In situ metal fluxes for the assessment of metal bioavailability in sediments

Elvio D. Amato[1,2,3], Stuart L. Simpson[3], David A. Spadaro[3], Chamani P.M. Marasinghe Wadige[4], William A. Maher[4], Anne M. Taylor[4], Dianne F. Jolley[2]

[1]Department of Biology, Systemic Physiological and Ecotoxicological Research Group, University of Antwerp, Antwerp, Belgium
[2]School of Chemistry, University of Wollongong, Wollongong, NSW, Australia
[3]CSIRO Land and Water, Lucas Heights, NSW, Australia
[4]Ecochemistry Laboratory, Institute for Applied Ecology, University of Canberra, Canberra, ACT 2601, Australia

E-mail contact: elvio.amato@uantwerpen.be

1. Introduction

Analysis of pore waters, dilute-acid extractable metal (AEM) (equivalent to simultaneously extracted metals (SEM)), acid volatile sulfide (AVS), and organic carbon (OC) concentrations are frequently used to evaluate and predict metal bioavailability in sediments.[1] Where concentrations of bioavailable contaminants are determined to exceed sediment quality guideline levels, bioassays are usually performed to evaluate toxicity effects resulting from contaminant exposure. Although the chemical analyses used for bioavailability assessment have been shown to be useful for predicting metal toxicity in sediments,[1] the predictions for more oxidized surface sediments can be quite poor, frequently owing to a broader range of factors influencing metal bioavailability including variability in phases that are easily oxidized or reduced (e.g. AVS and Fe(II)). In addition, laboratory-based bioassays may provide inadequate predictions of metal bioavailability and toxicity due to their inability to adequately replicate field exposure conditions. Thus, techniques capable of providing reliable *in situ* assessments of metal bioavailability and toxicity are needed.

A comprehensive series of studies combining laboratory and field experiments were carried out to evaluate the performance of the diffusive gradients in thin films (DGT) technique for predicting metal bioavailability in sediments.[2] The DGT device uses an ion-exchange resin (Chelex) which selectively accumulates divalent metal (e.g., Cd, Cu, Fe, Ni, Mn, Pb, Zn) present in the sediment porewater and weakly-bound to the sediment particulate phase.[3] The DGT metal flux measured at the sediment water interface (SWI) was compared to biological responses of organisms (amphipods and bivalves) exposed to sediments contaminated with mixtures of metals, in the laboratory and in the field. The performance of the DGT technique for predicting biological responses was systematically compared to that of traditional methods relying on sediment chemical analysis (i.e., TRM, AVS-SEM).

2. Materials and methods

All laboratory bioassays were carried out using field-collected sediments placed in glass beakers and filled with filtered (0.45 µm) seawater. The DGT metal flux measured at the sediment-water interface was used to investigate relationships between DGT measurements and biological responses in both laboratory and field experiments. All DGT measurements were performed for 24 h.

Part 1. Dose-response relationships between DGT metal fluxes and adverse effects to an epi-benthic marine amphipod, *Melita plumulosa* (survival and reproduction) were assessed during a 10-day laboratory bioassay.

Part 2. Relatinships between bioaccumulation in a benthic marine bivalve, *Tellina deltoidalis,* exposed to estuarine sediments and DGT metal fluxes were investigated over an exposure period of 31 days in the laboratory and field.

Part 3. Metal bioaccumulation in a freshwater bivalve, *Hyridella australis,* and DGT metal fluxes were investigated in the laboratory and in the field for 28 days.

3. Results and discussion

In the sediments used to investigate relationships between the DGT metal flux and toxicity to the amphipod *M. plumulosa*, DGT veritcal profiles indicated release of DGT-labile metals at the SWI in correspondance of

increasing Fe(II) and Mn(II) fluxes, which generally occurred within 2 cm below the SWI. This indicated that metal mobility in sediments is linked to dissolution of Fe and Mn oxyhydroxides, but also oxidation of sulfides and degradation of organic matter may have contributed to this. DGT metal fluxes rapidly declined in the deeper sediment, consistently with increasing anoxic conditions and precipitation of metal sulfides. To assist in the analysis of effects from the mixtures of the metals (i.e., Cd, Cu, Ni, Pb, Zn), DGT metal fluxes were normalised using water quality guideline values (WQGVs) (ANZECC/ARMCANZ 2000) to account for predicted differences in the toxicity of the different metals. Strong dose-response relationships were found between the normalised DGT metal flux measured at the SWI (±0.5 cm) and adverse effects to reproducion and survival of the amphipod (Figure 1a). Normalised DGT metals fluxes appeared to provide stronger predictions of toxicity than normalised AEM concentrations.

In the comparison between laboratory and field experiments, greater DGT-Pb and -Zn fluxes were measured in the laboratory compared to the field. Bioaccumulation of these metals in the marine bivalve was also greater in laboraoty-exposed organisms, mainly due to release of metals from the sediment to the overlying water. Conversely, greater bioaccumulation of Cd and Zn was observed in the freshwater bivalve exposed to field conditions, likely due to fluctuations of metal concentrations in the water column occurring during the exposure. Consistently with bioaccumulation trends observed for the freshwater bivalve, also DGT-Cd and -Zn fluxes were greater in the field. Overall, DGT-metal fluxes measured across the sediment water interface (±1cm) were useful for predicting metal bioaccumulation in both the marine (Figure 1b) and freshwater bivalves irrespective of the type of sediment and exposure.

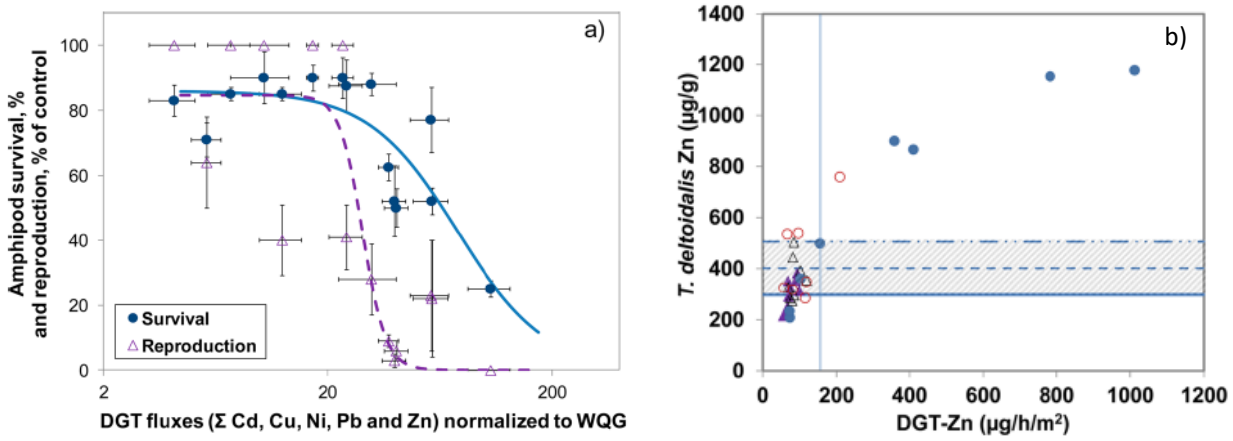

Figure 1: Relationships between DGT fluxes and toxicity to (a) marine amphipod and (b) bioaccumulation in the marine bivalve.

4. Conclusions

The DGT technique provided strong predictions of lethal and sub-lethal toxic effects to the epibenthic marine amphipod exposed to contaminated sediments with varying chemical and physical properties under laboratory conditions. Useful predictions of bioaccumulation were obtained for both marine and freshwater bivalves in both laboratory and field set-ups. Differences in bioaccumulation between organisms exposed to laboratory and field conditions highlighted the importance of including in sediment quality assessments lines of evidence based on *in situ* evaluations of metal bioavailability.

5. References

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