FATE, SPECIATION AND LONG-TERM TOXICITY OF METALS IN SEDIMENTS

DRAFT FINAL

Summary

Metals entering the aquatic compartment will quickly adsorb to suspended solids and sediment particles and as a result will be removed from the water column making the sediment compartment the main sink of metals in the environment. The largest portion of metals in non polluted sediment are present in the crystal lattice of minerals and other residual fractions which constitute the bottom sediment (Du Laing et al., 2009; Lin et al., 2013). However, the fate of metals entering the sediment compartment via the water column is more complex. A proper understanding of the processes that affect fate, such as inter-compartmental transfer, complexation, adsorption and precipitation reactions, remobilisation/burial phenomena and long-term ageing effects is key to understand the potential exposure of organisms (bioavailability) to metals.

The toxicity of metals (e.g., Cu, Ni, Zn) in sediments is modified by the presence and cycling of solid-phase ligands present in the sediment. Metals can be complexed and co-precipitated by reduced sulfur, chelated by functional groups on organic molecules, and adsorbed to iron and manganese oxide minerals; all of these reactions can render a fraction of the total pool of metal nontoxic to biota. The speciation of metals among these metal complexing agents is furthermore related to the residing physicochemical conditions (e.g., pH, redox potential). As, natural sediments vary temporally and spatially in physicochemical conditions, the diverse metal-complexing agents present in sediments may be more or less important for metal binding dependent on the conditions at fine (Costello 2015). Short term changes may even initially render metals more bioavailable. However, the binding of metals to sediments is not completely reversible because, with time, part of the metals is immobilized/fixated, which means that they will not be released into the porewater. (Cappuyns et al 2006). Aging processes redistribute the adsorbed metals to the interior stability of sorption sites of organic and mineral substrates (Burton et al., 2006) and as such increase retention of metals (Cappuyns and Swennen, 2006) and lower metal pore water concentrations are typically observed. As for metals the pore water route is still the predominant route in eliciting toxic effects, in comparison with the dietary route, the net result will be a decrease in toxicity in the long term. This has been confirmed in toxicity studies comparing the effects of ageing processes on the overall sediment toxicity observed in the field versus the toxicity of freshly metal spiked sediments used in the laboratory. All results indeed point into the direction of a reduced toxicity over the long term (Costello et al 2015, Costello et al, 2016).

Furthermore, in addition to the different chemical transformation processes that occur in the sediment over the long term, one needs to include sedimentation and burial processes into the equation. At a steady state situation, reached at long-term scale, the input of a metal via sedimentation and the output via resuspension will reach an equilibrium. In the long run as metals are being transported to deeper sediment layers the metals will also be less prone to resuspension. The burial process and the increasingly irreversible binding of the metals into the sediment matrix ensures that at the long term effects of metal contamination will be limited.

Questions addressed

In relation to the proposed T/DP-E method for measuring metal removal, this note clarifies the link between the speciation of metals and the ecotoxicological effects observed in sediments, including a consideration of exposure via the dietary route.

Fate and speciation of metals in bottom sediments

Metals in sediment mainly exist in the forms of soluble, ion-exchangeable, Fe–Mn oxides, organic matters/sulfides and carbonates and the distribution of different species indicates the bioavailability and migration of metals in sediment (Hou et al., 2013). There relative importance depend on the redox state of the sediment.

<u>Anaerobic sediments</u>

In anoxic sediments, sulfide produced by sulfate reduction reacts with Fe^{2+} and Mn^{2+} to form iron and manganese sulfide solids (Wang and Chapman, 1999). The amorphous iron monosulfides, quite often referred to with the term Acid Volatile Sulfides (AVS), are considered to be the more reactive sulfide pool which can be displaced by other metals (e.g. cadmium, copper, nickel, lead, zinc) on a mole-to-mole basis, forming more stable insoluble sulfide complexes with minimal biological availability (Ankley et al., 1996). Based on this principle Di Toro et al. (1990, 1992) have proposed the SEM-AVS model to predict situations in which toxicity should not occur. In general, the model has been found to be a good predictor of the non-toxicity of metals in sediments and has mostly been used in this context. If all the metal in sediment is in the form of $Me_{2/n}S(s)$ (i.e. AVS in excess), then the free metal ion activity is controlled by dissolution of $Me_{2/n}S(s)$. Sulfides are, however, not the only solid phase ligand present in anoxic sediments to bind metals. Particular organic carbon (POC) in the bulk sediment and Dissolved organic carbon (DOC) in the porewater are equally important in binding metals. The transient nature of sulfides under varying (temporal an spatial) conditions have give rise to concerns that metals could be remobilized again depending on the conditions at hand. This issue is being discussed in section 3.3.

<u>Aerobic sediments</u>

Iron oxides and particulate organic matter (carbon) are the two most important sediment components for metals partitioning in aerobic sediments (Yu et al, 2001). Binding to organic matter, Fe–Mn oxides, clay or silt can indeed stabilize heavy metals in sediments under elevated oxidative–reductive potential (ORP) conditions (Zhang et al., 2014). Under oxic conditions trace metals are strongly scavenged by iron and manganese oxide phases and adsorption and (co)precipitation processes will result in the binding of these metals (Cappuyns and Swennen 2006). Organic matter (OM) originating from various sources such as decay of plant material, animal detritus and its fecal matter has also a significant influence on trace metals solubility and bioavailability in sediment. Numerous studies have shown the importance of POC at reducing metal toxicity in sediments, with normalization of metal effects concentrations to the fraction of organic carbon in sediments improving the prediction of metal toxicity (Mahony et al, 1996, Correia and Costa, 2000, Besser et al, 2003). Finally the pH of the overlying water and sediment is also one of the key parameters that determines metal mobility in sediments (Cappuyns and Swennen, 2008). Adsorption sites in sediments are pH-dependent with the number of negative sites available for cation sorption decreasing with decreasing pH. Under alkaline conditions trace metals can precipitate as oxides, hydroxides, carbonates and phosphates. The pH dependent sorption reactions of cationic metals are partly due to the preferential sorption of hydrolysed metal species in comparison with the free metal ion.

In many sediments a mix of oxic and anoxic layered micro-environments will coexist. The oxic fraction of silty sediments usually extends to depths of 2 to 5mm. At greater depths, the sediment becomes suboxic, containing mixtures of oxic solid phases (e.g. iron and manganese (hydr)oxides in equilibrium with reduced dissolved phases (Fe^{2+} and Mn^{2+}) (Simpson and Batley, 2003). Once the easily reducible iron and manganese (hydr)oxides phases have been depleted, bacteria reduce sulfate to sulfide. The solubility of the metals is then controlled by the solubility of the metal sulfide phases.

Remobilisation and fixation of metals in bottom sediments

Short term

Particulate phase-bound metals may not be permanently sequestered in the bottom sediments (Kalnejais 2007). The burrowing activity of organisms, hydrological related events (increased flow rate, storm events) or occasional human activities (e.g. dredging) are all process that frequently will cause resuspension of sediments. During this process previously redox-stratified sediments will mix with oxygenated overlying water, thereby altering metal sediment-water partitioning and speciation (Simpson and Batley, 2007). But also, seasonally induced changes in redox zonation will have a pronounced influence on the chemical phase distribution. For example in winter oxygen penetration in the sediment is deemed to affect deeper layers.

Several studies have investigated the chemical composition and changes that occur when sedimentary metal phases are suspended in oxygenated water (Fetters et al, 2016, Kalnejais et al, 2007; Kalnejais et al, 2010, Kalnejais et al, 2015; Van Den Berg et al, 2001). Sulfides are thermodynamically unstable in oxidizing environments leading to a potential initial release of metals to the dissolved phase (De Jonge et al, 2012; Simpson et al, 2012, Kaljenais, 2007). However, the released trace metals are on their turn strongly scavenged by iron and manganese oxide phases so that precipitation of these oxides close to the sediment-water interface can lead to an enriched layer of trace metals close to the sediment-water interface (Sutherland et al., 2007). Costello et al (2015) indicated that copper liberated during CuS oxidation was not lost from the sediment but instead retained by other solid-phase ligands, likely organic matter and Fe and Mn oxides. The relative importance of these opposing processes will ultimately determine the net effect on trace metal bioavailability.

Long term

The binding of metals to sediments is not reversible because, with time, part of the metals is becoming immobilized, which means that they will not be released into the porewater (Cappuyns et al, 2006). In this regard, adsorption time is a factor to be considered in distribution and partitioning of metals. The prolonged aging of metals in sediment or soils has been demonstrated to be a major factor in determining their availability: the exchangeable and carbonate fractions decrease while the refractory fractions (organic and residual phase) increase (Guo et al., 2011; Jones et al., 2008; Peng et al., 2009; Zhong et al., 2012). For example, aging can redistribute the adsorbed metals to the interior stability of sorption sites of organic and mineral substrates (Burton et al., 2006) and as such increase retention of metals (Cappuyns and Swennen , 2006). A term that is used to indicate the increased retention of metals with aging time is fixation. Fixation of metals takes place by the slow diffusion of metals into Fe-(hydr)oxides (Brümmer et al., 1988), hydrous oxides of Al and Mn (Trivedi and Axe, 2000), clay minerals (Ma and Uren, 1998) and by diffusion or coprecipitation in carbonates (Nakhone and Young, 1993).

Next to the different chemical transformation processes that occur in the sediment over the long term one needs to include sedimentation and burial processes into the equation. At a steady state situation, reached at long-term scale, the input of a metal via sedimentation and the output via resuspension will reach an equilibrium. In the long run as metals are being transported to deeper sediment layers the metals will also be less prone to resuspension. The burial process and the increasing irreversible binding of the metals into the sediment matrix ensures that at the long term effects of metal contamination will be limited.

Long term toxicity and relative importance dietary route for metals in bottom sediments

Long term toxicity

Only recently, more studies have been conducted in relation to the effects of ageing processes to the overall sediment toxicity observed in the field versus the toxicity of freshly metal spiked sediments used in the laboratory. Costello et al. (2015) aged two sediments amended with copper and followed how they aged (natural oxidation) over a period of 213 days. As sediments aged oxygen penetrated sediment to a greater depth and AVS concentrations declined. Pore water concentrations and Cu bound to amorphous Fe oxides decreased while Cu associated with crystalline Fe oxides increased. These changes also resulted ia change in copper toxicity with "older" sediments eliciting less of a toxic response than freshly amended sediments containing the same total concentration of copper. A similar observation was observed when conducting the same type of experiments (this time 100 days experiments) with nickel spiked sediments. During oxidation of the two sediments again the partitioning and change in toxicity over time was monitored. The results showed that while in one sediment (low AVS, high iron), where nickel was bound to mostly iron oxides, the observed dose-response curve for the amphipod *Hyalella azteca* remained relatively constant the results were more dramatic in a sediment where Ni speciation is dominated by reduced ligands (high AVS). After ageing (oxidation) the EC10 values differed by 2 orders if magnitude from toxic freshly amended sediments (EC10 = 20 mg Ni/Kg dry wt.) to relatively benign aged sediment (> 3000 mg Ni/kg dry wt.) mainly due to the binding to the present high amorphous Fe oxide concentrations present in the sediment. The importance of sorption to Fe/Mn oxyhdroxides has also been demonstrated with other metals. Nedrich et al (2017) showed that the lack of toxicity observed in Vanadium contaminated sediments was mainly due to sorption to these oxic solid-phase ligands. Their importance has also been recognized in sediment remediation projects where in situ stabilization of sediment bound metals has been proposed as an alternative to ex-situ treatment. Adding birnessite (i.e. hydrous Mn oxide) reduced the toxicity of Pb and Cd spiked sediment by 92-100% (Lee et al, 2011).

Relative importance dietary exposure

Information on the relevance of the dietary route for metal toxicity to pelagic organisms has received increasing attention that provide a number of mainly laboratory studies utilizing systematic comparisons of toxicity of metals to an organism via water-only, diet-only, and combined water + diet exposures. DeForest and Meyer (2014) reviewed the state of science about dietborne-metal toxicity to aquatic biota, with a focus on 13 metals: Ag, Al, As, B, Cd, Co, Cu, Cr, Mo, Ni, Pb, V, and Zn. Of those metals, Ag, As, Cd, Cu, Ni, and Zn have been demonstrated to cause dietborne toxicity to aquatic organisms in laboratory exposures at potentially environmentally relevant concentrations. That is, waterborne concentrations at or near existing waterborne criteria and guidelines (e.g., AWQC, EQSs, PNECs) sometimes result in dietborne concentrations that contribute to added toxicity to the most sensitive species (usually filter-feeding herbivores like freshwater daphnids and saltwater copepods) beyond the toxicity caused by waterborne exposure alone. However, up to now dietborne exposures have not yet shown adverse ecological impacts, i.e, increased tissue concentrations have not been linked to adverse population/community effects for the metals listed above. Cardwell et al (2013) in their analysis showed that no relationship could be demonstrated between the magnitude of `trophic Transfer Factors and dietary toxicity to consumers/predators. Brix et al (2011) showed that for insects that diet is an important source if metal accumulation but that there have been no conclusive studies evaluating whether dietary metal accumulation causes toxicity.

In assessing risks for the sediment compartment the dietary route could be of a relative higher importance than the aquatic compartment. Whole sediment toxicity tests are typically conducted using an array of test species with different life strategies. Several of these organisms (oligochaetes, chironomids etc.) are dependent on the ingestion and assimilation of sediment particles to survive. If those sediments have been contaminated with the metal of concern the dietary route is intrinsically included in the assessment. For those species getting additional uncontaminated food the dietary exposure could be underestimated. Studies examining the bioaccumulation of metals in anaerobic sediments showed in general that in most of the cases metal accumulation is reduced when SEM-AVS < 0 (Ankley et al, 1996). However, in some case bioaccumulation was best correlated with total metal content in the sediment irrespective of the AVS content (Lee at al, 2000, Lee et al, 2001, De Jonge et al, 2009, De Jonge et al, 2010). It has been found that the dietary route seems to play an important role in explaining these observations. The observation that metals can be taken up under SEM-AVS conditions < 0 is strictly spoken not in contradiction with the overall SEM-AVS model or with our general understanding of metal bioaccumulation. It should, however, kept in mind that bioaccumulation does not represent a toxicological effect and an unambiguous connection between observed levels of accumulation and effects is not frequently observed. For species with no important detoxification mechanisms (e.g. *Hyalella azteca*), however a relationship between internal body concentration and effects is well documented (Environment Canada, 2011). But in general, when detoxification systems are in place toxicity does not depend on total accumulated metal concentration but is related to a threshold concentration of internal metabolically available metal (Rainbow, 2007). Toxicity ensues when the rate of metal uptake from all sources exceeds the combined rates of detoxification and excretion of the metal concerned. Subsequently the biological significance of accumulated metal concentrations under SEM-AVS conditions < 0 will depend on the way organisms cope with the increased metal exposure. Metals extracted in the gut from the ingested metal sulfides are detoxified and stored in granules for the benthic oligochaete *Tubifex tubifex* while at an overload of the AVS system metals can be found in a more easily accessible pool (De Jonge et al, 2011). Overall the results still support the tenet that AVS controls metal toxicity via the pore water in particular with relation to chronic effect. The results of Custer et al (2016) confirms this statement where waterborne Ni appeared to drive the survival and growth effects in the amphipod *H. azteca* and the snail *Lymnea stagnalis* followed by sediment and then food.

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