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Factors controlling dissolved organic carbon in soils: a database analysis and a model development

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SUMMARY

Carbon is constantly displaced along the land-ocean aquatic continuum, but, despite its crucial role in the global carbon cycle, this lateral transport of dissolved organic carbon (DOC) is usually neglected in Land Surface Models (LSM). Including these lateral DOC fluxes in global carbon cycle models is necessary for two main reasons: 1) Neglecting these fluxes can lead to an overestimation of terrestrial ecosystem carbon sequestration, and 2) In order to better understand and predict Earth's carbon cycle, we need to move towards a "boundless carbon cycle", that integrates terrestrial, freshwater and marine ecosystems. In this sense, some approaches for the modelling of processes and transport of DOC concentrations have been developed, but more accurate information is needed in order to better understand and predict DOC dynamics.

Therefore this thesis has a twofold objective: First, to compile and analyze a database on DOC concentrations in soil solution with the aim of better understanding which drivers determine their spatial and temporal variability. Second, to implement the processes of DOC production, retention and transport in the LSM ORCHIDEE. The thesis is, thus, half data-driven and half model-driven.

My database compiles DOC concentrations in soil solution at site level for different ecosystems around the world, giving special focus to the Northern Hemisphere and to forest ecosystems. I explored the differences in DOC concentrations amongst ecosystem types, climates and soil types first at global scale and then I focused on the site-to-site and the temporal variability in European forest soils. As expected, DOC concentrations were greater in organic soils than in mineral soils. I also found that DOC concentrations were lower in broadleaved forests than in coniferous forests, probably due to the slower decomposition rate of coniferous litter. There was evidence of an overall increasing trend in DOC concentrations in the organic layers, but no clear consistent temporal trend in concentrations of DOC in soil solution in the mineral soil was detected. The database analysis revealed a key role of site N availability and pH in controlling both the spatial and the temporal variability of DOC. I highlight the importance of internal soil processes as the ultimate factor controlling DOC concentrations in soils and as agent of the high heterogeneity among sites.

In the second part of the thesis, I implemented the processes of DOC decomposition, adsorption on- and desorption from soil minerals, and transport through and out of the soil in the land surface model ORCHIDEE. I also discretized the soil module down to 2 meters to allow the model to account for deep soil organic carbon and DOC dynamics. The resulting new model, ORCHIDEE-SOM, was evaluated against field data of DOC concentrations in a temperate forest site. The model-data agreement was very satisfactory for the dynamics and soil profiles of DOC concentrations, indicating that the most important processes of DOC production and transport are already well-represented in ORCHIDEE-SOM. However, the ORCHIDEE-SOM simulations of DOC and SOC dynamics at site level are not perfect yet because the physico-chemical soil properties that are important in determining DOC and SOC dynamics are not yet included in the model. My final recommendation is to keep improving ORCHIDEE-SOM by means of a multisite optimization in order to be able to use it at global scale, at the same time we advance in the representation of nutrients and pH controls in the land surface model ORCHIDEE-SOM.

SAMENVATTING

Koolstof wordt voortdurend uitgewisseld tussen waterstromen op het land en de oceanen. Ondanks de belangrijke rol van dit laterale transport van opgeloste organische koolstof (dissolved organic carbon; DOC) in de globale koolstofcyclus, wordt het meestal genegeerd in Land Surface Models (LSM). De laterale DOC stromen in bouwen in globale modellen is nochtans van belang om twee redenen: 1) het ontbreken van deze fluxen kan leiden tot een overschatting van koolstofopslag op het land, en 2) om de globale koolstofcyclus beter te begrijpen en te voorspellen moet onze visie veranderen naar een ‘grenzeloze koolstofcyclus’ waarbij terrestrische, zoetwater- en mariene ecosystemen geïntegreerd worden. Om deze reden werden enkele modellen ontwikkeld voor DOC-gerelateerde processen en transport. Er is echter nood aan nauwkeurigere informatie om de DOC-dynamieken beter te kunnen begrijpen en voorspellen.

Deze thesis had dan ook twee doelstellingen: (1) het opstellen en analyseren van een DOC database om te achterhalen welke omgevingsfactoren de spatiale en temporele variatie in DOC concentraties in bodemoplossing bepalen; (2) implementatie van productie-, retentie- en transportprocessen van DOC in het LSM ORCHIDEE. Deze thesis bestaat dus deels uit data-analyses, en deels uit modeltoepassingen.

Mijn database bevat DOC-concentraties in bodemoplossing op site-niveau voor verschillende ecosystemen verspreid over de Aarde, met veel aandacht vooral voor bossen in het Noordelijk halfrond. Ik heb eerst onderzocht hoe DOC-concentraties verschillen tussen ecosystemen, klimaten en bodemtypes op globale schaal, om vervolgens te focussen op de spatiale en temporele variatie in Europese bossen. Zoals verwacht waren de DOC-concentraties hoger voor organische dan voor minerale bodems. Ik vond ook dat DOC-concentraties lager waren in loofbossen dan in naaldbossen, waarschijnlijk vanwege de tragere ontbinding van afgevallen naalden. Over het algemeen stegen de DOC-concentraties in de organische bodemlagen, terwijl de temporele trends van DOC in bodemoplossing in de minerale bodemlagen geen consistent patroon vertoonden. De database-analyse suggereerde een belangrijk rol voor stikstofbeschikbaarheid en zuurtegraad van de bodem in het bepalen van zowel spatiale als temporele variatie in DOC-concentratie in de bodem. In deze thesis duid ik verder op het belang van de interne bodemprocessen als bepalende factor van de uiteindelijke DOC-concentraties in de bodem en de heterogeniteit ervan.

In het tweede deel van deze thesis heb ik de processen van DOC-decompositie, van adsorptie en desorptie van DOC aan mineralen, en van DOC-transport doorheen de bodem geïmplementeerd in ORCHIDEE. Ik heb ook de bodem-module gediscretiseerd tot 2 m om zo rekening te kunnen houden met de organische koolstof en DOC dynamieken in de diepere bodemlagen. Een evaluatie van het resulterende nieuwe model, ORCHIDEE-SOM, werd geëvalueerd met de DOC-concentratie-data van een gematigd bos. De overeenstemming tussen model en data was vrij goed wat betreft dynamieken en bodemprofiel, wat erop wijst dat de belangrijkste processen van DOC-productie en –transport goed weergegeven zijn in ORCHIDEE-SOM. Echter, ORCHIDEE-SOM kan voorlopig de DOC- en SOC-dynamieken op site-niveau nog niet perfect simuleren omdat de fysicochemische bodemeigenschappen die belangrijk zijn voor deze dynamieken nog niet opgenomen zijn in het model. Voor gebruik op globale schaal raad ik dan ook aan om, tijdens het inbouwen van de rol van nutriënten en pH in het model, ORCHIDEE-SOM ook te blijven verbeteren door middel van multi-site optimisatie.

THANK YOU

This PhD started as a real adventure, with a simple Skype interview from Córdoba (Spain), a new project without proposal, a move to Antwerp, and three main supervisors from two different countries. If I am able to write these words now, it is just thanks to all the wise people that surrounded me and the endless interest and support I received on the way. I think this was not an easy travel, but it was a very exciting and satisfactory one. As I said, like a real adventure.

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…And also dedicated to Luis. Because. Luis, you were the real motor that kept me working no matter how frustrating the results were. Your endless patience, love and optimism could always compensate my stress. You never doubted that I will finish the PhD, and I could feel it every morning. Believe me, I don't have words to thank you for your unconditional support.

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LIST OF PUBLICATIONS

Zenone, T., D. Zona, I. Gelfand, B. Gielen, **M. Camino-Serrano**, and R. Ceulemans (2015), CO_2 uptake is offset by CH_4 and N_2O emissions in a poplar short-rotation coppice, GCB Bioenergy, n/a-n/a.10.1111/gcbb.12269

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Vicca S, Gilgen AK, **Camino-Serrano M**, Dreesen FE, Dukes JS, Estiarte M, Gray, S.B., Guidolotti, G., Hoeppner, S. S., Leakey, A. D. B., Ogaya, R., Ort, D. R., Ostrogovic, M. Z., Rambal, S., Sardans, J., Schmitt, M., Siebers, M., van der Linden, L., van Straaten, O. and Granier, A. (2012). Urgent need for a common metric to make precipitation manipulation experiments comparable. New Phytologist.; 195(3):518-22. 10.1111/j.1469-8137.2012.04224.x

INTRODUCTION

1 The Boundless Carbon Cycle

Carbon in the biosphere is distributed among three reservoirs: terrestrial, oceanic and atmospheric. The atmospheric CO_2 has increased from approximately 277 parts per million (ppm) at the beginning of the Industrial Era, to 395 in 2013 (Le Quéré et al., 2014), and emissions from fossil-fuel combustion are the dominant source of anthropogenic emissions to the atmosphere. The traditional view of the carbon cycle considers only the vertical gas exchange between terrestrial and oceanic reservoirs with the atmosphere (Battin et al., 2009; Cole et al., 2007), which implies that all the CO_2 that is taken up from the atmosphere and is not respired, is stored on land (Regnier et al., 2013). However, this conventional view neglects the important role of inland waters as biogeochemical hot spots and as conduits between terrestrial and marine ecosystems. By assuming that all photosynthetically absorbed carbon that is not respired back to the atmosphere is sequestered by the ecosystem, the potential of land as a sink of anthropogenic CO_2 emissions is overestimated, but the magnitude of this overestimation is poorly constrained at ecosystem-level. In recent years, the awareness has increased that if we want to better understand the Earth’s carbon cycle and make reliable projections about its future, we need to move away from the traditional view towards a “boundless carbon cycle”, that integrates terrestrial, freshwater and marine ecosystems (Figure 1).

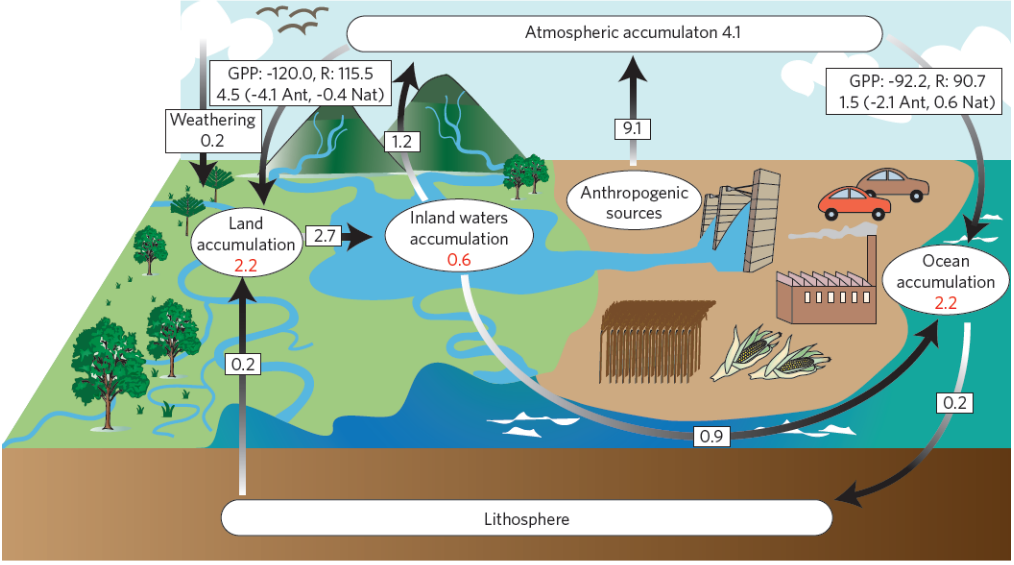


Figure 1. The boundless carbon cycle. Units are Pg C yr^{-1} and negative signs indicate a sink from the atmosphere. Source: Battin et al. (2009).

This need is illustrated for example by the gap in the global and European carbon budgets (Janssens et al., 2003; Regnier et al., 2013). Observation-based estimates of terrestrial carbon stock increases are considerably smaller than carbon dioxide uptake estimated by atmospheric models. One of the possible reasons for this imbalance lies in the C drainage from soils, C outgassing from lakes and rivers and storage in sediments. (Ciais et al., 2008; Regnier et al., 2013; Siemens, 2003).

The losses of C from terrestrial ecosystems to the sea have already been quantified since the 1970s and 1980s (e. g., Meybeck, 1982). These first attempts to quantify the role of aquatic systems in the global carbon cycle usually accounted only for the transport of C through the riverine pipe and consequently, assumed that the C flux going to the sea equals the C flux from land to inland water. However, it is known that C that enters the aquatic system can be transported, respired or stored in sediments elsewhere and thus, the rivers do not act as a simple passive pipe, but as a place of active transformations (Cole et al., 2007). Since then, studies account for the multiple factors affecting the fate of C in freshwater ecosystems and the quantification of C from land to rivers is becoming more accurate, showing that the transfer of terrestrial C to inland waters is considerably larger than delivery of C to the sea (Table 1). Processes occurring in the freshwater system are, however, beyond the scope of this thesis.

It is important highlighting that, even though recent studies made important improvements in the quantification of C fluxes from inland waters, there is still a need for improved and denser C observation systems covering a diversity of soil types and inland waters to properly asses the C fluxes to inland waters at global scales (Regnier et al., 2013). Therefore, the quantification of the C fluxes in the land-ocean aquatic continuum is still open to debate.

Table 1. Annual global soil C input to inland waters

Global flux of C from land to rivers (Pg C yr^{-1})	Reference	Remarks
0.9	(Meybeck, 1982)	No transformation occurring in rivers
0.4-0.9	(Hope et al., 1994)	No transformation occurring in rivers
0.36	(Aitkenhead and McDowell, 2000)	From empirical model (only accounts for DOC)
1.9	(Cole et al., 2007)	Consider reactions within the rivers
2.7	(Battin et al., 2009)	Consider reactions within the rivers
2.9	(Tranvik et al., 2009)	Consider reactions within the rivers
1.9	(Regnier et al., 2013)	Consider reactions within the rivers

The soil-derived C flux to the freshwater system encompasses three main components: DOC (dissolved organic carbon) (37%), DIC (dissolved inorganic carbon) (45%) and POC (particulate organic carbon)(18%) (Meybeck, 1993). This flux represents about 5% of soil heterotrophic respiration (Regnier et al., 2013) when considering both mineral and organic soils. DOC and DIC are the dominant sources of soil-derived inputs to stream waters. Because the dynamics of DOC fluxes from soils are not clear yet, this thesis focusses on the study of DOC concentrations.

1.1 The role of DOC leaching from soils in the net ecosystem carbon balance

Although DOC export from soils is higher from organic soils, such as peatlands, than from mineral soil (e.g., Billett et al., 2010), so far most of the research on DOC fluxes have focused on mineral, particularly forest, soils. In fact, the DOC export per area of organic soils is higher, but globally they cover a much smaller land area than mineral soils. Hence, from a global perspective, DOC export from mineral soils is very important. Moreover, reported DOC fluxes are highly variable, as DOC losses from forest soils have been estimated within a range of 1 to 20 g C m^{-2} yr^{-1} across Europe (Gielen et al., 2011; Kindler et al., 2011; Michalzik et al., 2001; Schulze et al., 2009). If we assume an average net biome productivity of European forests, excluding leaching losses, of 82 g C m^{-2} yr^{-1} (Schulze et al., 2009), DOC losses from forest soils thus represent between 0.12% and 24% of net biome productivity.

Although leaching of DOC represents a small flux of C compared to gross ecosystem carbon fluxes, considering these fluxes is particularly important for different reasons. First, DOC may represent a substantial part of the carbon balance of the site when studying the carbon flux at local scales over long time periods or in places where the net changes of biomass stocks are small. In these cases, outgassing of this carbon may occur outside the boundaries of the study system, leading to an overestimation of the estimated carbon storage of the site (Kindler et al., 2011). Second, this small lateral flux of C from forests is particularly important for the predictions of C storage on land under climate change. Not accounting for the C leaching from soils will introduce a systematic bias and may overestimate projections of terrestrial C sequestration.

Moving forward requires linking the aquatic and terrestrial ecosystems in the Earth System Models (ESMs) used to simulate and understand the evolution of climate including biogeochemical feedbacks. Nevertheless, the multiple processes involved in the production and transport of DOC remain poorly understood. The well-established riverine fluxes normally average carbon fluxes from various land use systems within a particular catchment (Kindler et al., 2011). Therefore, the missing link between C fluxes in rivers to those in terrestrial ecosystems is the leaching from soils. We will benefit from better data on factors affecting the leaching from soils as this information could considerably improve estimates and predictions of carbon budgets along the land-ocean continuum. In order to implement the link between terrestrial and aquatic ecosystems in global carbon cycles, we need:

1) to understand the drivers of DOC concentrations in soil solution;

2) to implement the main processes of DOC production in soils in global carbon models;

3) to model the transfer of DOC produced in soils to rivers and oceans, accounting for the in-stream transformations within the ESMs.

In this thesis, the first and second tasks were addressed. I first analyzed monitoring data to identify the main drivers of spatial and temporal changes in soil DOC concentrations, with the main focus on forests, and later I implemented the soil processes responsible for DOC production, removal and transport in the land surface model ORCHIDEE.

2 Drivers of DOC in soil solution

Because dissolved organic matter is a complex mixture of many organic compounds, it must be operationally defined. DOC is the carbon contained within organic matter in a solution that passes through a 0.45 µm filter and that might be derived from decomposing plant litter, root exudates, microbial biomass and exudates, and soil organic matter (Koehler et al., 2009).

Once in the soil, DOC experiences a combination of different processes that influence its concentration and molecular composition, namely, biological production and consumption, adsorption to- and desorption from soil minerals and transport. First, microbes can degrade DOC in soil solution (Kalbitz et al., 2003). Also, more DOC is produced as a product of the microbial decomposition of soil organic matter. Then, DOC mobilization occurs as a result of both solubilization and desorption within the soil profile. DOC sorbs to natural surfaces through several different mechanisms: ligand exchange reactions between carboxylate groups and mineral surface hydroxyls, anion exchange and physical adsorption (Gu et al., 1994; Jardine et al., 1989). The DOC that is not sorbed and remains free in solution can also move with soil water and finally leach out of the soil. Overall, microbial decomposition of organic matter plays a minor role at deeper horizons, where sorption processes have a greater effect on the fate of DOC (Kalbitz et al., 2000).

Consequently, the final DOC concentration in the soil will be the net result of DOC release (through soil organic matter decomposition, exudation and desorption from minerals) and DOC removal (through further decomposition, adsorption to minerals and leaching with water flux). These processes are affected by various environmental and soil factors operating at different scales, briefly described below and are summarized in Figure 2:

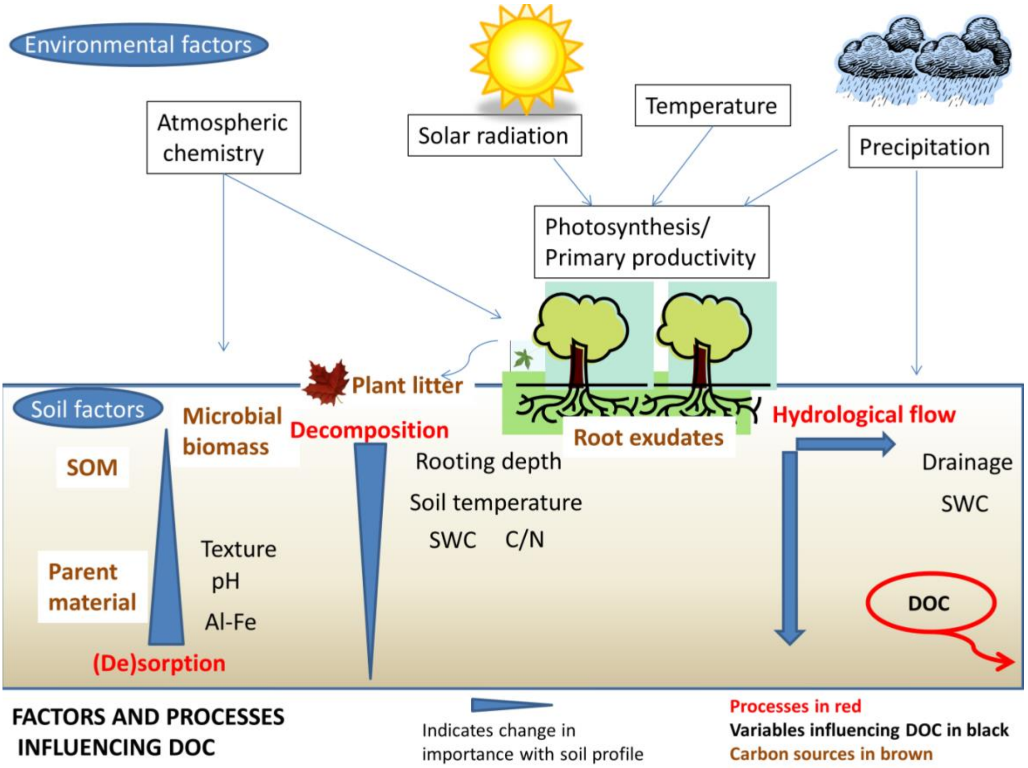


Figure 2. Schematic illustration of the factors and processes influencing dissolved organic carbon in soils. Processes are represented in red, factors in black and carbon sources in brown.

2.1 Environmental factors

2.1.1 Temperature

DOC is a product of organic matter decomposition and, as such, it is influenced by temperature (Davidson and Janssens, 2006). Positive relationships between DOC and temperature are reported under laboratory conditions (Moore and Dalva, 2001; Moore et al., 2008), but the effects of temperature on DOC are not always evident in the field, where biological and physicochemical controls over DOC occur simultaneously. DOC is an intermediate product of decomposition, and temperature changes will thus affect both the production and consumption of DOC. Hence, the temperature sensitivity of the DOC concentrations depends on the magnitude of both processes. In situ, increasing DOC concentrations with increasing temperature have been reported (e.g., Michalzik and Matzner, 1999), but predominantly for DOC in shallow forest soil horizons, where microbial activity is higher, while DOC in deeper soils is more stable and not affected by temperature changes.

2.1.2 Precipitation and soil water fluxes

Site hydrology has a strong influence over DOC transport through and out of the soil. (e.g., Gielen et al., 2011; Sanderman et al., 2009; van den Berg et al., 2012), since the DOC flux leaving the soil is directly proportional to the water flux (drainage and runoff). DOC mobility in soils is ultimately regulated by the variation in hydrological flowpaths of hillslopes, the hydrologic connectivity of different landscape units and the dynamics of shallow groundwater levels (Schelker et al., 2013). Moreover, the vertical transport of DOC through soil profiles is dominated by the flow regime and macropore transport, which are modified by changes in the frequency and intensity of the precipitation.

Recent studies focusing on the importance of short heavy rainfall events in the total export of DOC from forested catchments (Raymond and Saiers, 2010) showed that such events can significantly change DOC concentrations and fluxes by shifting dominant flowpaths towards preferential flow through macropores, runoff, and lateral flow, but this effect depends on the texture (Kalbitz et al., 2000). During heavy storms, the groundwater table will rise creating an hydraulic connectivity of surface horizons with streams and most of the DOC will rapidly leach from surface , thus, changing the preferential flowpath to runoff (Sanderman et al., 2009).

Finally, despite its diluting effect, increasing soil moisture may increase DOC concentrations after dry periods (when microbes massively excrete organic osmoprotectants to avoid osmotic burst, but also by the more optimal conditions for microbial decomposition) and in anaerobic conditions, for instance in peat soils, DOC decay is reduced by increasing anoxia.

2.1.3 Acid deposition

A factor with a possibly important influence on DOC concentrations is acid deposition. It has been hypothesized that the decreasing acidifying deposition over the last decades (Waldner et al., 2014) is an important driver of the increasing DOC concentrations in surface waters. Although this hypothesis has been proven for DOC concentrations in surface waters (Evans et al., 2005; Haaland et al., 2010; Hruška et al., 2009; Monteith et al., 2007), the picture is mixed for DOC concentrations in soils (Löfgren and Zetterberg, 2011; Vanguelova et al., 2010; Verstraeten et al., 2014; Wu et al., 2010). Decreasing atmospheric acid deposition may indirectly affect DOC concentrations by increasing soil pH and decreasing ionic strength. Both have been associated with enhanced solubility and mobilization of DOC (Evans et al., 2005).

2.2 Vegetation factors

DOC concentrations in soils are controlled by vegetation type, as the quality and amount of litter and root exudates, two important sources of DOC in forest soils, will change among ecosystem or forest types. While a study for 42 forests found no differences in DOC concentrations between forest types (Michalzik et al., 2001), other studies reported higher DOC concentrations under coniferous forests than under broadleaved forests (Currie et al., 1996; Fröberg et al., 2011; Khomutova et al., 2000), attributed to a thicker litter layer under coniferous forests. In fact, increasing litter production may result in increasing DOC concentrations, causing seasonal changes in the DOC concentrations in the organic layer that are related to seasonal changes in litter inputs (Kalbitz et al., 2000). Moreover, differences in the litter quality also influence DOC concentrations by changing the microbial decomposition and bioturbation rates (Cotrufo et al., 2013; Fröberg et al., 2011).

Nevertheless, the effect of vegetation type on DOC might be confounded with the effect of soil type, since the tree species have an effect on several chemical, physical and biological properties of the soil. For instance, tree species may modify the pH and the composition of the complexing organic acids of soil solutions. Also, the structural stability of soil may be lower under *Picea* spp. than under *Quercus* spp (Augusto et al., 2002). Both the soil pH and structural stability of soils influence DOC as discussed below.

2.3 Soil factors

Soil type determines the fertility, substrate quality and amount of organic matter, all these factor being key controls of the processes of production and solubility of DOC in soils. Some soil factors have been already identified in literature as important explanatory factors of DOC dynamics. Here, I describe how these factors affect DOC.

2.3.1 C/N ratio and N content

The importance of C:N ratio is well-established at regional and global scales (Aitkenhead and McDowell, 2000; van den Berg et al., 2012). At high C:N ratios, DOC concentrations increase due to the incomplete mineralization of DOC (Kindler et al., 2011; van den Berg et al., 2012). The soil C:N ratio is a good indicator of the decomposition rate and a good integrator of the biotic controls of DOC (for instance, of fertility) (Aitkenhead and McDowell, 2000; Kalbitz et al., 2000). Processing of nitrogen-poor organic matter results in production of more soluble residues, that is, more DOC is produced as leftover of soil organic matter degradation (Kindler et al., 2011). It also accounts for vegetation effects on soils, as the litter quality will partly determine the C:N ratio of the soil.

On the other hand, the effect of soil N on DOC concentrations is not well-established yet, with different studies showing contradictory results. The addition of N has been reported to increase DOC leaching in some studies (Bragazza et al., 2006; Pregitzer et al., 2004), but this effect is not always observed (Evans et al., 2008). Very likely, N will have an effect on DOC through vegetation activity: N-enrichment favors the above-ground tissue production in forests at the expense of C allocation to the root system (Janssens et al., 2010; Vicca et al., 2012), reducing an important source of DOC. Nevertheless, caution is needed when interpreting correlations between N and DOC, as N may co-vary with other factors affecting DOC, such as soil-nutrient availability or acidity (Evans et al., 2008; Janssens et al., 2010)

2.3.2 pH

Soil pH affects soil DOC via physico-chemical and biological processes, and thus both DOC production and consumption are influenced by pH, complicating the relationship between pH and DOC and leading to contradictory results from field studies. Regarding the physico-chemical effects of pH, the degree of DOC sorption to minerals is dependent on soil pH: it has been reported that decreasing pH enhances the adsorption of DOC to Fe oxides (Jardine et al., 1989; Kothawala, 2009). However, this relationship has been contradicted in other studies (e.g., Vance and David, 1989). On the other hand, pH reduces the solubility of DOC by promoting the release of Al^{3+} into soil solution. Increasing Al^{3+} in soil solution enhances DOC complexation and precipitation and, in turn, suppresses DOC solubility (Scheel et al., 2008; Vanguelova et al., 2010). The solubility of DOC is also impeded by high ionic strength in acid soils, but the effects of ionic strength in the DOC concentrations are ambiguous (Kalbitz et al., 2000).

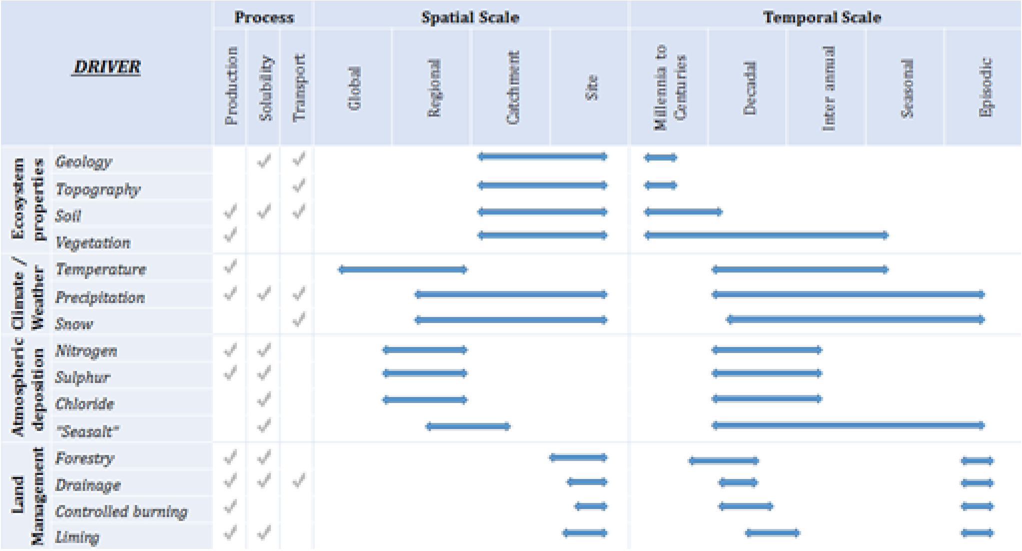
Regarding the effects of pH via biological processes, microbial decay may be suppressed under low pH by two mechanisms: first, the high Al^{3+} concentrations found at low pH may cause toxicity of Al^{3+} to soil microorganisms, and, second, the physical protection of organic matter through precipitation with Al^{3+} may reduce bioavailability of organic matter to be decomposed (Scheel et al., 2008).

2.3.3 Controls on DOC adsorption: Fe and Al (hydr)oxides, clay and organic carbon

The high affinity of DOC to the surfaces of Al and Fe oxides is well documented in literature (Kaiser et al., 1996; Kothawala, 2009; Moore et al., 1992). Also, high clay content has been associated to a higher adsorption capacity of soils (Jardine et al., 1989). Therefore, we can expect low concentrations of DOC in soils with high levels of Fe and Al (hydr)oxides and clay minerals, because in this type of soil, DOC is strongly adsorbed. The adsorption of DOC is even higher when the organic C content of the soil is low (Kaiser et al., 1996; Kothawala, 2009). The low adsorption capacity at high organic carbon content partly explains the typical decreasing profile of DOC in forest soils: in the organic layer, the organic carbon content is higher and DOC is mainly desorbed and free in soil solution; however, the adsorption of DOC in the mineral soil rises as the amount of organic carbon decreases with depth, removing DOC from soil solution.

Finally, soil texture will determine not only the adsorption capacity, but also the flowpath of DOC through the soil. In soils, the preferential flowpath during heavy rainfall events shifts towards the macropores, influencing the output of DOC. This shift is much more pronounced in clay soils than in sandy soils, where the influence of water flux on the DOC flowpath is small because there are relatively more macropores. The control of texture and soil aggregation on DOC concentrations can partly explain the disagreements found between laboratory and field studies, as laboratory studies does not account for the impact of soil aggregation on water pathways.

In conclusion, although the role of the factors affecting DOC in soil solution is relatively clear in laboratory studies, the results from field conditions are sometimes contradictory. The challenge is to disentangle the multitude of factors controlling DOC here presented that interact amongst them and act at a variety of spatial and temporal scales in field conditions (Figure 3). Therefore, future research should focus on understanding the controls of DOC concentrations under field conditions covering a wide range of soils, ecosystems and climates. Understanding the drivers underlying the mechanisms affecting DOC in soils will have two important implications: first, it will allow us to implement them in the global carbon models for future predictions. Second, it will help in designing efficient climate change mitigation strategies, particularly, strategies designed to enhance carbon sequestration will benefit from more detailed information about where and how it occurs.



	DRIVER	Process			Spatial Scale				Temporal Scale				
		Production	Solubility	Transport	Global	Regional	Catchment	Site	Millenia to Centuries	Decadal	Inter annual	Seasonal	Episodic
Ecosystem properties	*Geology*		✓	✓			↔	↔	↔				
	Topography			✓			↔	↔	↔				
	Soil	✓	✓	✓			↔	↔	↔	↔			
	Vegetation	✓					↔	↔	↔	↔	↔	↔	
Climate / Weather	*Temperature*	✓			↔	↔				↔	↔	↔	
	Precipitation	✓	✓	✓		↔	↔	↔		↔	↔	↔	↔
	Snow			✓		↔	↔	↔		↔	↔	↔	↔
Atmospheric deposition	*Nitrogen*	✓	✓			↔				↔	↔		
	Sulphur	✓	✓			↔				↔	↔		
	Chloride		✓			↔				↔	↔		
	"Seasalt"		✓			↔	↔			↔	↔	↔	↔
Land Management	*Forestry*	✓	✓					↔	↔	↔			↔
	Drainage	✓	✓	✓				↔		↔			↔
	Controlled burning	✓						↔		↔			↔
	Liming	✓	✓					↔		↔	↔		↔

Figure 3. Scale of spatial and temporal variation in drivers of DOC production, solubility and transport. Adapted from Clark et al. (2010).

3 Modelling the transfer of DOC from soils to streams and rivers

Earth System Models (ESMs) are mechanistic global models that represent physical, chemical and biological processes within and between the atmosphere, ocean, and terrestrial biosphere. ESMs include the important feedbacks from the biosphere to the atmosphere so that we can identify and understand effects of climate on vegetation and carbon and vice versa (Prentice and Cowling, 2013). ESMs have become an indispensable tool to predict the risks of continued environmental changes for future climate, ecosystem services and sustainable land management. For instance, a set of ESMs are used within the Intergovernmental Panel on Climate Change (IPCC) (Taylor et al., 2012) for assessment of the impacts of climate change and design of mitigation strategies. Hence, their predictions need to be as accurate as possible. However, ESMs are currently under development and some key processes in the global carbon cycle are still missing.

A Land Surface Model (LSM) is the component of an ESM that accounts for the carbon, energy and water cycles on land. Normally, LSMs simulate the vertical exchange of C between the atmosphere and the land, that is, NPP and soil heterotrophic respiration, but the fluvial C transport is currently ignored (Figure 4). The integration of the lateral C transport in LSMs will allow a more correct distribution of the land and ocean C sinks (Regnier et al., 2014). The first step towards the correct simulation of the C flux will require modifications in the typically very simple soil modules of the LSMs.

Despite the importance of soils as a large component of the global C storage, the soil compartments are the *overlooked* part in LSMs (Nishina et al., 2014; Todd-Brown et al., 2013). Typically, soil carbon dynamics described in LSMs are based on the CENTURY model (Parton et al., 1987) or the ROTH-C model (Coleman et al., 1997). Hence, soil carbon is divided in three pools (slow, active and passive) with different turnover rates. Basically, the different pools are decomposed and the fraction of the decomposed carbon being transferred from one pool to another is prescribed, with the rest fraction being lost to the atmosphere as heterotrophic respiration. Losses of soil carbon by dissolution and transport are neglected. Furthermore, soils are normally represented as a single layer box within LSMs, thus impeding a correct accounting for internal soil processes and soil organic carbon (SOC) at depth.

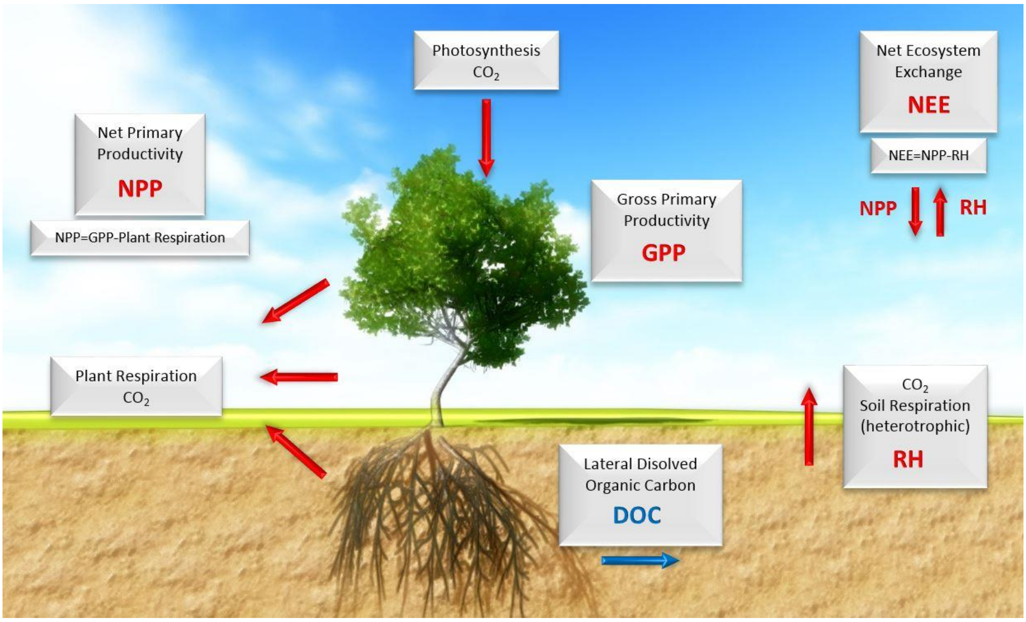


Figure 4. Carbon fluxes between the atmosphere and land typically represented within land surface models (in red) and missing lateral C transport (in blue).

To our knowledge, only one model accounts for the leaching of DOC at global scale (TEM model, McGuire et al. (2010)), but in this case, DOC export is simply calculated as a function of NPP, ignoring the underlying mechanisms of production and transport of DOC in soils. Nevertheless, several soil models exist that account for DOC dynamics and transport at smaller scales and for specific conditions (Table 2).

For instance, there are models that simulate DOC dynamics in peatlands and mires (Worrall and Burt, 2005; Yurova et al., 2008), in crops (Gjettermann et al., 2008) or in forests (Michalzik et al., 2003; Neff and Asner, 2001; Wu et al., 2013). These models generally differ in the definition of the SOC and DOC pools in soils, which may be characterized by their turnover time (e.g., Neff and Asner, 2001; Ota et al., 2013; Parton et al., 1987) or chemical composition (e.g., Laine-Kaulio et al., 2014; Michalzik et al., 2003; Yurova et al., 2008). They also differ in the level of detail in the process formulation (from simple first order kinetics to non-linear relationships) and the spatial and temporal resolution (from site to global, and from hourly to annual or longer time scales) (Table 2). Finally, most of these models do not represent a discretized soil depth yet and SOC and DOC dynamics are assumed to occur in one or two soil layers.

It is highly important to include the mechanisms of production, retention and transport of DOC in soils already presented in smaller-scales models, particularly in view of predictions of the C cycle change under future climate. DOC in soil is important in two ways: first, it is the primary source of DOC in inland waters and, second, it is one of the main sources of subsoil SOC. Future changes in environmental conditions may cause important, albeit still relatively unknown, soil-atmosphere-hydrosphere feedbacks, that will affect processes of carbon cycling, with consequences for the deep soil dynamics and the DOC leaching from soils. Currently, vertical transport and stabilization of C, where DOC plays a key role, are neglected in LSMs. Hence, improving the mechanistic representation of DOC formation in soils will lead to a more accurate prediction of the *anthropogenic carbon leakage* and the soil carbon storage under future climate change.

Table 2. Summary of DOC models described in literature. A brief description of their spatial definition, ecosystem of application, time step, definition of the carbon pools, the number of soil layers and processes represented is given.

Model	Reference	Spatial definition	Ecosystem	Time step	Number of soil layers	Definition of carbon pools	Processes
TerraFlux	(Neff and Asner, 2001)	Global?	Forests	Hourly	6	Turnover times (CENTURY)	Microbial decomposition Sorption/Desorption Leaching
INCA-C	(Futter et al., 2007)	Catchments	Forests, peat-forests	Daily	2	3 general pools: SOC, DOC, DIC	Decomposition+desorption (SOC->DOC) (%SOC pool) Sorption (DOC->SOC) Leaching
TEM model	(Kicklighter et al., 2013) (McGuire et al., 2010)	Global	Forests/peatlands	Monthly	1	2 general pools: C_{RS} (reactive soil organic carbon) DOC	Decomposition (% SOC decomposed/dt=f(NPP)) Leaching
DyDOC -MADOC model-	(Michalzik et al., 2003)*	Site	Forests	Hourly/daily	3	Chemically differentiated fractions of humic substances (3)	Decomposition Sorption Leaching
Worrall and Burt DOC model	(Worrall and Burt, 2005)	Catchment	Peatland and mires	Monthly	2 (Acrotelm, catotelm)	DOC	Production
ECOSSE	(Smith et al., 2010)	National/Global? (UK)	Different land uses: peatlands, grasslands	Monthly	5 cm layers. Soil depth?	5 pools chemically/turnover differentiated	Decomposition Sorption Leaching
Yurova DOC model	(Yurova et al., 2008)	Site	Boreal Mires	Daily to annual	2(Acrotelm, catotelm)	3 pools according to solubility/sorption: Solid, Sorbed, Dissolved	Production/Mineralization Sorption Leaching

DOC-3	(Jutras et al., 2011)	Catchment	Forest/ wetlands	Daily	3 Different flow paths in catchment	Not partitioning into pools	DOC produced and leached is calculated in an unique equation
TRIPLEX-DOC	(Wu et al., 2013)	Landscape	Upland forest	Daily		3 C pools chemically/ biologically differentiated and Two kinetically distinct DOC pools.	Interception of throughfall DOC Biological production and decomposition Sorption/desorption Transport by water percolation
WetQual-C	(Sharifi et al., 2013)	Catchment	Wetland	0.01 day, results averaged to daily	2 soil layers (aerobic and anaerobic)	3 carbon pools: labile POC, recalcitrant POC and DOC	Decomposition Soil and water diffusion Burial Denitrification Methanogenesis
ROMUL	(Laine-Kaulio et al., 2014)	Site	Mor	0.5 h	Mor layer	Chemically differentiated fractions of humic substances :3 C pools + 2 pools of DOC+2 pools of sorbed DOC.	Humification Mineralization Adsorption
Gogo et al. Model	(Gogo et al., 2014)	Site to global	Peatland			3 carbon pool (solid, aqueous and gaseous) or 4 (labile and recalcitrant solid pool)	Decomposition
SOLVEG-II	(Ota et al., 2013)	Site	Grassland	15 min	27 soil layers in 5.5 m	3 carbon pools based in turnover (CENTURY). One DOC pool (free)	Decomposition Sorption/Desorption Transport with water Root water uptake Diffusion
DocMod	(Currie and Aber, 1997)	Landscape	Forest	Monthly	1	3 litter fractions, microbial biomass, woody detritus and forest floor humus	Decomposition Leaching

SOMPROF	(Braakhekke et al., 2011)	Site	Forest		11 compartments (can be chosen)	5 OM pools :3 litter pools, non-leachable and leachable slow OM (dissolved and adsorbed)	Liquid phase transport
DAISY	(Gjettermann et al., 2008)	Ecosystem	Crops	hourly	14 horizons? Variable?	8 OM pools (3 for added organic matter, 3 SOM, 3 microbial biomass), 1 for DOC and 1for DON	Biological production and consumption Sorption (IM) Transport Convection-dispersion

**Rowe et al., 2014 integrated existing models of vegetation and soil in ‘MADOC’ model*

4 The methodology: a database and a modelling approach

The methodology I used in this thesis is based on two main tasks: 1) data gathering to compile a database on field data of DOC concentrations, leading to the data-driven chapters 1 and 2; and 2) modelling using the LSM ORCHIDEE, leading to the model-driven chapters 3 and 4.

4.1 The database

I collected data of DOC concentrations measured in the organic and mineral soil across different ecosystems and climates. I started the search with a global scope, but later I concentrated it at European level and mainly forests due to data availability (Figure 5), since most of the research on soil DOC has focused on temperate forest ecosystems (Karsten et al., 2007). DOC can be measured using different methods: 1) centrifugation or saturation extract of field-moist soil samples in laboratory, 2) in situ use of lysimeters (zero-tension or tension) to collect soil water DOC samples in the field (Ludwig et al., 1999), 3) Indirect estimation of DOC from water UV adsorption or water color (Hazen) (Worrall et al., 2003). Measurements using different methods should not be directly compared because different fractions of the soil solution may be collected (Karsten et al., 2007). For this reason, I only used the data obtained from tension or zero-tension lysimeters, the most commonly used methods in field monitoring. Apart from data on DOC concentrations, I gathered information on site properties (ecosystem type, dominant species, soil properties, soil solution chemistry and water flux, when available) for each plot.

The main sources of our data were from published literature, and from freely available databases. More specifically, we gathered data from 75 sites from literature, 9 sites from the Environmental Change Network (ECN) in UK and 281 sites from the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) network. While all the data was analyzed and compared in the first chapter of this thesis, later we concentrated on a more exhaustive statistical analysis using the ICP Forests Level

II plots since this pan-European dataset compiles plot information using a harmonized sampling protocol (Lorenz, 2010).

The ICP Forests is a European network that monitors forest condition at two monitoring intensity levels: the Level I and Level II plots. The Level I monitoring is based on around 6000 observation plots throughout Europe that were established to gain insight into the geographic and temporal variations in forest condition. The Level II intensive monitoring comprises more than 200 plots in selected forest ecosystems, covering a wide spatial range, from Italy to Northern Finland, with the aim to clarify cause-effect relationships. In this thesis, data from Level II plots have been used because, for these plots, long-term measurements of soil solution DOC (from 1995 to 2011, the period varying among plots) are available, as well as information on aboveground biomass, soil properties, atmospheric deposition, and climate across Europe. The quality assurance and control procedures include the participation in periodic laboratory ring tests (e.g., Marchetto et al. (2011)) to check the international comparability, therefore, reducing the uncertainty in the inter comparison of measurements across countries.

For the first chapter of this thesis, DOC data from published literature and from the ICP Forests program were harmonized using the same soil depth classification. In the ICP Forests program soil parameters were measured separately for the surface organic layer and for different depths in the mineral soil (0-10 cm, 10-20 cm, 20-40 cm and 40-80 cm). The soil and soil solution parameters from 0-10 cm and 10-20 cm were averaged into a 0-20 cm class and this ICP soil layer stratification into five soil depth classes (one organic and four mineral) was finally applied to all sites in the final database to harmonize the dataset. No data extrapolation was made to obtain DOC concentrations along the soil profile when a single measurement was available for one site. For instance, if only one measurement at one soil depth was available for an independent site from a published article, this measurement was simply classified as DOC within its soil depth interval, e.g., at 0-20 cm.

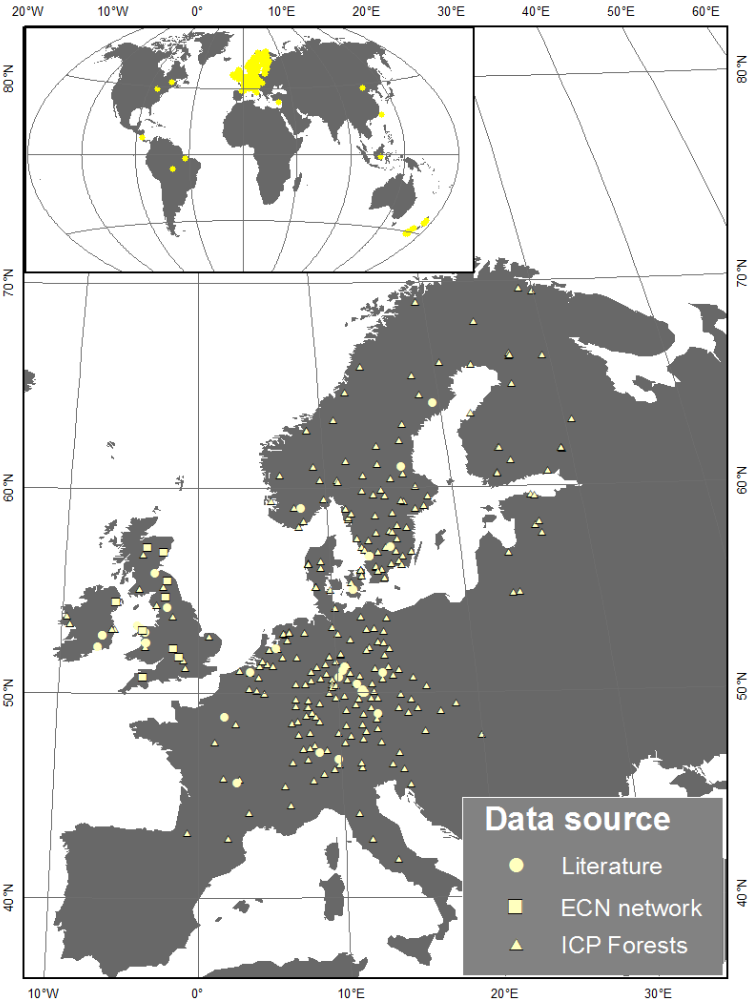


Figure 5. Location of sites contained in the database.

4.2 The Land Surface Model ORCHIDEE

ORCHIDEE is the land surface model of the IPSL (Institut Pierre Simon Laplace) Earth System Model. Its simulations were included in the IPCC assessments, as well as in the 3th, 4th and 5th Climate Model Intercomparison Project (CMIP5). ORCHIDEE can be run coupled with a global circulation model or as a stand-alone model in the offline mode. In this thesis ORCHIDEE has always been run in the offline version, because I focus only on changes in the land surface, not in the interaction with the atmosphere.

For the offline simulations, ORCHIDEE needs seven meteorological variables at a 30 min interval, i.e.: wind speed, air pressure, short-wave radiation, long-wave radiation, air temperature, precipitation and specific air humidity that are stored in the so-called *forcing files*. Atmospheric CO_2 concentrations and a representative soil texture for the site are also required.

ORCHIDEE represents the principal processes influencing the carbon cycle (photosynthesis, ecosystem respiration, soil carbon dynamics, fire, etc.) and energy exchanges at the biosphere. It consists of two modules: SECHIBA, which describes the fast processes of energy and water exchanges between the atmosphere and the biosphere at a time step of 30 minutes and STOMATE, that calculates the phenology and carbon dynamics of the terrestrial biosphere at a time step of 1 day (Figure 6). ORCHIDEE represents vegetation globally using 13 plant functional types (PFT): one PFT for bare soil, eight for forests, two for grasslands, and two for croplands (Krinner et al., 2005). Regarding the soil module, ORCHIDEE simulates soil carbon dynamics with a simple soil model based on CENTURY (see section 3) and assuming the soil column to be a single box.

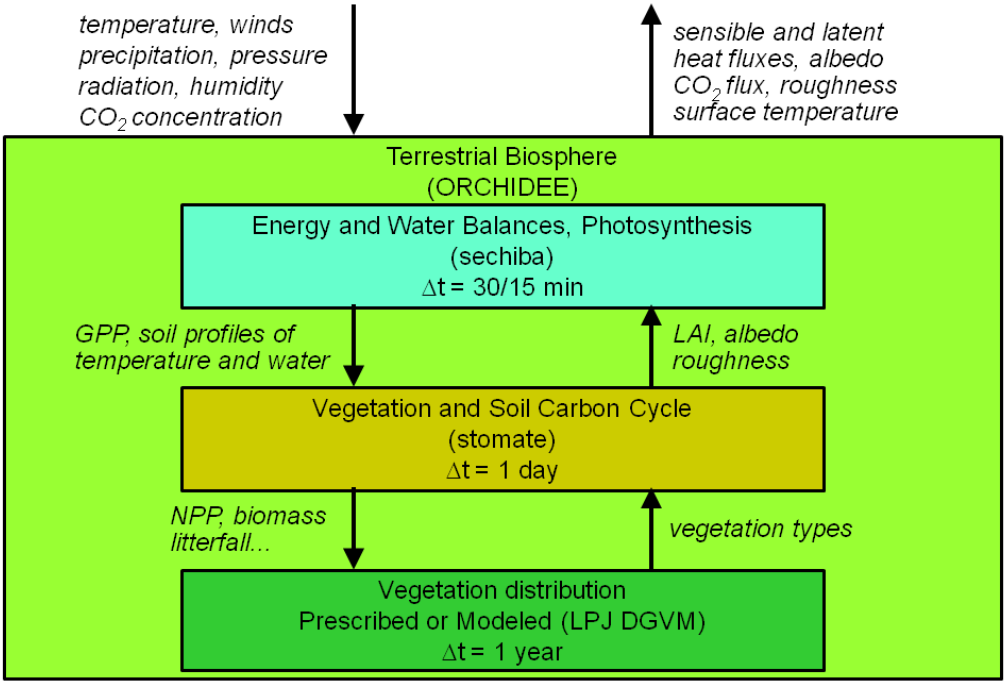


Figure 6. Modelled processes within ORCHIDEE and their time steps. Source: the ORCHIDEE website http://labex.ipsl.fr/orchidee/index.php/about-orchidee/#modelled_processes.

OBJECTIVES

The objectives of this thesis are twofold: first, to better understand and quantify the drivers of DOC concentrations in soil solution by means of a database analysis and, second, to implement the processes of DOC production and transport in soil within the land surface model ORCHIDEE to be able to simulate the export of DOC from soils to streams.

The specific objectives of each chapter of are then structured around the two main objectives of the thesis, with two data-driven chapters and two model-driven chapters (Figure 7):

Chapter 1. To quantify the differences in soil DOC concentrations between ecosystems and soil types and to identify potential drivers of the site-to-site variability of DOC concentration in soil solution.

Chapter 2. To understand the long-term temporal trends of DOC concentrations across European forests (ICP Forests Level II plots) and to identify the underlying environmental drivers.

Chapter 3. To modify the existing soil module of the LSM ORCHIDEE in order to enable simulations of DOC concentrations and fluxes in soil and out of the soil in a vertically discretized soil.

Chapter 4. To evaluate the new soil module ORCHIDEE-SOM against field data on DOC concentrations in soil solution from a temperate coniferous forest, and perform a sensitivity analysis to detect the most important parameters to be optimized in the future.

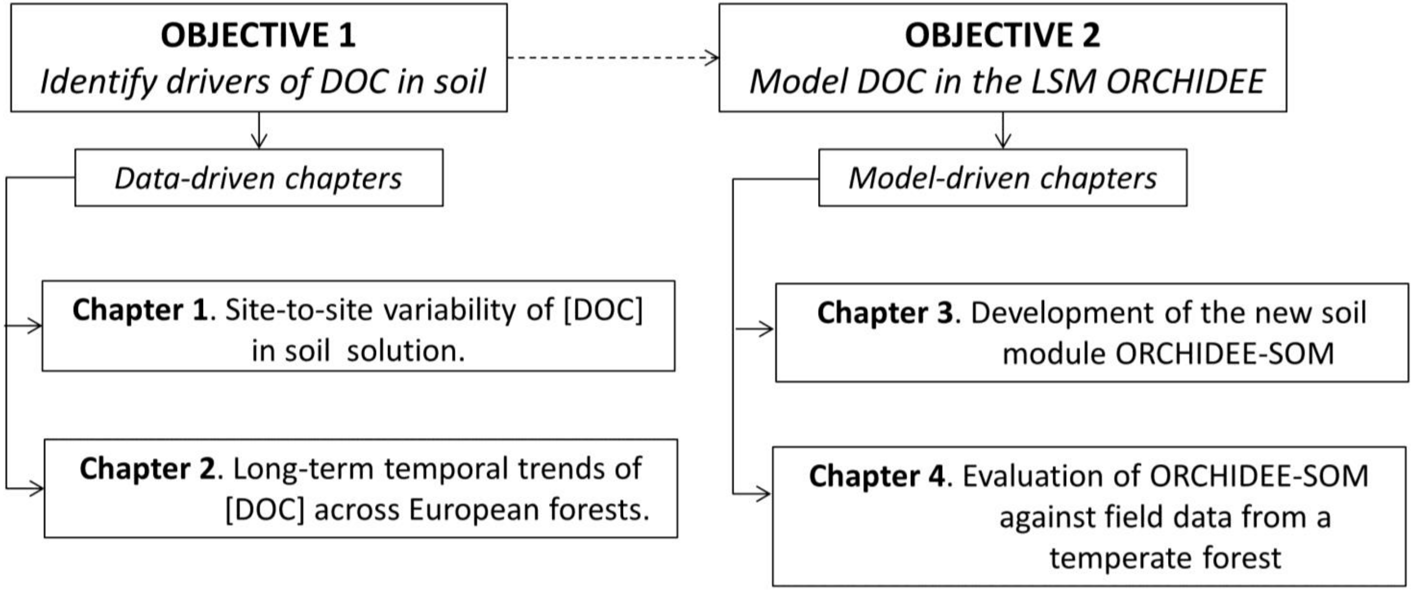


Figure 7. Conceptual scheme of the objectives of the thesis.

CHAPTER 1

CHAPTER 1. Linking variability in soil solution dissolved organic carbon to climate, soil type and vegetation type.

Camino-Serrano, M., Gielen, B., Luyssaert, S., Ciais, P., Vicca, S., Guenet, B., De Vos, B., Cools, N., Ahrens, B., Arain, A., Borken, W., Clarke, N., Clarkson, B., Cummins, T., Don, A., Graf Pannatier, E., Laudon, H., Moore, T., Nieminen, T., Nilsson, M. B., Peichl, M., Schwendenmann, L., Siemens, J., Janssens, I. (2014), Linking variability in soil solution dissolved organic carbon to climate, soil type, and vegetation type, Global Biogeochemical Cycles, 28, doi:10.1002/2013GB004726.xxx

Abstract

Lateral transport of carbon plays an important role in linking the carbon cycles of terrestrial and aquatic ecosystems. There is, however, a lack of information on the factors controlling one of the main C sources of this lateral flux i.e. the concentration of dissolved organic carbon (DOC) in soil solution across large spatial scales and under different soil, vegetation and climate conditions. We compiled a database on DOC in soil solution down to 80 cm and analyzed it with the aim, firstly, to quantify the differences in DOC concentrations among terrestrial ecosystems, climate zones, soil and vegetation types at global scale and, secondly, to identify potential determinants of the site-to-site variability of DOC concentration in soil solution across European broadleaved and coniferous forests. We found that DOC concentrations were 75% lower in mineral than in organic soil and temperate sites showed higher DOC concentrations than boreal and tropical sites. The majority of the variation (R^2=0.67-0.99) in DOC concentrations in mineral European forest soils correlates with NH_4^+, C/N, Al and Fe as the most important predictors. Overall, our results show that the magnitude

(23% lower in broadleaved than in coniferous forests) and the controlling factors of DOC in soil solution differ between forest types, with site productivity being more important in broadleaved forests and water balance in coniferous stands.

1 Introduction

Lateral transport of carbon is an important process linking terrestrial and aquatic ecosystems. The global transport of carbon from rivers to the ocean is about 0.8 Pg. C yr^{-1} (Regnier et al., 2013), of which ca. 20% is riverine dissolved organic carbon (DOC) flux into coastal oceans (Dai et al., 2012). While losses and transformations of DOC in inland waters, that is, outgassing as CO_2 and CH_4 emissions or burial in sediments, are well reported (Battin et al., 2009; Ciais et al., 2008; Cole et al., 2007; Nilsson et al., 2008), little is known about DOC transformations in soil solution across different ecosystems. Such information is, however, essential to understand processes controlling DOC leaching from soils in order to link terrestrial DOC fluxes to those in aquifers and rivers (Kindler et al., 2011).

The amount of DOC in soil solution is the balance of *inputs* and *outputs* of organic carbon to the soil water. DOC *inputs* to soil solution originate from biological decomposition, throughfall or litter-leaching, root exudates (Bolan et al., 2011), and from deposition of soot and dust (Schulze et al., 2011). The DOC *outputs* from soil solution are due to further mineralization and gaseous loss to the atmosphere, and to leaching into river headwaters (Bolan et al., 2011; Kalbitz et al., 2000). However, DOC may also interact with the soil matrix and can be adsorbed or desorbed depending on the soil conditions: Fe, Al and clay content, total organic carbon, cation exchange capacity (CEC) and pH (Kaiser et al., 1996; Kothawala et al., 2009). These factors governing DOC removal from soils can be allocated to three groups: biological control over the net DOC production and decomposition, edaphic control over the net DOC sorption, and hydrological control over drainage and lateral export from the ecosystem.

The relative importance of these three groups of processes varies across sites. There is evidence that soil DOC concentrations are influenced by vegetation type. Larger DOC concentrations in coniferous than in broadleaved stands have been reported (Currie et al., 1996; Fröberg et al., 2011). This difference is particularly pronounced in the forest floor organic layers, due to variations in humus type and organic matter composition among forest types (Borken et al., 2011). Tree species may also affect the size and quality of soil DOC (Lu et al., 2012). On the other hand, DOC export from peatland and forest soils has been shown to be dominated by extreme rainfall events (Dinsmore et al., 2013; Xu et al., 2012), which are expected to become larger and more frequent globally (IPCC, 2012).

A growing number of studies focusses on the controlling factors of variability in soil DOC concentrations at local, regional or national scale (Borken et al., 2011; Buckingham et al., 2008a; van den Berg et al., 2012), but much less information is available on effects of vegetation type, climate and soil properties on DOC variability at larger, continental to global scale. Two studies that address the larger scale variation in DOC include Michalzik et al. (2001), who presented a review on controls of DOC fluxes and concentrations across 42 temperate forests, and Kindler et al. (2011), who investigated variability in DOC concentration and fluxes across 12 European sites of different land use type. Both studies concluded that leaching of DOC from subsoils is controlled by retention in B horizons of the mineral soils (Kindler et al., 2011; Michalzik et al., 2001). However, while Kindler et al. (2011) found a close correlation between soil C/N ratio and DOC leaching from mineral topsoils, Michalzik et al. (2001) found no correlations between DOC leaching from litter layers and C/N. Hence, given the importance of DOC fluxes in the global carbon cycle, it is essential to analyze controlling factors of DOC concentrations and fluxes at larger scales with more complete datasets that cover different soil and vegetation types and various climate conditions.

To this aim we gathered data from the literature and from existing ecosystem monitoring networks (with a focus on European data) and compiled a database of DOC concentrations in soil solution and some key ancillary information. The database was analyzed to (1) quantify the differences in soil-solution DOC among near-natural terrestrial ecosystems, climate zones, soils, and vegetation types at the global scale, and (2) identify potential determinants of the site-to-site variability of DOC concentration in soil solution across European forests, differentiating between coniferous and broadleaved forests.

2 Material and methods

2.1 Database description

2.1.1 DOC concentrations in the soil solution

A database was designed to compile measurements of DOC concentrations in soil solution in different ecosystems around the world. The data were collected by means of two different approaches: 1) for published literature, figures were scanned using the free software Engauge Digitizer 4.1, tables were copied or the first author of the study was contacted to share the original data and; 2) we contacted the leaders of comprehensive networks such as the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) (http://icp-forests.net/) and the UK Environmental Change Network (ECN) (http://www.ecn.ac.uk/).

In total, there were 281 Level II plots from ICP Forests with available data on DOC in soil solution from the litter layer down to 80 cm deep, distributed over 20 different countries and ranging from Italy to Northern Finland. In addition to soil solution chemistry, also throughfall, litterfall, atmospheric deposition, and ground vegetation data are collected on a regular basis. The ICP Forests soil solution samples used for this analysis were collected between 1995 and 2008, with the majority sampled fortnightly. Soil solution was collected at different depths starting at 0 cm, defined as the interface between the organic layer and underlying mineral soil. Normally, lysimeters were installed at (at least) three depths: 0-20 cm, 20-40 cm and 40-80 cm (Nieminen, 2011). Full details of the

ICP-Forests sampling protocols can be found at http://icp-forests.net/page/icp-forests-manual.

These ICP Forests network data were complemented with observations from 75 independent sites taken from the literature and 9 terrestrial sites (3 grasslands, 1 forest and 5 peatlands) from ECN. For the latter, data on soil solution, soil properties, vegetation and meteorology were collected and analyzed by the network members. Soil solution in ECN terrestrial sites was collected fortnightly by using samplers in the A horizon and B horizon. Details of the ECN protocols can be found at http://www.ecn.ac.uk/measurements/terrestrial.

The final database thus contained information from 365 sites (311 of which are forests and 80% are located in Europe; Table 1, Figure S1, Table S1), with all soil solution DOC observations measured between 1988 and 2012. All the soil solutions were sampled in situ by using lysimeters or piezometers. Lysimeters are typically used in unsaturated soils, while piezometers are used where superficial water tables are present, for instance, in peatland soils. In most sites with unsaturated soils, zero-tension lysimeters are installed under the O horizon and tension lysimeters installed at depth in the mineral soil are used in combination (Kolka et al., 2008). Although comparative studies have shown larger DOC concentrations measured by zero-tension than by tension lysimeters (Buckingham et al., 2008b), when doing a cross-site comparison, no systematic differences between these techniques were found, because the effect of lysimeter type seems to be site-specific (Nieminen et al., 2013). For more information regarding the uncertainties in data collection see Appendix S1.

Table 1. Overview of the data contained in the database

Data Source	**# of sites**	**# of depths per site**				**Sites per ecosystem type**		
		1	2	3	>3	Forest	Non forest	
							Organic	Mineral
ICP Forests[1] dataset	281	66	60	68	86	281	-	-
ECN network[2]	9	-	9	-	-	1	2	6
Literature, site PIs[3] and researchers	75	26	22	20	7	29	27	20

[1] *International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests*

[2] *UK Environmental Change Network*

[3] *PI: Principal Investigator*

2.1.2 Ancillary data

Additional site information on soil properties, vegetation, climate, annual water balance and other soil solution parameters were also stored in the database.

Soil properties. Soil properties, such as texture, bulk density, pH, total organic carbon and nitrogen content, C/N ratio, exchangeable and extractable elements (such as Fe, Al or Mg), CEC and base saturation, as well as information on soil type according to the World Reference Base for Soil Resources (WRB) classification, were added to the database whenever available. A detailed list of variables, with descriptions and units can be found in Table S2. In the ICP Forests program this set of soil parameters was measured separately for the surface organic layer and for different depths in the mineral soil. A distinction was made between water-saturated (H) and unsaturated (O) organic layers, according to the FAO definition (Cools and de Vos, 2010). The mineral layer was sampled at fixed depth layers (0-10 cm, 10-20 cm, 20-40 cm and 40-80 cm). The ICP data network soil layer stratification was applied to all sites to harmonize the dataset. For aggregation of sites according to their acidity, soils were classified using pH

($CaCl_2$) as “Very acid” (<4.2), “Intermediate” (4.2-5),”Well Buffered” (5-6.2) and “Basic” (>6.2). In addition to DOC concentrations, other soil-solution chemical parameters, such as ammonium (NH_4^+), nitrate (NO_3^-), total dissolved iron (Fe) and aluminum (Al) and sulphate (SO_4^{2-}) concentrations were often available.

Vegetation related variables. A first classification of the data was made based on forest and non-forest ecosystems. In the non-forest sites, we further distinguished between mineral and organic soils, with the latter being mainly peatland sites. Within the forests, only one site was on organic soil, thus, no grouping into forests with mineral and organic soils was possible. Instead this single site with forest on organic soils was excluded in order to prevent it biasing the analyses. We split forests into two forest types, i.e., coniferous and broadleaved (evergreen and deciduous) forests. Based on the dominant and co-dominant tree species, a litter decomposability class (1-5 from fast to slow litter decomposition rate) was assigned for the forested sites, according to den Ouden et al. (2010). Monthly normalized difference vegetation index (NDVI) from 1982 to 2010 was extracted from the NDVI3g GIMMS (Global Inventory Modeling and Mapping Studies) dataset with a 4 km resolution (Pinzon et al., 2005). Moreover, monthly gross primary production (GPP) and Latent Heat or Evapotranspiration (ET) were extracted from a global dataset derived from upscaled eddy covariance data (Jung et al., 2011) for the period from January 1990 to December 2008 at 0.5 degree spatial resolution.

Climate and water balance variables. When available, measured mean annual and monthly precipitation, evapotranspiration, drainage and air temperature were added to the database. Due to inconsistencies and gaps in these measurements, in particular for precipitation and air temperature, monthly precipitation was also extracted for all sites for the period January 1990 to December 2008 from the Global Precipitation Climatology Centre (GPCC) dataset at a resolution of 0.5 degrees (Rudolf et al., 2010). Further, monthly air temperature at a height of 2 m, soil temperature and volumetric soil water content in three soil layers (0-0.07m, 0.07-0.28m and 0.28-1m) were extracted from the ERA interim dataset for the period 1990 to 2008. This dataset was obtained from the ECMWF Data Server. The resolution of these data was 0.75 degrees. Climate class for each site was determined via the Köppen-Geiger climate classification system (Kottek et al., 2006).

2.2 Pre-processing and statistical analysis

The data analysis focused on the potential controlling factors on site-to-site variability of DOC concentrations in soil solution. In order to relate the DOC concentrations with the set of drivers (Table S2), the median DOC concentration per site and per depth interval (organic layer, topsoil (0-20 cm), intermediate layer (20-40 cm) and subsoil (40-80 cm)) was taken to avoid the influence of outliers. Firstly, we used bootstrapping to test for statistical differences among ecosystem types including all sites (Table 2). Histosols are organic soils and behave differently from mineral soils that represent the bulk of the sites in this dataset. We therefore excluded Histosols from further comparison among forest types, pH classes, soil types, climate zones and latitude ranges. Secondly, we selected a subset of 83 Level II plots from the ICP Forests program based on the availability of all necessary predictor variables and used forward stepwise linear regression analysis (Hocking, 1976) to identify the most significant multivariate relationship between DOC concentrations and the predictor variables. Plots included in the 83 Level II sites subset are broadleaved deciduous and coniferous forests in the temperate and boreal zones (marked in bold in Table S1). Models with the highest explained variance (R^2) and the minimum root mean square error (RMSE) were selected. Co-linearity was checked with the Variation Inflation Factor (VIF) and Corrected Akaike's information criterion (AICc) was used to assess overfitting. The data were split into broadleaved and coniferous sites based on results from previous studies (Fröberg et al., 2011; Lu et al., 2012; Vestgarden et al., 2010) that indicate a difference in magnitude of DOC concentrations between vegetation types. For more information regarding the preparation of the dataset and the statistical analysis see Appendix S1.

Table 2. Distribution of sites across soil types, vegetation types and latitude zone. B: Boreal, Tem: Temperate, Tro: Tropical. Double values presented for forests are (# Coniferous / # Broadleaved)

	Forest			**Non_Forest mineral**			**Non_Forest organic**		
	B	**Tem**	**Tro**	**B**	**Tem**	**Tro**	**B**	**Tem**	**Tro**
Acrisol	-	-	-/2	-	-	-	-	-	-
Andosol	-	1/3	-/2	-	1	1	-	-	-
Arenosol	10/1	42/9	-	-	-	-	-	-	-
Cambisol	3/-	28/28	-	-	5	-	-	-	-
Ferralsol	-	-	-/5	-	-	2	-	-	-
Gleysol	-	3/8	-	-	1	-	-	-	-
Histosol	-	1/-	-	-	-	-	-	28	-
Leptosol	2/-	2/1	-	-	1	-	-	-	-
Luvisol	-	11/15	-	-	2	-	-	-	-
Podzol	22/1	58/11	-	1	2	-	-	1	-
Regosol	4/-	8/2	-	-	-	-	-	-	-
Others[1]	-	7/14	1/-	-	1	-	-	-	-
No Data	2/-	7/7	1/2	-	9	-	-	-	-

[1] *“Others” category includes the following soil types (number of sites in brackets for each soil type): Albeluvisol (1), Alisol (4), Anthrosol (3), Calcisol (1), Fluvisol (1), Lixisol (1), Planosol (1), Stagnosol (5), Umbrisol (5), Vertisol (1).*

3 Results

3.1 Variation in DOC concentration across ecosystem types, soil types and climate zones.

3.1.1 Effect of ecosystem type.

DOC concentrations were higher for non-forest sites located on organic soils than for forest and non-forest sites on mineral soils ($p<0.05$, Figure 1a, Table S3). DOC concentrations substantially decreased with increasing depth in forests (Figure 1b), while in organic soils (mainly peat) the opposite was observed (Figure 1a). Non-forest sites with mineral soils also exhibited decreasing DOC concentrations with increasing depth, albeit with lower DOC concentrations in the surface layer than in forest soils (Figure 1a). On average, broadleaved forests exhibited lower DOC concentrations than coniferous forests (23% lower, broadleaved DOC mean= 13 mg/l, 95% CI=11-17, n= 111; coniferous DOC mean= 17 mg/l, 95% CI= 15-19, n=219, Figure 1b), while the vertical distribution of DOC did not differ between coniferous and broadleaved forests (Figure 1b).

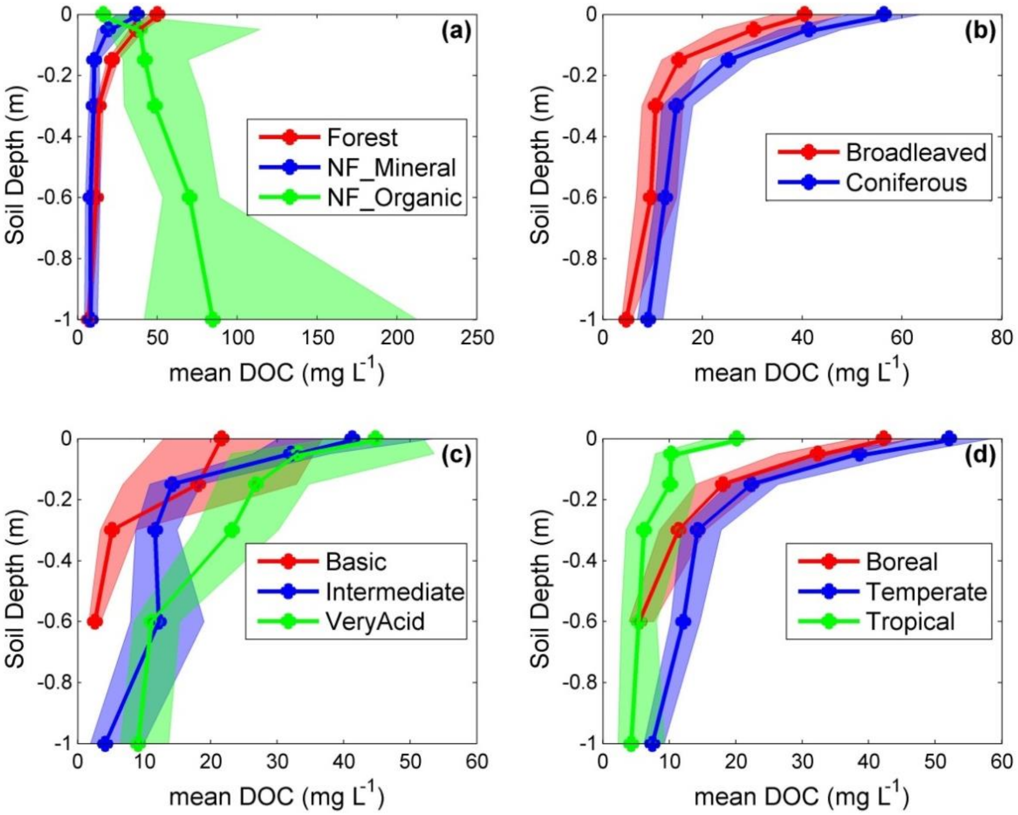


Figure 1. DOC profiles for a) Ecosystem type (NF: Non-forest), b) Forest type, c) pH classes with Basic (>6.2), Intermediate (5-4.2) and Very Acid (<4.2) and d) Latitude classification with Boreal (>60°), Temperate (35°-60°) and Tropical (<35°). Solid lines represent the bootstrapped line and shaded areas the bootstrapped 95% confidence interval. Points are placed in the mid-point of the depth interval.

3.1.2 Effect of soil type.

Among all soil types, Histosols (organic peatland soils), showed the largest DOC concentrations (Figure 2), with significant differences compared to other soil types from the 20-40 cm layer downwards (Table S3). The lowest DOC concentrations generally occurred in Andosols (volcanic soils) (Figure 2, Table S3). Podzols, Arenosols and Regosols showed intermediate DOC concentrations. We further observed that DOC concentrations were generally larger in very acid soils (pH($CaCl_2$) < 4.2) than in more basic soils, especially in the subsoil layers between 20 and 80 cm (Figure 1c).

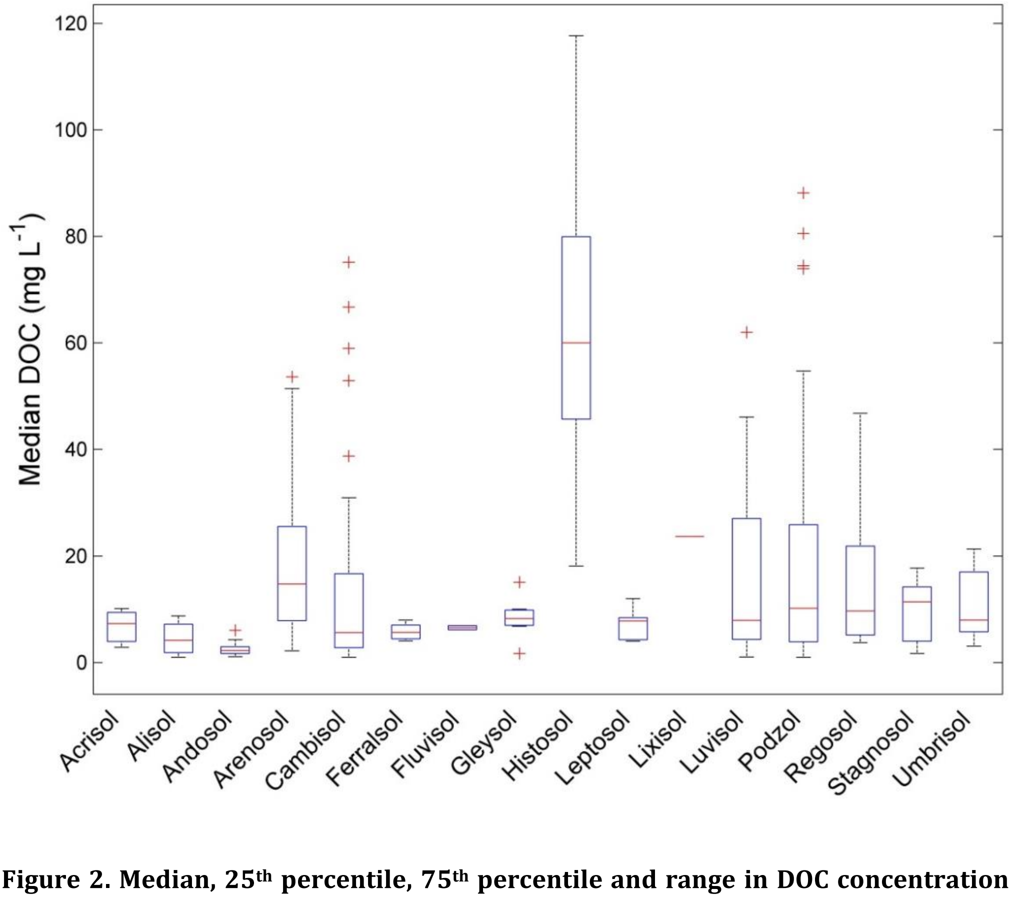


Figure 2. Median, 25th percentile, 75th percentile and range in DOC concentrations averaged (depth-weighted) over the soil profile, by soil type. Outliers are shown as crosses.

3.1.3 Effect of climate

DOC concentrations at lower latitudes (<35°) were significantly lower than in temperate regions (35°-60°) for all depths, except for the deepest layer ($p<0.05$, Figure 1d). Boreal (for simplicity here defined as sites located above a latitude of 60°N) and temperate sites showed similar DOC concentrations in soil solution in the upper soil layers, but not in the subsoil (40-80 cm), where DOC concentrations for the boreal sites were significantly lower ($p<0.05$, Figure 1d).

3.2 Site-to-site variability of DOC concentration in broadleaved and coniferous forests across Europe

Because coniferous forest soils exhibited larger DOC concentrations than broadleaved forests (see section 3.1) we separated both forest types for our model analysis of the controlling variables in the ICP Forests dataset. The stepwise linear models produced for both forest types were successful in attributing the variation in DOC concentrations in the mineral soil layers to their possible drivers (Figure 3, Table 3). For both forest types, only the model for DOC in the organic layer showed a poor fit (Figure 3a), although it was still statistically significant ($p<0.05$) for broadleaved forests (Table 3). At all depths, models for broadleaved forests showed a better fit than the models for coniferous forests. Overall, nitrogen-related variables (NH_4^+ in soil solution and C/N), as well as Fe and Al were most often selected as important drivers of variation in DOC concentrations across the sites (Figure 4, Table 3). The coefficients of the stepwise regressions are given in Table S4.

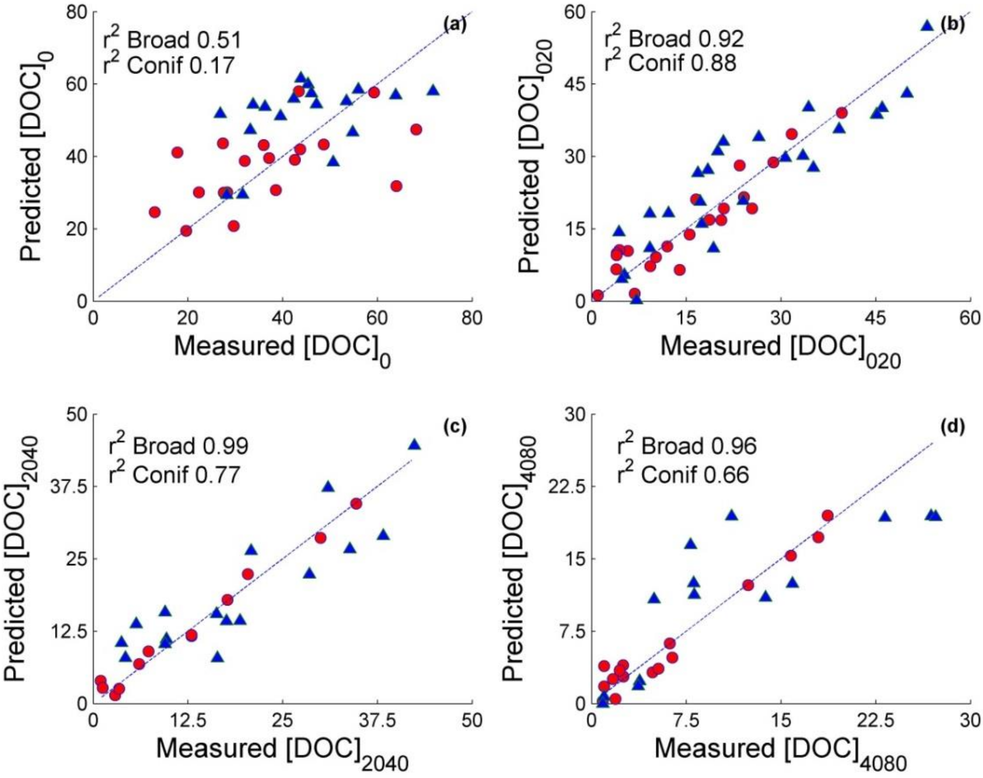


Figure 3. Predicted versus measured dissolved organic carbon (DOC) concentrations (mg L^{-1}) in soil solution in different soil depth intervals: a) organic layer (0 cm), b) topsoil (0-20 cm), c) intermediate layer (20-40 cm) and d) subsoil (40-80 cm). Predicted values have been calculated using stepwise linear regression. Circles represent the model for broadleaved (Broad) forests and triangles the model for coniferous (Conif) forests. The 1:1 line is shown. See Table 3 for additional information on the statistics.

Table 3. Dependent variable and final predictor variables, number of sites, R^2, RMSE and p value for each model

	CONIFEROUS					**BROADLEAVED**				
Dependent variable	Predictor variables	# sites	R^2	RMSE	p value	Predictor variables	# sites	R^2	RMSE	p value
Median DOC_0	Drainage summer (0.17)	21	0.17	20.44	0.06	C/N (0.27), LitterDecomp (0.25)	20	0.51	13.5	0.002
Median DOC_{0-20}	NH_4^+ in SS (0.18), ExchAl (0.17), avgDrainage (0.09), C/N (0.08), pH (0.07), ST (0.04), Fe in SS (0.02), Sand (0.017)	30	0.88	7.24	<0.0001	NH_4^+ in SS (0.25), Fe in SS (0.1), ExchAl (0.03), NDVI summer (0.03), avgET (0.02)	23	0.92	4.52	<0.0001
Median DOC_{20-40}	Fe in SS (0.25), Al in SS (0.13), Sand (0.09)	16	0.77	6.63	0.0003	NH_4 in SS (0.63),ET summer (0.065), avgPrec (0.02), C/N (0.003)	14	0.99	1.9	<0.0001
Median DOC_{40-80}	Prec in summer (0.6), NH_4 in SS (0.2)	14	0.67	5.78	0.0028	C/N (0.07), ExchFe (0.06), avgET (0.05), Temp autumn (0.05), LitterDecomp (0.03)	16	0.96	1.6	<0.0001

The predictor variables are listed in order of relative importance in the model and the partial R^2 (a measurement of the marginal contribution of one explanatory variable when all others are already included in the model) for each variable in the model is between parentheses. (SS= Soil Solution, LitterDecomp= categorical variable for litter decomposability based on site species, Prec= precipitation, Temp= Air Temperature, ST=Soil Temperature).

Different predictor variables were retained in the models explaining DOC concentrations across sites in the organic layer for broadleaved compared to coniferous forests. Vegetation characteristics, such as summer NDVI (a proxy of leaf production) and litter decomposability, were better correlated with the DOC concentrations under broadleaf than under conifer forests. In coniferous forests, on the other hand, DOC was strongly correlated to water-balance-related variables (Figure 4, Table 3).

DOC concentrations under conifer surface litter layers correlated negatively to drainage in summer, while DOC concentrations under broadleaf forest litter layers correlated best with C/N ratio of the forest floor and with litter decomposability (Figure 4). However, these models explained only 17% and 51% of the site-to-site variability in DOC concentrations in the organic layer for coniferous and broadleaved sites, respectively (Table 3).

The models for DOC concentrations in the upper layer of the mineral soil (0-20 cm) captured 88% (conifers) and 92% (broadleaf forests) of site-to-site variability (Table 3). For both coniferous and broadleaved models, NH_4^+ concentration in soil solution, together with exchangeable Al were the most important variables explaining variability in DOC concentrations in the upper layer of the mineral soil. While NH_4^+ was positively correlated with DOC, exchangeable Al was negatively correlated. C/N ratio also appeared important at coniferous sites, while Fe in soil solution was relevant in broadleaved forests. DOC in the intermediate soil layer (20-40 cm) was mainly positively related to soil solution variables, with ammonium concentration in soil solution having the highest partial R^2 in the model for broadleaved forests and Al and Fe concentrations in soil solution being more important in coniferous forests. The best explanatory variables in models for DOC concentrations in subsoil (40-80 cm) differed strongly between broadleaved and coniferous models (Table 3). Nevertheless, in the case of broadleaved forests, selected variables exhibited only very low partial R^2 (Table 3). In coniferous forests, mean precipitation in summer was the most important variable with a high partial R^2, and a model including precipitation in summer and NH_4 in soil solution explained 67% of the site-to-site variation in DOC at 40-80 cm depth in these forests (Figure 3d).

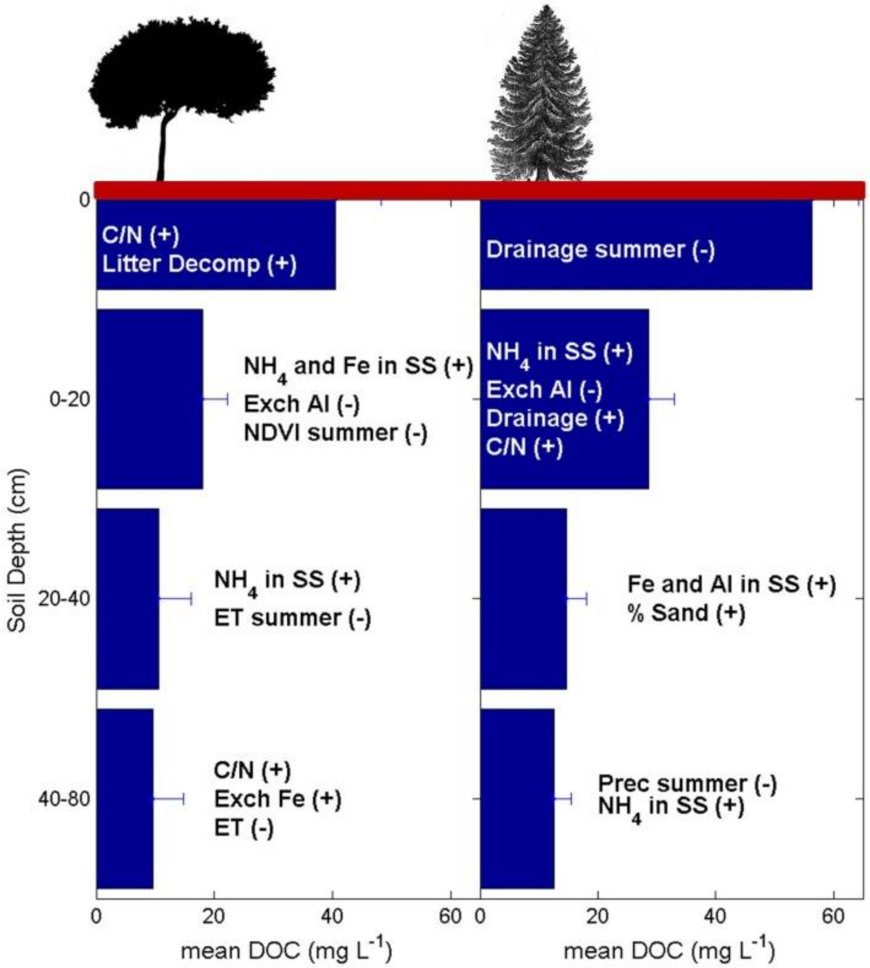


Figure 4. Most-important explanatory variables selected for the stepwise regression models. Linear models fitted for broadleaved and coniferous separated for four different layers (0 cm, 0-20 cm, 20-40 cm and 40-80 cm). The sign of the relationship is shown between parentheses. Mean DOC concentrations are based on all data. Most-important explanatory variables are based only on European data.

4 Discussion

4.1 Differences across ecosystem, climate and soil type

In total, 365 sites are included in this database, located primarily in the humid temperate zone, and with especially tropical sites being underrepresented (n= 13). Mediterranean and (semi-)arid sites were absent from the database. Although this is to be expected due to low potential for DOC production under these climate conditions, it hampers putting these fluxes into a global perspective. Furthermore, organic soils are scarce (29 organic soils with non-woody vegetation) compared to forests on mineral soils (311 forests). Only one forest was on organic soil. The first part of the analysis focusses on generalities across ecosystem types, climates and soil types, but due to the different sample size between soil types and vegetation cover (Table 2), discussions relying on this stratification will necessary confound the effects of soil and vegetation. Although this may appear as a shortcoming in the database, the spatial distribution of the sites correctly reflects our current knowledge basis. The second part of our analysis focuses on temperate and boreal forests only.

4.1.1 Effect of ecosystem type

Overall, we observed higher DOC concentrations in peatland soils than in mineral soils, and within ecosystems on mineral soils, higher concentrations (at least in the upper soil layers) in forests than in other vegetation types (Figure 1). However, our database contained only 26 non-forest ecosystems on mineral soils (compared to >300 forests), and no data for forests on organic soils, indicating that care needs to be taken when generalizing these differences.

The mean DOC concentrations recorded in our database (Figure 1 and 2, Table S3) are in the range reported in the literature. For example, we found an average DOC concentration of 50 mg L^{-1} (5th and 95th bootstrap confidence intervals: 45-56 mg L^{-1}) in the forest organic layers and a mean DOC concentration of 12 mg L^{-1} (5th and 95th confidence intervals: 10-14 mg L^{-1}) in the subsoil (40-80 cm). In their review, Michalzik et al. (2001) reported DOC concentrations in forest organic layers to range from 20 to 90 mg L^{-1} and from 2 to 30 mg L^{-1} in forest B horizons.

Our data compilation showed larger DOC concentrations for non-forest ecosystems on organic soils than for non-forest ecosystems on mineral soils (Figure 1, Table S3). This difference in DOC concentrations was in line with the reported values of 26-75 mg L^{-1} for organic soils and 2-42 mg L^{-1} for non-forests mineral soils in the UK (van den Berg et al., 2012). The one exceptionally high concentration in our dataset was observed for a cutover peatland undergoing restoration in New Zealand (Moore and Clarkson, 2007).

An early meta-analysis reported similar DOC concentrations for 42 broadleaved and coniferous forests, most of them temperate forests (Michalzik et al., 2001). These results were contradicted by other studies (Currie et al., 1996; Fröberg et al., 2011; Kalbitz et al., 2000; Khomutova et al., 2000) that, similar to our analysis, showed that DOC concentrations are on average lower in broadleaved forests than in coniferous forests. Including a larger number of forests, and covering a wider range of soils and climates, we found a consistent difference in DOC concentrations between forest types. However, while the temperate zone contains similar number of broadleaved and coniferous forests, tropical forests only contains broadleaved and boreal forests are mainly coniferous, thus, results should be carefully interpreted, as climate acts as a covariate. Nonetheless, restricting this analysis to the difference between conifers and deciduous forests in the temperate zone only, we can confirm the higher concentrations in the coniferous forests (Figure S2).

Concentration differences between upper soil layers in coniferous versus broadleaved forests have been attributed to the thicker litter layer in coniferous forests (Fröberg et al., 2011; Hansson et al., 2011), which in turn is caused by the slower decomposition rate of coniferous litter. It has been suggested that the thicker the litter layer, the longer the infiltrating water is in contact with the organic matter (Borken et al., 2011), thereby increasing the probability for organic molecules to dissolve as DOC. The thickness of the litter layer is largely determined by the prevailing climatic conditions and the quality of the litter, which is dependent on tree species. Decomposition of higher quality (lower C/N ratio) litters, typical for broadleaved forests, results in higher rates of DOC production (Cotrufo et al., 2013). However, DOC production and microbial decomposition of litter are competing pathways, and because higher litter quality also stimulates microbial processing, proportionally less DOC remains in soil solution in broadleaved forests.

Overall, our data compilation thus confirms that since the review of Michalzik et al. (2001), the range of DOC concentrations in temperate forest ecosystems is well established. However, tropical forests and non-forest ecosystems in general are underrepresented in our database, so novel observations should preferentially focus on these ecosystems.

4.1.2 Effect of soil type.

Not surprisingly, we found the highest DOC concentrations in Histosols (Figure 2), which are highly organic soils in which high water levels reduce mineralization rates (Blodau, 2002), such that incompletely decomposed plant material remains in the soil and acts as a source of DOC. On the contrary, we found the lowest DOC concentrations in Andosols. Andosols typically have a high content of soil organic matter (SOM), but this SOM is protected against decomposition through absorption to the volcanic minerals, resulting in stabilized SOM that does not take part in decomposition, yielding low DOC production (Óskarsson et al., 2004). In general, the effect of soil type on the DOC concentrations is partly determined by soil texture and mineralogy (Schwendenmann and Veldkamp, 2005), which determines DOC sorption capacity and thus SOM stabilization potential.

We further observed that DOC concentrations in Histosols increased with increasing depth, which is opposite to most mineral soils. The depth-profile of DOC concentrations in Histosols probably results from two mechanisms that reduce DOC consumption with increasing depth. Firstly, decomposition rates and therefore DOC consumption may decrease with increasing depth following the increasingly anaerobic conditions in the deeper layers (Moore and Dalva, 2001; Vicca et al., 2009). Secondly, the residence time of water increases with depth: in lower layers of histosols, hydraulic conductivity is very low and, even though DOC production rates are also slow, this can lead to the buildup of DOC.

Our data compilation supports the idea that larger DOC concentrations are found in more acid soil solutions ((e.g. Clarke et al., 2005; Löfgren and Zetterberg, 2011); Figure 1c/Table S3)). This relationship may be explained by the enhanced dissolution of organo-metal complexes at low pH (Kalbitz et al., 2000). pH has a strong direct effect on the solubility of DOC due to its acid-base properties (Hruška et al., 2003), and also an indirect effect through its impact on microbial activity (shifting between bacteria dominated microbial community at high pH to fungi dominated at low pH), making it difficult to isolate the direct effect of pH on DOC concentrations.

4.1.3 Effect of climate.

The different climate zones reflect differences in temperature, precipitation and nutrient availability. If we assume that no DOC is leached or adsorbed, the final DOC concentration in a soil solution is the outcome of two offsetting processes that both depend on climate i.e. DOC production and DOC decomposition (Kalbitz et al., 2000). It has been proven that the CO_2:DOC-production ratio increases with warming, suggesting that, although DOC production increases with temperature, its mineralization is even more temperature sensitive (Moore et al., 2008). Accordingly, in the tropics high production is offset by high decomposition resulting in DOC concentrations below those observed in the temperate and boreal zone. Under boreal and artic conditions, both DOC production and decomposition are lower, but frozen conditions limit transport and dissolution of DOC by reducing the connectivity between soil organic matter and soil water (Laudon et al., 2012), resulting in slightly smaller DOC concentrations than in the temperate zone (Figure 1d).

In conclusion, the observed DOC concentration in a soil solution is the balance between DOC production and decomposition (largely driven by biological activity) and adsorption and desorption (largely determined by soil type). The four processes share a dependency on the climatic conditions. While we found a consistently higher DOC under coniferous forests than under broadleaved forests, the database heterogeneity complicates the separation of significant factors for different climates and, thus, the processes behind this vegetation effect remain largely hidden at global scale. For this reason, we conducted an analysis on a restricted dataset, including only forests (both coniferous and deciduous) from the temperate and boreal zone, obtained from one network using standardized methodologies (the ICP Forests network). This allowed us to attribute the main controlling factors of DOC variability between forest types for the temperate and boreal zones.

4.2 Site-to-site variability in DOC concentration under broadleaved and coniferous forests in Europe

The statistical models used here to predict the site-to-site variability of DOC in the mineral soil outperformed (R^2=0.9) those describing the variability of DOC in the organic layer (R^2=0.5 to 0.17). This was to be expected because the organic layer is more dynamic than the mineral layer, due to the former's more intense contact with the atmosphere and its higher dependence on abiotic processes, such as infiltration rates and moisture changes (Michalzik and Matzner, 1999; Schulze et al., 2011). Therefore, the higher variability in DOC concentration in the organic layer across sites may largely be due to its higher temporal variability, which was not captured in the models. Moreover, we had fewer predictors available for the organic layer and some important drivers, such as variability in throughfall inputs or type of herbaceous layer, are missing in the selected models for the organic layer.

4.2.1 Common controlling factors in European forests.

In the mineral soil solution, the site-to-site variability of DOC concentrations strongly correlated with nitrogen availability, especially to NH_4^+ in soil solution and to a lesser extent, soil C/N ratio, and aluminum- and iron-related soil variables (Table 3, Figure 4). We observed that high DOC concentrations in soil solutions correlated with high NH_4^+ concentrations for both coniferous and broadleaved forests. Historical N deposition may have strengthened this relationship over Europe, because Level II plots of the ICP Forests program have often been located in areas with high N deposition (Fischer et al., 2007), particularly in the temperate zone. The addition of N has been reported to increase DOC leaching in some studies (Bragazza et al., 2006; Findlay, 2005; Pregitzer et al., 2004). Although this has not always been observed in fertilization studies (Evans et al., 2008), it has been suggested that increased soil NH_4^+ results in incomplete degradation of lignin and lead to increased levels of soil phenolics and thus greater production of DOC (Pregitzer et al., 2004).

Our analysis confirmed that sites with low soil C/N ratios tend to exhibit low DOC at both regional (Kindler et al., 2011; van den Berg et al., 2012) and global scale (Aitkenhead and McDowell, 2000). Different mechanisms influencing both inputs and outputs of DOC may contribute to this. On the one hand, low C/N litter was suggested to increase microbial carbon use efficiency and decrease SOM decomposition (Cotrufo et al., 2013; Schimel and Weintraub, 2003), which could thus decrease DOC production from SOM as well as promote the complete microbial assimilation of DOC. This idea was confirmed also by Janssens et al (2010), who found that N deposition leads to a change in microbial community and reduces decomposition rates. On the other hand, when N is limiting, trees typically allocate relatively more carbon belowground, in the form of root exudates or root symbionts, (Vicca et al., 2012) and a part of this extra C can end up in the soil solution (Moorhead and Sinsabaugh, 2006), resulting in higher DOC inputs at sites with higher C/N ratios.

Exchangeable Al and dissolved Fe and Al were also found to be important for explaining DOC variability across European forest sites (Table 3). In soils with high contents of exchangeable Al, less DOC was found in the top mineral soil solution in both broadleaved and coniferous stands. This relationship can be explained by the promoting effect of Al^{3+} on the sorption of SOM to clay minerals (e.g., Theng, 1976). Elevated concentrations of dissolved Al^{3+} also promote the flocculation of DOC-metal complexes (Nierop et al., 2002). In part, the relationship between exchangeable Al and DOC concentrations is probably caused by a co-variation with pH: Large contents of exchangeable Al occur at pH < 4.5 and the solubility of SOM strongly decreases with pH (You et al., 1999). Moreover, sorption of DOC to mineral soil horizons showed a maximum at pH values around 4 (Ussiri and Johnson, 2004) due to the balance between increasing positive charge of Fe- and Al-(hydr)oxides with decreasing pH and increasing protonation of DOC. The positive correlation between dissolved Fe and DOC concentrations we found from our dataset was also reported for a Swiss forest catchment (Hagedorn et al., 2000). Their analysis revealed that the dissolution of Fe-(hydr)oxides under reducing conditions increases not only dissolved Fe concentrations, but also DOC concentrations as a consequence of the diminished sorptive retention of DOC. Overall, soil properties, particularly pH and sorption capacity of the subsoil, influence DOC concentrations in soil solution, independently of the standing forest type.

Sorption of DOC derived from topsoils leads to a stabilization of the retained DOC against mineralization and may contribute to accumulation of organic C in subsoils (Kalbitz et al., 2005). Unfortunately, repeated soil samplings, which could verify an accumulation of C, have been carried out mainly for agricultural soils and almost exclusively for topsoils (e.g., Bellamy et al., 2005). Significant increases of organic carbon stocks in the B-horizon of a beech forest suggest that DOC sorption contributes to the buildup of SOC stocks also in forest soils (Schrumpf et al., 2014). Therefore, DOC sorption plays an important role in soil C sequestration, with the amount of carbon that is retained in subsoils being determined by the subsoils available sorption capacity (Kindler et al., 2011).

4.2.2 Difference in controlling factors between broadleaved and coniferous forests

The difference between coniferous and broadleaved forests may be related either to a characteristic inherent to the forest type, or it may be related to covarying factors. For example, conifers, especially pines, are more often located on sandy soils and in cold climates, where DOC concentration is primarily determined by the water balance, as drainage and precipitation, and the physico-chemical characteristics of the soil, such as texture. The transport of DOC in sandy soils was reported to be dominated by the flow regime and macropore transport (Kalbitz et al., 2000), because fast water movement might reduce adsorption and microbial processing of DOC (Don and Schulze, 2008; Kaiser and Kalbitz, 2012). Accordingly, we hypothesize that differences in soil texture between coniferous and broadleaved forests may have contributed to the observed difference in the importance of precipitation and drainage in the models of DOC concentration (Table 3). Under this hypothesis, conifer trees (particularly pines) are associated with more sandy soils (which have lower water holding capacity), whereas broadleaved trees are associated with more silt and clay soils.

However, this separation between growth strategies is imperfect. Among the conifers, for example, pines are normally planted on soils with higher sand content, at lower altitudes and warmer conditions than spruces (Barnes et al., 1998). To better test this hypothesis, future studies examining the differences in factors controlling spatial variability should be performed at genus or even species-level.

Broadleaved forests, on the other hand, generally grow more on fine-textured soils that are more fertile. These conditions stimulate also decomposition rates – often reflected in higher soil respiration (Raich and Tufekcioglu, 2000; Wang et al., 2006) - owing to the importance of biotic factors in the models of DOC concentration, which may in turn be responsible for the lower DOC concentrations in broadleaved forests.

The difference in DOC concentration in soil solution among forest types should be kept in mind when modeling DOC production, transport and decomposition at large scales and for different ecosystem types. These results suggest that different model formulations will be needed to develop models of DOC production and transport for the different plant functional types.

5 Conclusions

We present a database that substantially extends the scope of previous studies on the variability of DOC concentrations in soil solution. Using this database, we found that on average DOC concentrations were 75 % lower in mineral than in organic soil and that temperate sites showed higher DOC concentrations than boreal and tropical sites. Further, DOC concentrations in soil solution were 23 % lower in broadleaved sites than in coniferous forests. Overall, N availability, as indicated by C/N and NH_4^+ in soil solution, played a key role for the site-to-site variability of DOC in European forests, possibly by controlling microbial activity. Al and Fe are also important determinants of DOC site-to site-variability, reflecting pH controls on DOC concentrations. Biotic factors (litter decomposability or NDVI) become more important in explaining DOC in broadleaved forests, whereas water balance (drainage or precipitation) is more important in coniferous sites. We hypothesize that broadleaved sites are commonly more fertile and productive, and exhibit higher SOM mineralization rates, resulting in smaller DOC concentrations measured in soil solution.

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CHAPTER 2

CHAPTER 2. Long-term trends in soil solution dissolved organic carbon (DOC) across European forests

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Abstract

Dissolved organic carbon (DOC) in soil solution is connected to DOC in surface waters through hydrological flows. Therefore, it is expected that long-term dynamics of DOC in surface waters reflects trends of DOC in the soil solution. However, a multitude of site-studies has so far failed to establish consistent trends in soil solution DOC whereas increasing concentrations in European surface waters over the past decades appear to be the norm, possibly a result from recovering from acidification. The objectives of this study were therefore to understand the long-term monotonic trends of soil solution DOC from a large number of European forests (ICP Forests Level II plots) and determine their main physico-chemical and biological controls. We applied trend analysis at two levels: 1) to the entire European dataset and 2) to the individual time series and related trends with plot characteristics, i.e., soil and vegetation properties, soil solution chemistry and atmospheric deposition loads. Analyses of the entire dataset provided evidence of an overall increasing trend in DOC concentrations in the organic layers, but, at individual plots and depths, there was no clear overall trend in soil solution DOC across Europe with temporal slopes of soil solution DOC ranging between -16.8% yr^{-1} and 23% yr^{-1} (median= 0.4% yr^{-1}). The non-significant trends (40%) outnumbered the increasing (35%) and decreasing trends (25%) across the 97 ICP Level II sites retained for analysis. By means of multivariate statistics, we found a positive relationship between DOC trends and mean NO_3^- deposition and a negative correlation with mean SO_4^{2-} deposition, but the magnitude of these relationships depended on the plot deposition history. While the attribution of increasing trends in DOC due to the reduction of SO_4^{2-} deposition could be confirmed in N-poorer forests, in agreement with observations in surface waters, this was not the case in N-richer forests. In conclusion, long-term trends of soil solution DOC reflected the interactions between drivers acting at local (soil and vegetation properties) and regional (atmospheric deposition of S and N) scale.

1 Introduction

Dissolved organic carbon (DOC) in soil solution is the source of much of the terrestrially derived DOC in surface waters (Battin et al., 2009; Bianchi, 2011; Regnier et al., 2013). Soil solution DOC in forests is connected to streams through different hydrological pathways: e.g. through superficial run-off or through infiltration, DOC leaches from the forest floor into the mineral soil and then moves down from the rooting zone to the groundwater (Mcdowell and Likens, 1988). Therefore, it could be expected that long-term dynamics of DOC in ecosystem soil solutions mirror those observed in surface waters.

Drivers related to climate change (temperature increase, precipitation change, atmospheric CO_2 increase), to the decrease in acidifying deposition or to land use change and management can individually or jointly explain trends in surface water DOC concentrations (Evans et al., 2012; Freeman et al., 2004; Oulehle et al., 2011; Sarkkola et al., 2009; Worrall and Burt, 2004). Increasing air temperatures warm the soil and thus stimulate soil organic matter (SOM) decomposition through greater microbial activity (Davidson and Janssens, 2006; Hartley and Ineson, 2008; Kalbitz et al., 2000). Other drivers, such as increased atmospheric CO_2 and accumulation of atmospherically deposited nitrogen, are thought to increase the sources of DOC (i.e., root exudates, litterfall) by enhancing primary plant productivity (Sucker and Krause, 2010). Changes in precipitation and land use (e.g. draining of peatlands, changes in forest management or grazing systems) may alter the flux of DOC leaving the ecosystem, but no consistent trends in hydrology or land use changes were detected in areas where increasing DOC trends have been observed (Monteith et al., 2007).

Recent focus was mainly on the decreasing acidifying deposition as an explanatory factor for the increase in DOC concentrations in surface waters in Europe and North America by means of decreasing ionic strength (Hruška et al., 2009) and increasing pH of soil solution and the consequent increase in DOC solubility (Evans et al., 2005; Haaland et al., 2010; Monteith et al., 2007). Although the hypothesis of an increase in surface water DOC due to recovery from past acidification was confirmed in studies of soil solution DOC in the UK and Northern Belgium (Vanguelova et al., 2010; Verstraeten et al., 2014), it is not consistent with trends in soil solution DOC concentrations measured in Finnish, Norwegian and Swedish forests (Löfgren and Zetterberg, 2011; Ukonmaanaho et al., 2014; Wu et al., 2010). This inconsistency between soil solution DOC and stream dissolved DOC trends could suggest that DOC in surface water and soil solution responds differently to (changes in) environmental conditions in different regions (Akselsson et al., 2013; Clark et al., 2010; Löfgren et al., 2010). Alternatively, other factors such as tree species and soil type, may be co-governing organic matter dynamics and input, generation and retention of DOC in soils.

Trends of soil solution DOC vary not only among forests, but often also within the same site (Löfgren et al., 2010). Forest characteristics such as tree species composition, soil fertility, texture or sorption capacity may affect the response of soil solution DOC to environmental drivers, for instance, by controlling the rate of soil acidification through soil buffering and nutrient plant uptake processes (Vanguelova et al., 2010). Within a plot, depth variability is typically caused by different intensity of DOC production, transformation and sorption along the soil profile. Positive temporal trends in soil solution DOC (increasing concentrations over time) are frequently reported for the organic layers and shallow soils where production and decomposition processes control the DOC concentration (Löfgren and Zetterberg, 2011). However, no dominant trends are found for the mineral soil horizons, where physico-chemical processes, such as sorption, become more influential (Borken et al., 2011; Buckingham et al., 2008a). Furthermore, previous studies have used different temporal and spatial scales which may have further added to the inconsistency in the DOC trends reported in literature (Clark et al., 2010).

In this context, the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests, 2010) compiled a unique dataset containing data from more than 100 forest plots (Level II) which allows unraveling regional trends in soil solution DOC in forests at European scale, and statistical analysis of the drivers behind these regional trends. For these plots, long-term measurements of soil solution DOC are available, as well as information on aboveground biomass, soil properties and atmospheric deposition of N and S, collected using a harmonized sampling protocol across Europe. This dataset has previously been used to investigate the spatial variability of DOC in forests at European scale (Camino-Serrano et al., 2014), but an assessment of the temporal trends in soil solution DOC using this large dataset has not been attempted so far. The main objective of this study was to understand the long-term temporal trends of DOC concentrations in soil solution measured at the ICP Forests Level II plots across Europe. Following DOC trends in surface water, we hypothesized that temporal trends in soil solution DOC would also be positive, but with trends varying locally depending on plot characteristics. We further investigated whether plot characteristics, specifically climate, N and S deposition loads, forest type, soil properties and changes in soil solution chemistry can explain across-sites differences in DOC trends.

2 Materials and Methods

2.1 Data description

Soil solution chemistry has been monitored within the ICP Forests Programme since the nineties in most Level II plots. The ICP Forests data were extracted from the pan-European Forest Monitoring Database (Granke, 2013). A list of the Level II plots used for this study can be found in Appendix S1, Table S1. The methods for collection and analysis of soil solution used in the various countries (Switzerland: Pannatier et al. (2011); Flanders: Verstraeten et al. (2012); Finland: Lindroos et al. (2000); UK: Vanguelova et al. (2010), Denmark: Hansen et al. (2007)) follow the ICP Forests manual (Nieminen, 2011). Generally, lysimeters were installed at several fixed depth intervals starting at 0 cm, defined as the interface between the surface organic layer and underlying mineral soil. These depths are typically aligned with soil "organic layer", "mineral topsoil", "mineral subsoil" and "deeper mineral soil", but sampling depths vary among countries and even among plots within a country. Normally, zero-tension lysimeters are installed under the surface organic layer and tension lysimeters in the mineral soil, but zero-tension lysimeters are also used in mineral layers in some countries. Multiple collectors (replicates) were installed per plot and per depth to assess plots spatial variability. However, in some countries, samples from these replicates were often pooled before analyses or averaged prior to data transmission. The quality assurance and control procedures include the use of control charts for internal reference material to check long-term comparability within national laboratories as well as participation in periodic laboratory ring tests (e.g., Marchetto et al., 2011) to check the international comparability. Data were reported annually to the pan-European data center, checked for consistency and stored in the pan-European Forest Monitoring Database (Granke, 2013).

Soil water was usually collected fortnightly or monthly, although for some plots sampling periods with sufficient soil water for collection were scarce, especially in dry periods. After collection, the samples were filtered through a 0.45 µm membrane filter, stored below 4 °C and then analyzed for DOC, together with other soil solution ions and properties (NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{-2}, total dissolved Al^{3+}, total dissolved Fe, pH, electrical conductivity). The precision of DOC analysis differed among the laboratories. The coefficient of variation of repeatedly measured reference material was 3.7% on average. The time span of soil solution time series used for this study ranged from 1991 to 2011, although coverage of this period varied from plot to plot (Appendix S1, Table S1).

Soil properties, monthly bulk and throughfall atmospheric deposition of NO_3^-, NH_4^+ and SO_4^{2-}, meteorological variables and stem volume increment were also measured at the ICP Forests Level II plots. Stem volume growth was calculated by the ICP network from diameter at breast height (DBH), dead or alive status, and tree height which were assessed for every tree (DBH > 5 cm) within a monitoring plot approximately every five years since the early nineties. Tree stem volumes were derived from allometric relationships based on diameter and height measurements according to De Vries et al. (2003), accounting for species and regional differences. Stem volume growth (in m^3) between two consecutive inventories was calculated as the difference between stem volumes at the beginning and the end of one inventory period for living trees. Stem volume data were corrected for all trees that were lost during one inventory period, including thinning. Stem volume at the time of disappearance (assumed at half of the time of the inventory period) was estimated from functions relating stem volume of standing living trees at the end of the period *vs* volume at the beginning of the period. The methods used for collection of these data can be found in the Manuals of the ICP Forests Programme (ICP Forests, 2010). The soil properties used for this study were derived from the aggregated soil data of European ICP Forests Level II plots (Cools and De Vos, 2014).

Since continuous precipitation measurements are not commonly available for the Level II plots, we used the precipitation measurements extracted from the E-OBS gridded dataset to improve the temporal and spatial coverage and to reduce methodological differences of precipitation measurements across the sites. Precipitation measurements for the location of the Level II plots were extracted from the Observational station data of the European Climate Assessment & Dataset (ECA&D) and the ENSEMBLES Observations gridded dataset (E-OBS) (Haylock et al., 2008). The E-OBS dataset contains daily values of precipitation and temperature from stations data gridded at 0.25 degrees resolution. When E-OBS data was not available, it was gap-filled with ICP Forests precipitation values gained during deposition measurements, if available (open field, bulk deposition or throughfall deposition).

2.2 Data preparation

We extracted data only from plots whose data spanned time series of more than 10 years and included more than 60 observations of soil solution DOC concentrations of individual or groups of collectors. Outliers, defined as ± 3 interquartile range of the 25 and 75 quantiles of the time series, were removed from each time series to avoid influence of few extreme values in the long-term trend (Schwertman et al., 2004). Values under 1 mg L^{-1}, which is the detection limit for DOC in the ICP Level II plots, were replaced by 1 mg L^{-1}. After this filtering, 529 time series, from 118 plots spanning from Italy to Norway, were available for analysis. Soil solution, precipitation and temperature were aggregated to monthly data by the median of the observations in each month, and by the sum of daily values in the case of precipitation. Data of canopy throughfall and open field bulk inorganic N and S deposition measured at the Level II plots were also interpolated to monthly data (Waldner et al., 2014).

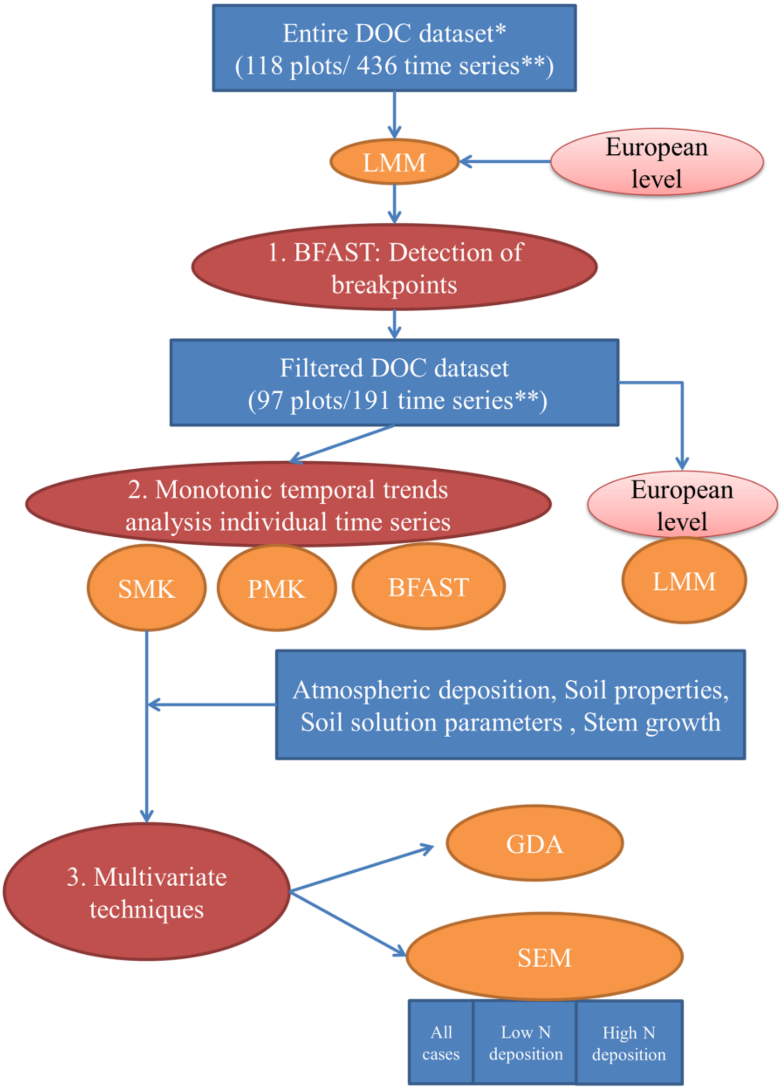
The Level II plots were classified according to their forest type (Broadleaved/Coniferous dominated), soil type (World Reference Base, Reference Soil Group (WRB 2006)), their stem growth (slow, < 6 m^3 ha^{-1} yr^{-1}, intermediate, 6 - 12 m^3 ha^{-1} yr^{-1}; and fast, > 12 m^3 ha^{-1} yr^{-1}) and soil pH (low, <4.2, intermediate, 4.2-5, high, >5). Plots were also classified based on throughfall N deposition level, defined as: high deposition (HD, >15 kg ha^{-1} yr^{-1}), medium deposition (MD, 5 - 15 kg ha^{-1} yr^{-1}), and low deposition (LD, <5 kg ha^{-1} yr^{-1}) and throughfall SO_4^{2-} level, defined as: high deposition (HD, >6 kg ha^{-1} yr^{-1}), and low deposition (LD, < 6 kg ha^{-1} yr^{-1}).

2.3 Statistical methods

The sequence of methods applied is summarized in Figure 1. The analysis of temporal trends in soil solution DOC concentrations was carried out at two levels: 1) at the European level and 2) at the plot scale in each individual time series. While the first analysis allows an evaluation of the overall trend in soil solution DOC at continental scale, the second analysis indicates whether the observed large scale trends are also occurring at local scales, and tests if local trends in DOC can be attributed to certain driver variables.

Linear mixed-effects models (LMM) were used to detect the temporal trends in soil solution DOC concentration at the European scale (Figure 1). For these models, the complete ICP Forests dataset was used. For the trend analysis of individual time series, however, we focused on the investigation of the potential long-term trends in soil solution DOC at European forests that show monotonicity. Therefore, DOC time series were first analyzed using the Breaks For Additive Seasonal and Trend (BFAST) algorithm to detect the presence of breakpoints (Verbesselt et al., 2010) and the time series showing breakpoints were discarded (see Appendix S2.2.) (Figure 1). The raw time series and their trends and breakpoints analyzed using the BFAST analysis can be visualized in Appendix S5. Then, monotonic trend analyses were carried out using the Seasonal Mann Kendall (SMK) test for monthly DOC concentrations (Hirsch et al., 1982; Marchetto et al., 2013). Partial Mann Kendall (PMK) test was also used since it allows to test the influence of precipitation as a co-variable to detect if the trend detection might be due to a DOC dilution/concentration effect (Libiseller and Grimvall, 2002). Moreover, LMMs were performed again with the filtered dataset to compare results with and without time series showing breakpoints (Figure 1).

For this study, five depth intervals were considered: the organic layer (0 cm), topsoil (0-20 cm), intermediate (20-40 cm), subsoil (40-80 cm) and deep subsoil (> 80 cm). The slopes of each time series were standardized by dividing them by the median DOC concentration over the sampling period, aggregated to a unique plot-soil depth slope and classified by the direction of the trend as significantly positive (P, $p < 0.05$), significantly negative (N, $p < 0.05$) and non-significant (NS, $p \geq 0.05$). When there was more than one collector per depth class, the median of the slopes was used when the direction of the trend (P, N or NS) was similar. When the different trends at the same plot-soil depth combination were either P and NS, or N and NS, it was marked as "Weighted positive" and "Weighted negative" to indicate that there was potential predominant direction of the trend but with less significance. Trends for soil solution parameters (NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{-2}, total dissolved Al^{3+}, total dissolved Fe, pH, electrical conductivity), precipitation and temperature were calculated using the same methodology as for DOC. Finally, we performed two multivariate statistical analyses, General Discriminant Analysis (GDA) and Structural Equation Models (SEM), to investigate the main factors explaining differences in DOC trends among the selected plots (Figure 1). All the statistical analysis were performed in R software version 3.1.2 (R Core Team, 2014) using the "rkt" (Marchetto et al., 2013), "bfast01" (de Jong et al., 2013) and "sem" (Fox et al., 2013) packages, except from the GDA that was performed using Statistica 6.0 (StatSoft, Inc. Tule, Oklahoma, USA) and the LMMs that were performed using SAS 9.3 (SAS institute, Inc., Cary, NC, USA). More detailed information on the statistical methods used can be found in Appendix S2.



* Time series > 10 years and > 60 obs.
* Time series aggregated per soil depth

Acronym	Model	Type of analysis
LMM	Linear mixed-effects models	Temporal trends
BFAST	Breaks For Additive Seasonal and Trend	Analysis of breakpoints in time series
SMK	Seasonal Mann Kendall test	Monotonic temporal trends
PMK	Partial Mann Kendall test	Monotonic temporal trends
GDA	General Discriminant Analysis	Multivariate analysis
SEM	Structural equation Model	Multivariate analysis (direct/indirect effects)

Figure 1. Flow-diagram of the sequence of methods applied for analysis of temporal trends of soil solution DOC and their drivers.

3 Results

3.1 Overall soil solution DOC trends at European scale

First, temporal trends in DOC were analyzed for all the European DOC data pooled together by means of LMM models to test for the presence of overall trends. A significantly increasing DOC trend ($p<0.05$) in soil solution collected with zero-tension lysimeters in the organic layer was observed mainly under coniferous forest sites (Table 1). Similarly, a significantly increasing DOC trend ($p<0.05$) in DOC for soil solution collected with tension lysimeters was found in deep mineral horizon (>80cm) for all sites, but mainly for coniferous forest sites (Table 1). By contrast, non-significant trends were found in other mineral horizons (0-20 cm, 20-40 cm, 40-80 cm) by means of the LMM models. When the same analysis was applied to the filtered European dataset, i.e., without the time series including breakpoints (see section 3.2), fewer significant trends were observed: only an overall positive trend was found for DOC in the organic layer using zero-tension lysimeters, again mainly under coniferous forest sites but no statistically significant trends were found in the mineral soil (Table 1).

Table 1. Summary of temporal trends obtained with the linear mixed models (LMM) built for different forest types, soil depth intervals and collector types with the entire dataset (with breakpoints) and with the dataset without time series showing breakpoints (without breakpoints) and the Seasonal Mann Kendal tests (SMK). The table shows the relative slope (rslope in % yr-1), the number of observations (n) and the P value. For the SMK tests, the number of time series showing significant negative (N), non-significant (NS) and significant positive (P) trends are shown. LMMs for which no statistically significant trend was detected (p<0.1) are represented in grey and the LMMs for which a significant trend (p<0.05) was detected are in bold.

Forest type	Collector type	Layer	LMM (with breakpoints)			LMM (without breakpoints)			SMK (without breakpoints)			
			n	rslope	p value	n	rslope	p value	rslope	N	NS	P
All	TL	O	3133	6.75	*0.0782*	1168	-0.30	n.t.	-1.03 (±1.65)	1	3	1
		M02	19311	0.10	n.t.	8917	-1.06	n.t.	0.16 (±4.78)	17	29	21
		M24	7700	2.69	n.t.	3404	3.66	n.t.	0.6 (±9.03)	11	12	11
		M48	24614	0.95	n.t.	11065	0.80	n.t.	0.67 (±4.76)	22	30	32
		M8	9378	**6.78**	**0.0036**	3394	3.41	n.t.	1.007 (±8.79)	8	9	16
	ZTL	O	8136	**3.75**	**<0.001**	4659	1.63	*0.0939*	**1.7 (±4.28)**	3	16	8
		M02	3389	-0.54	n.t.	445	0.17	n.t.	-0.7 (±1.85)		3	1
		M24	739	0.36	n.t.							
		M48	654	-3.37	n.t.	336	1.05	n.t.	1.07 (±3.08)	1	2	1
		M8	118	1.39	n.t.							
B	TL	O	637	-5.96	n.t.	475	-0.17	n.t.	-0.3 (±0.9)	0	2	0
		M02	8397	3.07	*0.0764*	3104	0.51	n.t.	0.89 (±5.94)	4	7	10

		M24	2584	-0.05	n.t.	928	6.01	n.t.	1.03 (±11.31)	3	5	4
		M48	10635	-0.93	n.t.	4634	2.46	n.t.	1.51 (±5.31)	11	8	16
		M8	4354	-6.85	*0.0672*	1797	-0.10	n.t.	0.3 (±6.28)	4	5	6
	ZTL	O	4057	0.37	n.t.	1956	-0.90	n.t.	0.96 (±5.47)	2	7	3
		M02	608	0.26	n.t.	192	1.88	n.t.	2.72			1
		M24	94	**11.80**	**0.026**							
		M48	427	-2.84	n.t.				0		1	
		M8	34	**-36.18**	**<0.001**							
C	TL	O	2496	8.15	*0.0633*	693	1.33	n.t.	-1.06 (±2.25)	1	1	1
		M02	10914	-0.97	n.t.	5813	-1.60	n.t.	-0.04 (±3.98)	13	22	11
		M24	5116	2.71	n.t.	2476	3.66	n.t.	-0.3 (±7.82)	7	7	8
		M48	13979	1.24	n.t.	6431	0.05	n.t.	0.3 (±4.32)	16	22	11
		M8	5024	**9.93**	**<0.001**	1597	7.58	n.t.	2.89 (±10.28)	4	4	10
	ZTL	O	4079	**3.59**	**0.0018**	2703	**3.09**	**0.0045**	**1.85 (±2.88)**	1	9	5
		M02	2781	-0.60	n.t.	253	-1.44	n.t.	-0.83 (±0.4)	0	3	0
		M24	645	0.23	n.t.							
		M48	227	-0.39	n.t.	251	-0.55	n.t.	2.14 (±3.66)	1	1	1
		M8	84	13.87	*0.0995*							

B: Broadleaved, C: Coniferous/O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm/TL: tension lysimeter, ZTL: zero-tension lysimeter/ n.t.: no trend detected.

3.2 Soil solution DOC trend analysis of individual time series

3.2.1 Comparison of methods of individual trend analysis

In order to assure that the overall detected trends were not influenced by breakpoints in the time series, we applied the BFAST analysis to select the monotonic time series for individual analysis of DOC trends. Time series with breakpoints represented more than 50% of the total time series aggregated by soil depth interval (245 out of 436). In total, 191 plot-soil depth combinations from 97 plots were analyzed after filtering out the time series showing breakpoints and 94% of the analyzed plot-depth combinations showed consistent trends among replicates collected at the same depth. In contrast, when considering also the time series with breakpoints, the trends calculated for plot-depth combinations agreed in only 75% of the cases, implying that the proportion of contradictory trends within plot-depth combinations increased from 6% in the dataset without breakpoints to 25% in the entire dataset (Figure 2). For both datasets, the majority of the trends were not statistically significant (44% and 41%, for the dataset with and without breakpoints, respectively). In other words, filtering the time series for breakpoints reduced the within-plot variability, while most of the plots showed similar aggregated trends per plot-depth combinations. For this reason, the results discussed from here on correspond only to the trends of monotonic (breakpoint filtered) time series of soil solution DOC concentrations.

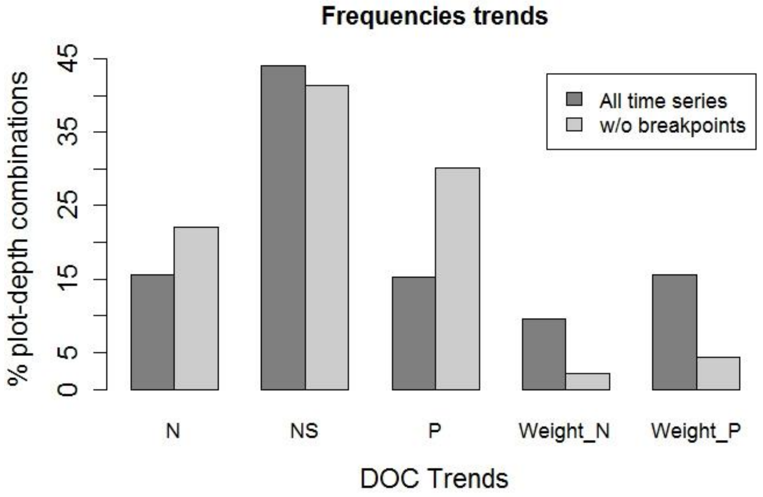


Figure 2. Percentage of plot-soil depth combinations for which negative (N), non-significant (NS), positive (P), negative and non-significant (Weight_N) and positive and non-significant (Weight_P) trends were found when 1) all the time series were used, 2) only time series without breakpoints (detected using the BFAST analysis) were used.

The results from the individual DOC trend analysis of monotonic time series showed that there was a good agreement between the three methods: BFAST, SMK and PMK (Table 2). The direction and significance of the trend agreed for 84.5% of the time series analyzed. For the majority of the remaining time series for which the trends did not agree, BFAST did not detect a trend when SMK and PMK did, thus, the latter two methods seemed to be more sensitive for trend detection than BFAST. Trends computed with SMK and PMK agreed very well.

For virtually all plots, including precipitation as a co-variable in the PMK test gave the same result as the SMK test, which indicates that precipitation (through dilution or concentration effects) did not affect the DOC trends. Dilution/concentration effect was only detected in four plots: one in France and 3 in Germany, but only for one collector in each plot (Appendix S1, Table S1).

Table 2. Median relative trend (rslope in % yr^{-1}) and interquartile range of rslope and number of time series with statistically significant ($p < 0.05$) positive trends (P), significant negative trends (N) or non-significant (NS) changes for trend analyses of DOC

Soil depth	SMK				PMK				BFAST			
	rslope	N	NS	P	rslope	N	NS	P	rslope	N	NS	P
O	1.18 (±3.37)	4	19	9	1.0 (±3.44)	4	18	9	1.15 (±3.47)	5	18	9
M02	0.04 (±3.41)	17	32	22	0.10 (±3.29)	16	33	21	-0.40 (±3.56)	19	34	18
M24	0.61 (±8.62)	11	12	11	-0.03 (±8.97)	10	11	11	0.83 (±9.31)	10	11	13
M48	1.01 (±4.79)	23	32	33	0.77 (±4.75)	22	31	33	0.59 (±6.32)	23	33	32
M8	1.18 (±9.39)	8	9	16	1.01 (±8.48)	8	11	14	1.75 (±9.59)	7	9	17

SMK: Seasonal Mann Kendall test, PMK: Partial Mann Kendall test, BFAST: Breaks For Additive Seasonal and Trend test/ O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm.

3.2.2 Soil solution DOC trends using the SMK test

Based on the results from the individual trend analysis using the SMK test, the temporal slopes of soil solution DOC concentration ranged from -16.8% yr^{-1} to 23% yr^{-1} (median= 0.4% yr^{-1}, interquartile range = 4.3% yr^{-1}). Among all the time series analyzed, there was a majority of not statistically significant trends (40%, 104 time series), followed by significantly positive trends (35%, 91 time series) and significantly negative trends (24%, 63 time series) (Table 2). There is, thus, no uniform trend in soil solution DOC in forests across a large part of the European continent. Although a slight tendency of increasing trends in central Europe and decreasing trends in North and South Europe could be observed (Figure 3), the uneven number of analyzed time series for each country (very few in Austria, Italy or Finland and many in Germany) made it difficult to draw firm conclusions about the spatial pattern of the trends in soil solution DOC in Europe.

Furthermore, the regional trend differences were inconsistent when looking at different soil depth intervals separately (Figure 4 and 5).

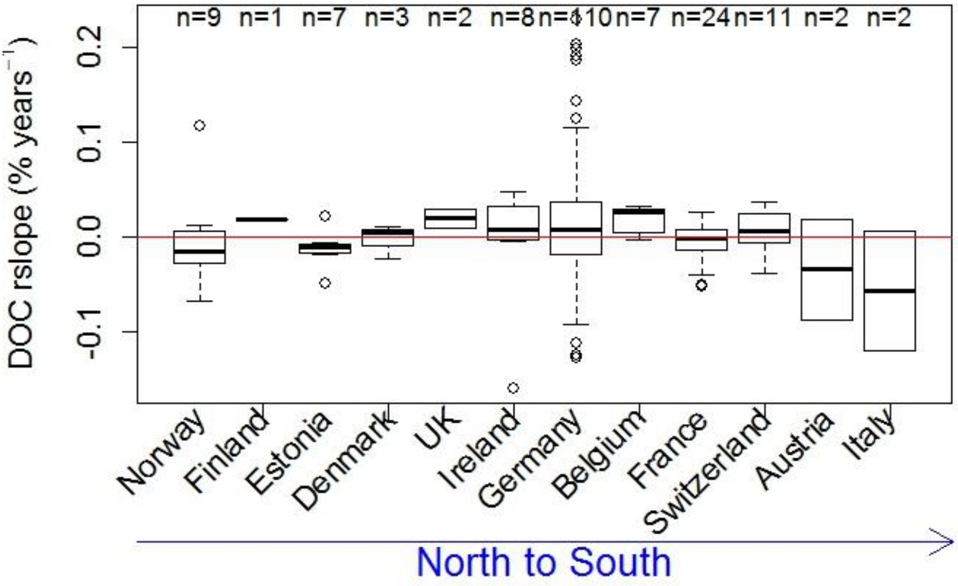


Figure 3. Relative slope of DOC trends calculated using the Seasonal Mann-Kendall test (SMK) for time series with more than 10 years of measurements and no breakpoints in 12 European countries, ranked from North to South.

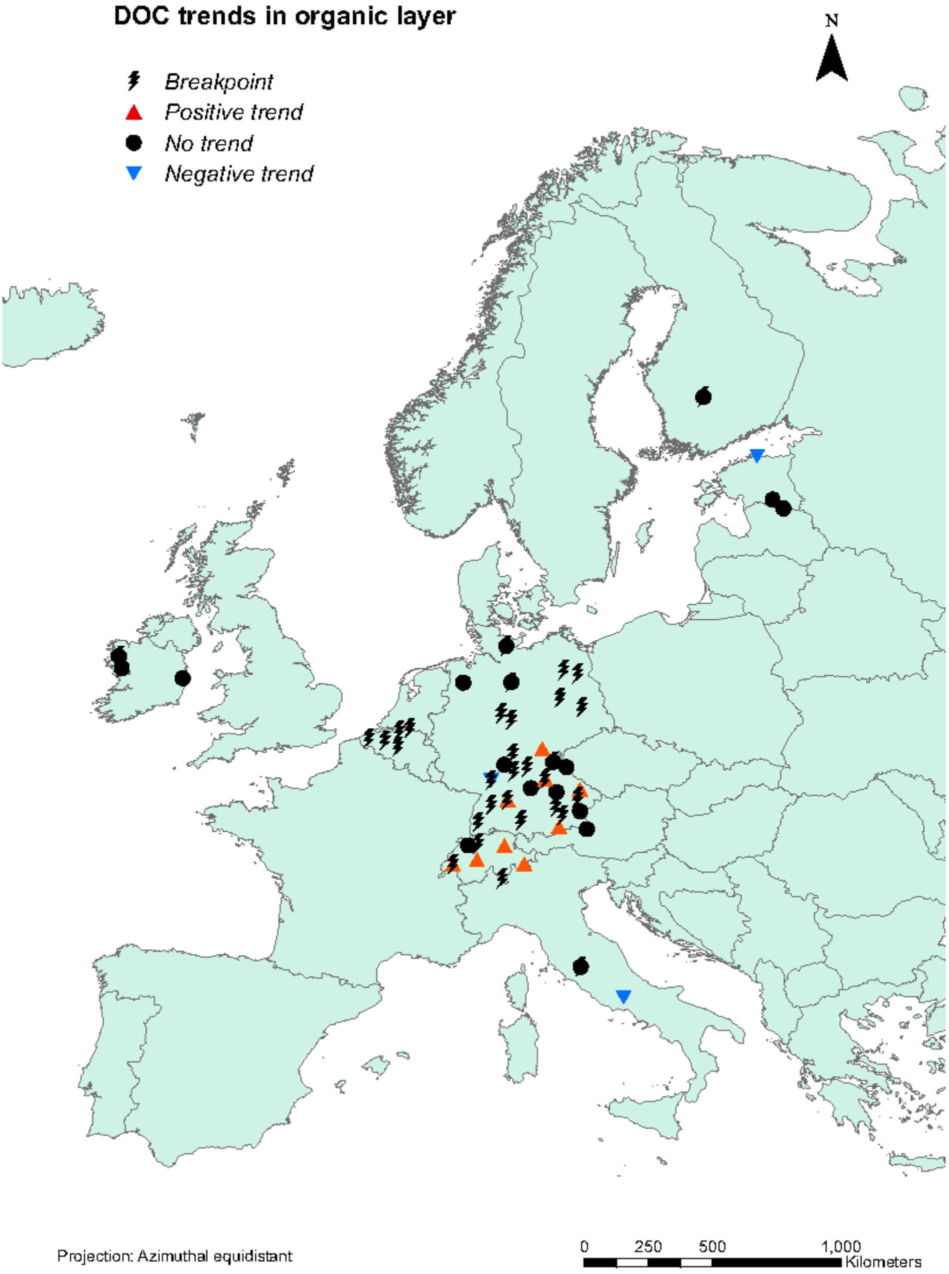


Figure 4. Directions of the temporal trends in soil solution DOC concentration in the organic layer at plot level. Trends were evaluated using the Seasonal Mann-Kendall test. Data span the period 1991-2011.

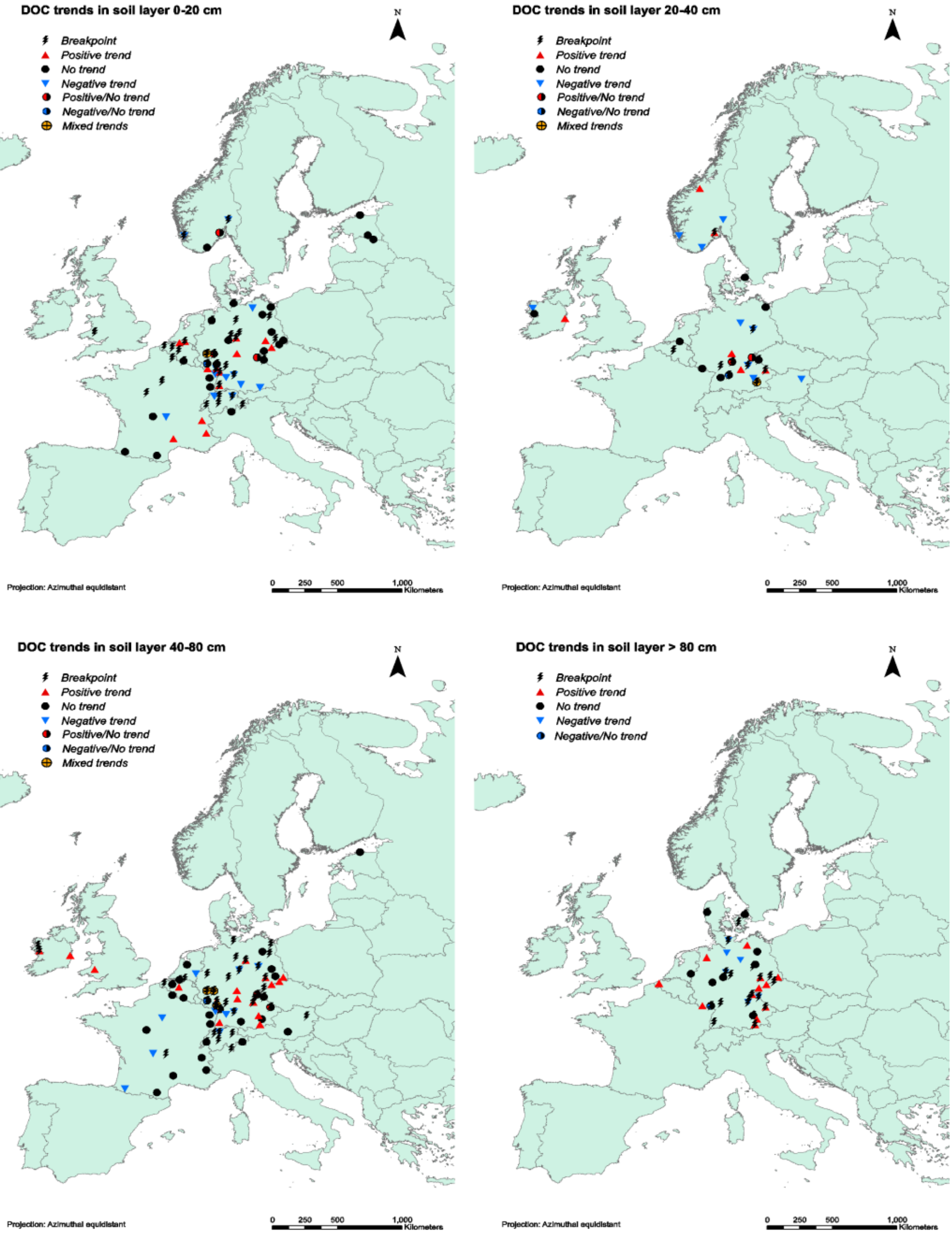


Figure 5. Directions of temporal trends in soil solution DOC concentration at plot level in the mineral soil for soil layers: a) topsoil (0-20 cm), b) intermediate (20-40 cm), c) subsoil (40-80 cm) and d) deep subsoil (> 80 cm). Trends were evaluated using the Seasonal Mann-Kendall test. Data span the period 1991-2011.

The variability in trends was high not only at continental scale, but also at plot level (Figure 6). We found consistent within-plot trends only for 50 out of the 97 sites. Moreover, some plots even showed different trends (P, N or NS) in DOC within the same depth interval, which was the case for 17 plot-depth combinations (16 in Germany and one in Norway), evidencing a high small-scale heterogeneity between collectors located at the same plot.

Trend directions often differed substantially among depths. For instance, in the organic layer, we found mainly non-significant trends and, when a trend was detected, it was more often positive than negative. Also in the subsoil (below 40 cm), non-significant and positive trends dominated (Table 2). Nevertheless, it is important to keep in mind that we could not test statistically if there was a real difference in DOC trends between depths as the set of plots differed between the different soil depth intervals. However, a visual comparison of trends for the few plots in which trends are evaluated for more than three soil depths showed that, at first sight, there was no difference in DOC trends between soil depths (Appendix S3, Figure S1).

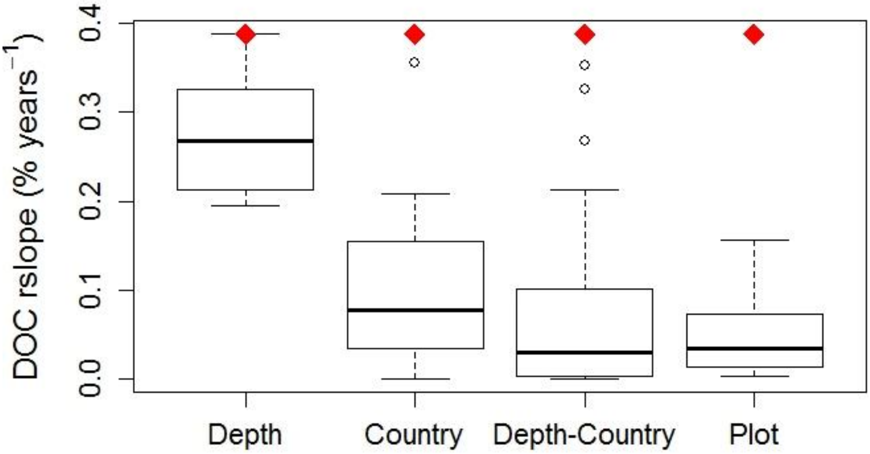


Figure 6. Range of relative slopes (max-min) for trends of DOC concentration in soil solution within each 1) Depth interval, 2) Country, 3) Depth interval per country, and 4) Plot. The boxplot shows the median, 25% and 75% quantiles (box), minimum and 1.5 times the interquartile range (whiskers) and higher values (circles). The red diamond marks the maximum range of slopes in soil solution trends in the entire dataset.

3.3 Factors explaining the direction and slopes of the soil solution DOC trends

A stratification of the forests based on forest type revealed no direct effect of forest type on the direction of the statistically significant trends in soil solution DOC (Figure 7C). Both positive and negative trends were equally found under broadleaved and coniferous forests ($\chi^2(1, N = 97) = 0.073$, $p = 0.8$). Increasing DOC trends, however, occurred more often under forests with a mean stem growth less than 6 m^3 ha^{-1} yr^{-1} during the study period, whereas decreasing DOC trends were more often associated to forests with a mean stem growth between 6 and 12 m^3 ha^{-1} yr^{-1} ($\chi^2(2, N = 53) = 5.8$, $p = 0.05$) (Figure 7D).

Mean annual throughfall SO_4^{2-} and N deposition both had a significant effect on the direction of the trends in soil solution DOC (Figure 7). Increasing trends were more frequent in forests with high or medium N deposition than in forests with low N deposition where only decreasing trends were found ($\chi^2(2, N = 57) = 9.58$, $p = 0.008$). Also throughfall SO_4^{2-} deposition significantly influenced the direction of the trend in soil solution DOC, with more positive trends found for sites with high mean throughfall SO_4^{2-} deposition (> 6 kg ha^{-1} yr^{-1}) than for sites with low SO_4^{2-} deposition ($\chi^2(1, N = 57) = 8.75$, $p = 0.003$). Correspondingly, the probability of positive trends in soil solution DOC was higher at high N deposition loads (Figure 8A). For SO_4^{2-} deposition loads, there were also relatively more positive trends at high and medium SO_4^{2-} than at low SO_4^{2-}, although this pattern is less clear (Figure 8B).

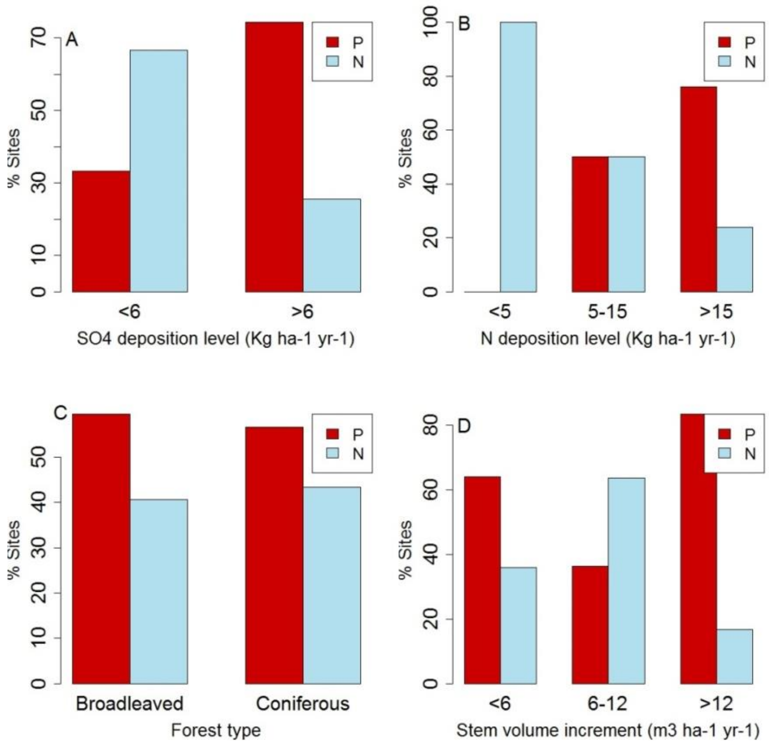


Figure 7. Percentage of occurrence of positive and negative trends in soil solution separated by A) throughfall SO_4^{2+} deposition level (kg ha^{-1} yr^{-1}), B) throughfall N deposition level (kg ha^{-1} yr^{-1}), C) Forest type and D) Stem volume increment (m^3 ha^{-1} yr^{-1}).

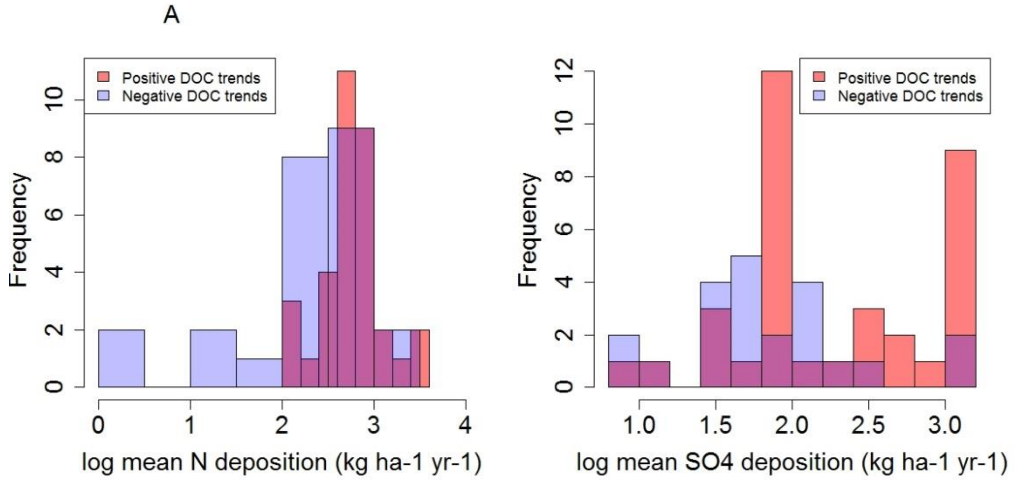


Figure 8. Histograms for log-transformed mean throughfall SO_4^{2-} deposition (A) and for log-transformed mean total N deposition (B) for positive and negative trends of DOC.

Regarding soil properties, more than half of the plots showing a consistent increasing DOC trend at all the evaluated soil depth intervals were located in Cambisols, (6 out of 11 plots), which are rather fertile soils, whereas plots showing consistent negative trends covered six different soil types. Other soil properties, like clay percentage, cation exchange capacity or pH, did not differ between sites with positive and negative DOC trends (Table 3). It is remarkable that trends in soil solution pH, Mg^{2+} and Ca^{2+} concentrations were similar across sites with both positive and negative DOC trends. Soil solution pH is distinctly increasing in almost all the sites, while Ca^{2+} and Mg^{2+} are markedly decreasing (Table 3). However, we found evidence that the soil acidity controlled the SO_4^{2-} deposition effect on the trends of DOC in soil solution (Figure 9). In very acid soils, a higher mean SO_4^{2-} deposition enhanced the increase of soil solution DOC, while in less acidified soils, there was no clear effect of mean SO_4^{2-} on DOC trends. Finally, no significant correlations were found between trends in temperature or precipitation and trends in soil solution DOC, with the exception of the trends in temperature in the soil depth interval 20-40 cm ($r = 0.47$, $p = 0.03$).

Table 3. Site properties for the 13 plots for which consistent negative trends (N) were found and for the 12 plots for which consistent positive trends (P) were found. Soil properties (Clay percentage, C/N ratio, pH($CaCl_2$), cation exchange capacity (CEC)) are for the soil depth interval 0-20 cm. Mean atmospheric deposition (N and SO_4^{2-}) is throughfall deposition. When throughfall deposition was not available, bulk deposition is presented with an asterisk. Trends in soil solution pH, Ca^{2+} and Mg^{2+} concentrations were calculated using the Seasonal Mann-Kendall test.

Country	Code Plot	Trend	Species	Soil Type (WRB)	Clay (%)	C/N	pH	CEC	MAP (mm)	MAT (°C)	N depos. (Kg ha^{-1} yr^{1})	SO_4^{2-} deposition (Kg ha^{-1} yr^{-1})	slope pH (%yr^{-1})	slope Ca^{2+} (% yr^{-1})	slope Mg^{2+} (% yr^{-1})
France	1_30	N	Quercus petraea	Cambic Podzols	3.79	16.8	3.96	1.55	567	11.9	7.28	4.25	0.10	-0.90	-1.00
France	1_41	N	Picea abies	Mollic Andosols	23.9	16.6	4.23	7.47	842	10.6	4.43	4.15	0.00	-1.10	-1.30
France	1_84	N	Pinus sylvestris	Cambic Podzols	4.09	22.8	3.39	4.07	774	10.5	7.66	3.77*	0.50	2.00	1.00
Germany	4_303	N	Picea abies	Haplic Podzols	17.3	16.5	3.05	8.77	1180	9.10	17.5		0.40	-5.00	-2.00
Germany	4_304	N	Fagus sylvatica	Dystric Cambisols	21.3	17.7	3.63	6.14	1110	6.20	16.4		0.00	-3.00	-0.40
Germany	4_308	N	Quercus robur		3.80	16.5	3.41	1.63	816	9.20	14.2*		0.00	-5.00	-2.00
Germany	4_802	N	Picea abies	Cambic Podzols	6.00	25.7	3.35	4.33	836	11.9	25.2	13.2	0.50	-2.40	-1.50
Germany	4_1502	N	Pinus sylvestris		4.40	23.8	3.78	2.35	593	9.40	9.79	5.66		-16.0	-14.0
Austria	14_9	N	Fagus	Eutric	20.1	12.8	5.26	25.9	679	10.8		3.80*	0.40	-1.50	-0.60

Country	Code Plot	Trend	Species	Soil Type (WRB)	Clay (%)	C/N	pH	CEC	MAP (mm)	MAT (°C)	N depos. (Kg ha^{-1} yr^{1})	SO_4^{2-} deposition (Kg ha^{-1} yr^{-1})	slope pH (%yr^{-1})	slope Ca^{2+} (% yr^{-1})	slope Mg^{2+} (% yr^{-1})
			sylvatica	Cambisols											
Norway	55_14	N	Picea abies	Cambic Arenosols	9.83	25.4	3.46				14.7	21.9	0.10	-1.70	-3.30
Norway	55_19	N	Picea abies		10.5	18.7	3.79		836	4.60	1.54	2.61	0.50	-7.00	-4.00
Italy	5_1	N	Fagus sylvatica	Humic Acrisols	3.14	12.2	5.32	31.6	670	23.3			-0.30	-10.0	-10.0
Switzerland	50_15	N	Abies alba	Dystric Planosols	17.6	14.7	3.73	7.76	1201	8.90	15.1	4.67	-0.10	-13.0	-4.00
Belgium	2_11	P	Fagus sylvatica	Dystric Cambisols	3.54	17.7	2.81	6.22	805	11.0	18.7	13.2	0.40	-11.0	-8.00
Belgium	2_21	P	Fagus sylvatica	Dystric Podzoluvisols	11.2	15.4	3.59	2.41	804	10.3	16.8	13.2	0.00	-9.00	-5.00
Germany	4_306	P	Fagus sylvatica	Haplic Calcisols					782	10.2	13.9		0.50	2.00	2.00
Germany	4_707	P	Pinus sylvestris	Dystric Cambisols					704	10.7	18.3	8.49	0.00	-10.0	-2.00
Germany	4_806	P	Picea abies	Dystric Cambisols					1349	8.30	23.0	6.81	0.30	-7.00	-6.00
Germany	4_903	P	Fagus sylvatica	Dystric Cambisols					905	9.60			0.20	-5.00	-3.00

Country	**Code Plot**	**Trend**	**Species**	**Soil Type (WRB)**	**Clay (%)**	**C/N**	**pH**	**CEC**	**MAP (mm)**	**MAT (°C)**	**N depos. (Kg ha^{-1} yr^{1})**	**SO_4^{2-} deposition (Kg ha^{-1} yr^{-1})**	**slope pH (%yr^{-1})**	**slope Ca^{2+} (% yr^{-1})**	**slope Mg^{2+} (% yr^{-1})**
Germany	4_920	P	Picea abies	Dystric Cambisols					908	8.90			-1.00	-6.00	-0.50
Germany	4_1402	P	Picea abies	Haplic Podzols	8.65	26.2	3.24	9.04	805	6.90	13.5	24.3	1.20	-6.00	9.00
Germany	4_1406	P	Quercus petraea	Eutric Gleysols	15.9	23.1	3.59	6.67	670	8.80	15.3	6.23	1.11	-4.00	-3.00
United Kingdom	6_922	P	Picea sichensis	Umbric Gleysols	34.8	15.6	3.31	10.8	1355	9.50			0.40	-9.00	2.00
Switzerland	50_2	P	Picea abies	Haplic Podzols	14.7	18.3	3.17	3.59	1473	4.40			-0.80	-5.00	-3.00
Norway	55_18	P	Pinus sylvestris		3.05	29.5	3.69		1175	0.35		2.40	-0.90	0.00	0.00

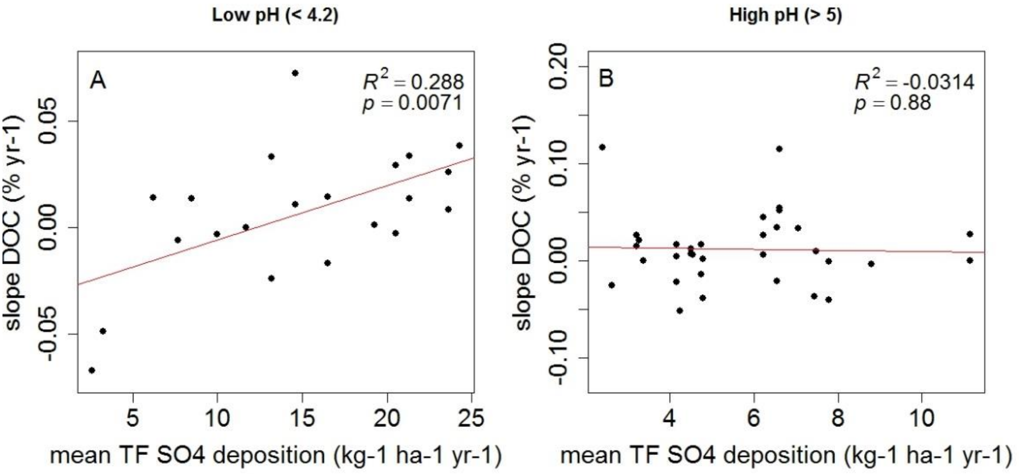


Figure 9. Relationship between mean throughfall SO_4^{2-} deposition and relative slopes of DOC for very acid soils (pH in soil solution < 4.2) (A) and no-acid soils (pH in soil solution > 5) (B).

Results from the General Discriminant Analysis showed a marginally significant separation of plot-soil depth combinations with negative and positive DOC trends (p = 0.06) (Figure 10). Median soil solution conductivity, median soil solution NO_3^- and median soil solution SO_4^{2-} were significant in the model and thus played an important role in the distinction between positive and negative DOC trends (Table 4). The fitted GDA model was able to predict 63.1% of the variance in DOC trends within the first axis (Figure 10).

Table 4. Statistics (Wilks' Lambda and p value) of the General Discriminant Analysis among groups of plot-soil depth combinations with different trend in DOC during the last years conducted with 10 different soil solution and deposition variables as independent continuous variables and different soil horizons as categorical independent variable. Bold type indicates a significant effect of the variable in the model ($p < 0.05$)

Independent variables	**Wilks' Lambda**	***p* value**
pH	0.913	0.158
log(NH4_TF)	0.973	0.575
log(NO3_BD)	0.944	0.308
log(SO_4^{2-}_BD)	0.920	0.182
log(SO_4^{2-}_SS)	0.857	**0.042**
log(NO3_SS)	0.814	**0.015**
log(NH4_SS)	0.947	0.331
log(AL_SS)	0.961	0.434
log(FE_SS)	0.930	0.224
log(CONDUCTIVITY_SS)	0.807	**0.012**

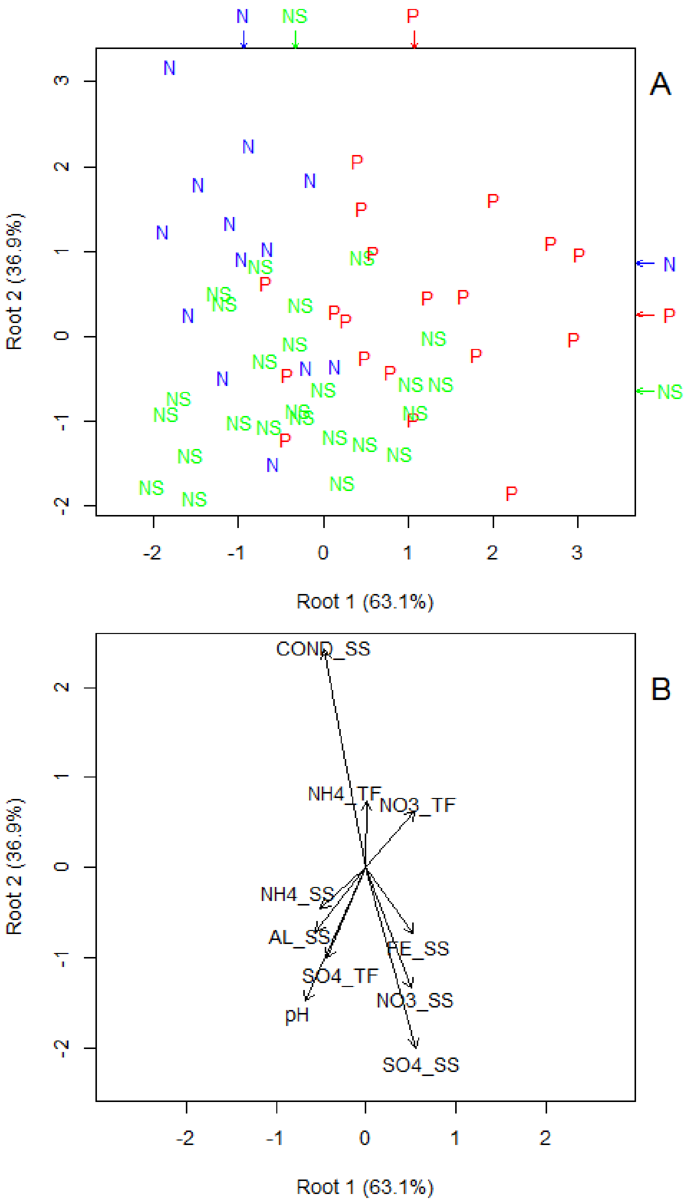


Figure 10. Biplot representing the scores for the single plot-soil depth combinations for the two roots of the General Discriminant Analysis (GDA). (B) Biplot representing the standardized canonical discriminate function coefficients for the two roots of this GDA. The GDA is generated to explain the variance among groups of plot-soil depth combinations with different trend in soil solution DOC (N for Negative trend, P for positive trend and NS for non-significant trends) during the last years conducted with 7 soil solution variables (pH, NH4_SS, NO3_SS, FE_SS, SO4_SS, COND_SS, AL_SS) and three throughfall deposition variables (NH4_TF, NO3_TF, SO4_TF) as independent continuous variables and different soil layers as categorical independent variable.

To test whether the influence of stem growth and soil solution chemistry was related to the effect of SO_4^{2-} and/or NO_3^- deposition on soil solution DOC, we applied structural equation models (SEM) to determine the capacity of these variables in explaining variability in the slope of DOC trends. We evaluated the influence of both the annual mean (Kg ha^{-1} yr^{-1}) and the trends (% yr^{-1}) in deposition and soil solution parameters.

3.3.1 Effect of mean deposition and soil solution parameters

Firstly, we analyzed different models that could explain the DOC trends using the overall dataset. This analysis indicated both direct and indirect effects of the annual mean SO_4^{2-} and NO_3^- throughfall atmospheric deposition on the slopes of DOC trends. The SEM accounted for 32.7% of the variance in DOC trend slopes (Figure 11A). This model identified a significantly negative direct effect of SO_4^{2-} deposition on trends in soil solution DOC. On the other hand, throughfall NO_3^- deposition had a significantly positive direct effect on DOC trends slopes (Figure 11A).

The variables in the model that best explained temporal changes in DOC were the same for the forests with low and medium N deposition; for both groups, NO_3^- deposition and SO_4^{2-} deposition (directly, or indirectly through its influence on plant growth) influenced the trend in DOC (Figure 11B). Mean SO_4^{2-} deposition had again a significant negative effect on DOC slopes, while NO_3^- deposition had a significantly positive effect. The percentage of variance in DOC trend slopes explained by the model was 33 %. For the forests with high N deposition, however, we found no model for explaining the trends in DOC using the mean annual SO_4^{2-} and NO_3^- throughfall deposition.

3.3.2 Effect of trends in deposition and soil solution parameters

When the SEM is applied for the overall dataset using the trends in SO_4^{2-} and NO_3^- deposition instead of the mean values, a positive effect of trend in NO_3^- deposition and a negative effect of trend in SO_4^{2-} deposition were also apparent, but the latter was non-significant (Appendix S4, Figure S3A). However, the percentage of variance in DOC trend slopes explained by the model was much lower (16%). The SEM applied with the trends in SO_4^{2-} and NO_3^- throughfall deposition for forests with low and medium N deposition explained 24.4% of the variance of DOC trends, and showed a significantly negative effect of trends in SO_4^{2-} deposition on trends in DOC (Appendix S4, Figure S3B).

For the forests with high N deposition, the best model selected as explaining variables the relative trends in SO_4^{2-}, NO_3^- deposition and in median soil solution conductivity (% yr^{-1}) (Figure 11C). The relative trend slopes of NO_3^- were positively related to the DOC trend slopes. Also, both the trend slopes of SO_4^{2-} and NO_3^- deposition indirectly affected the trend slopes of DOC through an effect on the trends of soil solution conductivity, although acting in opposite directions: while trends in NO_3^- deposition negatively affected the trends on soil solution conductivity, trends in SO_4^{2-} deposition had a marginally significant positive effect on the trends on soil solution conductivity. The trends in conductivity, in turn, positively affected the trend slopes of DOC. The percentage of the variance in DOC trend slopes explained by the model was 25% (Figure 11C).

In summary, long-term trends in soil solution DOC were negatively related to mean SO_4^{2-} deposition (except for sites with high N deposition, where the effect of mean and trends of SO_4^{2-} deposition was not significant, Figure 11A and 11B versus 11C) and positively related to N deposition (Figure 11). Also, trends of soil solution DOC negatively correlated with trends of SO_4^{2-} deposition when the N deposition was low or intermediate (Appendix S4, Figure S3).

4 Discussion

4.1 Trend analysis of soil solution DOC in Europe

4.1.1 Are the many non-significant trends real?

Results show a predominance of non-significant trends in site-level DOC concentrations across the ICP Forest network. Measurement precision, strength of the trend and the choice of the method can all affect trend detection (Sulkava et al., 2005; Waldner et al., 2014). To detect a small trend either very long time series or very accurate and precise data are needed. Evidently, strong trends are easier to detect than weak trends. In general, it is very difficult to find statistically significant trends with a highly uncertain dataset as it is the ICP Forests. The quality of the data is assured within the ICP Forests by means of repeated ring tests that are required for all participating laboratories and the accuracy of the data has been improved considerably over eight years period (Ferretti and König, 2013; König et al., 2013). However the precision and accuracy of the dataset varies across countries and plots. By filtering out the breakpoints from the dataset and removing outliers, we improved the overall quality of the data, and thus guaranteed that the detected positive and negative trends were real at a 0.05 significance level. Nevertheless, we found a majority of non-significant trends. For these cases, we cannot state with certainty that DOC did not change over time: it might be that the trend was not strong enough to be detected, or that the data quality was insufficient for the period length available for the trend analysis (more than 9 years in all the cases). As an example, the mixed-effects models detected a positive trend in the organic layer, and while many of the individual time series measured in the organic layer also showed a positive trend, most were classified as non-significant trends (Figure 4). This probably lead to an underestimation of trends that individually might not be strong enough to be detected by the individual trend analysis, but that in addition to the other European data can slightly contribute to an overall trend of increasing DOC concentrations in soils of European forests.

The uncertainty in the interpretation of the non-significant trends is compensated by using the SMK and PMK tests applied to monthly data for the trend analysis, which can detect smaller trends than other trend analyses techniques applied to annual data (Marchetto et al., 2013; Waldner et al., 2014). In summary, while there is certainty (at $p<0.05$) that the detected statistically significant trends are real and not influenced by artifacts in the time series, the group of non-significant trends in DOC might well contain sites with significant trends that could not (yet) be detected statistically. Nevertheless, the selected trend analysis technique is the most suitable to detect weak trends, thus reducing the chances of hidden trends within the non-significant trends category.

4.1.2 Analysis of breakpoints in the time series

Soil solution DOC time series measured with lysimeters are subject to possible interruptions of monotonicity, which is manifested by breakpoints. For instance, installation effect, collector replacement, local forest management, disturbance by small animals or by single or repeated canopy insect infestations can disrupt DOC time series through abrupt changes in soil disturbance (Akselsson et al., 2013; Kvaalen et al., 2002; Lange et al., 2006; Moffat et al., 2002; Pitman et al., 2010). In general, detailed information on the management history of the site in terms of local disturbances was not available for the majority of Level II plots, which hinders selection of individual monotonic time series based on specific site conditions. A preliminary inquiry sent to the responsible for soil solution measurements within the ICP Forests network in each country showed that, for instance, breakpoints in some German, Greek and Italian plots might be explained by very severe drought conditions that may cause an abrupt increase of DOC after rewetting of the soil. On the other hand, one of the breakpoints in an Austrian plots could be explained by replacement of instruments during that period. The BFAST analysis allowed us to filter out time series affected by local disturbances (natural or artefacts) from the dataset and retain time series that represented general monotonic trends. By doing this, we removed some of the within-plot variability (Figure 2) that might be caused by local factors that do not directly explain the long-term monotonic trends in DOC and would thus complicate or confound the trend analysis (Clark et al., 2010).

In view of these results, we recommend that testing for monotonicity of the individual time series is a necessary first step in this type of analyses and that the breakpoint analysis is an appropriate tool to filter out large datasets before analyzing the long-term temporal trends in DOC concentrations. It is worth mentioning that, since our main goal was to study general monotonic trends, we did not focus on finding the direct causes of breakpoints in time series. Further work is needed to interpret the causes of these abrupt changes and verify if these are artefacts or mechanisms, since it can also contain useful information on local factors affecting DOC trends, such as forest management or extreme events (Tetzlaff et al., 2007).

4.1.3 Variability in individual soil solution DOC trends

Even after removing sites with breakpoints in the time series, within-plot variability remained high (median within-plot range: 3.3 % yr-1), with different trends observed for different collectors from the same plot (Figure 6). This high small scale variability in soil solution DOC makes it difficult to draw conclusions about long-term DOC trends from individual site measurements, particularly in plots with heterogeneous soil conditions (Löfgren et al., 2010).

The trends in soil solution DOC were also variable across soil depth intervals. The mixed-effect models suggested an increasing trend in soil solution DOC concentration in the organic layer, and some evidence of an increasing trend in soil solution DOC concentration under 80 cm depth when the entire dataset (with breakpoints) was analyzed. The individual trend analyses seemed to confirm the increasing trend under the organic layer (Table 1), while more heterogeneous trends in the mineral soil were found, which is in line with previous findings (Borken et al., 2011; Evans et al., 2012; Hruška et al., 2009; Löfgren and Zetterberg, 2011; Vanguelova et al., 2010). This difference has been attributed to different processes affecting DOC in the organic and shallow soils and in the subsoil. External factors such as acid deposition may have a more direct effect in the organic layer where physico-chemical properties of soil do not interfere in the output of DOC (Fröberg et al., 2006). However, DOC measurements are not available for all depths at each site, complicating the comparison of trends across soil depth intervals. Hence, the depth-effect on trends in soil solution DOC cannot be ruled out (see Appendix S3).

Finally, the direction of the trends in soil solution DOC concentrations did not follow a clear regional pattern across Europe (Figure 4 and 5) and even contrasted with other soil solution parameters that showed widespread trends over Europe, such as decreasing SO_4^{2-} and increasing pH. This finding indicates that effects of environmental drivers on soil solution DOC concentrations may differ depending on local factors, like soil type and site and stand characteristics. Thus, the trends in DOC in soil solution appear to be the outcome of interactions between drivers acting at local and regional scales.

4.2 Controls on soil solution DOC temporal trends

4.2.1 Vegetation

Biological controls on DOC production and consumption, like stem growth, which operates at site or catchment level, are particularly important when studying soil solution because plant-derived carbon is the main source of DOC (Harrison et al., 2008). The 5-year mean stem growth was available only for 53 sites as the increment between inventories carried out every five years, and as such no annual growth estimates were available. Nevertheless, our results suggest that vegetation growth is an important driver of DOC temporal dynamics in forests, as it has been reported for peatlands (Billett et al., 2010; Dinsmore et al., 2013). In our study, differences in DOC temporal trends across all soil depths were not related to forest type, but were related to stem growth: more fertile plots, as indicated by higher stem volume increment, more often exhibited decreasing trends in DOC (Figure 7 and 11), possibly in response to reduced C allocation to belowground nutrient acquisition system.

It is well-established that N-enrichment favors the above-ground tissue production (as indicated by a higher stem volume increment) in forests (Janssens et al., 2010; Vicca et al., 2012) at the expense of C allocation to the root system. Hence, reducing an important source of DOC. Also, compared to vigorously growing forests, slower forest growth is likely associated with sparser canopies, which in turn leads to less interception and higher soil water input. This in turn could stimulate litter decomposition and thus DOC production. Finally, forest growth might indirectly affect DOC trends through changes in soil solution chemistry (via cation uptake) (Vanguelova et al., 2007), but our data did not allow to test these pathways and thus the DOC response to vegetation uptake remains hypothetical.

4.2.2 Acidifying deposition

Decreased atmospheric SO_4^{2-} deposition and accumulation of atmospherically deposited nitrogen were hypothesized to increase DOC in European surface waters over the last 20 years (Evans et al., 2005; Hruška et al., 2009; Monteith et al., 2007). SO_4^{2-} and N deposition decreased in Europe during the past decades (Waldner et al., 2014), but trends in soil solution DOC concentrations varied largely, with increases, decreases, as well as steady states being observed across respectively 56, 41 and 77 time series in European forests (Figure 4 and 5). Although we could not demonstrate a direct effect of trends in SO_4^{2-} and N deposition on the trends of soil solution DOC, we observed a switch in the direction of the DOC trends according to the mean SO_4^{2-} and N deposition levels (Figure 7 and 8), with increasing soil solution DOC trends occurring more often in forests with high N and, to a lesser extent, SO_4^{2-} deposition. This finding suggests an interaction between the deposition load and the mechanisms underlying the temporal change of soil solution DOC. In the following paragraphs, we discuss the influence of N and SO_4^{2-} deposition separately.

Nitrogen

The role of atmospheric N deposition in increasing DOC leaching from soils has been well documented (Bragazza et al., 2006; Pregitzer et al., 2004; Rosemond et al., 2015). The mechanisms behind this relationship are either physico-chemical or biological. Chemical changes in soil solution through the increase of NO_3^- ions can trigger desorption of DOC (Pregitzer et al., 2004), and biotic forest responses to N deposition, namely, enhanced photosynthesis, altered carbon allocation and reduced soil microbial activity (Bragazza et al., 2006; de Vries et al., 2009; Janssens et al., 2010), can affect the final amount of DOC in soil. One proposed mechanism is the incomplete lignin degradation and greater production of DOC in response to increased soil NH_4^+ (Pregitzer et al., 2004; Zech et al., 1994). Alternatively, N-induced reductions of forest heterotrophic respiration (Janssens et al., 2010) may lead to greater accumulation of DOC.

Overall, our results suggest that at sites with lower N deposition and lower soil NO_3^-, DOC concentration in the soil solution is predominantly decreasing (Figure 8A and Figure 10) and in these forests, we showed that decreasing trends in SO_4^{2-} deposition coincided with increasing trends in soil solution DOC (Figure S3). The response of DOC to changes in atmospheric deposition thus seems to be controlled by the past and present N deposition loads. It suggests that the mechanisms of recovery from sulphur deposition and acidification take place only in non-N-saturated forests, as it has been observed for N deposition effects (de Vries et al., 2009). In high N deposition areas, it is likely that impacts of N-induced acidification on forest health and soil condition lead to more DOC leaching, even though SO_4^{2-} deposition is decreasing.

Sulphur

Similar to our observation for soil solution DOC, decreasing SO_4^{2-} deposition has been linked to increasing surface water DOC (Evans et al., 2006; Monteith et al., 2007; Oulehle and Hruska, 2009). SO_4^{2-} deposition triggers soil acidification and a subsequent release of Al^{3+}. The amount of Al^{3+} is negatively related to soil solution DOC due to two plausible mechanisms: 1) The released Al^{3+} can bind with organic molecules, enhancing DOC complexation and precipitation and, in turn, suppress DOC solubility, that is, decreasing DOC concentrations in soil solution (de Wit et al., 2001; Tipping and Woof, 1991; Vanguelova et al., 2010), and 2) at higher levels of soil solution Al^{3+} in combination with low pH, DOC production through SOM decomposition decrease due to toxicity of Al^{3+} to soil organisms (Mulder et al., 2001). Consequently, when SO_4^{2-} deposition is lower, increases of soil solution DOC concentration could be expected (Figure 11A and 11B). Finally, an indirect effect of plant response to the trend in soil solution DOC could contribute. Acidified soils are nutrient-limited and plants respond to a decrease in nutrient availability, e.g., with changes in belowground C allocation (Vicca et al., 2012) (see section 4.2.1.).

The SO_4^{2-} deposition effect on the trends of DOC in soil solution depended on the soil acidity (Figure 9). Moreover, the soil chemical characteristics, more specifically the conductivity (which is an indirect measure of ionic strength (Griffin and Jurinak, 1973)), soil solution NO_3^- and SO_4^{2-} concentrations, were the most important factors determining whether DOC concentrations increased or decreased over time (Figure 10).

Ultimately, internal soil processes control the final concentration of DOC in the soil solution. The solubility and biological production and consumption of DOC are regulated by pH, ionic strength of the soil solution and the presence of Al^{3+} and Fe (Bolan et al., 2011; De Wit et al., 2007; Schwesig et al., 2003). These conditions are modulated by changes in atmospheric deposition, but not uniformly across sites: soils differ in acid-buffering capacity (Tian and Niu, 2015), and thus the response of DOC concentrations to sulphur deposition changes will be a function of the initial soil acidification and buffer status (Figure 9 and 11). Finally, modifications of soil properties induced by atmospheric deposition changes are probably an order of magnitude lower than the spatial variation of these soil properties across sites, making it difficult to isolate controlling factors on the final observed response of soil solution DOC at continental scale (Clark et al., 2010).

To sum up, our results highlight that the relative importance of the mechanisms behind the long-term temporal dynamics of DOC in soil solution may depend on the past and present status of the forest in terms of N and S deposition loads and acidification of soils (Clark et al., 2010; Evans et al., 2012; Tian and Niu, 2015). Therefore, soil solution DOC concentrations responded as expected to changes in acid deposition, particularly in non N-saturated sites, but the hypothesis of recovery from acidity cannot fully explain overall trends in soil solution DOC, as was also previously suggested in local or national studies of long-term trends in soil solution DOC (Löfgren et al., 2010; Stutter et al., 2011; Ukonmaanaho et al., 2014; Verstraeten et al., 2014).

Finally, although our results confirm that the long-term monotonic trends of DOC in soil solution are the consequence of the interactions between local (soil properties, forest growth), and regional (atmospheric deposition) drivers acting at different temporal scales, further work is needed to quantify the role of each mechanism underlying the final response of soil solution DOC to environmental drivers. We recommend that particular attention should be paid to the biological controls (e.g., stem growth, root exudates or litterfall) on soil solution DOC long-term trends, which remains poorly understood.

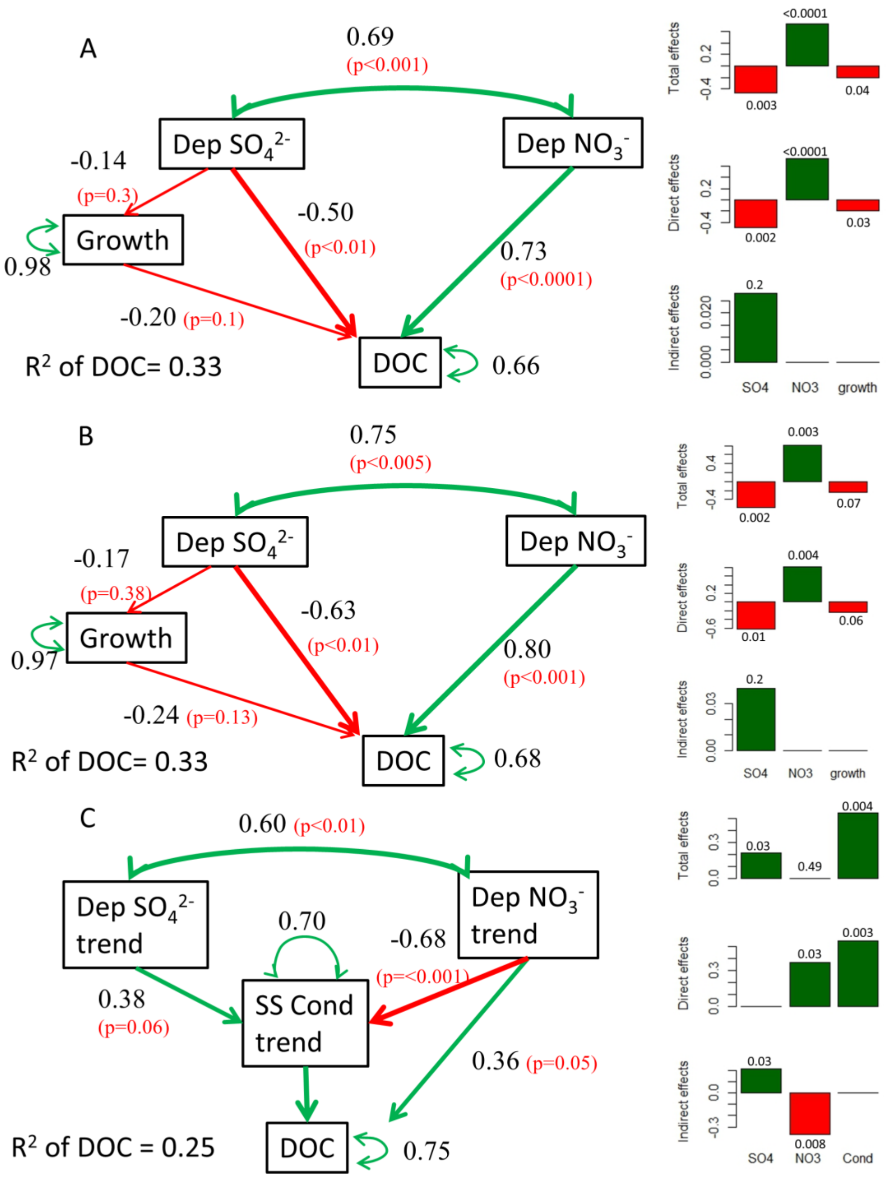


Figure 11. Diagrams of the structural equation models (SEM) that better explain the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases , B) cases with low or medium total nitrogen deposition (> 15 Kg ha^{-1} yr^{-1}), and C) cases with high total nitrogen deposition with mean or trends in annual SO_4^{2-} and NO_3^- deposition (Kg ha^{-1} yr^{-1}) with direct effects and indirect effects through effects on soil solution parameters (trends of conductivity in µS/cm) and mean annual stem volume increment (Growth) in m^3 ha^{-1} yr^{-1}). P-values of the significance of the corresponding effect between brackets. Green arrows indicate positive effects and red arrows indicate negative effects. Side bar graphs indicate the magnitude of the total, direct and indirect effects and their p-value.

4.3 Link between DOC trends in soil and streams

An underlying question is how DOC trends in soil solution relate to DOC trends in stream waters. Several studies have reported increasing DOC trends in surface waters as a recovery from acidification (Dawson et al., 2009; Evans et al., 2012; Monteith et al., 2007; Skjelkvåle et al., 2003). Overall, our results point to a noticeable increasing trend in DOC in the organic layer of forest soils, which is qualitatively consistent with the increasing trends found in stream waters and in line with positive DOC trends reported for the soil organic layer or at maximum 10 cm depth of the mineral soil in Europe (Borken et al., 2011; Hruška et al., 2009; Vanguelova et al., 2010). On the other hand, while there was also evidence of increasing trends in the deep mineral horizon (> 80 cm), trends at different soil horizons along the mineral soil were more variable and responded to other soil internal processes.

Hence, the results from the trend analysis for the overall European dataset points out to a link between the long-term dynamics in surface and deep soil and surface water DOC. However, the individual trend analysis reflects a high heterogeneity in the long-term response of soil DOC to environmental drivers. In fact, it is currently difficult to link long-term dynamics in soil and surface water DOC. Large scale processes become more important than local factors when looking at DOC trends in surface waters (Lepistö et al., 2014), while the opposite seems to apply for soil solution DOC trends. Furthermore, stream water DOC mainly reflects the processes occurring in areas with a high hydraulic connectivity in the catchment, such as peat soils or floodplains, which normally yield most of the DOC (Löfgren and Zetterberg, 2011). Further monitoring studies in forest soils with high hydraulic connectivity to streams are needed to be able to properly link dynamics of DOC in forest soil with dynamics of DOC in stream waters.

5 Conclusions

Different monotonic long-term trends of soil solution DOC have been found across European forests at plot scale, with the majority of the plot-depth trends being not statistically significant (40%), followed by significantly positive (35%) and significantly negative trends (25%). The distribution of the trends did not follow a specific regional pattern. There was evidence that an overall increasing trend occurred in the organic layers and, to a lesser extent, in the deep mineral soil, however, there is less agreement on the trends found in different soil horizons along the mineral soils.

A multivariate analysis revealed that long-term trends in soil solution DOC were negatively related to mean SO_4^{2-} deposition and positively to mean NO_3^- deposition. While the hypothesis of increasing trends of DOC due to reductions of SO_4^{2-} deposition could be confirmed in more N-limited forests, the role of SO_4^{2-} deposition in more N-enriched forests was not significant. We found evidence that soil pH determine the response of trends of DOC soil solution to SO_4^{2-} deposition, indicating that internal soil processes control the final response of DOC in soil solution. Although correlative, our results suggest that there is not one single mechanism responsible for soil solution DOC trends operating at large scale across Europe, but that interactions between drivers that operate at local (soil properties, site and stand characteristics) and regional (atmospheric deposition changes) scales are taking place at the same time.

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CHAPTER 3

CHAPTER 3. ORCHIDEE-SOM: Discretizing soil carbon and modelling dissolved organic carbon (DOC) dynamics in the Land Surface Model ORCHIDEE

Marta Camino-Serrano, Bertrand Guenet, Sebastiaan Luyssaert, Philippe Ciais, Sara Vicca, Bert Gielen, Ivan A. Janssens, ORCHIDEE-SOM: *Discretizing soil carbon and modelling dissolved organic carbon (DOC) dynamics in the Land Surface Model ORCHIDEE*. In preparation

Abstract

A fraction of the atmospheric carbon taken up by the land is displaced along the land-aquatic continuum in form of dissolved organic carbon (DOC). Current Earth System Models (ESM) do not account for this lateral flux of C and, therefore, the global simulations of C sequestration on land are overestimated. ESMs typically represent soils in a very simplistic way with a single layer box scheme, impeding a correct representation of soil carbon dynamics at depth. In this study, we present a new soil carbon module called ORCHIDEE-SOM, embedded within the land surface model ORCHIDEE, which is able to reproduce the DOC dynamics in a vertically discretized soil down to 2 meters. The model includes processes of biological production and consumption of DOC, DOC adsorption on- and desorption from soil minerals and DOC transport through and out of the soils. It is able to simulate concentrations of DOC solution and soil carbon stocks at 11 different soil layers and DOC fluxes out of the soil through runoff and/or drainage, and can also simulate carbon dynamics in deep soils. Combining this modified soil module with the –pending- river routing scheme of ORCHIDEE, which would couple draining soil water to the freshwater system, the estuaries and the oceans, will allow us to account for the lateral transport of carbon along

the land-ocean continuum and thereby better represent the global carbon cycle. Here, we describe the model structure and discuss the overall improvements compared to the trunk version of ORCHIDEE as well as the future work needed before being able to apply ORCHIDEE-SOM at global scales.

1 Introduction

Not all the CO_2 taken up from the atmosphere by terrestrial ecosystems is sequestered in soil or biomass. A fraction of this carbon is displaced along the land-aquatic continuum in the form of DOC (dissolved organic carbon), DIC (dissolved inorganic carbon) and POC (particulate organic carbon) and this fraction has been altered due to anthropogenic activity (Le Quéré et al., 2013; Regnier et al., 2013). These aqueous carbon transfers represent a source of carbon out of terrestrial ecosystems that should be taken into account when closing ecosystem carbon budgets. Soil DOC that is transported with drainage and runoff is eventually respired to the atmosphere, or buried in sediments elsewhere. Despite the importance of the lateral flux of carbon, losses of soil carbon by dissolution and transport are normally neglected in Earth System Models (ESMs). Incorporating the processes of C transport in the ESMs is relevant not only for calculating more accurate C budgets, but also to forecast future evolution of these fluxes. A correct representation of the lateral transport of DOC will have consequences for the mitigation strategies for climate change (Battin et al., 2009; Regnier et al., 2013). Particularly, strategies designed to enhance carbon sequestration will benefit from more detailed information about where lateral transport occurs and what are the processes involved.

Deep soil C seems to play an important role in controlling future soil carbon stock trajectories (Jobbagy and Jackson, 2000) because it is especially vulnerable to the global warming effects especially in permafrost soils or peatlands (Koven et al., 2013; Ota et al., 2013). Despite the role of deep C, it is usually not represented in

ESMs. To date, only one ESM incorporates mechanisms for vertical mixing and subsequent stabilization of C (Koven et al., 2013).

DOC is one of the main sources of subsoil SOC, particularly under humid conditions (Rumpel and Kogel-Knabner, 2011). Two processes cause the vertical movement of soil C: dispersal of SOC during mixing, which is represented in models as a diffusion process, and is mainly due to bioturbation caused by animals (and plant) activity in soil; and advection, which is the displacement of carbon with the liquid phase moving through the soil and affects only the soluble C pool (Braakhekke et al., 2013). Indeed, a substantial amount of C in deep soil layers is DOC transported through the water fluxes within the soil column and it is considered as an important substrate for microorganisms in deep soils (Neff and Asner, 2001; Rumpel and Kogel-Knabner, 2011). Moreover, because soil microbial activity in deep layers is limited by fresh and labile substrate (Fontaine et al., 2007), DOC may participate actively in the C dynamics in deep soils. Nevertheless, the flux of C into deep layers is difficult to model because multiple mechanisms co-occur, which hampers the isolation of their effects from soil organic carbon (SOC) profiles measurements only (Braakhekke et al., 2013).

DOC concentration and fluxes are controlled by three main processes: 1) Biological production and consumption of DOC, 2) Adsorption to – and desorption from soil minerals, and 3) Transport between layers and out of the system. Although only one model exists that is able to predict DOC in soil at global scale (McGuire et al., 2010), several models can predict DOC at site, landscape or catchment scale. For instance, Neff and Asner (2001) and DyDOC (Michalzik et al., 2003) already presented a model able to simulate soil profiles of DOC taking into account processes of decomposition, sorption and leaching, although the representation of decomposition and sorption processes differs among these models. DyDOC is based on chemically-differentiated fractions of humic substances, whereas Neff and Asner (2001) defined C pools according to their turnover times. Moreover, DyDOC represent adsorption with an equilibrium partition coefficient, while Neff and Asner (2001) used sorption isotherms.

More recently, modelling approaches for DOC at landscape or catchment scale have been developed (Futter et al., 2007; Gjettermann et al., 2008; Jutras et al., 2011; McGuire et al., 2010; Ota et al., 2013; Wu et al., 2013). These models differ in the definitions of the soil carbon pools (from turnover times to chemically differentiated fractions), in the level of detail in the process formulation (from simple first order kinetics to non-linear relationships) and in the spatial and temporal resolution (from site to global, and from hourly to annual or longer time scales). Although these models have been successfully tested and are able to reasonably simulate DOC dynamics, at present, there is no global land surface model embedded within ESM that represents a vertically solved module of DOC production, consumption, sorption and transport.

For this reason, the aim of the present study is to develop and describe a new soil carbon module, which is able to reproduce the DOC dynamics in a vertically discretized soil down to 2 meters. This new soil carbon has been embedded in the land surface model ORCHIDEE.

2 Description of the new soil carbon module ORCHIDEE-SOM

2.1 General description of the module ORCHIDEE-SOM

ORCHIDEE-SOM is an extension to the soil module in the land surface model ORCHIDEE, based on the version SVN r1652. ORCHIDEE represents the principal processes influencing the carbon cycle (photosynthesis, ecosystem respiration, soil carbon dynamics, fire, etc.) and energy exchanges in the biosphere (Krinner et al., 2005). It consists of two modules: SECHIBA, which describes the fast processes of energy and water exchanges between the atmosphere and the biosphere at a time step of 30 minutes (de Rosnay et al., 2002) and STOMATE, which calculates the phenology and carbon dynamics of the terrestrial biosphere at a time step of 1 day. ORCHIDEE represents vegetation globally using 13 plant functional types (PFT): one PFT for bare soil, eight for forests, two for grasslands, and two for croplands (Krinner et al., 2005).

In the trunk version of ORCHIDEE, soil carbon is based on the CENTURY model following Parton et al. (1988). Hence, soil carbon is divided in two litter pools (metabolic and structural) and three SOC pools (slow, active and passive) with different turnover rates. Metabolic activity in the soil is controlled by temperature, moisture and clay content, and results in carbon fluxes from the three carbon pools. The fraction of the decomposed carbon being transferred from one pool to another is prescribed and the rest is lost to the atmosphere as heterotrophic respiration. The soil C profile with particular dynamics at each depth is not considered and losses of soil carbon by dissolution and transport are not accounted for in the model (Figure 1).

In contrast, ORCHIDEE-SOM simulates carbon dynamics in the soil column down to 2 m-depth, partitioned in 11 layers following the same scheme as in the hydrological module ORC11 (Campoy et al., 2013; Guimberteau et al., 2014). The improvements of ORCHIDEE-SOM compared to the standard version of ORCHIDEE are that 1) the concentration of DOC in each layer and transport between layers are (mechanistically) modeled; 2) soil carbon and DOC is discretized with depth down to 2 meters, and; 3) it links SOC decomposition with the amount of fresh organic matter as a way of accounting for the priming effect (Guenet et al., 2013) (Figure 1).

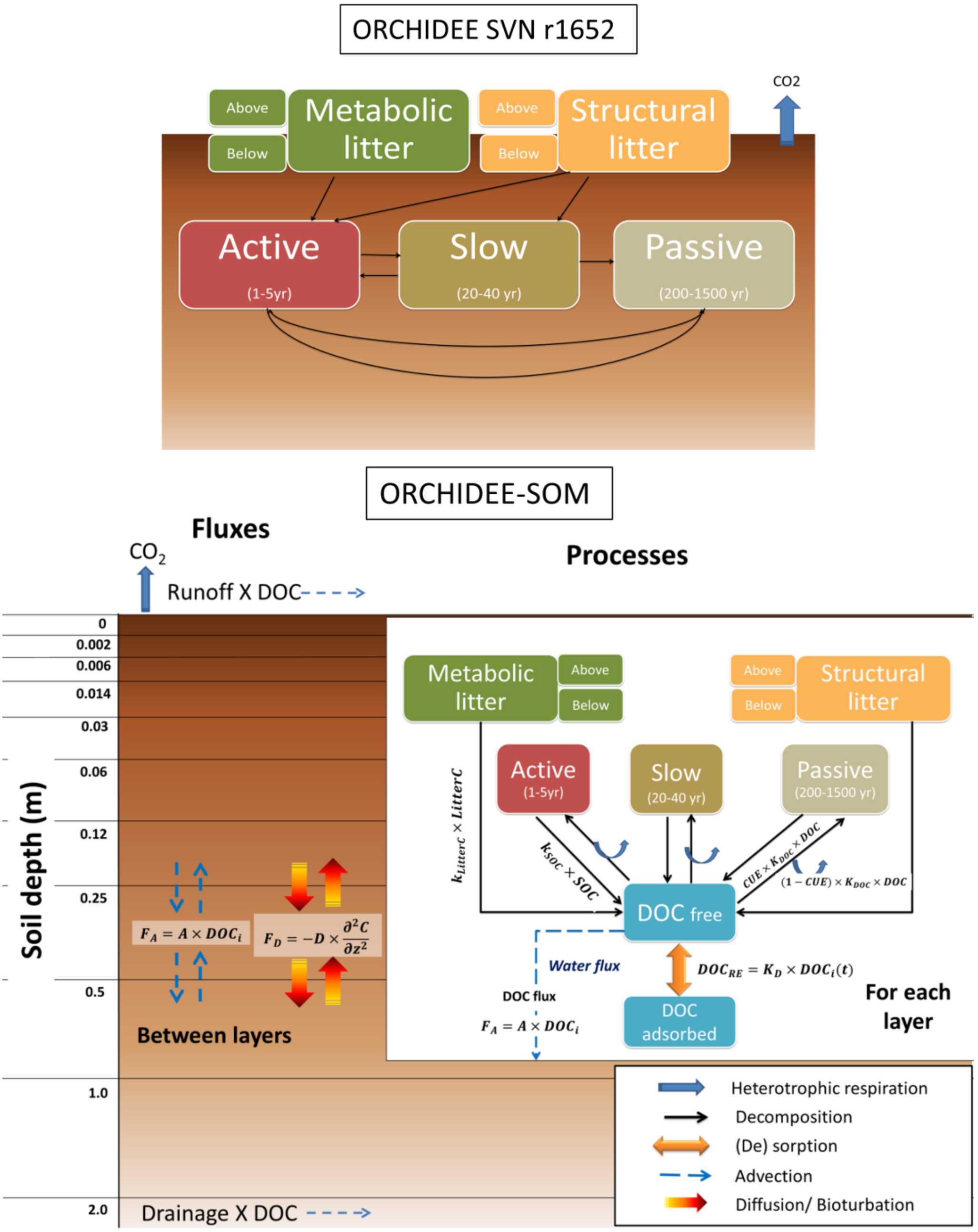


Figure 1. Overview of the changes in ORCHIDEE-SOM compared to the soil module in the trunk version of ORCHIDEE SVN r1652. The equations used for the processes occurring within and between layers are represented (see text for details).

2.2 Vertical discretization of the soil carbon module

For mathematical reasons, ORCHIDEE SVN r1652 has two different discretized schemes for soil physics: one for energy and one for hydrology. Since we need the transport of water between layers and drainage for the DOC module, we adopted the discretization used for the soil hydrology scheme whose performance has already been tested against tropical (Guimberteau et al., 2014), boreal (Gouttevin et al., 2012) and temperate datasets (Campoy et al., 2013). Therefore, ORCHIDEE-SOM represents a 2 m soil column with 11 discrete layers, whose thickness increases geometrically with depth. This kind of geometric configuration is used in most land surface models describing the vertical soil water fluxes based on the Richards equation, which is the case for ORCHIDEE (Campoy et al., 2013). The midpoint depths (in m) of the layers in the discretized soil column are: 0.00098, 0.00391, 0.00978, 0.02151, 0.04497, 0.09189, 0.18573, 0.37341, 0.74878, and 1.49951, respectively. The first layers in the soil hydrology discretization scheme are thinner (1 mm) than needed in terms of biological process-representation. Nevertheless, we decided to integrate the 11-layers scheme for technical reasons: it simplifies the coding and the understanding of the code for the users. At each time step, each soil layer is updated with all the sources and sinks of DOC due to the represented biological and physical processes.

The new 11-layers scheme applies to the soil carbon in the mineral soil and to the belowground litter (see Section 2.3.1.). However, the aboveground litter layer in ORCHIDEE is dimensionless: processes of production and decomposition of aboveground litter occur independently of the litter layer thickness. In ORCHIDEE-SOM, a new parameter to define the thickness of the litter layer has been added in order to be able to calculate the process of diffusion of aboveground litter into the mineral soil (Table 1).

2.3 Physical and biological processes affecting DOC

2.3.1 DOC, SOC and litter dynamic within each layers.

Enzymatic decomposition of litter and SOC is the primary source of DOC in soils and, thus, plays an important role in controlling DOC dynamics. DOC also originates from root exudates and from microbial residues. Simultaneously, microbial consumption of DOC is the main process of DOC removal from soil. Both being biological processes, DOC production and consumption are both controlled by the same factors that control biological activity, particularly temperature and moisture. Both processes will therefore vary with soil depth, land use type, and soil fertility (Bolan et al., 2011).

The rate of DOC production is controlled by its properties, such as organic matter fragment size, chemical composition, polarity, acidity, as well as the chemical characteristics of the solution (pH, nutrient content and oxygen and metal concentrations) (Kalbitz et al., 2000). Process-based models necessarily simplify the diversity of DOC sizes and composition by stratifying DOC in different pools, which may be characterized by their turnover time (e.g., Neff and Asner, 2001; Ota et al., 2013; Parton et al., 1987) or chemical composition (e.g., Laine-Kaulio et al., 2014; Michalzik et al., 2003; Yurova et al., 2008). The pool-based models assume that the different residence times or the different chemical composition are a reflection of all the factors affecting DOC biodegradation (Wu et al., 2010).

In ORCHIDEE-SOM, DOC is described using two pools that are defined by their decomposition rates, the labile DOC pool with a high decomposition rate and the recalcitrant DOC pool with a lower decomposition rate. The labile pool corresponds to the DOC coming from litter and active carbon, while the recalcitrant pool corresponds to the DOC coming from slow and passive carbon. Each pool may be free in the soil solution or adsorbed to the soil minerals. Only the free DOC is decomposed following a first order kinetics equation (Equation 1), based on the DOC mineralization model of Kalbitz et al. (2003).

As the Kalbitz et al. (2003) model calculates mineralization rates and not the decomposition rates, a parameter called microbial carbon use efficiency (CUE) has been added. The CUE parameter controls the amount of DOC that is decomposed but not respired in relation to the total amount of DOC decomposed. By default, we assume a microbial carbon use efficiency of 0.5, a largely accepted standard value of CUE (Manzoni et al., 2012). That means that half of the decomposed DOC goes back to the carbon pools and the other half is mineralized during heterotrophic respiration.

Therefore, the change in DOC for each pool due to biological activity at each time step is described as:

$$\frac{\partial DOC}{\partial t} = I(t) - \frac{1}{1-CUE} k_{DOC} \times DOC(t) \qquad (1)$$

With I being the input coming from litter and SOC decomposition (described below) in g C m^{-2} ground , k_{DOC} a parameter representing the decomposition rates of each free DOC pool (labile, and recalcitrant) in days^{-1} , which corresponds to the inverse of the *DOC_tau_stable* or *DOC_tau_labile* ORCHIDEE-SOM parameters (Table 1). Then, the decomposed DOC is partially respired and partially redistributed in the SOC pools, with the fraction of respired DOC being controlled by the carbon use efficiency (CUE).

Litter is defined by two pools called metabolic and structural with a high and a low decomposition rates, respectively. Above- and belowground litter are separate pools. While belowground litter is discretized over the 11-layers scheme down to 2 meters, aboveground litter layer is simply defined by a fixed thickness parameter (*z_litter*) (Table 1). Litter decomposition is also described by first order kinetics (Equation 2) similar to Equation 1 but for litter, I is coming from deceased plant tissues. The litter decomposition parameters are fixed and similar to the parameters used in ORCHIDEE SVN r1652. The main difference with the DOC decomposition is the presence of two rates modifiers, θ and τ, to take into account the effect of moisture and temperature, respectively:

$$\frac{\partial LitterC}{\partial t} = I(t) - k_{LitterC} \times LitterC(t) \times \theta(t) \times \tau(t) \qquad (2)$$

$$\theta(t) = \max(0.25, \min(1, 1.1 \times M(t)^2 + 2.4 \times M(t) + 0.29)) \qquad (3)$$

$$\tau(t) = \min(1, e^{0.69 \times (T(t) - 303.15)/10)}) \qquad (4)$$

With M and T being the soil moisture (m^3 m^{-3}) and the temperature (K) of the layer considered.

The SOC is defined by three pools, so called active, slow and passive, with different turnover rates. The decomposition is based on Guenet et al. (2013)with a parameter set obtained by Guenet et al., (In prep) (Table 1):

$$\frac{\partial SOC}{\partial t} = I(t) - k_{SOC} \times (1 - e^{-c \times LOC}) \times SOC(t) \times \theta(t) \times \tau(t) \qquad (5)$$

With I being the input of C into the pool considered in g C m^{-2} ground, k_{SOC} a SOC decomposition rate ($days^{-1}$), LOC the stock of labile organic C defined as the sum of the C pools with a higher decomposition rate than the pool considered. This means that for the active carbon pool LOC is the litter, but for slow carbon pool LOC is the litter and the active pool, and finally, for the passive carbon pool LOC is the sum of litter, active and slow carbon donor pools. Finally, c is a parameter controlling the interaction of the LOC pool with the SOC mineralization (Table 1).

2.3.2 DOC sorption to soil minerals

Sorption isotherms are commonly used to examine relationships between solution concentration and soil surface association. There are two main sorption isotherm approaches used to represent the amount of DOC adsorbed in soil: the modified Langmuir equation and the Initial Mass (IM) isotherm (Kothawala et al., 2008). The original Langmuir equation (Equation 6) is not able to cope with the desorption of dissolved organic carbon from native soil organic matter, which occurs in natural soils, because it lacks the intercept term (Nodvin et al., 1986).

$$RE = \frac{k \times Q_{max} \times DOC}{1 + k \times DOC} \qquad (6)$$

With RE being the desorption (negative value) or adsorption (positive value) of DOC, k the binding affinity, DOC the initial concentration of free DOC in solution and Q_{max} the maximum adsorption capacity.

Several researchers have attempted to include desorption of dissolved organic carbon using modified forms of the Langmuir equations that, however, do not provide meaningful values of maximum sorption capacity (Kaiser, K., personal communication). On the other hand, the IM isotherm (Equation 7) represents well DOC sorption processes when sorption does not approach the sorption maximum, that is, for deeper subsoils. However, for soil horizons receiving high amounts of DOC, IM isotherm might not be the best solution (Kothawala et al., 2008).

$$RE = m \times DOC - b \tag{7}$$

With RE being the desorption (negative value) or adsorption (positive value) of DOC, m a regression coefficient similar to the partitioning coefficient, DOC the initial concentration of free DOC in solution and b the intercept (the desorption parameter).

Most of the DOC models that represent adsorption use the IM linear isotherm (Neff and Asner, 2001; Wu et al., 2013) (Equation 7) or use a first order kinetic reaction to represent a linear adsorption (Laine-Kaulio et al., 2014; Michalzik et al., 2003). In principle, these two approaches are expressions of a simple partitioning process, where the tendency of the soil to adsorb DOC is described by an equilibrium partition coefficient.

The linear adsorption isotherm slope (m in Equation 7) is the distribution coefficient (K_D) when the reactive substance present in the soil is assumed to be insignificant. Hence, K_D is defined as a measure of the affinity of the substances for the soil when the reactive substance present in the soil (DOC in our case) is assumed to be insignificant. The distribution coefficient can be related to the regression coefficient (m) in the IM isotherm following Nodvin et al. (1986) (Equation 8):

$$K_D = \frac{m}{1-m} \times \frac{(volume\ of\ solution)}{(mass\ of\ soil)} \tag{8}$$

K_D (m^3 kg $^{-1}$ soil) represents the distribution between the adsorbed and dissolved organic carbon and thus it will vary depending on the adsorption capacity of the soil profile.

ORCHIDEE-SOM assumes that adsorption/desorption occurs due to the deviation between the actual concentration of adsorbed DOC and the equilibrium adsorbed DOC according to K_D. Therefore, the DOC adsorption in soil minerals in ORCHIDEE-SOM is formulated as follows:

$$DOC_{RE} = K_D \times DOC_i(t) \times BD \times \frac{1}{\theta} \tag{9}$$

$$\frac{\partial DOC_i}{\partial t} = DOC_i(t) - (DOC_{RE}(t) - DOCad_i(t)) \tag{10}$$

$$\frac{\partial DOCad_i}{\partial t} = DOCad_i(\mathrm{t}) + (\mathrm{DOC_{RE}}(\mathrm{t}) - DOCad_i(\mathrm{t})) \tag{11}$$

In equation 9, DOC_{RE} is the amount of adsorbed DOC in equilibrium according to the partition coefficient K_D. As K_D is expressed in m^3 kg $^{-1}$ soil, we use bulk density (BD) and soil moisture (θ) to convert DOC from g C kg $^{-1}$ soil into g C m^{-3} water. $DOC_i(t)$ and $DOCad_i(t)$ are the concentration of free DOC in soil solution and the concentration of adsorbed DOC for each pool i in g C m^{-3} water, respectively. This approach assumes that the produced DOC at every time step of the model (30 minutes) is immediately distributed between the adsorbed and free pools to reach equilibrium. It also assumes that, although K_D may depend on soil properties (Equation 12), it is independent on the quality of DOC (labile or recalcitrant).

Dependence of the sorption distribution coefficient on soil properties

The adsorption characteristics of soils have previously been related to several soil properties. The desorption parameter (b) of the Initial Mass (IM) isotherm (Equation 7) has been related to the organic carbon content in the soil profile and the partition coefficient (m) with oxalate-extractable aluminum (Al_o) and dithionite-extractable iron (Fe_d) and organic carbon content (Kaiser et al., 1996). On the other hand, the maximum adsorption capacity of a soil (from the modified Langmuir isotherm) was found to correlate to Al in soil and, to a lesser extent, to Fe (Kothawala et al., 2008). Despite the accepted importance of Al and Fe in controlling DOC adsorption in soils, these variables are not globally available and hence not included in the land surface model ORCHIDEE. Therefore, we focus on the role of clay, OC, and pH in explaining the K_D coefficient of DOC sorption in soils (Figure 2).

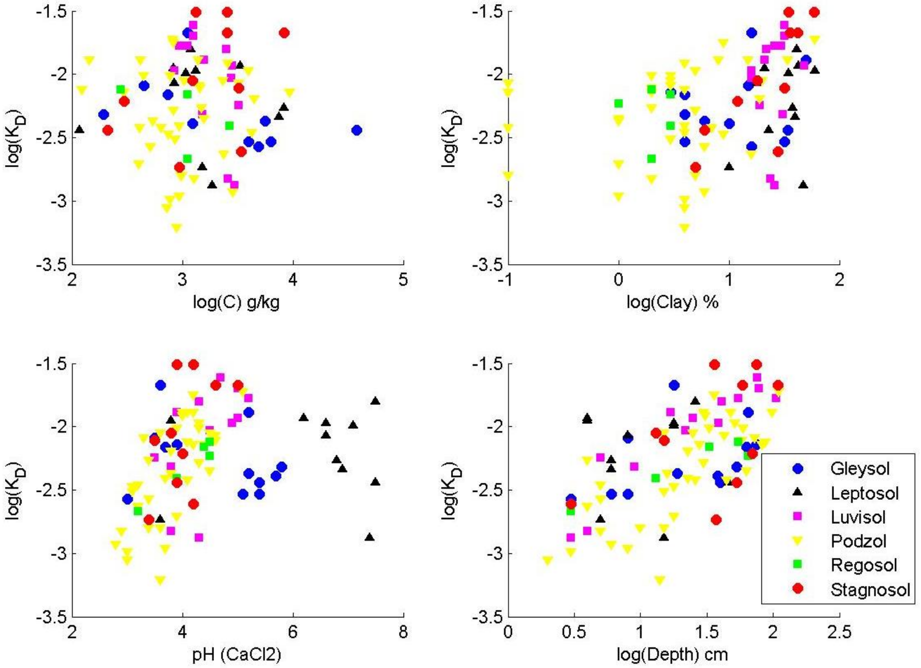


Figure 2. Relationships K_D with organic carbon (OC) in g/kg (upper left panel), Clay in % (upper right panel), pH ($CaCl_2$) (bottom left panel) and soil depth in cm (bottom right panel), based on the dataset from Kaiser et al. (1996) for 6 different soil types (WRB).

In order to produce a statistical model that predicts the K_D parameter as a soil-type dependent variable, we collected two different datasets: one with adsorption isotherms for soils in Canada (Kothawala et al., 2008) and another with soils from Germany, Sweden and The Netherlands (Kaiser et al., 1996). In total, the dataset contained data on the IM isotherm coefficients and pH ($CaCl_2$), OC(g kg^{-1}), % of sand, silt and clay and depth of the soil horizon for 184 soil horizons, 49 for Canadian soil profiles, 120 for Germany, 10 for The Netherlands and 5 for Sweden. However, due to important differences in both datasets that were influencing the statistical models, we decided to use only the European soils for the models to be used in ORCHIDEE-SOM in order to avoid artefacts in the statistical relationships.

Thus, we calculated the distribution coefficient K_D from the IM isotherm partition coefficient (m) measured in batch experiments on 34 European soil profiles (Kaiser et al., 1996), according to Equation 8, and built an empirical model that related K_D with soil depth, clay, pH and organic carbon. We selected the best model by means of stepwise regressions. The distribution of the residuals was checked and models whose residuals were not normally distributed were discarded. The selected model included only clay and depth as explanatory variables and was able to explain 50% of the variability in K_D (adjusted $R^2 = 0.5$, $p < 0.0001$) (Equation 12, Figure 3):

$$\log K_D = -3.1 + 0.2 * \log Clay + \log Depth \tag{12}$$

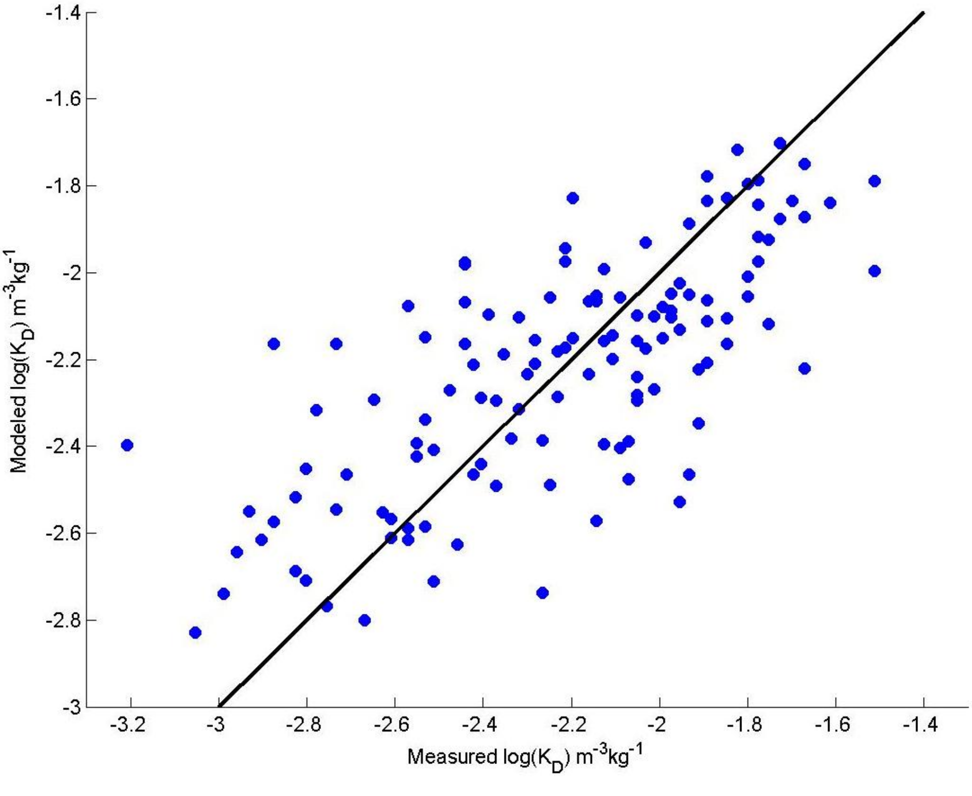


Figure 3. Measured (Kaiser et al., 1996) and modeled (Equation 12) distribution coefficient K_D as a function of clay and soil depth. The black line is the 1:1 line.

By using this relationship, the effects of soil texture and depth in the adsorption capacity of the soil are accounted for in the model. It is worth highlighting that interactions between explanatory variables were tested and some significant interactions came out, more particularly the interactions between carbon content and depth and clay and pH. However, introducing these interactions improved the model only slightly (adjusted R^2= 0.57 versus adjusted R^2=0.50), but inflated the number of parameters. Therefore, based on the Akaike Information Criterion, we used the most parsimonious model, which did not include interaction terms.

Although we tested this empirical relationship a posteriori (Figure 4), this is not included in the default version of ORCHIDEE-SOM, because the development of

Equation 12 and the validation of ORCHIDEE-SOM took place in parallel. For the moment, ORCHIDEE-SOM assumes a fixed K_D (Table 1).

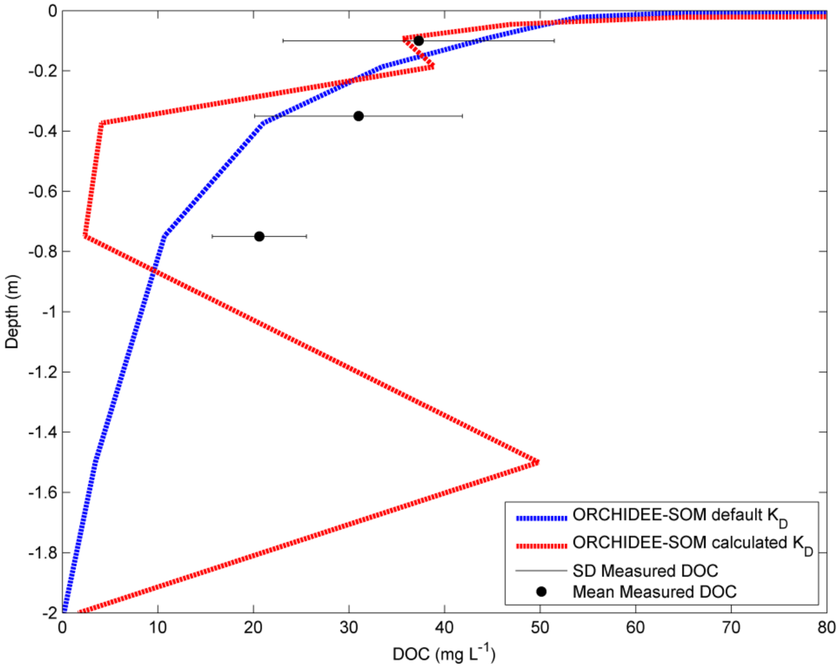


Figure 4. Comparison of model outputs using ORCHIDEE-SOM with default K_D parameter and with empirical relationship for K_D. Measurements correspond to a Scots pine forest in Belgium.

2.3.3 Vertical fluxes of DOC and SOC

Bioturbation, i.e. transport of plant debris and soil organic matter by soil fauna, is commonly represented in models as a diffusion process, whereas advection is used to represent C transport with the liquid phase (Braakhekke et al., 2011; Obrien and Stout, 1978; Wynn et al., 2005).

Diffusion

Soil fauna, like earthworms, termites, etc., move through the soil and displace organic matter, all the while disturbing the porewaters trapped between the grains and thus reworking the soil by mixing the soil matrix. This activity is called bioturbation. In general, bioturbation causes homogenization of soil properties, i.e., net transport of soil constituents proportional to the concentration gradient. For this reason, the effects of bioturbation on the distribution of soil properties has often been modelled using Fick's diffusion equation (e.g., Braakhekke et al., 2011; Elzein and Balesdent, 1995). However, some conditions must be respected to use Fick's law in the context of bioturbation. 1) the time between mixing events must be short compared to other processes. 2) the size of each layer must be small compared to the total length of the profile and 3) the mixing should be isotropic (bottom-up and top-down) (Braakhekke et al., 2011). Boudreau (1986) proved that, if these conditions are fulfilled, bioturbation can lead to diffusive behaviour of soil constituents and can be represented following the Fick's diffusion law. At small spatial scales, bioturbation may not meet these criteria. However, at sufficiently large spatial scales, the assumption of diffusive behaviour is reasonable (Braakhekke et al., 2011). Hence, we assume that bioturbation can be modelled as a diffusion process at global scale, for which ORCHIDEE-SOM is designed.

Therefore, in ORCHIDEE-SOM, we represented bioturbation by a diffusion equation based on Fick's second law (Equation 13):

$$F_D = -D \times \frac{\partial^2 C}{\partial z^2} \tag{13}$$

where F_D is the flux of C transported by diffusion, -*D* the diffusion coefficient (m^2 day^{-1}) and *C* the amount of carbon in the pool subject to transport (g C m^{-3} soil). In ORCHIDEE-SOM, bioturbation represented as diffusion applies to the SOC pools and the belowground litter.

Because soil fauna activity may vary with depth, one could argue that diffusion coefficient should be depth-dependent. However, models with depth-dependent diffusion coefficients have been proposed, with no apparent improvement from models with a fixed diffusion coefficient (Boudreau, 1986). In fact, most of the developed models of diffusion at ecosystem level assumes a diffusion parameter constant with depth (Braakhekke et al., 2011; Bruun et al., 2007; Obrien and Stout, 1978; Wynn et al., 2005).For the time being, we assume that soil fauna is present everywhere along the soil profile and, thus, the diffusion parameter is assumed to be constant across the soil profile in ORCHIDEE-SOM.

DOC transport through the soil column is represented by two mechanisms. First DOC is transported following the flux of water between layers, which is described below. Then, DOC may also be transported by diffusion following Equation 13, but with different parameters than for SOC. Unlike for SOC, diffusion of DOC is not a representation of bioturbation processes, but a representation of DOC movement due to actual diffusion (movements of molecules due to concentration gradients). For this, we assume that the water distribution is continuous over the soil column (i.e., there are no dry places).

Advection

The soil hydrology module is based on the 2 m vertical discretization of the soil column (see section 2.2.). A physically-based description of the unsaturated water flow was introduced in ORCHIDEE by de Rosnay et al. (2002). Soil water fluxes calculation relies on a one-dimensional Fokker-Planck equation, combining the mass and momentum conservation equations using volumetric water content as a state variable (Campoy et al., 2013). Due to the large scale at which ORCHIDEE is usually applied, the lateral fluxes between adjacent grid cells are neglected. Also, all variables are assumed to be horizontally homogeneous. The flux field q along the soil profile comes from the equation of motion known as Darcy (1856) equation in the saturated zone, and extended to unsaturated conditions by Buckingham (1907) (Equation 14):

$$q(z,t) = -D\big(\theta(z,t)\big)\frac{\partial\theta(z,t)}{\partial z} + K(\theta(z,t)) \qquad (14)$$

In this equation, z is the depth (in m) below the soil surface, t (in s) is the time, K(θ) (in m s^{-1}) is the hydraulic conductivity and D(θ) (in m^2 s^{-1}) is the diffusivity.

The soil hydrological module counts with the following boundary conditions at the soil surface and at the bottom layer. First, the water flux at the soil surface is defined by the difference between infiltration into the soil and soil evaporation. Precipitation is partitioned between surface runoff and infiltration into the soil, by characterizing the wetting front speed through the top soil layers (d'Orgeval et al., 2008). Soil evaporation is calculated assuming that it can proceed at the potential rate, unless water becomes limiting. Second, ORCHIDEE assumes conditions of free gravitational drainage at the soil bottom. This boundary condition implies that soil moisture is constant below the lower node, which is not always found in nature. In particular, when a shallow water table is present, water saturation within the soil column cannot be modelled within ORCHIDEE. More information on the calculation of the water flux, runoff and drainage can be found in Campoy et al. (2013).

The transport of DOC within the liquid phase occurs due to advection flux and it is modelled as the flow of water calculated by the hydrology module multiplied by the concentration of DOC at each layer according to Equation 15 (Futter et al., 2007):

$$F_A = A \times DOC_i \tag{15}$$

With F_A the advection flux of DOC, A the flux of water calculated by the hydrological module in m^3, and DOC_i the concentration of DOC free in solution in pool *i* in g C m^{-3} water.

At each time step, DOC in each layer is updated with the DOC fluxes entering and leaving the soil layer. The final DOC concentration in the last and first layer is multiplied by drainage and runoff, respectively, to calculate the amount of DOC leaving the system (in g C m^{-2} ground).

Table 1. List of parameters of ORCHIDEE-SOM, with their description, value, units, the parameterization used for each parameter

Parameter	Description	Value	Units	Parameterization
Fixed				
Z_litter (*z_litter*)	Thickness litter above	10	mm	Parameter dependent and change with time
Soil carbon parameters				
frac_carb_ap (*frac_carb_ap*)	fraction of the active pool going into the passive pool	0.004	-	Parton et al. (1987)
frac_carb_sa (*frac_carb_sa*)	fraction of the slow pool going into the active pool	0.42	-	Parton et al. (1987)
frac_carb_sp (*frac_carb_sp*)	fraction of the slow pool going into the passive pool	0.03	-	Parton et al. (1987)
frac_carb_pa (*frac_carb_pa*)	fraction of the passive pool going into the active pool	0.45	-	Parton et al. (1987)
frac_carb_ps (*frac_carb_ps*)	fraction of the passive pool going into the slow pool	0	-	Parton et al. (1987)
active_to_pass_clay_frac (*active_to_pass_clay_frac*)		0.68		Parton et al. (1987)
carbon_tau active (*carbon_tau_iactive*)	Residence times in carbon pools	0.149	days	Guenet et al., in prep
carbon_tau slow (*carbon_tau_islow*)	Residence times in carbon pools	5.48	days	Guenet et al., in prep
carbon_tau passive (*carbon_tau_ipassive*)	Residence times in carbon pools	241	days	Guenet et al., in prep
priming_param (c) active (*priming_param_iactive*)	Priming parameter for mineralization active	493.66		Guenet et al., in prep

Parameter	**Description**	**Value**	**Units**	**Parameterization**
priming_param (c) slow (*priming_param_islow*)	Priming parameter for mineralization slow	194.03		Guenet et al., in prep
priming_param (c) passive (*priming_param_ipassive*)	Priming parameter for mineralization passive	136.54		Guenet et al., in prep
FLUX_TOT_COEFF (*flux_tot_coeff*)	Coefficient modifying the fluxes (1.2 and 1.4 increase decomposition due to tillage, 0.75 modify the flux depending on clay content	1.2, 1.4, .75	days	Gervois et al. (2008) for 1.2 and 1.4; Parton et al. (1987) for 0.75
D (*Dif*)	Diffusion coefficient used for bioturbation litter and soil carbon	1.94E-7	m^2 day^{-1}	Guenet et al. (2013) Bruun et al. (2007)
		DOC parameters		
DOC_tau_stable (*DOC_TAU_STABLE*)	Residence time of stable DOC	60.0	days	Value within the range(5-5000) found in literature (Boddy et al., 2007; Boddy et al., 2008; Kalbitz et al., 2003; Qualls and Haines, 1992; Turgeon, 2008)
DOC_tau_labile (*DOC_TAU_LABILE*)	Residence time of labile DOC	0.3	days	Value within the range (0.07-100) found in literature (Boddy et al., 2008; Kalbitz et al., 2003; Qualls

Parameter	Description	Value	Units	Parameterization
				and Haines, 1992; Turgeon, 2008)
D_DOC (*D_DOC*)	Diffusion coefficient used for DOC diffusion (mm2 dt-1)	1.05e-5	m^2 day^{-1}	Ota et al., 2013
CUE (*CUE*)	Percentage of DOC decomposed that releases to CO_2	0.5	-	Manzoni et al. (2012)
K_D (*kd_ads*)	Distribution coefficient of adsorbed DOC	8.05E-3	m^3 water kg^{-1} soil	Moore et al. (1992)

2.4 Model testing

Once all processes described above were implemented in ORCHIDEE-SOM, we performed a preliminary model testing exercise using the default version of ORCHIDEE-SOM for PFTs 4, 6 and 10 (temperate needleaf evergreen forest, temperate broadleaved summergreen, and grassland, respectively) in order to assess if ORCHIDEE-SOM was able to reproduce the DOC soil profile within a normal range of values of DOC field measurements (Figure 5). Although the DOC measurements represented in Figure 5 correspond only to forest sites (PFT 4 and 6) coming from different European regions and soil types, it gives an idea of the range of DOC concentrations in the field, which is relatively well captured by the model.

Finally, ORCHIDEE-SOM was run for a particular site with PFT 4 for 14 years for four different cases: 1) All the transport processes were activated, 2) The advection flux was deactivated, 3) The DOC diffusion was deactivated and 4) The SOC diffusion was deactivated. These simulations allowed us to identify the relative importance of each transport process with depth (Figure 6) and with time (Figure 7). It is important to note that the relative importance of each process is subject to the limited time span used for these simulations. Further model validation work should extend these simulations to longer time scales.

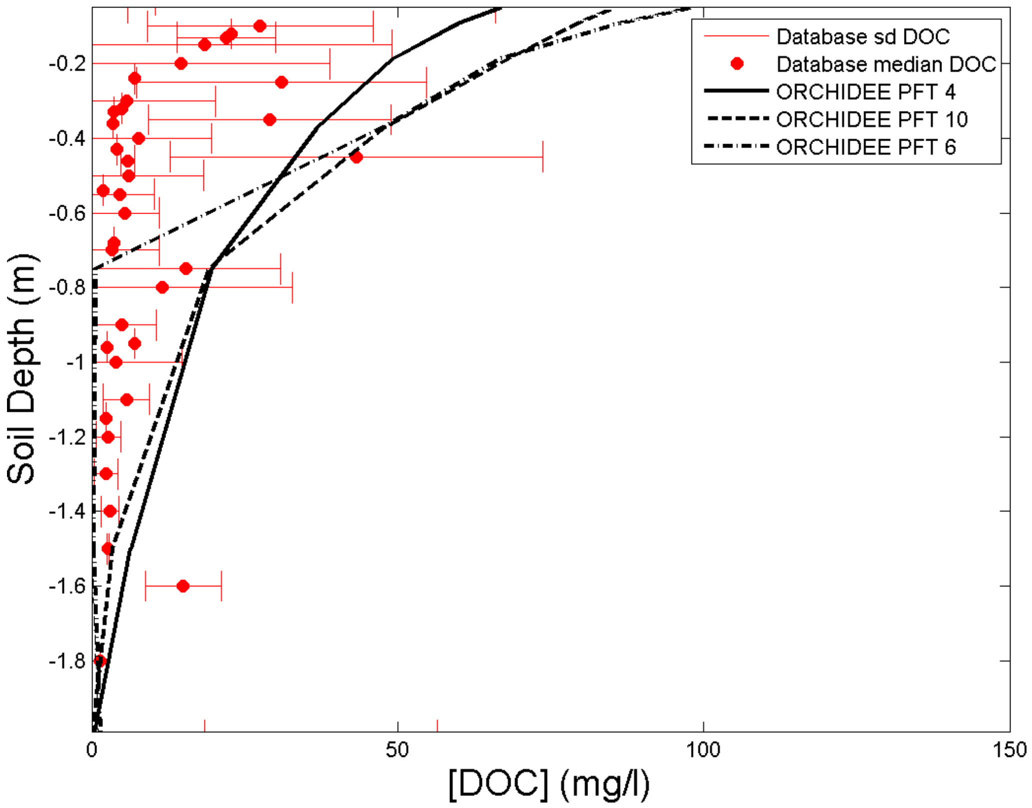


Figure 5. DOC profiles for the data on DOC concentrations (± standard deviation) in forest soils from ICP Level II plots (both needleleaf and broadleaf), and profiles modeled using the default version of ORCHIDEE-SOM for PFT 4 (temperate needleleaf evergreen), PFT 6 (temperate broadleaf summergreen) and PFT 10 (C3 grassland).

3 Discussion and future directions

Lateral C transport from soils to the water system is currently neglected in ESMs and ORCHIDEE-SOM is the first known land surface model embedded within an ESM that quantifies the production and transport of DOC out of terrestrial ecosystems. ORCHIDEE-SOM is an extension of the soil module of ORCHIDEE SVN r1652 that allows the simulation of concentrations of DOC solution in 11 different soil layers (g C m^{-3} ground or g C L^{-1} soil water) and DOC fluxes out of the soil through runoff and/or drainage (in g C m^{-2} ground), as well as the simulation of soil carbon dynamics in deep soils. A preliminary model testing showed that DOC measurements are within the range of DOC field observations (Figure 5), which indicates that the most important processes of DOC production and transport are already well-represented in ORCHIDEE-SOM.

However, to connect the land to the ocean, a river routing scheme able to transport DOC is needed. These developments are ongoing and lead by the Université Libre de Bruxelles (Lauerwald et al. in prep). Hence, the new features for modelling DOC in soil presented in this study will be the link between the soil and water reservoirs, therefore enabling the carbon cycle closure in ORCHIDEE by taking into account the lateral transport of carbon along the land-ocean continuum.

Another ongoing development in ORCHIDEE is the inclusion of the nitrogen and phosphorous cycles. Therefore, in the not-so-distant future, modelling the leaching of DOC as well as nutrients out of soils and into the water system should become possible.

Moreover, ORCHIDEE-SOM presents a more comprehensive representation of biological and physical mechanisms affecting SOC, which has been claimed to be critical for improving global simulations of soil carbon distribution in ESMs (Nishina et al., 2014; Schmidt et al., 2011; Todd-Brown et al., 2013). Nevertheless, representing soil processes that take place at microbial scales (<10^{-3} m) in an ESM that runs at global scale (with a normal grid cell area >10^{10} m^{2}) is a major challenge and implies some model assumptions and simplifications, especially in the early stages of the development. Next, the model simplifications and assumptions made for each process representation are discussed.

3.1 Biological SOC and DOC production and consumption

Soil organic carbon decomposition was already implemented in ORCHIDEE, but in a very simplified way (Krinner et al., 2005). Indeed, it was mainly based on

CENTURY (Parton et al., 1987) without vertical discretization, C export or interaction between labile organic carbon and SOC decomposition (i.e. priming). Recently, priming was added into ORCHIDEE, with significant impact on SOC dynamics at regional scale (Guenet et al., 2013). We started our developments from this last version. DOC decomposition is a new feature in ORCHIDEE-SOM. One main difference between SOC and DOC decomposition in ORCHIDEE-SOM is that DOC decomposition is not controlled by temperature, an assumption that was already made in previous DOC models (Kalbitz et al., 2003; Wu et al., 2013). This assumption seems reasonable as Boddy et al. (2008) showed that DOC decomposition in boreal ecosystems was relatively insensitive to temperature. Moreover, the DOC turnover rates in the model range from 0.3 to 60 days, which might be considered as high turnover rates in comparison with the SOC (Table 1). Thus, we may consider DOC as labile material. In that case, the assumption of temperature insensitivity is a simplification of reality, but it is still in accordance with the theory, which predicts a direct and positive relationship between temperature sensitivity and stability (Davidson and Janssens, 2006).

In reality, DOC is produced from soil microbial biomass, litter, soil organic carbon, root exudates and desorption from minerals. While litter, root exudates (we assumed that DOC coming from belowground metabolic litter represents root exudates and that DOC coming from belowground structural litter represents root-derived material) and soil organic carbon are DOC inputs in ORCHIDEE-SOM, soil microbial biomass is not explicitly represented in the model, as is the case in most of the current global-scale land surface models (Schmidt et al., 2011; Todd-Brown et al., 2013).

ORCHIDEE-SOM is an improvement of the already existing C module of ORCHIDEE, and thus, the distribution of SOC over the different pools based on their turnover rate (CENTURY model) was adopted, while new soluble pools (free and adsorbed DOC) were added. CENTURY-like models have proven to work effectively in reproducing changes in SOC stocks across large scales (Davidson and Janssens, 2006). However, understanding and implementing the microbial responses to environmental changes is crucial if the models want to be applied for predictions under climate change (Davidson and Janssens, 2006; Sulman et al., 2014; Wieder et al., 2013). Hence, recent studies have claimed the importance of the implementation of a mechanistic description of microbial biomass and activity, as well as the interactions between SOM quality and decomposition rate (priming effect), that are normally neglected in the representation of SOC decomposition in process-based models (Davidson and Janssens, 2006; Sinsabaugh et al., 2013). ORCHIDEE-SOM counts with a simple representation of the priming effect on decomposition (Equation 5) that allows a more realistic global prediction of SOC changes (Guenet et al., in prep). Moreover, efforts to define a model framework for soil microbial biomass in ORCHIDEE have already started. However, these changes, although necessary, requires a long time to be implemented. This is because each new development in an ESM should be designed, programmed, parameterized and validated at different spatial (site, regional, global) and temporal (daily and annual cycle, long term trends) scales through data assimilation before they are implemented in the trunk version of the model.

3.2 DOC mineral adsorption

It has been suggested that the long-term preservation of SOC is not controlled by turnover rate alone. On the contrary, its accessibility to microbial decomposers plays a more important role (Cotrufo et al., 2013; Schmidt et al., 2011). In that context, the representation of C protection against microbial decomposition by different processes (physical protection, energy limitation, adsorption on the mineral matrix) is highly important. In the original CENTURY model, physical protection by clay was already accounted for, but other SOC-protection mechanisms were not. The incorporation of adsorption processes in ORCHIDEE is thus a step forward in land surface models to represent such protection mechanisms (Sulman et al., 2014) since adsorbed DOC is not decomposed in the model.

Nevertheless, the selection of the adsorption equations responded to a great extent to computational restrictions. The adequacy of the Langmuir and IM isotherms depends on the soil type, but ORCHIDEE is designed to work for all soil types. Therefore, we selected the least parameter-dependent equation: the IM isotherm (Equation 7). First attempts to run the model using the IM isotherm failed due to the presence of an intercept term, which gave numerical instability during the spinup phase, when the soil carbon content is very low. For that reason, we selected the equilibrium equation (Equations 9 to 11). Although this approach assumes that DOC is immediately distributed between the adsorbed and free pools to reach equilibrium, the soil profiles obtained when applying this equation show the expected decreasing exponential shape (more free DOC in surface than in subsoils) (Camino-Serrano et al., 2014) (Figure 4).

By using the data from Kaiser et al. (1996), we obtained a relatively simple statistical relationship that explained half of the variability of the K_D coefficient. This relationship has a great potential to incorporate part of the soil-dependence of the mineral adsorption into ORCHIDEE in a very simple and not very computation expensive way. However, a first test at site level showed a poorer fit to measured free DOC data when applying the empirical relationship than when using the default adsorption parameter defined in ORCHIDEE-SOM (Figure 4). Also, the soil DOC profile could not be properly captured using the empirical relationship, probably indicating a high sensitivity of the simulated DOC profile to the adsorption distribution coefficient. This result might be influenced by the specific characteristics of this particular soil (very sandy and acid) and a more exhaustive evaluation is needed before we can draw conclusions on the best representation of the adsorption coefficient in ORCHIDEE-SOM.

However, we should note that this relationship has some weaknesses. For instance, not surprisingly, the amount of free DOC under 1 meter depth is overestimated when using this statistical relationship (Figure 4). The soil dataset used to develop the empirical relationship has measured K_D data down to 1 m, while in ORCHIDEE we modeled K_D by applying this relationship until 2 m.

Therefore, the K_D simulated in ORCHIDEE-SOM between 1 and 2 m of soil depth are calculated by extrapolating the empirical relationships obtained for the first meter of soil to the very deep soil. Further parameterization work is clearly needed before integrating this relationship in the final version of ORCHIDEE-SOM.

Moreover, we used depth as an explanatory variable, although depth as a variable has no ecological meaning (Figure 2d). In fact, different soil types will show different characteristics at the same depth. Currently, ORCHIDEE reads a unique non-depth-dependent value of pH and clay % per site and, therefore, we use soil depth as an integrative measure of soil-depth dependent variables that are not available in ORCHIDEE, but affect the sorption of DOC, such as Al and Fe (Kaiser et al., 1996; Kothawala et al., 2009; Moore et al., 1992). The inclusion of soil depth in the empirical model will allow to reproduce the decreasing DOC profile in soil. Ideally, the model should be enabled to use different soil characteristics at different soil layers (for the moment, a single value of clay and pH is defined per site). This should be a priority for future improvements in ORCHIDEE-SOM.

3.3 DOC and SOC vertical transport

ORCHIDEE-SOM includes an explicit representation of advection (for DOC) and diffusion (for SOC and DOC) processes, which are the main mechanisms by which organic carbon is transported to deep soil (Jenkinson and Coleman, 2008). Modeling these two mechanisms separately represents an improvement compared to models that represent only advection or diffusion. The two mechanisms are independent in terms of their environmental, physical and biological controls and, hence, a separate parameterization for each mechanism will allow to quantify the relative importance of each process under different conditions (Koven et al., 2013).

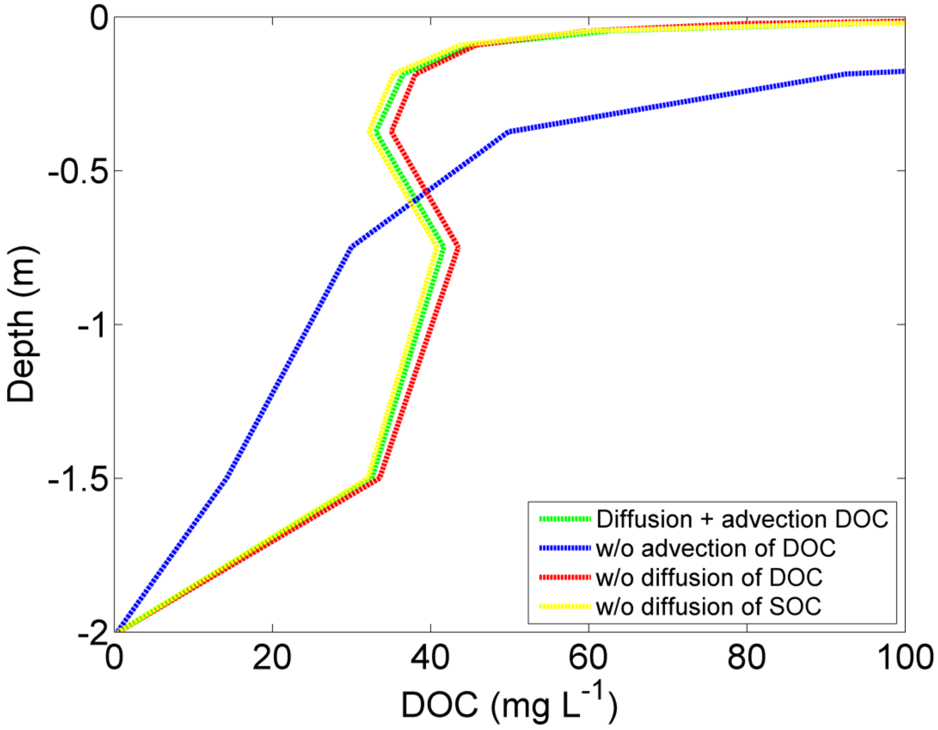


Figure 6. Soil profile of DOC concentrations modelled using ORCHIDEE-SOM for a PFT=4 site for 4 different cases: 1) All transport processes activated (in green), 2) Without advection of DOC (in blue), 3) without diffusion of DOC, and 4) without diffusion of SOC.

For instance, we found that the advection flux of DOC is the most important transport process defining the DOC profile (Figure 6 and 7). Soil profile of DOC changed when the advection flux is deactivated, while deactivating diffusion of DOC and SOC slightly changed the magnitude of DOC compared to the simulation using all the processes, but it did not influence the shape of the soil profile. The advection flux, therefore, seems to be key in determining the performance of ORCHIDEE-SOM when simulating DOC concentrations along the soil profile.

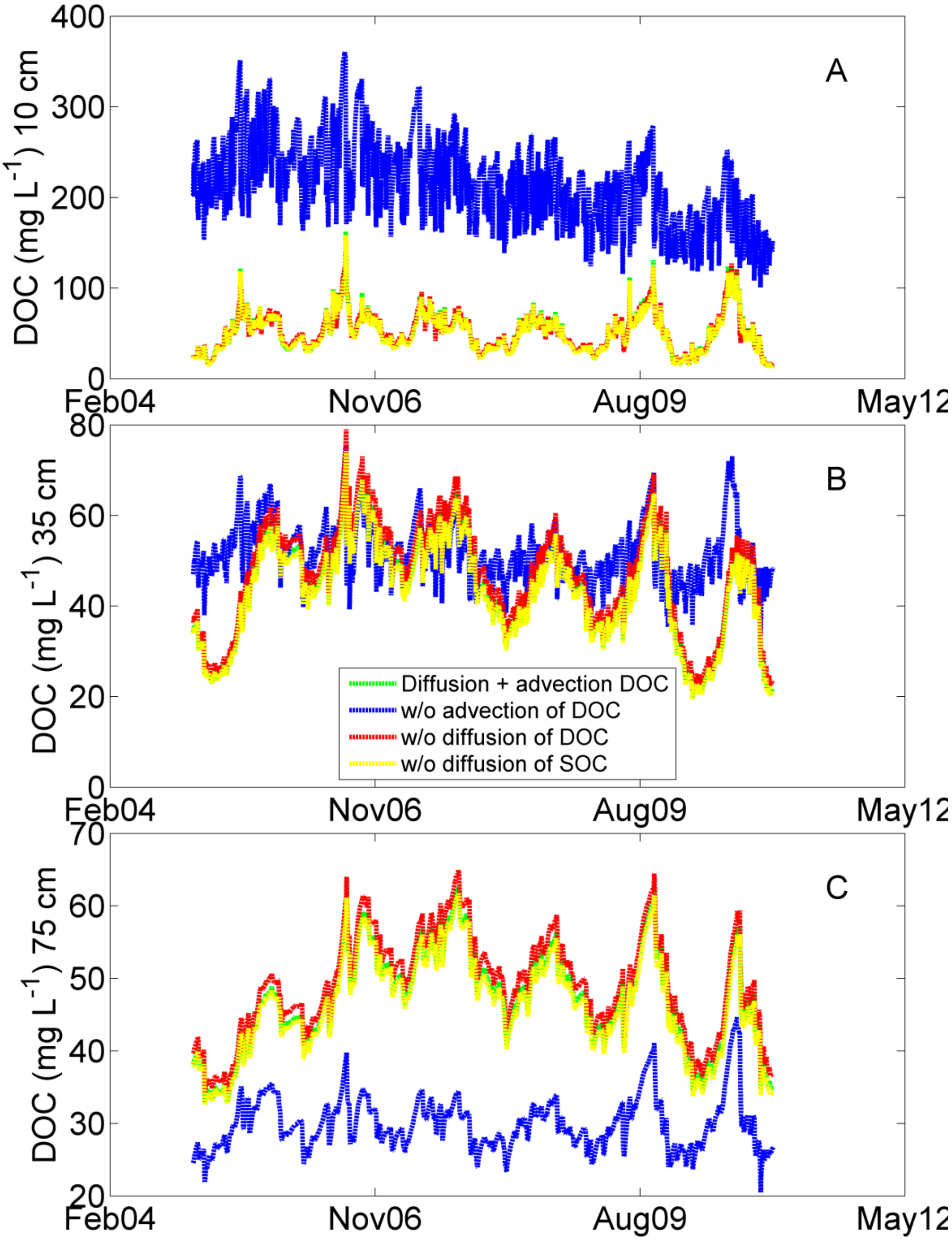


Figure 7. DOC concentrations over time modelled using ORCHIDEE-SOM for a PFT=4 site at three soil layers (A) 10 cm, B) 35 cm and C) 75 cm) for four different cases: 1) All transport processes activated (in green), 2) Without advection of DOC (in blue), 3) without diffusion of DOC, and 4) without diffusion of SOC.

Regarding the transport of DOC with the water drainage flux, limitations of the hydrological module of ORCHIDEE currently still limit the application of ORCHIDEE-SOM, as the advection flux is proportional to the water flux in the soil (Equation 15). The 11-layers hydrological module implies that there is free drainage in the bottom layer. This is not always the case in nature, as a shallow water table can lead to local increases of soil moisture with depth or saturation within the soil column (Campoy et al., 2013). This boundary condition currently limits the representation of more humid ecosystems such as wetlands or peatlands, and also needs to be addressed in the near future.

Another consequence of the free drainage boundary condition is the extremely low values of DOC concentrations at 2 meters deep (Figure 5). The module of DOC export with drainage assumes that all DOC available at 2 meters is subject to leaching with drainage, which occurs continuously since saturation conditions cannot be modelled. Consequently, DOC concentrations remain low because the DOC pool cannot build up, as it is quickly leached out of the system. The low DOC concentrations at 2 meters deep, in turn, lead to a very low DOC flux with drainage. Therefore, this boundary condition should be revised before applying our model for global predictions of DOC export with drainage.

Moreover, the profile of DOC in the soil strongly depends on the input from the hydrology module (Figure 6), and thus the accuracy of the DOC output relies on the quality of the soil water flux simulation. However, soil water fluxes between layers cannot be validated against observations (as there is no measurements of internal soil water flux) and, in this sense, a new source of uncertainty is introduced in ORCHIDEE-SOM.

Finally, it is important to note that, even though the same formulation has been used for transport of SOC and DOC, the represented mechanisms are different. Diffusion of DOC fits with the original definition of diffusion (movements of molecules due to a concentration difference), whereas diffusion of SOC is a simplification of complex soil-mixing mechanisms controlled by different actors (roots, earthworms, frost churning, etc.). In other words, diffusion of DOC and SOC in ORCHIDEE-SOM are represented with the same theoretical framework, but the reasons for this choice are different. The D term in the case of SOC is representative for the presence of ecosystem-engineers or for cryoturbation. Even though this diffusion approach for processes of soil carbon bioturbation is the most widely applied so far (e.g., Braakhekke et al., 2011; Bruun et al., 2007; Wynn et al., 2005), we need to keep in mind that this assumption may be subject to further development in latter versions of this model. For instance, the D term could be made soil depth-dependent.

3.4 Future parameterization and optimization

For further use of ORCHIDEE-SOM, a model parameterization is needed. Firstly, parameters that have proven to be variable with vegetation types (or PFTs) and soil type should be defined at PFT- or soil-type level or made PFT- or soil type-dependent in ORCHIDEE by means of empirical equations. A preliminary model testing exercise using the default version of ORCHIDEE-SOM showed that the model was able to reasonably reproduce DOC profiles and dynamics for a coniferous forests (see Chapter 4), but the results were not satisfactory for a beech forest and even less for a grassland site (Figure 5), suggesting that ORCHIDEE-SOM will benefit from parameters that are defined based on PFTs or soil type. Many studies highlight the importance of soil properties and vegetation characteristics in SOC-related parameters, for instance, the effect of soil type and litter decomposability on microbial response (Sulman et al., 2014) or the effect of soil texture, organic carbon content and bulk density in the moisture-soil respiration relationship (Moyano et al., 2012). An empirical relationship that links the adsorption coefficient (K_D) which is highly dependent on soil properties was suggested in this chapter (Equation 12), but it is still under development. Representation of other processes, particularly decomposition and diffusion rates, will benefit from a similar exercise.

Secondly, before being applicable to large scales simulations, ORCHIDEE-SOM needs to be optimized at both site and multisite level. Bayesian data assimilation has been successfully applied to constrain parameters with site level data (Braakhekke et al., 2013) or global datasets (Hararuk et al., 2014). Calibration of the new parameters of ORCHIDEE-SOM by data assimilation will give insight in the relative importance of processes affecting SOC and DOC in different ecosystem types (Braakhekke et al., 2013). For this version of the model, we used default parameters that are reasonable compared to prior knowledge (Table 1). However, a Bayesian optimization using site measurements of DOC and total soil carbon stock will reduce the uncertainty range of the new parameters, which is an essential part of any process-based large scale model (Zaehle et al., 2005). Currently, there is an on-going work on a Bayesian-based data assimilation exercise using DOC concentrations at three soil depths for three sites differing in PFT soil types.

4 Conclusions

To conclude, ORCHIDEE-SOM is a vertically explicit model of soil organic carbon and litter dynamics, embedded in the land surface model ORCHIDEE, which includes processes of DOC production and transport in soil. ORCHIDEE-SOM can provide insight into several processes that cannot be addressed with the trunk version of ORCHIDEE, such as deep SOC dynamics and loss of organic carbon through leaching.

With our work on ORCHIDEE-SOM, we prepared the necessary model structure to implement the new processes of DOC production and decomposition, DOC adsorption/desorption in mineral soils and SOC and DOC transport through water flux and bioturbation. Although the current model parameters are fixed based on prior literature and thus still require exhaustive parameterization, by improving each of these new elements we have the opportunity to end up with a robust, albeit simple and general, global tool for prediction of soil C movement and leaching to rivers and lakes.

CHAPTER 4

CHAPTER 4. Modelling the dynamics of DOC concentrations in the soil solution of a temperate forest using ORCHIDEE-SOM

Marta Camino-Serrano, Bertrand Guenet, Sebastiaan Luyssaert, Philippe Ciais, Sara Vicca, Bert Gielen, Johan Neirynck, Ivan A. Janssens. *Modelling the dynamics of DOC concentrations in the soil solution of a temperate forest using ORCHIDEE-SOM.* In preparation.

Abstract

ORCHIDEE-SOM is the first soil module within a land surface model able to simulate the soil organic carbon (SOC) and dissolved organic carbon (DOC) dynamics in a discretized soil profile, and to calculate the leaching of DOC from soils. The model includes representation of the biological consumption and production of DOC, the adsorption on- and desorption from soil minerals and the vertical transport of DOC and SOC through the soil profile down to 2 meters. In this study, we tested the model based on measurements of DOC concentrations at three soil depths in a temperate coniferous forest. Furthermore, we performed a sensitivity analysis of the seven new parameters in ORCHIDEE-SOM on the simulated DOC profile and dynamics. Finally, we evaluated which parameter change from the sensitivity analysis gave the best model-data fit. Model results compared well with measured DOC concentration profiles and dynamics, except for an underestimation of DOC concentrations in the deep soil. This finding indicates that the main processes of DOC production, stabilization and transport are correctly represented in the model. The sensitivity analysis demonstrated the importance of the processes of sorption in simulating the profile of DOC, while the dynamics of DOC were more linked to the residence time of DOC, which

controls the biological consumption rate of DOC. Increasing the residence time of recalcitrant DOC improved the simulation of the seasonal dynamics and also of the vertical profile of DOC. On the other hand, ORCHIDEE-SOM failed to reproduce SOC stocks and heterotrophic respiration. This failure can be partly explained by the missing representation of physico-chemical controls within ORCHIDEE, such as pH or Al and Fe concentrations in soil. However, also the evaluation exercise at site level could explain part of the failure, because ORCHIDEE has been designed for global simulations, with parameters optimized to work well at an average site, not at specific sites. In conclusion, this study is a first step in the evaluation of the new soil module ORCHIDEE-SOM that should be extended to a multi-site optimization to successfully simulate DOC and SOC dynamics and profiles at larger scales (continental or global).

1 Introduction

The importance of dissolved organic carbon (DOC) in soil processes is well-known: DOC is a carbon source for soil microorganisms, its mobilization is related to soil-formation processes and to transport of heavy metals (Kalbitz et al., 2000) and it contributes to the carbon sequestration in mineral soils (Neff and Asner, 2001; Rumpel and Kogel-Knabner, 2011). DOC constitutes also a C loss from forests that is normally neglected in European carbon budgets (Siemens, 2003). Although the magnitude of C losses through DOC leaching is small compared to the gross ecosystem carbon fluxes (between 5% and 2% of soil heterotrophic respiration - see Regnier et al. (2013); and Schulze et al. (2009)), neglecting the DOC fluxes can lead to a systematic bias of the atmosphere-based estimates of terrestrial ecosystem fluxes, probably overestimating the soil organic carbon sink (Jackson et al., 2002; Janssens et al., 2003).

Currently, no large-scale Land Surface Models (LSMs) accounts for DOC leaching from soils and thus, their prediction of terrestrial carbon uptake may be overestimated. Moreover, representation of soil organic carbon (SOC) in LSMs is generally highly simplified, with a single-layer box modelling approach, impeding correctly accounting for deep soil carbon dynamics. Soil carbon stocks in LSMs are normally modelled as a single carbon pool, and therefore it has not been possible to simulate DOC or SOC profiles (Todd-Brown et al., 2013).

This single-layer approach adopted in almost all LSMs assumes that deeper SOC and DOC do not play an active role in carbon cycle (Koven et al., 2013). However, deep soil carbon contributes to more than half of the global soil carbon stocks (Schmidt et al., 2011). DOC is an active agent of C dynamics in deep soil, as a substantial amount of C in deep soil layers is DOC transported through the water fluxes within the soil column. Moreover, DOC is considered as an important substrate for microorganisms in deep soils (Rumpel and Kogel-Knabner, 2011). A more realistic representation of the mechanisms of SOC and DOC dynamics in the soil profile will be needed to predict the vulnerability of deep SOC and DOC to climate change, which is one of the main objectives of LSMs.

Recently, a new multi-layer soil module has been developed within the LSM ORCHIDEE. This new module, called ORCHIDEE-SOM, simulates internal physico-chemical processes affecting SOC and DOC dynamics, namely biological DOC production and consumption, DOC adsorption on- and desorption from soil minerals and vertical movement of SOC and DOC due to advection and diffusion. Therefore, ORCHIDEE-SOM represents the processes that enable it to simulate SOC and DOC concentrations in 11 layers along a 2 meters deep soil profile, as well as the DOC flux contained in runoff and drainage. A detailed description of this model is given in Chapter 3. Although ORCHIDEE-SOM has been developed to work with all plant functional types (PFTs) of ORCHIDEE, a detailed evaluation of the model outputs against observational data has yet to be undertaken. If the model structure is valid, ORCHIDEE-SOM should be able to reproduce, not only the values of DOC concentrations within the range of the observations, but also the internal soil processes leading to a decreasing profile of DOC.

Therefore, the goal of the present work was to perform a first evaluation of the ability of the new soil module ORCHIDEE-SOM to reproduce the dynamics and soil profile of DOC concentrations. For that purpose, we made a comparison between model predictions and observations at a long-term monitored temperate coniferous forest in Belgium. We also performed a sensitivity analysis. evaluate the most suitable combination of parameters to simulate DOC concentrations at that site and to detect the main areas of improvement of the model.

2 Methods

2.1 Brief description of ORCHIDEE-SOM

ORCHIDEE-SOM is based on the trunk version of ORCHIDEE SVN r1652. ORCHIDEE calculates water and energy fluxes at a time step of 30 minutes and phenology and carbon dynamics at a time step of 1 day. The basic structure of the soil module in ORCHIDEE SVN r1652 is presented in Krinner et al. (2005). Here, a brief overview of the new features in ORCHIDEE-SOM is presented. A more detailed presentation can be found in Chapter 3.

In ORCHIDEE-SOM, the soil profile is divided in 11 layers. The first layer has a thickness of 0.001 m and with every additional layer it thickness increases geometrically up to a cumulative thickness of 2 meters. Litter is divided in 4 pools: metabolic aboveground litter, metabolic belowground litter, structural aboveground litter and structural belowground litter. Metabolic and structural litter have a different chemical composition and therefore a high and low decomposition rate, respectively. Regarding the soil carbon, three pools are distinguished based on their turnover rate. This approach follows Parton et al. (1988) who also distinguished an active, slow and passive soil carbon pool. In ORCHIDEE-SOM two new pools were added to represent the DOC defined by their decomposition rate: the labile DOC with a high decomposition rate and the recalcitrant DOC with a low decomposition rate. Each pool may be free (free DOC) in the soil solution or adsorbed (adsorbed DOC) on the mineral matrix.

In ORCHIDEE-SOM, SOC decomposition is modified to account for the priming effect (Guenet et al, in prep). The products of litter- and SOC decomposition go to free DOC, which, in turn, is decomposed following first order kinetics equation. One part of the decomposed DOC goes back to SOC pools, according to a fixed carbon use efficiency (CUE) parameter, the other part is converted into CO_2 and contributes to heterotrophic respiration. The free DOC can then be adsorbed to soil minerals or remain in solution following an equilibrium distribution coefficient (K_D) (Nodvin et al., 1986). Adsorbed DOC is assumed to be protected and thus it is neither decomposed nor transported within the soil column. Free DOC is subject to transport with the water flux between layers calculated by the hydrological module of ORCHIDEE, *i.e.* advection, and is represented following Futter et al. (2007). Also, SOC and DOC are subject to diffusion, and are represented using the Fick's law. SOC diffusion is actually a representation of bioturbation processes caused by animal (and plant) activity in soil or by freeze-frost cycles in permafrost. Logically, the diffusion parameter used in the equations for SOC and DOC is different.

All the described processes occur within each soil layer. At the end of every time step, the flux of DOC (expressed in g C m^{-2} d^{-1}) leaving the soil with runoff (upper layer) and drainage (bottom layer) is calculated by multiplying DOC concentrations in the solution with the runoff and drainage flux calculated by the already existing hydrological module of ORCHIDEE.

2.2 Site characteristics

Brasschaat is an 80-year-old even aged Scots pine (*Pinus sylvestris* L.) forest located in Belgium (51°18′N, 4°31′E). The stand is part of the ICP Forests Level II and Fluxnet/CarboEuropeIP/ICOS networks. The site has a temperate maritime climate, with a long-term mean annual temperature of 10 °C. The long-term mean temperatures of the coldest and warmest months are 3 and 19 °C, respectively, and mean annual precipitation is 830 mm.

The soil is classified as Arenosol. It is a moist soil, because of a clay layer at variable depth, but still rarely saturated, because of the high hydraulic conductivity in the upper horizons due to the sandy texture (Gielen et al., 2011). The soil is covered with an organic surface layer of 6 cm depth. The total stock of carbon in soil and litter was estimated in 144.5 t ha^{-1} (Janssens et al., 1999). More information on the soil properties of Brasschaat can be found in Janssens et al. (1999). Mean annual soil respiration is approximately 400 g C m^{-2} yr^{-1} (Gielen et al., 2011) (Table 1).

DOC concentrations were measured biweekly using tension lysimeters installed at three horizons corresponding to the Al/Ap horizon (±10 cm), the A/E horizon (±30–40 cm) and the Cg horizon (±70–80 cm) (hereafter referred as layer 10cm, layer 35 cm and layer 75 cm, respectively). Samples were collected and pooled into one composite sample per layer for analysis. In total, 6 samples were pooled to get one measurement at each date and horizon (Gielen et al., 2011) (Table 1).

Table 1. Site characteristics for Brasschaat

Site characteristics	
Location	51°18’N, 4°31’E
Ecosystem	Evergreen forest
Dominant species	*Pinus sylvestris* L.
mean annual GPP (g C m^{-2} year^{-1})	1173
Aboveground C storage (t ha^{-1})	104.4
Soil properties	
Soil classification	Arenosol
pH	4

Clay (%)	3.4
BD (g cm^{-3})	1.4
Soil and litter C storage (t ha^{-1})	144.5
mean annual soil respiration (g C m^{-2} year^{-1})	411.4
mean DOC (mg L^{-1}) (2000-2010)	
DOC at 10 cm	36.8
DOC at 35 cm	30.0
DOC at 75 cm	20.5

pH, Clay and Bulk Density are averages over the soil profile from data in Janssens et al. (1999) for Brasschaat. Aboveground, soil and litter C storage is taken from Janssens et al. (1999). GPP and soil respiration are means over 7 years from Gielen et al., 2011.

2.3 Sensitivity analysis set-up

As the site is part of the FLUXNET network, the in-situ measured meteorological variables were available to be used as forcing data for the simulations in ORCHIDEE. The in-situ meteorological data was gap-filled using the ERA-interim 3-hourly product, following the method developed by Vuichard and Papale (2015).

Prior to the sensitivity analysis, we initialized the model by using iteratively the meteorological data for the period 1997-2010 until all the soil variables reached a steady state. This procedure, known as the spin-up, took about 3000 years of simulation and was run with the default parameters values (Table 2). For pH, clay content and bulk density, site-specific observed values (Janssens et al., 1999; Table 1) were used. The atmospheric CO_2 concentration was held at 363.2 ppm representing the year 1997 (Keeling and Whorf, 2006).

To reduce the computational cost, part of the spin-up was executed with a simplified version of the model, called forcesoil, that only uses ORCHIDEE's soil carbon module. For this spin-up, the full model was first run for 266 years, followed by 2996 years with forcesoil and finally another 112 years of the full model. The final 112 years guarantee that there are no inconsistencies between biomass production, litter production and the soil carbon pools. The state of the ecosystem at the last time step of the spin-up is then used as the initial state for the actual simulations in the sensitivity analysis.

Then, we performed a sensitivity analysis in order to detect the main areas of improvement of the model. For this, we focused on the seven new parameters introduced in ORCHIDEE-SOM: the thickness of the litter layer (*z_litter,* mm), the SOC diffusion coefficient (*D,* m^2 day^{-1}), the DOC diffusion coefficient (*D_DOC,* m^2 hr^{-1}), the DOC sorption distribution coefficient (K_{D}, m^3 water kg^{-1} soil), the microbial carbon use efficiency (*CUE,* -), the residence time of recalcitrant DOC (*DOC_tau_stable,* days) and the residence time of labile DOC (*DOC_tau_labile,* days) (see Table 1 in Chapter 3). We ran 19 ORCHIDEE simulations, varying each parameter one by one in the range of observations, first adding 50% and second removing 50% of its value. For some highly variable parameters, we used a more extreme value (*z_litter*=200, *D*=1.95E-6 and K_D=0.05) in order to detect the model behavior with very different values (Table 2). We ran the model for 14 years (from 1997 to 2010).

Table 2. Parameter sets for the 19 simulations for the sensitivity analysis.

RUN		**PARAMETERS**						
Name	**Description**	**z_litter (mm)**	**D (m^2 day^{-1})**	**D_DOC (m^2 hr^{-1})**	**K_D (m^3 kg^{-1})**	**CUE (-)**	**DOC_tau_stable (days)**	**DOC_tau_labile (days)**
SEN1	Default	10	1.95E-7	4.428E-7	0.00805	0.5	60	0.3
SEN2	z_litter+50	**15**	1.95E-7	4.428E-7	0.00805	0.5	60	0.3
SEN3	z_litter-50	**5**	1.95E-7	4.428E-7	0.00805	0.5	60	0.3
SEN4	z_litter_other	**200**	1.95E-7	4.428E-7	0.00805	0.5	60	0.3
SEN5	D+50	10	**2.92E-7**	4.428E-7	0.00805	0.5	60	0.3
SEN6	D-50	10	**9.73E-8**	4.428E-7	0.00805	0.5	60	0.3
SEN7	D*10	10	**1.95E-6**	4.428E-7	0.00805	0.5	60	0.3
SEN8	D/10	10	**1.95E-8**	4.428E-7	0.00805	0.5	60	0.3
SEN9	D_DOC+50	10	1.95E-7	**6.642E-7**	0.00805	0.5	60	0.3
SEN10	D_DOC-50	10	1.95E-7	**2.214E-7**	0.00805	0.5	60	0.3
SEN11	kd+50	10	1.95E-7	4.428E-7	**0.0121**	0.5	60	0.3
SEN12	Kd-50	10	1.95E-7	4.428E-7	**0.004**	0.5	60	0.3
SEN13	kd_other	10	1.95E-7	4.428E-7	**0.05**	0.5	60	0.3
SEN14	CUE+50	10	1.95E-7	4.428E-7	0.00805	**0.75**	60	0.3
SEN15	CUE-50	10	1.95E-7	4.428E-7	0.00805	**0.25**	60	0.3
SEN16	DOC_tau_stable+50	10	1.95E-7	4.428E-7	0.00805	0.5	**90**	0.3
SEN17	DOC_tau_stable-50	10	1.95E-7	4.428E-7	0.00805	0.5	**30**	0.3
SEN18	DOC_tau_labile+50	10	1.95E-7	4.428E-7	0.00805	0.5	60	**0.5**
SEN19	DOC_tau_labile-50	10	1.95E-7	4.428E-7	0.00805	0.5	60	**0.1**

2.4 Comparison of model results with data

DOC concentrations measured in Brasschaat fortnightly at approximately 10 cm, 35 cm and 75 cm were compared with DOC concentrations simulated with ORCHIDEE-SOM for each measurement date from the soil layers 6 (~ 9.2 cm depth), 8 (~ 37 cm) and 9 (~ 75 cm) respectively. Moreover, measured soil carbon stocks (t ha^{-1}) were compared with the simulated soil carbon stock.

The simulated and measured DOC concentrations for the three layers were compared using the Mean Squared Deviation (MSD) and its three components: the Squared Bias (SB), the Non-Unity slope (NU) and the Lack of Correlation (LC) (Gauch et al., 2003). The SB is an indicator of the mean bias of the simulation from the measurement, the NU provides information on the ability of the model to reproduce the magnitude of fluctuation among the measurements, and LC indicates the ability of the model to reproduce the shape of the data. The lower the value of MSD, SB, NU and LC are, the better the fit is. The value amplitude of these statistics indicators will depend on the measured variable and the units used (in this case, DOC concentrations in mg L^{-1}). These are very useful to compare model-observations fit among models (e.g., Guenet et al., 2013).

The four statistical indices were calculated for the 19 simulations of the sensitivity analysis by comparing 1) measurements of DOC concentrations at 10 cm, 35 cm and 75 cm, and 2) mean DOC concentrations (from 10 cm, 35 cm and 75 cm), in order to detect which parameter change gave the best fit to the measured DOC data (lowest MSD). The model-data comparison was done for each measurement date and, therefore, the statistical indices gave an idea of the performance of the model in terms of temporal dynamics.

3 Results

3.1 Simulation of the magnitude, dynamics and soil profile of DOC with the default parameter set

Overall, ORCHIDEE-SOM with default parameters was able to capture reasonably well the magnitude of soil solution DOC at the Brasschaat site, particularly for the uppermost layer (10 cm) (Figure 1 and 2), with measured mean values of 37±14, 31±11 and 21±5 mg L^{-1} and simulated mean values of 42±20, 22±7 and 10±3 mg L^{-1} for DOC concentrations at 10, 35 and 75 cm, respectively. Similarly, the temporal dynamics (intra-annual variations) were well reproduced (Figure 1). Nevertheless, for the uppermost layer, ORCHIDEE-SOM simulated peaks of DOC concentrations (normally in summer) that were outside the range observed from soil solution DOC measurements (Figure 1A).

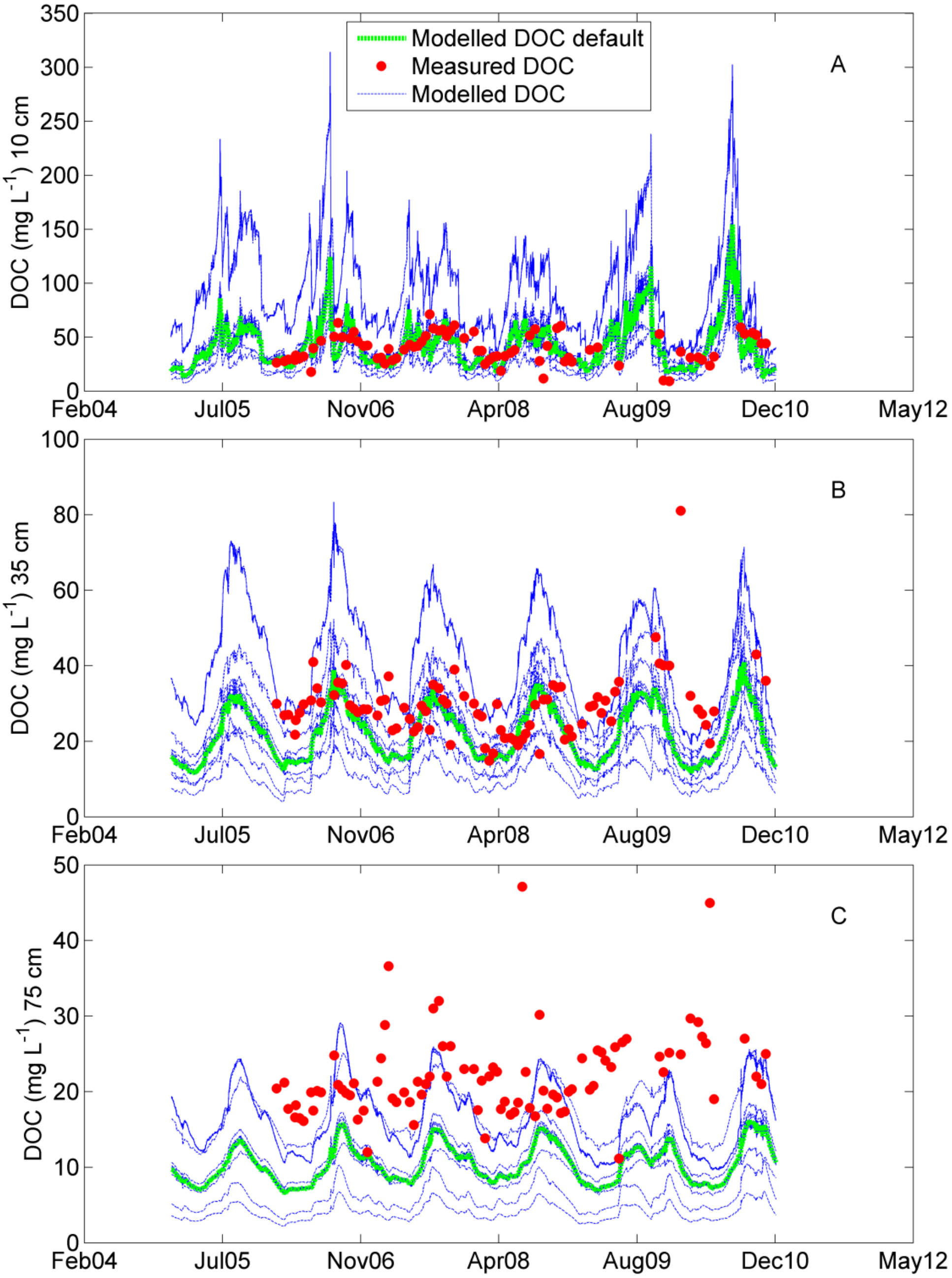


Figure 1. Modelled versus observed DOC concentrations in soil solution (mg L^{-1}) in Brasschaat at different soil depths: A) 10 cm, B) 35 cm and C) 75 cm. The 19 sensitivity tests are shown in blue, the simulation using the default parameters settings is shown in green.

Overall, our statistical approach confirmed that the simulation using the default parameters was able to reproduce reasonably well the seasonal cycle in soil solution DOC, particularly for the upper and middle soil layer. The default run was ranked at 5th and 7th place when simulations were sorted by the goodness of fit (lowest MSD) for the layers at 10 cm and 35 cm, albeit with very similar MSD values than the simulations with higher ranks, respectively (Figure 3, Table 3). On the other hand, the ability of the model to simulate DOC dynamics at 75 cm was improved by using another set of parameters than the default parameter set. In particular, changing the parameters related to sorption, DOC decomposition rates and litter layer depth improved the MSD values.

Table 3. Values of Squared Bias (SB), Non-Unity Slope (NU), Lack of correlation (LC) and Mean Squared Deviation (MSD) for the default simulation and the range associated to the 19 simulations for the sensitivity analysis between brackets.

	SB	NU	LC	MSD
Mean DOC	27.3 (2.19-344.4)	32.4 (9.85-178.4)	28.3 (28.3-28.3)	88 (78.7-551.3)
DOC 10 cm	6.8 (0-1858)	62.6 (5.78-642)	173.8 (173.6-174.3)	225.4 (222.7-2658)
DOC 35 cm	64.1 (0.8-374.9)	26.9 (5-156)	71.5 (71.2-71.6)	161.2 (123-451)
DOC 75 cm	137.9 (22.4-326)	5.29 (0.29-23.1)	32.1 (32-32.1)	175.5 (68.1-358.4)

With the default parameter set, the SB of DOC at 10 cm depth was close to 0, but the LC was high, indicating that at 10 cm the model was able to capture the mean values, but was not very good at reproducing the shape of the data, *i.e.* the seasonal variation (Figure 1A). At 35 cm, the model-data bias increased (higher SB), but the reproduction of the seasonal variation improved (lower LC). At 75cm, the NU was close to zero and SB was high, suggesting that the model was able to reproduce the variability of the data, but the reproduction of the seasonal variation was not perfect (LC ≠0) and there was a clear systematic underestimation of DOC concentrations at 75 cm (Figure 1C).

The vertical profile of free DOC in soil solution obtained using the model with the default parameters agreed well with the observed data (Figure 2), except for the simulations in the bottom layer (75 cm) underestimating the observed DOC concentrations.

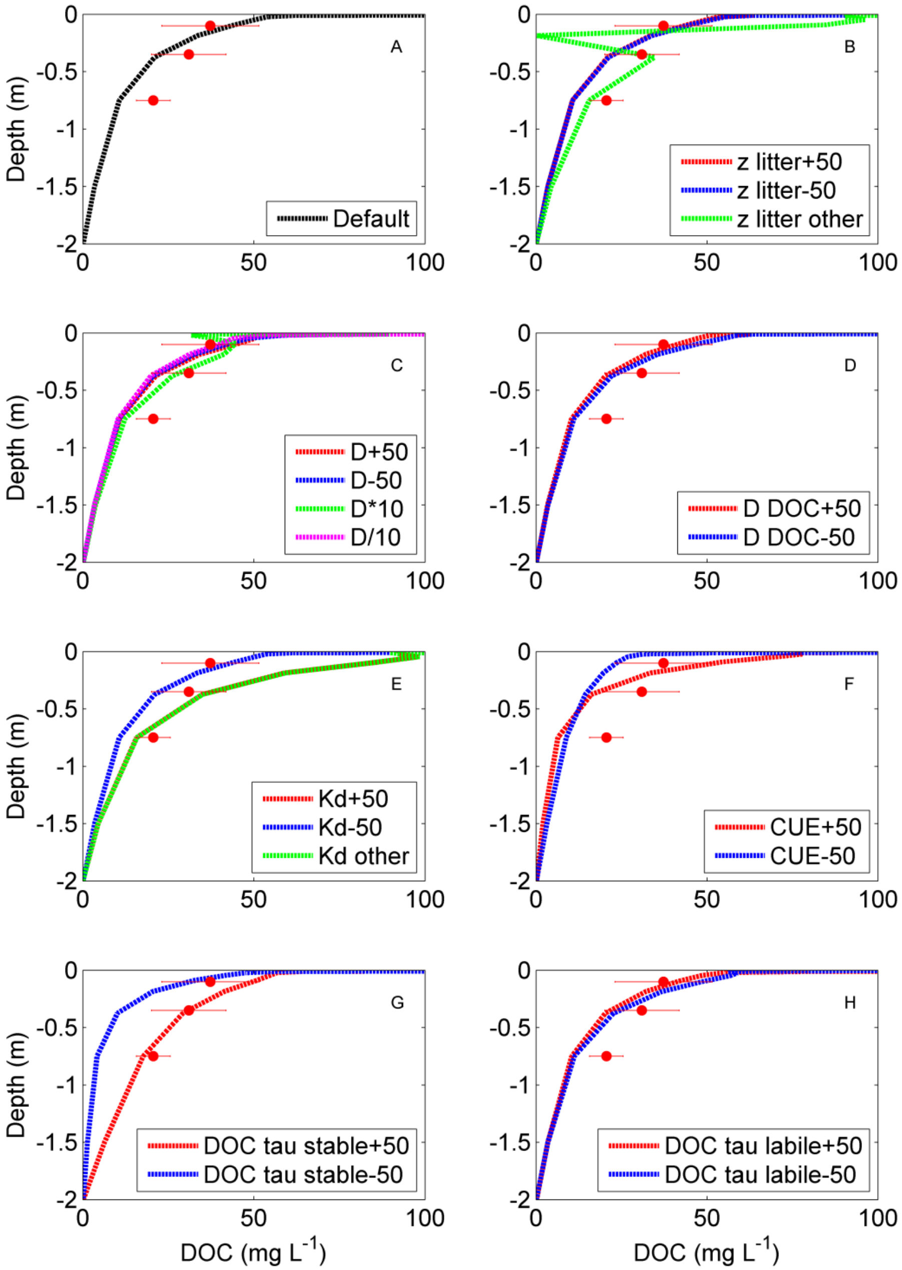


Figure 2. Profile of modelled (dashed lines) versus observed (red dots) DOC concentrations in soil solution (mg L^{-1}) in Brasschaat. Each panel represents the simulations for each parameter used in the sensitivity analysis. The default simulation corresponds to the following parameters: *z_litter*=10, *D*=1.95e-7, *D_DOC*=4.428e-7, *K_D*=0.00805, *CUE*=0.5, *DOC_tau_stable*=60, *DOC_tau_labile*=0.3. *z_litter_other* is the simulation with *z_litter*=200, *Kd_other* is the simulation with *K_D*=0.05

3.2 The sensitivity analysis

Simulated free and adsorbed DOC concentrations -averaged over the soil profile- were most sensitive to the sorption distribution coefficient (K_D) (Table 4). Free DOC concentrations decreased also notably when the residence time of recalcitrant DOC decreased by 50%. Adsorbed DOC was highly sensitive to the thickness of the litter layer (*z_litter_other*) when this was increased with one order of magnitude.

Table 4. Results from the sensitivity analysis. In color the three simulations showing the largest relative change from default simulation for total soil carbon, free and adsorbed DOC and heterotrophic respiration (HR). GPP was constant for all the sensitivity tests, except for the test *z_litter_other*, that reduced GPP by 1.5%.

RUN	Total Soil Carbon (t ha^{-1})	% change	free DOC (mg L^{-1})	% change	adsorbed DOC (g C m^{-3} soil)	% change	HR (g C m^{-2} year^{-1})	% change
Default	243.4	0.00	19.79	0.00	0.13	0.00	685.8	0.00
z_litter+50	242.2	-0.48	19.73	-0.29	0.13	-0.04	685.7	-0.02
z_litter-50	246.7	1.36	19.95	0.83	0.13	0.11	686.1	0.04
z_litter_other	251.7	3.39	25.61	29.41	1.07	**707.4**	715.4	**4.31**
D+50	245.0	0.65	19.90	0.55	0.13	0.11	686.0	0.03
D-50	241.8	-0.68	19.64	-0.74	0.13	-0.11	685.6	-0.03
D*10	263.6	**8.28**	21.12	6.72	0.14	3.06	689.7	0.57
D/10	240.5	-1.21	19.35	-2.18	0.13	-0.19	685.4	-0.06
D_DOC+50	242.3	-0.45	19.13	-3.34	0.13	0.01	686.6	0.12
D_DOC-50	245.0	0.67	20.70	4.59	0.14	5.13	684.0	-0.27
Kd+50	255.5	4.98	31.33	**58.33**	0.28	**110.8**	718.9	**4.82**
Kd-50	243.5	0.02	19.64	-0.75	0.08	-43.11	685.6	-0.04
kd_other	256.7	5.45	31.32	**58.29**	0.97	**630.4**	716.8	**4.51**
CUE+50	283.5	**16.48**	16.94	-14.40	0.15	9.44	663.5	-3.25
CUE-50	210.0	**-13.71**	14.93	-24.55	0.13	-5.70	701.6	2.30
DOC_tau_stable+50	243.3	-0.05	27.31	38.01	0.13	0.08	685.8	0.00
DOC_tau_stable-50	243.6	0.06	11.53	**-41.74**	0.13	-0.11	685.8	0.00
DOC_tau_labile+50	242.0	-0.56	20.17	1.94	0.14	2.22	686.9	0.15
DOC_tau_labile-50	246.1	1.09	20.05	1.33	0.14	6.59	682.7	-0.46

The simulation best reproducing DOC concentrations (averaged over the soil profile) was the simulation using a residence time of labile DOC reduced by 50 % (lowest MSD and lowest LC). The simulation with the lowest bias from the measurements (lowest SB) was the simulation that used a 50% increased residence time of recalcitrant DOC (*DOC_stable+50*), while the simulation with the best capacity to reproduce the temporal variation in the data (lowest NU) used a 50% lower *CUE* (Figure 4).

When focusing on the top soil layer, the best simulation to reproduce the dynamics of DOC was the simulation with the diffusion coefficient reduced by 50% (*D-50*). The lowest bias, however, occurred when decreasing the diffusion coefficient of DOC by 50% (*D_DOC-50*). As with the overall average DOC concentration, the best simulation of the temporal dynamics of the DOC concentration in the top layer was achieved when decreasing the *CUE* by 50% (Figure 3).

In the case of the 35 cm layer, the best simulation of the DOC dynamics was with the SOC diffusion coefficient increased by one order of magnitude (*D*10*). The lowest bias was achieved for the test with the residence time of recalcitrant DOC increased by 50% (*DOC_stable+50*), while the best reproduction of the seasonal variation (lowest LC) was for the test with *CUE* decreased by 50% (Figure 3).

Finally, the best simulation of DOC dynamics in the 75 cm layer was the test with the residence time of recalcitrant DOC increased by 50% (*DOC_stable+50*), which also gave the best model-data bias, followed by the simulations with an increased sorption distribution coefficient (K_D). Similar to the layer 35 cm, the best reproduction of the seasonal variation occurred when decreasing the *CUE* by 50% (Figure 3).

The sensitivity analysis showed that the simulated soil profile of DOC concentrations is mainly affected by the sorption distribution coefficient (K_D) and the residence time of the recalcitrant DOC (Figure 2). Increasing the K_D parameter by 50% led to a worse model-data fit of the free DOC at 10 and 35 cm.

Paradoxically, increasing this parameter substantially improved the fit in the bottom layer (Figure 3). On the other hand, the parameters for diffusion of SOC and DOC did not substantially affect the soil profile of DOC (Figure 2C and Figure 2D).

Overall, decreasing the *CUE* parameter seemed to improve the representation of data scattering (NU) and of the data seasonal variation (LC) in the subsoil. In general, the best fit of the model (lowest MSD) suggested that the coefficients of diffusion and DOC residence times play a key role in the model's capacity to accurately represent the dynamics of DOC concentrations in soil solution in Brasschaat. More specifically, increasing the residence time of recalcitrant DOC (*DOC_tau_stable*) decreased the bias between simulated and observed DOC concentrations in the subsoil, while still giving a good overall fit (MSD=261) for the topsoil. We can conclude that increasing the residence time of recalcitrant DOC by 50% (to approximately 100 days) gave the best overall reproduction of the dynamics of the free DOC in soil solution, as well as the best model-data fit for the three soil layers and the mean DOC over the profile.

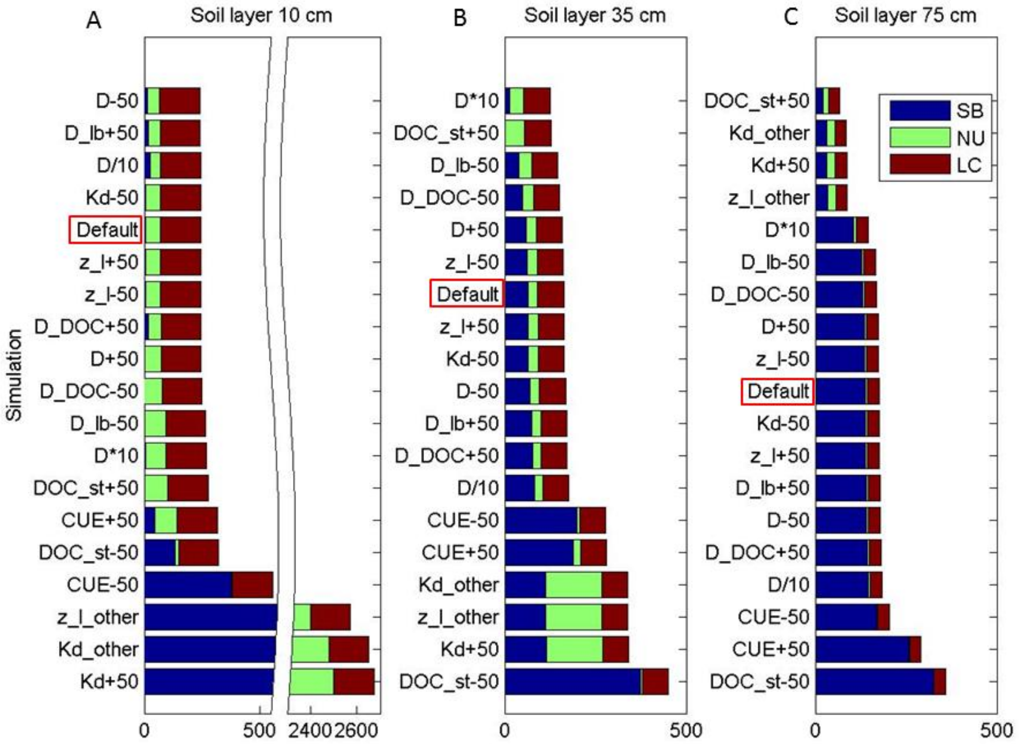


Figure 3. Components of the mean squared deviation (MSD) for the 19 sensitivity test for A) 10 cm, B) 35 cm and C) 75 cm. The three components are squared bias (SB), non-unity slope (NU) and lack of correlation (LC). Sensitivity tests are sorted from smallest to largest MSD, which corresponds to the best and worst fit. *DOC_st* stands for *DOC_tau_stable*, *DOC_lb* stands for *DOC_tau_labile* and *z_l* for *z_litter*. The Default simulation is highlighted in red.

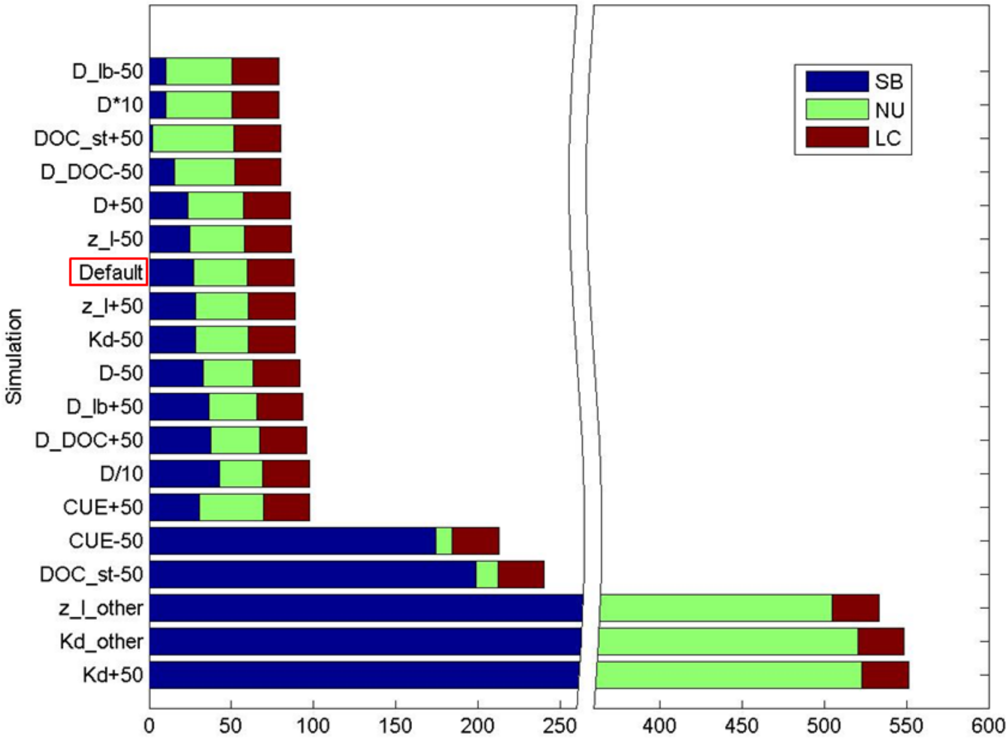


Figure 4. Components of the mean squared deviation (MSD) for the 19 sensitivity tests for the mean DOC along the three soil depths. The three components are squared bias (SB), non-unity slope (NU) and lack of correlation (LC). Simulations are sorted from smallest to largest MSD, which corresponds to the best and worst fit. *DOC_st* stands for *DOC_tau_stable*, *DOC_lb* stands for *DOC_tau_labile* and *z_l* for *z_litter*. The Default simulation is highlighted in red.

3.3 Simulations of other C concentrations and fluxes in Brasschaat

Although the magnitude, dynamics and soil profiles of DOC are reasonably well captured by the model, simulated heterotrophic respiration and total soil carbon stocks were clearly overestimated. ORCHIDEE-SOM simulated values of mean annual heterotrophic respiration around 700 g C m^{-2} yr^{-1}, whereas reported values for Brasschaat of soil respiration, which includes both heterotrophic and autotrophic respiration, were approximately 400 g C m^{-2} yr^{-1} (Table 1 and 3). Given that, on average, heterotrophic respiration accounts for half of the soil respiration (Hanson et al., 2000), the estimation of heterotrophic respiration by

ORCHIDEE-SOM was likely more than three times the observed heterotrophic respiration at the site.

Total soil carbon stock simulated by ORCHIDEE-SOM was twice the observed carbon stock (simulated mean value=243 t ha^{-1}, measured mean value= 118 t ha^{-1}). The shape of the measured soil carbon profile was well simulated for the subsoil, but the model failed to capture it in the topsoil (Figure 5), where the simulated values of soil carbon concentrations were very high. Therefore, the overestimation of total soil carbon stocks originates from the very high simulated carbon concentrations in the first 30 cm of soil.

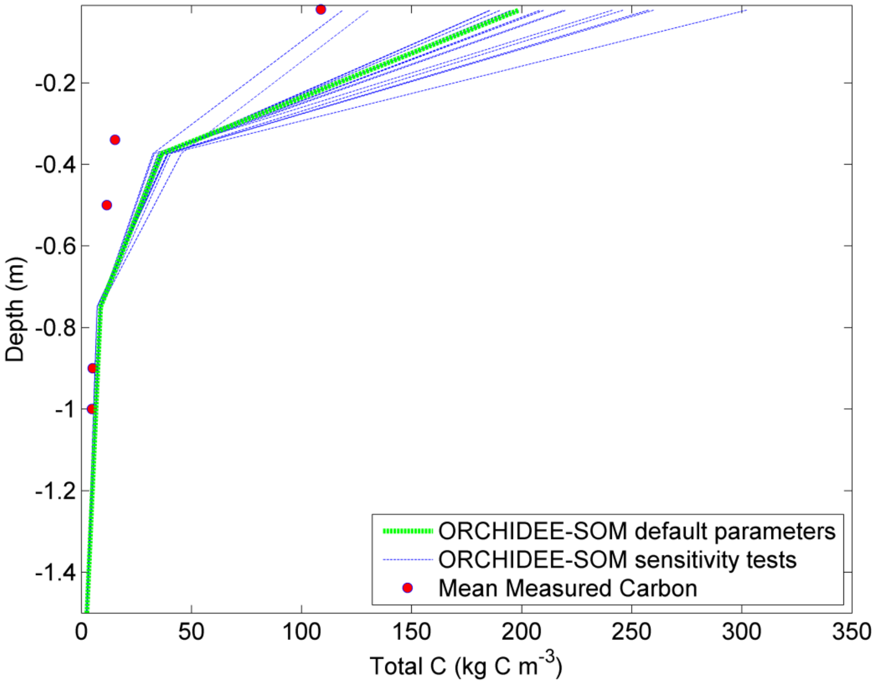


Figure 5. Profile of modelled versus observed total soil carbon stocks (kg C m^{-3}) in Brasschaat. The 19 sensitivity tests are shown in blue, the simulation based on the default parameters settings in green.

Total soil carbon and heterotrophic respiration sensitivity to changes in the seven parameters tested were less pronounced with maximum changes of 17% (Table 4). Heterotrophic respiration is mostly affected by the same parameters as adsorbed DOC, that is, the sorption distribution coefficient (K_D) and the thickness of the litter layer when it was increased one order of magnitude (*z_litter_other*). Not surprisingly, simulated total soil carbon was especially sensitive to changes in the parameter controlling the carbon use efficiency (CUE) and diffusion coefficient (D), which are the two parameters affecting directly the SOC dynamics in ORCHIDEE-SOM. The residence time of recalcitrant DOC (*DOC_tau_stable*) had no effect on heterotrophic respiration, and also its effect on total soil carbon stock was negligible (Table 4). Overall, among the different simulations in the sensitivity analysis, relative changes in heterotrophic respiration and total soil carbon stocks were smaller than changes in DOC.

4 Discussion

4.1 Simulated DOC dynamics and profiles with default parameters

This study is the first attempt to evaluate the recently developed module of DOC production and transport in the LSM ORCHIDEE-SOM. Our results suggest that the model can simulate the magnitude and temporal dynamics of DOC concentrations in the soil of a temperate coniferous forest, even when applying default parameters according to prior knowledge. For the particular case of Brasschaat, model-data bias was less than 4 mg L^{-1} out of an average of 37 mg L^{-1} for the soil layer at 10 cm, DOC concentrations at 35 cm were underestimated by 9 mg L^{-1}, but were still in the range of 14-81 mg L^{-1} of the observations, whereas the DOC values at 75 cm were underestimated by 10 mg L^{-1}. Measured soil DOC concentrations at Brasschaat are within the range of 2-90 mg L^{-1} of DOC concentrations in soil solution reported in the literature for European forests (Michalzik et al., 2001). ORCHIDEE-SOM thus, seems to be able to simulate DOC concentrations in soil solution within the range of measurements for a European forest site in terms of DOC concentrations.

More specifically, in the topsoil (10 cm layer) the model was able to catch the mean values, but was not very good at reproducing the shape of the temporal variation of the data, because the modelled amplitude of the seasonal cycle was too high (Figure 1a). Two possible reasons are considered for the overestimated seasonal amplitude of the modelled DOC in the topsoil. First, SOC decomposition in ORCHIDEE-SOM may be too sensitive to temperature, thus increasing decomposition during periods of high temperature, such as summer, and producing a large amount of DOC that exceeds normal values found in nature. Indeed, seasonal changes in DOC concentrations in the topsoil have been reported under field conditions due to increases in soil temperature (Michalzik and Matzner, 1999), but this effect is not always clear because soil moisture conditions also play an important role in the temperature effects on DOC release (Kalbitz et al., 2000). Therefore, the second possible reason for these high peaks of DOC in summer may be found in the hydrological module of ORCHIDEE: simulated soil moisture in the top layer may be too low, leading to too high concentrations of DOC.

In the intermediate soil layer (35 cm) the model-data bias is higher than for the topsoil, but the shape of the measurement data is better simulated (Figure 1B and 3). At a soil depth of 75 cm the model was able to reproduce the variability of the data (NU was very low) but there was a systematic bias with a clear underestimation of DOC concentrations (SB was high) (Figure 1C and 3).

The fact that simulations of DOC concentrations were better in topsoil than in subsoil suggest that production of DOC by microbial decomposition, which is the predominant process affecting surface DOC concentrations, is well-represented in the model, while some internal soil processes, more related with the physico-chemical characteristics of the soil, such as DOC stabilization, are not fully captured by the model. The observed DOC concentrations closer to the surface (10 and 35 cm) showed a clear seasonal dynamic, while DOC in the subsoil (75 cm) did not exhibit a clear seasonal pattern. This is in line with other observations and was suggested to indicate that DOC concentrations in subsoil depend more on soil characteristics, contrary to DOC concentrations in the top soil that depend more on climatic or biological factors (Qualls and Haines, 1992). Given the small scale variation in soil characteristics, the large scale of the model simulations may fail to reproduce the small scale variation of the mineral subsoil. Simulations of DOC for the 75 cm layer indeed showed a smoother seasonal pattern compared to the upper layers, but this simulated seasonal cycle was still more pronounced compared to that of the observations (Figure 1). The smoother seasonal variation in lower soil layers in the model is due to soil temperature and soil moisture that are more stable in deep soil.

DOC in soil solution is highly dependent on soil acidity and the soil solution concentration of NH_4^+, Al^{3+} or Fe^{2+} (Chapter 1 and 2). However, these parameters are not explicitly represented within ORCHIDEE-SOM, as is the case for all LSMs (Falloon and Smith, 2009; Todd-Brown et al., 2013). This means that essential physico-chemical controls on DOC cannot be captured by the model. The measured high DOC concentrations at 75 cm at Brasschaat may be due to the particular soil properties of this forest. The soil at the study site is very acidic (pH_{H2O}<4) and very sandy. In fact, higher concentrations of DOC are often found in acid forest soils, due to their high concentration of Al^{3+} in the soil solution, which affects DOC decomposition through two different mechanisms: microorganisms toxicity to Al^{3+} and decreased bioavailability through the formation of Al-DOC precipitates (Scheel et al., 2008; Schwesig et al., 2003). In addition, the clay content of soils is known to enhance the mineral adsorption of DOC, reducing the amount of DOC free in soil solution (Jardine et al., 1989). Therefore, these two factors (pH and texture) are key in explaining the high observed DOC concentrations in the subsoil, but pH is currently not considered in ORCHIDEE-SOM and texture in ORCHIDEE can only adopt default values (sand-loam, loam or clay-loam) for the whole soil column. Consequently DOC concentrations at depth are underestimated by the model.

Another possible reason for the underestimation of DOC concentrations in the layer 75 cm is the incapacity of ORCHIDEE-SOM to simulate conditions of high groundwater table (Campoy et al., 2013). During wet periods in winter, a shallow water table is often present, even above 1 m depth (Table 5). The presence of groundwater at 75 cm could influence the measurements by DOC coming from the groundwater that cannot be simulated by ORCHIDEE-SOM. Nevertheless, this situation happens only during few months in winter and thus could explain isolated cases of model-data disagreements (Figure 6), but not the systematic bias.

Table 5. Monthly groundwater levels in Brasschaat for the period 2006-2011 in cm below surface.

	jan	feb	mar	april	may	jun	jul	aug	sep	oct	nov	dec
2006		-85	-86	-103	-136	-143	-184	-188	-171	-182	-178	-135
2007	-105	-93	-76	-106	-144	-146	-130	-119	-139	-141	-104	-79
2008	-75	-72	-60	-69	-101	-121	-128	-113	-128	-126	-106	-74
2009	-89	-77	-105	-107	-129	-125	-149	-166	-181	-189	-163	-80
2010	-84	-85	-79	-102	-141	-175	-196	-210	-197	-183	-110	-88
2011	-75	-88	-100	-150	-189	-196	-197	-191	-180	-189	-193	-178

Regarding the vertical profile of DOC, the model was able to simulate the decreasing profile of soil DOC for the test site (Figure 2). This exponential decreasing shape is typical for soil DOC distribution in temperate forests soils (Chapter 1). The fact that we obtained a similar shape of the DOC profile in the soil column as in the observational data points out to a correct representation of the processes of DOC transport (advection and diffusion) within the soil.

Although the overall soil profile of DOC is correctly simulated, DOC at the bottom layer was underestimated, as previously mentioned. A potential explanation of the failure to capture mean DOC concentrations in the deep soil is that the default parameters used in this first version of ORCHIDEE-SOM are not soil depth-dependent yet. Parameters involved in processes of biological decomposition (*DOC_tau_stable, DOC_tau_labile*), mineral adsorption or desorption (K_D) or vertical transport of DOC (*D_DOC*) are expected to change along the soil profile, as the relative importance of the processes change, because soil conditions vary across soil horizons (Braakhekke et al., 2013). Further parameterization work needed is discussed in section 5.

Finally, it is important to highlight that the root profile, which influences the vertical distribution of soil carbon in ORCHIDEE-SOM, is fixed for each PFT and does not interact with environmental condition or soil properties. While this assumption may work well for regional or global simulations, it may impede a correct model-data fit at site level. In reality, it is well-known that the root profile is highly dependent on vegetation type, soil and climate conditions (Jackson et al., 1996; Rudd et al., 2014), but the latter factors are omitted in the model. Hence, the simplification in the representation of the root profile in ORCHIDEE-SOM might create a bias in modelled versus measured SOC and DOC profiles in site-level simulations.

4.2 The sensitivity analysis

In our sensitivity analysis the residence time of the recalcitrant DOC is detected as a key parameter controlling the magnitude (Table 4), dynamics (Figure 3 and 4) and soil profile (Figure 2) of DOC. This is not surprising because the residence time of DOC controls the amount of DOC available for biodegradation. We observed that increasing the residence time of recalcitrant DOC by 50% (to approximately 100 days) yields the best overall fit of the observed dynamics of free DOC in soil solution (Figure 6). This residence time of recalcitrant DOC of 100 days is in line with previously reported DOC residence times (Turgeon, 2008), but is still smaller than others (Kalbitz et al., 2003; Qualls and Haines, 1992). For the moment, the residence time of DOC in ORCHIDEE is fixed and no dependency on temperature is taken into account. Due to this high sensitivity of ORCHIDEE-SOM to DOC residence times, we recommend to model DOC decay rate as a function of substrate properties (labile or recalcitrant DOC) and soil conditions including pH, temperature and moisture, as was previously suggested by Schmidt et al. (2011). In contrast to what is typically assumed in LSMs, the temperature sensitivity of decay is not constant along the wide range of substrate quality: recalcitrant material is more sensitive to temperature (Davidson and

Janssens, 2006). Therefore, we suggest making the temperature response (Q10) of decomposition dependent on the DOC decomposition rate in future model developments.

Even though DOC was not very sensitive to the diffusion coefficient for DOC or SOC, it seemed that the goodness of fit of the simulations of the dynamics of DOC improved when changing the SOC diffusion coefficient (Figure 3 and 4). In ORCHIDEE-SOM, diffusion of DOC represents the movements of dissolved C due to a differential concentration, but diffusion of SOC is a simplification of complex bioturbation mechanisms controlled by different actors (roots, earthworms, etc.). The negligible relative importance of the DOC diffusion compared with the SOC diffusion points out the importance of bioturbation to improve predictions of DOC dynamics. Although this biological activity (e.g. earthworms activity) is not yet explicitly incorporated in LSMs (Falloon and Smith, 2009), a fine parameterization of the SOC diffusion coefficient can help in integrating this process. Moreover, the contrasting results for the top layer (fit improvement with decreased SOC diffusion rate) and the subsoil (fit improvement with increased SOC diffusion rate) bring to light the urgency to make the diffusion coefficient soil depth-dependent, as the biotic activity declines non-linearly with depth, with important differences between soil horizons (Wilkinson et al., 2009), and strongly depends on litter quality and soil properties such as pH and base saturation (Braakhekke et al., 2011).

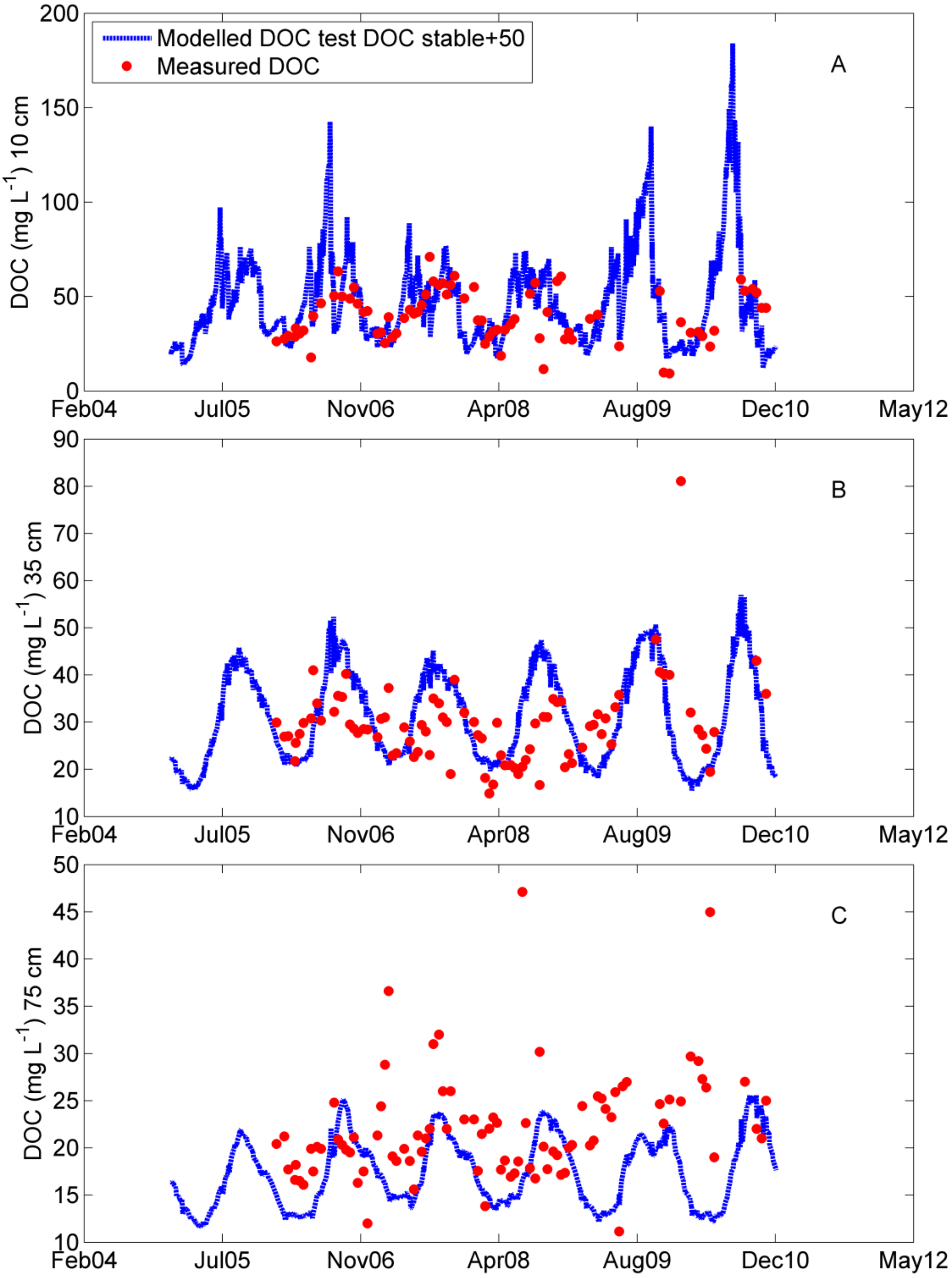


Figure 6. Modelled versus observed DOC concentrations in soil solution (mg L^{-1}) in Brasschaat at different soil depths: A) 10 cm , B) 35 cm and C) 75 cm for the sensitivity test selected for best simulating the dynamics and soil profile of DOC, which corresponds to the residence time of recalcitrant DOC increased by 50% (*DOC_stable+50*).

One of the main findings of this study was the high sensitivity of the simulated free DOC concentration along the soil profile to the sorption distribution coefficient (K_D). The model's performance could improve with a lower K_D in the upper layer and a higher K_D in the subsoil, suggesting that we need to make the sorption distribution coefficient soil depth-dependent. The higher sorption (higher K_D) of the lower B and C horizons compared to A, E and B/E horizons in forest soils has been frequently described in literature (e.g., Jardine et al., 2006; Kaiser et al., 1996; Sanderman and Amundson, 2008). This is because B and C horizons in forest soils are normally more acidic, clay- and Al- and Fe- oxide richer and have less organic C, all factors that enhance adsorption of DOC (Kaiser and Guggenberger, 2000; Kaiser et al., 1996; Karavanova, 2013).

4.3 Simulation of other C concentrations and fluxes in Brasschaat

While ORCHIDEE-SOM captured the dynamics and soil profile of DOC concentration, the model failed to correctly simulating CO_2 fluxes and SOC stocks. Simulated soil carbon stocks were twice as large as the observations and heterotrophic respiration was overestimated by more than 100%.

Reducing CUE by 50 % (that is, to a value of 0.25) produced a better fit of the simulation to the observed value of total soil carbon (Table 4). This result is in line with the recommendation of using a CUE value of 0.3 in broad spatial scale models operating at long time steps (Sinsabaugh et al., 2013), because many of the reported values of CUE for terrestrial ecosystems are inflated due to methodological limitations inherent to measurements of microbial community growth in soils (Manzoni et al., 2012; Sinsabaugh et al., 2013). However, the simulations with a reduced CUE did not perform well when compared with DOC measurements, with a considerable underestimation of DOC at the three soil layers. Moreover, the sensitivity of total SOC stock and heterotrophic respiration to the seven studied parameters was very low (Table 4), which indicates that the mismatch between simulated and observed heterotrophic respiration and total soil carbon stocks is not a problem of parameterization of the new soil module ORCHIDEE-SOM.

Instead, the main reason for the incorrect simulation of heterotrophic respiration and total soil carbon probably lies in the particular characteristics of the study forest. Due to the lack of forest management between the 1930s and the 1980s, trees are very tall and thin, posing hydraulic constraints on transpiration. Moreover, due to sandy parent material and decades of acidification, trees are limited by phosphorous and base cations (Ivan Janssens, personal communication). As a result of both the nutrient limitation and the limited hydraulic conductivity, leaf area index (LAI) is very low (<2 at its peak). As a consequence of the limited leaf area, the Brasschaat site is a highly unproductive site (measured mean GPP= 1173 g C m^{-2} yr^{-1} (Gielen et al., 2011), compared to 1760 for a typical temperate zone coniferous forest (Luyssaert et al., 2007)). Because ORCHIDEE is a LSM that does not take into account historic mismanagement and nutrient limitations on tree productivity, and, moreover is parameterized for a typical forest, its simulated LAI and GPP are overestimated for the Brasschaat forest, with a modelled LAI of 4.8 (instead of <2) and GPP of 1770 g C m^{-2} yr^{-1} (instead of 1173). Because the C inputs to the soil are necessarily also overestimated in the model, also the simulated soil carbon stocks and heterotrophic respiration rate are overestimated.

In the light of these results, the same simulation as explained in section 2.3. was repeated (only for ORCHIDEE-SOM with default parameters), but with a maximum LAI fixed to 1.8, according to field measurements in Brasschaat (Ivan Janssens, personal communication). Then, simulated GPP (1026 g C m^{-2} yr^{-1}) and heterotrophic respiration (328 g C m^{-2} yr^{-1}) were closer to the observational data (1173 g C m^{-2} yr^{-1} and 411 g C m^{-2} yr^{-1}, respectively) than with the default parameterization of LAI in ORCHIDEE (Table 6). Consequently, the simulated carbon inputs to the soil were also considerably reduced and soil carbon concentrations were even lower than the measured carbon concentrations in Brasschaat (Table 6). With this new LAI parameterization, soil carbon in the mineral soil was better simulated (Figure 7A), while soil carbon in the litter layer was underestimated.

In addition to the low carbon inputs, which can be corrected by changing the LAI parameterization, low heterotrophic respiration in Brasschaat is further caused by the site-specific soil characteristics that are hostile to many microbial groups. Very low pH and high NH_4^+ content both decrease microbial activity, since only few organisms can produce enzymes that function optimally at this pH (Janssens et al., 1999). Finally, the site is saturated with N, which also retards long-term decomposition (Janssens et al., 2010), probably leading to, not only a reduction in soil respiration, but also a higher accumulation of litter. Again, these carbon responses are not captured by the model and thus it is not surprising that we find bias in the model-data agreement in observations of heterotrophic respiration or carbon concentration in the litter layer that highly depend on pH or nutrient conditions, even after correction of LAI and GPP.

Table 6. Comparison of modelled C pools and fluxes for the simulations with ORCHIDEE default parameterization and with maximum LAI set to 1.8 against Brasschaat field observations.

Modelled variables	Modelled default ORCHIDEE parameterization	Modelled ORCHIDEE lai max=1.8	Measured in Brasschaat
Total Soil Carbon (T ha^{-1})	242.2	81.68	144
Heterotrophic respiration (g C m^{-2} yr^{-1})	686	328	411*
GPP (g C m^{-2} yr^{-1})	1768	1026	1173
DOC free (mg L^{-1})	19.8	61.2	30
Litter metabolic above (g C m^{-2})	283.9	110.6	
Litter metabolic below (g C m^{-3})	65.7	62.4	
Litter structural above (g C m^{-2})	4501.6	1105.8	
Litter structural below (g C m^{-3})	2208	1005	
Carbon active (g C m^{-3})	482	239.5	
C slow (g C m^{-3})	517.5	208.9	
C passive (g C m^{-3})	2868	829.9	

** This value corresponds to Soil respiration, which includes both heterotrophic and autotrophic respiration.*

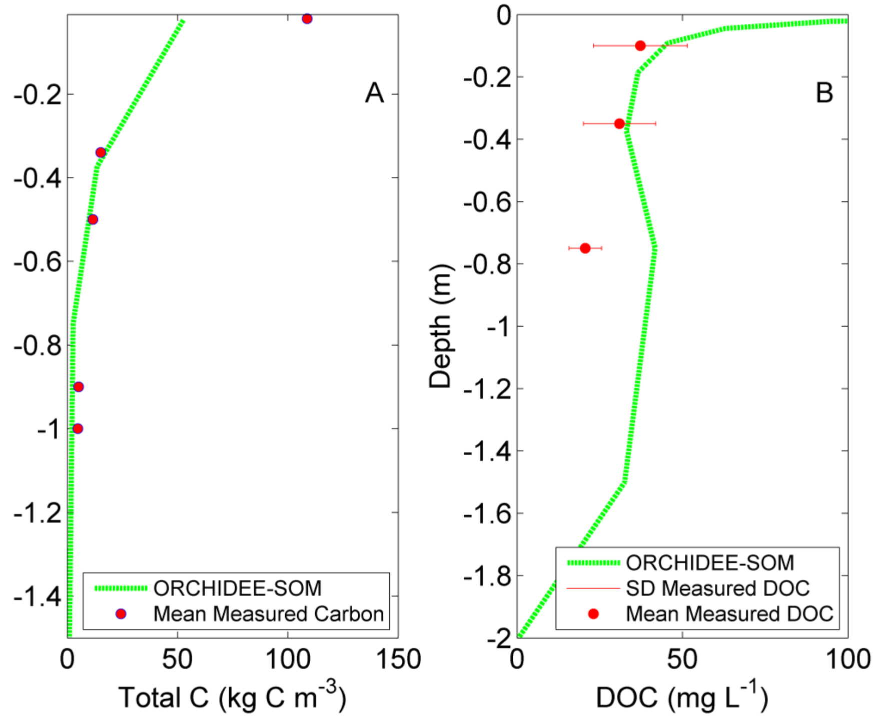


Figure 7. Modelled and measured soil profiles of A) DOC concentrations (mg L^{-1}) and B) Soil carbon concentrations (kg C m^{-3}) for the ORCHIDEE-SOM simulation with a fixed maximum LAI of 1.8.

On the other hand, the simulation of ORCHIDEE-SOM adapted to this specific LAI parameterization for Brasschaat gave a good model-data fit for DOC concentrations in the upper and intermediate layers, as it was the case for the default parameterization of ORCHIDEE. However, for the subsoil (75 cm), DOC was overestimated in this case (Figure 7B). This fact confirms our hypothesis that we cannot get a satisfactory model-data fit for DOC concentrations in subsoil because some internal soil processes, more related with the physico-chemical characteristics of the soil, such as DOC stabilization, cannot be captured by the model.

In summary, there are two main reasons for the high modeled heterotrophic respiration and soil carbon stocks: 1) high simulated soil carbon inputs due to the high modeled GPP by ORCHIDEE, and, 2) missing representation of key parameters and mechanisms controlling C dynamics, such as N and pH controls. While the high soil carbon inputs due to a high modeled GPP could be corrected by a site-specific parameterization of LAI (Table 6), the model-data mismatch due to missing N and internal soil controls on DOC still requires further model development work to be solved (see Section 5).

With the first attempt to evaluate the new soil module ORCHIDEE-SOM, we found that the represented processes of DOC production, sorption and transport can reproduce well the magnitude of DOC in Brasschaat, a representative European forest in terms of DOC. It is able to also reproduce well the seasonality of DOC and, to some extent, the DOC soil profile. The model however failed in reproducing vertical fluxes of C for reasons that are beyond the modifications introduced in ORCHIDEE-SOM. The evaluation exercise addressed in this study allows us to confirm and illustrate that the main processes of DOC production and transport are successfully represented in ORCHIDEE-SOM, and to detect main areas of model improvement (see section 5). However, conclusions from this site-level validation cannot be extrapolated as ORCHIDEE is a global model not designed for site-scale application, unless parameterized.

5 Conclusions and further work

The current version of ORCHIDEE-SOM was able to reasonably capture the DOC dynamics in a temperate coniferous forest, using input parameters that are realistic compared to prior knowledge. The model-data agreement for free DOC was better for the upper soil layers than for subsoil. On the other hand, heterotrophic respiration, soil carbon stocks and GPP were first overestimated by the model. The particular site characteristics of Brasschaat (very acidic and sandy soils) result in a highly unproductive site, conditions that ORCHIDEE-SOM was not able to capture, leading to an overestimation of GPP and heterotrophic respiration. Although this overestimation of carbon fluxes could be partly corrected by adopting a site-specific LAI parameterization, part of this model failure can only be solved by implementing some missing mechanisms affecting soil C and DOC in ORCHIDEE.

Moving forward requires parameterizing the key parameters detected in the sensitivity analysis through data assimilation and testing the new optimized ORCHIDEE-SOM model against observation of SOC and DOC at larger scales (continental or global).

More specifically, we recommend two main steps in future improvements of ORCHIDEE-SOM:

1) Parameterization for different ecosystem and soils: The results from our sensitivity analysis evidence that the new ORCHIDEE-SOM is sensitive to parameters that should be made PFT dependent, particularly the parameter CUE and the diffusion coefficients. Therefore, an ecosystem differentiated multi-site optimization is needed before being able to apply ORCHIDEE-SOM to continental or global scales. Moreover, some parameters importance and performance highly depended on the soil depth, especially the sorption and diffusion coefficients, as they control the C storage in depth. Moreover, the parameter CUE could be soil-depth dependent, allowing us to control the DOC/heterotrophic respiration ratio at different soil layers, which seems to be very important in terms of the high sensitivity of simulated DOC in subsoil. We recommend making these parameters soil dependent by introducing empirical relationships that will make them variable with soil characteristics, such as texture, that in turn, should be defined per soil layer to account for their depth dependence. Finally, we suggest that a multi-site Bayesian optimization is applied by taking into account DOC, SOC and GPP observations simultaneously. The dependence of soil carbon stocks on NPP in LSMs has already been reported (Todd-Brown et al., 2013). This highlights the necessity to optimize the modelled LAI and GPP previously to try a soil parameterization for optimization of DOC in order to assure that the ORCHIDEE inputs coming from plant production are correct.

2) ORCHIDEE improvements: Our results highlight the importance of some missing parameters in current LSMs to predict SOC and DOC dynamics with reliability. For instance, SOC and DOC decomposition and adsorption/desorption highly depend on soil pH and the amount of Al and Fe in soil, but ORCHIDEE has not yet the ability to account for these factors. Similarly, it is known that nutrient limitations, such as N and P, modulate soil C dynamics (Wieder et al., 2015b), but the version of ORCHIDEE we used to start the development does not explicitly considered these nutrient dynamics. Moreover, soil properties should be defined per soil layer to account for soil horizons differences. For instance, the recommended empirical relationships to make the parameters dependent to soil properties will be only possible once the basic structure of ORCHIDEE-SOM has been adapted to account for pH or texture defined by soil layer. However, these recommended changes would add complexity to the models, possibly leading to an over parameterization.

Now that new global or large scale products with soil properties, such as pH or clay are becoming available (e.g., FAO/IIASA/ISRIC/ISSCAS/JRC, 2012; Rossel, 2011), including these parameters as inputs in the forcing files for ORCHIDEE-SOM is a relatively easy task. Nevertheless, the challenge is to find a trade-off between implementing these key factors in explaining DOC at small scales and the increased uncertainty associated to these estimates at global scale. In order to use ORCHIDEE-SOM globally, we will need a global soil map with information on pH, clay, Fe, etc., and these products come with a very high uncertainty for the soil properties (Malone et al., 2011). Thus, the high uncertainty on the new parameters may be propagated to the model outputs, and soil C pools are particularly sensitive to the model uncertainty (Zaehle et al., 2005). Therefore, we first need to assess if the improvements produced by these recommendations will be offset by the associated uncertainty introduced in ORCHIDEE-SOM.

Finally, the simulation of DOC concentrations and fluxes rely on the water balance calculated by the hydrological module. A revision of the boundary condition of free drainage at the bottom layer should be considered before being able to simulate DOC and SOC in humid ecosystems with a temporal high water table (temperate forests) or permanently waterlogged (peatlands or wetlands). We highlight this point as a high priority improvement in ORCHIDEE-SOM in order to be able to simulate the lateral transport of DOC from soils.

SYNTHESIS

SYNTHESIS

1 MAIN FINDINGS

1.1 Variability of DOC

In total, 365 sites were included in the global database on DOC in soil solution, located primarily in the humid temperate zone. There was an underrepresentation of tropical sites (n= 13) and organic soils (n=29). Moreover, mediterranean and (semi-)arid sites were absent. Hence, care should be taken when extrapolating our conclusions to global scale. I used the database to analyze the spatial and temporal variability of DOC with the aim, firstly, to quantify the differences in DOC concentrations among terrestrial ecosystems, climate zones, soil and vegetation types at global scale (Chapter 1) and, second, to understand the long-term monotonic trends of soil solution DOC from a large number of European forests, focusing only on the ICP Forests Level II plots (Chapter 2).

1.1.1 Site-to-site variability

DOC concentrations reported in our database differed strongly among sites, and within sites among sampling locations. Nonetheless, the observed ranges showed good agreement with values of soil DOC concentrations within the range 2-90 mg L^{-1} previously reported in literature (Michalzik et al., 2001). I further quantified DOC by latitude, ecosystem type and soil type. DOC concentrations at lower latitudes (<35°) were smaller than at temperate (35°-60°) and boreal latitudes (>60°). On average, I found larger DOC concentrations for non-forest ecosystems on organic soils (mean=53 mg L^{-1}, 95% CI= 40-69) than for non-forest ecosystems on mineral soils (mean=10 mg L^{-1}, 95% CI=8-13). In addition, broadleaved forests exhibited lower DOC concentrations than coniferous forests (23% lower, broadleaved DOC mean= 13 mg L^{-1}, 95% CI=11-17; coniferous DOC mean= 17 mg L^{-1}, 95% CI= 15-19), a finding that is in line with previous studies (Currie et al., 1996; Fröberg et al., 2011; Khomutova et al., 2000).

An important finding is that DOC substantially decreased with increasing depth in forests, while in organic soils (mainly peat) the opposite was observed, probably due to decreasing decomposition rates with depth due to anaerobic conditions (Vicca et al., 2009). No differences were found in the vertical distribution of DOC in the soil profile between coniferous and broadleaved forests.

1.1.2 Temporal trends

The DOC concentrations measured at sites from the ICP Forests network that had more than 10 years of data (from 1991 to 2011) were analyzed to detect temporal trends of DOC in soil solution. For this purpose, I applied two techniques: a mixed-effect model to analyze all the European data together and an individual trend analysis using the Seasonal Mann-Kendall tests. The mixed-effect models suggested an increasing trend in soil solution DOC concentration in the organic layer and in deep subsoil (> 80 cm) when the entire dataset (with breakpoints) was analyzed. The individual trend analyses seemed to confirm the increasing trend under the organic layer, while more heterogeneous trends in the mineral soil were found, which is in line with previous findings (Borken et al., 2011; Evans et al., 2012; Hruška et al., 2009; Löfgren and Zetterberg, 2011; Vanguelova et al., 2010). Furthermore, by using the individual trend analysis, I found a majority of non-significant trends, indicating that either DOC in soil solution is not changing over time or that we will need longer time series to detect trends that have not yet resulted in changes large enough to be detected against the highly variable background.

In conclusion, applying the Seasonal Mann-Kendall tests at individual time series, I could not find an overall trend of DOC concentrations in soil solution across Europe. Nevertheless, the analysis of all the European data together suggested that DOC is increasing in both the organic layer and deep subsoil. This finding implies that, even though the heterogeneity at plot scale is very large, it might be an overall increasing trend of DOC concentrations from soils, as for DOC concentrations in surface waters that have been increasing over the past decades (De Wit et al., 2007; Evans et al., 2006; Monteith et al., 2007).

1.2 Identified controlling factors of dynamics in soil solution DOC

Further statistical analyses focusing on the ICP Level II plots revealed the most important factors affecting the site-to-site variability of DOC (Chapter 1) and its temporal trends (Chapter 2). I considered climate (precipitation and temperature), soil properties, soil solution chemistry, atmospheric deposition and vegetation type amongst the possible determinants of DOC concentrations.

Overall, I identified N availability and soil pH as the most important controlling factors of DOC spatial and temporal variability (Chapter 1 and Chapter 2). In the first chapter, I found that N availability, as indicated by C/N ratio and NH_4^+ concentration in soil solution, played a key role for the site-to-site variability of soil solution DOC concentrations in European forests, possibly by controlling microbial activity. High DOC concentrations in soil solutions correlated with high NH_4^+ concentrations and I propose the incomplete degradation of lignin under high NH_4^+, leading to greater production of DOC (Pregitzer et al., 2004) as an explanatory mechanism. On the other hand, low soil C/N ratios tended to exhibit low DOC, possibly due to increased microbial carbon use efficiency and high rates of DOC consumption (Cotrufo et al., 2013). Al and Fe are also important determinants of site-to-site variability in DOC, reflecting pH and mineralogy controls on DOC concentrations. The reported effects of pH on DOC in soil solution are contradictory (Kalbitz et al., 2000). I found that DOC in soil solution increases when pH is lower, and this effect might be due to a shift of the microbial community towards a fungi-dominated community at low pH (Blagodatskaya and Anderson, 1998): taking into account the importance of fungi for the release of DOC (Moller et al., 1999), decreasing pH can lead to elevated DOC production.

Nevertheless, the relationship between these factors and DOC concentrations in soil solution are only correlative and therefore they do not imply causation. For instance, the relationship between Al and Fe and DOC is bidirectional: Al and Fe are not only drivers of variation of DOC, but also they may be the consequence, as higher DOC keeps more Al and Fe in solution. Similarly, both NH_4^+ and DOC are partly results from incomplete mineralization, and thus, the correlation of these two variables is a reflection of the same mechanism. Therefore, some of the correlations reported in this thesis should be further examined in targeted experiments in order to test whether or not they are indeed causal, as implied by our models.

In the second chapter, I tested whether the well-established pattern that decreasing acidifying deposition leads to increased DOC concentrations in surface waters in Europe and North America also leads to long-term increasing trends of DOC concentrations in soil solution across European forests. I found that the response of trends of DOC to the reduction in the acidic deposition depends on the N deposition loads of the forest. While the hypothesis of increasing trends of DOC due to reductions of SO_4^{2-} deposition could be confirmed in more N-limited forests, the role of SO_4^{2-} deposition in more N-enriched forests was not significant. Moreover, I found that also soil pH determines the response of trends in DOC to SO_4^{2-} deposition. In very acid soils, a higher mean SO_4^{2-} deposition enhanced the temporal increase of soil solution DOC, while in less acidified soils, there was no clear effect of mean SO_4^{2-} on DOC trends.

Regarding the effect of vegetation, it is important to highlight that absolute DOC concentrations differed between forest types (Chapter 1), whereas I did not find any effect of forest type on the temporal trends of DOC (Chapter 2). Not only did DOC concentrations differ between forest types, also the identified drivers were different for broadleaved and coniferous forests, with biotic factors being more important in explaining DOC in broadleaved forests, and water balance more important in coniferous sites.

Summarizing, the results from Chapter 1 and Chapter 2 identified N availability and soil pH as important controlling factors of the dynamics of DOC in European forest soils. Surprisingly, neither precipitation nor temperature seemed to play a key role in controlling spatial and temporal dynamics of DOC. Hence, I conclude that factors controlling DOC acting at local scale, like site characteristics, dominate over factors acting at regional scales, like climate (Clark et al., 2010).

1.3 Modelling DOC in ORCHIDEE: improvement of the representation of SOC and DOC dynamics

In the second part of this thesis, I developed a new soil module within the Land Surface Model (LSM) ORCHIDEE, called ORCHIDEE-SOM. Chapter 3 describes the processes implemented in ORCHIDEE-SOM and Chapter 4 is an evaluation of the model performance against field data from a temperate coniferous forest. With this work, I contributed to the current soil modelling research mainly with two developments: 1) Presentation of a vertically discretized soil module in a LSM, 2) Representation of all the processes affecting DOC in soils in a LSM. To our knowledge, only one LSM currently represents a discretized soil module (Koven et al., 2013), but there is no large scale LSM that accounts for the production and transport of DOC in soils.

1.3.1 Model improvements: C discretization in a global model and framework for DOC leaching

The previously identified primary tasks for improving LSMs include: a depth specific representation of decomposition, mineral-SOC interactions, and transport; a mechanistic description of microbial biomass and the priming effect (Schmidt et al., 2011; Todd-Brown et al., 2014); incorporating nutrient dynamics in LSMs (Nishina et al., 2014; Todd-Brown et al., 2014; Wieder et al., 2015b); and finally, modelling the leaching of DOC to streams and rivers (Battin et al., 2009).

Recently, priming was added into ORCHIDEE, with significant impact on SOC dynamics at regional scale (Guenet et al., in prep) and ORCHIDEE-SOM was developed from this last version. ORCHIDEE-SOM enables the simulation of DOC concentrations in soil solution at 11 different soil layers and DOC fluxes out of the soil through runoff and/or drainage, as well as the simulation of soil carbon dynamics in deep soils. The new processes that I implemented (Chapter 3) are the decomposition of DOC, following first order kinetics, the adsorption of free DOC to the mineral matrix according to the linear adsorption following Nodvin et al. (1986), and the transport of DOC by advection (with water flux) and diffusion of DOC and SOC (through bioturbation). Therefore, our developments deal with many of the urgent model development needs described above, except for the incorporation of nutrients and a mechanistic representation of microbial activity.

Moreover, with ORCHIDEE-SOM, we can simulate and predict deep soil organic carbon separately from surface carbon. This is an important step forward as it has been demonstrated that deep soil carbon plays an important role in the carbon cycle (Jobbagy and Jackson, 2000). The representation of a discretized soil carbon model will have a high impact on the predictions of future global carbon stocks under future climate, as demonstrated by Koven et al. (2013).

The representation of DOC adsorption to the mineral matrix also adds value to ORCHIDEE-SOM. It has been suggested that the long-term preservation of SOC is controlled by its accessibility to microbial decomposers (Cotrufo et al., 2013; Schmidt et al., 2011). In this context, the representation of C protection to microbial decomposition by different process (physical protection, energy limitation, adsorption on the mineral matrix) is highly important. My work is a step forward in LSMs because it represents C protection mechanisms (adsorbed DOC is not decomposed in the model). Furthermore, I set the model structure needed to account for the dependence of mineral adsorption to soil properties, such as clay content, but this is work in progress.

Overall, the modelling work of this thesis set the framework for a model able to predict SOC and DOC dynamics down to 2 meters deep in the soil and the export of C to rivers globally. Further parameterization and optimization work is needed before using it at global scale.

1.3.2 Model evaluation

In Chapter 4, ORCHIDEE-SOM was evaluated against DOC concentrations measured in a temperate coniferous forest, Brasschaat. The results showed that the current version of ORCHIDEE-SOM was able to reasonably capture the DOC dynamics in this particular forest, using input parameters that are realistic compared to prior knowledge. Moreover, the DOC profile was well simulated by the model, although the model-data agreement for free DOC was better for the upper soil layers than for subsoil.

On the other hand, heterotrophic respiration, soil carbon stocks and GPP were all overestimated by the model. The particular site characteristics of Brasschaat (very low leaf area and highly acidic sandy soils) resulted in an unproductive site, conditions that ORCHIDEE-SOM was not able to capture, because its parameterization is aimed to work well at the mean coniferous forest, with much higher leaf area and thus GPP. Therefore, biological activity is overestimated in Brasschaat, explaining why soil C stocks and heterotrophic respiration were overestimated. In fact, this overestimation could be corrected by adjusting the maximum LAI to the observed value in Brasschaat (max_lai = 1.8), suggesting that an optimization of the modelled LAI and GPP is needed previous to a soil parameterization for optimization of DOC, in order to assure that the ORCHIDEE inputs coming from plant production are correct.

Moreover, I performed a sensitivity analysis to detect the main areas of model improvement. The sensitivity analysis allowed us to gain information about which parameters are most important in determining DOC dynamics and thus, should be prioritized in the subsequent parameterization. Results of the sensitivity analysis showed that the sorption distribution coefficient is the most important parameter for successful simulation of DOC profiles. The residence time of the recalcitrant DOC is detected as a key parameter controlling the magnitude, dynamics and soil profile of DOC. I concluded that increasing the residence time of recalcitrant DOC by 50% will give the best overall reproduction of the dynamics of the free DOC in soil solution. These findings demonstrated one limitation of the current parameterization in ORCHIDEE-SOM. For the moment, parameters, such as sorption distribution or the diffusion coefficient, are not soil depth-dependent, even though their relative importance differs between soil depths. In reality, the diffusion coefficient declines non-linearly with depth, with important differences between soil horizons (Wilkinson et al., 2009). Furthermore, the adsorption distribution coefficient should be higher in the B and C soil horizons compared to A, E and B/E soil horizons in forest soils (Jardine et al., 2006; Kaiser et al., 1996; Sanderman and Amundson, 2008).

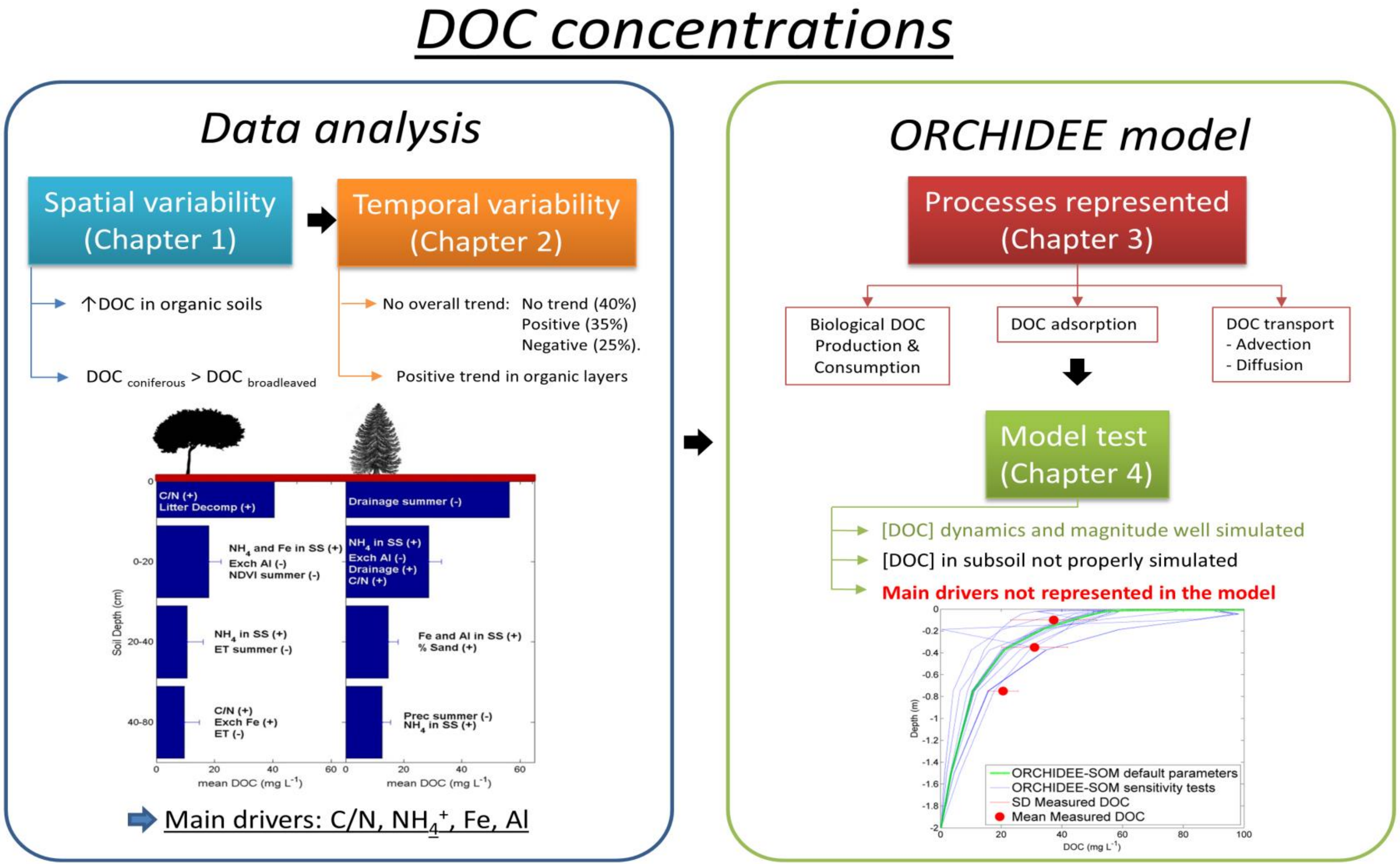
1.4 Identified drivers versus model limitations

Although I already implemented the main processes affecting soil DOC dynamics (Chapter 3) with a reasonable output for one European study site (Chapter 4), the main detected drivers of the spatial and temporal dynamics of DOC in soil solution, soil solution Fe and Al and, exchangeable Al and N (Chapters 1 and 2), are not represented in ORCHIDEE yet (Figure 1).

As found in chapters 1 and 2, the pH and the amount of Al and Fe in soil solution are key in controlling DOC dynamics. In fact, I argued that the missing representation of pH controls in ORCHIDEE might have contributed to the model's failure to capture the carbon stocks and fluxes of the acid forest soil in Brasschaat. Within ORCHIDEE-SOM, I can account for the texture control on DOC adsorption by means of an empirical relationship (Chapter 3) that links unique values of clay per site with the sorption distribution coefficient. However, these properties are very variable in space (among sites and within the soil profile), which thus far has hampered the implementation in global models.

Second, my data-driven chapters showed a high importance of the soil and atmospheric N in controlling DOC in soil solution. However, at the moment of our model development, the trunk version of ORCHIDEE did not include the N cycle yet, impeding the representation of the interactions between the C and N cycle. This means that ORCHIDEE cannot account with important mechanisms, such as the response of DOC to atmospheric deposition, and thus we should be cautious when extrapolating their prediction to future climate conditions. Many researchers have recently put the focus on the importance of nutrient (N and P) representations in ESMs (Schmidt et al., 2011; Todd-Brown et al., 2013; Wieder et al., 2015b; Zaehle et al., 2010). The representation of the P and N cycles in the trunk version of ORCHIDEE is imminent. This will bring the opportunity to modify our model equations with empirical models accounting for the detected relationships between DOC and N soon.

Finally, the study of the temporal trends of DOC (Chapter 2) suggested that complex interactions exist between factors influencing DOC in soil. These complex interactions might lead to a shift in the trend of DOC in a complicated direction under future climate and forest management scenarios that global models might not be able to predict.



DOC concentrations

Data analysis

Spatial variability (Chapter 1)

- ↑DOC in organic soils
- DOC $_{coniferous}$ > DOC $_{broadleaved}$

Temporal variability (Chapter 2)

- No overall trend: No trend (40%), Positive (35%), Negative (25%).
- Positive trend in organic layers

Main drivers: C/N, NH_4^+, Fe, Al

ORCHIDEE model

Processes represented (Chapter 3)

- Biological DOC Production & Consumption
- DOC adsorption
- DOC transport
  - Advection
  - Diffusion

Model test (Chapter 4)

- [DOC] dynamics and magnitude well simulated
- [DOC] in subsoil not properly simulated
- **Main drivers not represented in the model**

Figure 1. Synthesis of main objectives and findings in this thesis.

2 FUTURE DIRECTIONS

2.1 Study of the lateral transport of C and N at global scales

The present study focuses on the leaching of C from soils and its potential controlling factors with the aim to better predict the future carbon cycle along the land-ocean continuum. Nevertheless, no differentiation between natural and anthropogenic causes of DOC transport was made when studying the drivers of DOC changes in soil. The reallocation of terrestrial C fluxes within the land-ocean continuum is particularly important taking into account the increasing CO_2 emissions due to anthropogenic causes, as mentioned in the introduction of this thesis. As a consequence, further research on the past, present and future leaching of DOC from soils should assess the anthropogenic contribution of DOC fluxes to allow a complete estimation of the anthropogenic effects on the global C cycle (Regnier et al., 2013).

On the other hand, the C that is transported within inland waters is composed by DOC, DIC (mainly pCO2) and POC, but in this thesis only DOC has been modelled within ORCHIDEE. Therefore, a next step in going towards the boundless carbon cycle should necessarily implement the processes of production and transport of DIC and POC from soils into inland waters. The implementation of release and movement of DIC within the soil in ORCHIDEE is already under development. Once both soil and stream DIC is modelled within ORCHIDEE, we can use river pCO2 as an additional model constraint for validation of soil and streams DOC fluxes.

Similarly, the scope of this thesis is restricted to closing the "boundless carbon cycle", even though the close linkage between the C and N biogeochemical cycles has recently been claimed (Wieder et al., 2015b; Zaehle et al., 2010). In fact, the results from this thesis highlighted the importance of linking the C and N cycle. Lateral transport of dissolved nitrogen, and not only dissolved carbon, contribute to greenhouse emissions from inland waters, with nitrogen emissions being highly impacted by anthropogenic activity (Seitzinger et al., 2005). Going a step forward will require to couple C and N cycles in LSMs, from land to the ocean, with the aim to fully account for the greenhouse gasses emissions from inland waters in global models in order to assess the impacts of climate change under different climate scenarios.

Finally, the outputs from a LSM that includes leaching of C and N from soils will be useful, not only to predict the impacts of climate change under future climate scenarios, but also to better understanding the contributing processes to the observed spatial and temporal trends in DOC (Chapter 1 and 2) that cannot be measured simultaneously in the field (e.g., DOC production and decomposition, or the amount of adsorbed DOC). In other words, once the model accounts for the important drivers of DOC, it can be used to test if the observed DOC responses to environmental changes are indeed explained by the model. In conclusion, the link between the data analysis and the modelling work is bidirectional: not only the monitoring data can help in developing the model, but also the model outputs can shed light on the mechanisms taking place in the field.

2.2 Data availability

DOC fluxes

The link between terrestrial DOC and riverine DOC flux seems to be dominantly controlled by catchment hydrology (Sebestyen et al., 2009; Stutter et al., 2011; Tranvik and Jansson, 2002). Although I focused on DOC concentrations, an increase in concentration does not necessarily result in increased river transport, which is the product of concentration and drainage and/or runoff. Therefore, information on the hydrology of the site will be key in determining the amount of DOC leaching to the streams and waters. While our findings on the soil processes and drivers will be very important to improve predictions of DOC in future climates, the correct link between soils and streams should focus on hydrology (precipitation, runoff and drainage).

The lack of quality hydrological data in this thesis, more specifically drainage and runoff, hampered a correct quantification of the DOC fluxes at European scale.

The study of the drivers of DOC concentrations (Chapter 1) could be extended to DOC fluxes if estimates of drainage were made available for the ICP Forest Level II plots. On the other hand, I was able to simulate the DOC export with water drainage and runoff calculated from ORCHIDEE. However, the absence of hydrology information at site level impeded the calculation of DOC export for our sites and consequently, an independent validation of DOC fluxes using field data was not possible. I therefore recommend that modelling the water balance of the sites is prioritized for large scale monitoring networks.

Broaden the study ecosystems

To our knowledge, our study is the first to report the drivers of DOC concentrations at European level. Nevertheless, our results cannot be extrapolated to larger scales or other ecosystems since the majority of our sites were temperate forests. Particularly peatlands and tropical ecosystems are currently understudied.

Peatlands cover a small fraction of the land area (only 3%), but represent a major terrestrial carbon store (30% of the global soil carbon) (Blodau, 2002). Thus, the long-term stability of this carbon stored in peatlands is of high priority to avoid land C emissions. Recently, concern has been raised because peatland waters are associated with high concentrations of DOC (Billett et al., 2004), representing an important mechanism of peatland C loss. Hence, it is highly important to understand and predict the mechanisms behind the peatlands DOC export and several studies have already focused on it (e.g., Clay et al., 2009; Dinsmore et al., 2011; Evans et al., 2006). However, there has been no attempt to explore the drivers of spatial variability in DOC export from peatlands.

Tropical ecosystems were also underrepresented in this study. Although reported DOC leaching from tropical ecosystems is small compared to other ecosystem's leaching (Camino-Serrano et al., 2014; Schrumpf et al., 2006), the mechanisms of DOC production and transport under tropical conditions are not clear yet.

2.3 Modelling DOC in ORCHIDEE

Model improvements and optimization

In this thesis, I implemented a new soil module with the ability to model the main processes affecting DOC and SOC dynamics. However, for this version of the model, I used default parameters that are reasonable compared to prior knowledge and therefore an ecosystem differentiated multisite optimization is needed before being able to apply ORCHIDEE-SOM to continental or global scales. A Bayesian optimization using site measurements of DOC and total soil carbon stock will reduce the uncertainty range of the new parameters, which is an essential part of any process-based large scale model (Zaehle et al., 2005). Currently, we are working on a Bayesian-based data assimilation exercise using DOC concentrations at three soil depths for three sites with different ecosystem and soil types. I recommend extending this work to a larger data assimilation work using data of DOC and soil carbon stocks from multiple sites covering a wide range of climate, ecosystem and soil types.

Furthermore, I suggested making some ORCHIDEE-SOM parameters soil dependent by introducing empirical relationships that will make them variable with soil characteristics, such as texture. This improvement is relevant to fully-capture internal soil processes, but we need to keep in mind that when improving global models a dilemma appears: increasing the level of detail according to new scientific findings without increasing the uncertainty of the global model too much. Finding the good trade-off between model complexity and the ability to parameterize the model from observations will require further uncertainty analysis (Wieder et al., 2015a).

Large scale application of the model

A final aim of the development of ORCHIDEE-SOM is to produce global simulations of DOC concentrations in soils and its transport to rivers, estuaries and oceans. For the global simulations of DOC concentrations in soils, we first need to optimize the new parameters as mentioned above and then test the model outputs against field data at sites from different biomes. Global simulations of DOC concentrations and export from soils will bring a unique opportunity to quantify and predict the contribution of DOC leaching to the global carbon cycle. Then, it will be possible to identify hotspot areas in which strategies of carbon conservation could be prioritized.

For the simulations of DOC transport to oceans, a river routing scheme able to transport DOC is needed. These developments are ongoing and are led by Université Libre de Bruxelles (Lauerwald et al. in prep). Once the soil module in ORCHIDEE-SOM is validated and linked to the new DOC river scheme, it will improve the allocation of terrestrial and ocean C sinks and will allow the prediction of the present and future contribution of the aquatic continuum fluxes to the global C cycle.

3 CHALLENGES WHEN STUDYING DOC IN SOIL SOLUTION

3.1 Two separated worlds: aquatic and terrestrial

DOC in soil solution is where the soil carbon and the water cycles meet. In other words, studying DOC in soil requires bridging the gap between the hydrological and terrestrial scientific communities. This is not an easy task as terrestrial and aquatic ecology differ in terms of units, scale, research focus and detail of processes represented (Stergiou and Browman, 2005).

As an example, our work is the first attempt to link the soil hydrology and soil carbon dynamics in ORCHIDEE, as the DOC dynamics can only be modeled once soil water content and water fluxes are incorporated into the soil carbon module. However, time steps for the hydrological and carbon processes in ORCHIDEE do not match. In the same line, the 11-layers soil discretization applied for the hydrological module and found to be optimal for representation of soil water fluxes (de Rosnay et al., 2002) corresponds to soil layers in the topsoil that are extremely thin for the representation of soil ecological processes. These discrepancies between carbon and hydrological modelling add challenges to the modelling of DOC using a pre-existing global model.

Aquatic and terrestrial ecology also differs in their research focus: a search for the key words “DOC GPP” in the Web of Knowledge database shows an important number of studies on the relationships between lake or ocean GPP and DOC, but no references occur to studies on terrestrial GPP and DOC, even though it is a very interesting research question if we want to assess the contribution of DOC to the terrestrial carbon cycle and model its transfer to streams.

Nevertheless, the tendency towards a separation of the marine and terrestrial ecology is slowly changing. Nowadays there is growing interest in linking the aquatic and terrestrial worlds, particularly with some pressing problems occurring in globally distributed reservoirs like the ocean and the atmosphere. As climate change acts globally, it is nonsensical to interpret the land and ocean responses of the carbon cycle to environmental changes separately. Studying DOC in soils is thus a new and exciting research challenge that will likely enhance communication among scientist on different ecosystems (terrestrial, freshwater, marine).

3.2 DOC as an intermediate product

The fact that DOC is an intermediate product of decomposition complicates the quantification of drivers affecting the production and consumption of DOC. That is, factors affecting the decomposition of soil organic matter, such as temperature, control DOC in two directions: increasing inputs of DOC, but also increasing the outputs. This complicates isolation of the effect of a single driver on the biological production or removal of DOC from field data. For instance, laboratory experiments may shed light on the different temperature sensitivities of the processes of DOC production and DOC decomposition, allowing disentangling the effect of temperature in the final DOC concentrations in soil, but it is not possible to reach this level of detail from monitoring sites. Therefore, relating DOC concentrations in soils to environmental factors is not a straightforward work.

3.3 Mismatch between levels of study (field/laboratory/model)

The scientific interest in DOC is not new; however, the scale at which DOC is studied has been increasing in the last decades. Published studies about DOC have shifted from mainly laboratory experiments to site level field studies and, more recently, to multisite comparisons. DOC models have also evolved towards more complex representations of DOC. As a result of this variety of studies, we can find much information about DOC in literature, but these results are most of the time not comparable, or even contradictory (Kalbitz et al., 2000), for at least two reasons:

First, the definition of DOC may vary between studies: for instance, in many studies the terms dissolved organic matter (DOM) and DOC are used as synonyms, but dissolved organic matter includes not only organic carbon, but also dissolved organic N among other components. Second, the method used for extraction is very variable, especially between laboratory and field studies, and the selection of the method also affects the final amount of DOC (Zsolnay, 2003).

Finally, communication between experimentalists and modelers should be strengthen to facilitate the model-data integration in the future (Bahn et al., 2010). Currently, definitions and approaches used in modelling are different from the terminology used in field and laboratory studies. Further studies on soil DOC will benefit if the link between experiments, monitoring studies and process modelling is improved.

3.4 Overlapping scales

The mechanisms governing diversity in soils are highly scale dependent (Bardgett and van der Putten, 2014). More specifically, processes affecting DOC occur at very small scales (microsites in soils) and very short times (minutes or seconds), but these processes are part of the long-term carbon cycle that occurs over centuries and thus are being integrated in global carbon models, as it has been done in this thesis. In order to model DOC we need to find a trade-off between adding the high DOC variability governed by many mechanisms taking place at small scales and the simplicity needed to be able to run a global land surface model.

CONCLUSIONS

1. The results of this thesis highlight the interactions between DOC and N dynamics. NH_4^+ in soil solution and C/N ratio are key controlling factors of the site-to-site variability of DOC in European forests (Chapter 1), while N atmospheric deposition levels will determine the response of DOC to temporal changes in environmental drivers (Chapter 2). The N cycle should be included in global carbon models in order to be able to simulate and predict DOC leaching.

2. This thesis also highlights the important role that soil pH plays in soil processes affecting production, retention and transport of DOC. Al and Fe in soil solution are important determinants of DOC site-to site-variability, reflecting pH controls on DOC concentrations (Chapter 1), and also pH determines the response of temporal trends of DOC soil solution to SO_4^{2-} deposition (Chapter 2).

3. Long-term trends of soil solution DOC across European forests are not uniform (Chapter 2), with the majority of the trends being not statistically significant (40%), followed by increasing trends (35%) and decreasing trends (25%). I found evidence that an overall increasing trend occurred in the organic layers, while more heterogeneous trends were found in the mineral soils.

4. Factors controlling DOC concentrations acting at local scale, like site characteristics, dominate over factors acting at regional scales, like climate, in explaining soil solution DOC concentrations in Europe.

5. The soil module developed in this study, ORCHIDEE-SOM, is the first land surface model able to simulate processes of DOC production and transport at different soil layers, as well as DOC export with drainage and runoff (Chapter 3). The model is able to reproduce soil profiles and temporal dynamics of DOC in a temperate forest soil (Chapter 4). However, further parameterization work is needed to be able to apply ORCHIDEE-SOM at global scales.

6. I argued that the missing representation of pH and nutrient controls in ORCHIDEE-SOM might have contributed to the model's failure when modelling SOC in a particularly acidic forest site. We need to account for these important ecological drivers in land surface models before being able to fully understand and predict DOC dynamics at large spatial and temporal scales.

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APPENDICES

Chapter 1 Appendix S1. Pre-processing of the dataset and statistical analysis

Uncertainties on DOC measurements from different sources

Both the ICP Forests dataset and the ECN count with their own quality assessment procedures (Ferretti and König, 2013; Sykes and Lane, 1996). Within the ICP Forests, the participation in ring tests is required for all participating laboratories. The qualification criterion states that >50% of the results of all ring test samples for a particular variable must be within the appropriate tolerable limit. Laboratories who have failed the ring test for a particular variable have the opportunity to requalify by reanalyzing the ring test samples. Up to now, 5 water ring test have been organized as part of the ICP program since 1998. The percentage of results exceeding tolerable limits has been reduced considerably over eight years period (König et al., 2013). To our knowledge, no cross-validation has been done between the ICP Forests and UK ECN network (which also has a quality control for procedures for the Analysis of Water Samples). However, it is worth to note that the majority of the sites in our database (281) comes from the ICP Forests and only 9 sites comes from the UK ECN Network. Regarding the measurements taken from literature (75), errors in sampling are only rarely reported. Because we collected data from published literature, different laboratory analysis and errors in sampling are intrinsic of this kind of research. Nevertheless, in literature, we found the majority of the protocols for measurements of DOC (in the field and laboratories) very similar. To minimize possible systematic errors, DOC data reported in literature were gathered only when samples were taken in the field using lysimeters or piezometers and samples were properly stored until laboratory analysis. Data with insufficient methodological information were discarded.

We presume negligible differences caused by off-sets between networks and sources in comparison with the natural DOC variation. Even though we acknowledge the existing high uncertainty in the measurements of DOC, we consider it unlikely that potential sampling errors could bias the natural variability of DOC across different ecosystems and climates around the world.

Preparation of the dataset

The data analysis focused on the drivers that may explain the spatial site-to-site gradients of DOC concentrations in soil solutions. Each variable was aggregated over the study period in order to proceed with the statistical analysis. The median DOC concentration per site and per depth range was taken to avoid the influence of outliers. In order to link soil solution data with soil properties, the soil solution data were aggregated using the same layers as defined in the ICP Forests soil properties dataset. Soil solution samples taken from the bottom of the organic layer (0 cm) were kept separately in order to link them to the properties of the organic layer. In addition, the weighted mean DOC over the soil profile up to 80 cm depth was calculated using the depth intervals as weighting factor. Soil properties that were available only per layer were also aggregated to have a depth-weighted average for the entire profile, defined in this study from 0 to 80 cm.

The long-term mean annual and seasonal GPP, NDVI, ET, temperature, precipitation and volumetric soil water content were calculated. Seasons were defined as follows: spring (March-May), summer (June-August), autumn (September-November) and winter (December-February). Finally, mean annual and mean seasonal drainage were calculated as the difference between precipitation and evapotranspiration assuming that the long term change in soil water content was zero.

Statistical analysis

Differences across ecosystems, climates and soil types

We used bootstrapping to test for statistical differences among different ecosystem types, forest types, pH classes, soil types, climate zones and latitude ranges. Within each group, we provide bootstrap results for the different soil layers and also for the entire soil profile. We used bootstrapping because this non-parametric procedure is distribution-independent and therefore does not assume normal distribution of the data or equality of variance, which is important for the small sample sizes (n<30) of some of our groups (Efron, 1981). Also, bootstrapping provides a way to account for the distortions caused by the samples that may not be fully representative of the population. A bootstrapped mean and 95% confidence interval were calculated for each group by using the resampling method (2500 iterations) (Table S3).

Statistical modeling of the spatial distribution of DOC across European sites

To correlate the spatial variability in DOC concentrations against our set of drivers, the relationships between the observed DOC concentrations and potential drivers in different depth intervals were analyzed via linear models. This analysis was performed on a subset of the complete database, containing only Level II plots from the ICP Forests program. This was done to explore how DOC depends upon a wide range of potential drivers that were only available within the ICP Forests measurements.

The complete global database contains a large number of available drivers (predictors; see Table S2) with a potential strong correlation between some of them. In addition, this database contains a large number of missing values amongst the predictor variables. Therefore, the interdependencies between predictor variables were examined with a factor analysis and a correlation matrix. Based on the observed groups of significantly correlated drivers, a reduced set of variables was defined, taking into account data availability for most sites. Nevertheless, we chose to include correlated variables in the analysis because literature suggested them to have a strong influence on the spatial variability in DOC concentration. This approach allowed us to continue the analysis with 83 Level II plots from the ICP Forests program and fewer drivers. The selected drivers were climate variables (annual and seasonal drainage, NDVI, GPP, precipitation and ET), soil properties (CEC, pH, Exchangeable Al and Fe, soil solution ions, sand and clay content, C and N content and C/N ratio, amongst others) and vegetation characteristics (litter decomposability and thickness of the litter layer).

Since some of the predictor variables were correlated, a forward stepwise linear regression (Hocking, 1976) was used to identify the most significant multivariate relationship between DOC concentrations and the predictor variables in the organic layer (0 cm), and in the mineral soil—topsoil (0-20 cm), intermediate layer (20-40 cm) and subsoil (40-80 cm). An entrance and exit tolerance of 0.1 on the p-values was used. Data were standardized by their standard deviation before performing the stepwise fit. Regressions with the highest explained variance (R^2) and the minimum root mean square error (RMSE) were selected. In addition, the distribution of residuals was examined to evaluate model structure. Variation Inflation Factor (VIF) for the variables in the final regression models was calculated to check for co-linearity. When VIF is higher than five, the predictor variable with the lowest significance is removed from the model. Corrected Akaike's information criterion (AICc) was also used to assess overfitting when comparing two possible models with a different number of variables. Finally, the coefficients of partial determination (partial R^2) were calculated in order to assess the relative importance of each variable in the final model. While partial R^2 measures the marginal contribution of one predictor variable when all others are already included in the model, the absolute value of the final model linear regression coefficients represents the sensitivity of DOC to the predictor variable. Partial R^2 and regression coefficients can be combined to assess the relative importance of each variable in accounting for DOC gradients.

The data were split into broadleaved and coniferous sites based on results from previous studies (Fröberg et al., 2011; Lu et al., 2012; Vestgarden et al., 2010) that indicate a difference in magnitude of DOC concentrations between vegetation types. We separated between forest types after confirming that model performance for coniferous and broadleaved models was better than for the models built without forest type distinction. Creating a model for each forest type gave us the opportunity to understand the reason for such differences by investigating the relative importance of the soil and climate factors in each model. The coefficients of the final models are presented in Table S4. All statistical analyses were performed using MATLAB (R2012a; The Mathworks Inc., Natick, MA), except the calculation of the partial R^2 which was carried out using R software.

Table S1. List of sites, sites characteristics and site references for additional site information. For information on ICP Forests sites, go to http://icp-forests.net/ and for information on ECN network sites, go to http://www.ecn.ac.uk/. ICP Forests sites used for the stepwise regression (see 3.2) are marked in bold.

Site	Lat	Lon	Vegetation type	Climate	Site Reference
Amoeboid	-45.49	167.63	Not drained: peatland	Cfc	Moore and Clarkson (2007)
Asa	57.13	14.75	Coniferous forest	Cfb	Fröberg et al. (2006)
Awarua	-46.58	168.50	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Bayswater	-46.14	168.04	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Borland	-46.75	167.50	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Cairngorms	57.11	-3.82	Drained/ managed: grassland	Cfc	ECN network
CarlowC	52.84	-6.90	Cropland	Cfb	Kindler et al. (2011)
CarlowG	52.84	-6.90	Grassland	Cfb	Kindler et al. (2011)
CarlowG2	52.84	-6.90	Grassland	Cfb	Kindler et al. (2011)
CastleDowns	-45.79	168.21	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Coulissenhieb	50.14	11.86	Coniferous forest	Cfb	Michalzik and Matzner (1999)
Drayton	52.19	-1.76	Grassland	Cfb	ECN network
Dunearn	-46.00	168.16	Partially drained	Cfb	Moore and Clarkson (2007)
Easter_Bush	55.86	-3.20	Grassland	Cfb	Kindler et al. (2011)
FazendaVitoria_DP	-2.98	-47.31	Grassland	Am	Markewitz et al. (2004)
FazendaVitoria_MF	-2.98	-47.31	Broadleaved forest	Am	Markewitz et al. (2004)
FazendaVitoria_MP	-2.98	-47.31	Grassland	Am	Markewitz et al. (2004)
FazendaVitoria_	-2.98	-47.31	Broadleaved	Am	Markewitz et al. (2004)

SF			forest		
Flakaliden	64.11	19.45	Coniferous forest	Dfc	Fröberg et al. (2006)
Fruebuel	47.11	8.54	Grassland	Cfb	Kindler et al. (2011)
Glensaugh	56.90	-2.55	Grassland	Cfb	ECN network
GorsGoch	53.28	-4.36	Not drained: peatland	Cfb	Kang et al. (2001)
Grignon	48.84	1.96	Cropland	Cfb	Kindler et al. (2011)
Guandaushi_NH	24.06	121.50	Broadleaved forest	Cfb	Liu and Sheu (2003)
Guandaushi_SH	24.06	121.50	Broadleaved forest	Cfb	Liu and Sheu (2003)
Guandaushi_fir	24.06	121.50	Coniferous forest	Cfb	Liu and Sheu (2003)
Hainich	51.07	10.45	Broadleaved forest	Cfb	Kindler et al. (2011)
Hillsborough	54.45	-6.07	Grassland	Cfb	ECN network
Hohe_Matzen	50.00	11.93	Coniferous forest	Cfb	Guggenberger and Zech (1993)
Kaltenborn	50.78	10.21	Grassland	Cfb	Don and Schulze (2008)
Kepler	-45.53	167.69	Not drained: peatland	Cfc	Moore and Clarkson (2007)
Ketetahi	-39.06	175.56	Not drained: peatland	Cfb	Moore and Clarkson (2007)
KiniSwamp	-43.61	169.60	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Klingenberg	50.96	13.33	Cropland	Cfb	Kindler et al. (2011)
Knåttasen	61.00	16.20	Coniferous forest	Dfc	Fröberg et al. (2006)
Kopuatai	-37.40	175.55	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Kuaro	-1.85	116.03	Broadleaved forest	Af	Fujii et al. (2011)
LaSelva	10.43	-83.98	Broadleaved forest	Af	Schwendenmann and Veldkamp (2005)
Laois	52.28	-7.25	Coniferous forest	Cfb	Kindler et al. (2011)

Laqueuille	45.64	2.73	Grassland	Cfb	Kindler et al. (2011)
Lochristi	51.01	3.85	Broadleaved forest	Cfb	Broeckx et al. (2012)
Loobos	52.16	5.74	Coniferous forest	Cfb	Kindler et al. (2011)
LowerAfonHafren	52.47	-3.70	Coniferous forest	Cfb	Neal et al. (2005)
MatoGrosso	-10.46	-58.46	Forest	Aw	Johnson et al. (2006)
Mehrstedt	51.26	10.64	Grassland	Cfb	Don and Schulze (2008)
Migneint	52.99	-3.77	Not drained: peatland	Cfb	Freeman et al. (2004)
MoorHouse	54.69	-2.38	Not drained: peatland	Cfb	ECN network
MtBurns	-45.75	167.38	Not drained: peatland	Cfc	Moore and Clarkson (2007)
MtKili_Mf			Forest		Schrumpf et al. (2006)
MtKili_SF			Forest		Schrumpf et al. (2006)
MtKili_Sv			Forest		Schrumpf et al. (2006)
NantFfrancon	53.15	-4.06	Not drained: peatland	Cfb	Bonnett et al. (2006)
NationalPark_Culvert	-39.18	175.39	Not drained: peatland	Cfb	Moore and Clarkson (2007)
NationalPark_Wet	-39.18	175.39	Not drained: peatland	Cfb	Moore and Clarkson (2007)
NorthWyke	50.78	-3.91	Grassland	Cfb	ECN network
Oberwarmensteinach	50.00	11.80	Coniferous forest	Cfb	Guggenberger and Zech (1993)
Opuatia	-37.43	175.06	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Opuatia_WT	-37.43	175.06	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Plynlimon	52.46	-3.78	Not drained: peatland	Cfb	Freeman et al. (2004)
Pukerau	-46.15	169.25	Not drained: peatland	Cfb	Moore and Clarkson (2007)
RiviereDuLoup	47.79	-69.46	Drained/ managed:	Dfb	Glatzel et al. (2003)

			grassland		
Shearer	-42.91	170.75	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Soro	55.04	11.63	Broadleaved forest	Cfb	Kindler et al. (2011)
Sourhope	55.48	-2.21	Grassland	Cfb	ECN Network
Stillberg	46.77	9.86	Grassland/ Coniferous forest	Cfb	Hagedorn et al. (2008)
Storgama	59.00	8.05	Heathland	Dfc	Haaland et al. (2008)
Taipusi_C10	41.84	115.22	Cropland	BSk	Jiao et al. (2009)
Taipusi_C15	41.84	115.23	Cropland	BSk	Jiao et al. (2009)
Taipusi_C20	41.84	115.25	Cropland	BSk	Jiao et al. (2009)
Taipusi_F	41.83	115.25	Broadleaved forest	BSk	Jiao et al. (2009)
Taipusi_G	41.83	115.22	Grassland	BSk	Jiao et al. (2009)
TePonanga	-39.00	175.73	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Tönnersjöheden_NS	56.66	13.07	Coniferous forest	Cfb	Fröberg et al. (2011)
Tönnersjöheden_SB	56.66	13.07	Broadleaved forest	Cfb	Fröberg et al. (2011)
Tönnersjöheden_SP	56.66	13.07	Broadleaved forest	Cfb	Fröberg et al. (2011)
Torehape	-37.31	175.44	Drained/ managed: grassland	Cfb	Moore and Clarkson (2007)
TurkeyPoint	42.66	-80.55	Coniferous forest	Dfb	Peichl et al. (2007)
UpperWharfedale	54.21	-2.20	Drained/managed: grassland	Cfb	Neal et al. (2005)
Wetzstein	50.45	11.45	Coniferous forest	Cfb	Kindler et al. (2011)
Whangamarino	-37.29	175.13	Not drained: peatland	Cfb	Moore and Clarkson (2007)
Wulfersreuth	50.05	11.75	Coniferous	Cfb	Guggenberger and Zech

			forest		(1993)
Wytham	51.78	-1.33	Broadleaved forest	Cfb	ECN network
YrWyddfa	53.07	-4.03	Grassland	Cfb	ECN network
13_1301	57.50	12.25	Coniferous forest	Cfb	ICP Forests
13_1403	58.43	11.73	Coniferous forest	Cfb	ICP Forests
13_5201	59.57	18.05	Coniferous forest	Dfb	ICP Forests
13_5202	59.08	17.63	Coniferous forest	Dfb	ICP Forests
13_5301	60.02	17.18	Coniferous forest	Dfc	ICP Forests
13_5401	58.95	16.98	Coniferous forest	Dfb	ICP Forests
13_5404	59.30	16.12	Coniferous forest	Dfc	ICP Forests
13_5501	58.15	15.42	Coniferous forest	Dfb	ICP Forests
13_5502	58.75	15.15	Coniferous forest	Dfb	ICP Forests
13_5601	57.87	14.75	Coniferous forest	Cfb	ICP Forests
13_5602	57.83	14.98	Coniferous forest	Dfb	ICP Forests
13_5603	57.50	15.33	Coniferous forest	Dfb	ICP Forests
13_5701	56.88	15.12	Coniferous forest	Cfb	ICP Forests
13_5702	57.05	14.37	Coniferous forest	Cfb	ICP Forests
13_5703	56.83	13.73	Coniferous forest	Cfb	ICP Forests
13_5801	58.05	16.10	Coniferous forest	Cfb	ICP Forests
13_5802	56.63	15.62	Coniferous	Cfb	ICP Forests

			forest		
13_5804	56.85	16.32	Coniferous forest	Cfb	ICP Forests
13_6001	56.28	14.65	Broadleaved forest	Cfb	ICP Forests
13_6002	56.40	15.30	Broadleaved forest	Cfb	ICP Forests
13_6003	56.22	15.43	Coniferous forest	Cfb	ICP Forests
13_6101	56.02	13.92	Broadleaved forest	Cfb	ICP Forests
13_6102	56.10	13.52	Broadleaved forest	Cfb	ICP Forests
13_6103	56.13	13.50	Coniferous forest	Cfb	ICP Forests
13_6109	55.60	14.10	Coniferous forest	Cfb	ICP Forests
13_6201	55.92	13.60	Broadleaved forest	Cfb	ICP Forests
13_6301	57.07	12.55	Broadleaved forest	Cfb	ICP Forests
13_6302	56.93	12.72	Coniferous forest	Cfb	ICP Forests
13_6303	56.77	13.13	Coniferous forest	Cfb	ICP Forests
13_6401	58.53	11.72	Coniferous forest	Cfb	ICP Forests
13_6501	57.40	13.10	Coniferous forest	Cfb	ICP Forests
13_6503	57.77	13.75	Coniferous forest	Cfb	ICP Forests
13_6507	58.72	11.97	Coniferous forest	Dfb	ICP Forests
13_6601	58.62	13.77	Coniferous forest	Dfb	ICP Forests
13_6701	59.65	13.80	Coniferous forest	Dfc	ICP Forests

13_6702	59.82	12.90	Coniferous forest	Dfc	ICP Forests
13_6703	60.58	13.12	Coniferous forest	Dfc	ICP Forests
13_6802	59.58	14.70	Coniferous forest	Dfc	ICP Forests
13_6803	59.87	14.43	Coniferous forest	Dfc	ICP Forests
13_6901	59.33	15.93	Coniferous forest	Dfc	ICP Forests
13_7001	61.12	14.35	Coniferous forest	Dfc	ICP Forests
13_7002	60.40	15.27	Coniferous forest	Dfc	ICP Forests
13_7106	60.65	16.30	Coniferous forest	Dfc	ICP Forests
13_7201	62.27	16.33	Coniferous forest	Dfc	ICP Forests
13_7301	62.00	14.42	Coniferous forest	Dfc	ICP Forests
13_7302	63.07	16.73	Coniferous forest	Dfc	ICP Forests
13_7402	64.48	18.47	Coniferous forest	Dfc	ICP Forests
13_7404	65.40	18.10	Coniferous forest	Dfc	ICP Forests
13_7501	65.95	23.25	Coniferous forest	Dfc	ICP Forests
13_7502	66.07	20.62	Coniferous forest	Dfc	ICP Forests
14_16	47.06	14.11	Coniferous forest	Dfc	ICP Forests
14_9	48.12	16.05	Broadleaved forest	Cfb	ICP Forests
15_1	69.58	28.90	Coniferous forest	Dfc	ICP Forests
15_10	61.87	24.21	Coniferous	Dfc	ICP Forests

			forest		
15_11	61.85	24.31	Coniferous forest	Dfc	ICP Forests
15_12	60.65	23.81	Coniferous forest	Dfc	ICP Forests
15_13	60.62	23.84	Coniferous forest	Dfc	ICP Forests
15_16	61.77	29.34	Coniferous forest	Dfc	ICP Forests
15_17	61.81	29.32	Coniferous forest	Dfc	ICP Forests
15_18	60.70	27.85	Coniferous forest	Dfb	ICP Forests
15_19	61.24	25.07	Coniferous forest	Dfc	ICP Forests
15_20	63.16	30.71	Coniferous forest	Dfc	ICP Forests
15_21	66.30	29.50	Coniferous forest	Dfc	ICP Forests
15_23	63.56	22.49	Coniferous forest	Dfc	ICP Forests
15_3	68.00	24.24	Coniferous forest	Dfc	ICP Forests
15_32	66.43	26.69	Broadleaved forest	Dfc	ICP Forests
15_33	61.82	29.32	Broadleaved forest	Dfc	ICP Forests
15_5	66.33	26.65	Coniferous forest	Dfc	ICP Forests
15_6	66.36	26.73	Coniferous forest	Dfc	ICP Forests
15_9	64.97	26.39	Coniferous forest	Dfc	ICP Forests
1_100	47.93	7.12	Coniferous forest	Cfb	ICP Forests
1_17	47.57	1.25	Broadleaved forest	Cfb	ICP Forests

1_30	48.45	2.72	Broadleaved forest	Cfb	ICP Forests
1_37	49.95	4.81	Coniferous forest	Cfb	ICP Forests
1_41	45.76	2.97	Coniferous forest	Cfb	ICP Forests
1_46	45.80	1.82	Coniferous forest	Cfb	ICP Forests
1_57	44.12	3.54	Broadleaved forest	Cfb	ICP Forests
1_59	48.50	6.70	Broadleaved forest	Cfb	ICP Forests
1_6	50.17	3.75	Broadleaved forest	Cfb	ICP Forests
1_63	43.15	-0.66	Broadleaved forest	Cfb	ICP Forests
1_84	48.85	7.71	Coniferous forest	Cfb	ICP Forests
1_90	44.48	6.45	Coniferous forest	Cfc	ICP Forests
1_93	42.87	2.10	Coniferous forest	Cfb	ICP Forests
1_96	45.42	6.12	Coniferous forest	Cfb	ICP Forests
1_98	48.61	7.13	Coniferous forest	Cfb	ICP Forests
2_1	49.95	4.83	Coniferous forest	Cfb	ICP Forests
2_11	51.07	3.04	Broadleaved forest	Cfb	ICP Forests
2_14	51.40	5.05	Coniferous forest	Cfb	ICP Forests
2_15	51.31	4.52	Coniferous forest	Cfb	ICP Forests
2_16	50.98	3.80	Broadleaved forest	Cfb	ICP Forests
2_21	50.75	4.41	Broadleaved	Cfb	ICP Forests

			forest		
2_8	50.10	4.27	Broadleaved forest	Cfb	ICP Forests
3_1012	52.23	5.63	Broadleaved forest	Cfb	ICP Forests
3_1040	52.10	5.22	Broadleaved forest	Cfb	ICP Forests
3_106	52.53	6.55	Coniferous forest	Cfb	ICP Forests
3_129	52.17	5.75	Coniferous forest	Cfb	ICP Forests
3_174	51.32	5.52	Coniferous forest	Cfb	ICP Forests
3_175	51.32	5.52	Coniferous forest	Cfb	ICP Forests
3_2080	52.15	5.88	Broadleaved forest	Cfb	ICP Forests
3_2084	52.27	5.73	Coniferous forest	Cfb	ICP Forests
3_2085	52.83	6.43	Coniferous forest	Cfb	ICP Forests
3_226	51.55	4.77	Broadleaved forest	Cfb	ICP Forests
3_39	52.97	6.73	Coniferous forest	Cfb	ICP Forests
3_58	52.87	6.33	Coniferous forest	Cfb	ICP Forests
3_61	52.87	6.35	Coniferous forest	Cfb	ICP Forests
3_82	52.90	6.72	Coniferous forest	Cfb	ICP Forests
4_1001	49.32	7.02	Broadleaved forest	Cfb	ICP Forests
4_101	54.10	10.24	Broadleaved forest	Cfb	ICP Forests
4_1101	52.47	13.22	Coniferous forest	Cfb	ICP Forests

4_1102	52.47	13.22	Coniferous forest	Cfb	ICP Forests
4_1103	52.42	13.60	Coniferous forest	Cfb	ICP Forests
4_1201	53.10	12.42	Coniferous forest	Cfb	ICP Forests
4_1202	53.13	12.97	Coniferous forest	Cfb	ICP Forests
4_1203	52.97	13.64	Coniferous forest	Cfb	ICP Forests
4_1204	52.19	12.56	Coniferous forest	Cfb	ICP Forests
4_1205	51.80	13.56	Coniferous forest	Cfb	ICP Forests
4_1206	52.13	14.00	Coniferous forest	Cfb	ICP Forests
4_1302	53.67	12.06	Broadleaved forest	Cfb	ICP Forests
4_1303	53.64	13.94	Coniferous forest	Cfb	ICP Forests
4_1401	50.42	12.53	Coniferous forest	Cfb	ICP Forests
4_1402	50.64	13.30	Coniferous forest	Cfb	ICP Forests
4_1403	50.83	14.10	Coniferous forest	Cfb	ICP Forests
4_1404	51.12	14.55	Coniferous forest	Cfb	ICP Forests
4_1405	51.24	13.82	Coniferous forest	Cfb	ICP Forests
4_1406	51.18	12.83	Broadleaved forest	Cfb	ICP Forests
4_1501	52.58	11.17	Coniferous forest	Cfb	ICP Forests
4_1502	52.05	12.31	Coniferous forest	Cfb	ICP Forests
4_1605	50.62	10.79	Coniferous	Cfb	ICP Forests

			forest		
4_1606	51.34	10.87	Broadleaved forest	Cfb	ICP Forests
4_1607	50.79	11.66	Coniferous forest	Cfb	ICP Forests
4_1608	50.93	11.02	Broadleaved forest	Cfb	ICP Forests
4_1609	50.48	11.50	Coniferous forest	Cfb	ICP Forests
4_301	52.84	10.27	Broadleaved forest	Cfb	ICP Forests
4_302	51.85	10.40	Coniferous forest	Cfb	ICP Forests
4_303	51.86	10.42	Coniferous forest	Cfb	ICP Forests
4_304	51.76	9.58	Broadleaved forest	Cfb	ICP Forests
4_305	51.75	9.57	Coniferous forest	Cfb	ICP Forests
4_306	51.52	10.03	Broadleaved forest	Cfb	ICP Forests
4_307	52.91	7.86	Coniferous forest	Cfb	ICP Forests
4_308	53.18	9.90	Broadleaved forest	Cfb	ICP Forests
4_502	51.73	6.17	Broadleaved forest	Cfb	ICP Forests
4_503	51.69	7.26	Broadleaved forest	Cfb	ICP Forests
4_505	51.22	8.67	Broadleaved forest	Cfb	ICP Forests
4_506	51.02	8.18	Coniferous forest	Cfb	ICP Forests
4_601	50.63	9.67	Broadleaved forest	Cfb	ICP Forests
4_602	50.42	9.67	Broadleaved forest	Cfb	ICP Forests

4_603	50.70	8.88	Broadleaved forest	Cfb	ICP Forests
4_604	50.26	9.66	Broadleaved forest	Cfb	ICP Forests
4_605	50.57	8.20	Broadleaved forest	Cfb	ICP Forests
4_606	51.37	9.27	Broadleaved forest	Cfb	ICP Forests
4_607	50.92	9.33	Broadleaved forest	Cfb	ICP Forests
4_701	49.68	7.02	Coniferous forest	Cfb	ICP Forests
4_702	50.42	7.08	Coniferous forest	Cfb	ICP Forests
4_703	49.63	7.92	Broadleaved forest	Cfb	ICP Forests
4_704	50.41	7.73	Broadleaved forest	Cfb	ICP Forests
4_705	49.27	7.81	Broadleaved forest	Cfb	ICP Forests
4_706	49.02	8.13	Broadleaved forest	Cfb	ICP Forests
4_707	49.30	7.87	Coniferous forest	Cfb	ICP Forests
4_801	48.80	8.40	Coniferous forest	Cfb	ICP Forests
4_802	49.46	8.75	Coniferous forest	Cfb	ICP Forests
4_806	48.02	7.97	Coniferous forest	Cfb	ICP Forests
4_808	48.01	9.96	Coniferous forest	Cfb	ICP Forests
4_809	48.60	8.63	Coniferous forest	Cfb	ICP Forests
4_812		9.42	Coniferous forest		ICP Forests
4_901	49.40	11.32	Coniferous	Cfb	ICP Forests

			forest		
4_902	48.22	12.73	Coniferous forest	Cfb	ICP Forests
4_903	50.35	9.93	Broadleaved forest	Cfb	ICP Forests
4_904	47.57	12.93	Coniferous forest	Cfb	ICP Forests
4_905	49.12	10.58	Coniferous forest	Cfb	ICP Forests
4_906	48.12	11.92	Coniferous forest	Cfb	ICP Forests
4_907	49.85	10.52	Broadleaved forest	Cfb	ICP Forests
4_908	49.75	12.38	Coniferous forest	Cfb	ICP Forests
4_909	49.97	11.80	Coniferous forest	Cfb	ICP Forests
4_910	48.70	12.73	Broadleaved forest	Cfb	ICP Forests
4_911	48.98	12.88	Broadleaved forest	Cfb	ICP Forests
4_912	49.68	11.50	Coniferous forest	Cfb	ICP Forests
4_913	48.93	11.76	Broadleaved forest	Cfb	ICP Forests
4_914	49.97	9.45	Broadleaved forest	Cfb	ICP Forests
4_915	47.87	10.78	Broadleaved forest	Cfb	ICP Forests
4_916	47.57	10.38	Coniferous forest	Cfb	ICP Forests
4_917	48.40	10.53	Coniferous forest	Cfb	ICP Forests
4_918	49.27	12.38	Coniferous forest	Cfb	ICP Forests
4_919	48.41	11.66	Broadleaved forest	Cfb	ICP Forests

4_920	50.45	11.35	Coniferous forest	Cfb	ICP Forests
4_921	49.73	9.89	Broadleaved forest	Cfb	ICP Forests
4_922	47.73	11.68	Coniferous forest	Cfb	ICP Forests
50_12	46.02	8.84	Broadleaved forest	Cfc	ICP Forests
50_13	47.40	8.23	Broadleaved forest	Cfb	ICP Forests
50_15	47.28	7.89	Coniferous forest	Cfb	ICP Forests
50_16	47.17	9.07	Broadleaved forest	Cfb	ICP Forests
50_2	46.72	7.76	Coniferous forest	Cfb	ICP Forests
50_3	47.23	7.42	Broadleaved forest	Cfb	ICP Forests
50_4	46.49	9.89	Coniferous forest	ET	ICP Forests
50_8	46.59	6.66	Broadleaved forest	Cfb	ICP Forests
51_1	47.89	19.96	Broadleaved forest	Cfb	ICP Forests
55_1	58.38	8.23	Coniferous forest	Dfc	ICP Forests
55_10	61.00	9.22	Coniferous forest	ET	ICP Forests
55_11	60.37	9.73	Coniferous forest	Dfc	ICP Forests
55_12	62.77	8.88	Coniferous forest	Cfc	ICP Forests
55_13	58.08	7.85	Coniferous forest	Cfb	ICP Forests
55_14	59.33	5.78	Coniferous forest	Cfb	ICP Forests
55_15	63.28	11.18	Coniferous	Cfc	ICP Forests

			forest		
55_16	64.65	12.27	Coniferous forest	Dfc	ICP Forests
55_17	68.98	19.42	Coniferous forest	Dfc	ICP Forests
55_18	62.77	8.88	Coniferous forest	Cfc	ICP Forests
55_19	60.37	11.07	Coniferous forest	Dfc	ICP Forests
55_2	60.25	11.10	Coniferous forest	Dfc	ICP Forests
55_3	59.03	7.57	Coniferous forest	Dfc	ICP Forests
55_4	65.88	13.80	Coniferous forest	Dfc	ICP Forests
55_5	69.45	30.03	Coniferous forest	Dfc	ICP Forests
55_6	58.97	11.52	Coniferous forest	Cfb	ICP Forests
55_7	61.27	11.85	Coniferous forest	Dfc	ICP Forests
55_8	60.60	6.52	Coniferous forest	Cfc	ICP Forests
55_9	59.43	9.87	Coniferous forest	Dfc	ICP Forests
56_10			Forest		ICP Forests
56_3	54.78	23.58	Coniferous forest	Dfb	ICP Forests
56_6	54.82	24.08	Coniferous forest	Dfb	ICP Forests
58_2015	50.73	15.54	Broadleaved forest	Cfb	ICP Forests
58_2061	49.74	12.86	Coniferous forest	Cfb	ICP Forests
58_2102	49.90	14.55	Broadleaved forest	Cfb	ICP Forests
58_2103	49.23	14.30	Broadleaved	Cfb	ICP Forests

			forest		
58_2161	49.68	15.23	Coniferous forest	Cfb	ICP Forests
58_2163	49.03	14.98	Coniferous forest	Cfb	ICP Forests
58_2251	50.29	16.39	Coniferous forest	Cfb	ICP Forests
58_2361	49.07	17.27	Broadleaved forest	Cfb	ICP Forests
58_2401	49.45	18.40	Coniferous forest	Cfb	ICP Forests
58_521	50.04	12.63	Coniferous forest	Cfb	ICP Forests
58_561	49.26	15.70	Coniferous forest	Cfb	ICP Forests
59_2	59.58	26.13	Coniferous forest	Dfb	ICP Forests
59_3	58.06	26.11	Coniferous forest	Dfb	ICP Forests
59_7	57.70	26.52	Coniferous forest	Dfb	ICP Forests
59_8	59.53	26.40	Coniferous forest	Dfb	ICP Forests
59_9	58.27	26.46	Coniferous forest	Dfb	ICP Forests
5_1	41.85	13.59	Broadleaved forest	Cfb	ICP Forests
5_10	46.24	9.59	Coniferous forest	Dfc	ICP Forests
5_12	45.68	8.07	Broadleaved forest	Dfc	ICP Forests
5_17	46.36	11.49	Coniferous forest	Dfc	ICP Forests
5_27	46.59	11.43	Coniferous forest	Dfc	ICP Forests
5_6	44.11	11.12	Broadleaved forest	Cfb	ICP Forests

5_8	46.49	13.59	Coniferous forest	Dfc	ICP Forests
5_9	42.83	11.90	Broadleaved forest	Cfb	ICP Forests
60_4	46.29	14.40	Coniferous forest	Dfb	ICP Forests
60_5	45.54	14.80	Broadleaved forest	Cfb	ICP Forests
64_5	56.74	23.70	Coniferous forest	Dfb	ICP Forests
66_101	35.01	33.05	Coniferous forest	Csa	ICP Forests
66_102	34.95	32.83	Coniferous forest	Csa	ICP Forests
6_512	51.20	-0.86	Broadleaved forest	Cfb	ICP Forests
6_516	51.58	-1.00	Broadleaved forest	Cfb	ICP Forests
6_517	54.30	-3.00	Broadleaved forest	Cfb	ICP Forests
6_715	52.73	0.87	Coniferous forest	Cfb	ICP Forests
6_716	53.70	-1.76	Coniferous forest	Cfb	ICP Forests
6_717	55.08	-4.29	Coniferous forest	Cfb	ICP Forests
6_919	55.17	-2.48	Coniferous forest	Cfb	ICP Forests
6_920	56.73	-4.06	Coniferous forest	Cfc	ICP Forests
6_922	52.21	-3.74	Coniferous forest	Cfb	ICP Forests
7_1	53.10	-6.00	Coniferous forest	Cfb	ICP Forests
7_10	53.36	-9.35	Coniferous forest	Cfb	ICP Forests
7_109	52.14	-8.41	Coniferous	Cfb	ICP Forests

			forest		
7_11	53.76	-9.56	Broadleaved forest	Cfb	ICP Forests
7_16	53.11	-6.24	Coniferous forest	Cfb	ICP Forests
8_11	56.29	8.43	Coniferous forest	Cfb	ICP Forests
8_12	56.28	8.42	Coniferous forest	Cfb	ICP Forests
8_13	56.28	8.42	Coniferous forest	Cfb	ICP Forests
8_14	56.28	8.42	Broadleaved forest	Cfb	ICP Forests
8_15	56.28	8.42	Coniferous forest	Cfb	ICP Forests
8_21	55.13	8.88	Coniferous forest	Cfb	ICP Forests
8_22	55.13	8.88	Coniferous forest	Cfb	ICP Forests
8_23	55.13	8.88	Coniferous forest	Cfb	ICP Forests
8_24	55.13	8.88	Broadleaved forest	Cfb	ICP Forests
8_25	55.13	8.88	Broadleaved forest	Cfb	ICP Forests
8_26	55.13	8.88	Coniferous forest	Cfb	ICP Forests
8_31	55.95	12.35	Coniferous forest	Cfb	ICP Forests
8_32	55.95	12.35	Coniferous forest	Cfb	ICP Forests
8_33	55.95	12.35	Coniferous forest	Cfb	ICP Forests
8_34	55.96	12.35	Broadleaved forest	Cfb	ICP Forests
8_35	55.95	12.35	Broadleaved forest	Cfb	ICP Forests

8_51	56.08	9.35	Coniferous forest	Cfb	ICP Forests
8_64	55.01	9.93	Broadleaved forest	Cfb	ICP Forests
8_74	55.38	11.56	Broadleaved forest	Cfb	ICP Forests
8_85	55.70	12.35	Broadleaved forest	Cfb	ICP Forests
8_95	56.40	9.34	Broadleaved forest	Cfb	ICP Forests

Table S2. Database content: variables, description of the variable and units.

	Variable		Brief description	Unit
	Short name	**Long name**		
Location	Site	Site name		
	Lat	Latitude	Latitude in DD.dd	Degrees North
	Lon	Longitude	Longitude in DD.dd	Degrees East
Climate	MAT	Mean annual temperature	ERA interim dataset for the period 1990 to 2008	°C
	TempSpring	Temperature in spring	Mean temperature from March to May for the period 1990 to 2008	°C
	TempSummer	Temperature in summer	Mean temperature from June to August for the period 1990 to 2008	°C
	TempAutumn	Temperature in autumn	Mean temperature from September to November for the period 1990 to 2008	°C
	TempWinter	Temperature in winter	Mean temperature from December to February for the period 1990 to 2008	°C
	MAP	Mean annual precipitation	GPCC dataset for the period 1990 to 2008	mm
	PrecSpring	Precipitation in spring	Mean precipitation from March to May for the period 1990 to 2008	mm
	PrecSummer	Precipitation in summer	Mean precipitation from June to August for the period 1990 to 2008	mm
	PrecAutumn	Precipitation in autumn	Mean precipitation from September to November for	mm

			the period 1990 to 2008	
	PrecWinter	Precipitation in winter	Mean precipitation from December to February for the period 1990 to 2008	mm
	ET	Mean evapotranspiration	Evapotranspiration extracted from Jung et al., 2011 for the period 1990 to 2008	mm
	ETspring	Evapotranspiration in spring	Mean evapotranspiration from March to May for the period 1990 to 2008	mm
	ETsummer	Evapotranspiration in summer	Mean evapotranspiration from June to August for the period 1990 to 2008	mm
	ETautumn	Evapotranspiration in autumn	Mean evapotranspiration from September to November for the period 1990 to 2008	mm
	ETwinter	Evapotranspiration in winter	Mean evapotranspiration from December to February for the period 1990 to 2008	mm
	Mean_Drainage	Mean annual drainage	Calculated as the difference between MAP and ET	mm
	DrainageSpring	Drainage in spring	Calculated as the difference between PrecSpring and ETspring	mm
	DrainageSummer	Drainage in summer	Calculated as the difference between PrecSummer and ETsummer	mm
	DrainageAutumn	Drainage in autumn	Calculated as the difference between PrecAutumn and ETautumn	mm
	DrainageWinter	Drainage in winter	Calculated as the difference between PrecWinter and	mm

			ETwinter	
Soil Solution	MedianDOC	Median DOC concentration	Median DOC (dissolved organic carbon) concentration in soil solution throughout the period of measurement.	mg L^{-1}
	MedianNH4	Median NH_4^+ concentration	Median NH_4^+ concentration in soil solution throughout the period of measurement.	mg L^{-1}
	MedianNO3	Median NO_3^- concentration	Median NO_3^- concentration in soil solution throughout the period of measurement.	mg L^{-1}
	MedianSO4	Median SO_4^{2-} concentration	Median SO_4^{2-} concentration in soil solution throughout the period of measurement.	mg L^{-1}
	MedianFe	Median $Fe^{2+/3+}$ concentration	Median $Fe^{2+/3+}$ concentration in soil solution throughout the period of measurement.	mg L^{-1}
	MedianAl	Median Al^{3+} concentration	Median Al^{3+} concentration in soil solution throughout the period of measurement.	mg L^{-1}
Soil properties	Soil Type	Reference soil group	Soil classification according to World Reference Base for Soil Resources (WRB)	
	Texture	Texture class	USDA texture class (SiCL, SC, SCL, SL, LS, S)	
	Clay	Fraction of clay	Mass fraction of clay (0 - 2 µm)	g $100g^{-1}$
	Silt	Fraction of silt	Mass fraction of silt (2 - 63 µm)	g $100g^{-1}$
	Sand	Fraction of sand	Mass fraction of sand (63 - 2000 ųm)	g $100g^{-1}$
	BD	Bulk density	Mean bulk density of fine	kg m^{-3}

			earth	
	CFmass	Coarse fragments mass	Mass of coarse fragments (stones and gravel with diameter > 2 mm)	g 100g^{-1}
	FFTH	Forest Floor Thickness	Average thickness of forest floor	cm
	FFM	Forest Floor Mass	Average mass of forest floor	kg m^{-2}
	FFC	Forest Floor Carbon	Average carbon stock in forest floor	t C ha^{-1}
	FFN	Forest Floor Nitrogen	Average nitrogen stock in forest floor	t C ha^{-1}
	FFS	Forest Floor Sulfur	Average Sulfur stock in forest floor	t C ha^{-1}
	FFP	Forest Floor Phosphorous	Average Phosphorous stock in forest floor	t C ha^{-1}
	pHCaCl2	pH ($CaCl_2$)	pH measured using a solution of calcium chloride $CaCl_2$	
	pHH2O	pH (H_2O)	pH measured in water	
	OrgC	Organic Carbon	Organic carbon content	g kg^{-1}
	SOC	Soil Organic Carbon	Carbon stock	t C ha
	N	Nitrogen	Total nitrogen content	g kg^{-1}
	C/N	C/N ratio	C:N ratio of the concerning layer	
	Carbonates	Carbonates	Carbonate content	g kg^{-1}
	ExchAcid	Exchangeable Acidity	Total exchangeable acidity	cmol$_+$ kg^{-1}
	ExchAl	Exchangeable Al		cmol$_+$ kg^{-1}
	ExchCa	Exchangeable Ca		cmol$_+$ kg^{-1}

	ExchFe	Exchangeable Fe		cmol$_+$ kg^{-1}
	ExchK	Exchangeable K		cmol$_+$ kg^{-1}
	ExchMg	Exchangeable Mg		cmol$_+$ kg^{-1}
	ExchMn	Exchangeable Mn		cmol$_+$ kg^{-1}
	ExchNa	Exchangeable Na		cmol$_+$ kg^{-1}
	FreeH	Free H$^+$	Free H$^+$ acidity	cmol$_+$ kg^{-1}
	BCE	Base Cations Exchangeable	Sum of exchangeable Ca, K, Mg, Na	cmol$_+$ kg^{-1}
	ACE	Acid Cations Exchangeable	Sum of exchangeable Al, Fe, Mn, Free H+	cmol$_+$ kg^{-1}
	CEC	Cation Exchange Capacity	Sum of BCE and ACE	cmol$_+$ kg^{-1}
	BaseSat	Base Saturation	BCE/CEC*100	cmol$_+$ kg^{-1}
	ExtracAl	Extractable Al	Aqua regia extractable Al	mg kg^{-1}
	ExtracCa	Extractable Ca	Aqua regia extractable Ca	mg kg^{-1}
	ExtracFe	Extractable Fe	Aqua regia extractable Fe	mg kg^{-1}
	ExtracK	Extractable K	Aqua regia extractable K	mg kg^{-1}
	ExtracMG	Extractable Mg	Aqua regia extractable Mg	mg kg^{-1}
	ExtracMn	Extractable Mn	Aqua regia extractable Mn	mg kg^{-1}
	ExtracNa	Extractable Na	Aqua regia extractable Na	mg kg^{-1}
	ExtracP	Extractable P	Aqua regia extractable P	mg kg^{-1}
	ExtracS	Extractable S	Aqua regia extractable S	mg kg^{-1}
	MeanST	Mean annual soil temperature	ERA interim dataset for the period 1990 to 2008: datasets for layer 1 (0-0.07	°C

			m), layer 2(0.07-0.28 m), layer 3 (0.28-1 m)	
	MeanSWV	Mean annual volumetric soil water	ERA interim dataset for the period 1990 to 2008: datasets for layer 1 (0-0.07 m), layer 2(0.07-0.28 m), layer 3 (0.28-1 m)	$m^3\ m^{-3}$
Vegetation and productivity	LU	Land use	Categorical variable for land use type with classes: *Forest*, *Non forest-mineral soils* and *Non forest-organic soils*	
	TreeSpecies	Tree species	Name of the main tree species in the site	
	VegType	Vegetation type	Dichotomous variable for forest type with classes: *Coniferous* and *Broadleaved*	
	LFWeight	Litterfall weight	Dry weight of litterfall per m^2	$kg\ m^{-2}$
	LitterDecomp	Litter decomposability	Categorical variable for litter decomposability classes based on tree species ranging from 1 to 5	
	avgNDVI	Mean annual NDVI	Mean annual NDVI for the period 1982-2010 extracted from the GIMMS dataset. Range from 0 to 1.	
	NDVIspring	NDVI in spring	Mean NVDI from March to May for the period 1982 to 2010. Range from 0-1.	
	NDVIsummer	NDVI in summer	Mean NDVI from June to August for the period 1982 to 2010. Range from 0-1.	
	NDVIautumn	NDVI in autumn	Mean NDVI from September to November for the period	

		1982 to 2010. Range from 0-1.	
NDVIwinter	NDVI in winter	Mean NDVI from December to February for the period 1982 to 2010. Range from 0-1.	
avgGPP	Mean annual Gross Primary production	GPP extracted from Jung et al., 2011 for the period 1990 to 2008	g m^{-2} yr^{-1}
GPPspring	Gross Primary production in spring	Mean GPP from March to May for the period 1990 to 2008	g m^{-2} spring^{-1}
GPPsummer	Gross Primary Production in summer	Mean GPP from June to August for the period 1990 to 2008	g m^{-2} summer^{-1}
GPPwinter	Gross Primary Production in autumn	Mean GPP from September to November for the period 1990 to 2008	g m^{-2} winter^{-1}
GPPautumn	Gross Primary production in winter	Mean GPP from December to February for the period 1990 to 2008	g m^{-2} autumn^{-1}

Note: All soil properties (except “Soil Type”) and soil solution variables are defined for the organic layer, and for the mineral soil in the intervals 0-20 cm, 20-40 cm and 40-80 cm.

Table S3. Bootstrap mean and 5th and 95th confidence intervals of the bootstrapped mean (in brackets) for the median DOC concentrations (mg L^{-1}) in different ecosystems, forest types, climate zones, soil types, pH classes and latitude classification. The number of sites per group is indicated in superscript. Only groups with more than 3 sites have been included. Climate zones are classified according to the Köppen climate classification (Af: Tropical rainforest climate, Am: Tropical monsoon climate, Bsk: dry (steppe) climate, Cfb and Cfc: Maritime Temperate climates, Dfb: Warm Summer Continental climate, Dfc: Continental Subartic or Boreal climates). Histosols have been removed from the dataset in the classification according to forest types, climate zones, pH classes and latitude classification.

	Soil profile (0- 80 cm)	**Layer 0 (0 cm)**	**Layer 1 (0-10 cm)**	**Layer 2 (10-20 cm)**	**Layer 3 (20-40 cm)**	**Layer 4 (40-80 cm)**	**Layer 5 (>80 cm)**
				Ecosystem			
Forest	16 (14 -17)^{329}	50 (45-56)^{139}	37 (32-43)^{102}	22 (19-25)^{174}	13 (11-16)^{131}	12 (10-14)^{211}	7 (6-9)^{121}
Non forests: Mineral	10 (8-13)^{25}	37 (26-44)^{6}	19 (12-29)^{11}	11 (9-14)^{14}	10 (7-14)^{16}	8 (5-14)^{6}	8 (4-13)^{9}
Non forests: Organic	53 (40-69)^{19}	16 (13-21)^{3}	40 (19-97)^{8}	42 (28-66)^{7}	48 (32-79)^{5}	70 (53-89)^{12}	86 (42-213)^{6}
				Forest type			
Broadleaved	13 (11-17)^{111}	40 (35-48)^{50}	30 (23-39)^{32}	15 (12-20)^{65}	11 (8-16)^{45}	10 (7-15)^{69}	5 (4-6)^{53}
Coniferous	17 (15-19)^{219}	56 (50-64)^{90}	41 (36-48)^{70}	25 (22-30)^{111}	15 (12-18)^{88}	13 (10-15)^{143}	9 (7-12)^{68}
				Climate zone			
Af	6 (3-8)^{4}	19 (9-25)^{3}	11 (7-14)^{4}	-	4 (2-4)^{4}	-	-
Am	5 (4-6)^{4}	17 (16-20)^{3}	-	11 (9-13)^{4}	2 (2-3)^{4}	-	7 (3-13)^{4}

BSk	14 (10-22)^{5}	-	12 (9-18)^{5}	14 (10-20)^{5}	15 (11-22)^{5}	-	-
Cfb	15 (13-18)^{239}	53 (48-60)^{115}	43 (35-53)^{53}	23 (19-28)^{122}	15 (12-19)^{90}	12 (10-15)^{168}	8 (6-9)^{121}
Cfc	7 (5-12)^{7}	-	15 (8-25)^{5}	8 (5-10)^{6}	4 (2-5)^{4}	7 (3-14)^{3}	-
Dfb	19 (15-25)^{23}	50 (38-61)^{8}	35 (30-44)^{11}	20 (12-33)^{5}	12 (2-18)^{3}	14 (11-21)^{17}	-
Dfc	15 (12-20)^{61}	34 (21-42)^{7}	34 (28-41)^{32}	18 (14-23)^{37}	11 (8-15)^{33}	5 (4-7)^{25}	-
Soil type							
Acrisol	7 (3-9)^{3}	19 (9-24)^{3}	10 (6-14)^{3}	-	-	-	-
Alisol	5 (2-8)^{4}	35 (26-45)^{4}	-	-	4 (2-7)^{3}	2 (1-3)^{3}	2 (1-2)^{4}
Andosol	3 (2-4)^{9}	25 (23-29)^{4}	-	3 (2-4)^{6}	4 (2-7)^{3}	2 (1-3)^{3}	2 (1-2)^{7}
Anthrosol	63 (52-70)^{3}	103 (97-113)^{3}	82 (73-89)^{3}	63 (53-80)^{3}	-	59 (43-69)^{3}	-
Arenosol	18 (15-22)^{59}	75 (57-101)^{18}	48 (38-60)^{22}	32 (26-42)^{29}	19 (13-25)^{17}	14 (12-17)^{46}	10 (7-14)^{21}
Cambisol	12 (9-17)^{72}	42 (37-50)^{34}	23 (17-30)^{12}	11 (8-14)^{38}	13 (9-21)^{33}	8 (6-14)^{41}	7 (5-12)^{35}
Ferralsol	6 (5-7)^{7}	18 (14-23)^{5}	11 (8-13)^{3}	10 (6-12)^{5}	3 (2-4)^{6}	-	6 (3-12)^{5}
Gleysol	8 (6-11)^{8}	-	19 (9-29)^{3}	13 (8-19)^{5}	-	4 (2-5)^{5}	3 (2-5)^{5}
Histosol	65 (51-81)^{13}	53 (51-58)^{4}	-	-	64 (53-87)^{5}	64 (49-83)^{13}	76 (38-188)^{7}
Leptosol	7 (6-9)^{9}	-	11 (8-17)^{5}	7 (5-15)^{6}	4 (3-5)^{4}	6 (3-10)^{4}	-
Luvisol	19 (13-27)^{33}	45 (36-53)^{14}	45 (35-54)^{10}	16 (11-22)^{15}	7 (5-10)^{14}	4 (3-7)^{14}	4 (3-6)^{19}
Podzol	18 (14-22)^{90}	57 (48-68)^{42}	42 (31-54)^{28}	29 (22-39)^{46}	15 (11-20)^{36}	15 (11-21)^{58}	9 (6-14)^{25}

Regosol	14 (9-22)^{14}	-	48 (36-58)^{4}	29 (20-46)^{5}	21 (14-32)^{4}	7 (5-8)^{10}	-
Stagnosol	10 (5-15)^{5}	-	-	-	-	8 (4-13)^{5}	-
Umbrisol	11 (5-17)^{5}	24 (20-32)^{3}	-	18 (11-25)^{5}	-	9 (5-15)^{5}	-
pH							
Very Acid (<4,2)	18 (15-22)^{71}	45 (39-52)^{42}	33 (23-53)^{13}	27 (21-36)^{38}	23 (18-30)^{36}	11 (9-15)^{46}	9 (6-13)^{34}
Intermediate (4.2-5)	15 (13-19)^{40}	41 (31-55)^{9}	32 (27- 38)^{25}	14 (11- 19)^{28}	12 (9-15)^{21}	12 (8-19)^{18}	4 (2-10)^{6}
Well buffered (5-6.2)	13 (8-20)^{11}	-	26 (17-37)^{5}	12 (7-17)^{9}	17 (8-30) ^{5}	7 (4-10)^{8}	4 (2-6)^{5}
Basic (>6.2)	10 (4-26)^{7}	22 (13-37)^{4}	-	18 (7-34)^{5}	5 (3-9)^{3}	3 (2 -4)^{5}	-
Latitude							
Boreal (>60)	14 (11-17)^{45}	42 (38-47)^{5}	32 (26-38)^{29}	18 (14-24)^{31}	11(8-15)^{31}	6 (4-8)^{14}	-
Temperate(35-60)	16 (14-18)^{290}	52 (47-59)^{127}	39 (33-47)^{78}	22 (19-26)^{144}	14 (12-18)^{102}	12 (10-15)^{197}	7 (6-9)^{122}
Tropical (<35)	7 (5-11)^{17}	20 (16-24)^{11}	10 (8-13)^{6}	10(7-14)^{12}	6 (3-12)^{12}	5 (3-8)^{4}	4 (2-10)^{8}

Table S4. Value, p value and standard error (S.E.) of the coefficients of each model.

CONIFEROUS					**BROADLEAVED**				
Model	**Variables**	**Coefficients**	**p value**	**S.E.**	**Model**	**Variables**	**Coefficients**	**p value**	**S.E.**
0 cm					**0 cm**				
	Intercept	51.94	<0.0001	4.46		Intercept	32.65	<0.0001	3.76
	Drainage summer	-9.11	0.0607	4.57		C/N	-9.56	0.0069	3.11
						Litter Decomp	18.59	0.0094	6.35
0-20 cm					**0-20 cm**				
	Intercept	25.87	<0.0001	1.33		Intercept	17.44	<0.0001	0.94
	NH4 in SS	10.03	0.0007	1.81		NH4 in SS	8.08	0.0275	1.11
	ExchAl	-12.23	0.0212	2.26		Fe in SS	5.69	0.0479	1.27
	avgDrainage	7.89	0.0027	1.99		ExchAl	-2.68	0.0158	1.00
	C/N	7.28	0.001	1.90		NDVI summer	-3.02	0.0003	1.25
	pH	-8.00	<0.0001	2.35		avg ET	-2.39	<0.0001	1.12
	avgST	5.32	0.071	2.14					
	Fe in SS	3.25	<0.0001	1.71					
	% Sand	-4.20	0.0945	2.40					

20-40 cm					**20-40 cm**				
	Intercept	19.19	<0.0001	1.66		Intercept	16.30	<0.0001	0.51
	Fe in SS	6.34	0.0035	1.75		NH4 in SS	22.49	<0.0001	0.74
	Al in SS	5.01	0.0213	1.89		ET summer	-6.62	<0.0001	0.68
	% Sand	4.12	0.0468	1.86		avgPrec	6.40	0.0003	1.13
						C_NM24	-2.03	0.0436	0.86
40-80 cm					**40-80 cm**				
	Intercept	11.19	<0.0001	1.54		Intercept	5.05	<0.0001	0.62
	Prec in summer	-7.21	0.0011	1.65		C/N	1.95	0.002	0.47
	NH4 in SS	3.90	0.0376	1.65		ExchFe	2.14	0.0036	0.57
						avgET	-2.28	0.0053	0.64
						Temp autumn	1.89	0.0078	0.57
						Litter	2.56	0.0219	0.94

The coefficients have been obtained by stepwise fit regressions using the dataset after standardization.

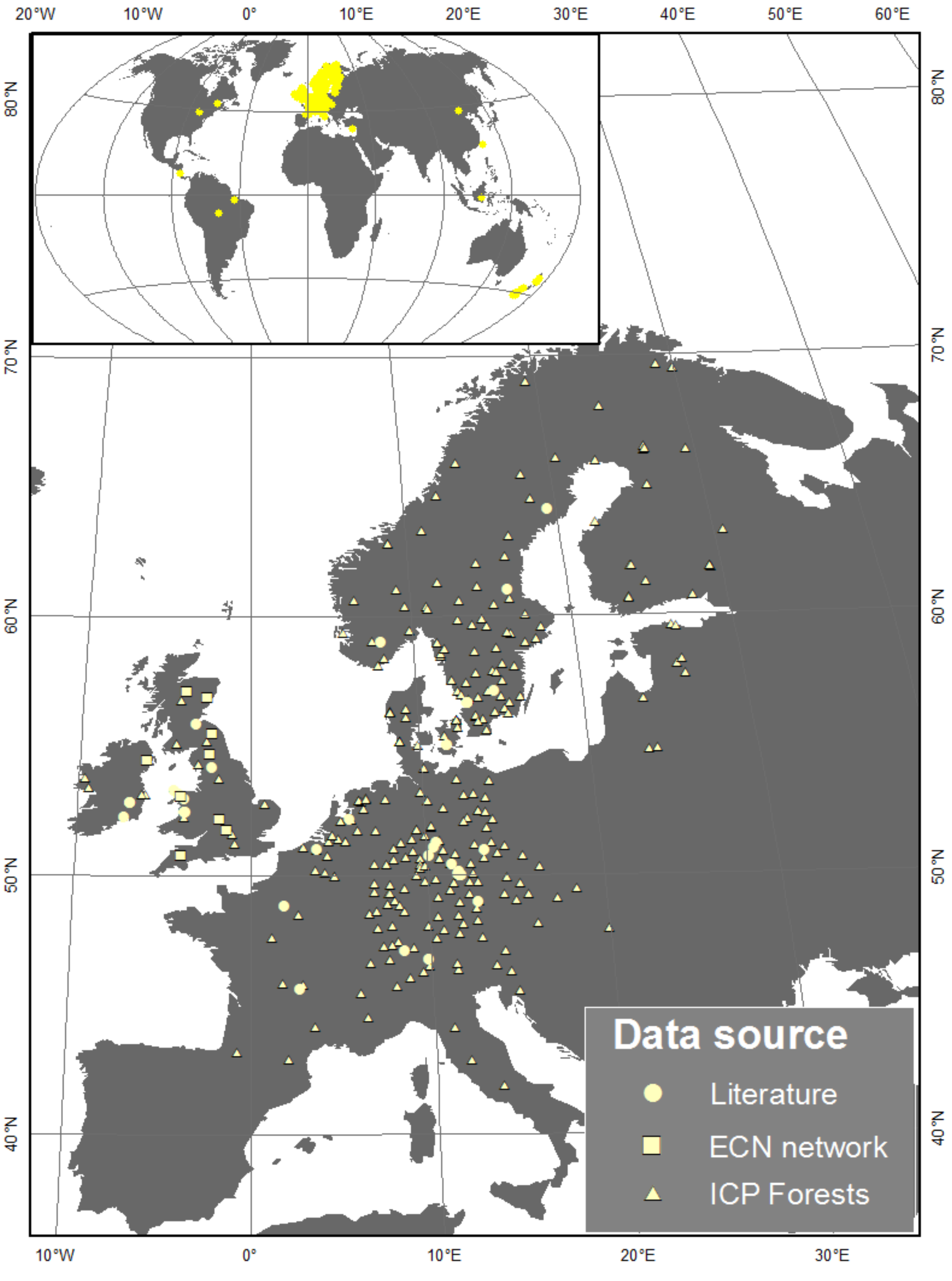
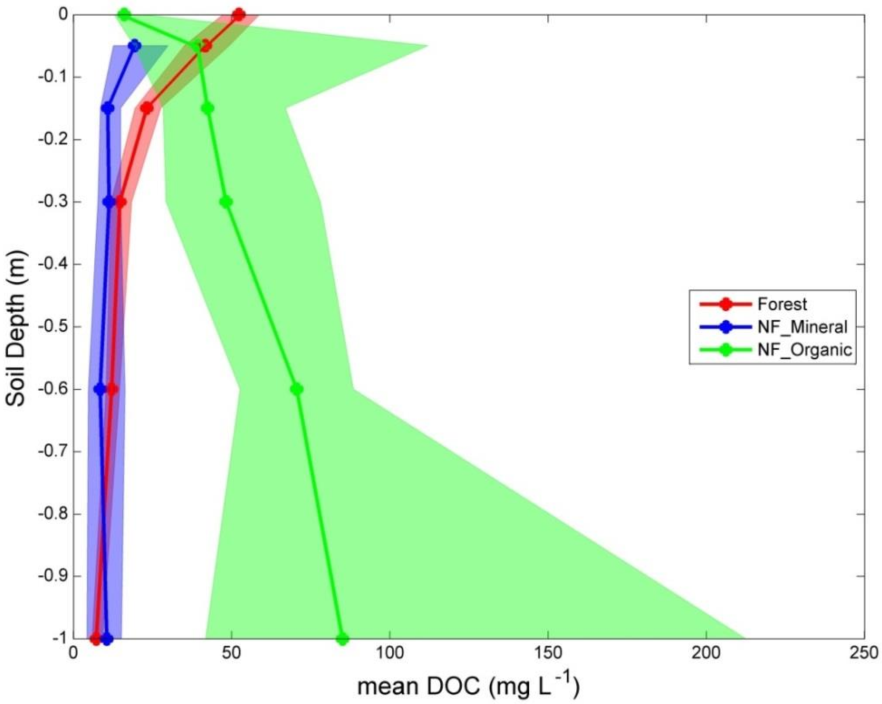


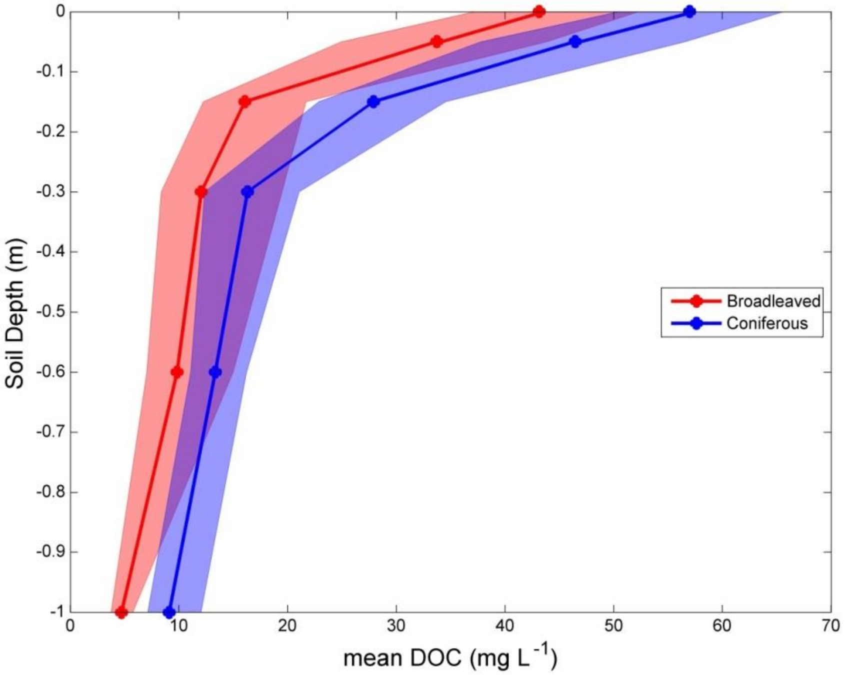
Figure S1. Location of sites contained in the database.

Figure S2. DOC profiles only for temperate zone a) Ecosystem type (NF: Non-forest), b) Forest type, and c) pH classes with Basic (>6.2), Intermediate (5-4.2) and Very Acid (<4.2). Solid lines represent the bootstrapped line and shaded areas the bootstrapped 95% confidence interval. Points are placed in the mid-point of the depth interval. Sites on Histosols are not present in Figure b) and c).

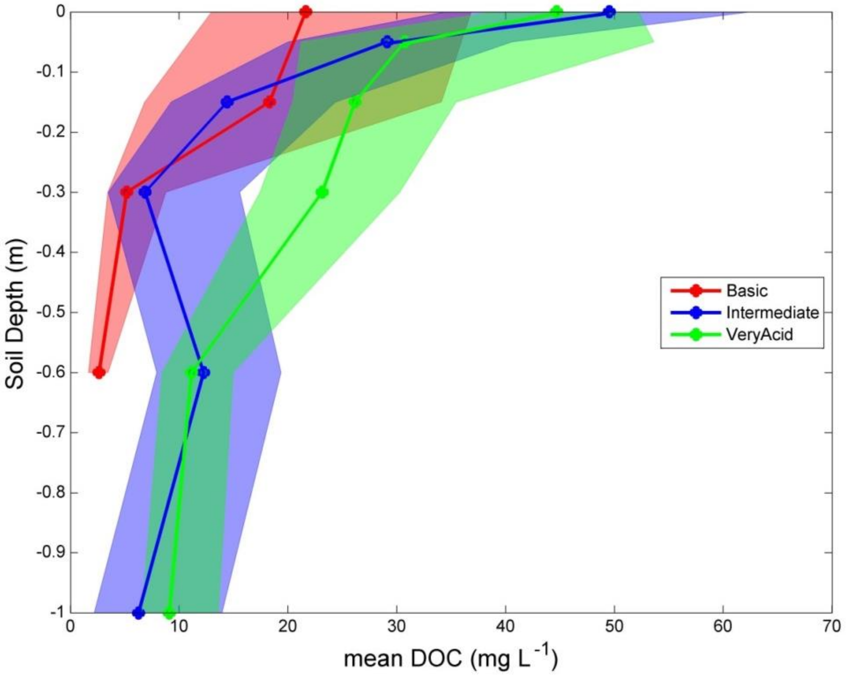
a)



b)


0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
Soil Depth (m)
0
10
20
30
40
50
60
70
mean DOC (mg L $^{-1}$)
Broadleaved
Coniferous

c)


0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
Soil Depth (m)
0
10
20
30
40
50
60
70
mean DOC (mg L $^{-1}$)
Basic
Intermediate
VeryAcid

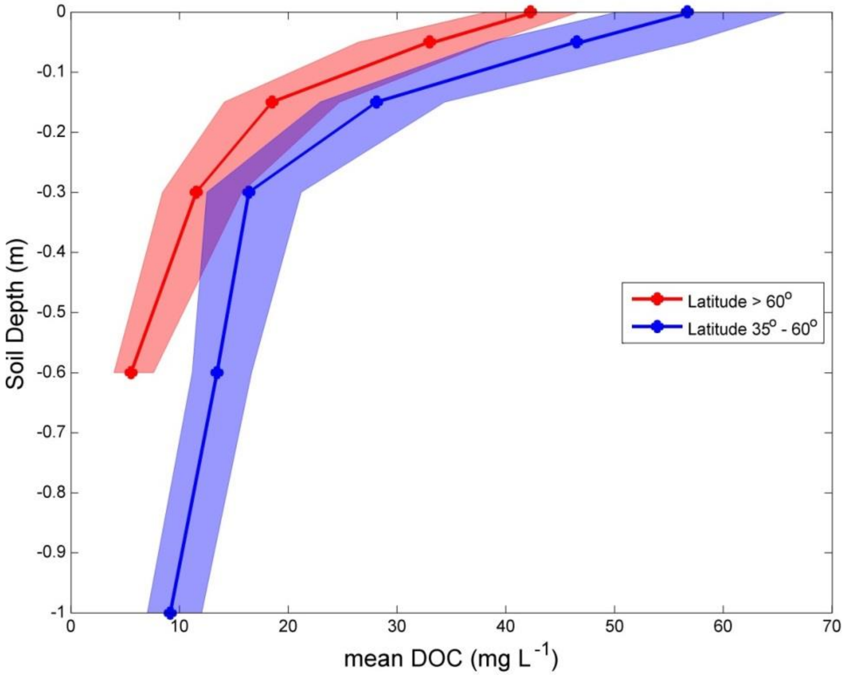


Figure S3. DOC profiles only for coniferous forests split by latitude classification with Boreal (>60°) and Temperate (35°-60). Solid lines represent the bootstrapped line and shaded areas the bootstrapped 95% confidence interval. Points are placed in the mid-point of the depth interval. Sites on Histosols are not present.

Chapter 2 Appendix S1. List of ICP Forests Level II plots used for the trend analysis

Table S1. List of ICP Forests Level II plots used for the trend analysis and their dominant forest species and resulting trend calculated using the Seasonal Mann-Kendall test (NS; non-significant, P: positive, N: negative). Rows in green correspond to the plots where at least one time series has been used for the individual trend analysis after filtering out the breakpoints. Rows in red correspond to the plots with measurements of DOC in soil solution that have not been used for the individual trend analysis because there was not enough data (Lack data) or breakpoints were detected (BP). Collector type are tension lysimeters (TL) or zero-tension lysimeters (ZTL).

Country	Code country	Code plot	Start year	End year	Collector type	Tree species	Trend	Dilution effect
France	1	6	1998	2011	TL	*Quercus robur*	NS	
France	1	17	1998	2011	TL	*Quercus petraea*	NS	
France	1	30	1998	2011	TL	*Quercus petraea*	N	
France	1	37	1998	2011	TL	*Picea abies*	NS	
France	1	41	1998	2011	TL	*Picea abies*	N	
France	1	46	1998	2011	TL	*Picea abies*	NS/N	
France	1	57	1998	2011	ZTL	*Fagus sylvatica*	P/NS	
France	1	63	1998	2011	TL	*Fagus sylvatica*	NS/N	
France	1	84	1998	2011	TL	*Pinus sylvestris*	N	
France	1	90	1998	2011	TL	*Abies alba*	NS/P	depth= -0.2, coll=1
France	1	93	1998	2011	TL	*Abies alba*	NS	
France	1	96	1998	2011	TL	*Abies alba*	P/NS	
France	1	98	1998	2011	TL	*Abies alba*	NS	
France	1	100	1998	2011	TL	*Abies alba*	NS	
Belgium	2	1	2000	2005		*Picea abies*	Lack data	
Belgium	2	8				*Quercus petraea*	Lack data	

Belgium	2	11	1999	2011	ZTL/TL	*Fagus sylvatica*	P	
Belgium	2	14	1999	2011	ZTL/TL	*Pinus nigra*	NS/P	
Belgium	2	15	1999	2011	ZTL/TL	*Pinus sylvestris*	NS/P	
Belgium	2	16	1999	2011	ZTL/TL	*Quercus robur*	NS	
Belgium	2	21	1999	2011	ZTL/TL	*Fagus sylvatica*	P	
Germany	4	101	1996	2011	TL	*Fagus sylvatica*	NS/N	
Germany	4	301	1997	2011	TL	*Fagus sylvatica*	NS	
Germany	4	302	1997	2011		*Picea abies*	BP	
Germany	4	303	1998	2011	TL	*Picea abies*	N	
Germany	4	304	1998	2011	TL	*Fagus sylvatica*	N	
Germany	4	305	1998	2011		*Picea abies*	BP	
Germany	4	306	1996	2011	TL	*Fagus sylvatica*	P	
Germany	4	307	1996	2011	TL	*Pinus sylvestris*	NS/P	depth=-2.5, coll=3
Germany	4	308	1993	2011	TL	*Quercus robur*	N	
Germany	4	502	1998	2011	TL	*Quercus robur*	N/NS	
Germany	4	503	1997	2011		*Fagus sylvatica*	BP	
Germany	4	506	1997	2011	TL	*Picea abies*	NS	
Germany	4	603	1998	2005		*Fagus sylvatica*	Lack data	
Germany	4	604	1998	2001		*Fagus sylvatica*	Lack data	
Germany	4	605	1998	2005		*Fagus sylvatica*	Lack data	
Germany	4	606	1996	2011	TL	*Fagus sylvatica*	NS	
Germany	4	607	1998	2010		*Fagus sylvatica*	Lack data	
Germany	4	701	1996	2011	TL	*Picea abies*	Weight_N	

Germany	4	702	1996	2011	TL	*Picea abies*		
Germany	4	703	1996	2011	TL	*Fagus sylvatica*	NS/P	
Germany	4	704	1996	2011	TL	*Fagus sylvatica*	Weight_P	
Germany	4	705	1996	2011	TL	*Quercus petraea*	N/Weight_N	
Germany	4	706	1996	2011	TL	*Quercus robur*	P/Weight_P	
Germany	4	707	1996	2011	TL	*Pinus sylvestris*	P	
Germany	4	802	1997	2011	TL	*Picea abies*	N	
Germany	4	806	1997	2011	TL	*Picea abies*	P	
Germany	4	808	1997	2011	TL	*Picea abies*	N/NS	
Germany	4	809	1997	2010	TL	*Picea abies*	N/NS	
Germany	4	812	1997	2011	TL	*Picea abies*	P/N/Weight_N	
Germany	4	901	1996	2011	ZTL/TL	*Pinus sylvestris*	P/N	
Germany	4	902	1996	2011	ZTL/TL	*Picea abies*	NS	
Germany	4	903	1998	2011	ZTL/TL	*Fagus sylvatica*	P	
Germany	4	904	1996	2011	ZTL/TL	*Larix decidua*	NS	
Germany	4	905	1996	2011	ZTL/TL	*Pinus sylvestris*	P/NS	
Germany	4	906	1996	2011	ZTL/TL	*Picea abies*	NS/P	
Germany	4	907	1996	2006		*Fagus sylvatica*	Lack data/BP	
Germany	4	908	1996	2011	ZTL/TL	*Picea abies*	NS/N	
Germany	4	909	1996	2011	ZTL/TL	*Picea abies*	NS/Weight_P/P	depth=-1.2, coll=15
Germany	4	910	1996	2006		*Quercus robur*	Lack data/BP	
Germany	4	911	1996	2011	ZTL/TL	*Fagus sylvatica*	P/Weight_P	
Germany	4	912	1996	2006		*Pinus sylvestris*	Lack data/BP	

Germany	4	913	1996	2011	ZTL/TL	*Quercus petraea*	NS	
Germany	4	914	1996	2011	ZTL/TL	*Quercus petraea*	NS	
Germany	4	915	1996	2006		*Fagus sylvatica*	Lack data	
Germany	4	916	1996	2006		*Picea abies*	Lack data	
Germany	4	917	1996	2006		*Picea abies*	Lack data	
Germany	4	918	1996	2006		*Pinus sylvestris*	Lack data	
Germany	4	919	1996	2011	ZTL/TL	*Fagus sylvatica*	N/P/NS	
Germany	4	920	1998	2011	ZTL/TL	*Picea abies*	P	
Germany	4	921	1997	2011	ZTL/TL	*Quercus petraea*	P/Weight_P	
Germany	4	922	1997	2011	ZTL/TL	*Picea abies*	P/N	depth=-0.5, coll=6
Germany	4	1001	1998	2011	TL	*Quercus robur*	P/NS	
Germany	4	1201	2001	2007		*Pinus sylvestris*	Lack data	
Germany	4	1202	2001	2011	TL	*Pinus sylvestris*	NS	
Germany	4	1203	2000	2011		*Pinus sylvestris*	BP	
Germany	4	1204	2000	2011	TL	*Pinus sylvestris*	NS	
Germany	4	1205	2000	2011	TL	*Pinus sylvestris*	NS	
Germany	4	1206	2000	2007		*Pinus sylvestris*	Lack data	
Germany	4	1302	1998	2011	TL	*Fagus sylvatica*	N/P	
Germany	4	1303	1997	2011	TL	*Pinus sylvestris*	NS	
Germany	4	1401	1996	2012	TL	*Picea abies*	NS/P	
Germany	4	1402	1996	2012	TL	*Picea abies*	P	
Germany	4	1403	1996	2012	TL	*Picea abies*	NS/P	
Germany	4	1404	1996	2012	TL	*Picea abies*	NS/P	

Germany	4	1405	1996	2012	TL	*Pinus sylvestris*	NS
Germany	4	1406	1996	2011	TL	*Quercus petraea*	P
Germany	4	1501	1998	2011	TL	*Pinus sylvestris*	N/P
Germany	4	1502	1998	2011	TL	*Pinus sylvestris*	N
Germany	4	1605	2007	2011		*Picea abies*	Lack data
Germany	4	1606	2007	2011		*Fagus sylvatica*	Lack data
Germany	4	1607	2007	2011		*Pinus sylvestris*	Lack data
Germany	4	1608				*Quercus petraea*	Lack data
Germany	4	1609				*Abies alba*	Lack data
Italy	5	1	1999	2011	ZTL	*Fagus sylvatica*	N
Italy	5	9	1999	2011	ZTL	*Quercus cerris*	NS
UK	6	512	2004	2011		*Quercus robur*	Lack data
UK	6	517	2002	2010		*Quercus robur*	Lack data
UK	6	715	2002	2011	TL	*Pinus sylvestris*	NS
UK	6	716	2002	2009		*Pinus sylvestris*	Lack data
UK	6	919	2004	2011		*Picea sichensis*	Lack data
UK	6	920				*Picea sichensis*	Lack data
UK	6	922	1997	2011	TL	*Picea sichensis*	P
Ireland	7	1	1991	2000	ZTL/TL	*Picea sichensis*	P/NS
Ireland	7	10	1991	2011	ZTL and others/ TL	*Picea sichensis*	NS/P
Ireland	7	11	1991	2011	ZTL/TL	*Quercus petraea*	N/NS
Denmark	8	11	1996	2011	TL	*Picea abies*	NS
Denmark	8	34	1997	2011	TL	*Fagus sylvatica*	NS

Denmark	8	74	2002	2012	*Fagus sylvatica*	Lack data/BP
Denmark	8	85	2003	2011	*Quercus robur*	Lack data
Greece	9	3				Lack data
Greece	9	4				Lack data
Sweden	13	1301	1996	2006	*Pinus sylvestris*	Lack data
Sweden	13	1403	1996	2006	*Picea abies*	Lack data
Sweden	13	5201	1996	2006	*Pinus sylvestris*	Lack data
Sweden	13	5202	1996	2006	*Picea abies*	Lack data
Sweden	13	5401	1996	2006	*Picea abies*	Lack data
Sweden	13	5501	1996	2006	*Picea abies*	Lack data
Sweden	13	5502	1996	2006	*Pinus sylvestris*	Lack data
Sweden	13	5601	1996	2006	*Pinus sylvestris*	Lack data
Sweden	13	5602	1996	2006	*Picea abies*	Lack data
Sweden	13	5603	1996	2006	*Picea abies*	Lack data
Sweden	13	5701	1996	2006	*Pinus sylvestris*	Lack data
Sweden	13	5702	1996	2006	*Picea abies*	Lack data
Sweden	13	5703	1996	2006	*Picea abies*	Lack data
Sweden	13	5801	1996	2006	*Pinus sylvestris*	Lack data
Sweden	13	6001	1996	2006	*Fagus sylvatica*	Lack data
Sweden	13	6002	1996	2006	*Quercus robur*	Lack data
Sweden	13	6003	1996	2006	*Picea abies*	Lack data
Sweden	13	6102	1996	2006	*Fagus sylvatica*	Lack data
Sweden	13	6103	1996	2006	*Picea abies*	Lack data

Sweden	13	6301	2000	2006		*Fagus sylvatica*	Lack data
Sweden	13	6302	1996	2006		*Picea abies*	Lack data
Sweden	13	6401	1996	2006		*Pinus sylvestris*	Lack data
Sweden	13	6501	1996	2006		*Picea abies*	Lack data
Sweden	13	6503	1996	2006		*Pinus sylvestris*	Lack data
Sweden	13	6507	1996	2006		*Picea abies*	Lack data
Sweden	13	6601	1996	2006		*Picea abies*	Lack data
Sweden	13	6702	1996	2006		*Picea abies*	Lack data
Sweden	13	6703	1996	2006		*Picea abies*	Lack data
Sweden	13	6802	1996	2006		*Picea abies*	Lack data
Sweden	13	6803	1996	2006		*Pinus sylvestris*	Lack data
Sweden	13	6901	1996	2006		*Picea abies*	Lack data
Sweden	13	7402	1996	2006		*Pinus sylvestris*	Lack data
Sweden	13	7404	1996	2006		*Picea abies*	Lack data
Sweden	13	7501	1996	2006		*Pinus sylvestris*	Lack data
Sweden	13	7502	1996	2006		*Picea abies*	Lack data
Austria	14	9	1997	2010	TL	*Fagus sylvatica*	N
Austria	14	16	2001	2010	TL	*Picea abies*	NS
Finland	15	1	1998	2011		*Pinus sylvestris*	Lack data
Finland	15	3	1998	2011		*Picea abies*	Lack data
Finland	15	5	1997	2011		*Picea abies*	Lack data
Finland	15	6	1997	2011		*Pinus sylvestris*	Lack data
Finland	15	11	1997	2011	ZTL	*Picea abies*	NS

Finland	15	16	1998	2011		*Pinus sylvestris*	Lack data
Finland	15	17	1998	2011		*Picea abies*	Lack data
Finland	15	19	1999	2011		*Picea abies*	Lack data
Finland	15	20	1998	2011		*Pinus sylvestris*	Lack data
Finland	15	21	2000	2010		*Picea abies*	Lack data
Finland	15	23	1998	2010		*Picea abies*	Lack data
Switzerland	50	2	1999	2012	ZTL/TL	*Picea abies*	P
Switzerland	50	3	1999	2012	Mix collector	*Fagus sylvatica*	N/NS
Switzerland	50	4	1999	2011	ZTL/TL	*Pinus cembra*	NS/P
Switzerland	50	8	1999	2012	ZTL/TL	*Fagus sylvatica*	NS/P
Switzerland	50	12	1999	2012	ZTL/TL	*Quercus cerris*	NS
Switzerland	50	15	1999	2011	ZTL/TL	*Abies alba*	N
Switzerland	50	16	1999	2012	Mix collector	*Fagus sylvatica*	N/P
Norway	55	1	1996	2011	ZTL/TL	*Picea abies*	NS/N
Norway	55	9	1996	2011	TL	*Picea abies*	P/Weight_P
Norway	55	14	1996	2011	TL	*Picea abies*	N
Norway	55	18	1999	2010	TL	*Pinus sylvestris*	P
Norway	55	19	1998	2011	TL	*Picea abies*	N
Czech Republic	58	521	2006	2011		*Picea abies*	Lack data
Czech Republic	58	2015	2006	2011		*Fagus sylvatica*	Lack data
Czech Republic	58	2361	2006	2011		*Quercus fruticosa*	Lack data
Estonia	59	2	1999	2011	ZTL	*Pinus sylvestris*	NS/N
Estonia	59	3	1999	2011	ZTL	*Pinus sylvestris*	NS

Estonia	59	7	2002	2011	ZTL	*Pinus sylvestris*	NS	

Chapter 2 Appendix S2. Description of the statistical methods

1) Overall trend analysis at European scale

Linear mixed-effects models (LMM) were used to detect the temporal trends in soil solution DOC concentration at the European scale. For these models, the complete ICP Forests dataset was used. Because the dependent variable (DOC concentration) was usually not normally distributed, it was log-transformed to improve normality. Different models were built per depth and per collector type (tension or zero-tension lysimeters). For each model, the variable describing the temporal effect was the year, centered on the year 2000 (year-2000), which was considered as fixed effect. Also, month (1-12) was considered as fixed effect to account for seasonality. Two random factors describing the country ($ctry_{int}$) and plot ($plot_{int}$) effects and one random coefficient accounting for the between plot variation of the temporal effect ($plot_{slp}$) were considered in each LMM (Equation 1). The LMM were further adjusted by stratification of data according to forest type in order to investigate possible differences in DOC trends between broadleaved and coniferous forests. The models were built following Jonard et al. (2015).

$$logDOC = \left[a + month + ctry_{int}\,(0,\sigma_{ci}^2) + plot_{int}(0,\sigma_{pi}^2)\right] + \left[b + plot_{slp}(0,\sigma_{ps}^2)\ \right] \cdot (year - 2000) + \varepsilon(0,\sigma^2) \qquad (1)$$

where σ_{ci}^2, σ_{pi}^2, σ_{ps}^2 and σ^2 are the variances of the random factors ‘country’ and ‘plot’, of the random coefficient ‘plot’ and of the residual term (ε), respectively.

2) Trend analysis of individual time series

Temporal changes in terrestrial ecosystems can either be monotonic (continuous) changes, or discontinuous with abrupt changes resulting in break points (de Jong et al., 2013). Monotonicity of time series is generally assumed when analyzing DOC data for temporal trends (Filella and Rodriguez-Murillo, 2014). However, it is rarely statistically tested and, thus, potential abrupt changes in the time series may be overlooked. This issue becomes important in temporal trend analysis since a breakpoint may cause changes in the direction of the trend and could lead us, for example, to classify a time series as constant, when in reality we may have averaged out separate periods with significant changes (de Jong et al., 2013). On the contrary, breakpoints may erroneously induce the detection of a significant trend in long-term time series due to artifacts.

For these reasons, we focused on the investigation of the potential long-term trends in soil solution DOC at European forests that show monotonicity. Therefore, DOC time series were first analyzed using the Breaks For Additive Seasonal and Trend (BFAST) algorithm to detect the presence of breakpoints (Verbesselt et al., 2010). When a breakpoint was detected in a time series, there were two possibilities: first, one of the segments (before or after the detected breakpoint) was longer than 9 years, and, in this case, only the longest segment was used for the subsequent analysis of monotonic trends; second, the breakpoint split the time series in two segments shorter than 9 years and the time series was not used for the analysis of monotonic trends. We used a length threshold of 9 years, which is the minimum time series length recommended for long-term trend analysis (Libiseller and Grimvall, 2002; Waldner et al., 2014). In total, 258 time series from 97 plots were selected for analysis of monotonic trends. No clear pattern could be observed in the distribution of time series of DOC with breakpoints, which appeared to occur randomly across the study plots (Figure 4 and 5).

Monotonic trend analyses were carried out using the Seasonal Mann Kendall (SMK) test for monthly DOC concentrations (Hirsch et al., 1982; Marchetto et al., 2013). Partial Mann Kendall (PMK) test was also used since it allows to test the influence of a co-variable. We selected monthly precipitation as a co-variable to test if the trend detection might be due to a DOC dilution/concentration effect (Libiseller and Grimvall, 2002). For the SMK and PMK tests, the trend slopes were estimated following Sen (1968), as the median of all the slopes determined by all pairs of sample points. The SMK and PMK account for seasonality of the time series by computing the test on each of the seasons (in our case months) separately. The resulting slopes were also tested against the slopes calculated by BFAST. Finally, the individual slopes calculated according to Sen (1968) for each time series using the SMK or PMK method were standardized by dividing them by the median DOC concentration over the sampling period to avoid the influence of the magnitude of DOC concentration in the between-site comparison.

For this study, five depth intervals were considered: the organic layer (0 cm), topsoil (0-20 cm), intermediate (20-40 cm), subsoil (40-80 cm) and deep subsoil (> 80 cm). The slopes of each time series were then aggregated to a unique plot-soil depth slope and classified by the direction of the trend as significantly positive (P, $p < 0.05$), significantly negative (N, $p < 0.05$) and not significant (NS, $p \geq 0.05$). When there was more than one collector per depth class, the median of the slopes was used when the direction of the trend (P, N or NS) was similar. When the different trends at the same plot-soil depth combination were either P and NS, or N and NS, it was marked as "Weighted positive" and "Weighted negative". The five plot-soil depth combinations for which the calculated slopes showed opposite trend directions were discarded. All aggregated trend slopes came from time series measured using the same collector type.

Trends for soil solution parameters (NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{-2}, total dissolved Al, total dissolved Fe, pH, electrical conductivity), precipitation and temperature were calculated using the same methodology as for DOC: individual time series were analyzed using the SMK test and the relative slopes were calculated and aggregated to plot-soil depth combinations.

Finally, we performed multivariate statistical analyses to investigate the main factors explaining differences in DOC trends among the selected plots. Firstly, we used General Discriminant Analysis (GDA) (Raamsdonk et al., 2001) to determine the importance of soil solution and deposition variables in the separation of groups with different trend classes (P, N, NS) in DOC. We also accounted for the part of the variance due to the different soil layers (depth interval) as an independent categorical variable. Secondly, we applied Structural Equation Models (SEM) to test whether deposition variables had an effect (direct, indirect or total) on DOC trends through different pathways (Grace et al., 2010). For the SEMs, we assumed that there is no effect of soil depth on the DOC trends (see Appendix S3). We applied three SEM models: 1) for all the slopes in DOC, 2) only for the forests with low or medium total N deposition, and, 3) only for the forests with high total N deposition. For each case, we searched for the most parsimonious adequate model using the AIC and R^2. The significance level (*p* value) of the total, direct and indirect effects were calculated using the bootstrap (with 1200 repetitions) technique (Davison et al., 1986). Dependent variables were log-transformed to improve normality of the continuous variables and then standardized before performing the GDA and SEM. All the statistical analysis were performed in R software version 3.1.2 (R Core Team, 2014) using the "rkt" (Marchetto et al., 2013), "bfast01" (de Jong et al., 2013) and "sem" (Fox et al., 2013) packages, except from the GDA that was performed using Statistica 6.0 (StatSoft, Inc. Tule, Oklahoma, USA) and the LMMs that were performed using SAS 9.3 (SAS institute, Inc., Cary, NC, USA).

Chapter 2 Appendix S3. Depth-effect on the individual trends in soil solution DOC

Trends in soil solution from different soil depth intervals were mixed for the Pearson's chi-squared test performed for Figure 6 and the Structural Equation Models (SEM) (Figure 11), as the number of cases available for each depth will be insufficient to compute the statistics if we separate per soil depth interval. To check if the trends calculated at different depths were actually independent from the soil depth interval, we performed a Pearson's chi-squared test and found that the differences in trends among soil depth intervals were not statistically significant $\chi^2(8, N = 174) = 10.94$, $p = 0.21$) (Figure S1). Therefore, we assumed that there is no difference in trends among soil depth layers and performed the subsequent statistical analysis mixing the trends from different soil depths.

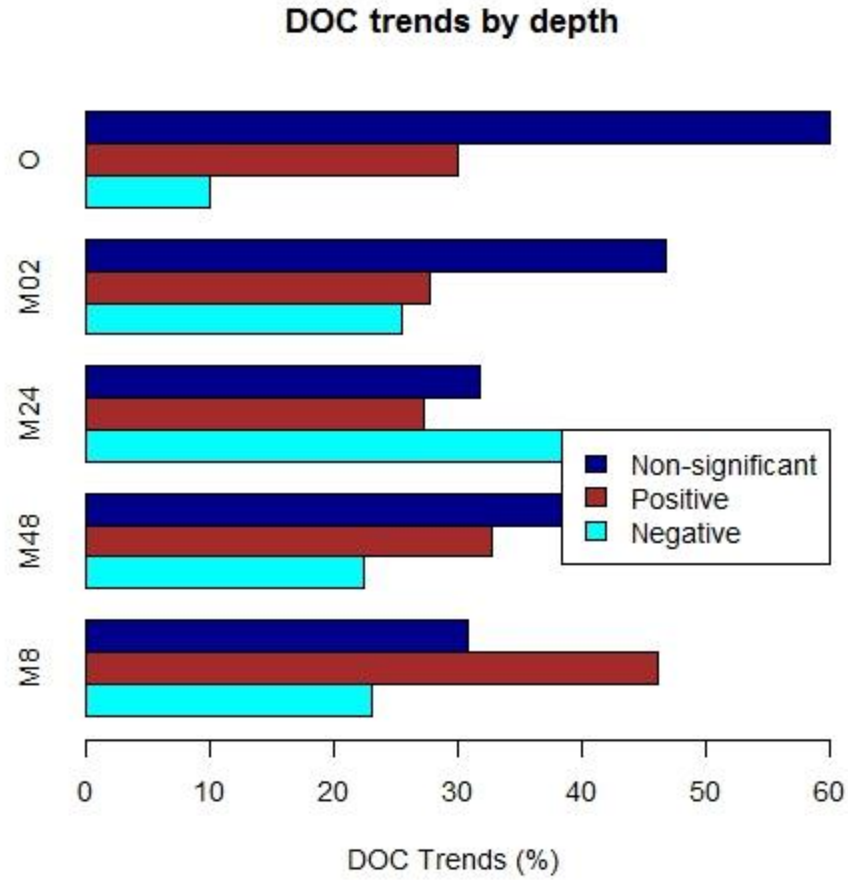


Figure S1. Percentage of non-significant, positive and negative trends per soil depth interval (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm).

However, a real difference in DOC trends between soil depths may be obscured by the fact that datasets differ between different depths (not all the sites count with DOC time series that could be analyzed for trends at all the soil depth intervals) and thus, we cannot rule out that there exist a difference in trends per soil depth. Although the number of sites with DOC trends analyzed at more than three soil depths (including organic layer) is not enough to apply the same statistics for this subset, we visually compared the 11 sites with this information available and found that, at first sight, it was confirmed that there is no a real difference in trends between soil depth interval (Figure S2).

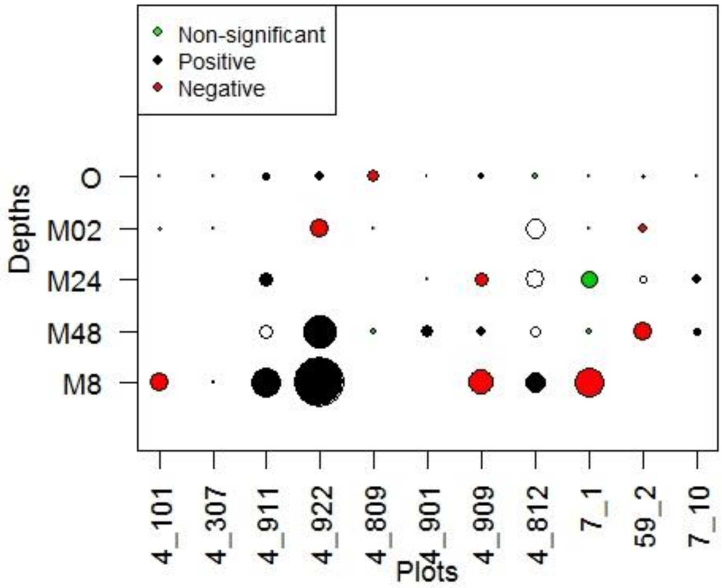


Figure S2. Direction of the trend (non-significant, positive and negative) per soil depth interval (O: organic layer, M02: mineral soil 0-20 cm, M24: mineral soil 20-40 cm, M48: mineral soil 40-80 cm, M8: mineral soil > 80 cm) for the 11 plots with DOC measured at least at 3 soil depth intervals including the organic layer. The size of the circle is proportional to the magnitude of the trend slope.

Chapter 2 Appendix S4. Structural equation model with trends in SO_4^{2-} and NO_3^- deposition

The same structural equation models (SEM) represented in Figure 11 were performed using the trends in SO_4^{2-} and NO_3^- deposition (% yr-1) instead of the mean values of SO_4^{2-} and NO_3^- throughfall deposition (kg ha^{-1} yr^{-1}) (Figure S3). The SEM for all the cases and for cases with low and medium N deposition are shown in Figure S3.

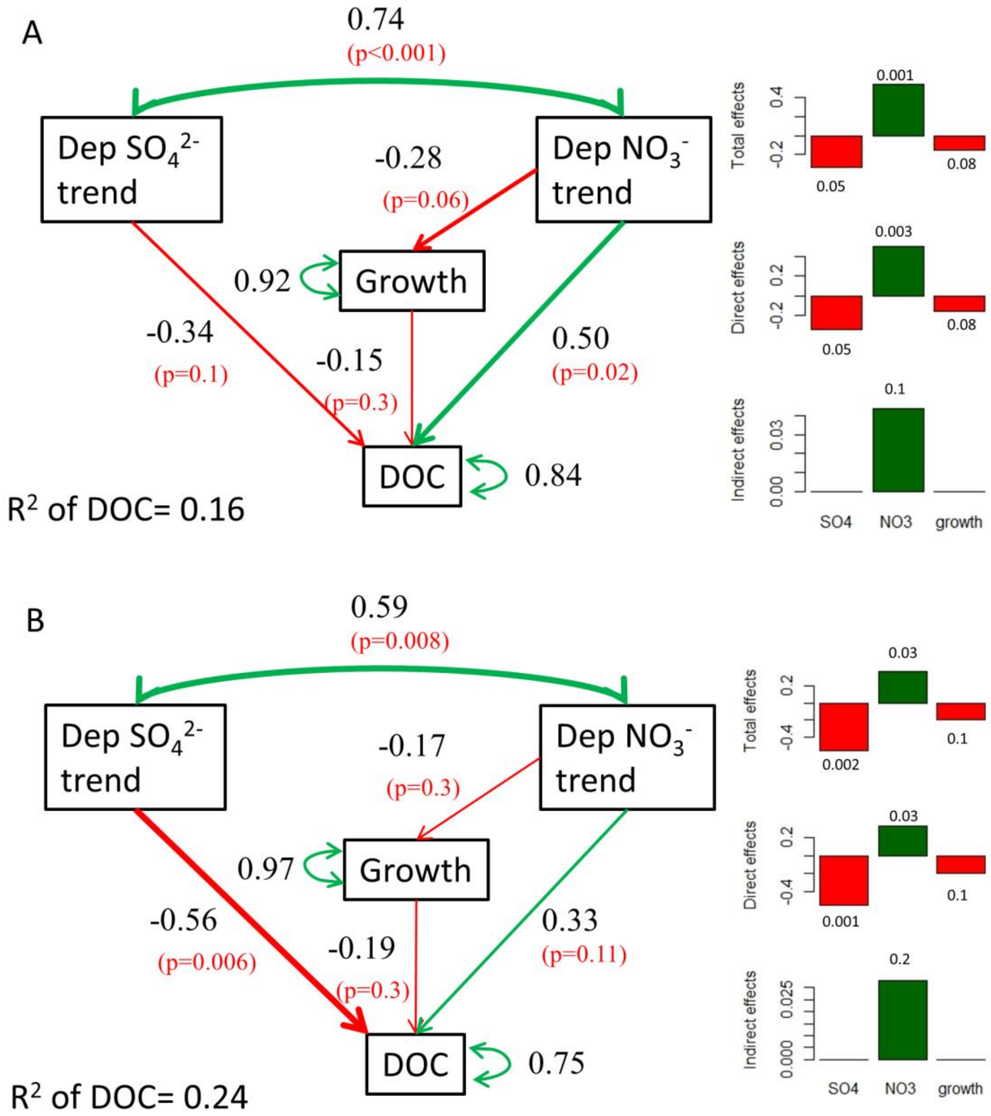


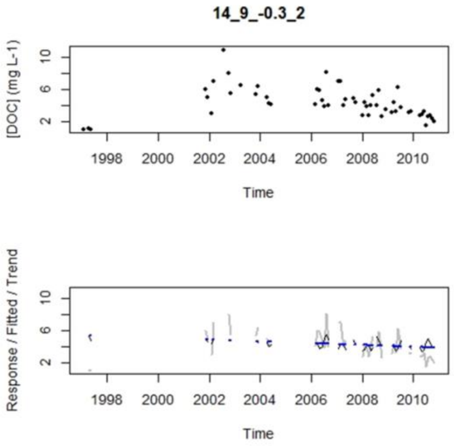
Figure S3. Diagram of the structural equation model (SEM) that better explain the maximum variance of the resulting trends of DOC concentrations in soil solution for: A) all the cases and B) cases with low or medium N deposition, with trends in SO_4^{2-} and NO_3^- deposition (% yr^{-1}) with direct effects and indirect effects through effects on mean annual stem volume increment (Growth) in m^3 ha^{-1} yr^{-1}). P-values of the significance of the corresponding effect between brackets. Green arrows indicate positive effects and red arrows indicate negative effects.

Chapter 2 Appendix S5. Raw time series showing temporal trends and breakpoints

The following figures show, for each individual collector, the raw DOC time series data (Outliers have been removed and DOC values below detection limit (<0.1), have been set to 0.1 and the observations have been aggregated to monthly data.) in the upper graph and the lower graph, the result from the BFAST analysis to detect abrupt changes in the time series and the trend line. Only the time series with a minimum of 60 data points are represented.

The title of each figure is the name of the collector as follows:

“Country code_Plot code_ Depth_collector ID”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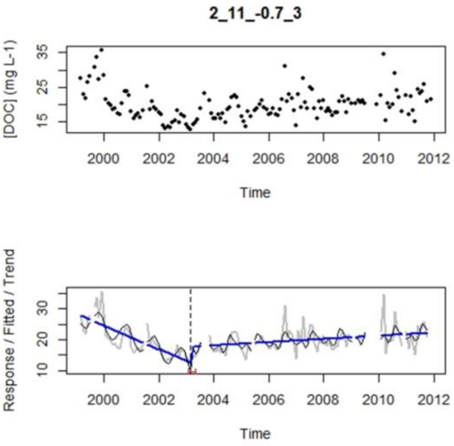
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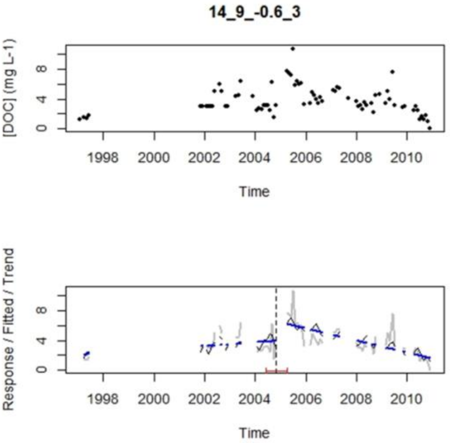
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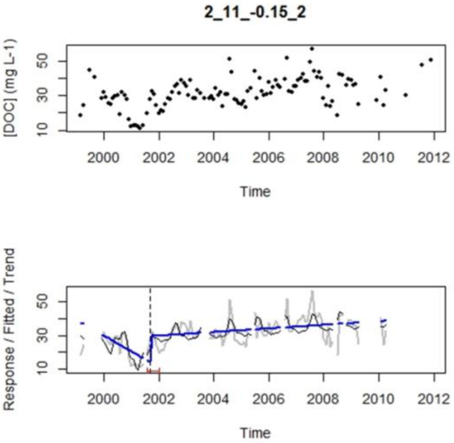
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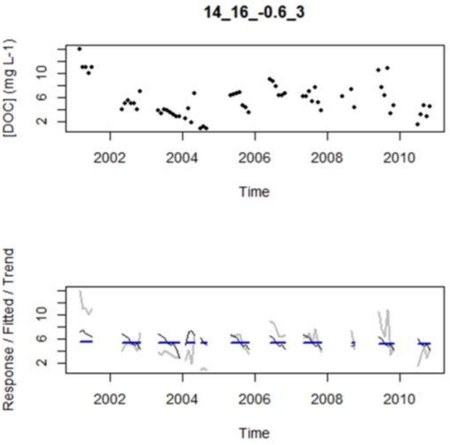
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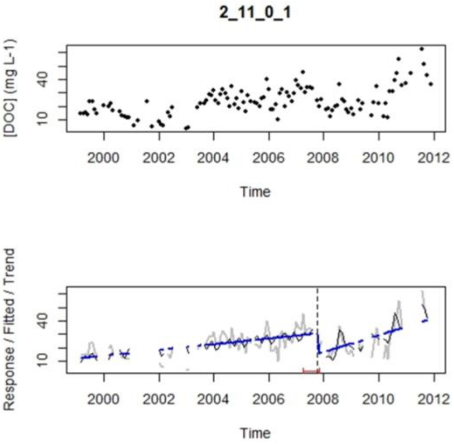
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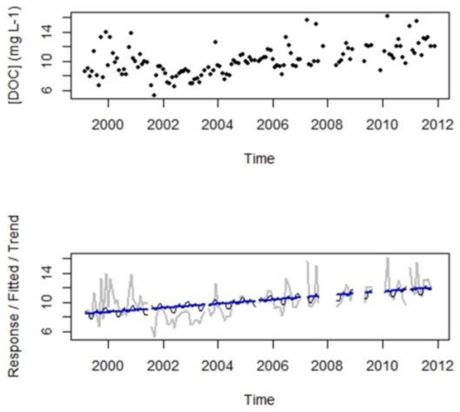
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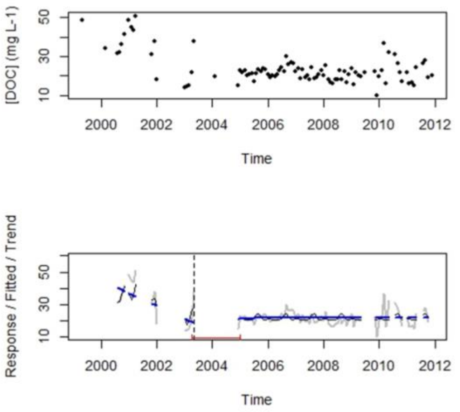
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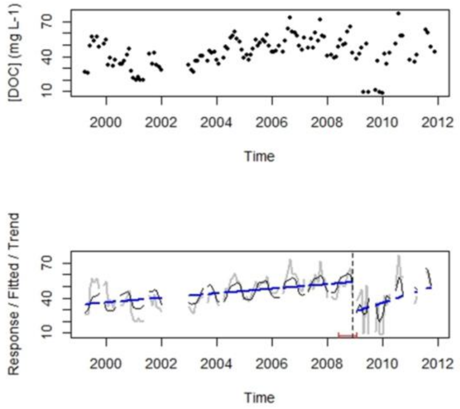
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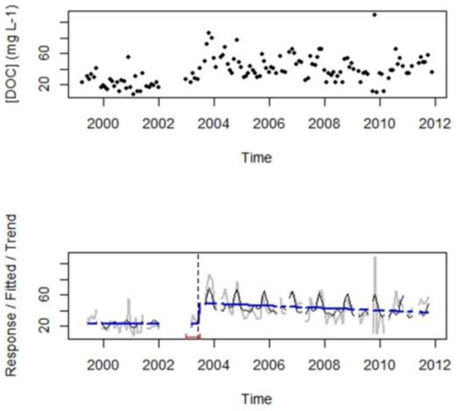
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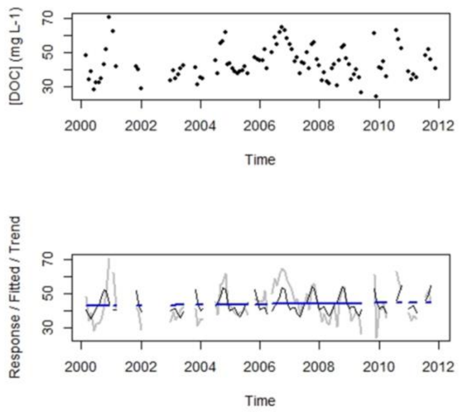
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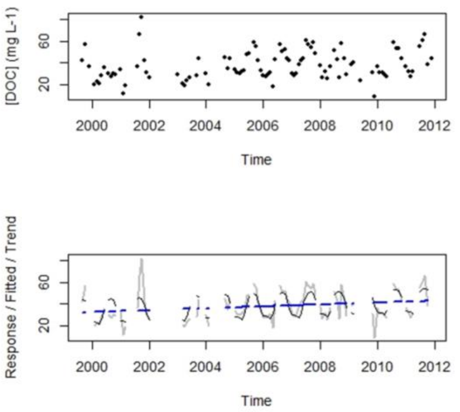
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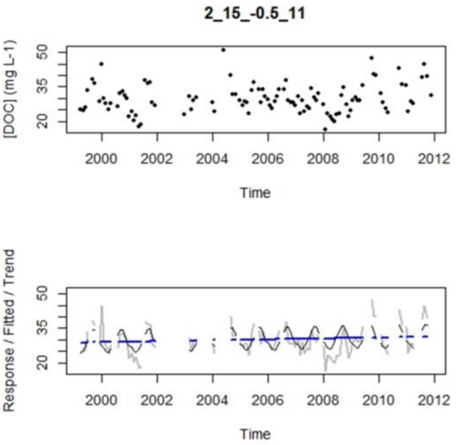
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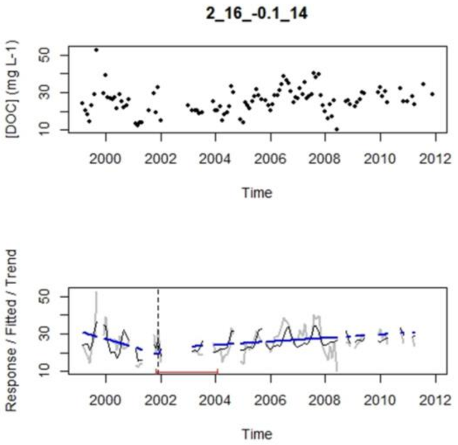
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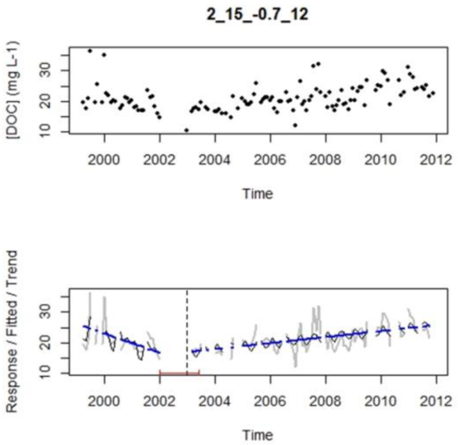
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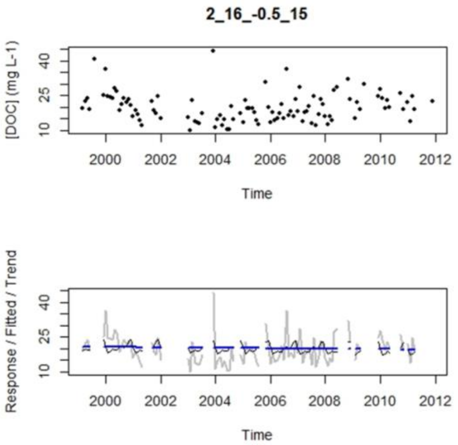
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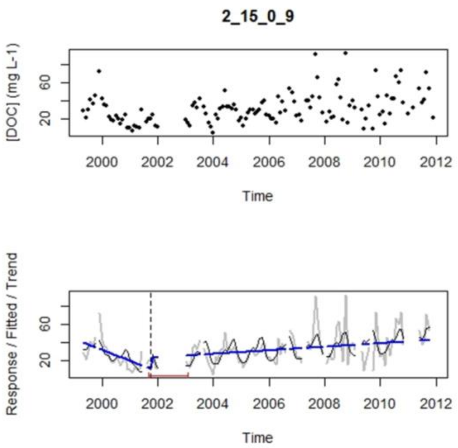
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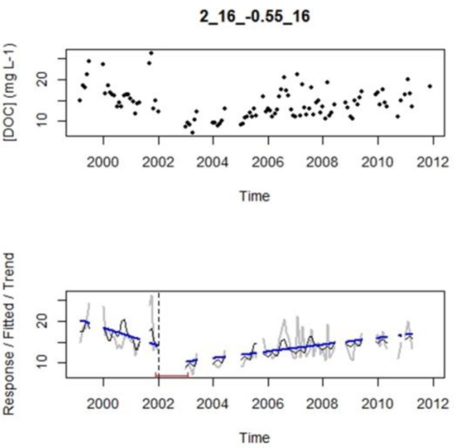
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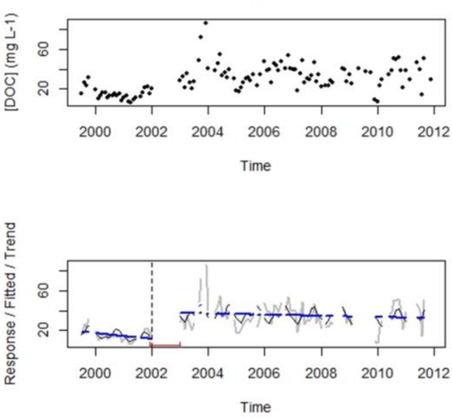

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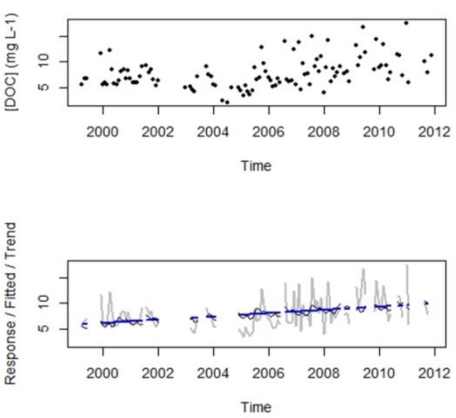

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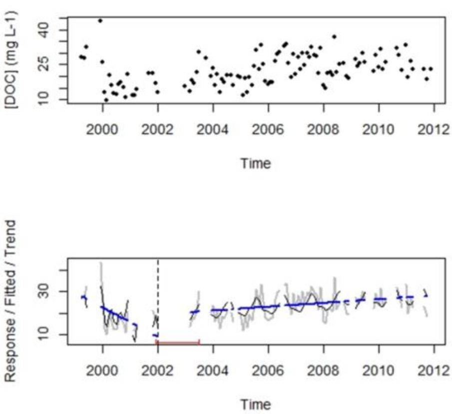

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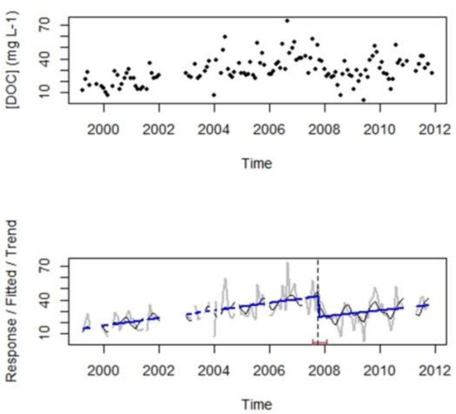

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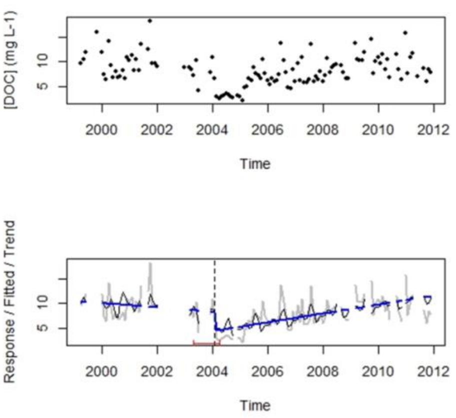

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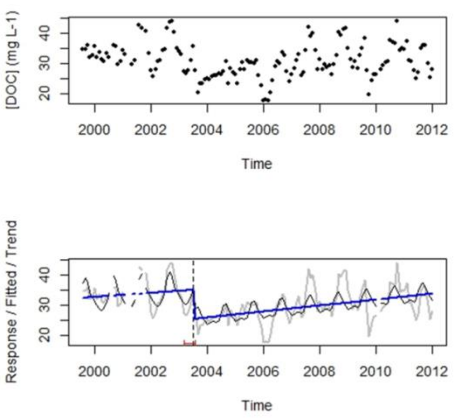

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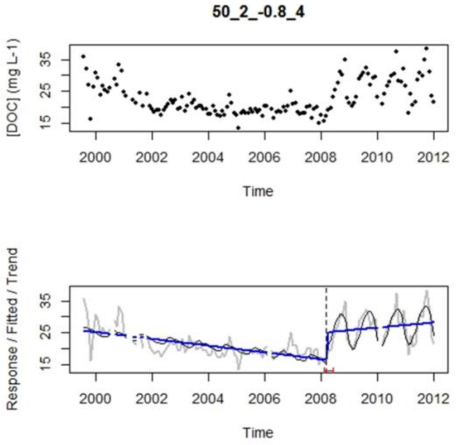
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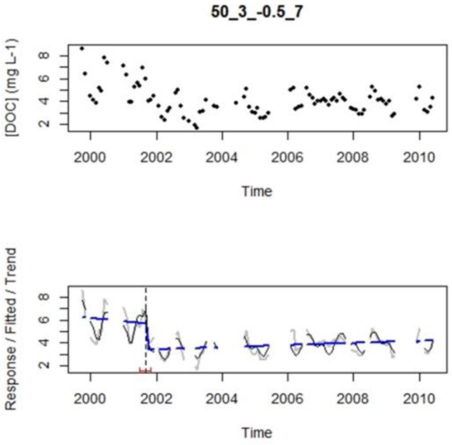
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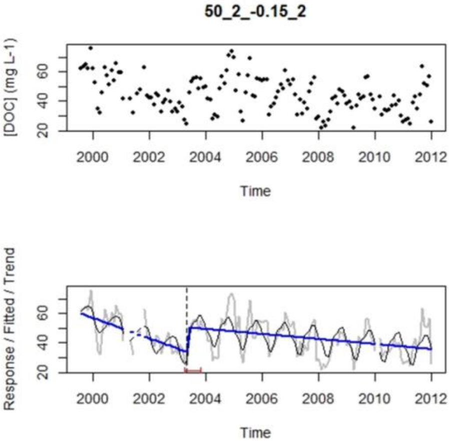
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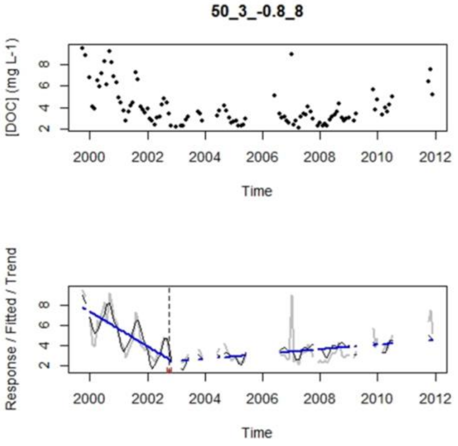
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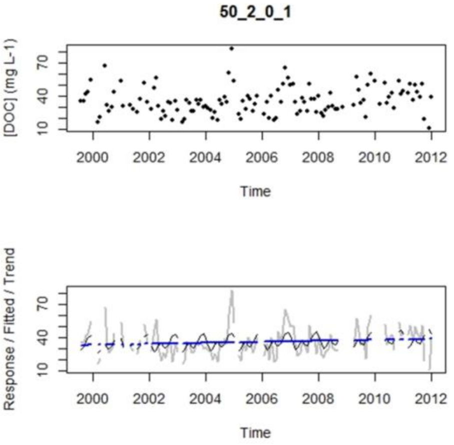
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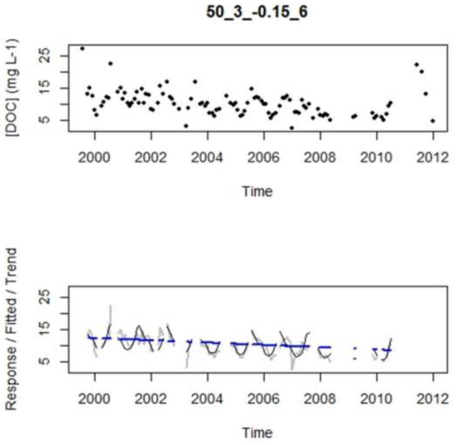
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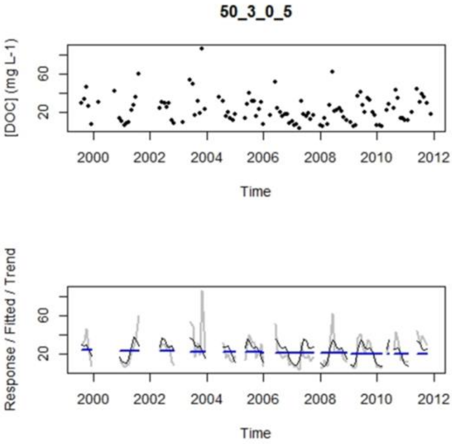
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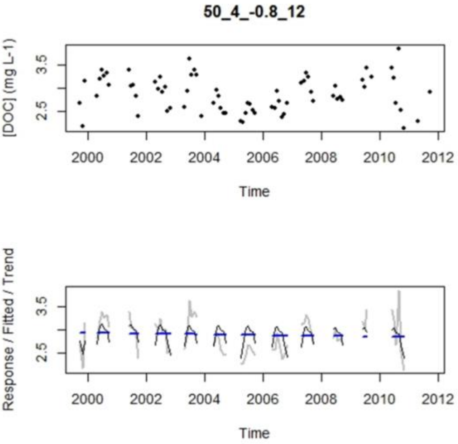
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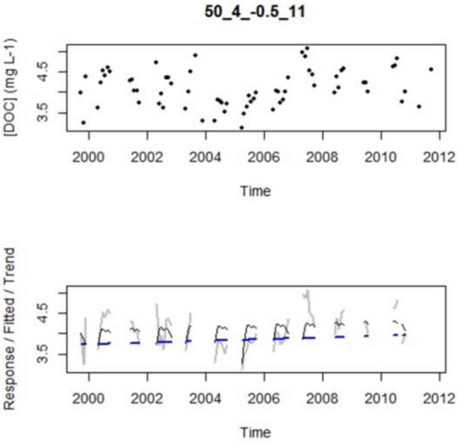
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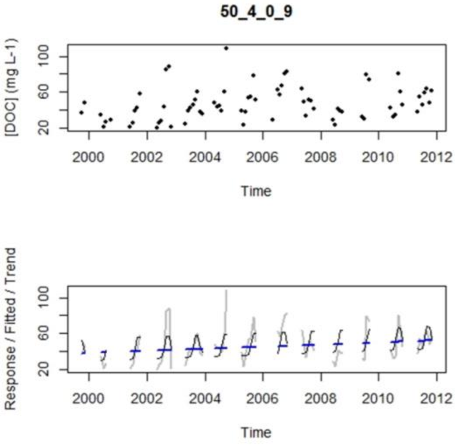
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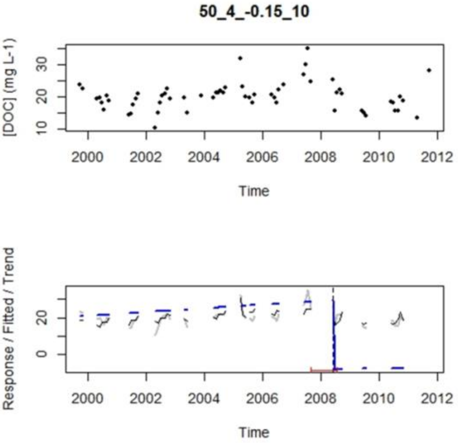
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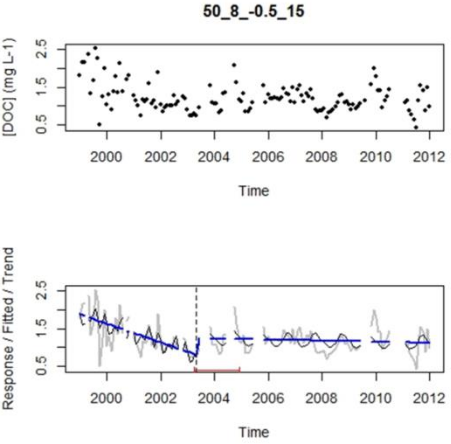
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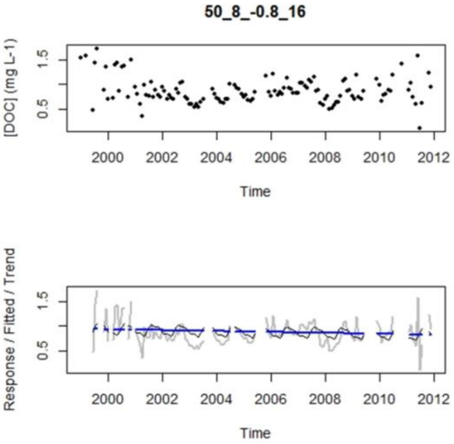
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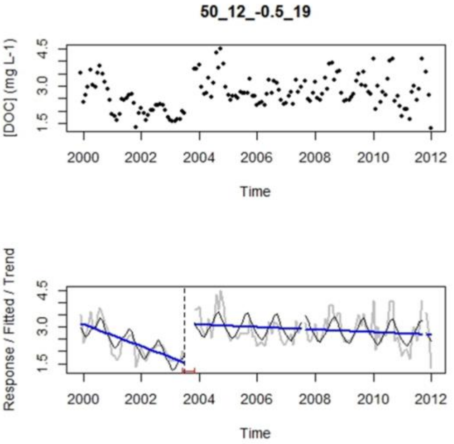
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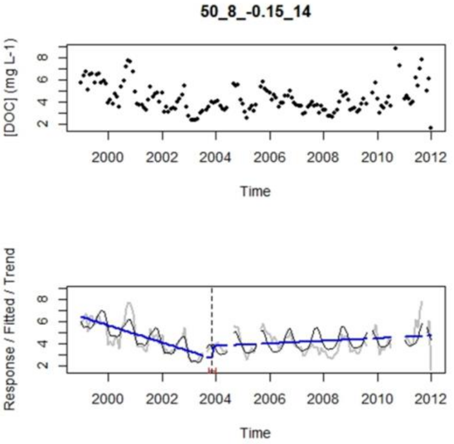
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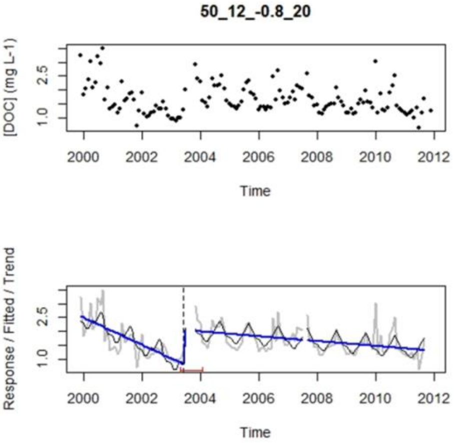
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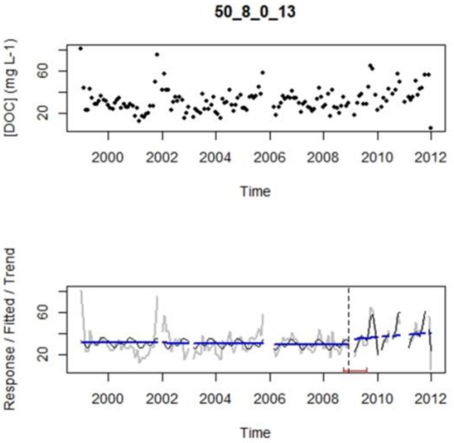
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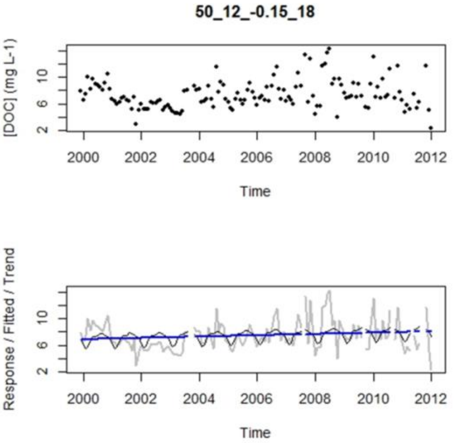
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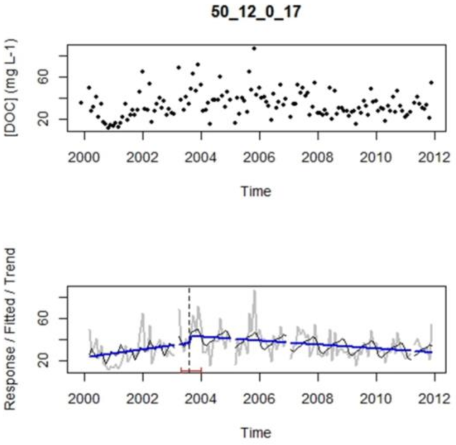
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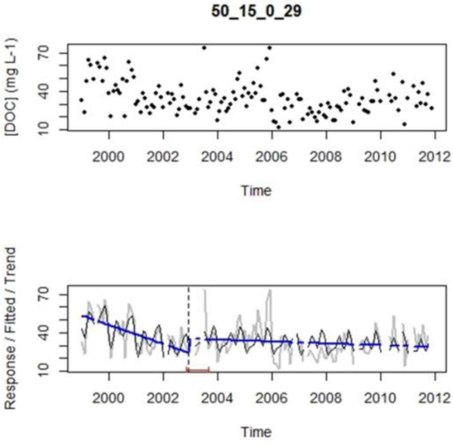
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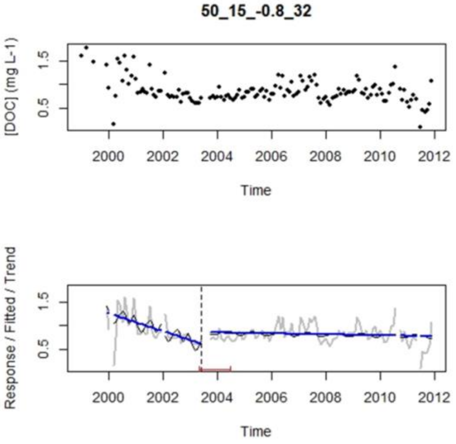
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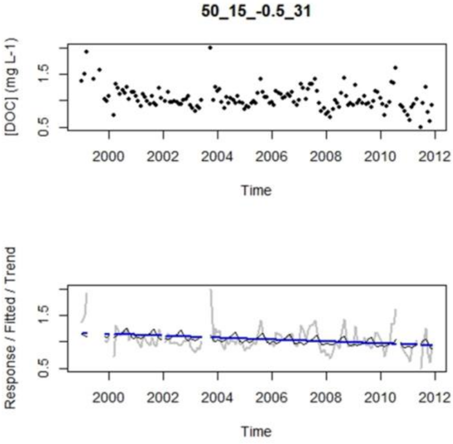
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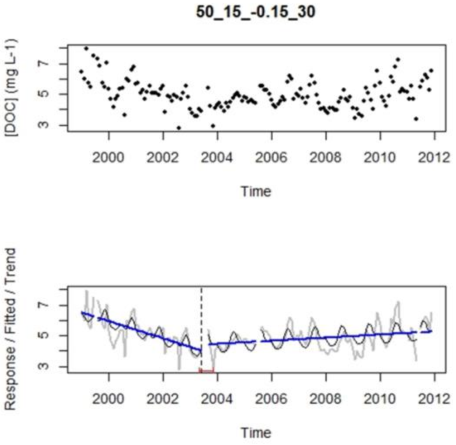
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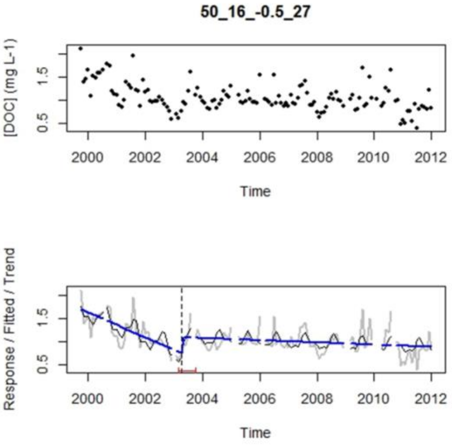
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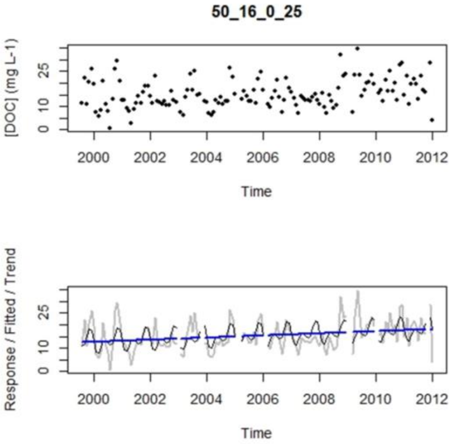
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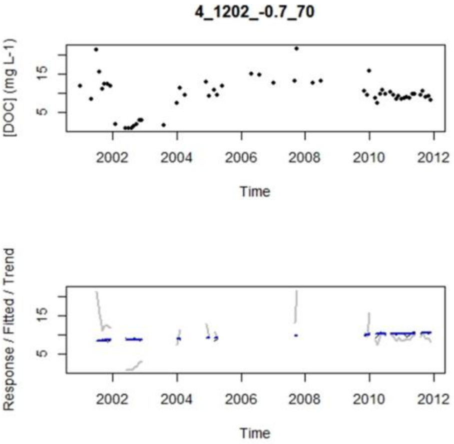
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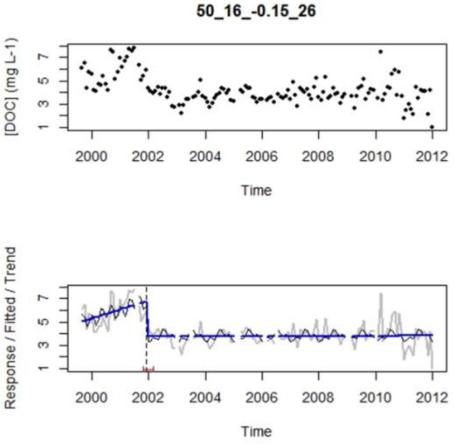
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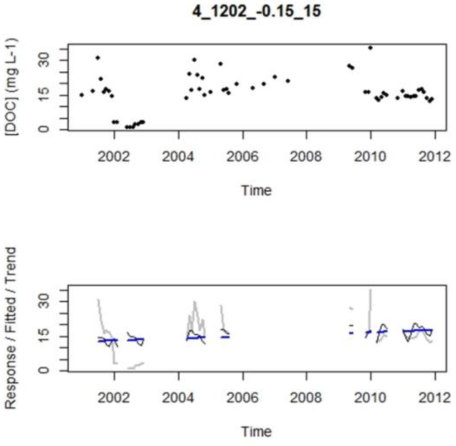
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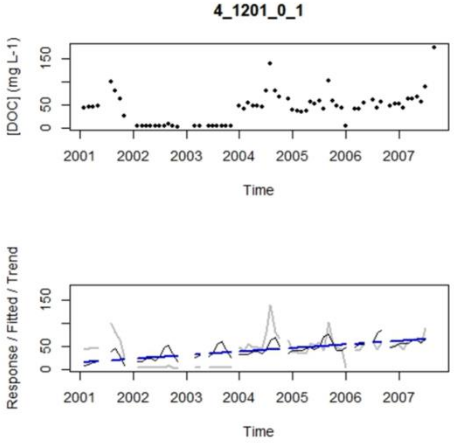
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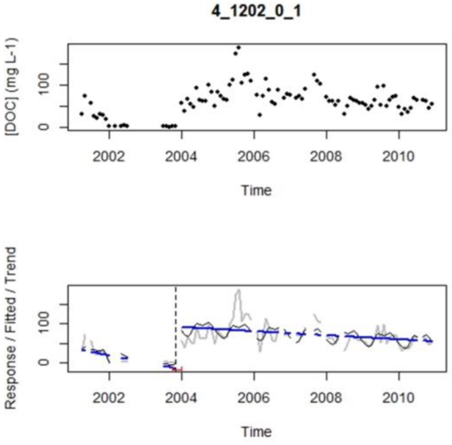
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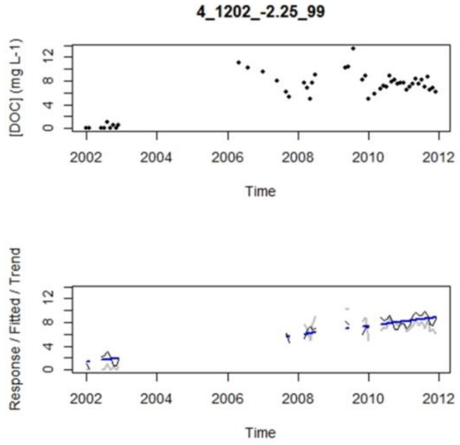
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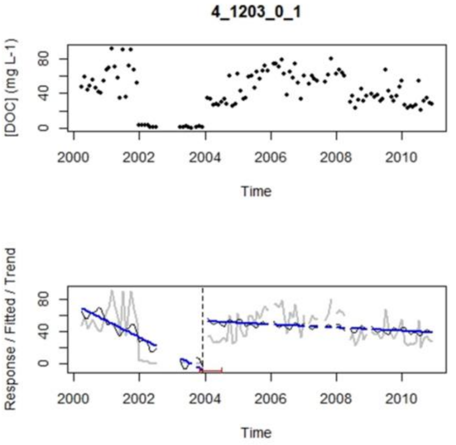
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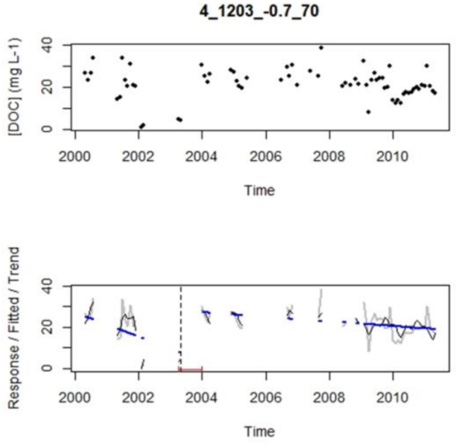
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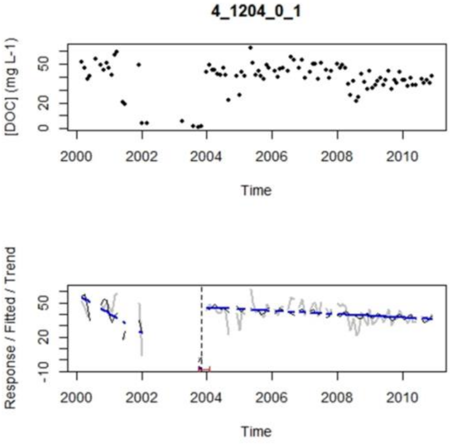
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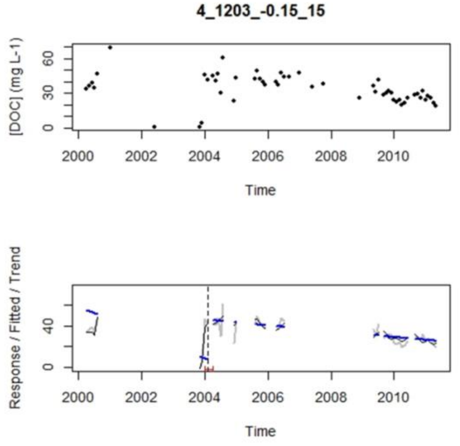
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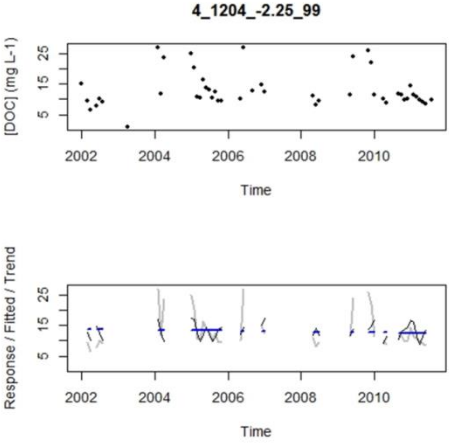
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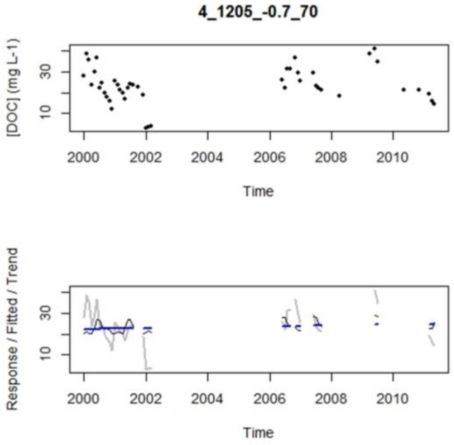
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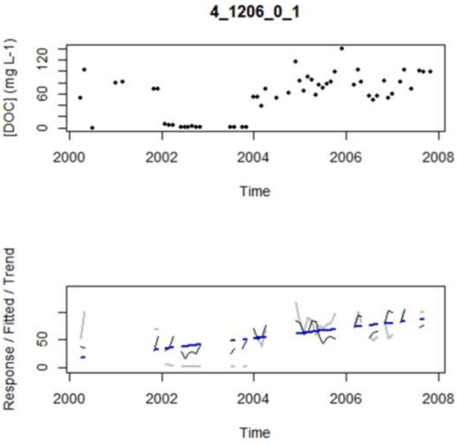
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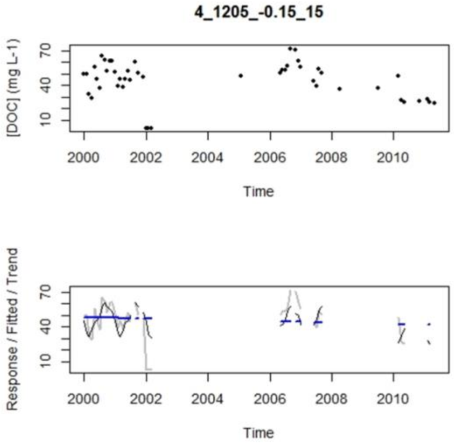
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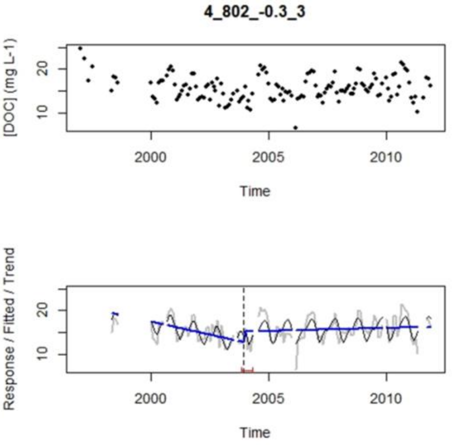
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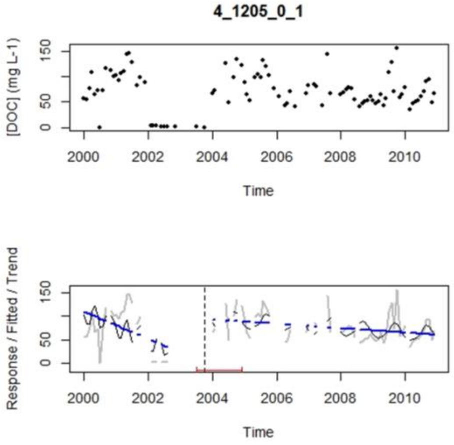
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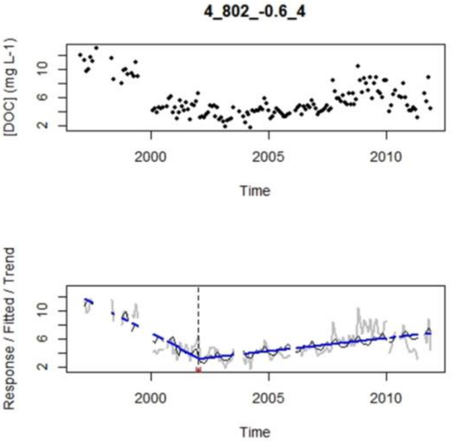
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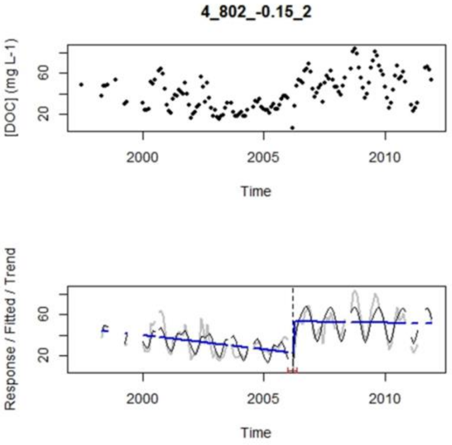
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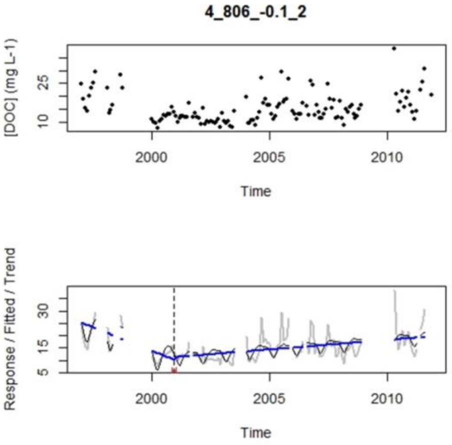
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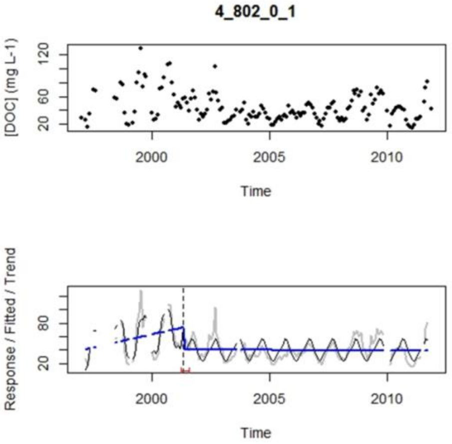
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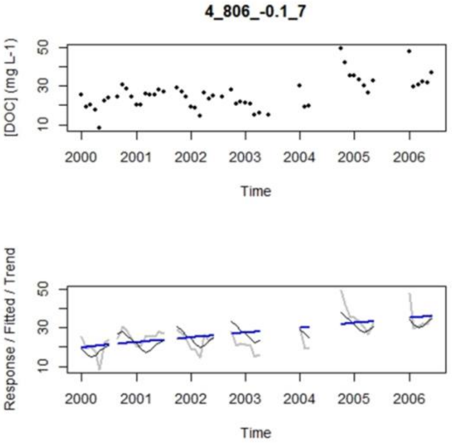
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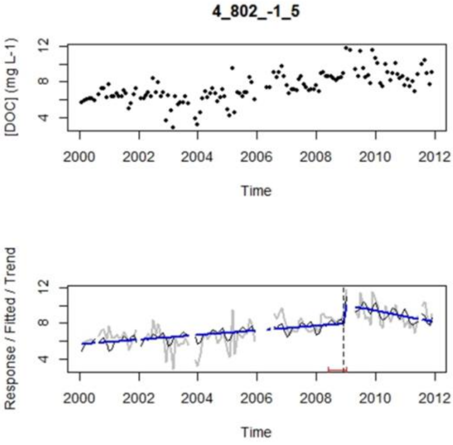
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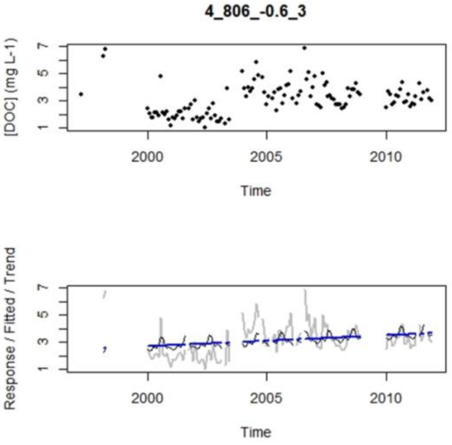
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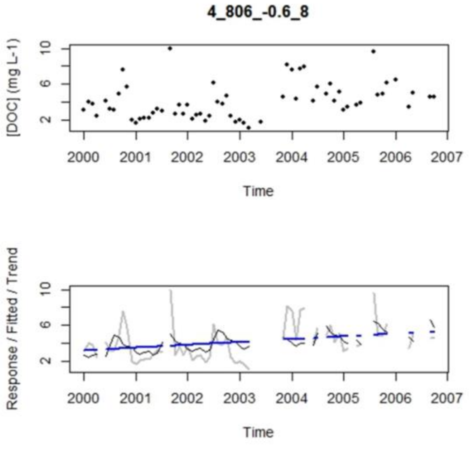
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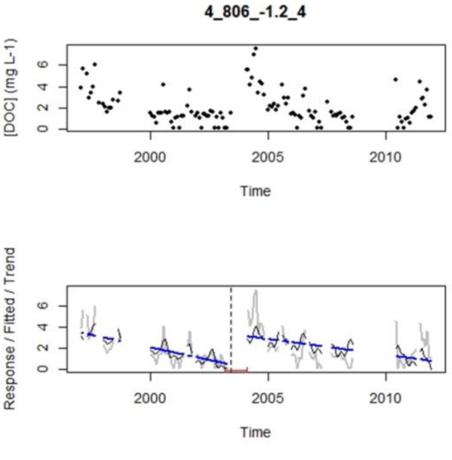
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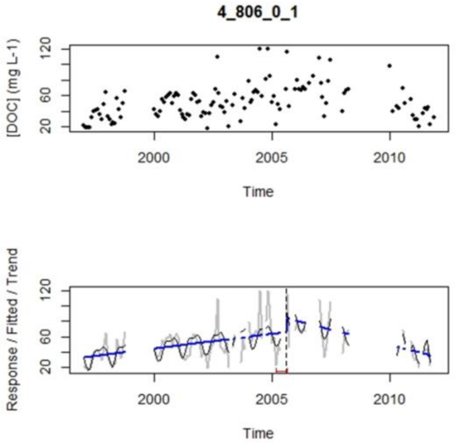
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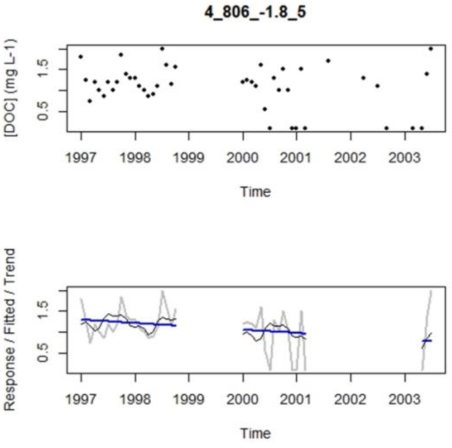
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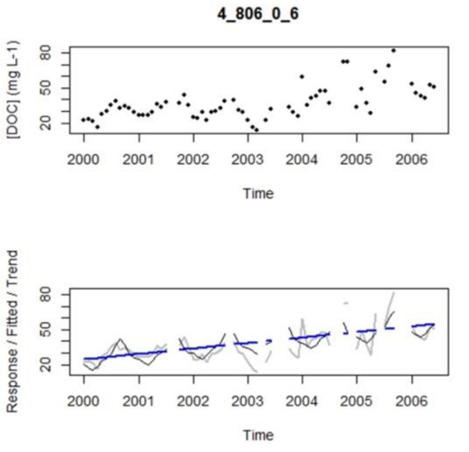
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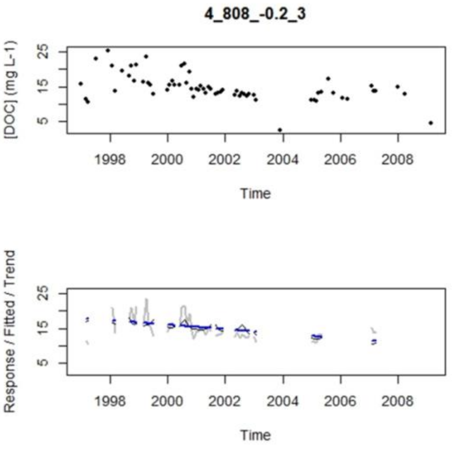
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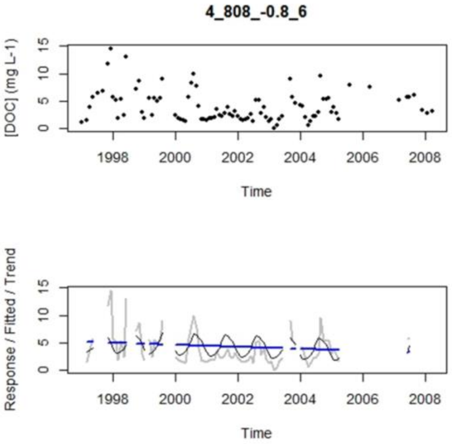
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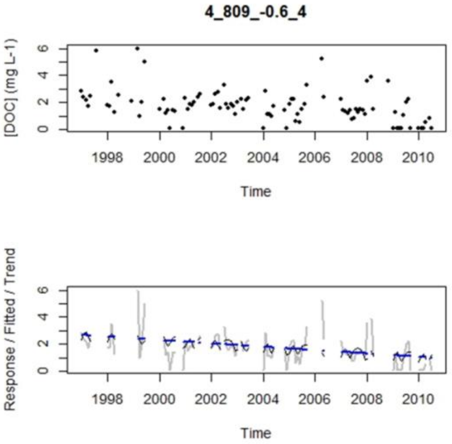
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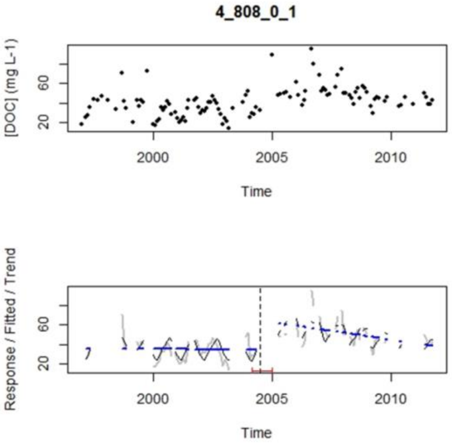
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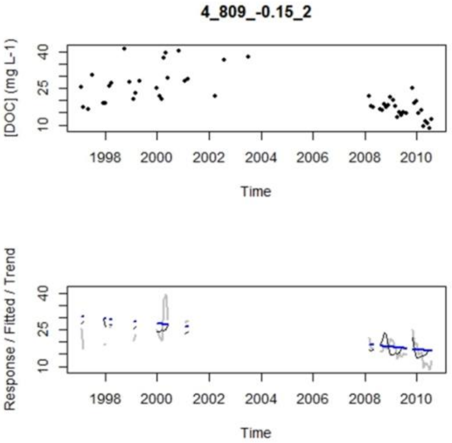
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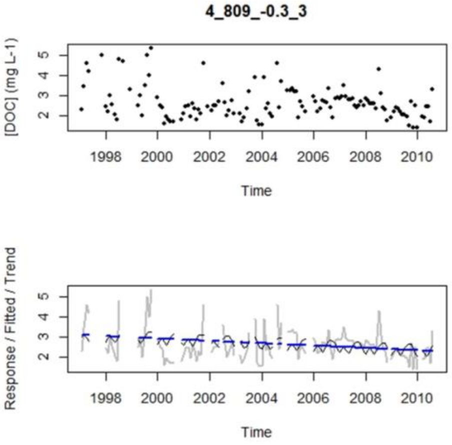
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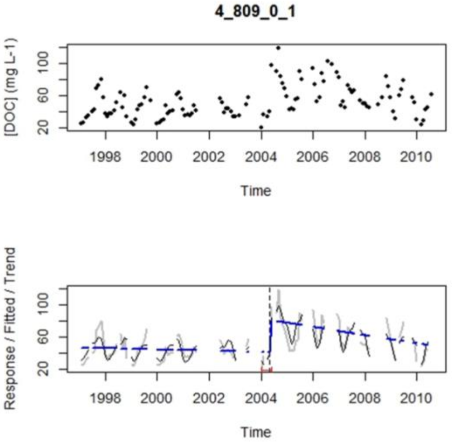
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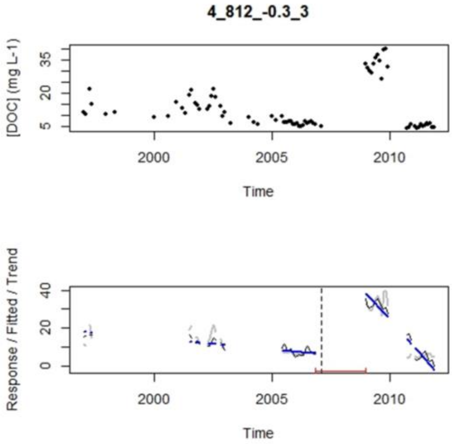
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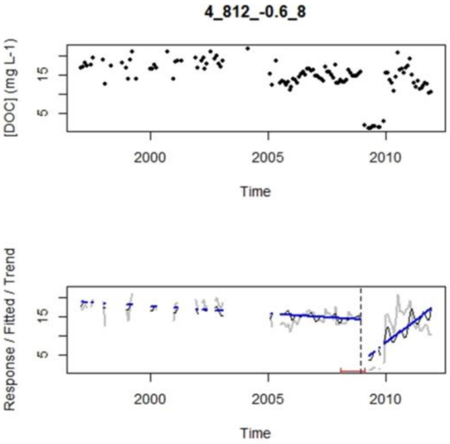
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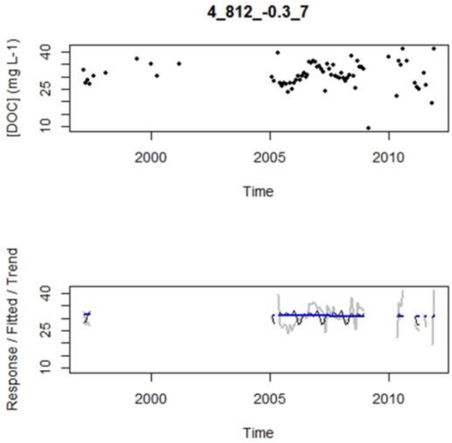
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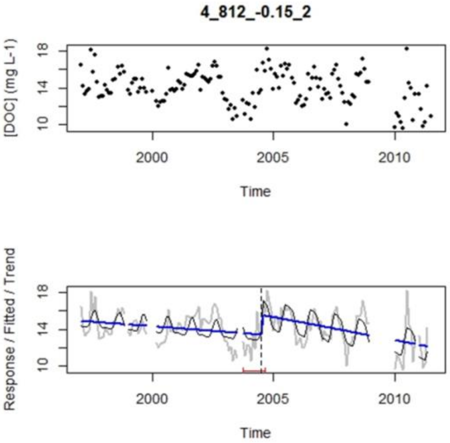
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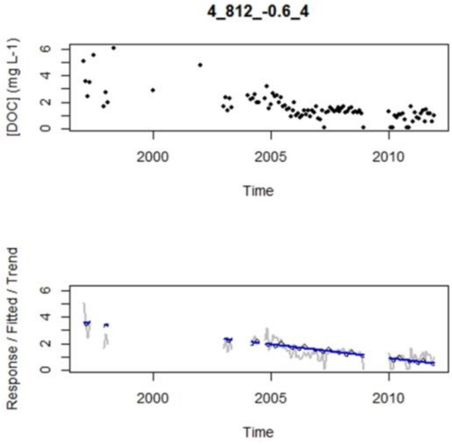
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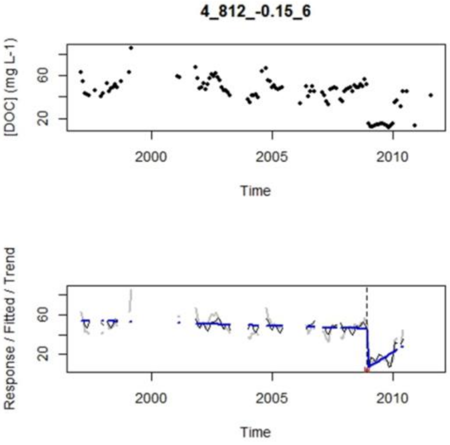
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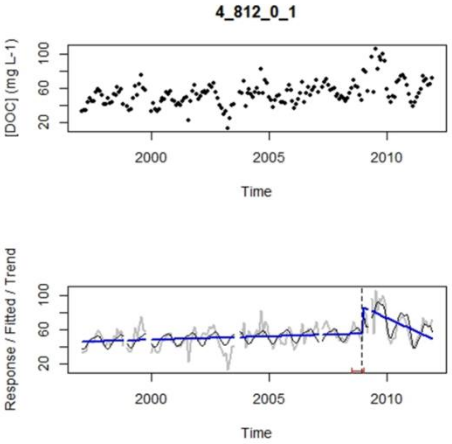
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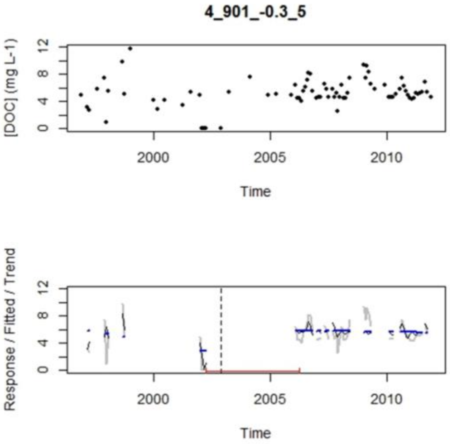
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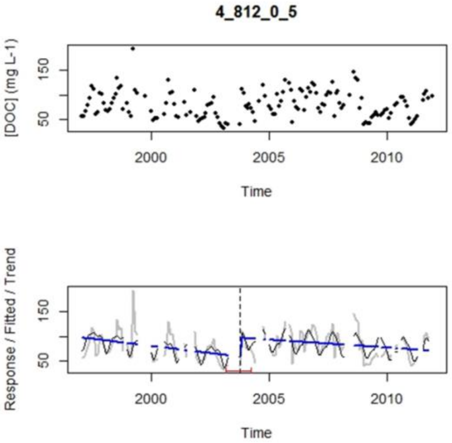
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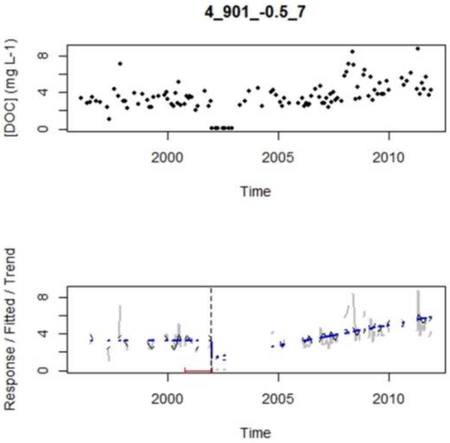
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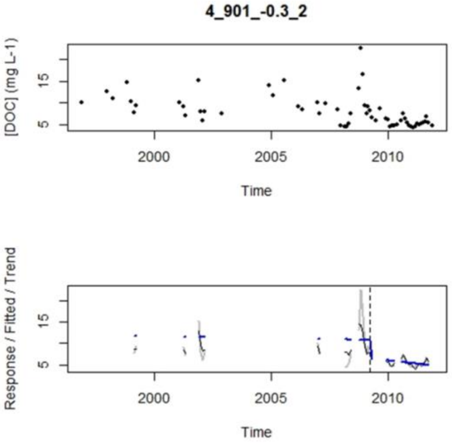
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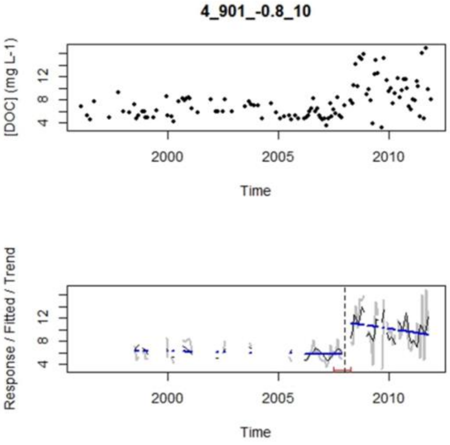
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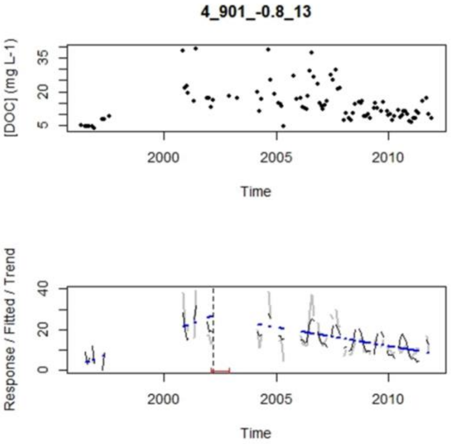
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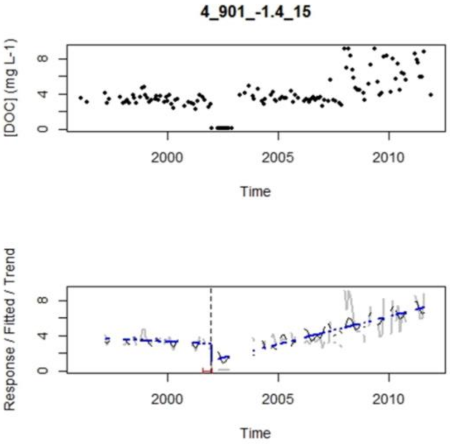
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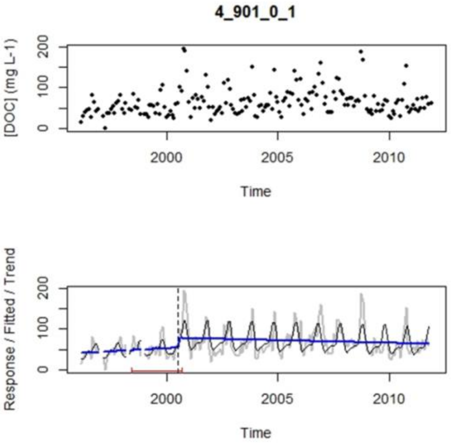
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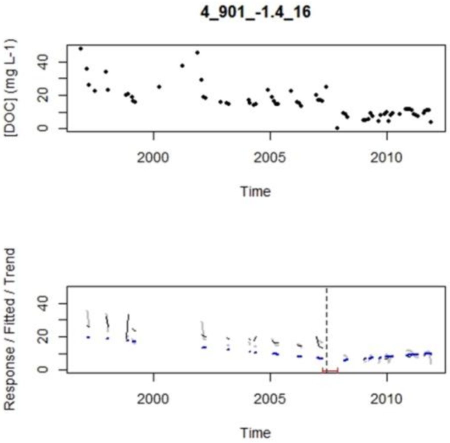
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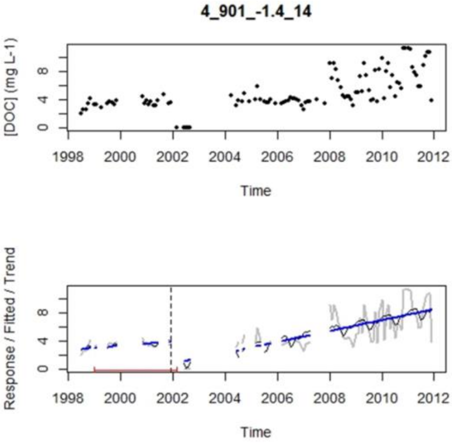
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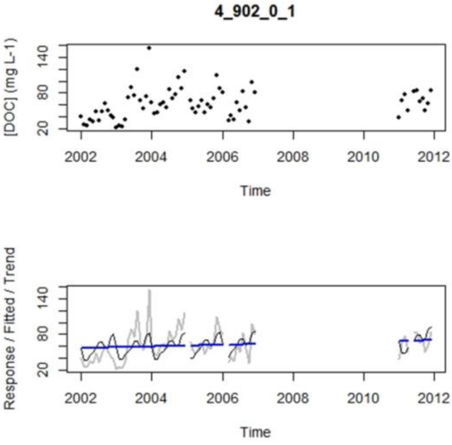
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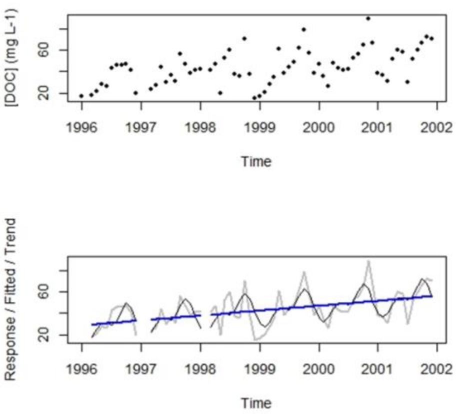
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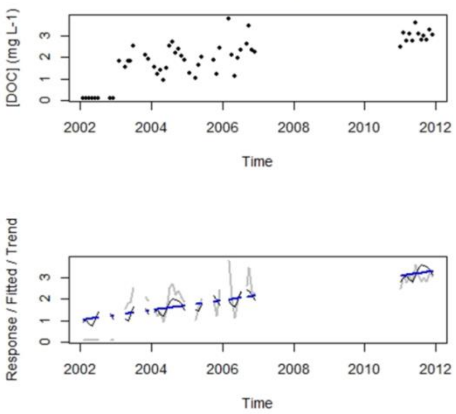
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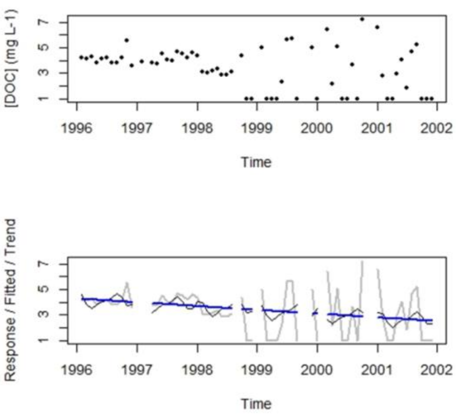
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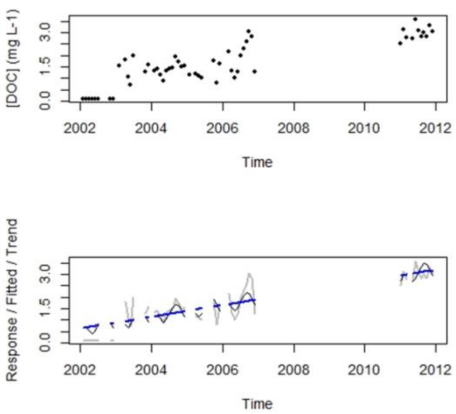
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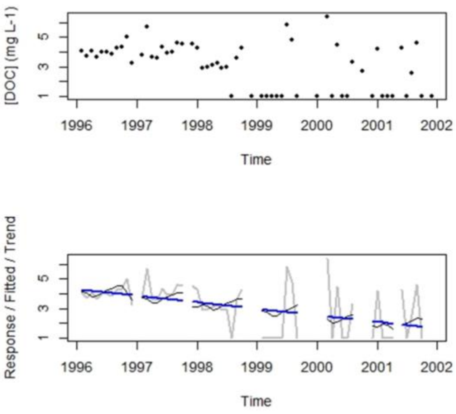
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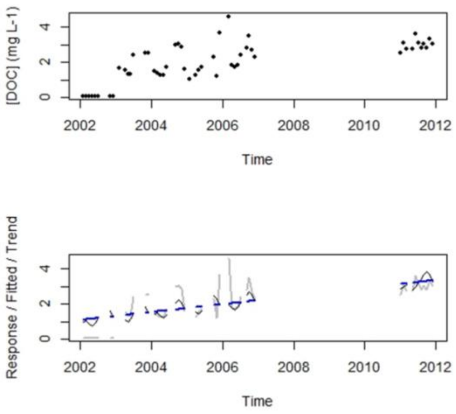
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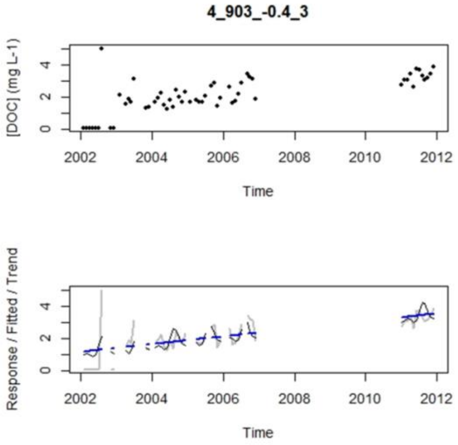
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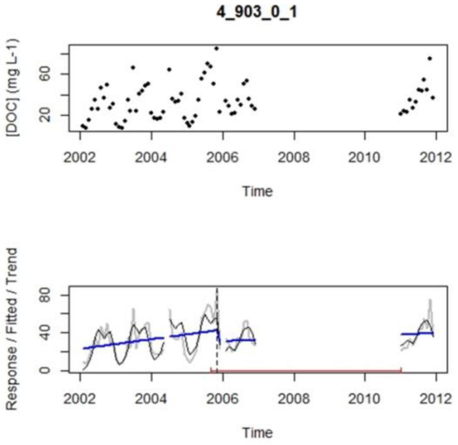
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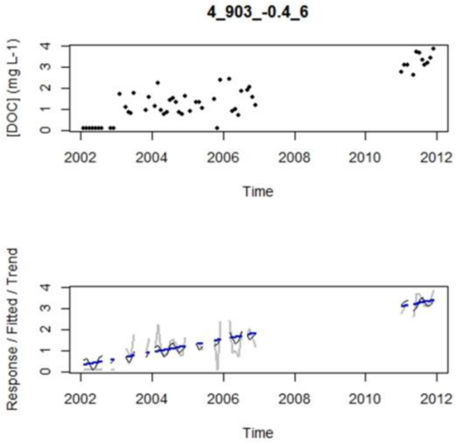
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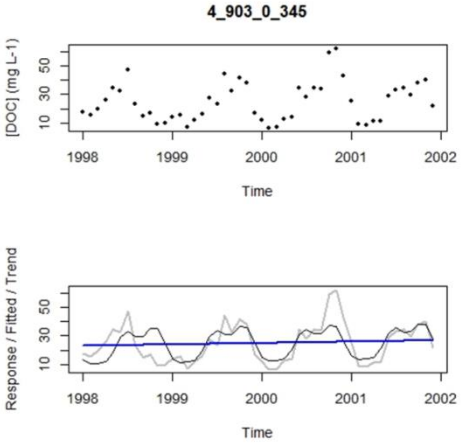
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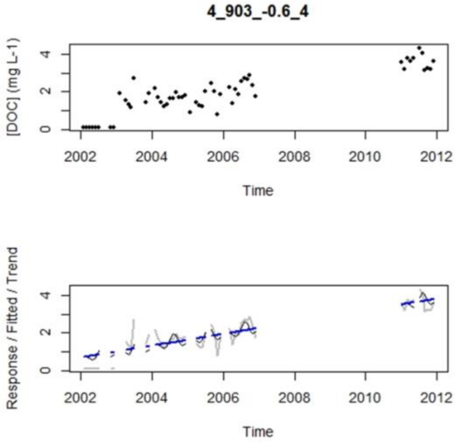
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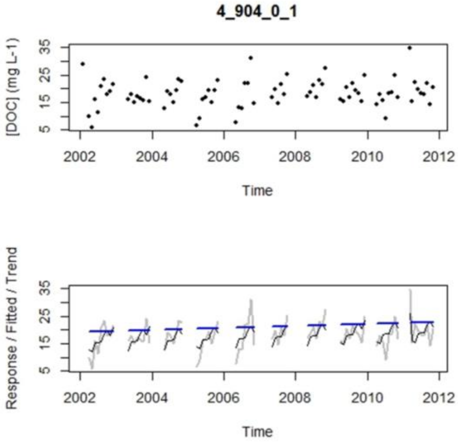
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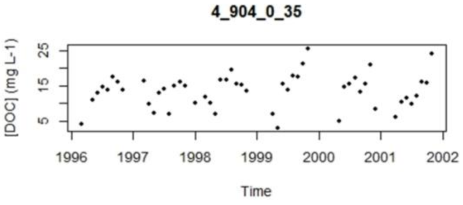
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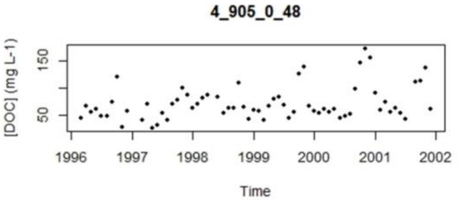
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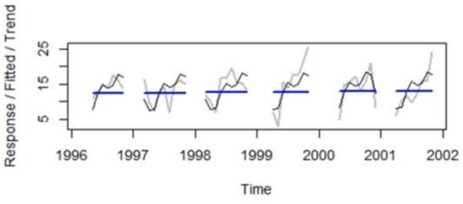
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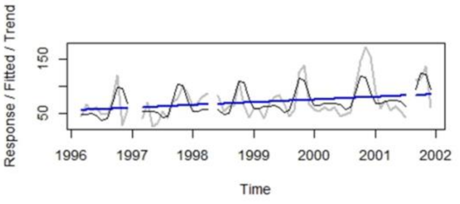
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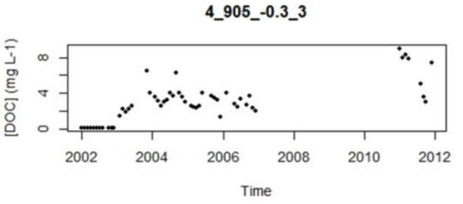
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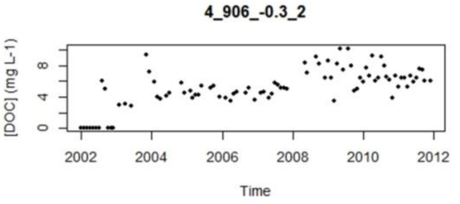
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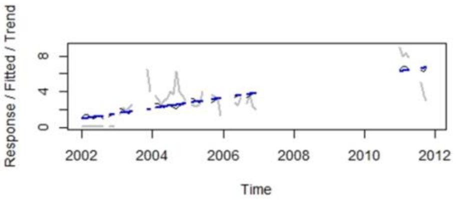
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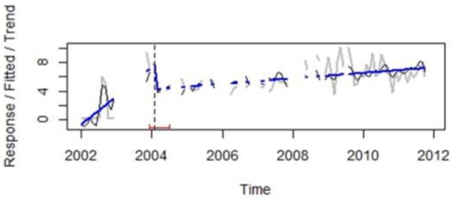
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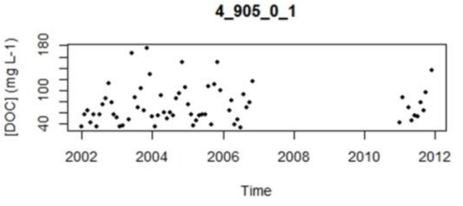
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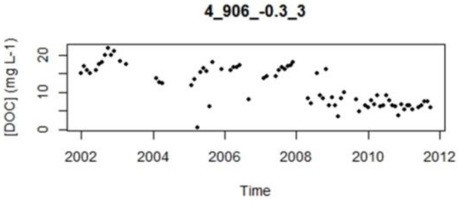
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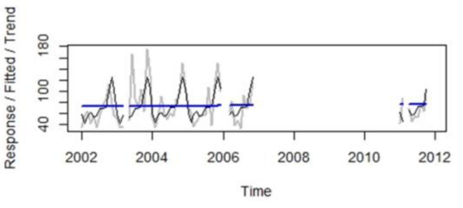
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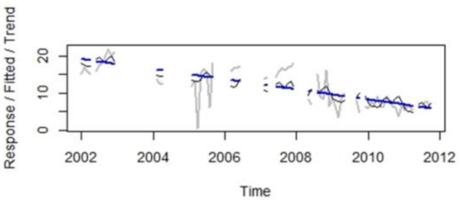
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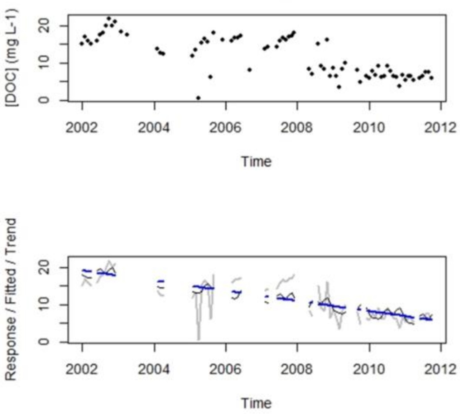

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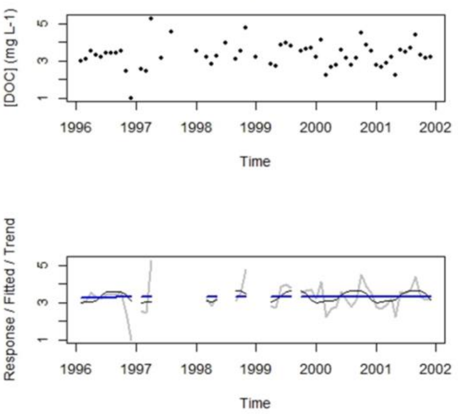

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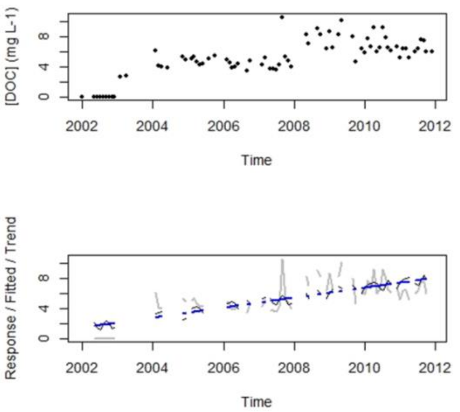

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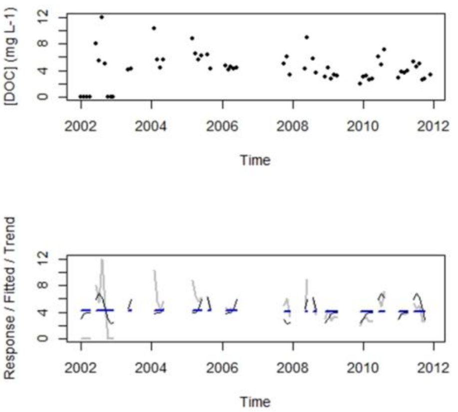

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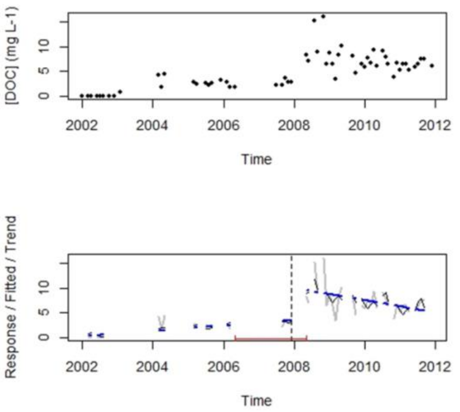

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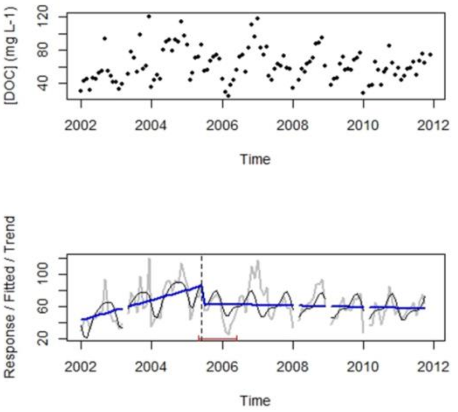

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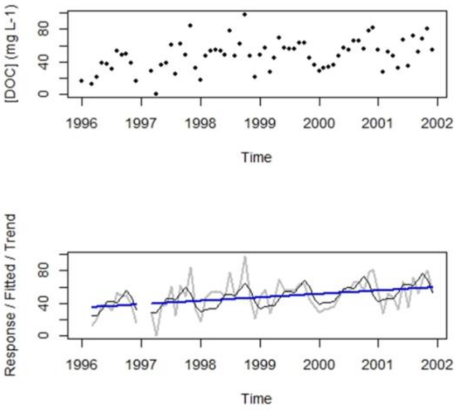

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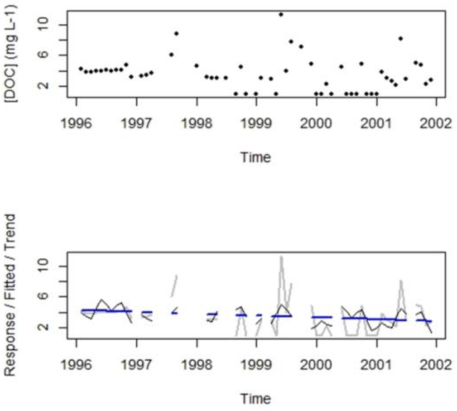

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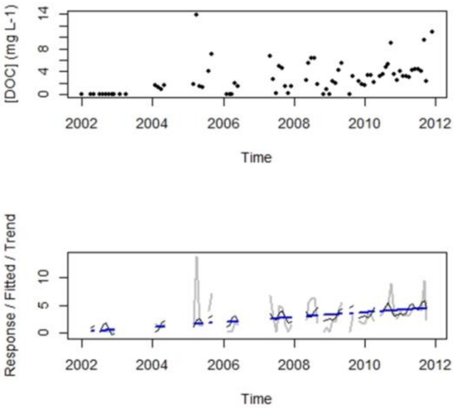

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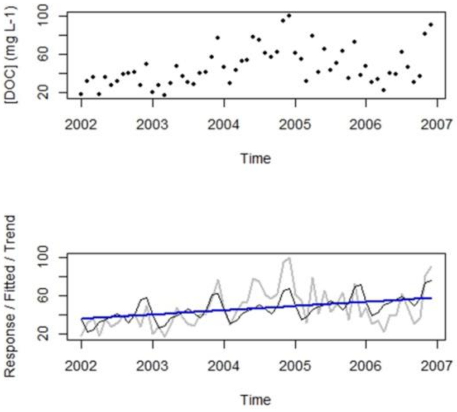

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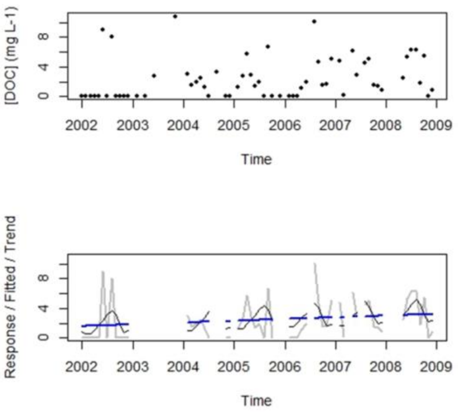

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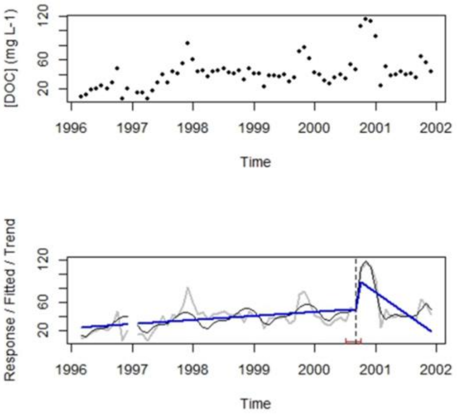

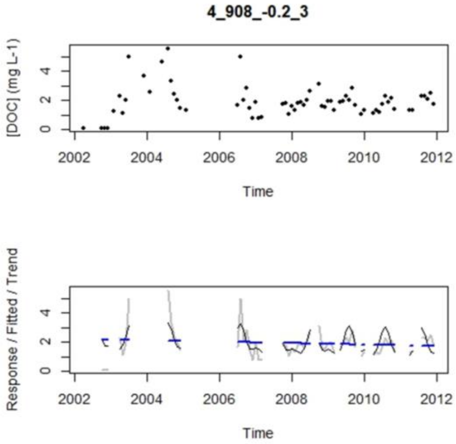
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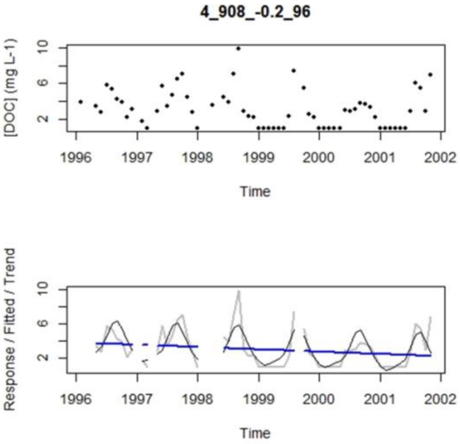
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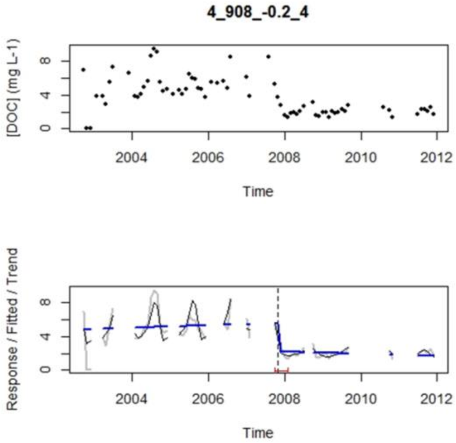
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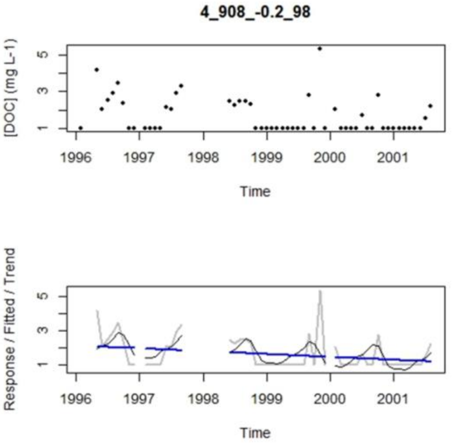
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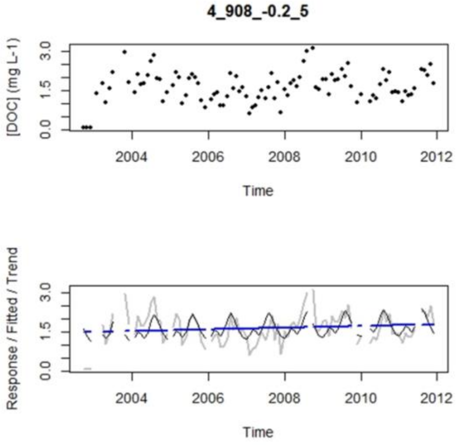
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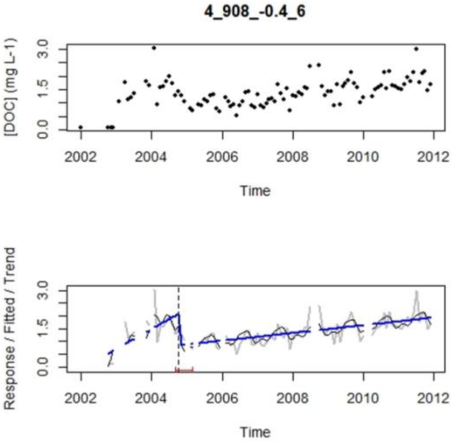
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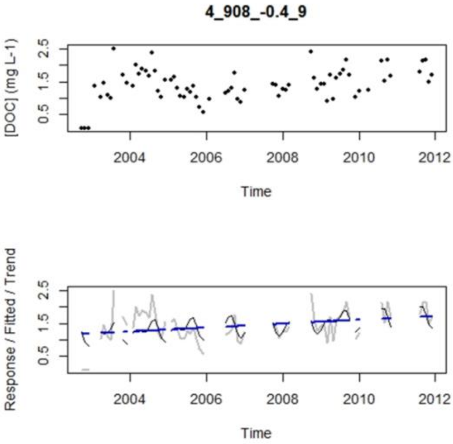
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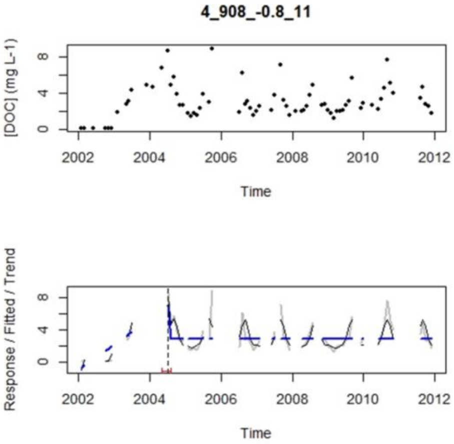
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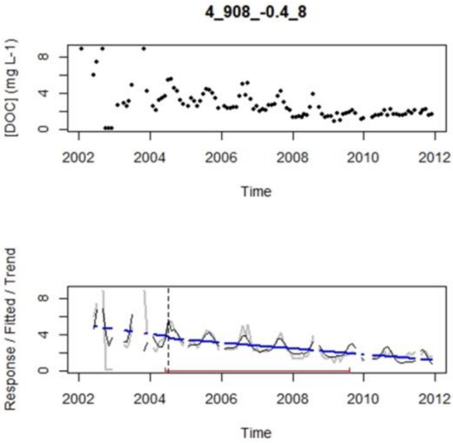
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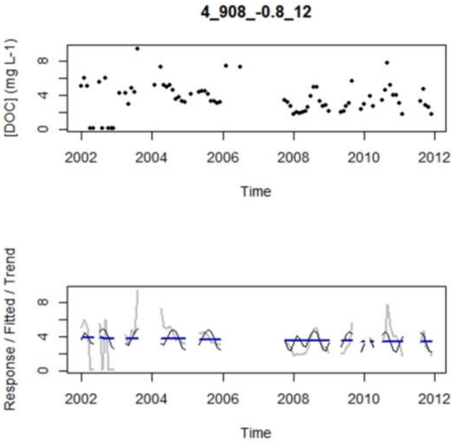
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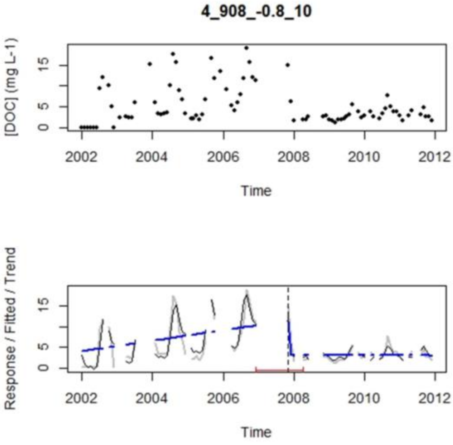
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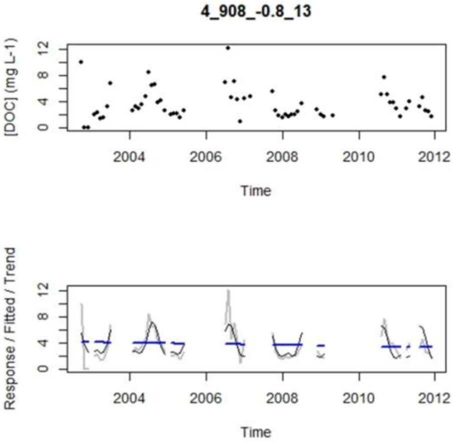
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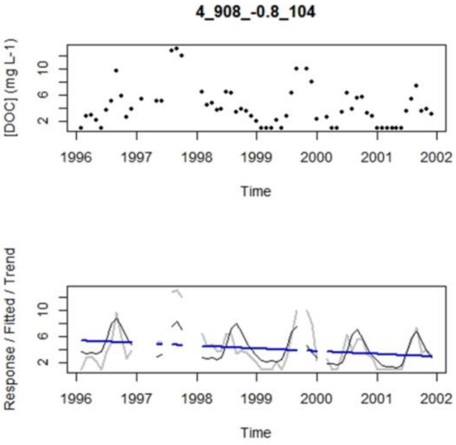
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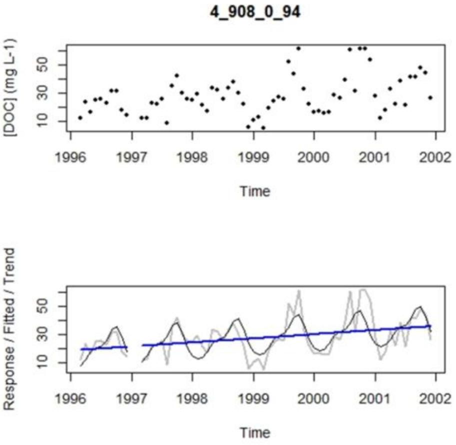
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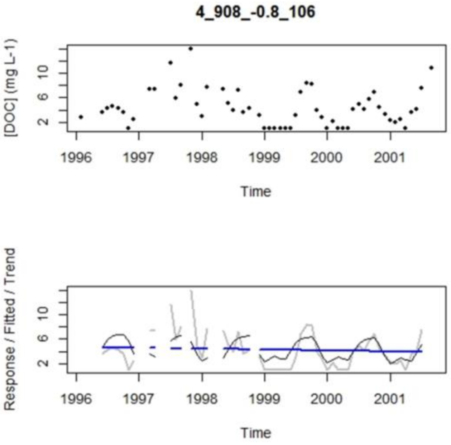
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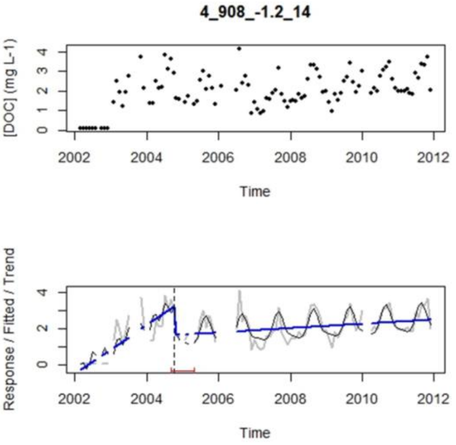
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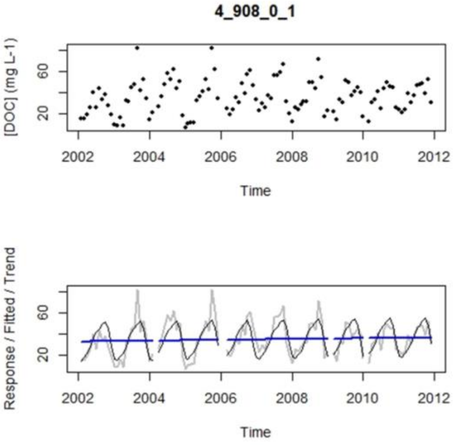
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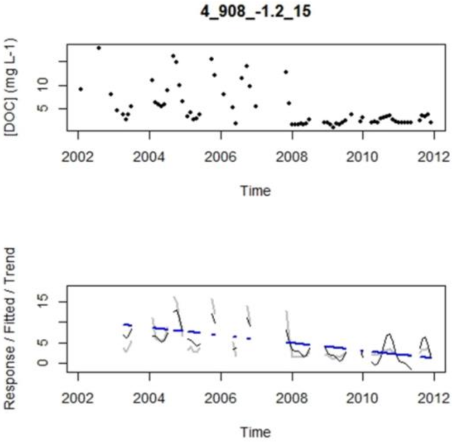
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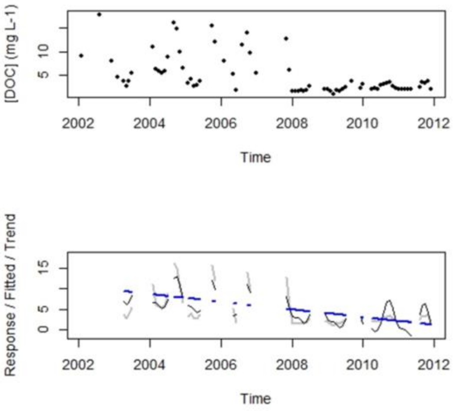

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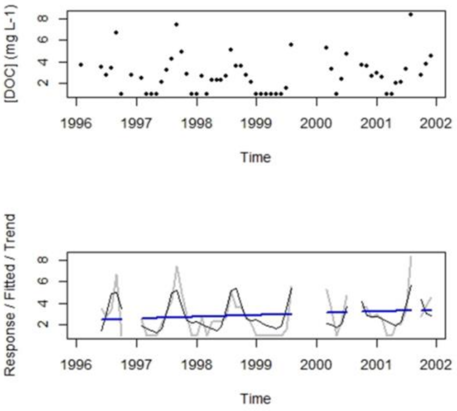

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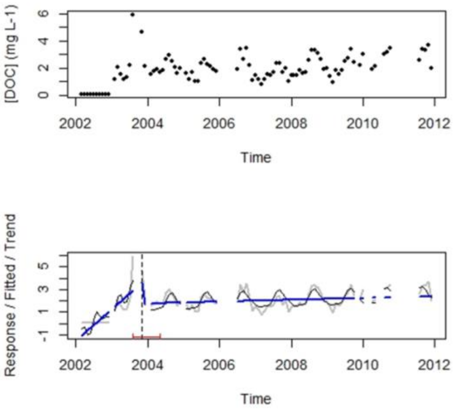

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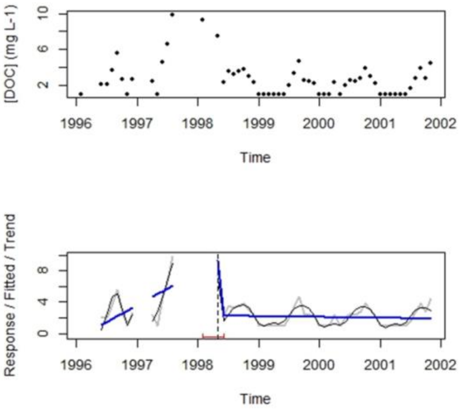

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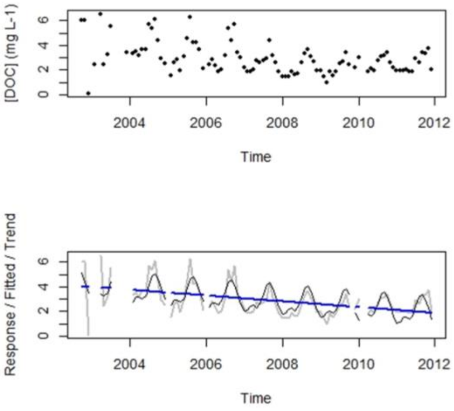

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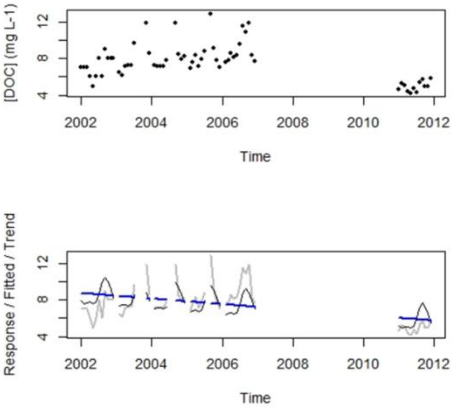

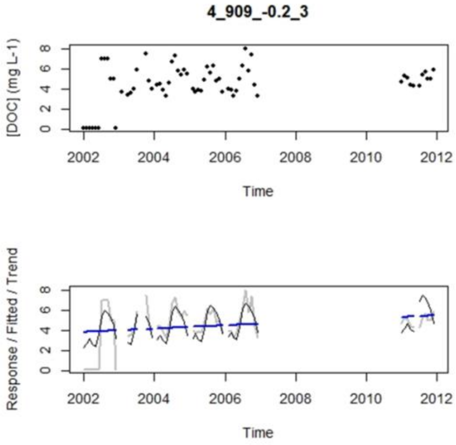
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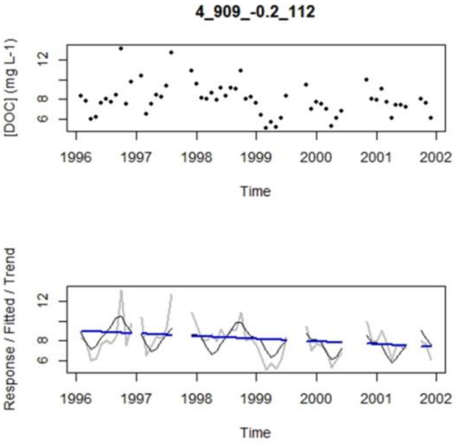
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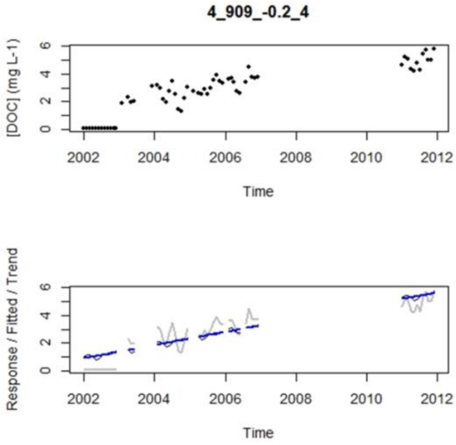
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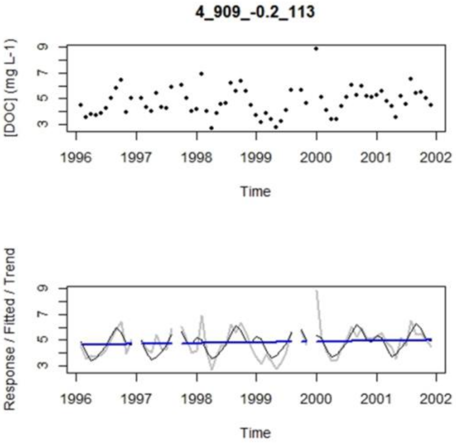
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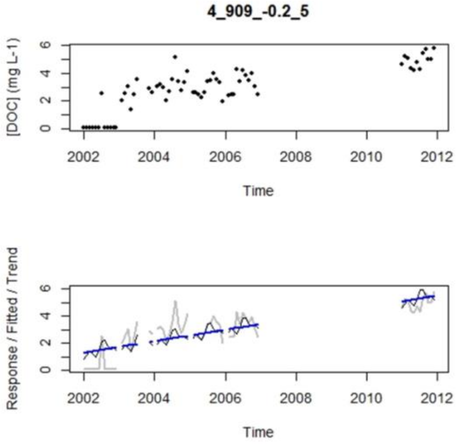
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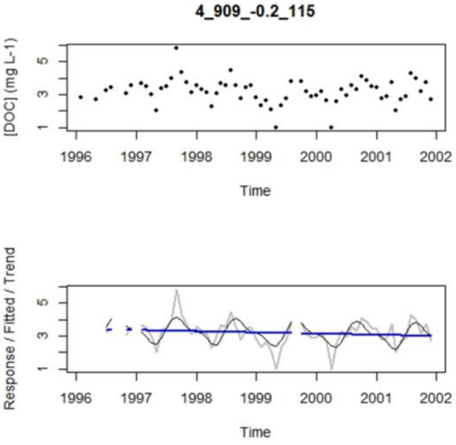
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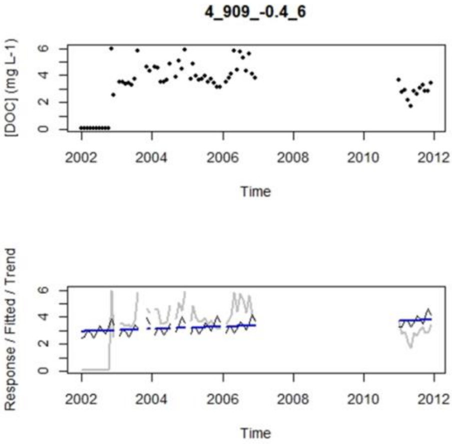
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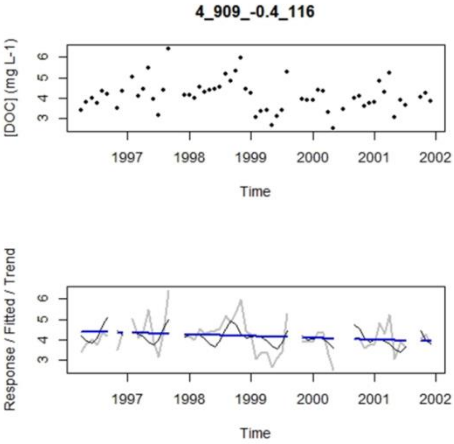
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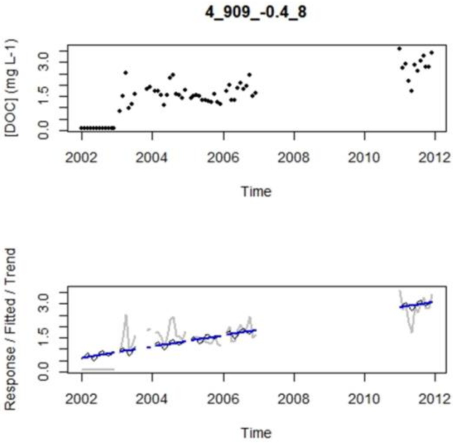
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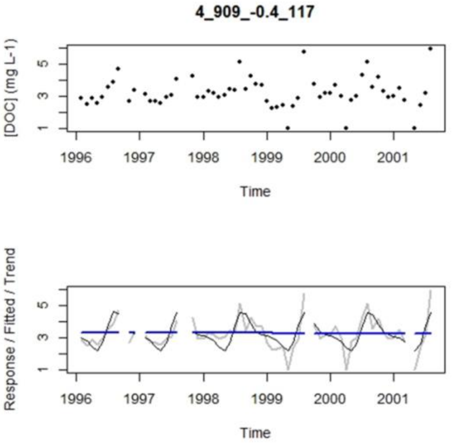
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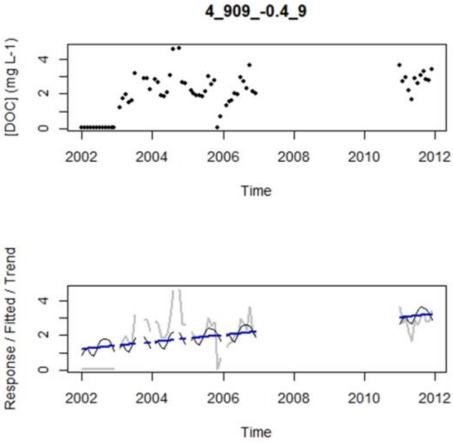
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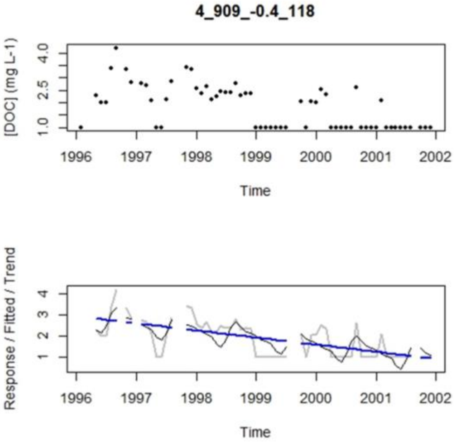
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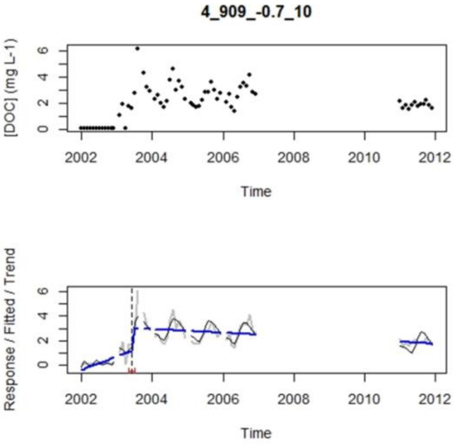
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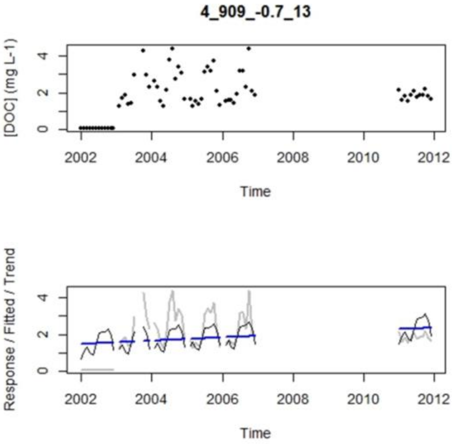
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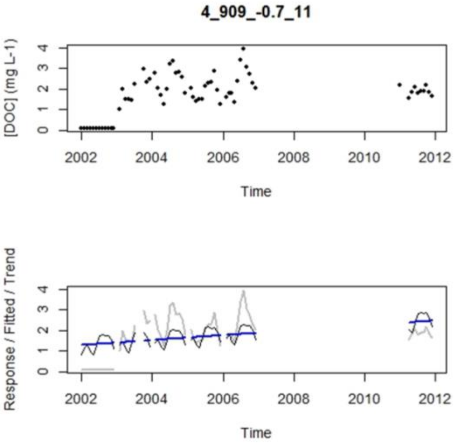
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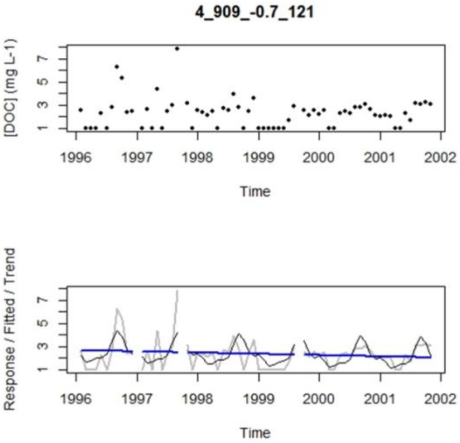
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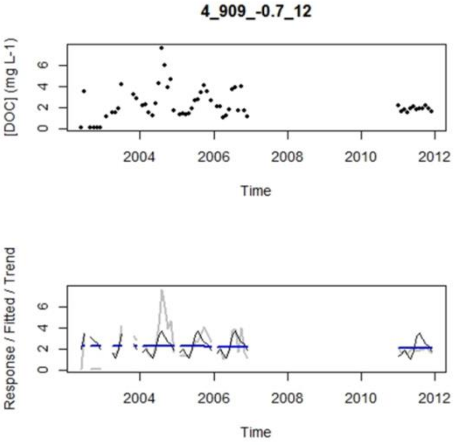
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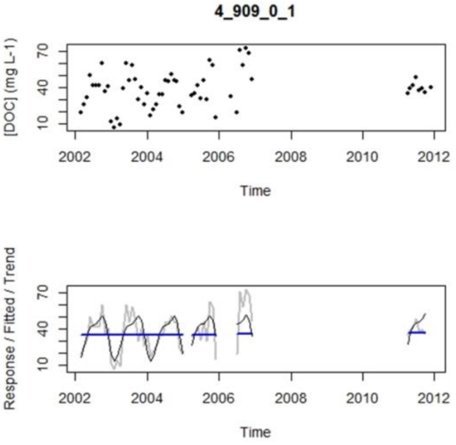
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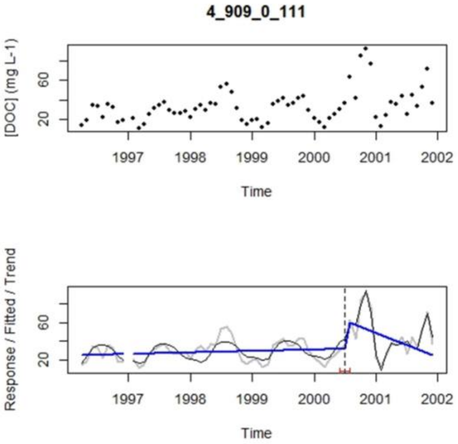
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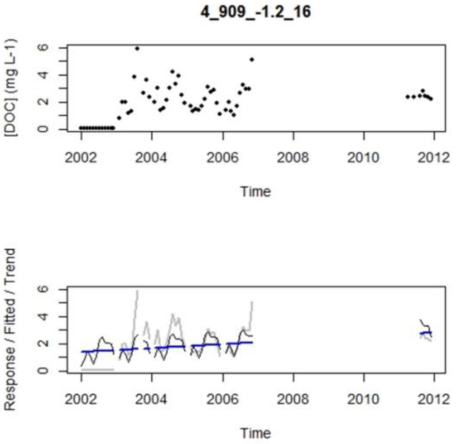
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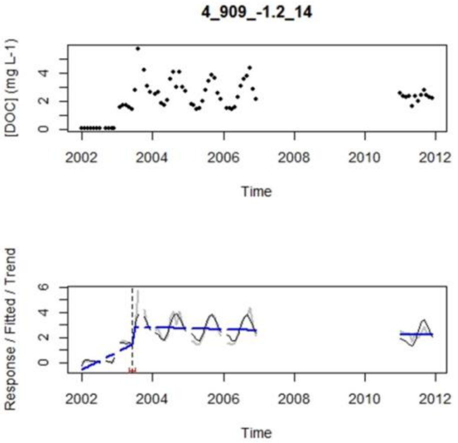
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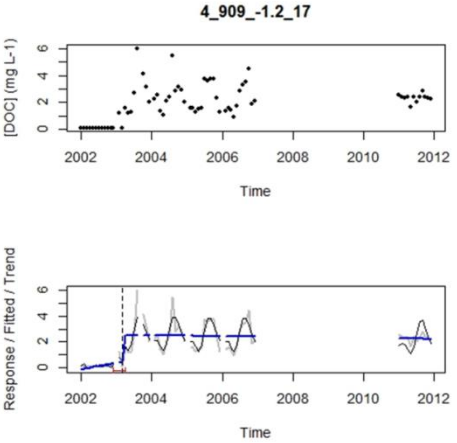
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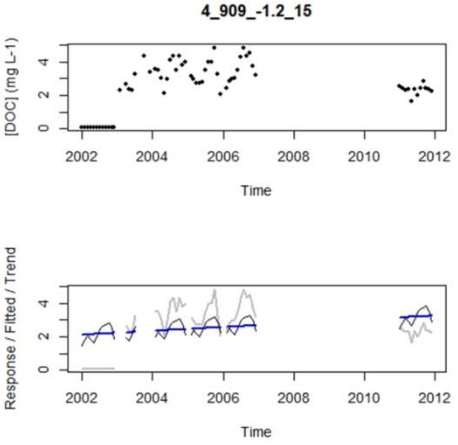
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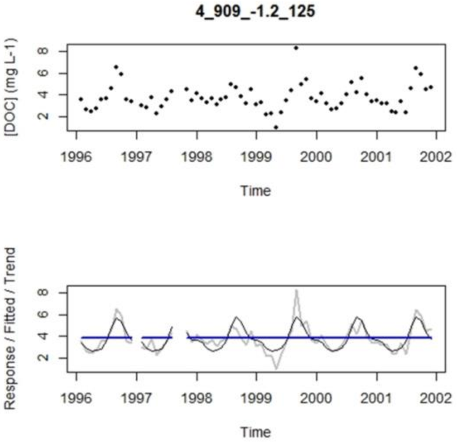
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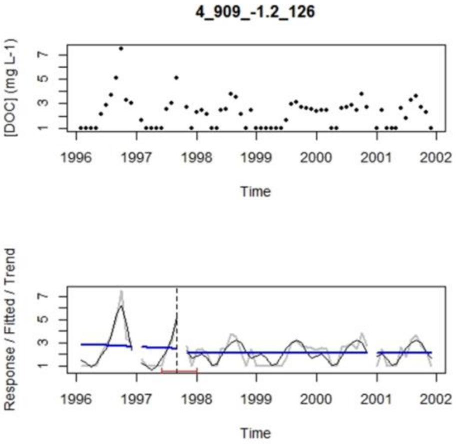
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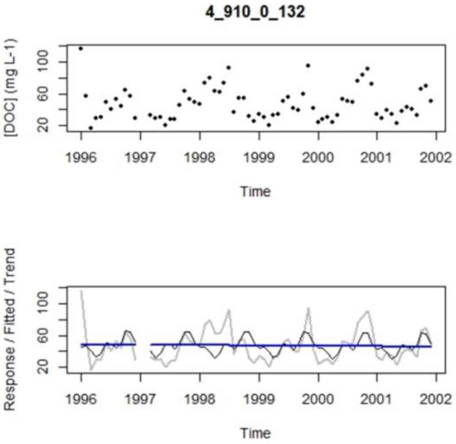
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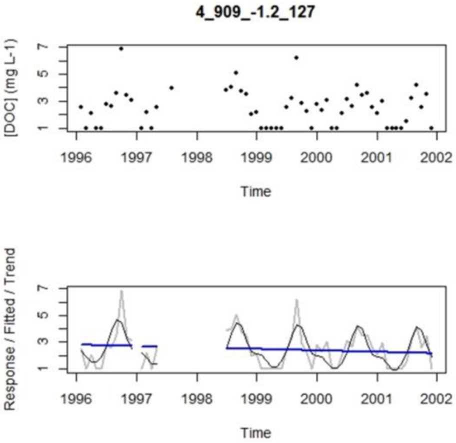
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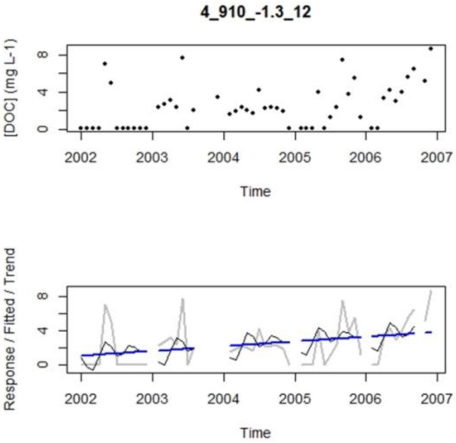
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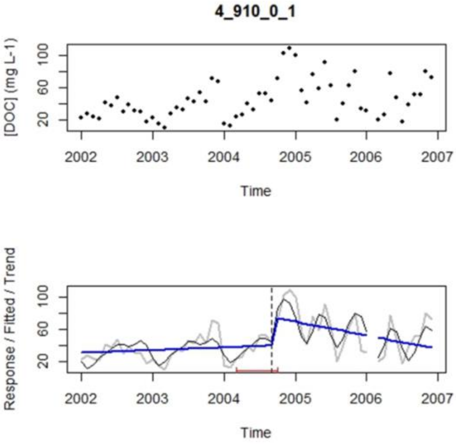
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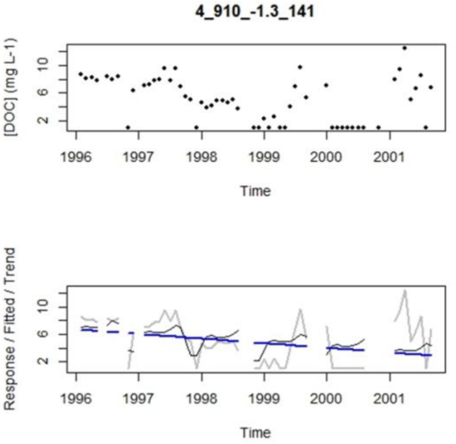
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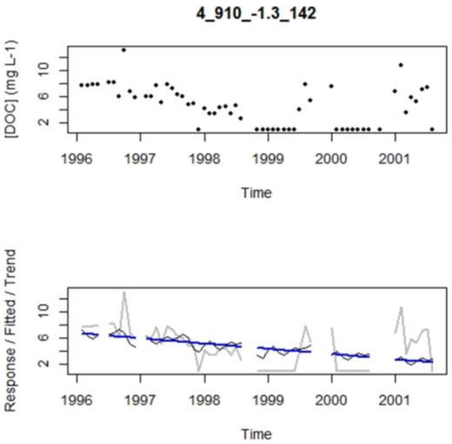
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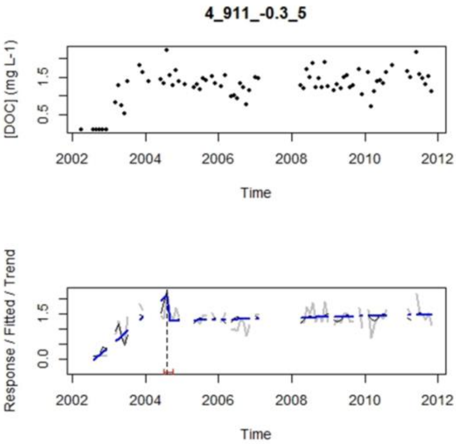
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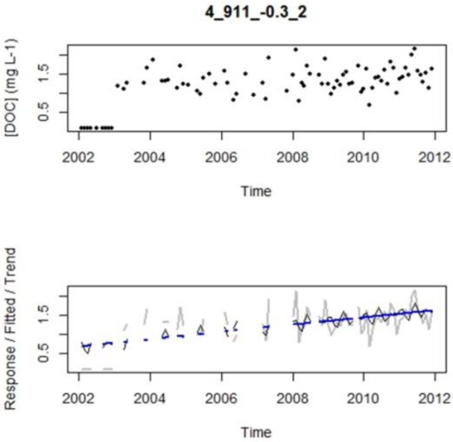
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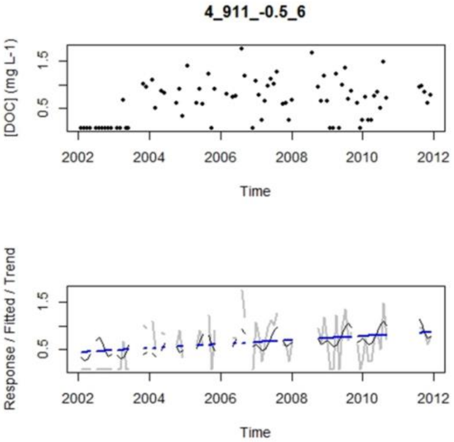
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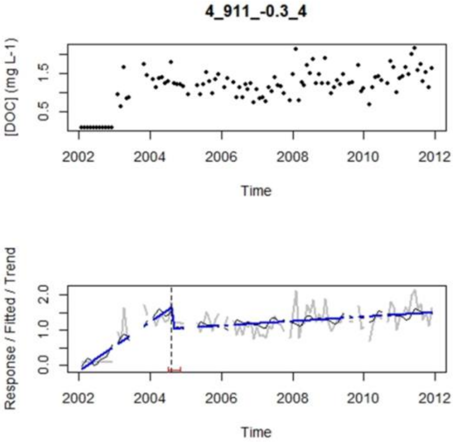
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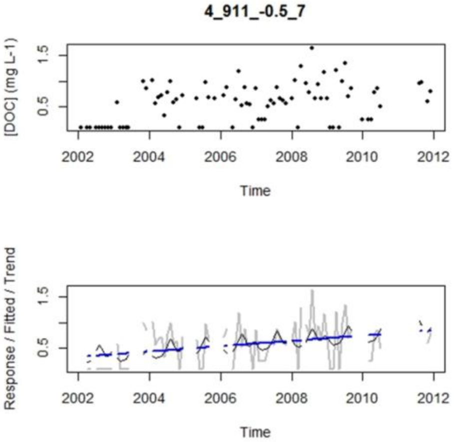
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Response / Fitted / Trend
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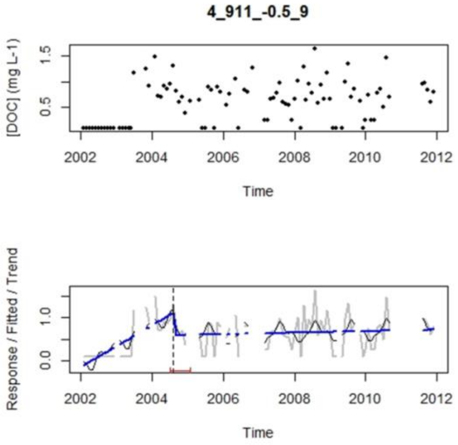
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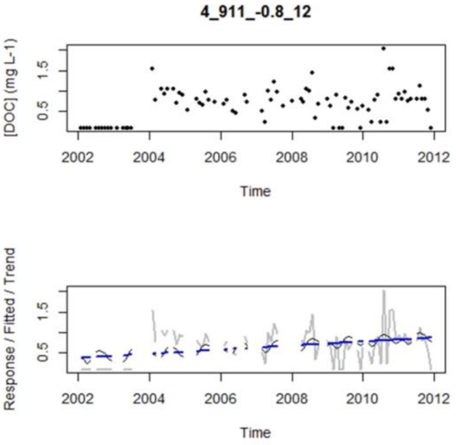
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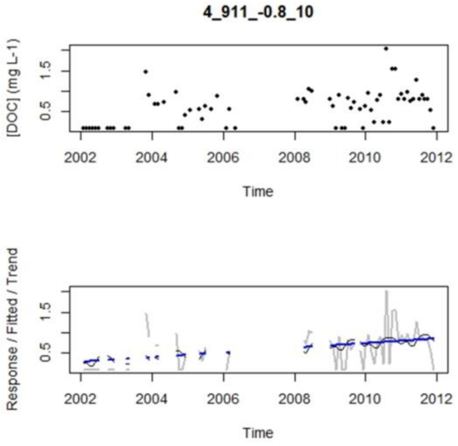
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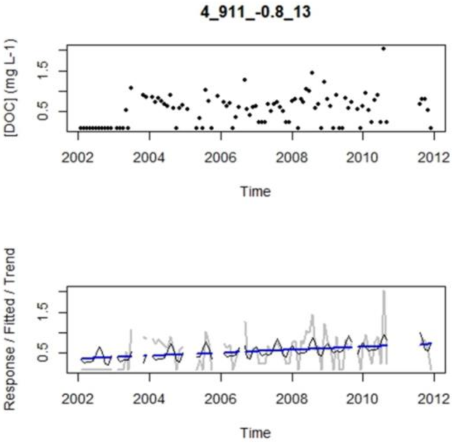
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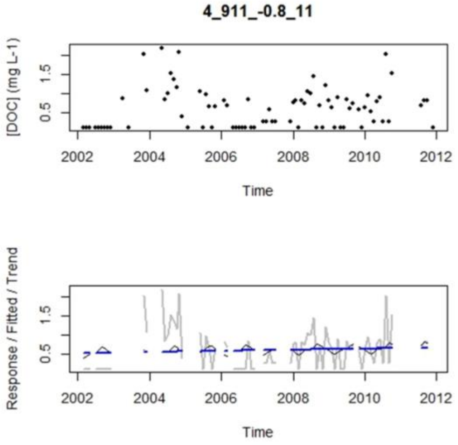
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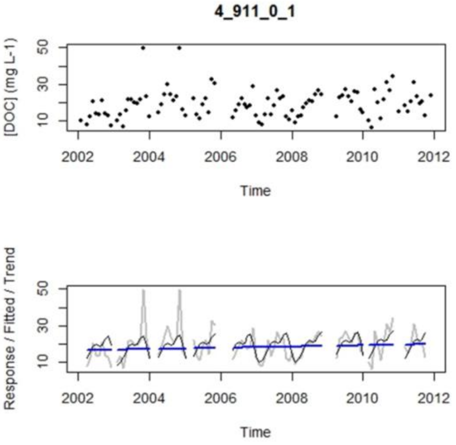
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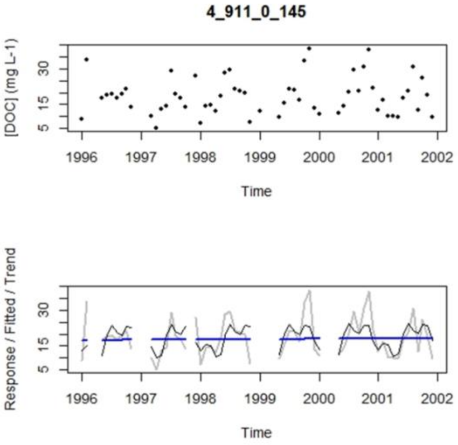
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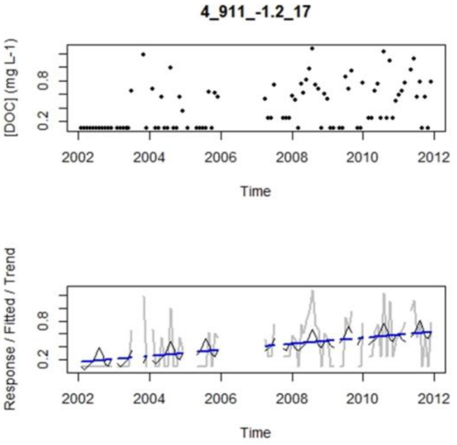
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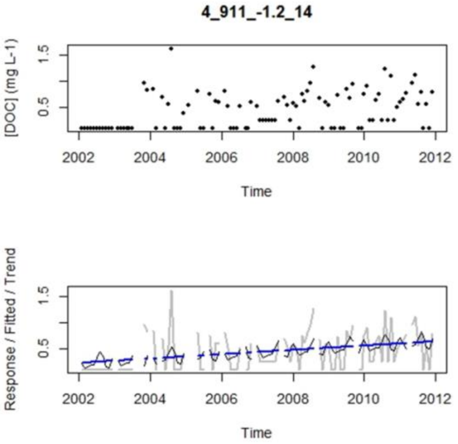
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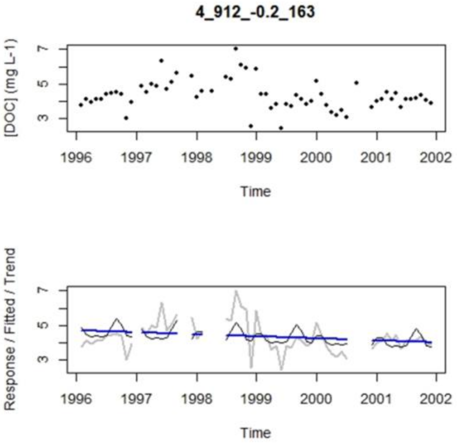
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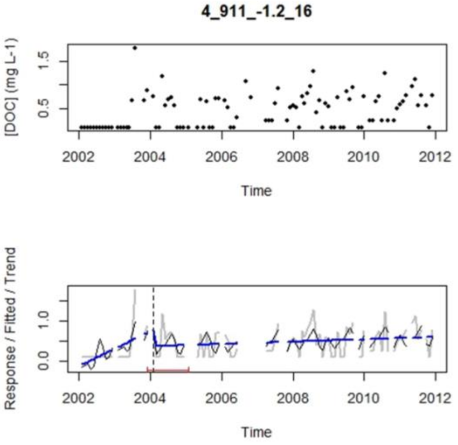
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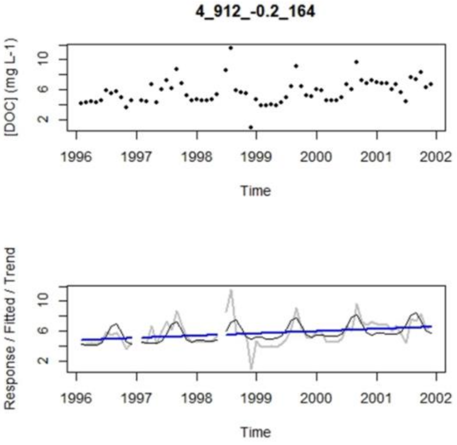
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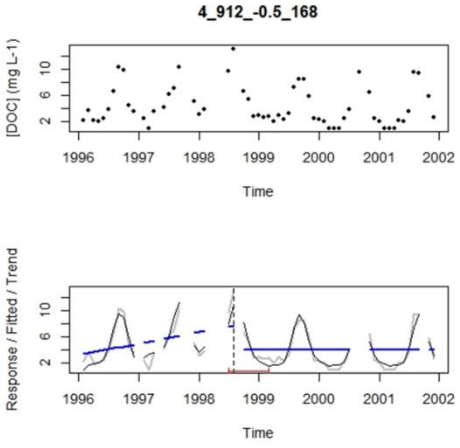
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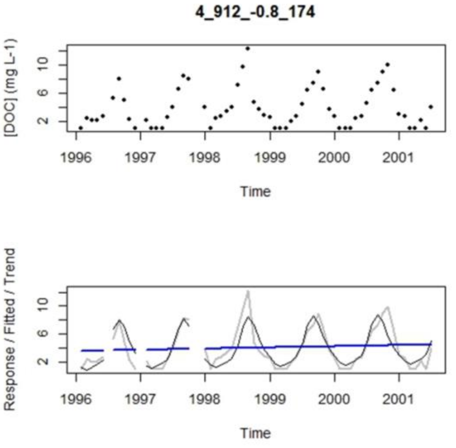
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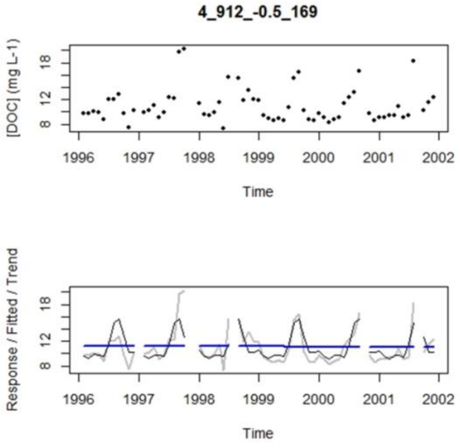
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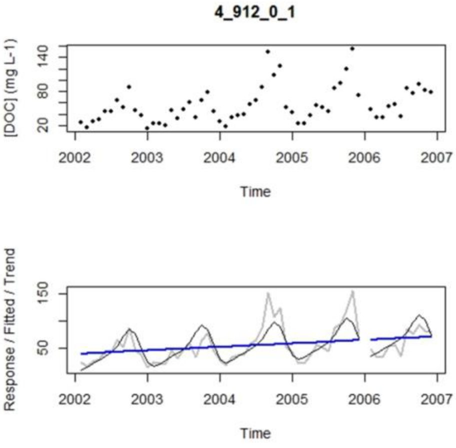
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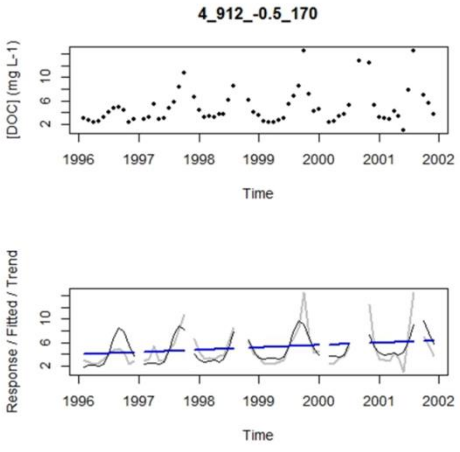
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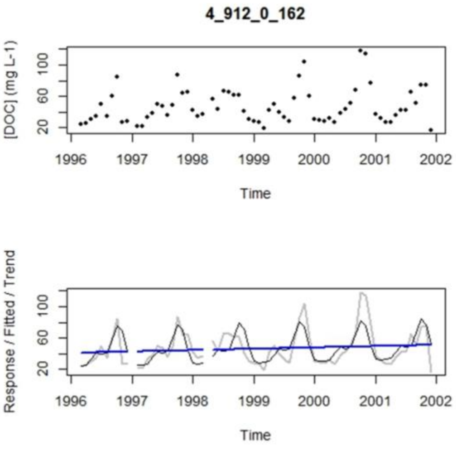
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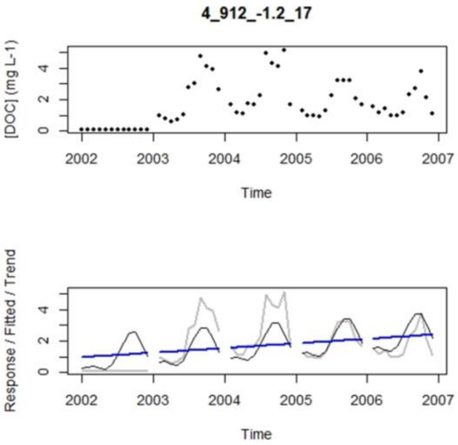

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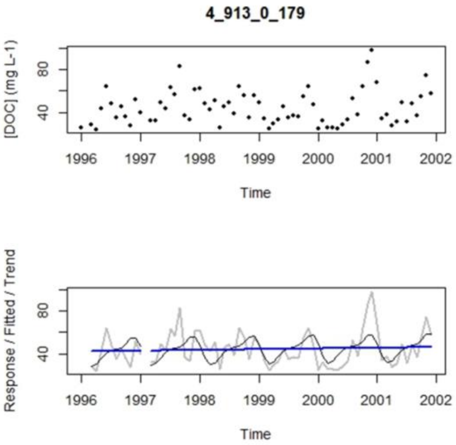

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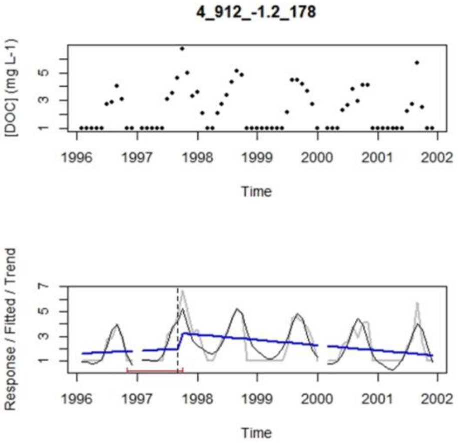

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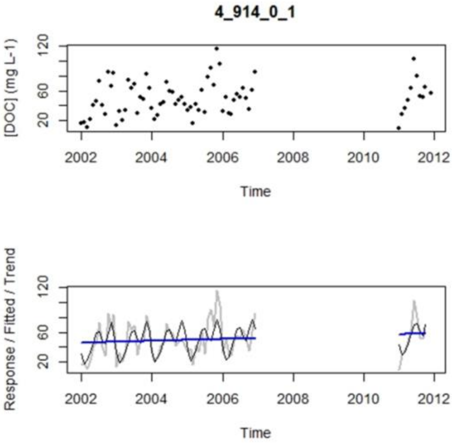

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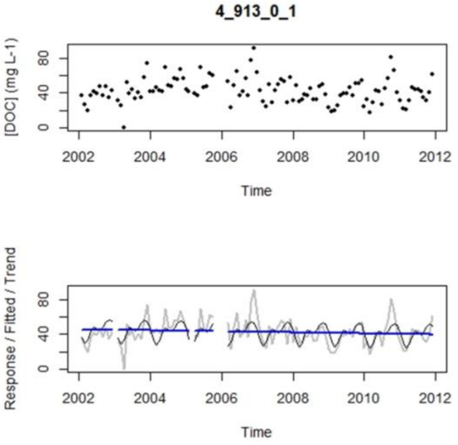

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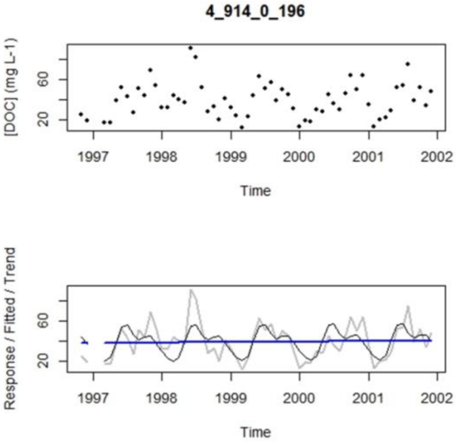

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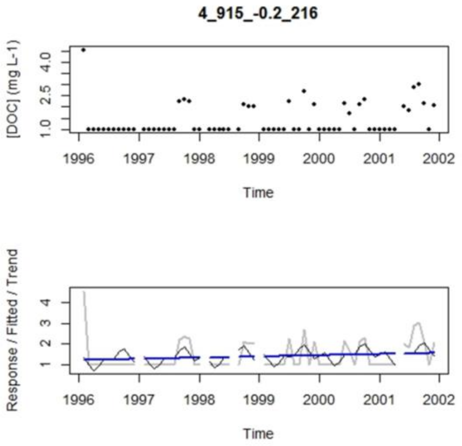
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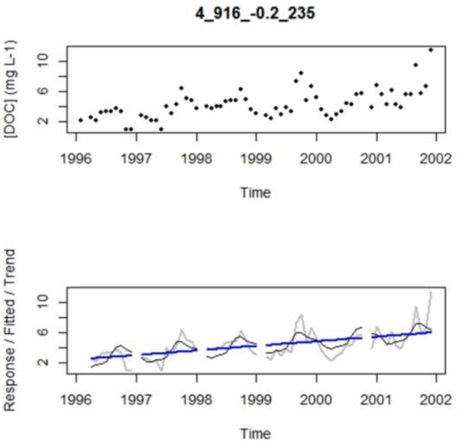
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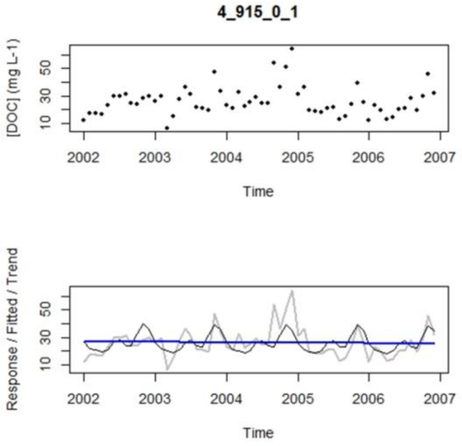
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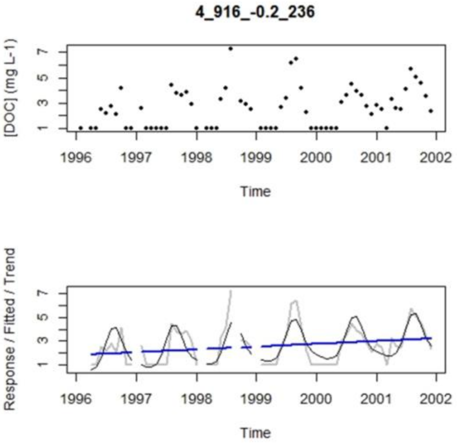
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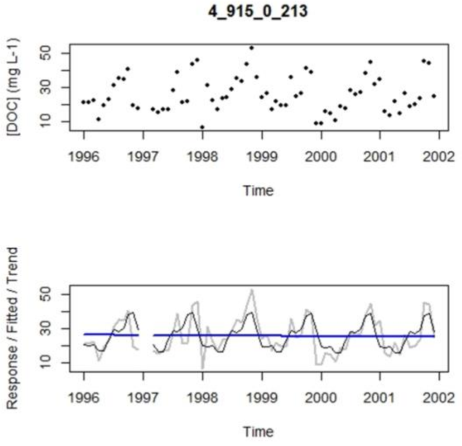
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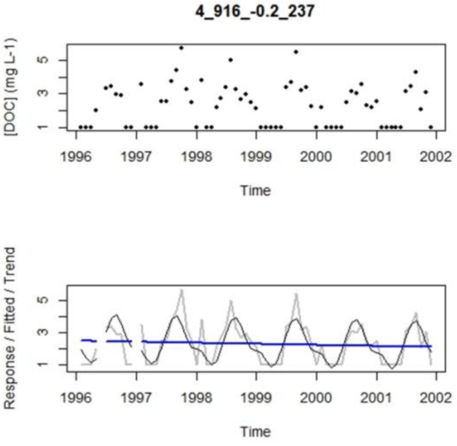
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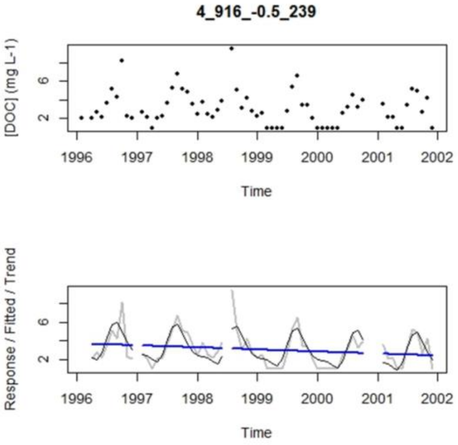
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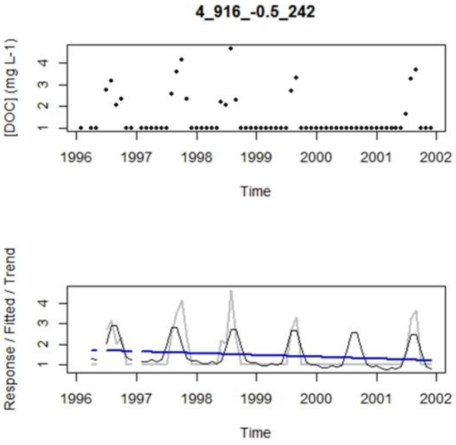
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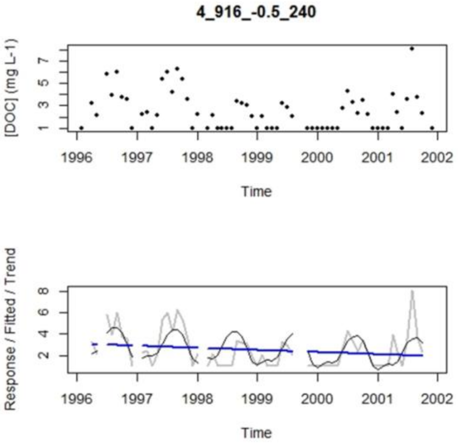
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Response / Fitted / Trend
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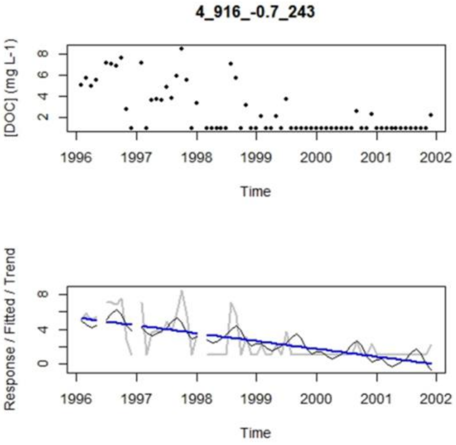
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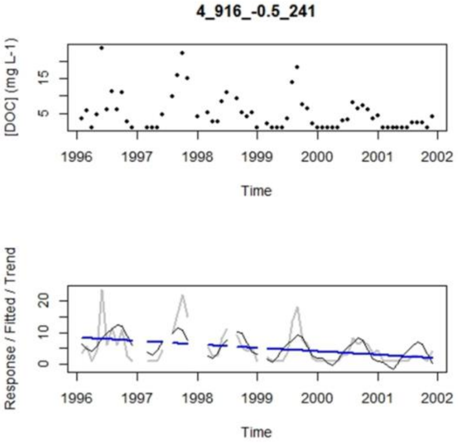
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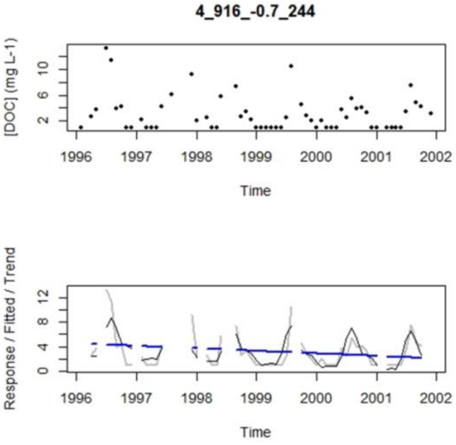
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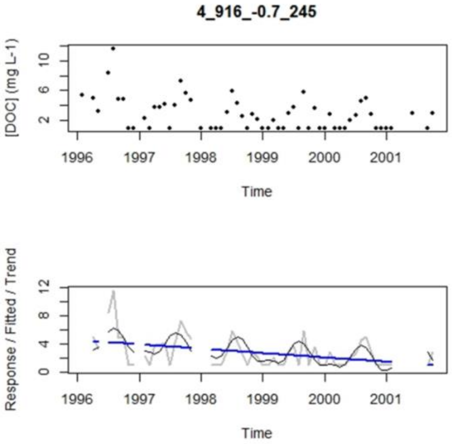
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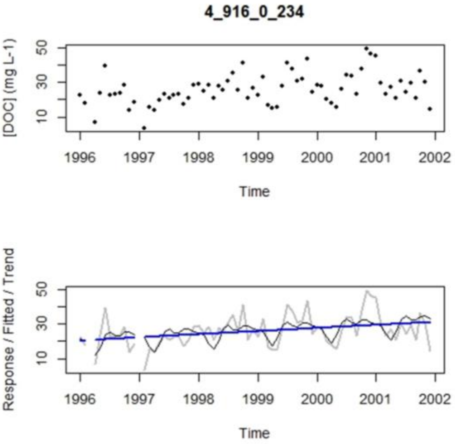
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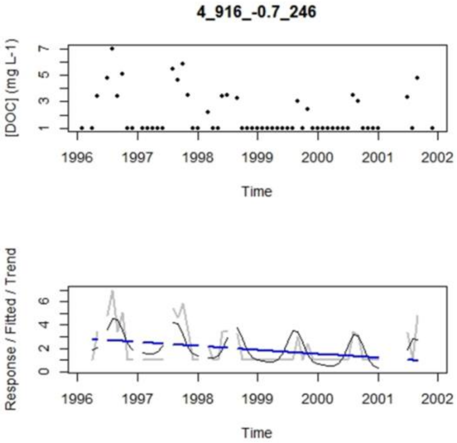
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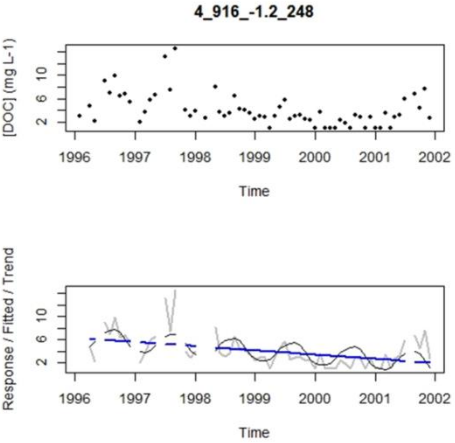
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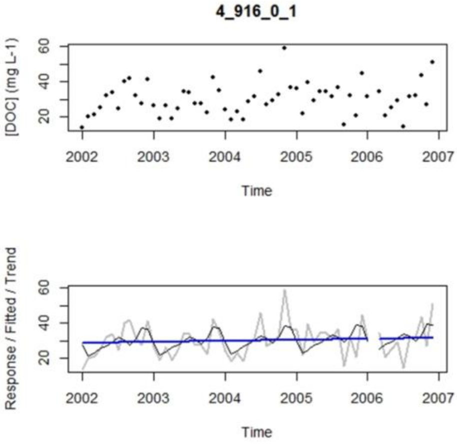
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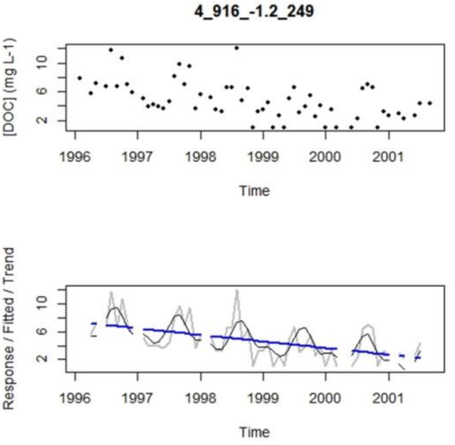
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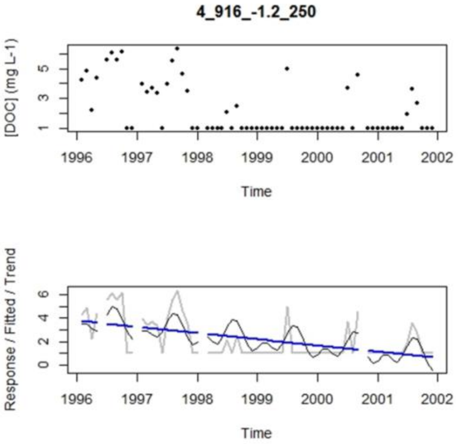
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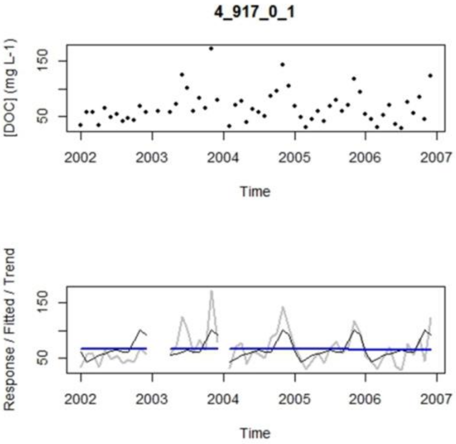
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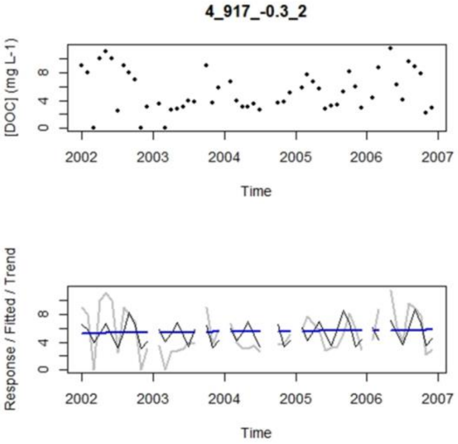
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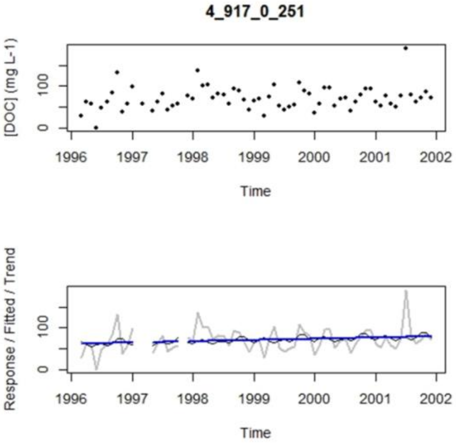
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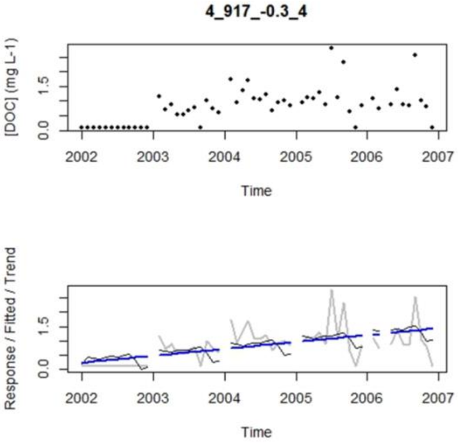
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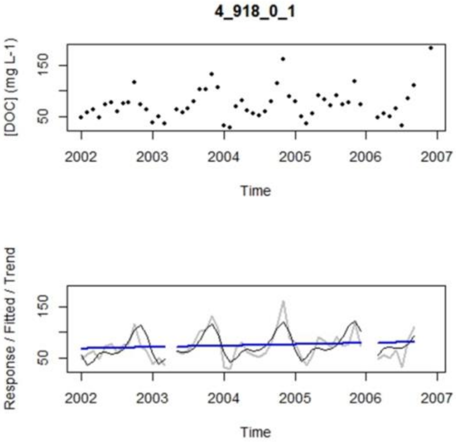
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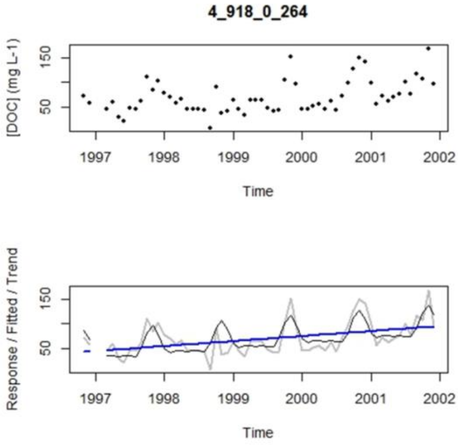
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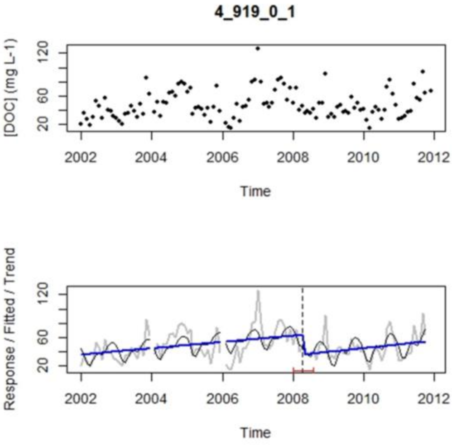
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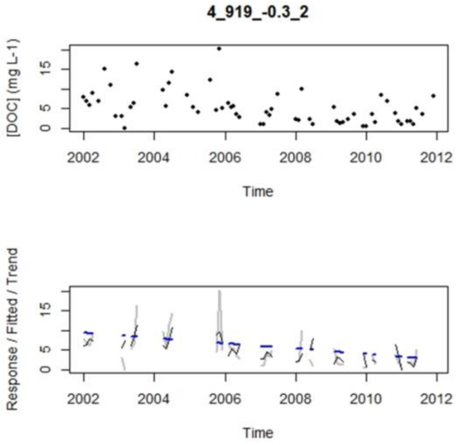
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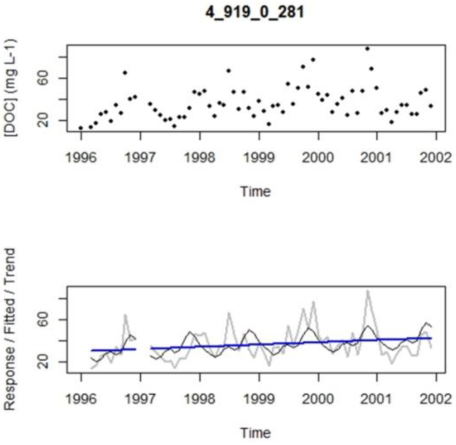
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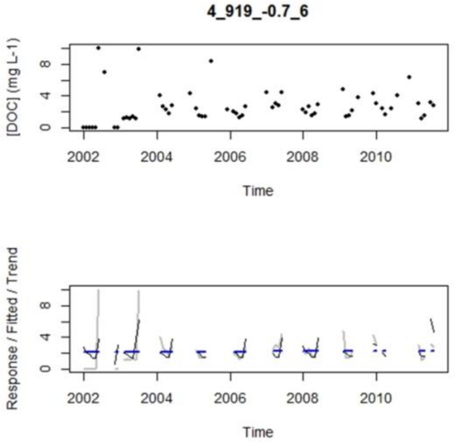
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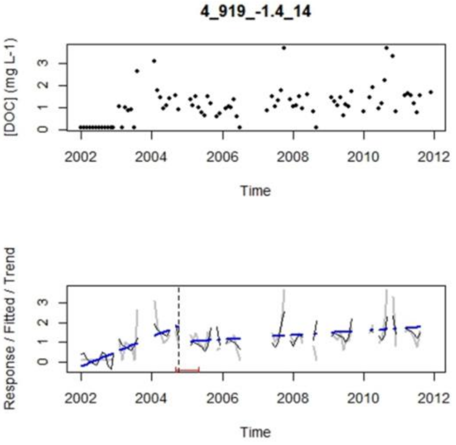
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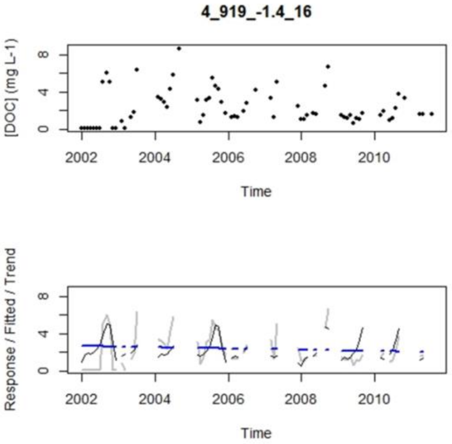
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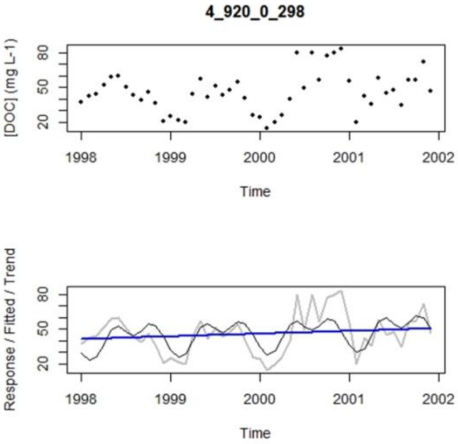
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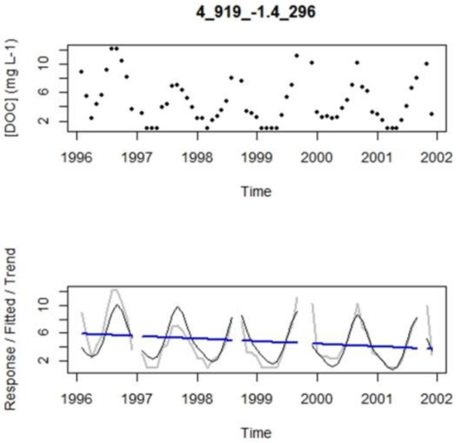
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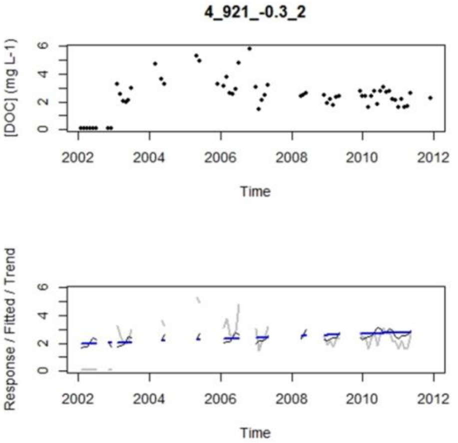
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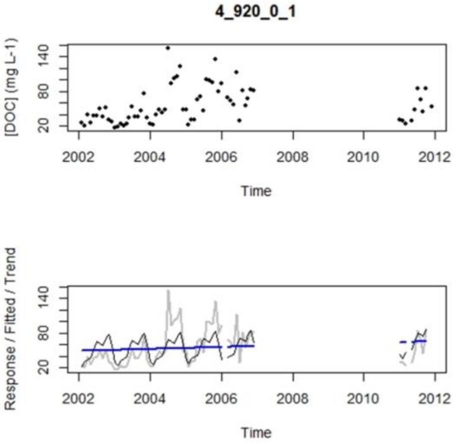
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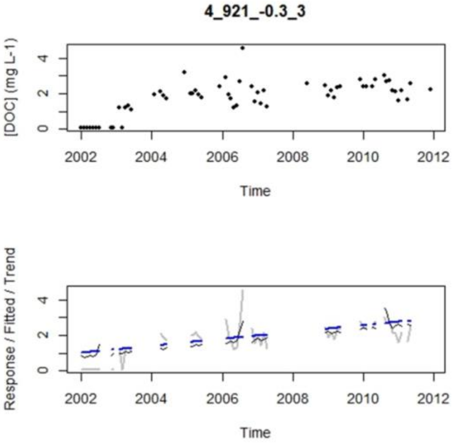
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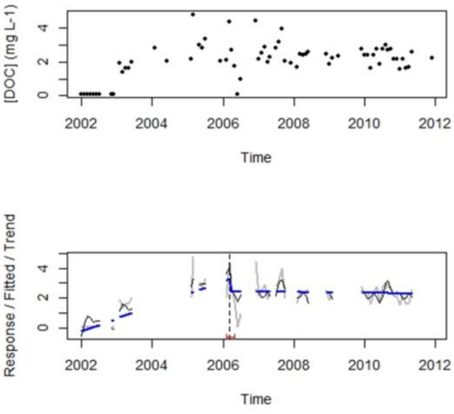

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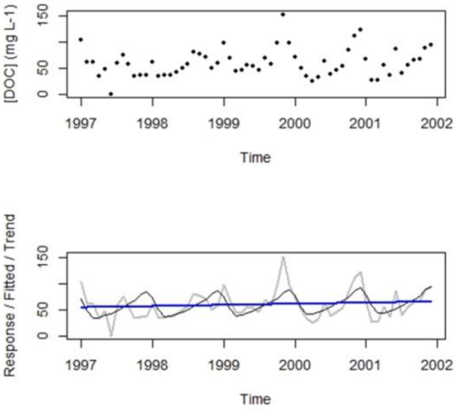

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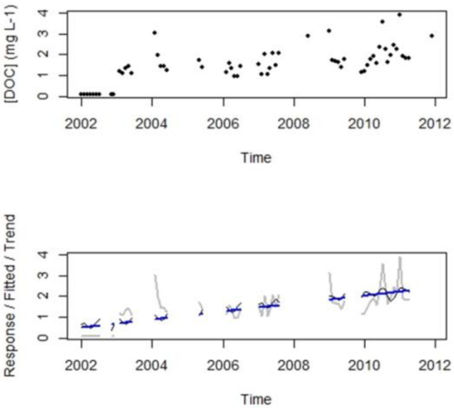

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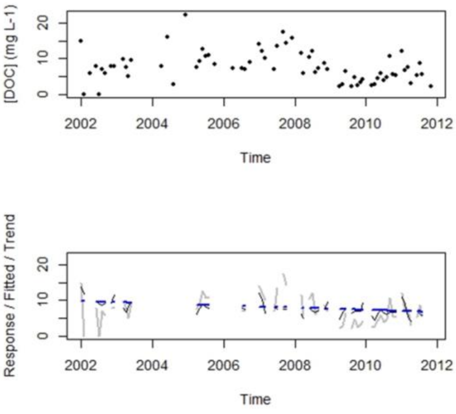

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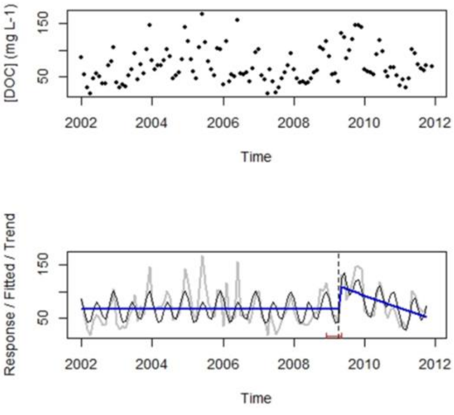

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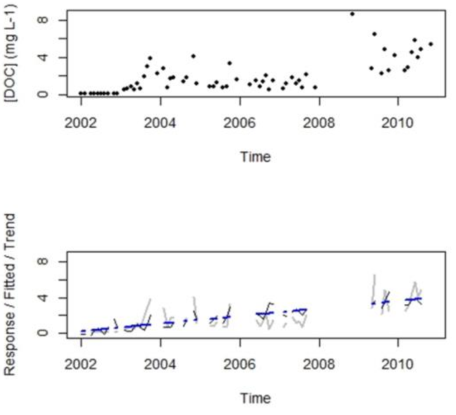

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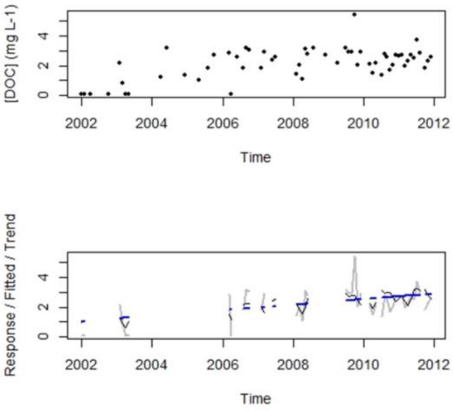

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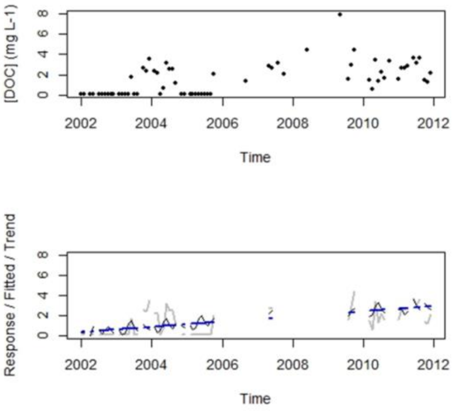

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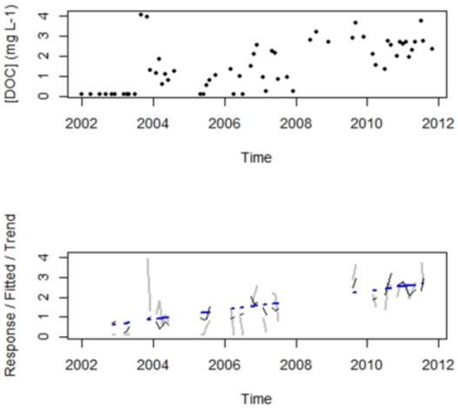

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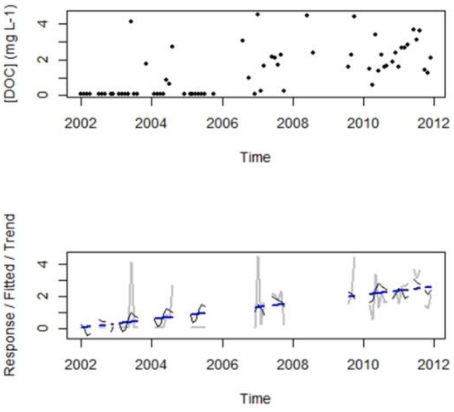

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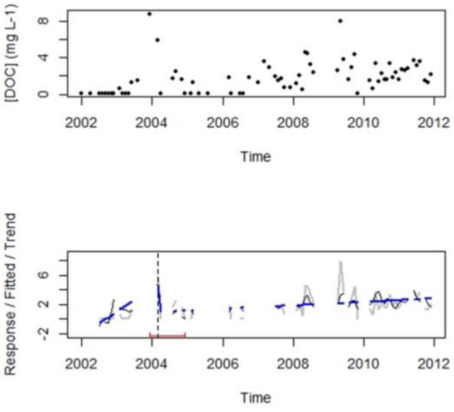

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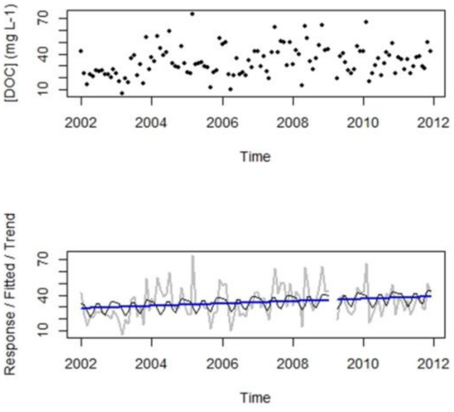

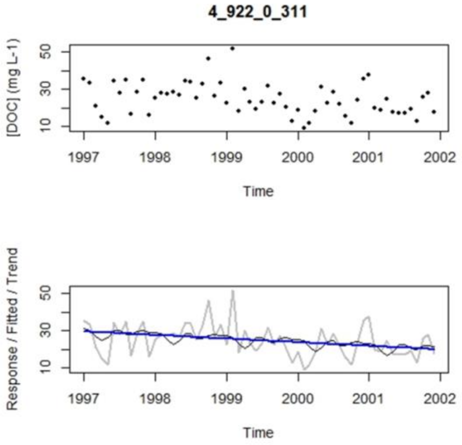
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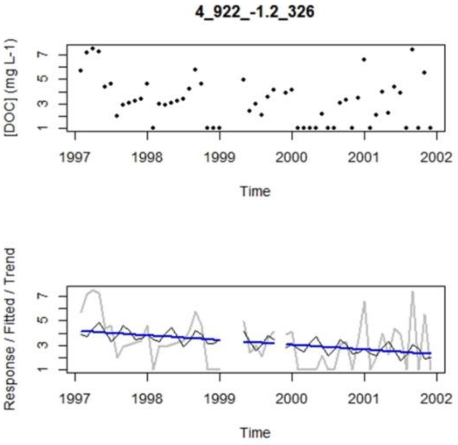
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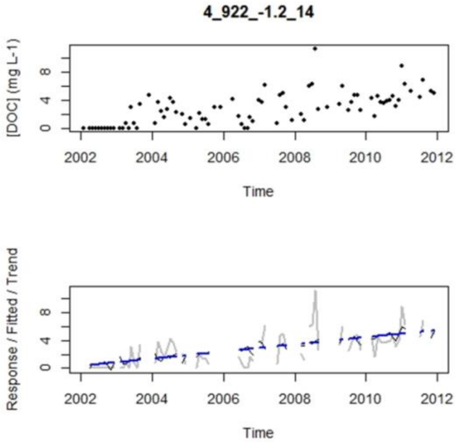
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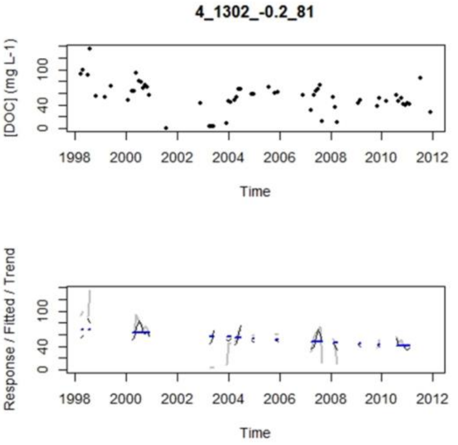
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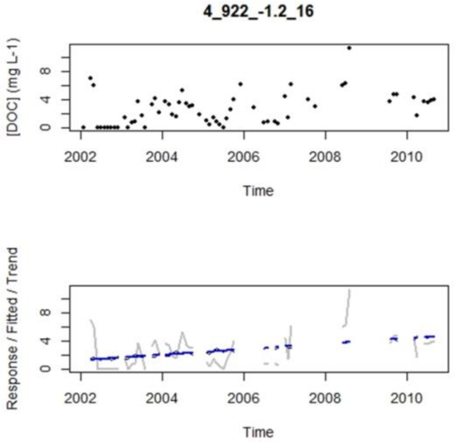
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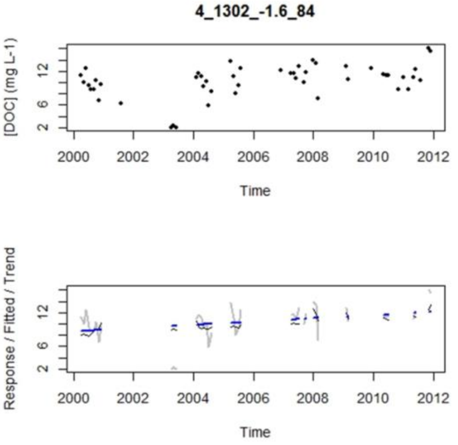
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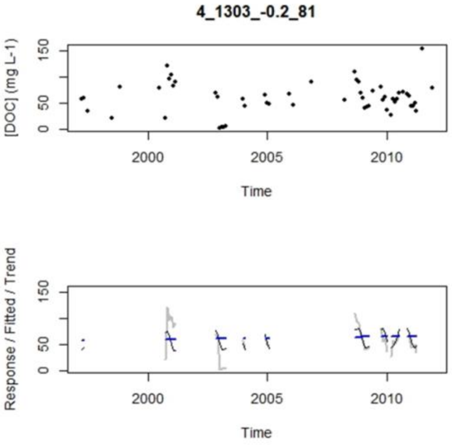
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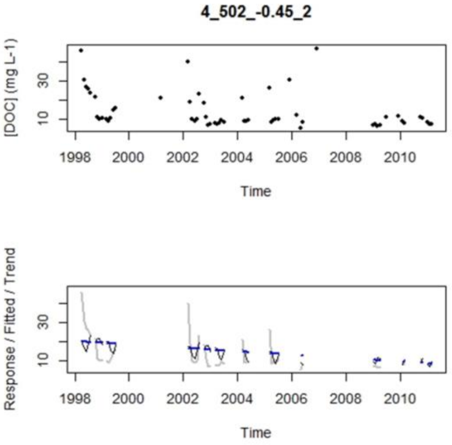
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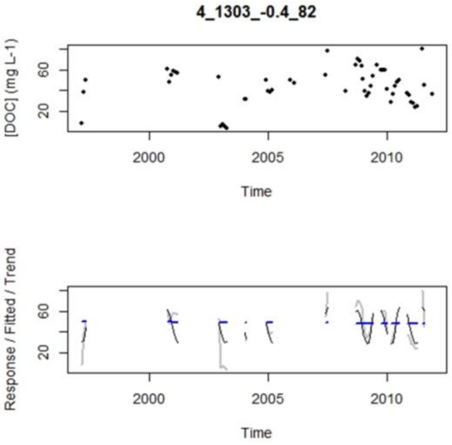
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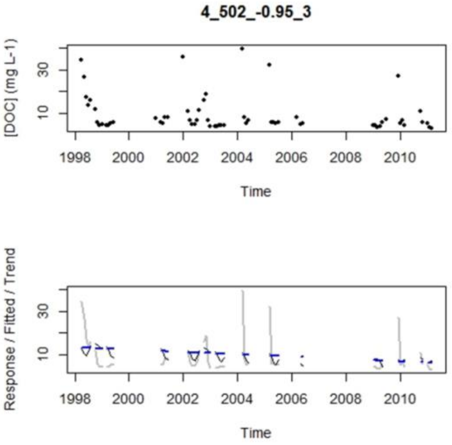
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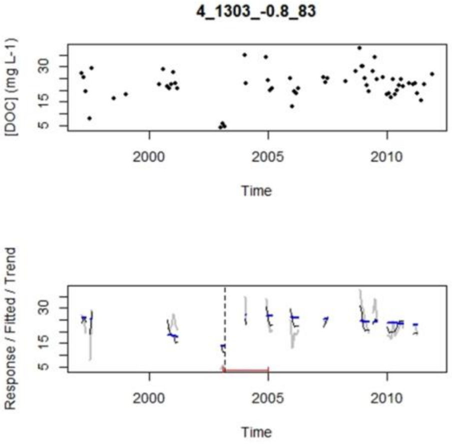
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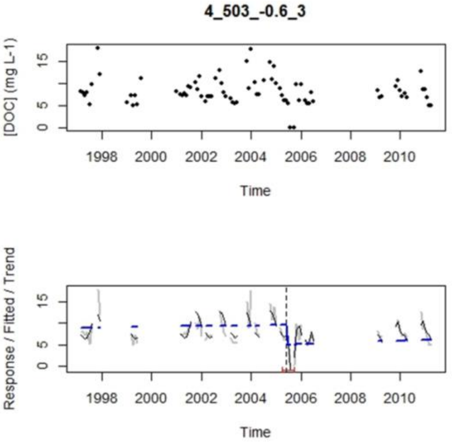
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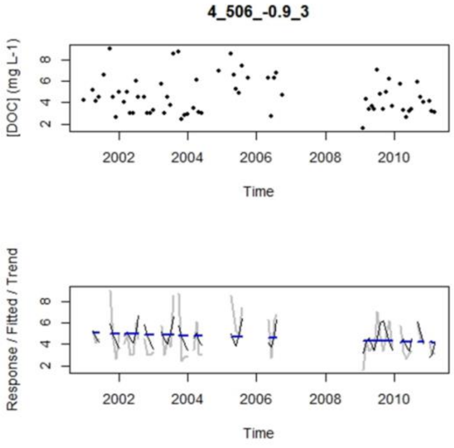
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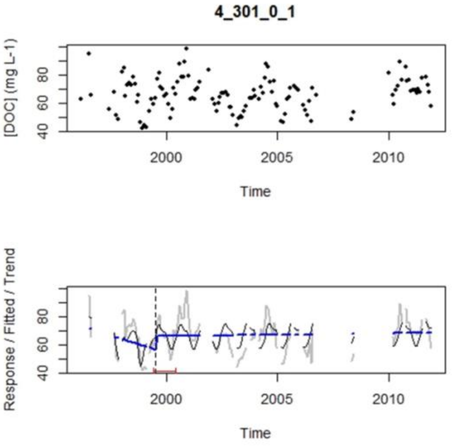
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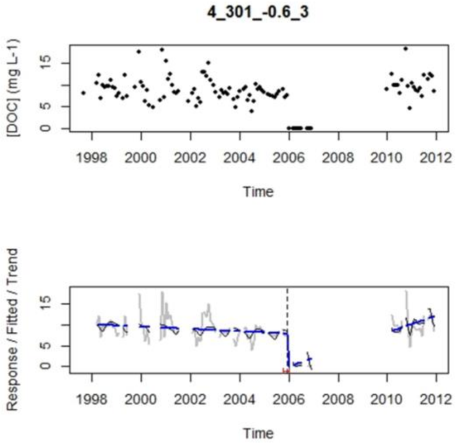
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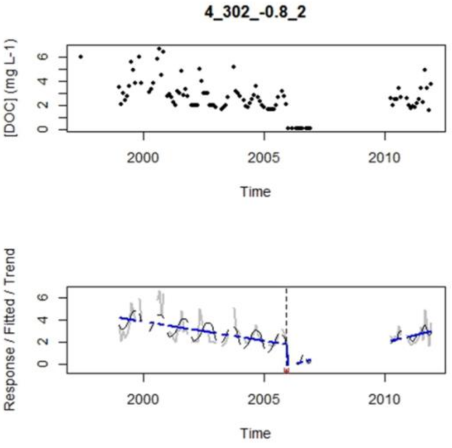
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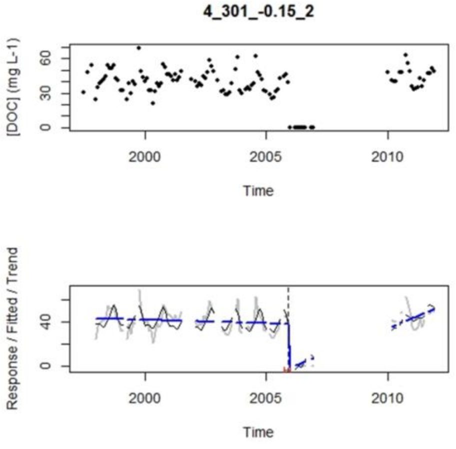
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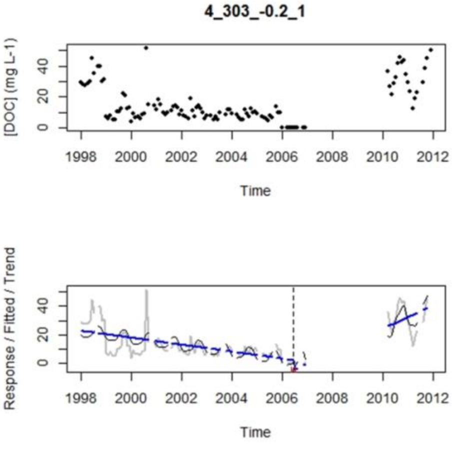
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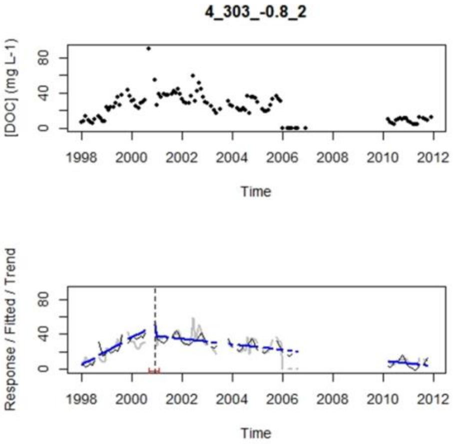
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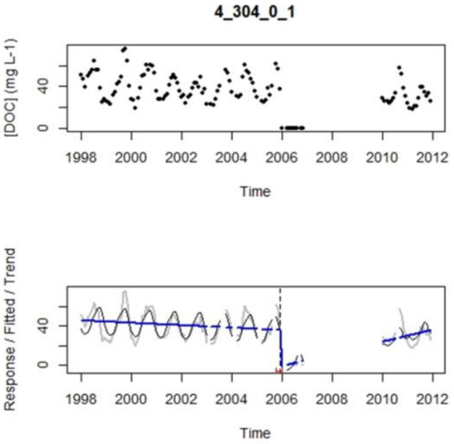
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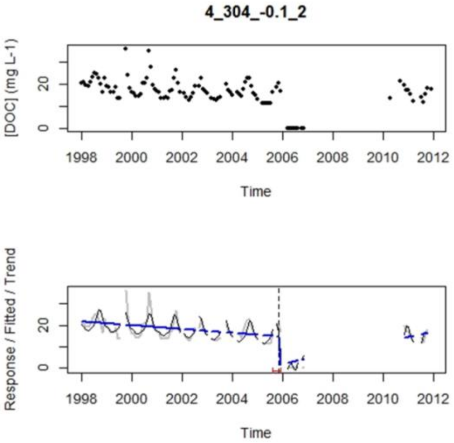
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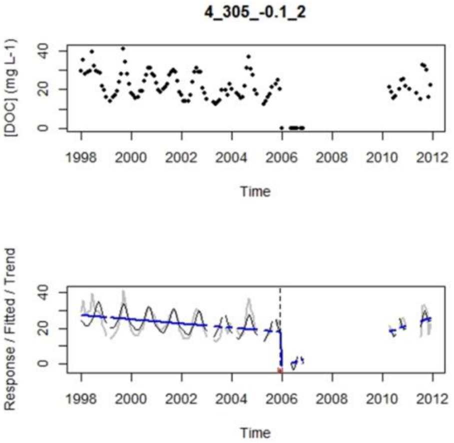
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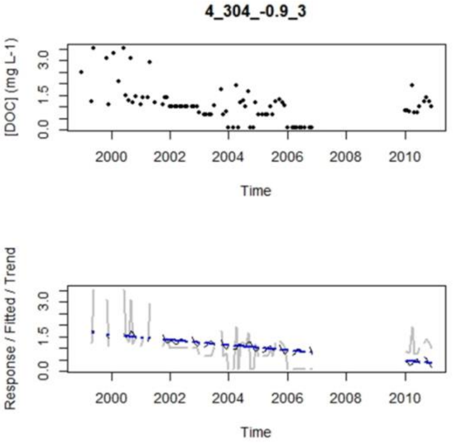
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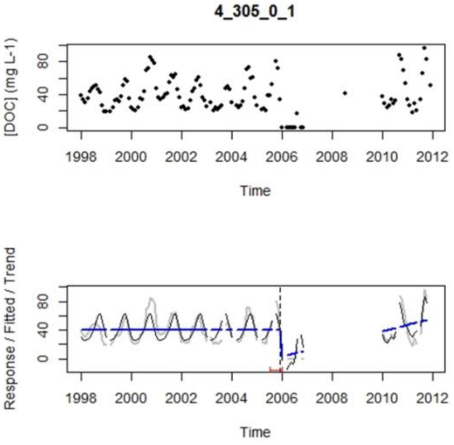
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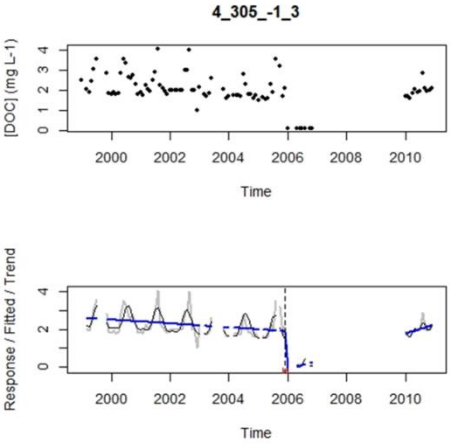
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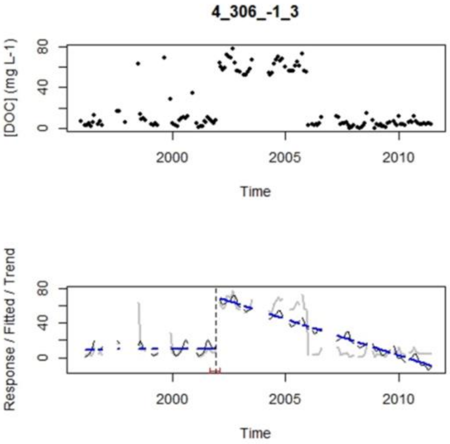
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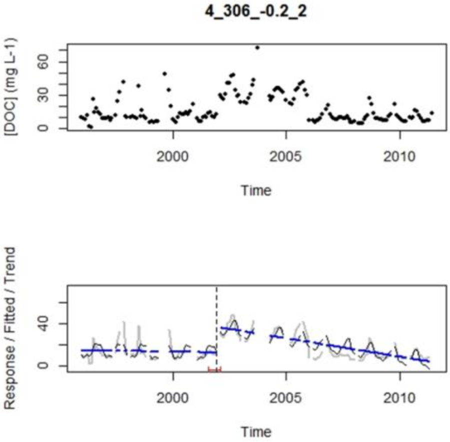
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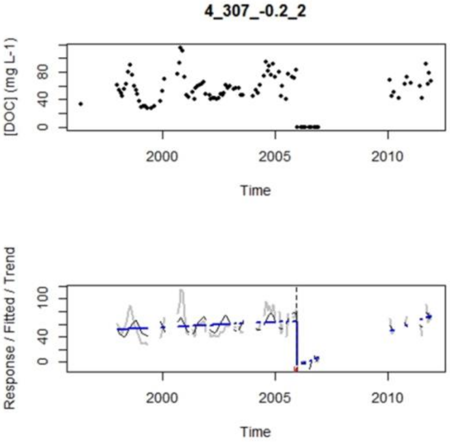
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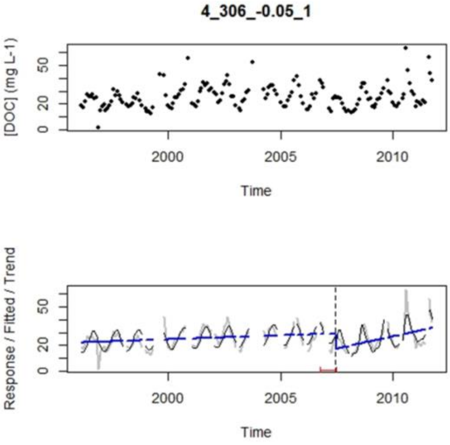
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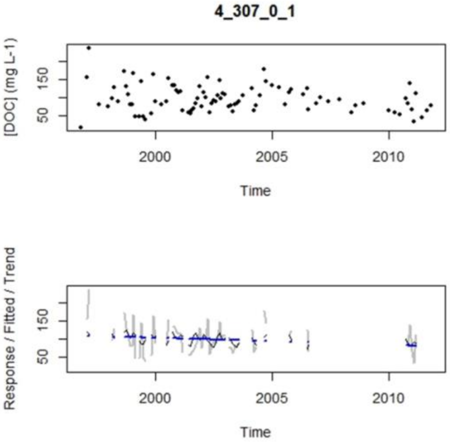
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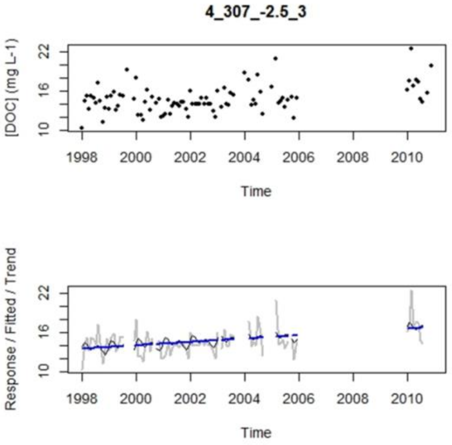
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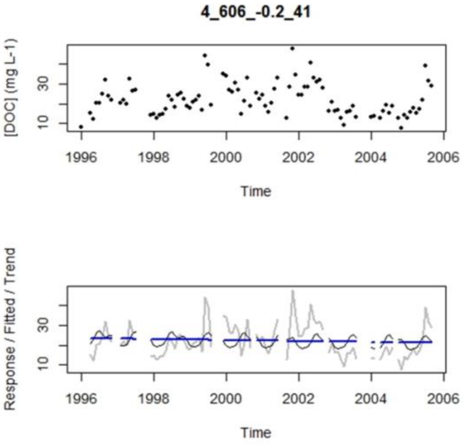
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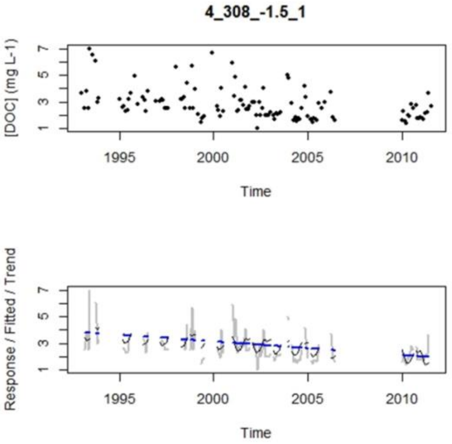
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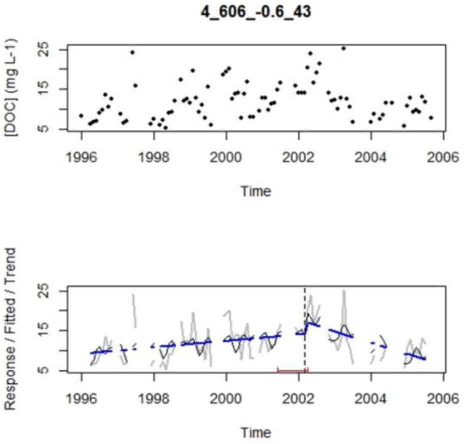
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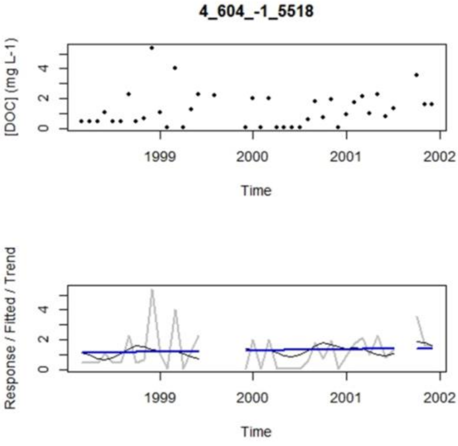
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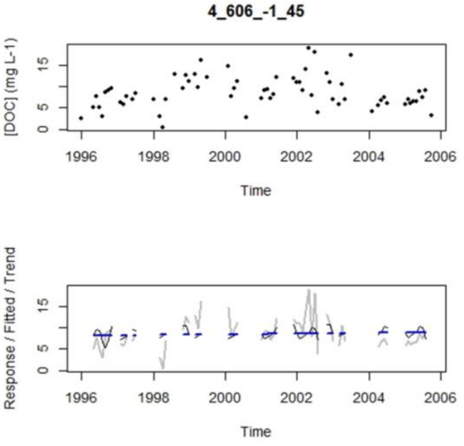
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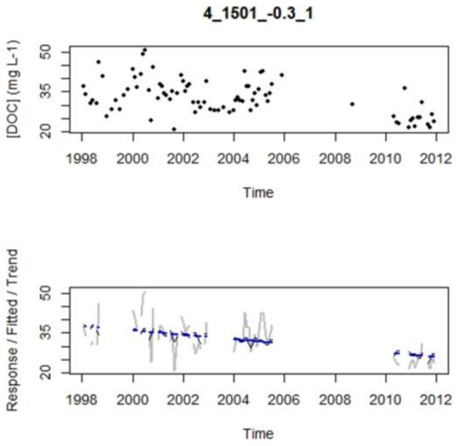
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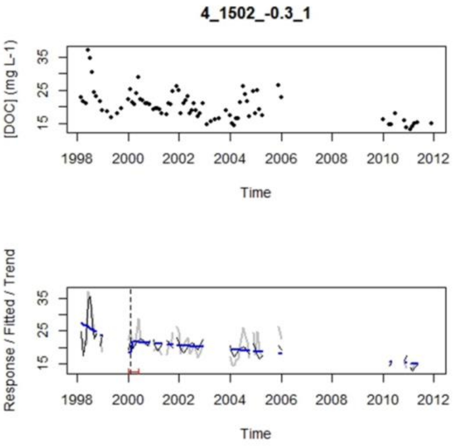
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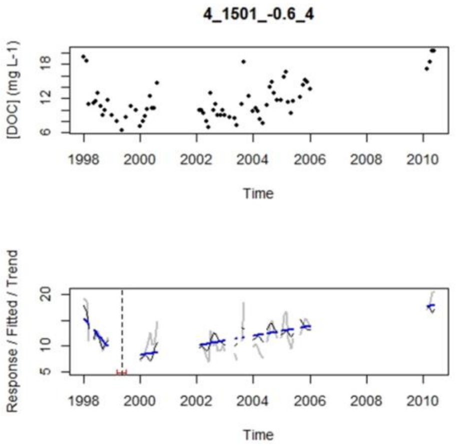
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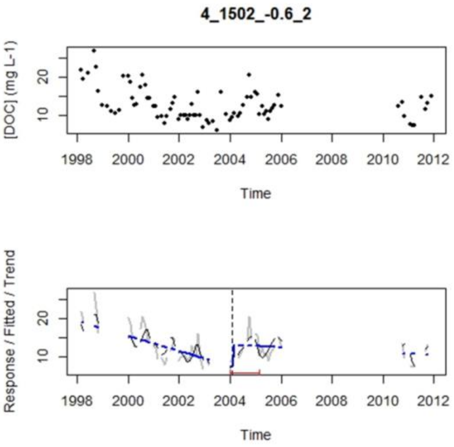
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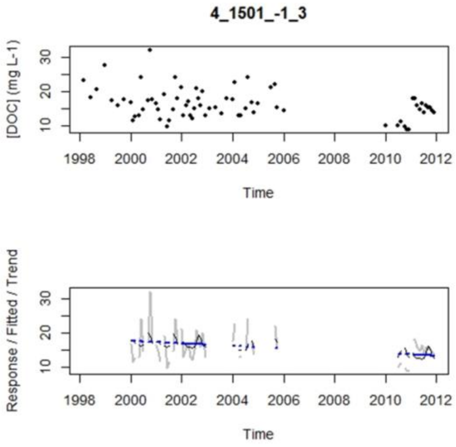
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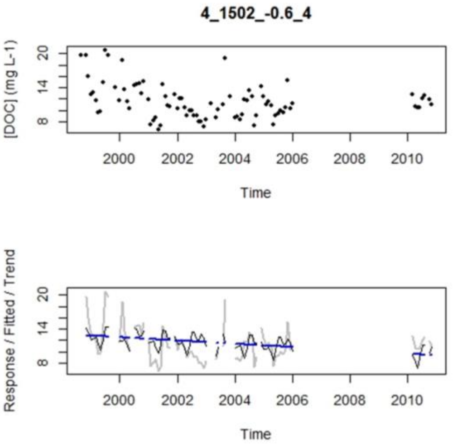
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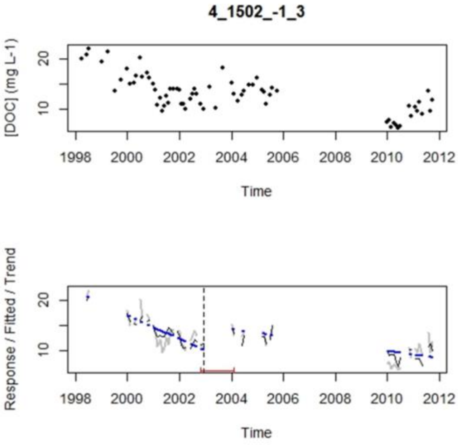
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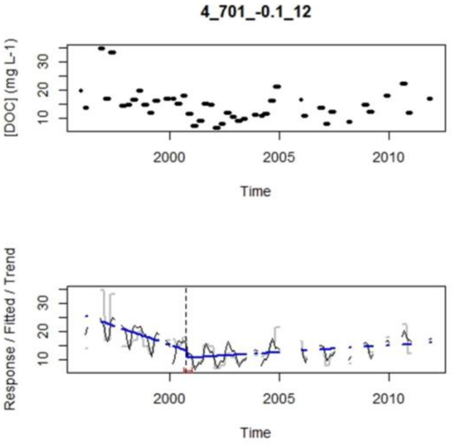
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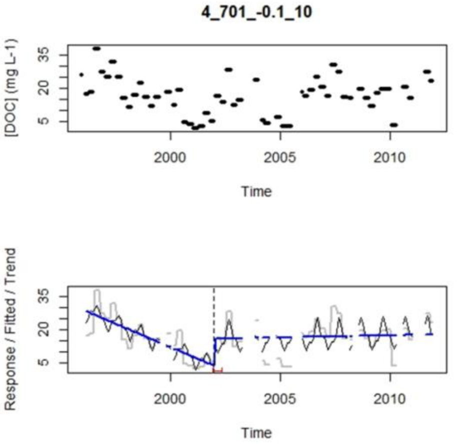
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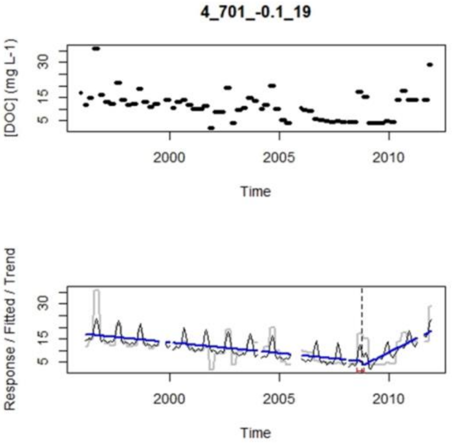
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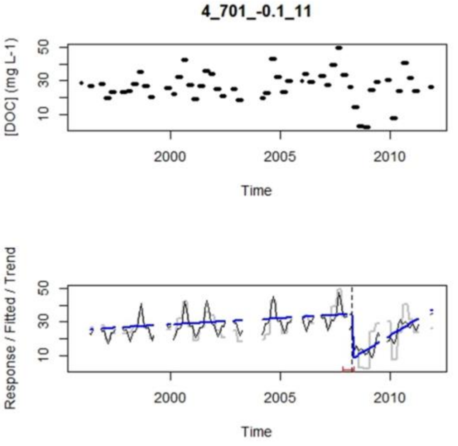
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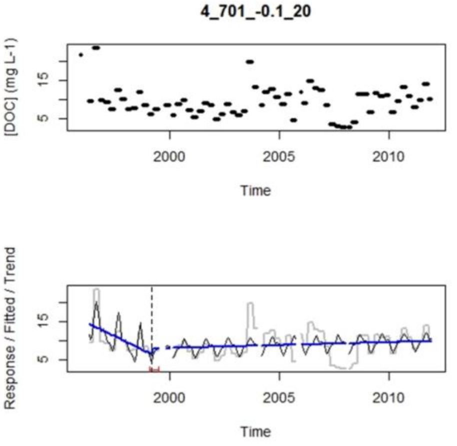
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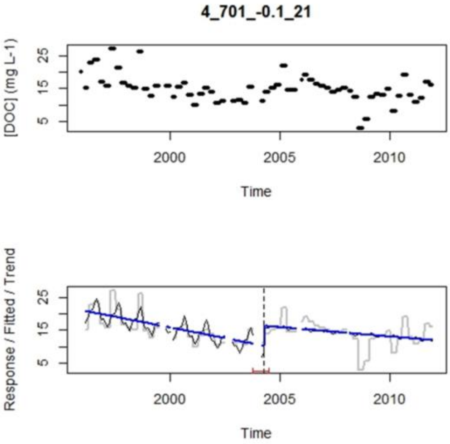
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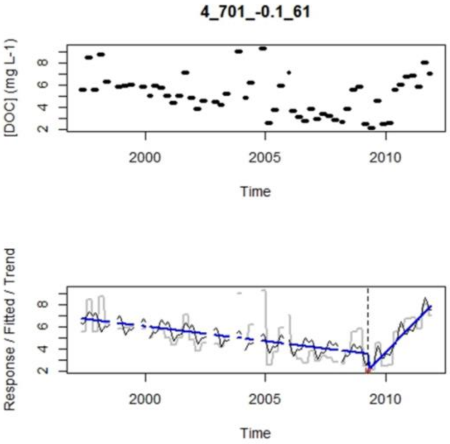
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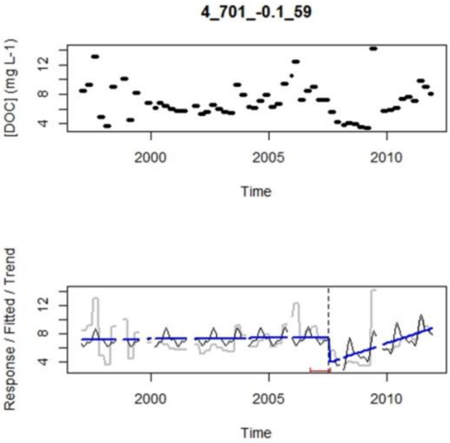
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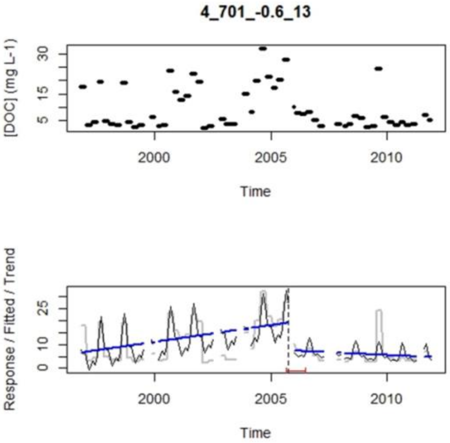
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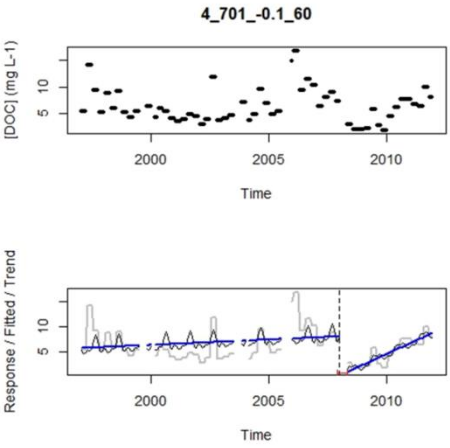
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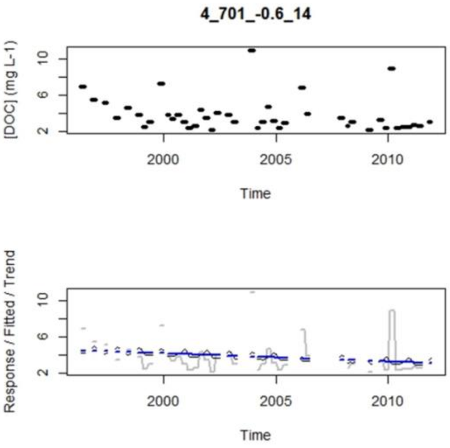
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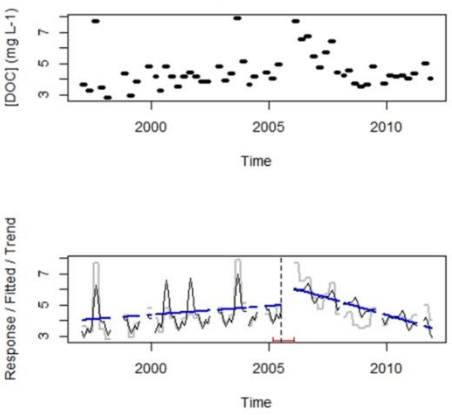

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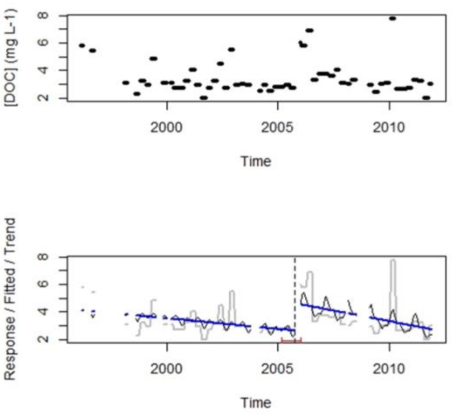

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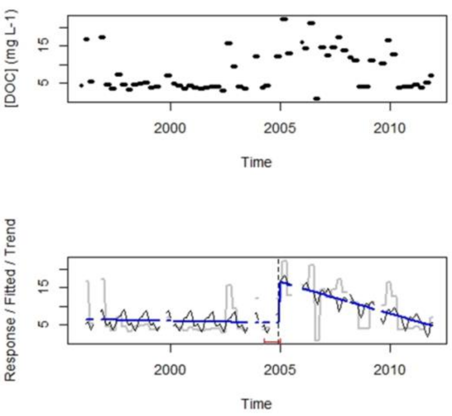

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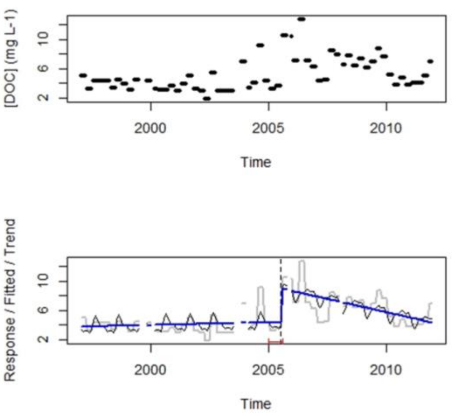

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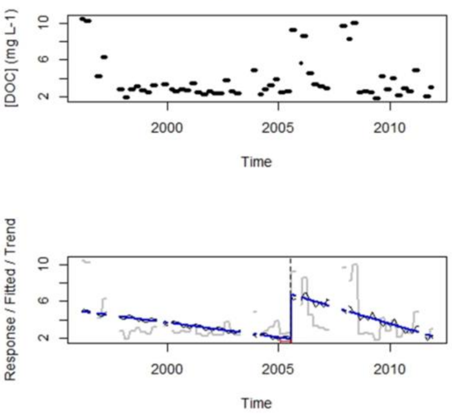

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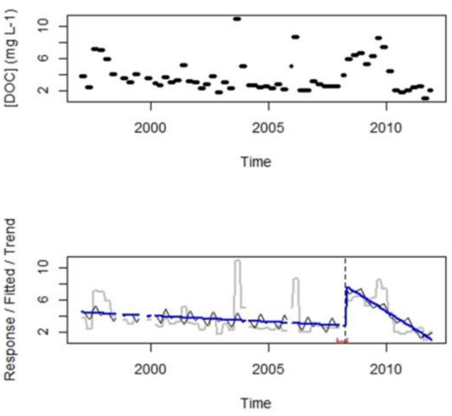

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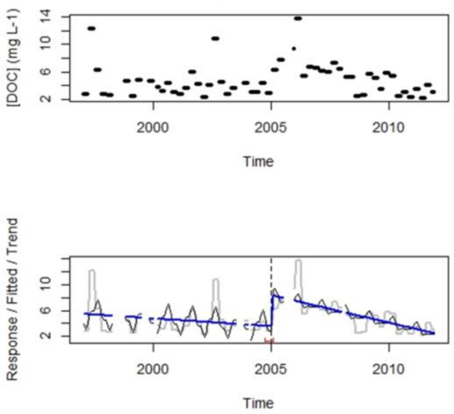

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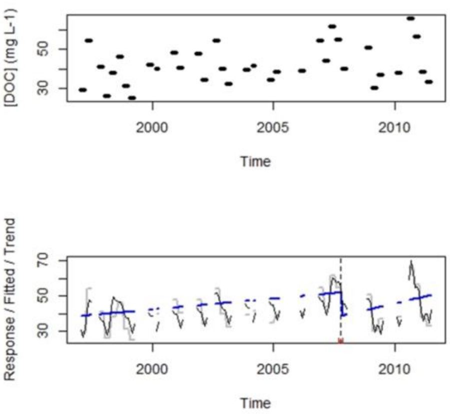

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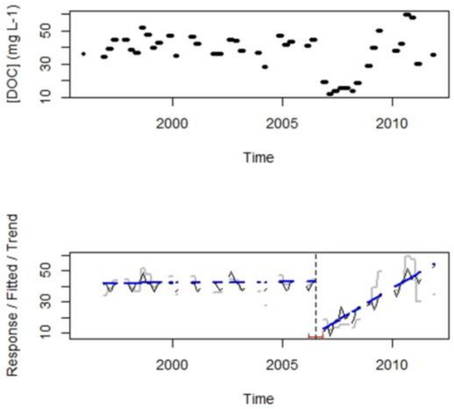

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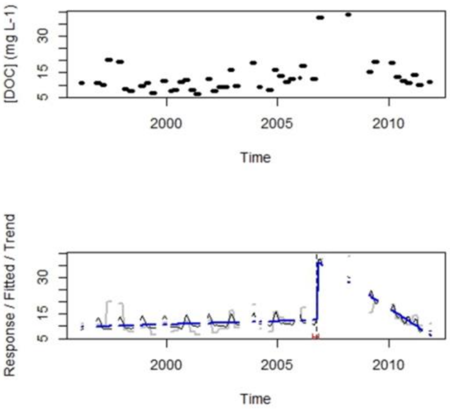

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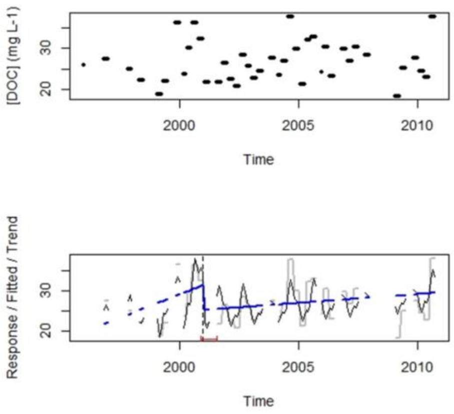

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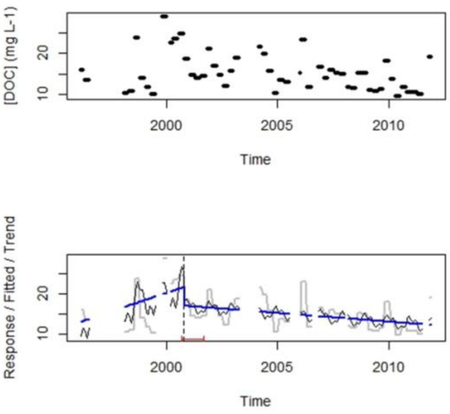

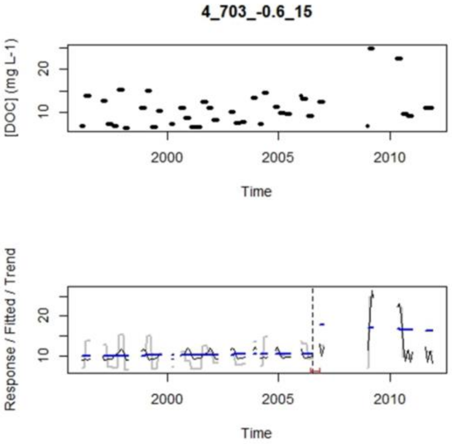
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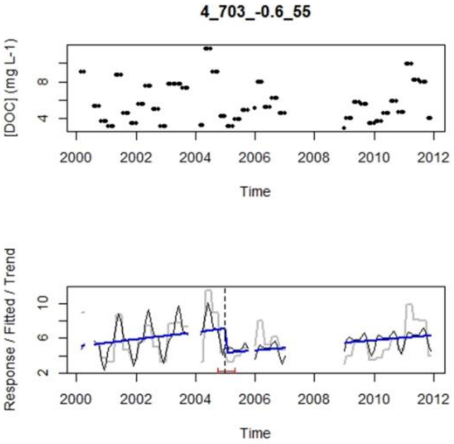
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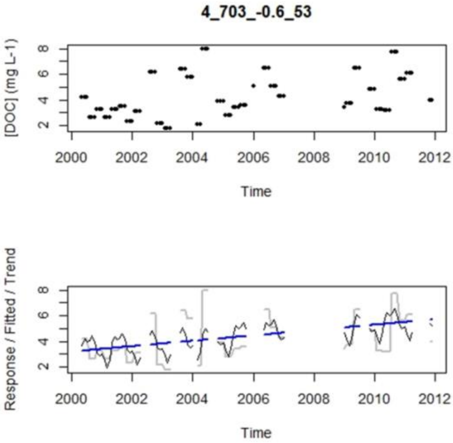
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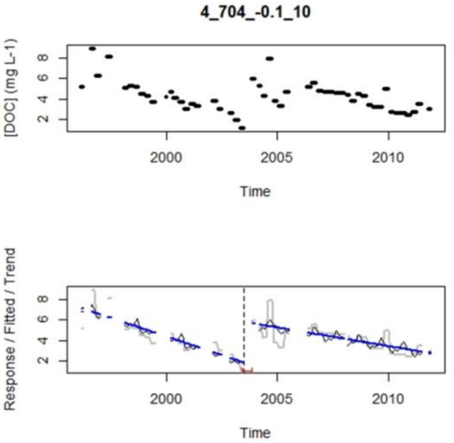
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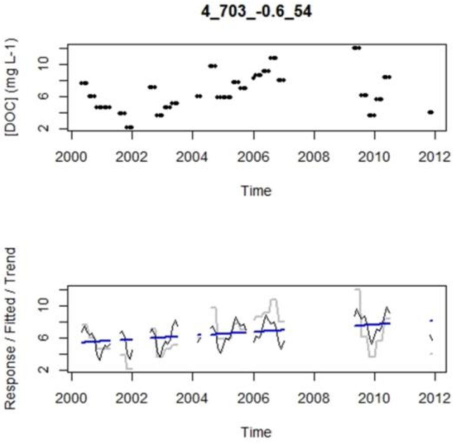
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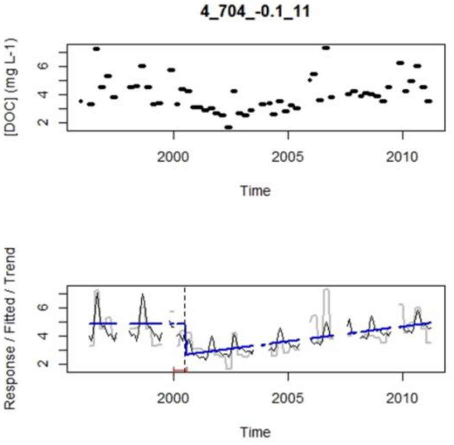
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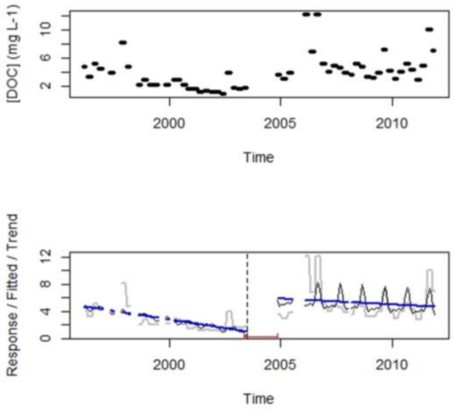
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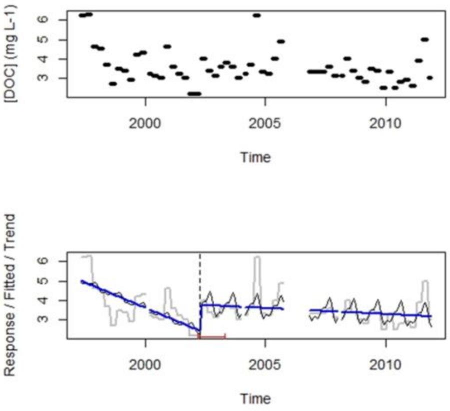
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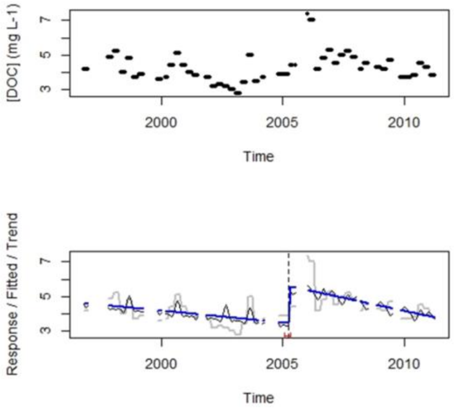
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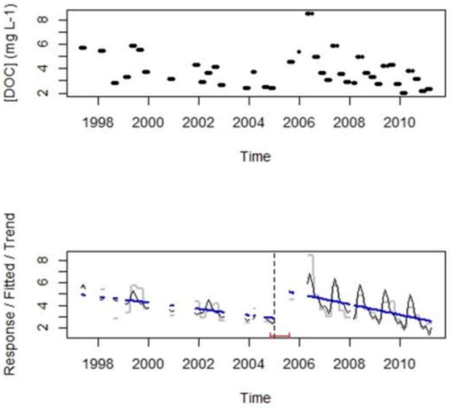
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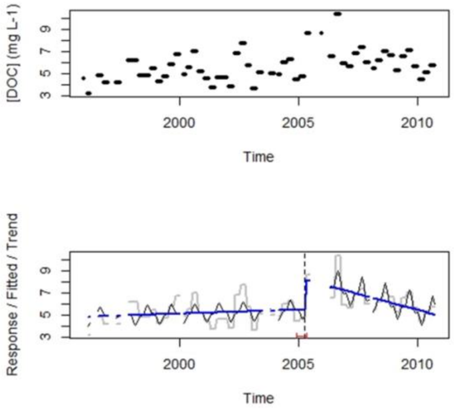
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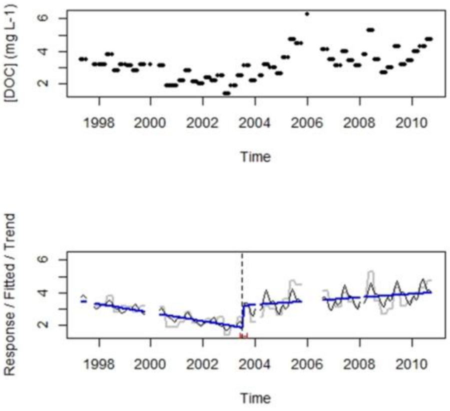
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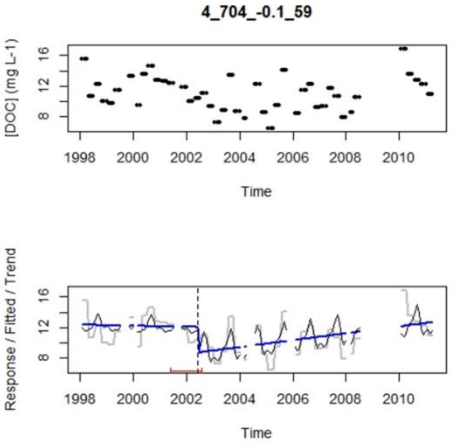
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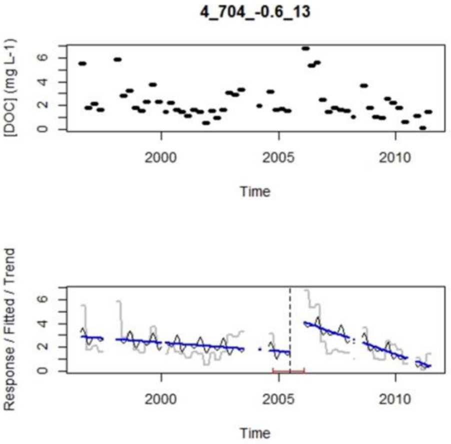
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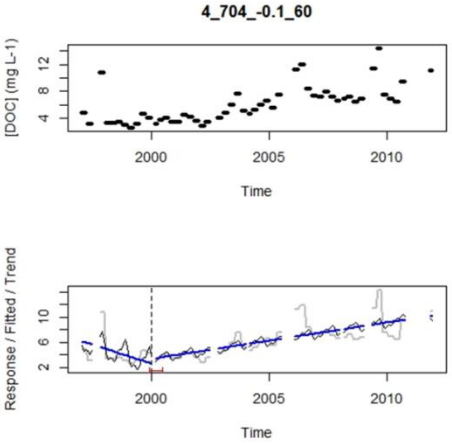
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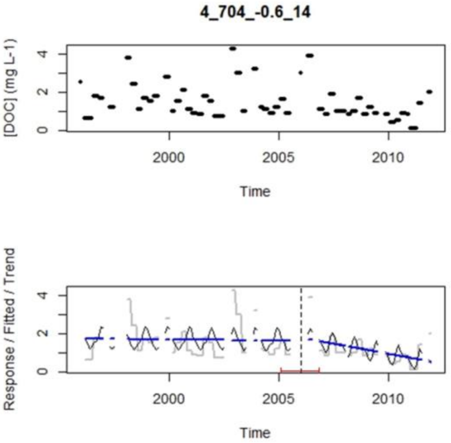
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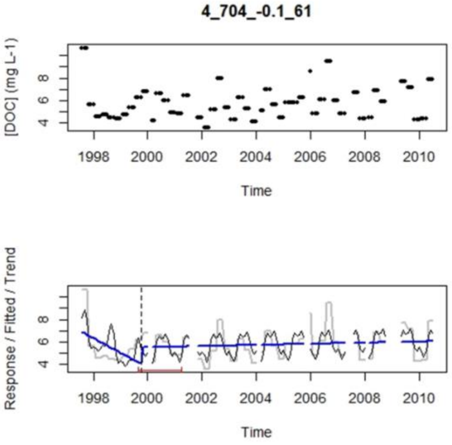
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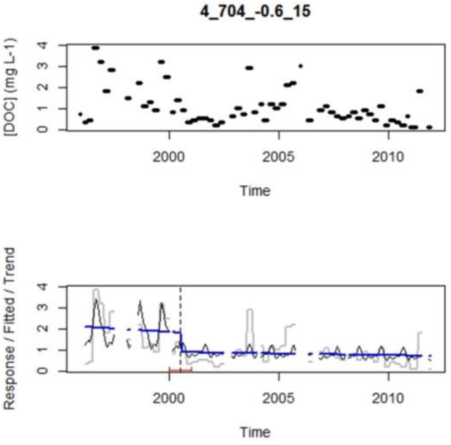
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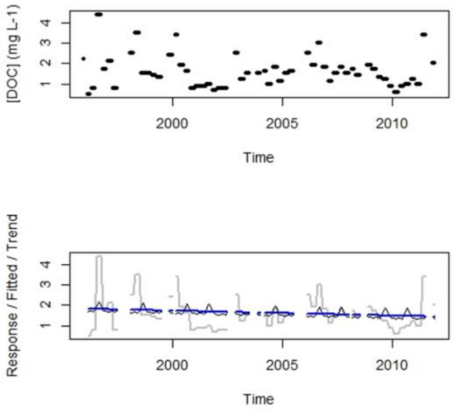

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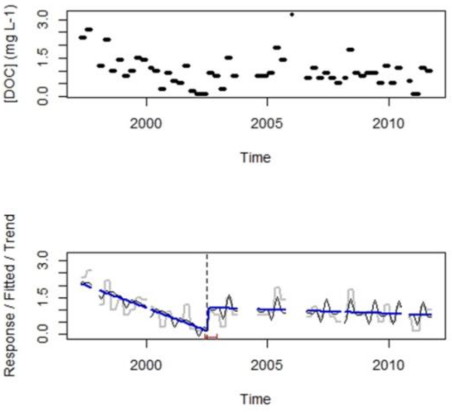

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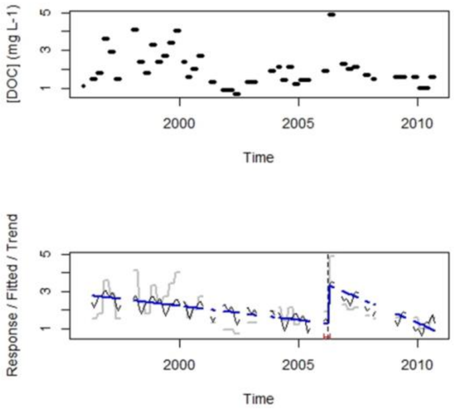

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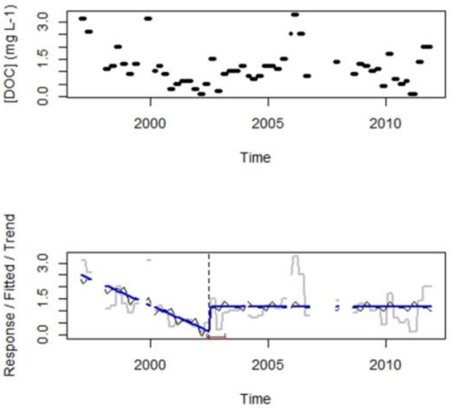

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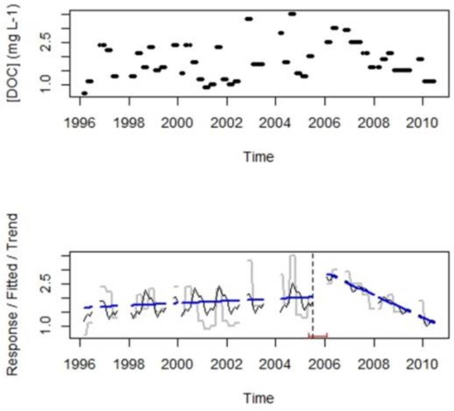

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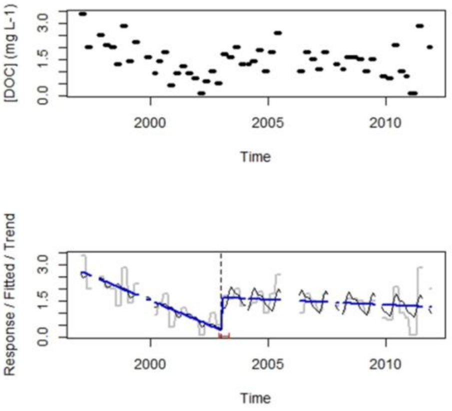

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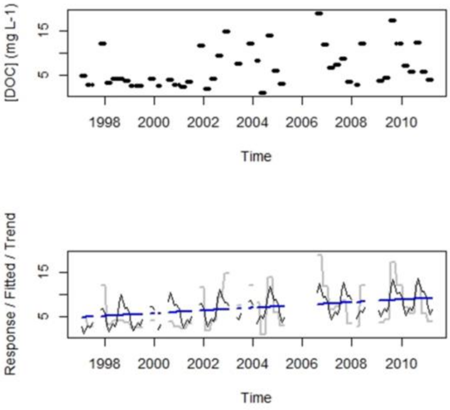

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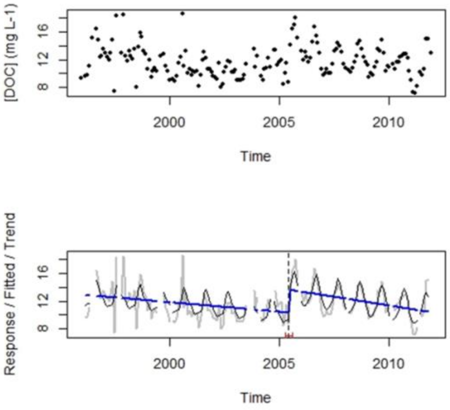

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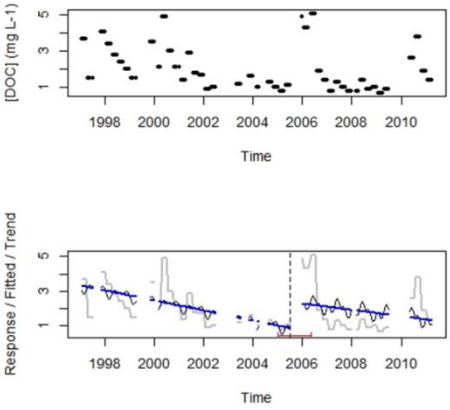

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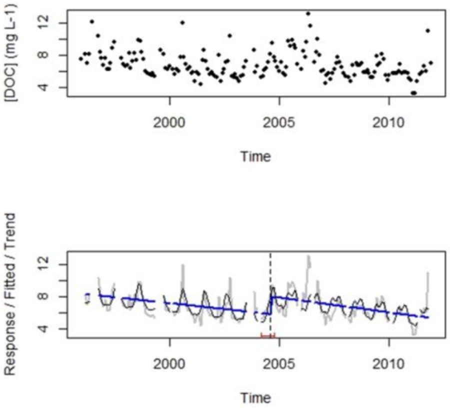

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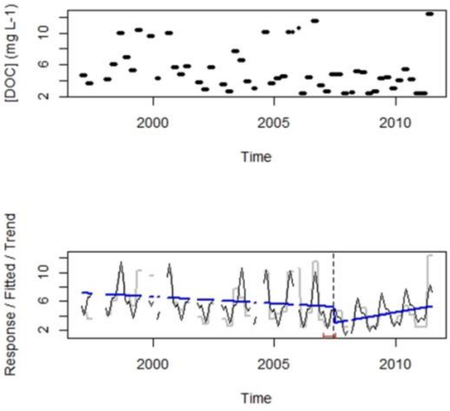

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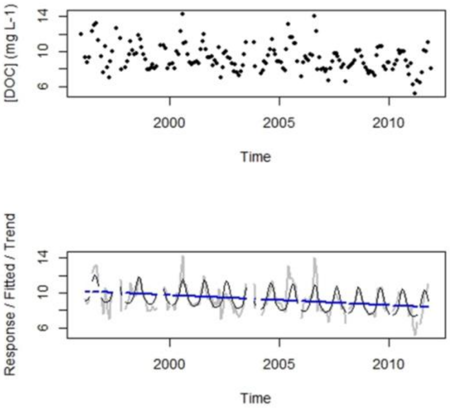

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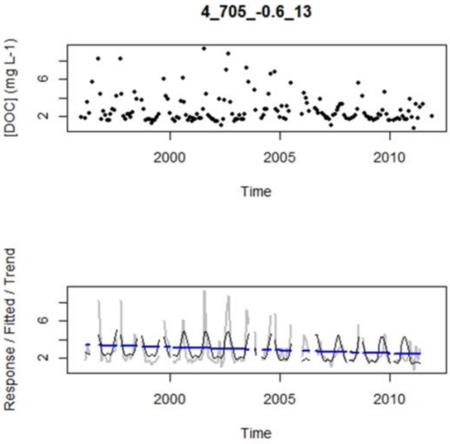
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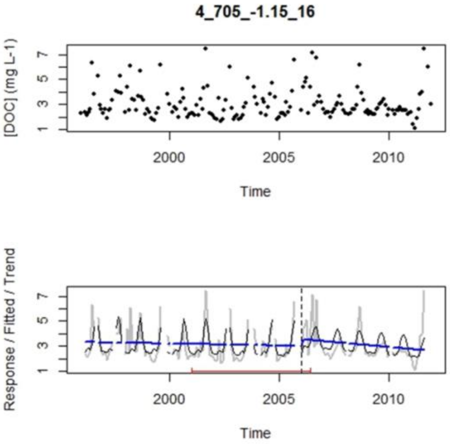
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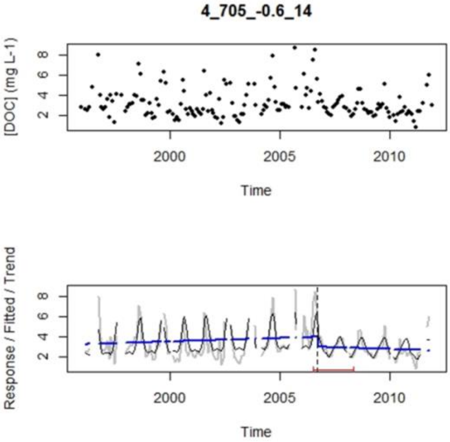
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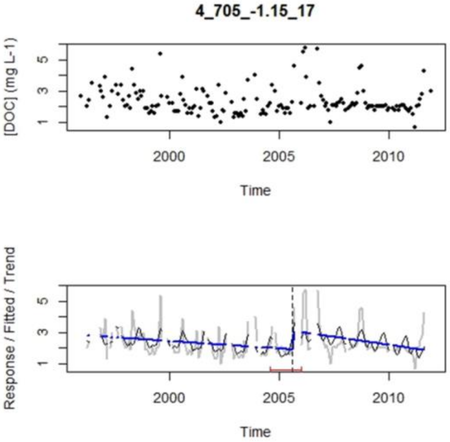
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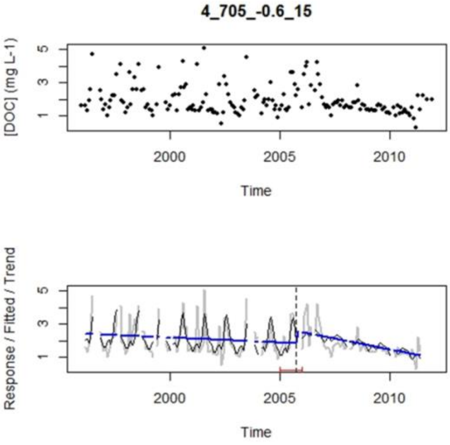
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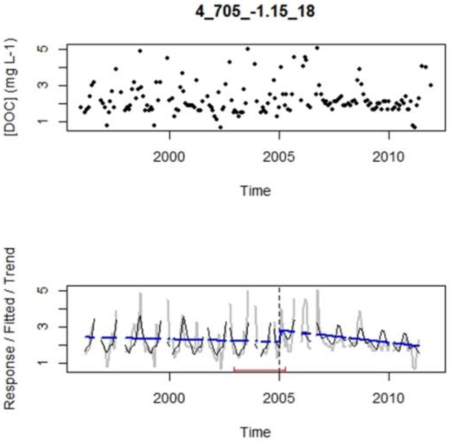
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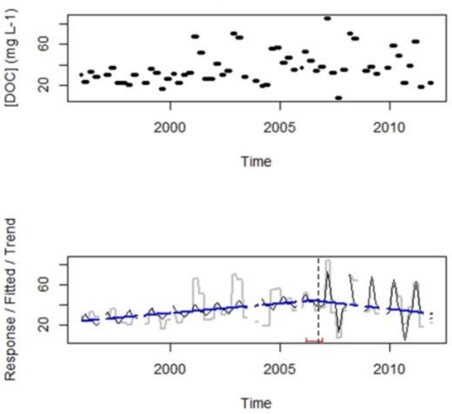

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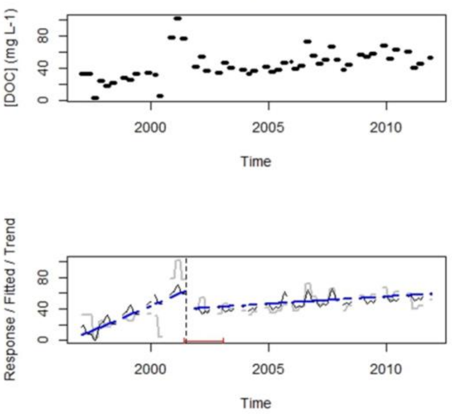

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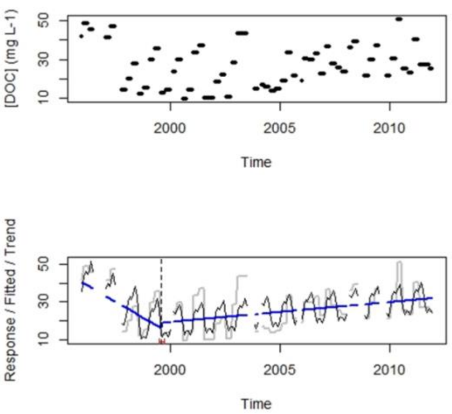

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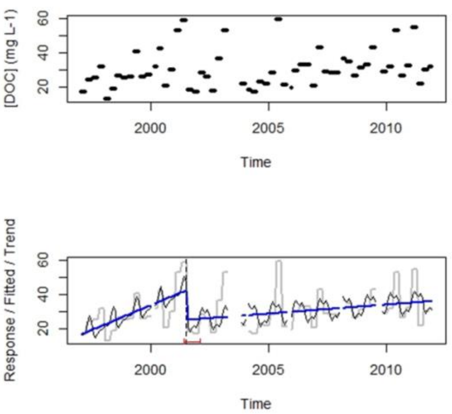

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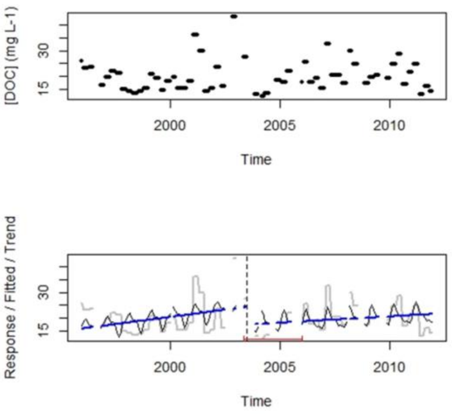

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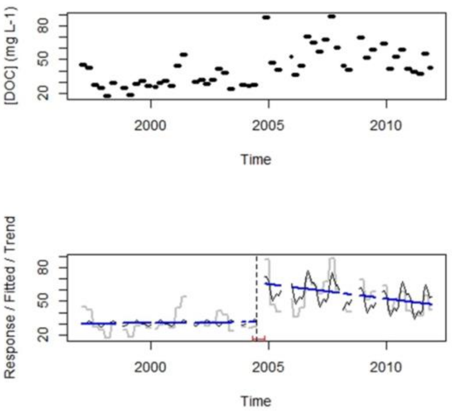

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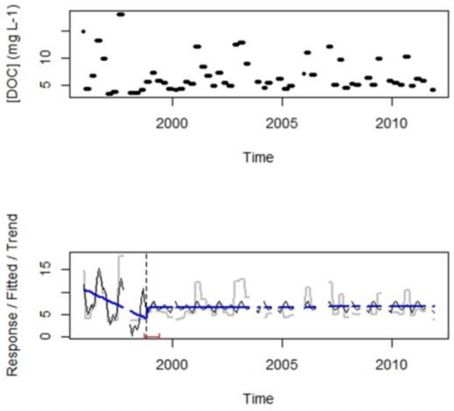

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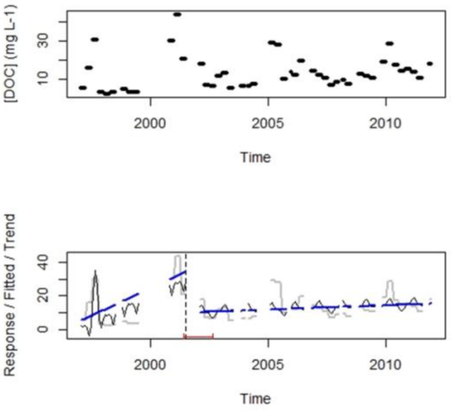

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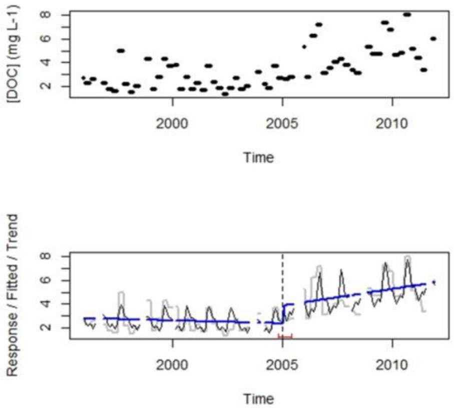

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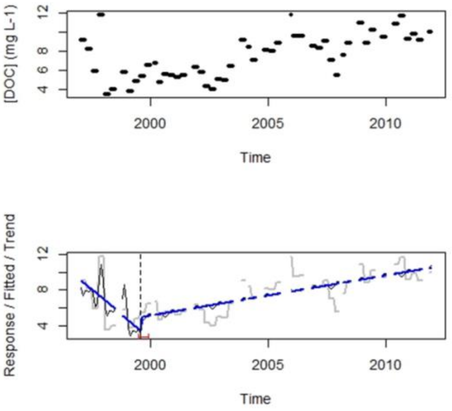

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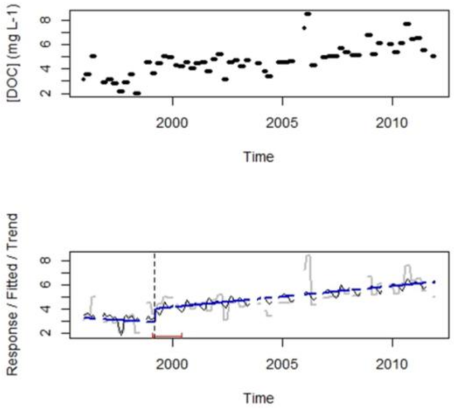

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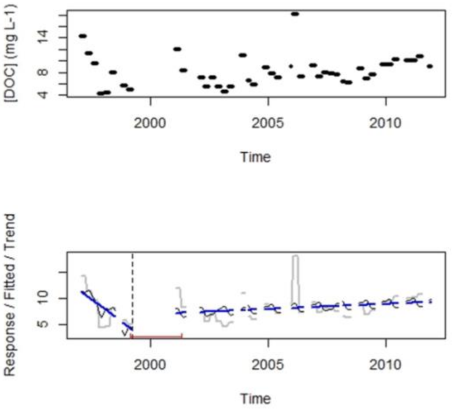

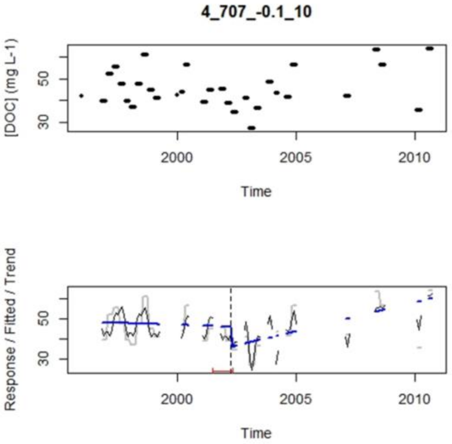
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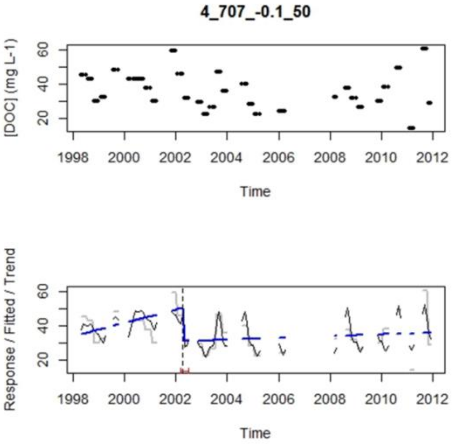
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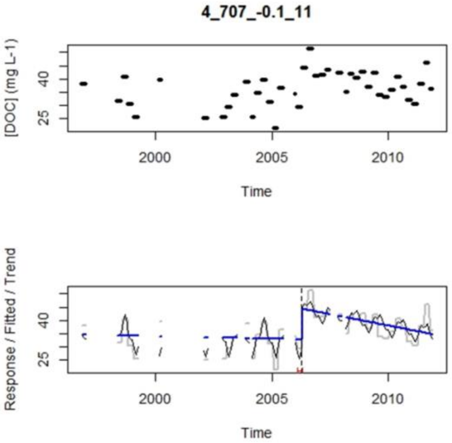
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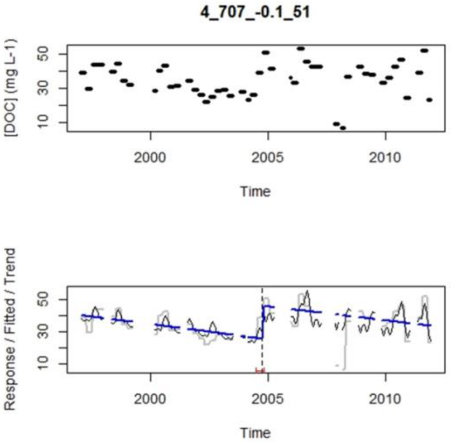
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Time
Response / Fitted / Trend
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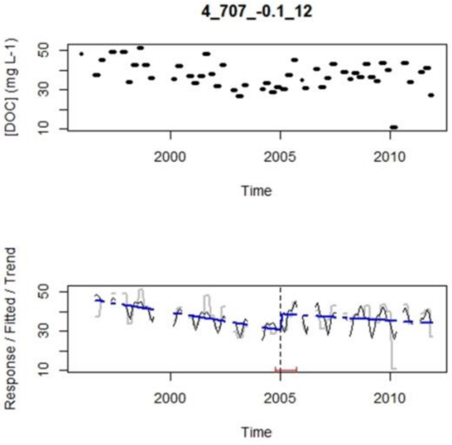
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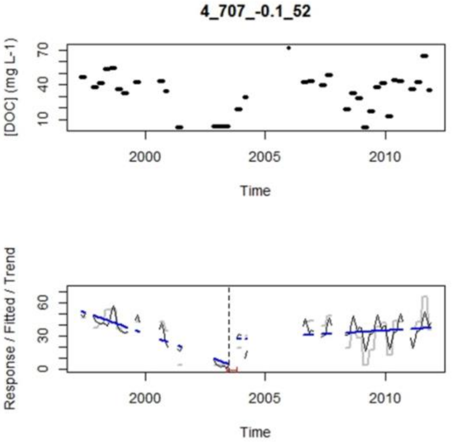
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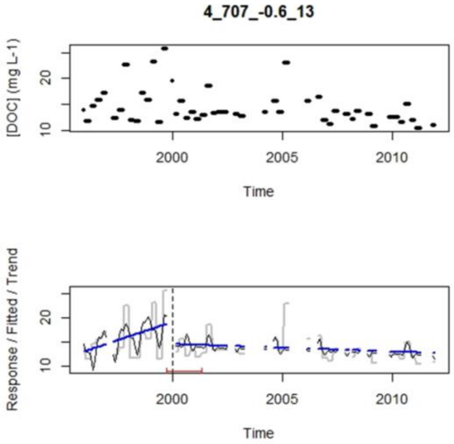
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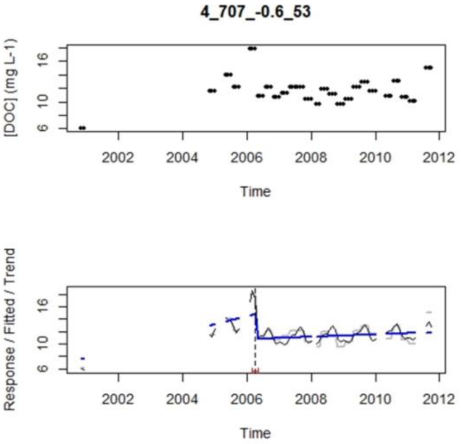
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Response / Fitted / Trend
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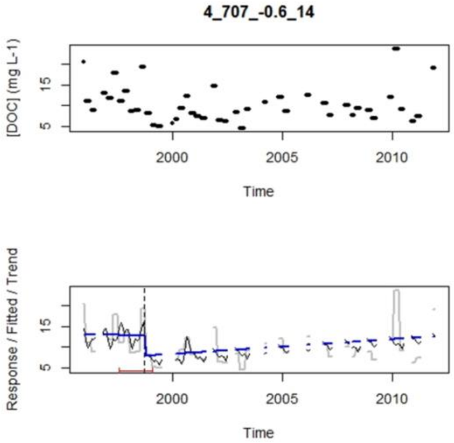
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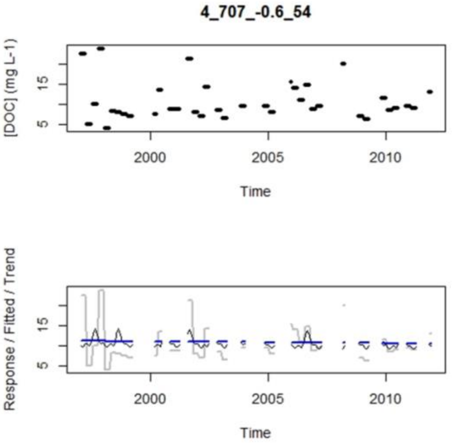
Time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Response / Fitted / Trend
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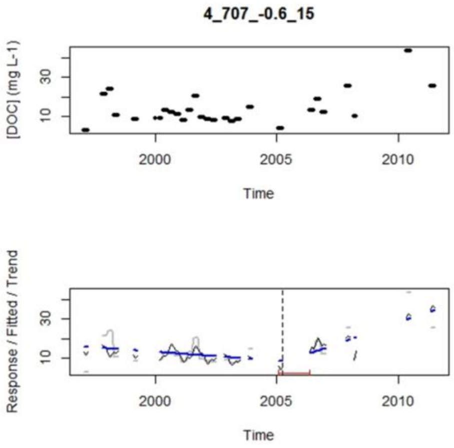
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Response / Fitted / Trend
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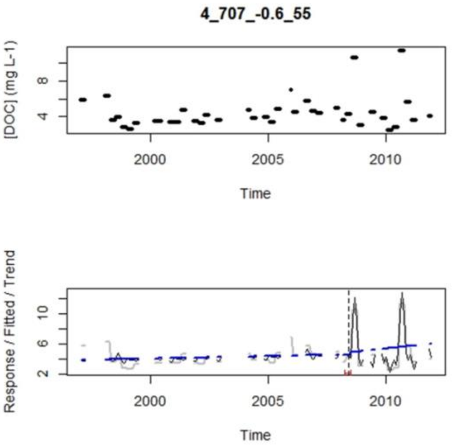
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Response / Fitted / Trend
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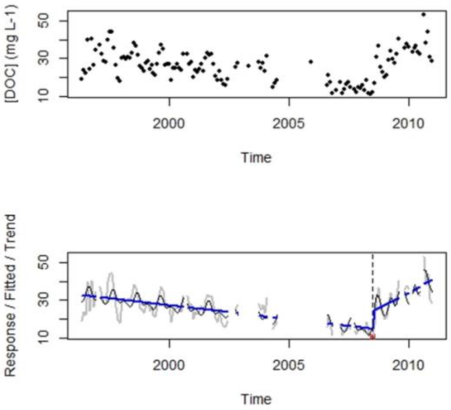
Time

4_101_-0.05_2



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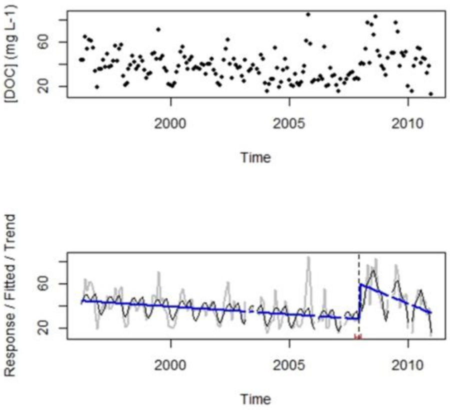

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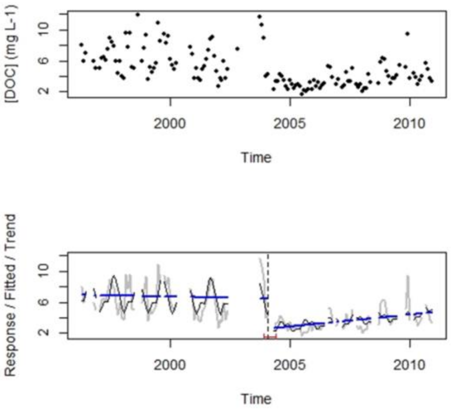
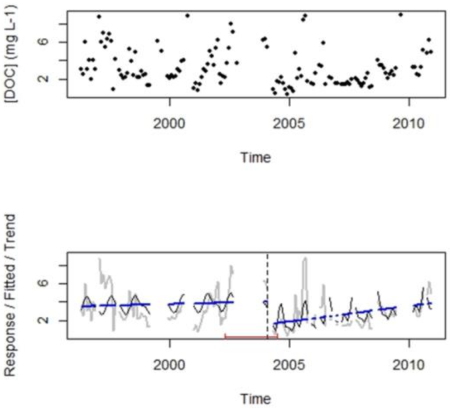


4_101_-1.5_5



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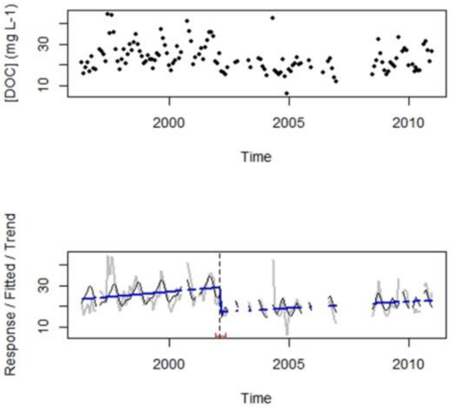

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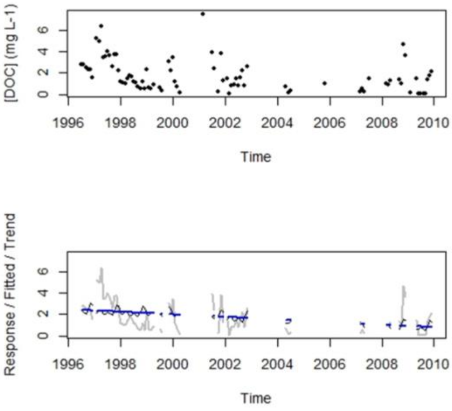

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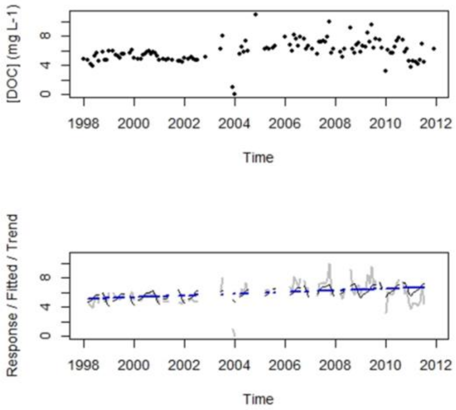

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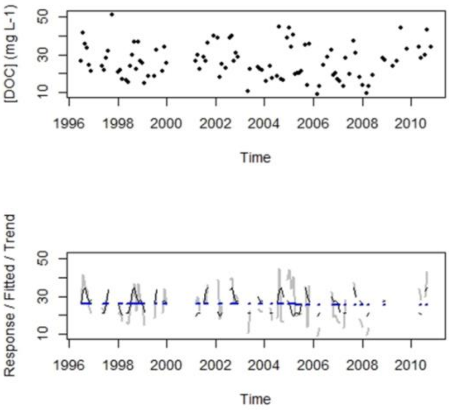

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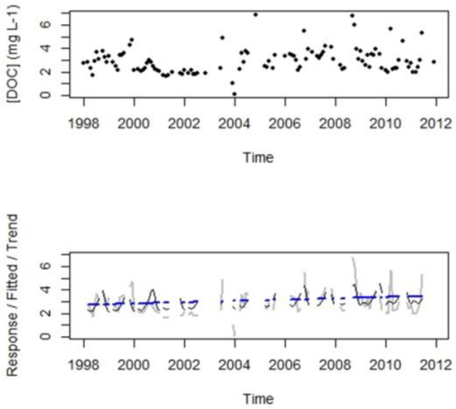

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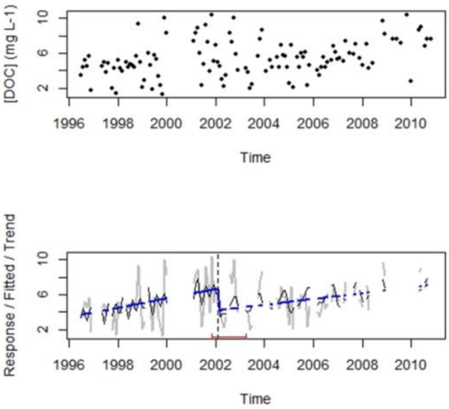

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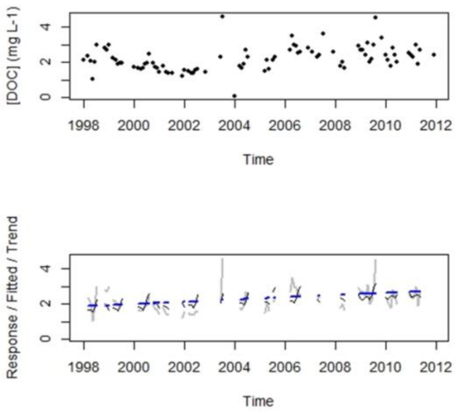

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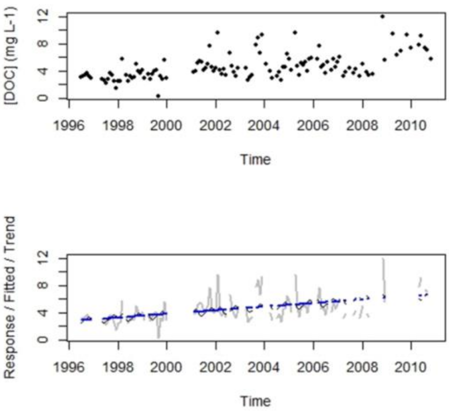

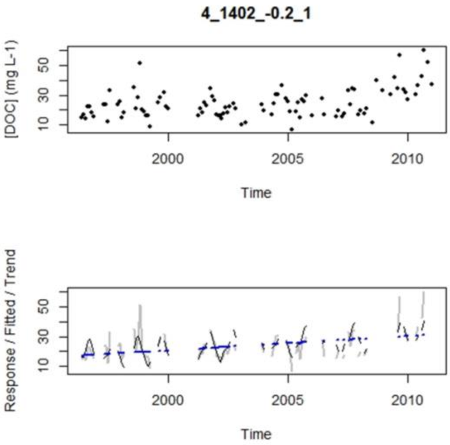
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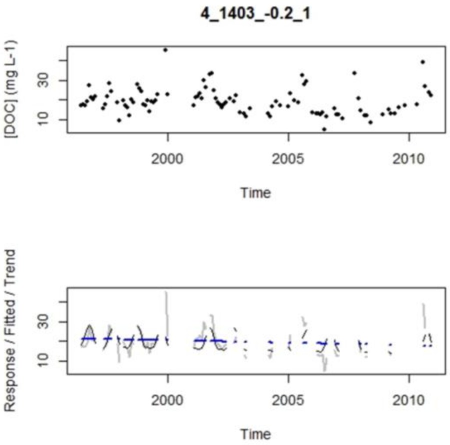
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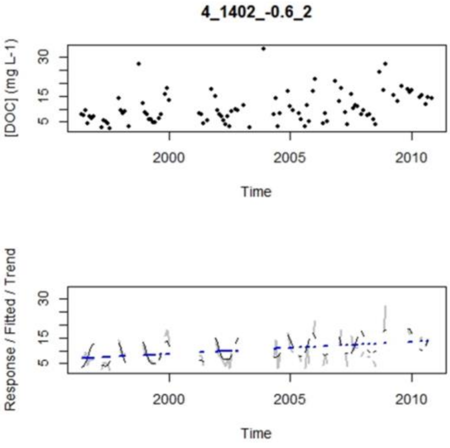
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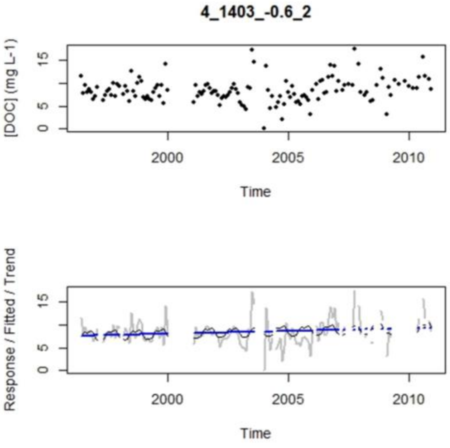
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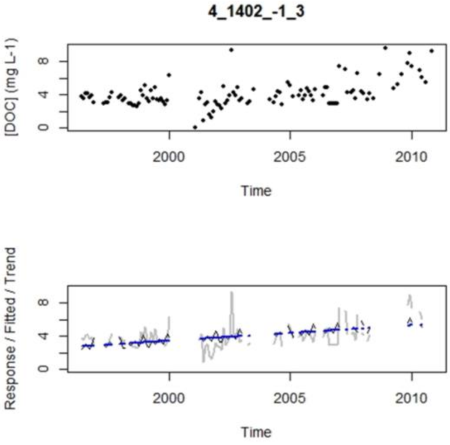
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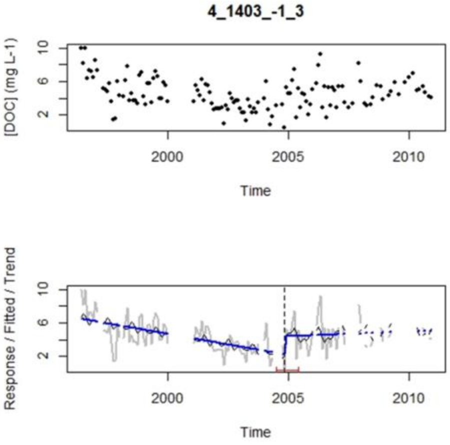
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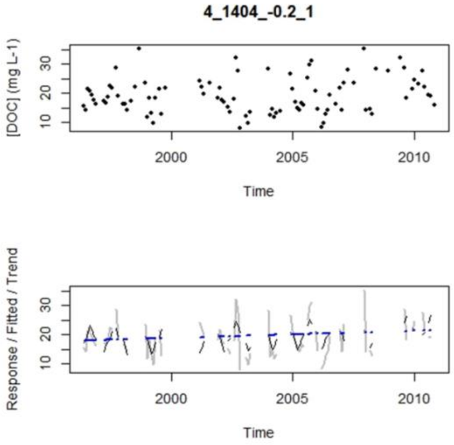
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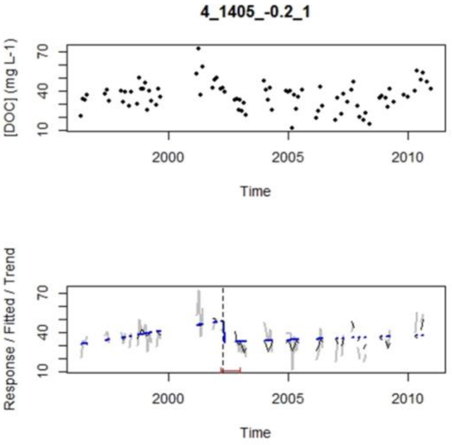
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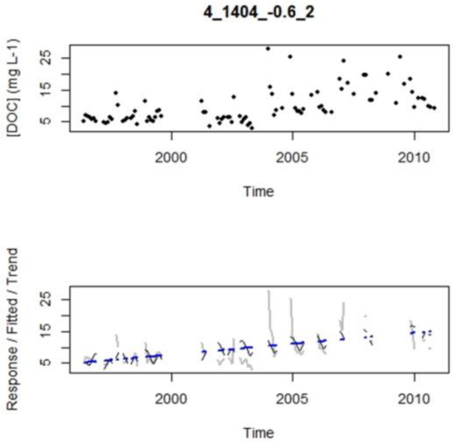
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Response / Fitted / Trend
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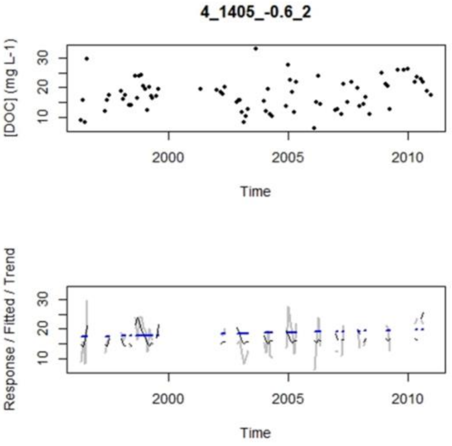
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Response / Fitted / Trend
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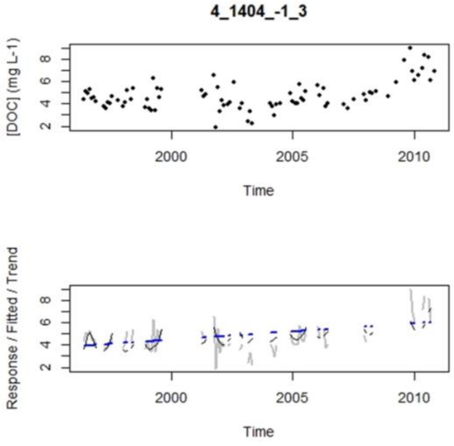
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Response / Fitted / Trend
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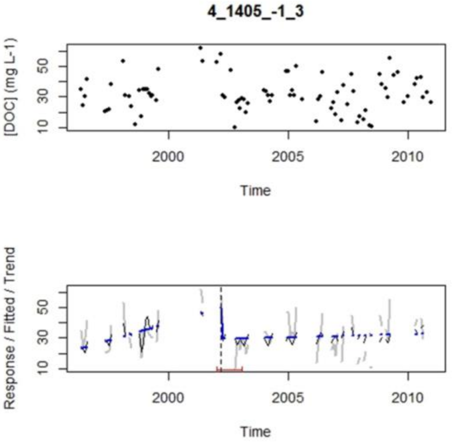
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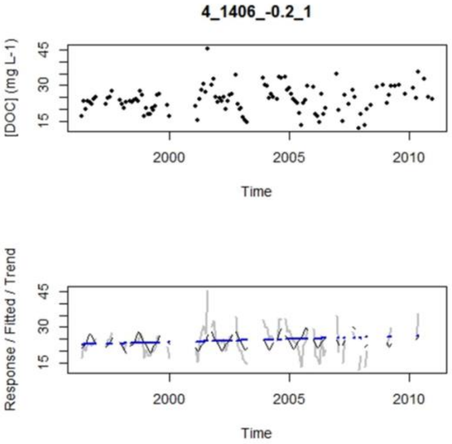
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Response / Fitted / Trend
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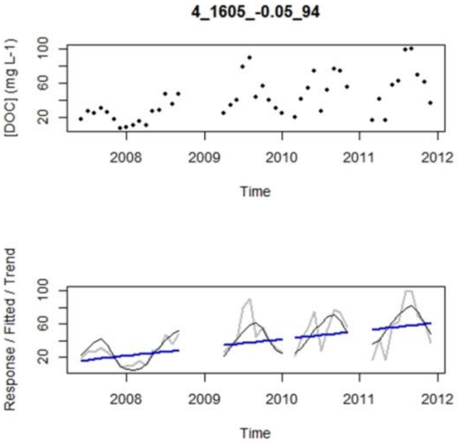
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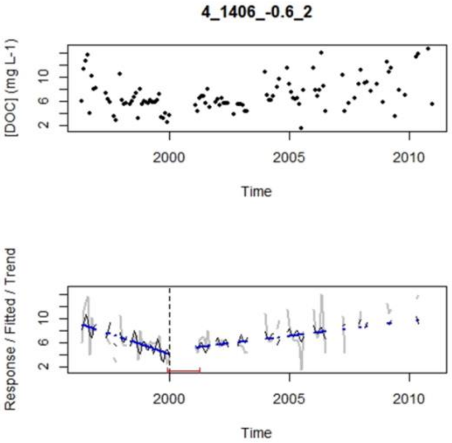
Time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Response / Fitted / Trend
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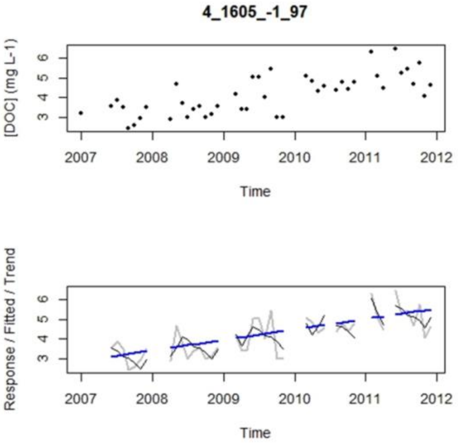
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Response / Fitted / Trend
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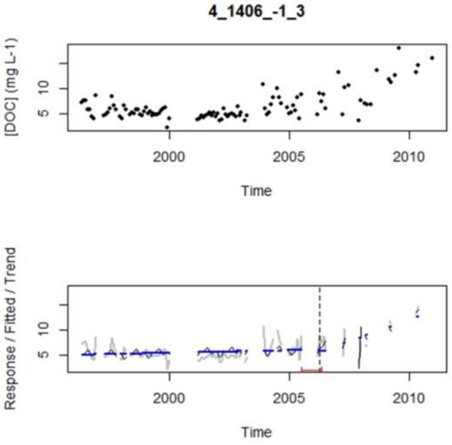
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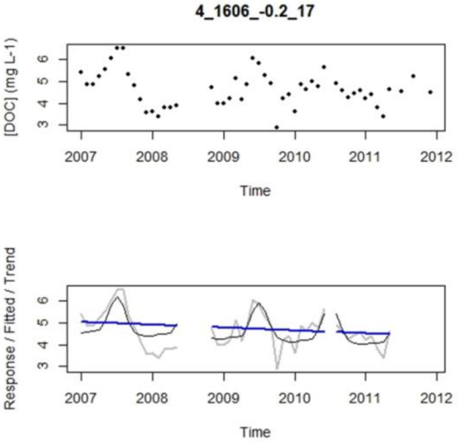
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Time

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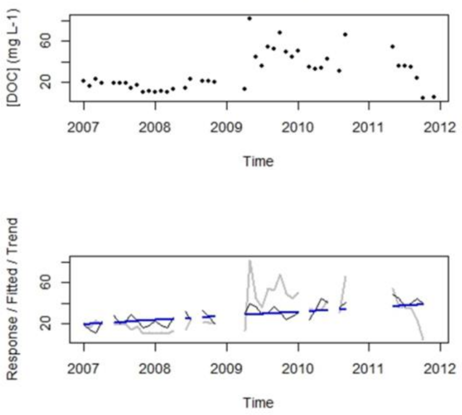

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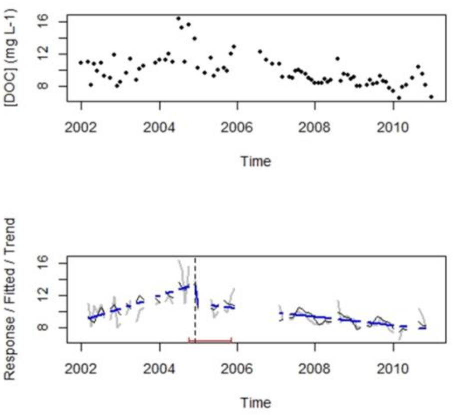

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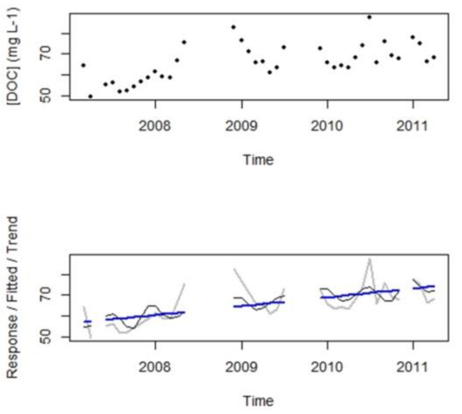
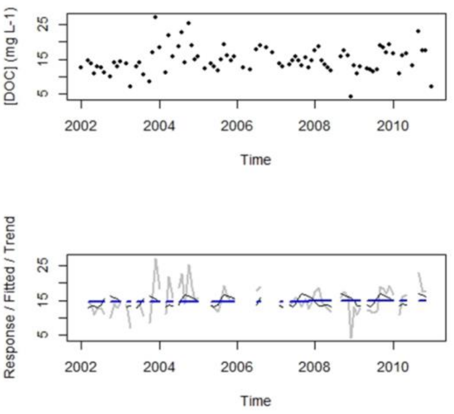
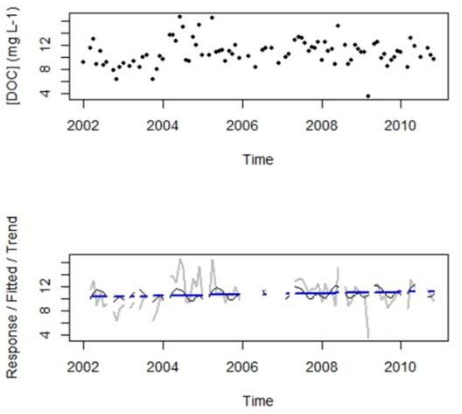


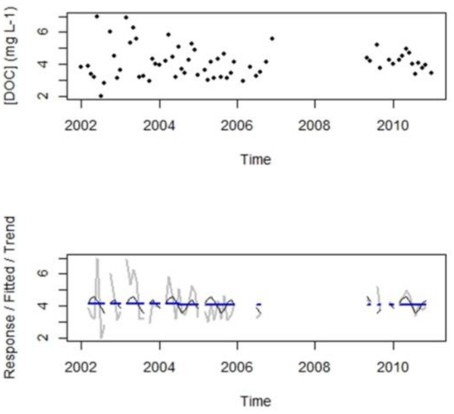
8_11_-0.9_20

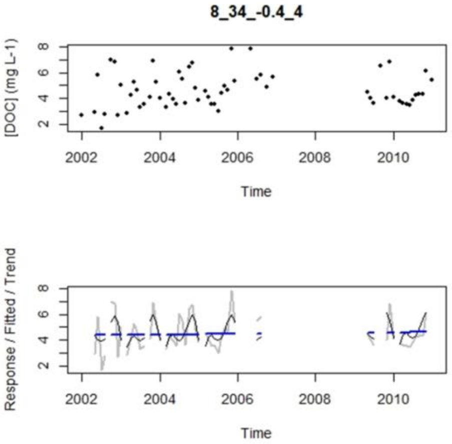


8_11_-0.9_13



8_34_-0.4_1

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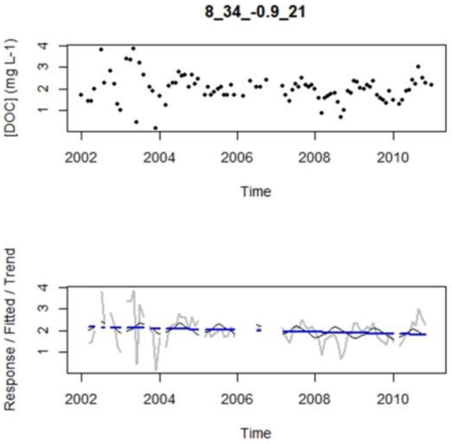
2010
Time
Response / Fitted / Trend
Time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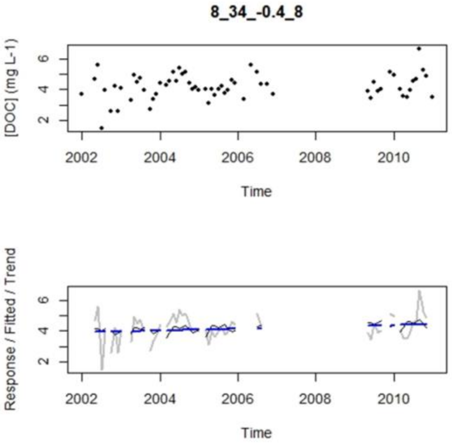
Time
Response / Fitted / Trend
Time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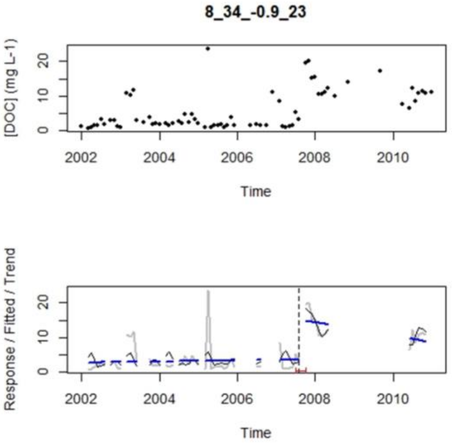
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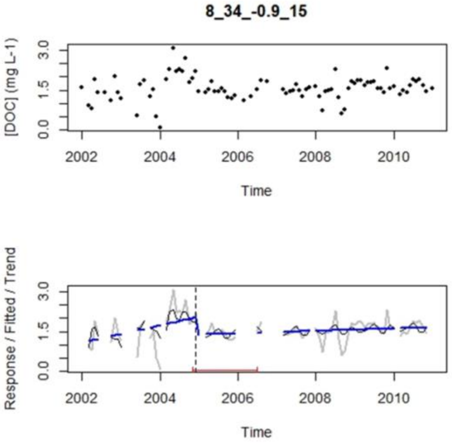
Time
Response / Fitted / Trend
Time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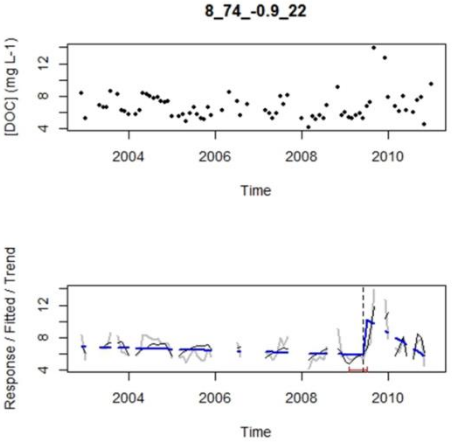
Response / Fitted / Trend
Time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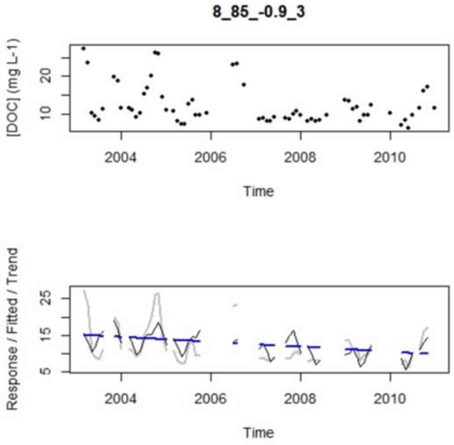
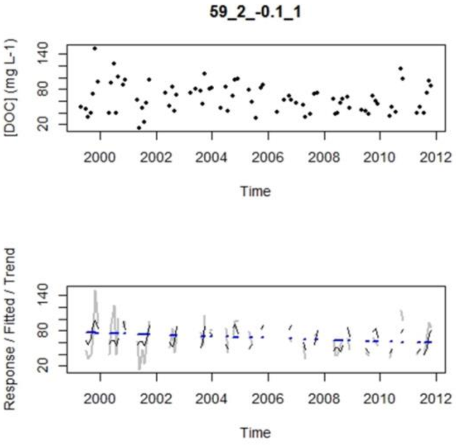
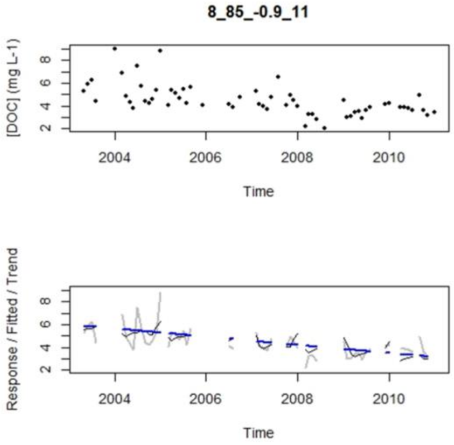
Time
Response / Fitted / Trend
Time


8_85_-0.9_3


59_2_-0.1_1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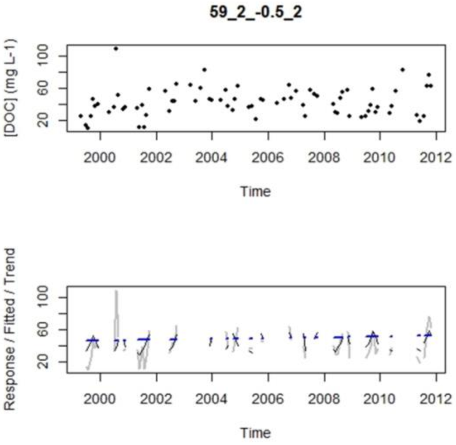
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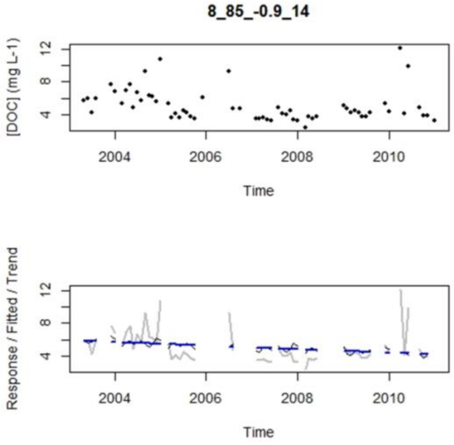
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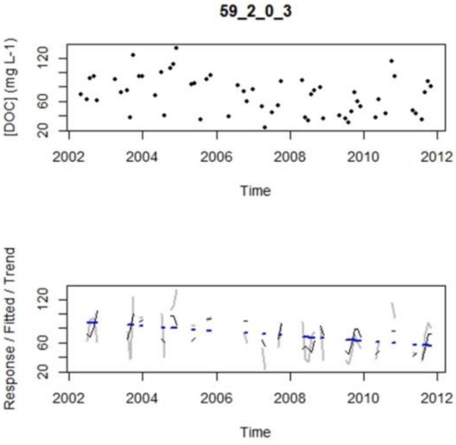
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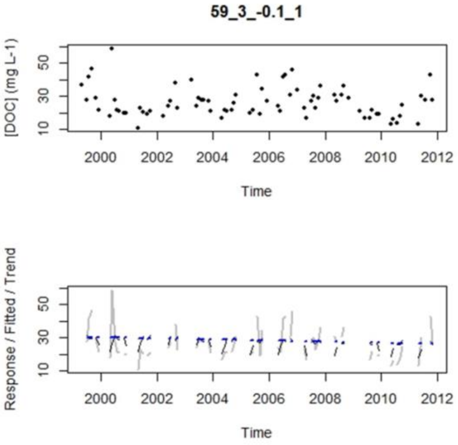
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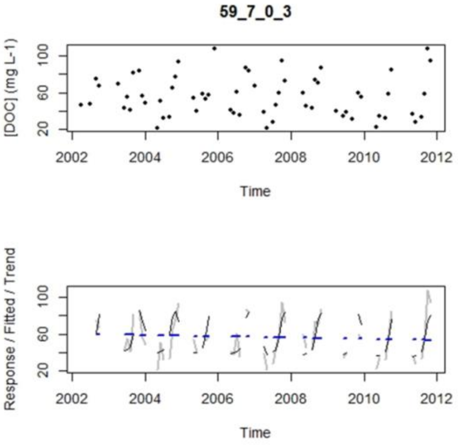
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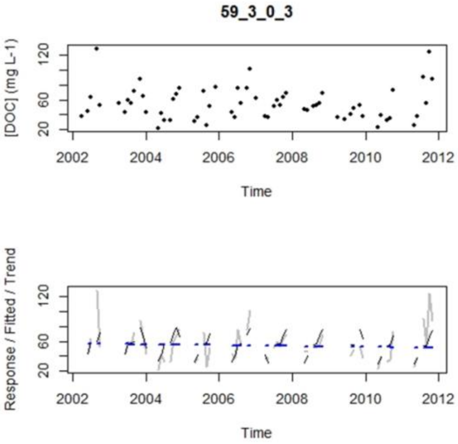
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Response / Fitted / Trend
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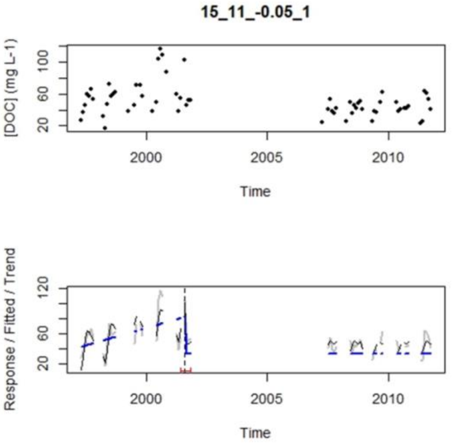
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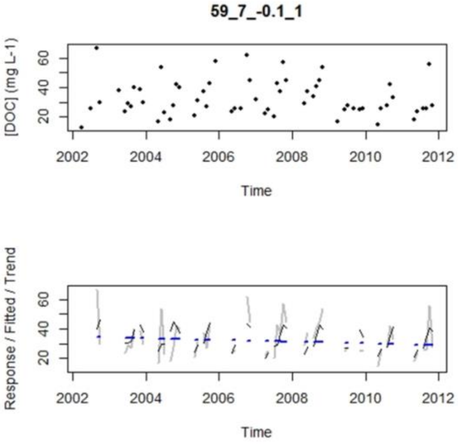
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Response / Fitted / Trend
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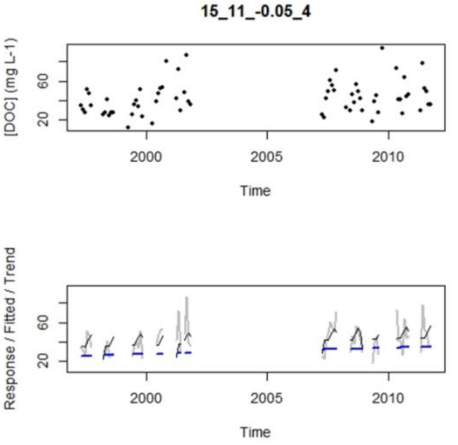
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Response / Fitted / Trend
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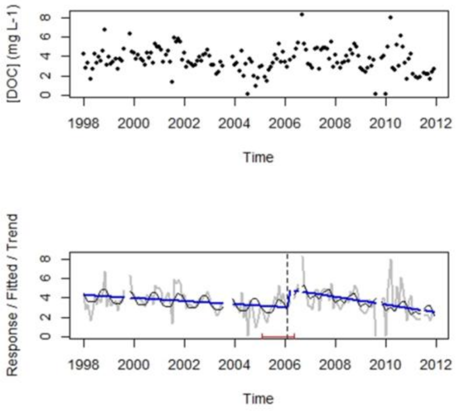
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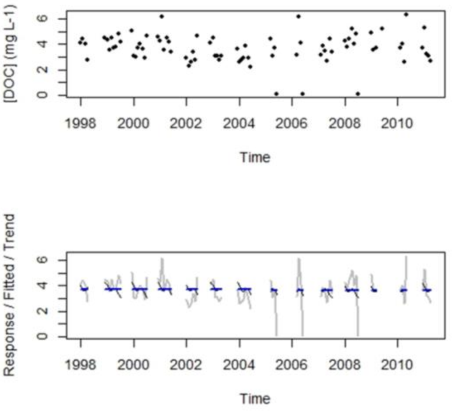
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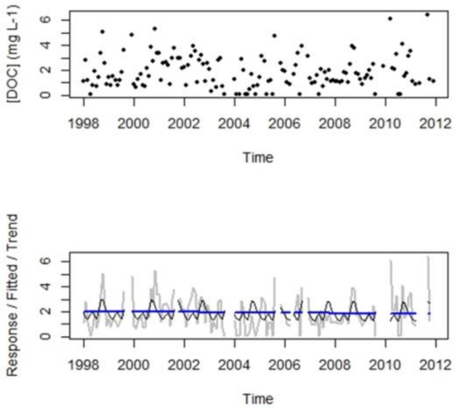
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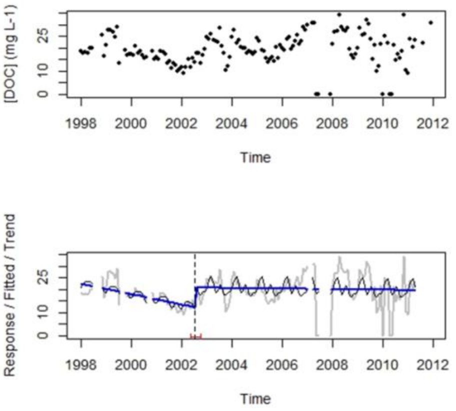
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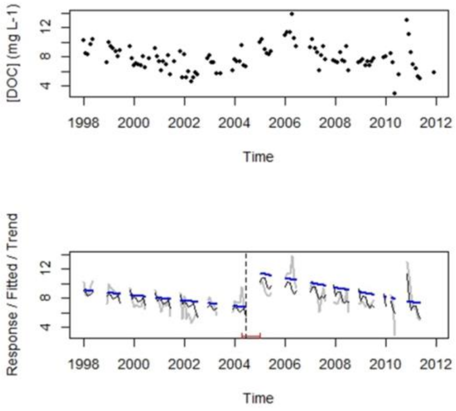
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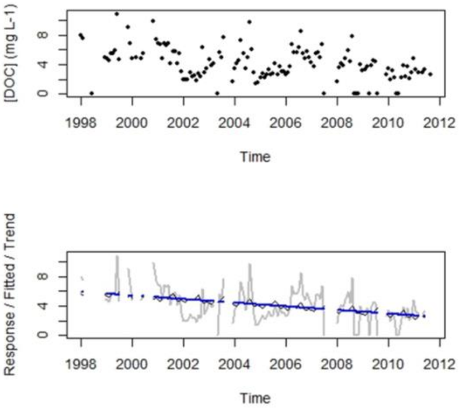
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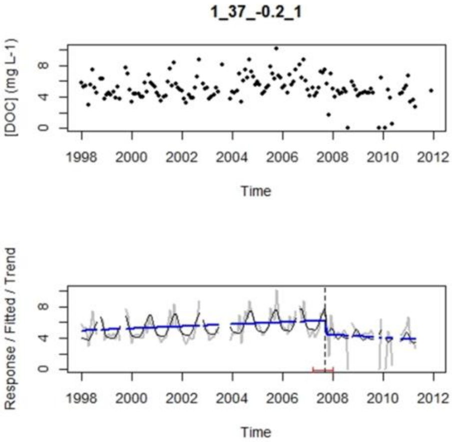

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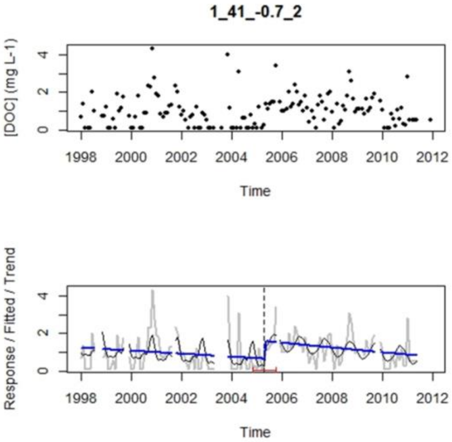

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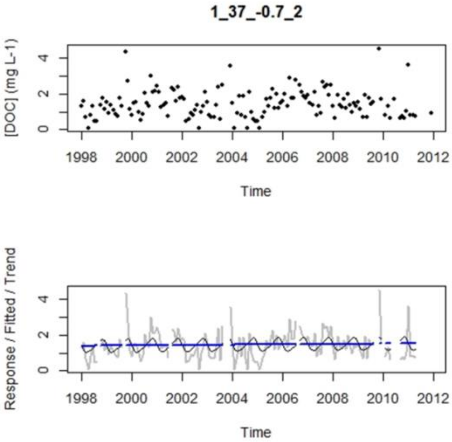

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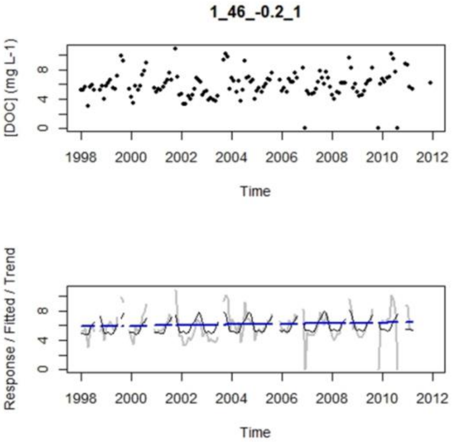

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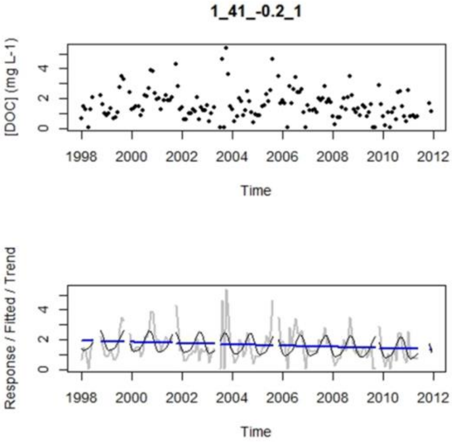

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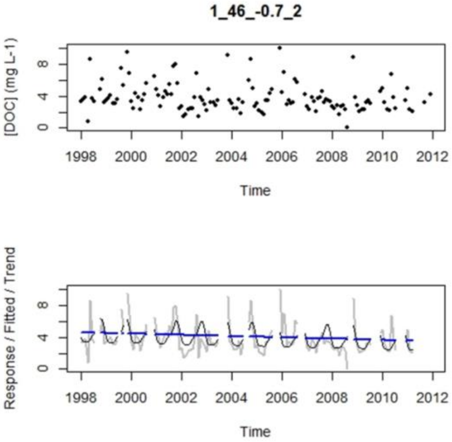

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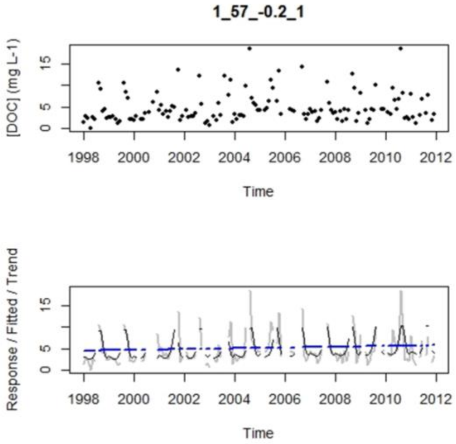
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Response / Fitted / Trend
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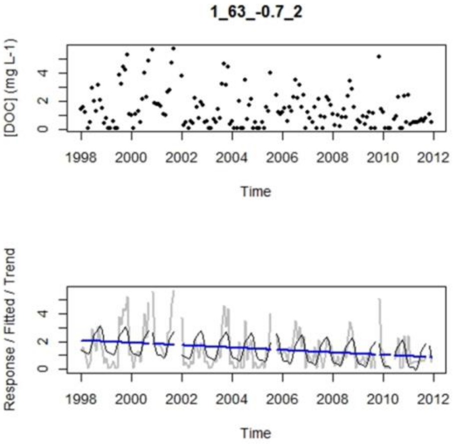
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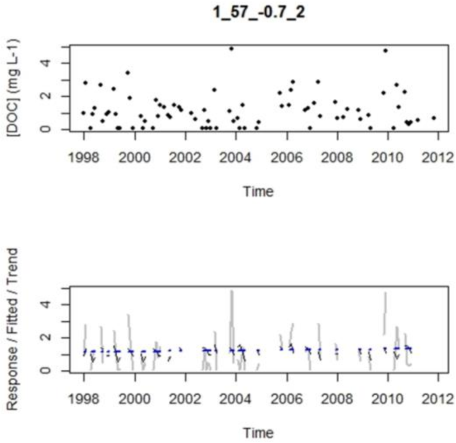
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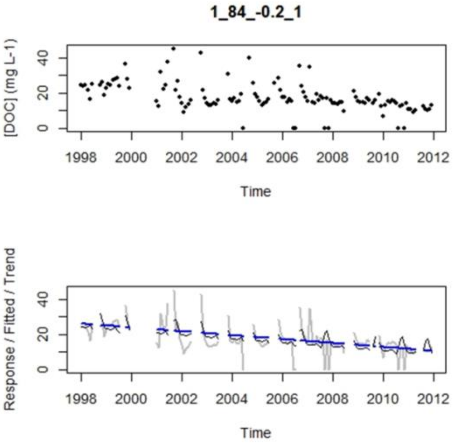
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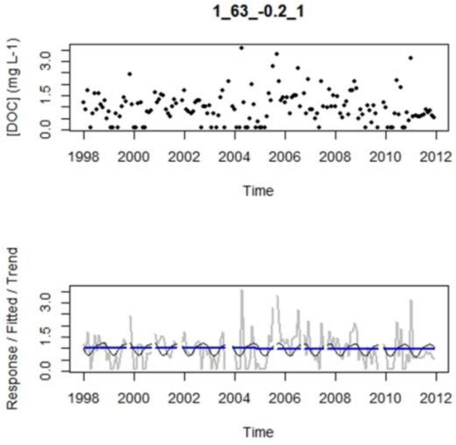
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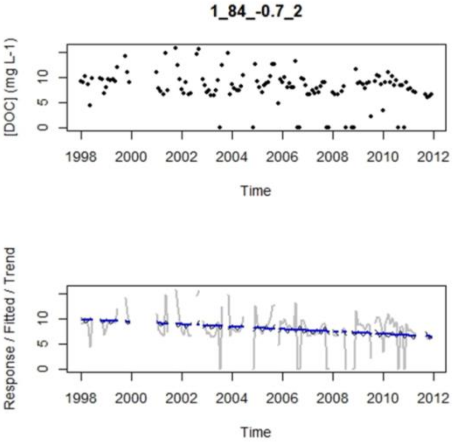
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Response / Fitted / Trend
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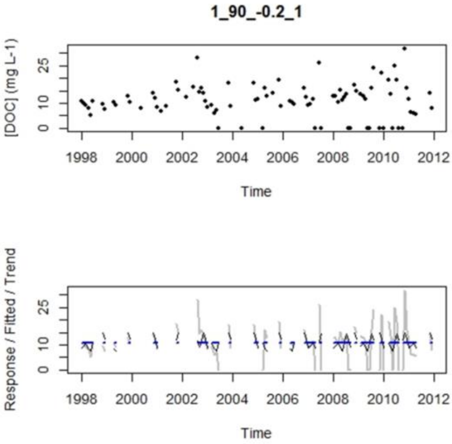
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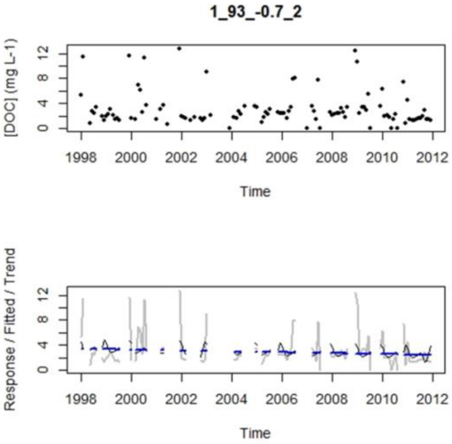
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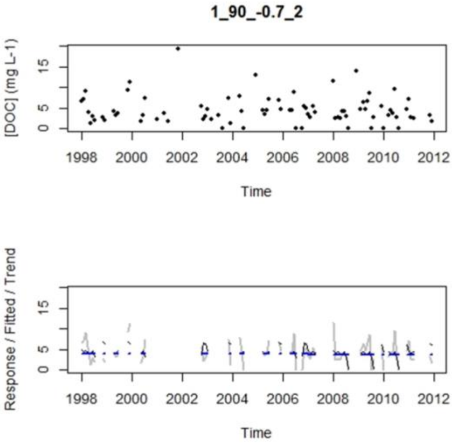
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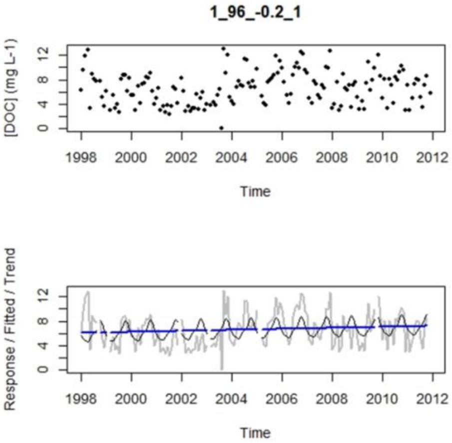
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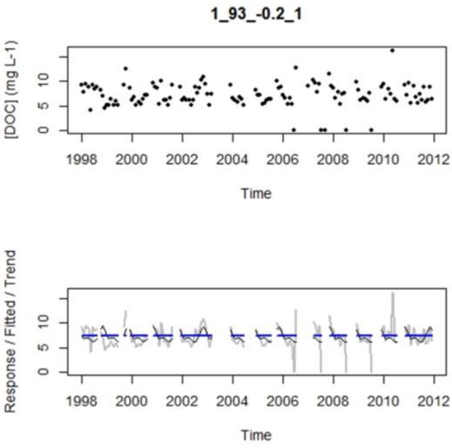
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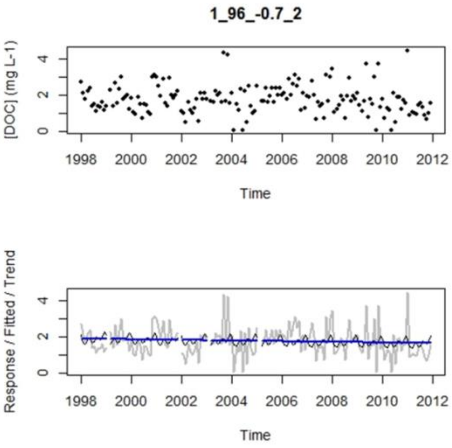
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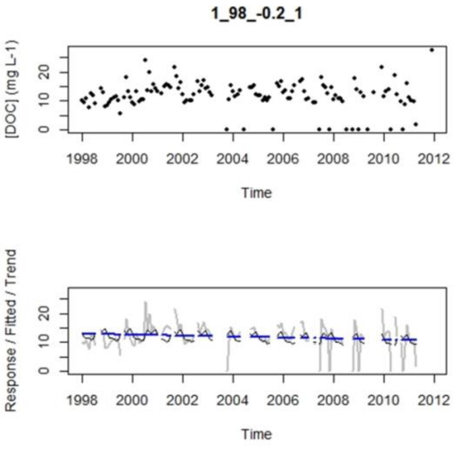
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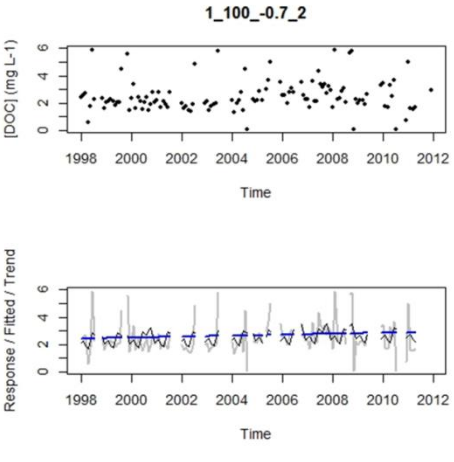
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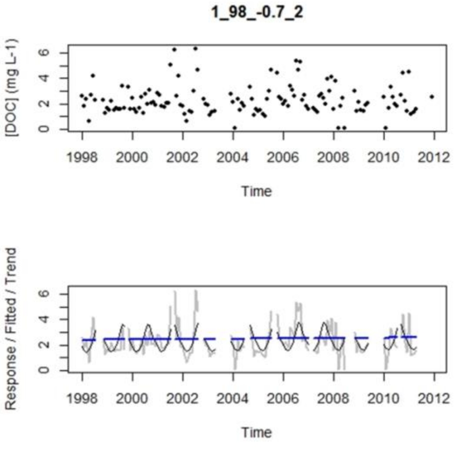
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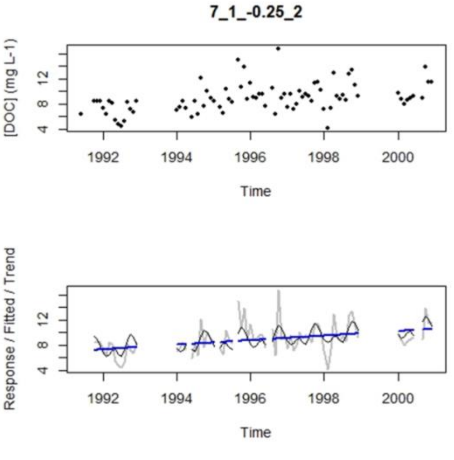
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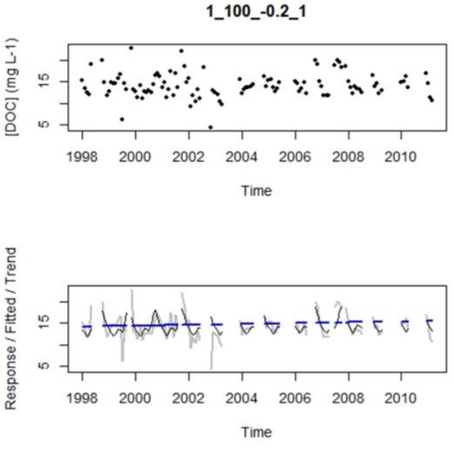
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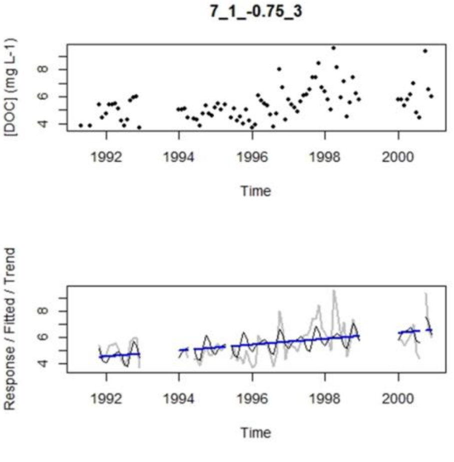
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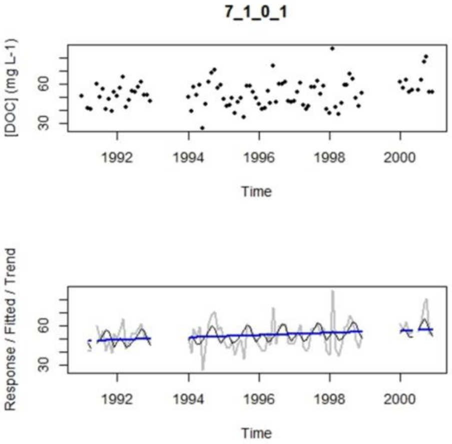
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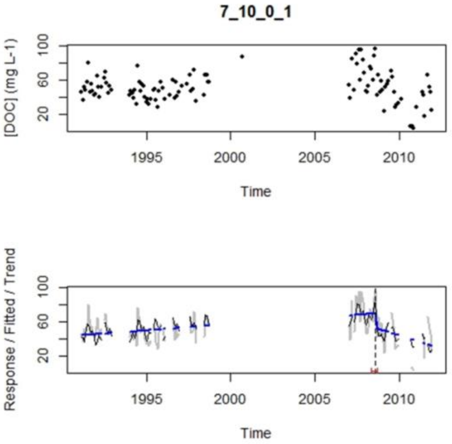
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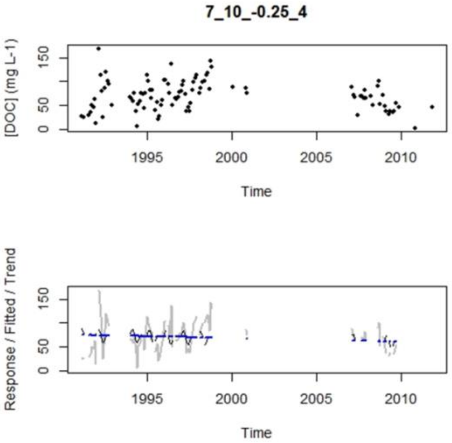
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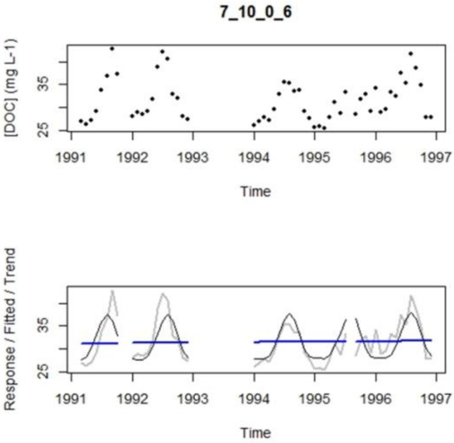
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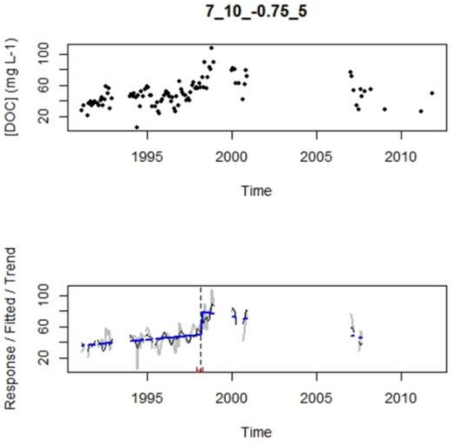
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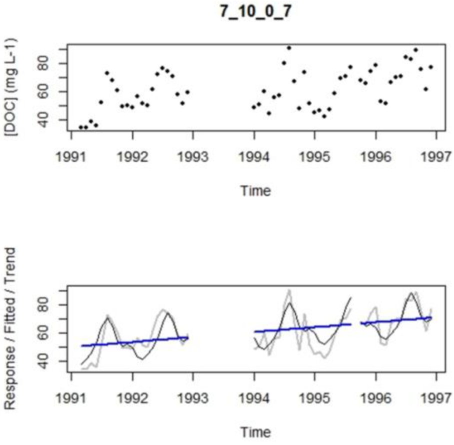
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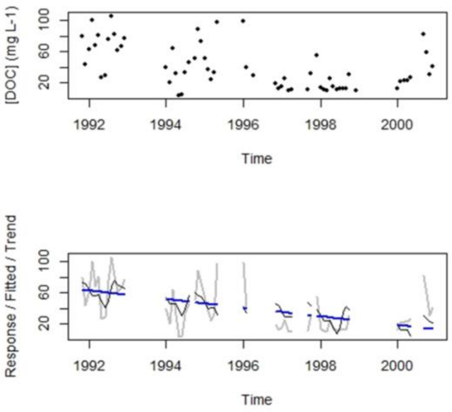

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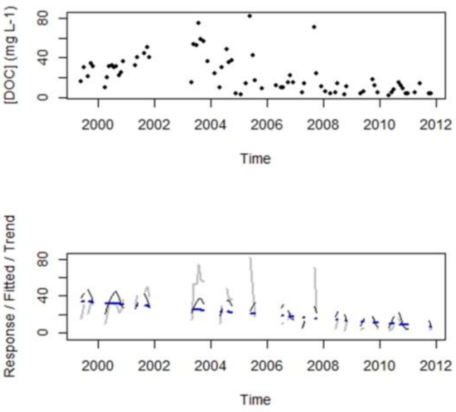

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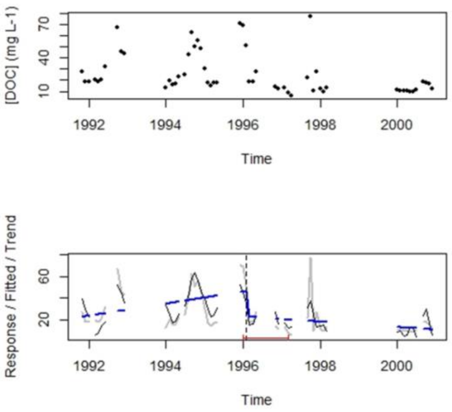

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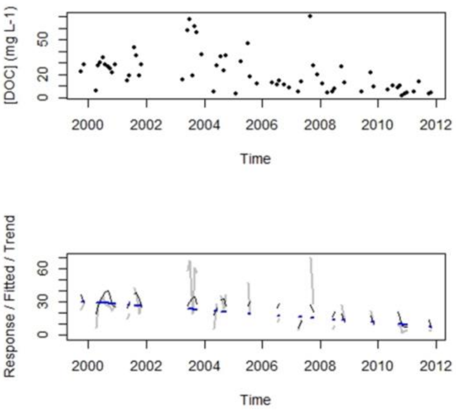

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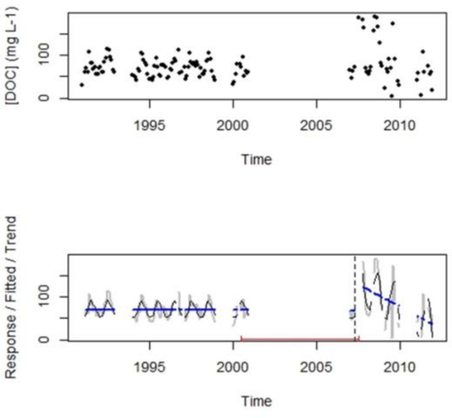

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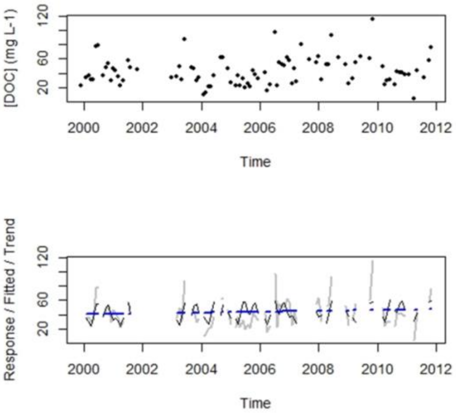

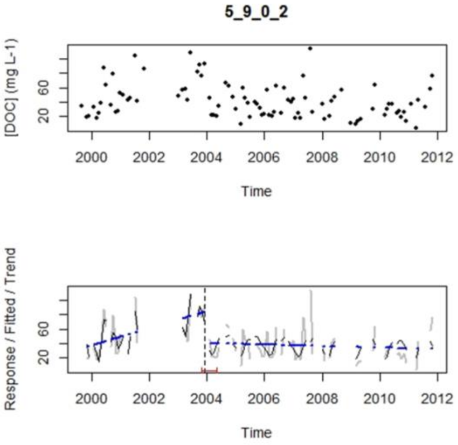
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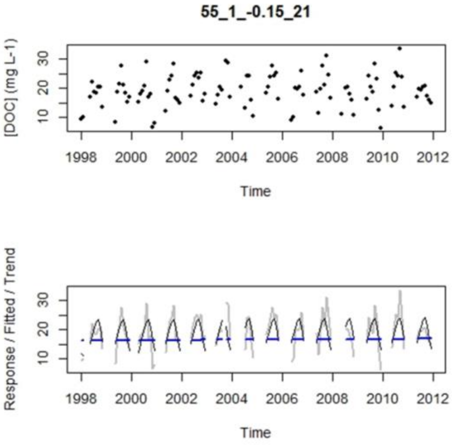
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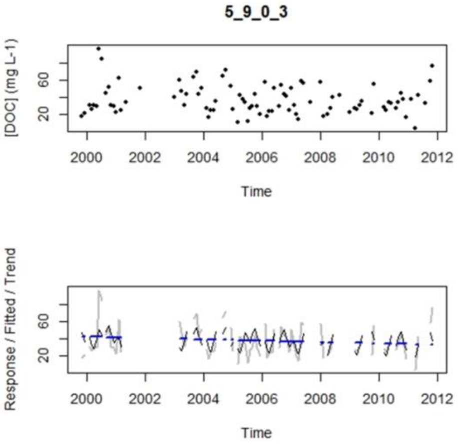
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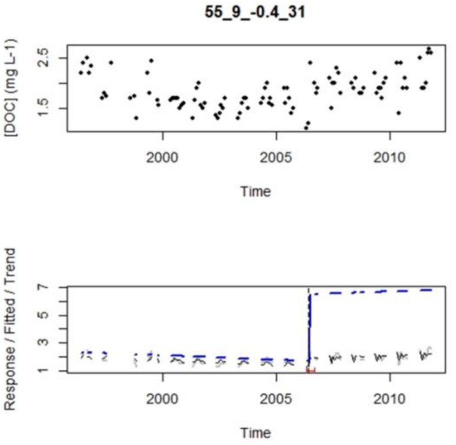
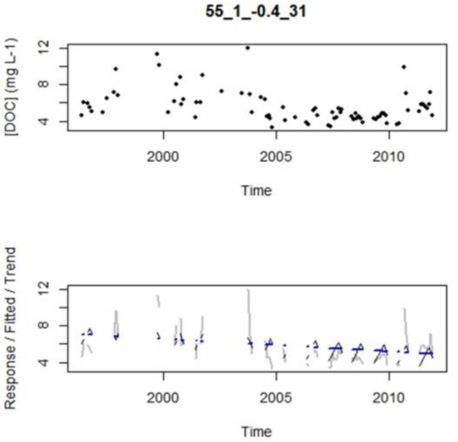

55_9_-0.4_31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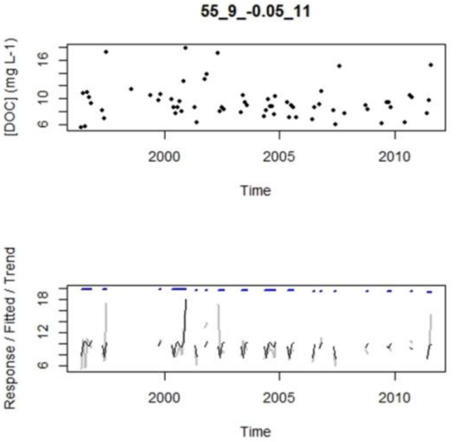
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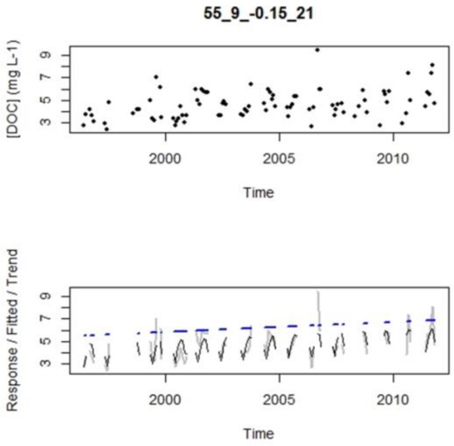
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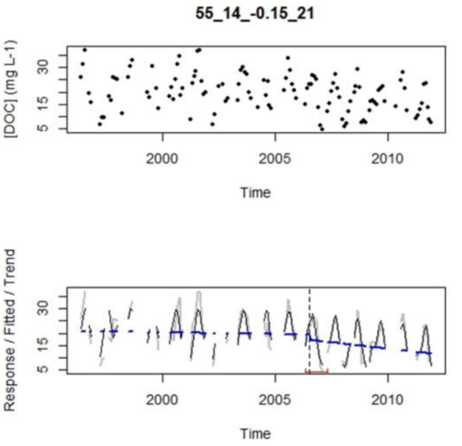
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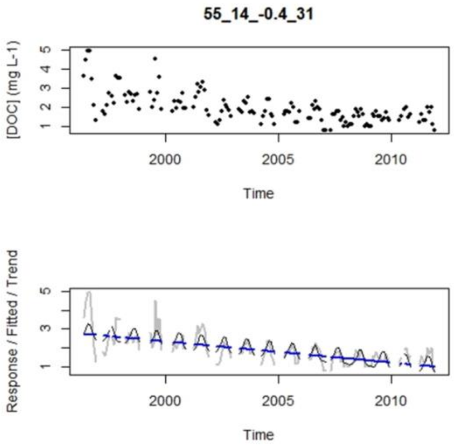
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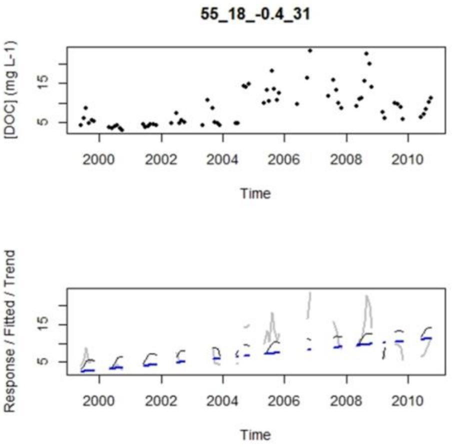
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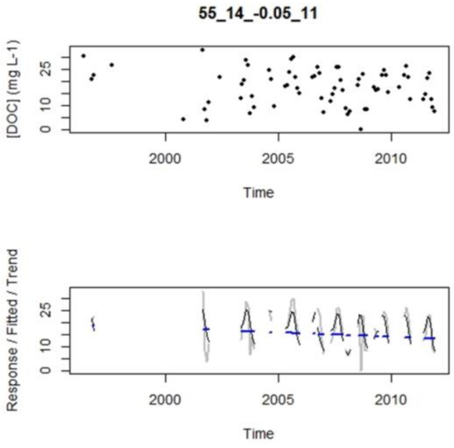
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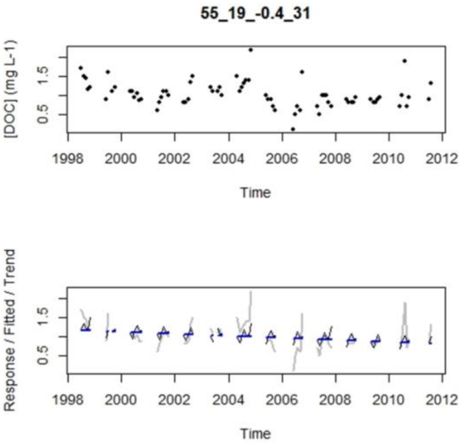
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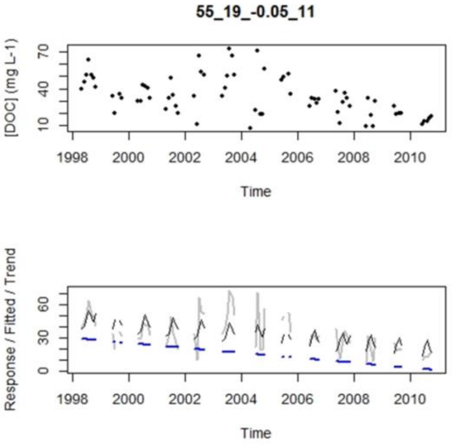
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Response / Fitted / Trend
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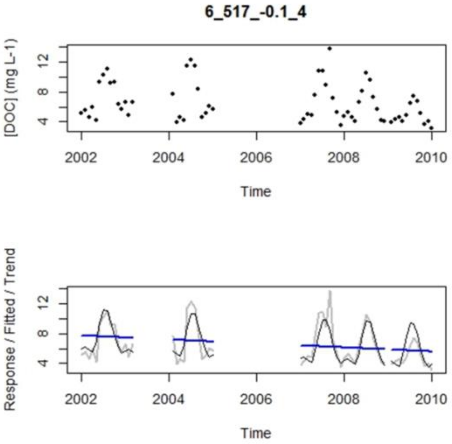
6_517_-0.1_4
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Time
Response / Fitted / Trend
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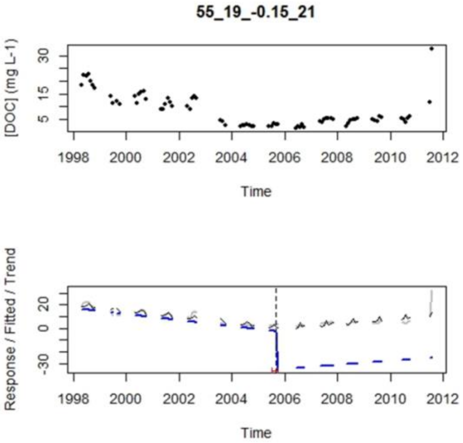
4
Time


55_19_-0.15_21
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Time
Response / Fitted / Trend
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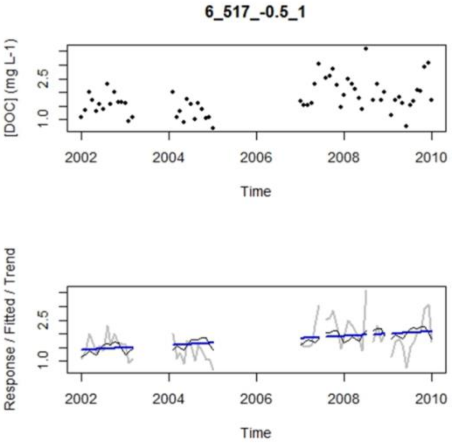
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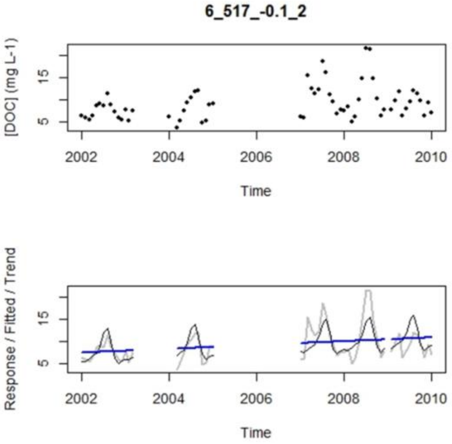
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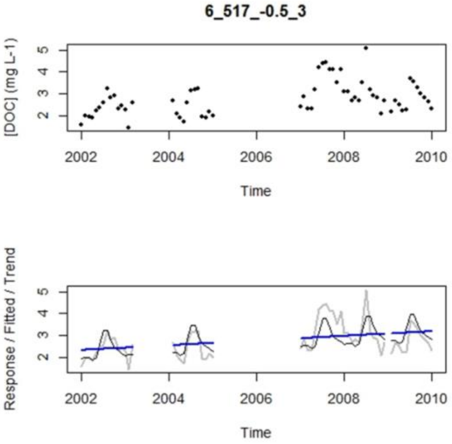
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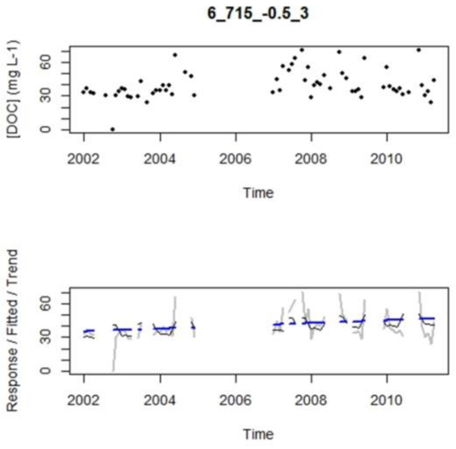

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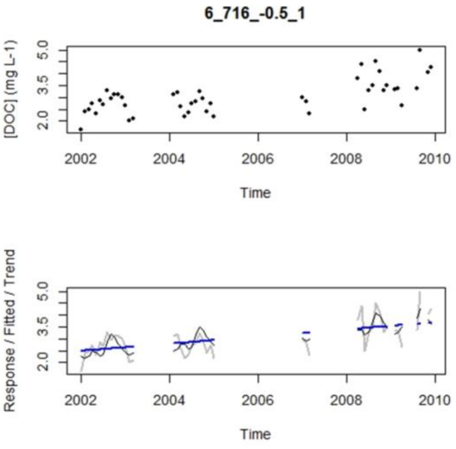

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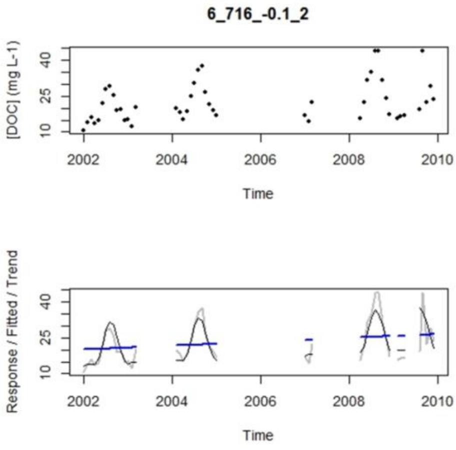

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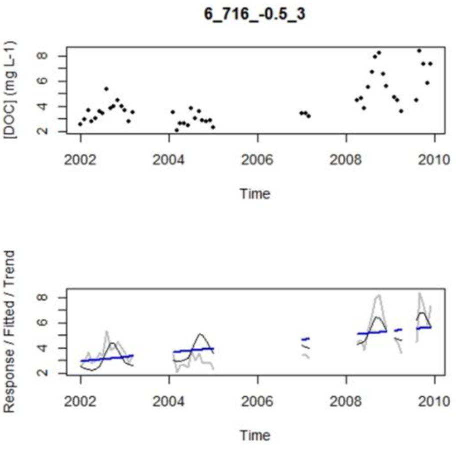

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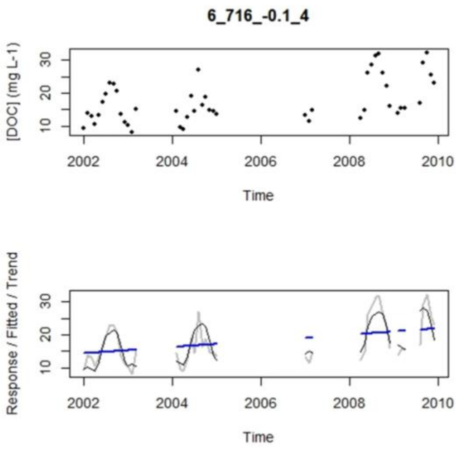

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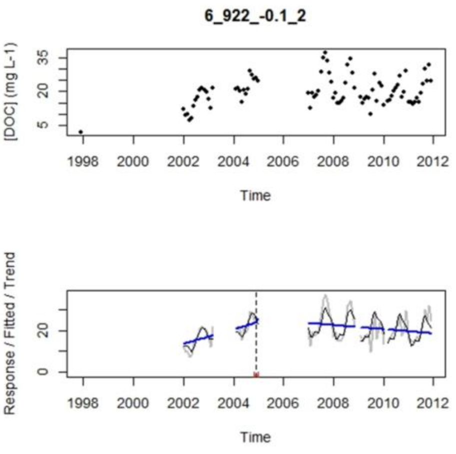

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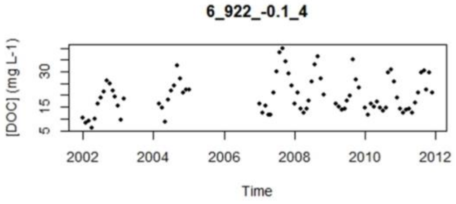
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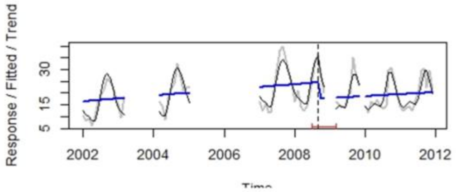
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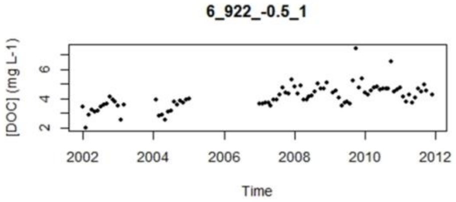
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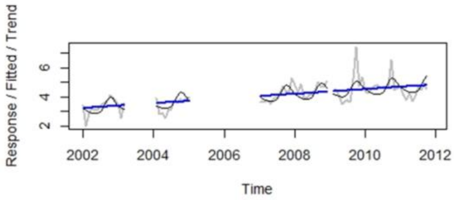
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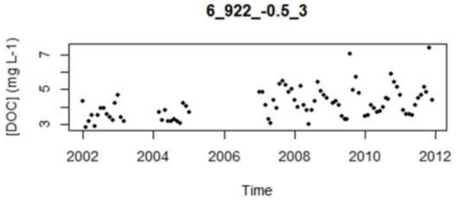
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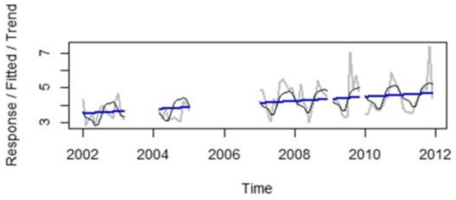
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