Speciation of Metals in Sediments: Sulfide Precipitation and Adsorption

Toxic metals in sediments often are not completely available for uptake by organisms. Metals bound to sediment solids in various forms are largely unavailable to organisms and therefore are far less toxic than metals dissolved in the pore water. Chemists use the term speciation to describe ways of calculating the various forms or species of metals that may be present in the sediments. Two main processes are assumed to control the equilibrium between metals on the sediment and dissolved metals in the porewater: precipitation of metal sulfides (acid volatile sulfides or AVS) and adsorption onto sediment surfaces.

Precipitation by AVS : Acid volatile sulfide (AVS) is an operationally defined measurement of metal sulfides that naturally occur in sediments. AVS represents the iron and manganese sulfide minerals in the sediments that react with toxic metals. (Some forms of metal sulfides, such as pyrite, are unreactive and are excluded from the measurement of AVS). Toxic metals, such as mercury or lead, form sulfide minerals less soluble than natural AVS. As a result, these toxic metals displace iron or manganese from AVS and are themselves sequestered in a very insoluble and biologically unavailable form. (U.S. EPA 1994; DiToro et al. 1996). The precipitation of metals by AVS is assumed to eliminate the mobility and toxicity of that metal, so it is important to account for this removal when computing the porewater concentration of metal from the concentration on the solids Only the residual metals present in excess of the measured AVS concentration are considered to be available for release into the porewater. This residual fraction, in turn, is corrected for adsorption by the sediment particles.

Metal-AVS calculations typically include the six toxic metals of greatest concern: mercury (Hg), copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), and nickel (Ni). The subtraction scheme for metals in the presence of AVS is as follows. We assume the total amount of each metal has been measured in sediment samples. We also assume the total amount of AVS has been measured. Because the metals are extracted and measured in the same process by which the AVS is measured, the metals are collectively called the simultaneously extracted metals or SEM. We convert all measurements into uniform units of moles of compound per kilogram of dry sediment (mol/kg). Unlike the more familiar units of milligrams per kilogram, molar units allow us to compare "apples with apples" for all metals and the AVS. In practice, the concentration ranges are more conveniently expressed in micromoles per kilogram (10^{-6} mol/kg or μmol/kg). One micromole of metal combines with one micromole of AVS to form one micromole of metal sulfide solid.

Because metals react rapidly with AVS with virtually 100% conversion, the calculations of metal-AVS interactions are a fairly simple exercise in bookkeeping (U.S. EPA 1994). Consider first the case where the AVS is greater than the amount of all of the metals combined (SEM). In this case AVS - SEM > 0 and we can assume that all of the metals have reacted with AVS and are present as insoluble sulfides.   In this desirable situation, we assume no metal is present in the porewater. (In reality a tiny amount of metal dissolves but the sulfide solubility is so low that this can be safely neglected and the dissolved metal concentration set to zero).

If the total of the SEMs is greater than the AVS (AVS - SEM < 0), then all of the AVS is bound to toxic metals but some residual of the SEM must be _not_ associated with

sulfide. This excess metal may adsorb to other sediment components or it may go into the porewater. Calculating the types and concentrations of metals that remain in this excess fraction is revealed by some further "bookkeeping."

The sulfide form of each toxic metal has its own solubility. Hg sulfide (HgS) is less soluble than all of the others. Cu sulfide (CuS) is the next most soluble, and so on. The complete order of sulfide solubilities is:

$$Hg < Cu < Pb < Cd < Zn < Ni.$$
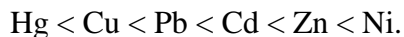
This means that for a given amount of AVS, HgS will always precipitate before any others. If the total Hg is greater than the AVS, then all the AVS will be HgS. The excess Hg, along with all the other metals, will be present in a more available form (dissolved or adsorbed).

> **Example**: AVS = 20 µmol/kg
> Hg = 23 µmol/kg
> Cu = 35 µmol/kg   SEM = 58 µmol/kg > AVS
>
> HgS = AVS = 20 µmol/kg
> Residual Hg(non-sulfide) = 3 µmol/kg
> Cu (non-sulfide) = 35 µmol/kg

If AVS is greater than the total Hg, all the Hg will precipitate and then Cu will also begin to precipitate.

> **Example**: AVS = 30 µmol/kg
> Hg = 23 µmol/kg
> Cu = 35 µmol/kg   SEM = 58 µmol/kg > AVS
>
> HgS = AVS = 23 µmol/kg
> Residual Hg(non-sulfide) = 0 µmol/kg
> CuS = 7 µmol/kg
> Cu (non-sulfide) = (35 – 7) = 28 µmol/kg

If the AVS exceeds the total Hg and Cu, then PbS will precipitate, and so on through the sequence. We can calculate this by subtracting the total Hg concentration from the AVS, then subtracting the Cu from the residual AVS (if any) and then subtracting the Pb from that residual AVS (if any) and so on for each of the other metals, in the order of their sulfide solubility. Note that as you calculate each metal in sequence (for SEM > AVS) , there eventually is a point where the AVS runs out in the "middle" of a metal. (In the last example above, AVS runs out in the Cu step.) The residual metal is assumes to remain isn non-sulfide form. And, the residual (non-sulfide)concentrations of all metals more soluble than the metal in the current iteration are equal to the total concentrations of those metals.

The complete process is illustrated by the example presented in Table 1.

Table 1. Example situation where the total AVS is greater than the total concentrations of several metals but less than the total of all metals. Concentrations specified are for illustration purposes.

	C^{tot}, µmol/kg	C_r, µmol/kg
AVS	100	0
Hg	10	0
Cu	75	0
Pb	25	10
Cd	15	15
Zn	80	80
Ni	60	60

The output of this process is an estimate of the so-called residual concentrations of metals, i.e., metals not bound as insoluble sulfides. The actual interstitial water concentrations of metals are then calculated from residual concentrations by factoring in the partitioning of residual metals to adsorptive surfaces on sediment particles. Interstitial water concentrations are the final output. Interstitial water concentrations are thought to be the most accurate representation of the bioavailable fraction of metals and are the input needed for calculating exposure and risk assessment for contaminated sediments.

Partitioning of Residual Metals between Interstitial Water and Sediment Solids

The dissolved or interstitial water concentration of metals is calculated by assuming the residual metals are partitioned between the solid surface and the liquid phase. We use a simple linear partition model of the form

$$C_s = K_d C_w \quad \text{or} \quad C_w = C_s/K_d$$

The assumption that the porewater metal is linearly (directly) proportional to the amount on the sediment implies there is an excess of available adsorption biding sites compared to the amount of metal present. This is usually a good assumption in sediments.

Several compilations suggest appropriate generic values for adsorption coefficients, and some appropriate values are given in Table 2. These generic values provide only a rough estimate of adsorption for a given sediment material but are useful for assessing the factors that control bioavailability of metals at a disposal site. More refined values of adsorption coefficients can be obtained if we incorporate information about the organic carbon content of sediments. Where such data are available we can scale the adsorption coefficient in proportion to the fraction of organic carbon. Also, because some metals

such as Cu show a particularly high affinity for natural organic matter, regressions are available for scaling the adsorption of these specific metals to the amount of organic carbon in the sediment. In the first stage of model development, we will use simple fixed values of adsorption coefficients (specific for each metal) and add more refined calculations to later versions of the model.

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Table 2.

Formulas for the values of K_d (adsorption coefficient)
Some depend on the percent organic content (%OC) of the sediment.
Example values calculated using %OC value shown at the bottom as 2%.

Metal	Example K_d	Formula
Hg	109	109
Cu	8,710	10^(0.33%OC + 3.28)
Pb	3,162	10^(0.20%OC + 3.1)
Cd	575	10^(0.21%OC + 2.34)
Zn	3,274	3274
Ni	150	150
%OC =	2	

Appendix: Notation Used

Unless otherwise noted, concentrations are in units of mol/kg

AVS_{tot} — Total acid volatile sulfides (AVS)

AVS_r — Residual AVS after precipitation with reactive metals

AVS_{virt} — Virtual AVS: AVS that would be present at a location in the absence of decay

C_j^{tot} — Total concentration of metal j in the deposited sediment

C_j^r — Residual concentration of metal j in the deposited sediment after reaction with AVS

C_j^{iw} — Interstitial water (dissolved) concentration of metal in the sediments (mol/L)

C_j^{ads} — Concentration of metal adsorbed to particle surfaces in the sediment

k_d — First-order decay coefficient for oxidative loss of AVS (sec^{-1})

Kj^{ads} — Adsorption coefficient for metal j (L/kg)

τ_i — Decay time interval for grid element i (sec)