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Critical Limits for Hg(II) in soils, derived from chronic toxicity data

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"Capsule"

Published laboratory toxicity data and chemical speciation modelling are used to derive Critical Limits expressed as either soil Hg(II) content or Hg^{2+} concentration.

Abstract

Published chronic toxicity data for Hg(II) added to soils were assembled and evaluated to produce a data set comprising 52 chronic endpoints, five each for plants and invertebrates and 42 for microbes. With endpoints expressed in terms of added soil Hg(II) contents, Critical Limits were derived from the 5th percentiles of species sensitivity distributions, values of 0.13 µg (g soil)$^{-1}$ and 3.3 µg (g soil organic matter)$^{-1}$ being obtained. The latter value exceeds the currently-recommended Critical Limit, used to determine Hg(II) Critical Loads in Europe, of 0.5 µg (g soil organic matter)$^{-1}$. We also applied the WHAM/Model VI chemical speciation model to estimate concentrations of Hg^{2+} in soil solution, and derived an approximate Critical Limit Function (CLF) that includes pH; log $[Hg^{2+}]_{crit}$ = - 2.15 pH – 17.10. Because they take soil properties into account, the soil organic matter-based limit and the CLF provide the best assessment of toxic threat for different soils. For differing representative soils, each predicts a range of up to 100-fold in the dry weight-based content of mercury that corresponds to the Critical Limit.

Key words: chemical speciation, critical limit, free ion concentration, mercury (II), organic matter, soil

1. Introduction

Although current interest in the ecotoxicity of mercury is mainly focused on the bioaccumulative form methylmercury, inorganic mercury - Hg(II) - is also a significant environmental pollutant. The inorganic form of the metal exerts direct toxic effects towards a variety of organisms including microbes, invertebrates and plants. Protection of soil ecosystems against these toxic effects can be based on Critical Limits (or Environmental Quality Standards), expressed as soil concentrations of Hg(II) above which unacceptable effects are expected. In work on Critical Loads of heavy metals, De Vries et al. (2007) adopted a soil Critical Limit of 0.5 µg (g organic matter)$^{-1}$ based on the results of long-term (several years) experiments with Hg(II) added to the O horizons of Swedish forest soils (Bringmark and Bringmark, 2001a,b). This limit was used to estimate Hg Critical Loads for effects on European soil ecosystems (Hettelingh et al., 2006), and the results indicate Critical Load exceedance for 85% of the area of Europe.

The Critical Limit for Hg(II) used by De Vries et al. (2007) was derived differently from limits for other metals (Cu, Zn, Cd, Pb), for which experimental chronic (NOEC, EC_{10}) toxicity data have been assembled and analysed using the Species Sensitivity Distribution (SSD) concept (e.g. Crommentuijn et al., 1997). The work described here was performed in order to derive SSD-based limits from published laboratory toxicity data for Hg(II). We assembled all available and acceptable published soil toxicity data for Hg(II) and analysed them to derive Critical Limits based on the maximum information. The limit values were set at the 5% level, i.e. protective of 95% of soil organisms (see e.g. Posthuma et al., 2003; Van Straalen and Denneman, 1989). Our main purpose in conducting this work was to obtain Critical Limits that can be used to quantify the possible effects of atmospherically-deposited Hg on natural and semi-natural ecosystems. However, the values should be generally applicable.

We used three methods to express Hg(II) toxicity. Firstly we followed the conventional approach and expressed the end-points in terms of the soil metal content (µg g^{-1}), with no account taken of possible dependence on soil organic matter (SOM) content or pH. The second method is a variant in which the results are expressed in terms of the Hg:SOM ratio, following de Vries et al. (2007). Meili (1991) argued that this should be preferred because of the well-established strong interaction of Hg(II) with organic matter, and the strong parallels between Hg(II) adsorption to SOM and its uptake by organisms.

The third approach followed that of Lofts et al. (2004), who described toxic effects not in terms of the total metal added to the soil, but the metal free ion concentration in soil solution. They derived Critical Limit Functions, in which the logarithm of the critical free ion concentration was expressed as a linear function of pH. Although this does not involve an explicit mechanism of toxicity, it is consistent with the idea that toxic response is elicited by a quasi-complexation mechanism in which the reactivity of the metal, expressed through the free ion concentration, is a pH-dependent measure of toxicity. This takes bioavailability into account in a simple way, as is thought desirable (Peijnenburg et al., 2002; Janssen et al., 2003); there is much current interest in relating metal toxic effects to the chemistry of the metals in the solution phase by which exposure occurs. Lofts et al. (2004) used pedotransfer functions to estimate free metal ion concentrations in soil solution for published toxicity experiments. These functions were multiple regression equations that were derived from analysis of metal concentrations in the solutions of soils of differing pH, organic matter content and heavy metal content (Tipping et al., 2003). Because such pedotransfer functions are not currently available for Hg(II), we used the WHAM chemical speciation model (Tipping, 1994; 1998) to estimate Hg^{2+} concentrations, denoted by $[Hg^{2+}]$.

2. Methods

2.1 Toxicity data

Toxicity data were accepted for analysis if they met the following criteria set out by Lofts et al. (2004).

(i) Only tests carried out in soils were accepted. Tests carried out in other media (e.g. agar, nutrient solution) were not used.

(ii) The exposed organism was of a species living in intimate contact with and considered to take up metal directly from the pore water (e.g. earthworms and other soft-bodied invertebrates, plants, and soil microorganisms).

(iii) The metal was added singly to the soil in a soluble form. In all the tests accepted, the form of mercury added was $HgCl_2$.

(iv) The pH and organic carbon or organic matter content of the soil were quoted or referenced. Where organic carbon alone was quoted it was converted to organic matter by multiplying by 2.0. Measured pH values were converted from values obtained by soil extraction (using H_2O, KCl or $CaCl_2$) to soil solution pH using the equations given by de Vries et al. (2005).

(v) Chronic effect endpoints were used. For plants, data were available for growth (yield) and reproduction, and for soil-dwelling invertebrates reproduction rate. For microbes there were measurements of enzymatic activity, rates of soil processes (e.g. respiration, nitrification), and changes in Operational Taxonomic Units.

(vi) The endpoint metal concentration was taken to be the added Hg concentration. As noted by Lofts et al. (2004), the optimal Hg pool would be the 'geochemically active' concentration since this controls the solution free ion concentration. However the geochemically active concentration of metal is rarely measured in toxicity tests so for consistency the added metal concentration was used. Since it is highly likely that Hg undergoes fixation in soil solids following addition in soluble form, the added metal concentration represents an upper limit to the geochemically active concentration.

(vii) End point concentrations of metals (NOEC, EC10) were either quoted in the paper, could be clearly extracted from tables of dose-response relationships, or in the case of EC10 values were calculable from tabulated or graphed dose-response data. A log-logistic dose-response model was used to calculate EC10 values when required. A description of this model is given by Lofts et al. (2004).

Toxicity data were assembled from the published literature and from new results for soil microorganisms, obtained from experiments with Swiss soils (see Supplementary Content).

2.2 Chemical speciation modelling

Calculations of soil and water chemical speciation were performed using WHAM (Tipping, 1994) incorporating Humic Ion-Binding Model VI (Tipping, 1998). Model VI uses a structured formulation of discrete, chemically-plausible, binding sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. Metal aquo ions (Al^{3+}, Fe^{3+}, Hg^{2+} etc.) and their first hydrolysis products ($AlOH^{2+}$, $FeOH^{2+}$, $HgOH^{+}$ etc.) compete with each other, and with protons, for binding. The same intrinsic equilibrium constant (K_{MA}) for binding to carboxyl or type A groups is assumed to apply to the aquo ion and its first hydrolysis product. The constant (K_{MB}) for binding to weaker acid groups is related to K_{MA}, and the contribution of rarer “soft” ligand atoms is factored in. The intrinsic equilibrium constants are modified by empirical electrostatic terms that take into account the attractive or repulsive interactions between ions and the charged macromolecule. More information and parameter values are given in Table S1. The humic ion-binding model is combined with an inorganic speciation model, the species list and constants for which were given by Tipping (1994). The inorganic reactions in this database are restricted to monomeric complexes of metals. The effects of ionic strength on the inorganic reactions are taken into account using the extended Debye-Hückel equation. Temperature effects on reactions between inorganic species are taken into account using published or estimated enthalpy data, but in the absence of experimental information, reactions involving humic substances are assumed to be independent of temperature. Tipping (1998, 2002) showed that the model can account for the great majority of published data sets describing either proton binding by humic matter or the binding of individual metals. Results from laboratory experiments involving competition for binding between metal ions and protons, and between different metal ions, have also been described successfully.

Soil organic matter is considered to comprise humic and fulvic acids (HA and FA), together with “inert” organic matter. The solution phase contains FA and inert organic matter. Therefore to apply the model the amounts of the humic substances (active with respect to cation binding) have to be determined or assumed. Information relevant to the present study has been reported by Tipping (2002) and Tipping et al. (2003). Tipping et al. (2003) showed that the active organic matter could be represented by a combination of humic and fulvic acids, but their combined contribution to the total organic matter varied. If the soil contained less than 45% SOM, the active binding compounds accounted on average for 0.386 of the total SOM, but for soils with SOM contents of greater than 45 %, their combined amount was 0.174 of the total soil mass (i.e. SOM and mineral matter). These values were used in the present work to estimate the concentrations of soil humic substances. For soil water, 65% of the dissolved organic matter was assumed to be active FA (Tipping et al., 2003).

3. Results and discussion

3.1 Chemical speciation modelling of Hg(II) in soil

Values of the key parameter to describe metal binding in Model VI, log K_{MA}, have been estimated for Hg(II) from a range of published data from experiments with isolated humic substances (Tipping, 2007). The derived default values for the model were 3.5 and 2.9 for HA and FA respectively (Table S1). However, it should be noted that the experimental data used to derive these constants were both scattered and relatively few in number, compared to those for most other metals to which the model has been applied (Tipping, 1998; 2002). Furthermore, for other strongly-binding metals (e.g. Cu, Pb), the values of LKMA for HA and FA are quite similar (Table S1), so the difference for Hg is unusual. Consequently there is considerable uncertainty in the default values for Hg(II), and some adjustments can be justified in order to square the lab-based constants with observations relevant to the field.

The model should be able to reproduce the distribution of Hg(II) between the solid and solution phases, which is mainly controlled by the distribution of dissolved and solid-phase organic matter (Schuster, 1991). Åkerblom et al. (2008) demonstrated that in Swedish forest soils, the ratio of Hg to OC was very similar in solution to that in the solid phase. The similarity in Hg:OC ratios was not correctly predicted using the default log K_{MA} values in WHAM, because the FA value was appreciably lower than that for HA (see above), and FA is assumed to dominate the solution OC. To achieve the required equalisation of Hg:OC ratios in the solid and solution phases, it was found necessary to increase the log K_{MA} value for Hg(II)-FA binding from 2.9 to 3.5.

The model should also provide reasonable estimates of soil solution [Hg^{2+}]. However estimates of this variable are scarce, reflecting the extremely low values and absence of reliable direct methodologies. The only relevant study is that of Skyllberg et al. (2000), who measured total dissolved Hg(II) concentrations in suspensions of peat in 0.5 M NaBr, which permitted estimation of [Hg^{2+}] using equilibrium constants for Hg(II)-Br complexation. We applied WHAM / Model VI to the same data, and compared the predicted and experimentally estimated [Hg^{2+}]. The model outputs were insensitive to the value of log K_{MA} for FA; thus, increasing the log K_{MA} for FA from 2.9 to 3.5, as applied above to match Hg:OC ratios, made little difference to the simulated values because binding is dominated by solid phase HA. Therefore for consistency we used the value of 3.5. Agreement between the measured and calculated values of [Hg^{2+}] is only approximate (Table 1). The model predicts higher concentrations at low pH, with better agreement at higher pH. We examined competition due to Al and Fe(III) by varying their assumed soil contents. There was little dependence on the Al concentration for typical soil levels. Relatively large effects of Fe(III) were found. The results in Table 1 are based on a solubility product (log K_{so}) for the reaction $Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$ (log K_{so}) of 2.7 at 25°C. If a log K_{so} of 0.0 was assumed, agreement with the observations was good at low pH, but simulated $[Hg^{2+}]$ became too low at higher pH.

The observations and simulations are both consistent with strong binding of Hg(II) by organic matter and very low Hg^{2+} concentrations in soil solution. However the validation attempt is clearly not fully successful, in particular with respect to the pH dependence of Hg(II) binding. The stronger pH dependence predicted by WHAM is consistent with observations of Hg binding by isolated dissolved organic matter fractions covering the pH range 4.9 to 7.0 (Haitzer et al. 2002, 2003). It can also be argued that modification of the model on the basis of indirect estimates based on results obtained from experiments under unnatural chemical conditions (i.e. 0.5 M NaBr) is inappropriate. Furthermore, adjustment of the pH dependence of binding would require a major change to WHAM, the model assumes competition between metal ions and protons, the binding of which is determined separately. Therefore we decided not to make further model amendments, and it is applied to estimate $[Hg^{2+}]$ in the soils used for toxicity experiments with caution.

As noted, the low concentrations of Hg^{2+} reflect the very high affinity of Hg for organic matter. For reference, a free ion concentration of 1.66×10^{-24} mol l^{-1} (the reciprocal of Avogadro's number per litre) implies that there is on average one Hg^{2+} ion per litre of solution. In these circumstances, the free ion concentration is a notional quantity that provides a link between the concentrations of quantitatively dominant species. For example, in a soil system at equilibrium, a conditional equilibrium constant could be defined that relates the concentration of Hg sorbed by solid phase organic matter to the concentration of Hg bound by dissolved organic matter, both measurable quantities. But the same calculation result should be obtained by relating the interactions of both these Hg forms to the theoretical free ion concentration. Thus, there is no reason to abandon the formal chemical description based on the free ion master species. By the same token, Hg(II) interactions with soil organisms can be described in terms of the reactivity of the metal, as expressed through the free ion concentration (see section 3.3).

3.2 Critical Limits expressed in terms of Hg(II) soil contents

Fifty-two toxicity end-points were obtained from published data, and these are summarised in Table 2. The results refer to five studies each with plants and invertebrates, and 42 studies of microbial processes. For this analysis we used the published end-points for all studies except those of Semu et al. (1985), Gudbrandsen et al. (2007), Son et al. (2007), van Faassen (1973) and Landa and Fang (1978), and the new data reported here (see Supplementary Content), for which we estimated endpoints using the log–logistic dose response model used by Lofts et al. (2004). The data set of Table 2 represents a substantial increase in the number of data points (18) assembled by Slooff et al (1995), and is an up-to-date compilation providing the best current basis for assessing Hg(II) toxic effects in soils. The number of end-points is comparable to those used for other heavy metals (Table 3).

Plotting all the toxicity end-points expressed as µg (g soil)$^{-1}$, or their logarithms, against either pH or SOM did not reveal any significant relationships, neither did multiple regression combining pH and %OM. This may reflect the differences in toxicity processes. Welp and Brummer (1997) showed that for the same microbial process (Fe(III) reduction) in different soils the logarithm of the end-point depended significantly on both pH and %OM, and we found that multiple regression with these variables yielded an r^2 of 83% ($p < 0.001$). However, no such relationships were found in the new data reported here on other microbial processes (Table 2B).

Figure 1 shows SSDs for Hg(II) plotted in terms of both µg (g soil)$^{-1}$ and µg (g SOM)$^{-1}$. There is no clear indication of different sensitivities among species or processes, although the results are dominated by results for microbes. The Critical Limits are derived from the data by repeated bootstrap calculation of the lower 5th percentile value, values of 0.13 µg (g soil)$^{-1}$ and 3.3 µg (g SOM)$^{-1}$ being obtained. These values are assumed to apply under all conditions, i.e. they do not vary with pH or any other soil variables. Of course, the use of the SOM-based value implies that the Critical Limit does depend upon SOM. The Critical Limits for Hg(II) are substantially lower than those of other bivalent cationic metals (Table 3).

Regulatory agencies have estimated guideline soil levels of Hg, aimed at protecting either human health or the environment. UK soil guideline values for inorganic Hg, to protect human health depend upon the land-use, but the lowest value is 8 µg (g soil)$^{-1}$ (Environment Agency, 2002). The corresponding value for Canada is 6.6 µg (g soil)$^{-1}$, which is lower than the value of 12 µg (g soil)$^{-1}$ that applies to environmental health (Canadian Council of Ministers of the Environment, 1999). Both are considerably greater than the corresponding value derived here of 0.13 µg (g soil)$^{-1}$. For the Netherlands, Crommentuijn et al. (1997) recommended a maximum permissible added content of 1.9 µg (g soil)$^{-1}$ for a soil with 10% organic matter; our SOM-based Critical Limit would convert to 0.33 µg (g soil)$^{-1}$. In contrast, our SOM-based value is appreciably higher than the value of 0.5 µg (g SOM)$^{-1}$

suggested by De Vries et al. (2007) on the basis of experiments on forest floor soil samples (Bringmark and Bringmark, 2001). As noted in the Introduction, this value of 0.5 µg (g SOM)$^{-1}$ was used to determine that 85% of European sites are exceeded in the Critical Load (Hettelingh and Sliggers, 2006). Use of our new higher value would decrease the geographical area for which the Critical Load is exceeded..

3.3 Critical Limit Function in terms of [Hg^{2+}] and pH

We applied WHAM / Model VI to estimate [Hg^{2+}] from added Hg(II), pH and SOM content. The calculation required assumptions about the background electrolyte, and each soil had to be "titrated" with either strong acid or strong base to achieve the measured pH. The [Hg^{2+}] values finally used were obtained assuming all soils to contain 0.5 mM $Ca(NO_3)_2$ as background electrolyte, with calculated additions of either Na or Cl to adjust pH. However, very similar results were obtained if NaCl was used as background, and adjustments were made with Ca or NO_3. As discussed in Section 3.1, we set log K_{MA} to 3.5 for both HA and FA, and assumed log K_{so} = 2.7 for $Fe(OH)_3$ solubility. Since the toxicity data refer to added metal in laboratory toxicity experiments, we assume that all the metal is "reactive" or "geochemically active", i.e. able to participate in solid-solution partitioning, chemical speciation in solution, and to be bioavailable. The estimated free ion concentrations are included in Table 2, and plotted against pH in Figure 2. The calculated values of [Hg^{2+}] fall in a wide range, from as low as 10^{-35} to as high as 10^{-13} mol l^{-1}. The dashed line is the median linear regression ($p < 0.001$ by bootstrapping).

The Critical Limit Function (CLF) was calculated using an adjusted version of the method used by Lofts et al. (2004). The procedure involves firstly calculating an expression for the median toxicity of [Hg^{2+}] as a function of pH and then deriving a further expression for the critical limit concentration of [Hg^{2+}] by assuming the distribution of toxicity data around the median expression to represent the distribution of sensitivities of soil organisms to Hg^{2+}. This entailed the following steps.

(i) The toxicity dataset (comprising pairs of soil solution pH and log [Hg^{2+}] concentrations) was sampled 10,000 times with replacement and slope (α) and intercept (γ) values calculated using median linear regression.

(ii) For each sample, a sensitivity distribution of the regression residuals was calculated and the 95–percentile (δ) of this distribution calculated. A value of γ corresponding to the critical concentration of [Hg^{2+}], was calculated as $\gamma_{crit} = \gamma + \delta$. The critical concentration of [Hg^{2+}] is given by log [Hg^{2+}]$_{crit}$ = α.pH + γ_{crit}.

(iii) Using the sampled slope and intercept parameters α and γ_{crit}, 10,000 values of log [Hg^{2+}]$_{crit}$ were calculated at each of a series of pH values spanning the range found in the toxicological tests. The CLF was derived by linear regression of the median log [Hg^{2+}]$_{crit}$ against pH. The solid line in Figure 2 represents the CLF, with α = -2.15 and γ_{crit} = -17.10.

Figure 2 shows the CLF for Hg(II) and also CLFs derived for other heavy metals (Ni, Cu, Zn, Cd and Pb). It is clear that the Hg(II) CLF falls many orders of magnitude below those of the other metals. The range of end-points, on the logarithmic scale, is relatively large for Hg(II). Table 3 presents the full set of CLF parameters for six cationic metals.

The CLF approach is empirical, but is consistent with the more mechanistic Biotic Ligand Model (Niyogi and Wood, 2004; Thakali et al., 2006), in that chemical speciation is regarded as the key to metal interaction with organisms, and thereby to toxicity. The free metal ion concentration is central to this idea, but competition with other cations, notably H^+, is also taken into account, hence the pH term in the CLF. In the case of Hg(II) the free ion concentrations are very low (Table 2, Figure 2), which means that binding to both soil organic matter and the biota is very strong. It is important to recognise that the free ion approach does not suggest that the free ion is somehow the “toxic species” or the “bioavailable form” of the metal; rather, it is the main variable that predicts toxicity. In the chemical equilibrium-based approaches (i.e. the CLF or the Biotic Ligand Model) *all* the “reactive” or “geochemically active” metal (i.e. all metal in solution, adsorbed to soil organic matter or mineral particles, etc) is bioavailable, but the chemical reactions govern the extent to which the metal reacts with the organism, and therefore toxicity. Thus, if the concentrations of other chemical species are kept constant, the greater is [M^{z+}] the greater is the extent of reaction with the organism, and therefore the greater the toxic effect.

The speciation modelling results (Section 3.1) showed only partial validation of the model by comparison with experimentally-estimated soil [Hg^{2+}], in particular with regard to the pH dependence of Hg(II) binding. Accordingly, the derived CLF also is also uncertain with respect to the pH dependence. As long as WHAM is used to estimate [Hg^{2+}] then application of the CLF derived here will yield consistent results, since any errors will cancel. But in an absolute sense the CLF parameters are highly approximate.

3.4 Application of the Critical Limits for Hg(II)

For four hypothetical but representative soils differing in pH and OM content, we calculated the active Hg content corresponding to the three types of Critical Limit derived in the present work (Table 4). For the soil-based Hg content limit of 0.13 µg g^{-1} the value is the same in all cases, and variation in soil properties cannot be taken into account. The SOM-based limit of 3.3 µg g^{-1} yields a variation of 100-fold, from 0.03 to 3.3 µg g^{-1}. The CLF gives similar results but a slightly smaller range, from 0.04 to 1.2 µg g^{-1}. The differences between the SOM- and CLF-based values arise because the pH dependence of Hg(II) binding by soil differs from the pH-dependence of the CLF. These results demonstrate the superiority of approaches that take soil properties into account; the purely soil-based Critical Limit would be over-protective at low pH / high SOM and under-protective at high pH / low SOM.

The soil contents of Hg(II) at the Critical Limit refer to reactive metal, which is well-defined for toxicity experiments in which metal salts are added to soil, and in theoretical chemical speciation calculations, but less so when analysing samples of soils from the field. For the other cationic bivalent metals of Table 3, extraction with dilute acid or EDTA provides a reasonable estimate of reactive metal (see e.g. Tipping et al., 2003), but preliminary studies in our laboratory (A.J. Lawlor and E.Tipping, unpublished results) suggest that such reagents are ineffective for Hg(II); see also Ernst et al. (2008). The use of a more aggressive extractant such as aqua regia may therefore be needed to release Hg(II) from soils, but this could also mobilise unreactive metal that is part of parent mineral matter, leading to overestimation of both atmospherically-deposited and bioavailable mercury (Krug and Winstanley, 2004).

4. Conclusions

(a) Critical Limits for Hg expressed as added metal content of soil are 0.13 µg (g soil)$^{-1}$ and 3.30 µg (g SOM)$^{-1}$. These are substantially lower than values derived by the same method for other bivalent cationic metals (Ni, Cu, Zn, Cd, Pb).

(b) The SOM-based limit is appreciably higher than the value of 0.5 µg (g SOM)$^{-1}$ currently recommended for use in calculating Critical Loads.

(c) With Hg(II) toxicity expressed in terms of the free ion concentration, [Hg^{2+}], estimated using WHAM / Model VI, an approximate Critical Limit Function (CLF) is derived. This takes the form; $\log [Hg^{2+}]_{crit} = - 2.15\ pH – 17.10$.

(d) The SOM-based Critical Limit and the CLF provide the best assessments of permissible soil levels of reactive Hg(II), which vary from *c.* 2 µg (g soil)$^{-1}$ for acid organic soil to *c.* 0.05 µg (g soil)$^{-1}$ for neutral soil low in organic matter.

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Table 1. Free ion concentrations of Hg(II) in equilibrium with peat soil. The observed values are from Skyllberg et al. (2000), the simulations are from WHAM.

pH	mol Hg gC^{-1}	log [Hg^{2+}] mol l^{-1}	
		obs	sim
2.83	-8.68	-28.50	-23.73
3.15	-8.41	-28.19	-24.07
3.18	-8.41	-28.25	-24.14
3.20	-6.93	-25.40	-20.09
3.21	-7.40	-26.20	-21.70
3.22	-8.62	-28.80	-24.52
3.24	-8.35	-28.40	-24.20
3.24	-7.91	-27.50	-23.11
3.24	-7.67	-27.00	-22.37
3.34	-7.47	-25.65	-22.17
3.34	-7.52	-25.65	-22.27
3.51	-8.37	-28.68	-24.88
3.54	-8.37	-28.69	-24.95
3.66	-7.38	-25.67	-22.76
3.72	-7.35	-25.68	-22.84
5.23	-6.92	-25.90	-25.52
5.41	-6.91	-25.94	-26.01
5.59	-6.92	-25.90	-26.56
5.98	-6.76	-26.24	-27.24
6.40	-6.69	-26.75	-28.28

Table 2A. Chronic toxicity data for Hg(II) for plants and invertebrates. OM is organic matter; [Hg]$^{2+}$ estimated by modelling with WHAM/Model VI.

Toxicity variable	pH	OM %	addedHg flg gsoil"^{1}	log [Hg2+] mol r'	Reference
Plants					
Cynodon dactylon leaf dry weight	7.8	14	8.0	-26.5	Weaver 1984
Cynodon dactylon stem dry weight	4.6	04	25.0	-13.7	Weaver 1984
Lactuca sativa seed emergence	4.0	5.6	7.0	-20.1	Environment Canada 1995
Raphanus sativa seed emergence	4.0	5.6	51.0	-16.7	Environment Canada 1995
Phaseolus vulgaris straw yield	4.9	3.2	0.9	-24.3	Semu 1985
Invertebrates					
Eisenia fetida reproduction	64	10.0	10.0	-25.7	Lock & Janssen 2001
Eisenia fetida reproduction	6.2	3.2	4.8	-24.7	Gudbrandsen et al 2007
Enchytraeus albidus reproduction	64	10.0	18.0	-24.9	Lock & Janssen 2001
Folsomia candida reproduction	64	10.0	1.8	-28.9	Lock & Janssen 2001
Paronychiurus kimi progeny	64	10.0	00	-33.7	Son et al 2007

Table 2B. Chronic toxicity data for Hg(II) for microbial processes and community structure. OM is organic matter; $[Hg]^{2}+$ estimated by modelling with WHAM/Model VI.

Toxicity variable	pH	OM %	addedHg)Jg gsoil·^{1}	log [Hg2+] moll"^{1}	Reference
ammonification	7.9	1.5	26.0	-24.5	
amylase activity	7.4	3.8	70	-23.1	
ATP content	5.9	24.0	2.0	-29.0	
ATP content	6.4	3.2	3	-25.8	
dehydrogenase activity	7.5	2.2	0.1	-33.9	
Fe(III) reduction	5.8	4.0	0.1	-29.8	
Fe(III) reduction	5.6	2.4	0.2	-28.5	
Fe(III) reduction	5.6	2.4	0.2	-28.4	
Fe(III) reduction	8.0	3.4	0.2	-34.6	
Fe(III) reduction	7.3	3.2	0.3	-32.2	
Fe(III) reduction	8.2	2.2	0.4	-33.7	
Fe(III) reduction	5.8	6.6	2.0	-26.4	
Fe(III) reduction	6.0	5.2	2.0	-26.5	
Fe(III) reduction	4.5	11.0	2.0	-24.4	
Fe(III) reduction	7.9	9.6	3.0	-31.6	
Fe(III) reduction	5.7	6.6	5.0	-24.4	
Fe(III) reduction	4.4	15.6	6.0	-22.7	
Fe(III) reduction	5.2	22.8	125.0	-20.0	
fluorescein diacetate hydrolysis	6.4	3.2	4	-25.4	Zelles et al. 1985
microbial respiration - C mineralisation	8.2	3.2	10.0	-28.8	Landa & Fang 1978
microbial respiration - C mineralisation	6.6	13.4	0.5	-31.6	Landa & Fang 1978
nitrification	8.1	6.1	70.0	-25.9	vanFaassen 1973
nitrification	7.9	1.5	1.2	-30.2	vanFaassen 1973
nitrification	7.4	30.0	2.0	-32.8	Beck 1981
Operational Taxonomic Unit	3.2	5.8	0.4	-22.4	This study
Operational Taxonomic Unit	3.3	8.4	0.3	-23.4	This study
Operational Taxonomic Unit	4.4	7	0.5	-25.5	This study
Operational Taxonomic Unit	4.5	4.2	8.2	-20.5	This study
Operational Taxonomic Unit	4.5	8.2	5.9	-22.0	This study
Operational Taxonomic Unit	4.9	16.4	5.1	-24.2	This study
Operational Taxonomic Unit	5.7	6.4	3.2	-25.2	This study
Operational Taxonomic Unit	6.8	10	31.1	-24.9	This study
Operational Taxonomic Unit	7.5	8.8	19.6	-27.4	This study
respiration	3.2	5.8	2.0	-20.0	This study
respiration	3.3	8.4	0.6	-22.7	This study
respiration	4.4	7	6.9	-21.3	This study
respiration	4.5	4.2	1.8	-22.8	This study
respiration	4.5	8.2	0.4	-26.2	This study
respiration	4.9	16.4	2.5	-25.8	This study
respiration	5.7	6.4	2.8	-25.5	This study
respiration	6.8	10	0.4	-31.7	This study
respiration	7.4	3.8	70	-23.1	Tu 1998

Table 3 Summary of Critical Limits for heavy metals in soil. The values for Ni, Cu, Zn, Cd and Pb are from Ashmore et al. (2007).

Metal	no. of data	μg (gsoil)$^{-1}$	μg (gSOM)$^{-1}$	CLF α	CLF γ_{crit}
Ni	83	9.4	481	-0.42	-3.78
Cu	141	10.0	227	-1.26	-1.80
Zn	92	17.9	253	-0.25	-5.07
Cd	63	3.5	54	-0.31	-6.36
Hg	52	0.13	3.3	-2.15	-17.10
Pb	49	52.8	984	-0.93	-3.50

Table 4 Comparison of soil Hg contents at the Critical Limit, calculated from the three Critical Limit methods (soil, SOM, function) described in the text.

pH	%OM	log [Hg^{2+}]	soil Hg µg g^{-1} CL soil	 CL SOM	 CLF
4.0	100	-25.70	0.13	3.30	1.19
5.0	20	-27.85	0.13	0.66	0.64
6.0	5	-30.00	0.13	0.17	0.19
7.0	1	-32.15	0.13	0.033	0.048

Figure captions

Figure 1

Species sensitivity distributions for Hg(II) chronic toxicity endpoints in soil, expressed in terms of soil solids (upper panel) and soil organic matter (lower panel). The derivation of Critical Limits at the 5th percentile is demonstrated with the horizontal and vertical lines.

Figure 2

Toxic end-points expressed as [Hg^{2+}], symbols as for Figure 1. The dashed line is the median regression, and the solid line the derived Critical Limit Function (CLF). CLFs for Ni, Cu, Zn, Cd and Pb are also shown.

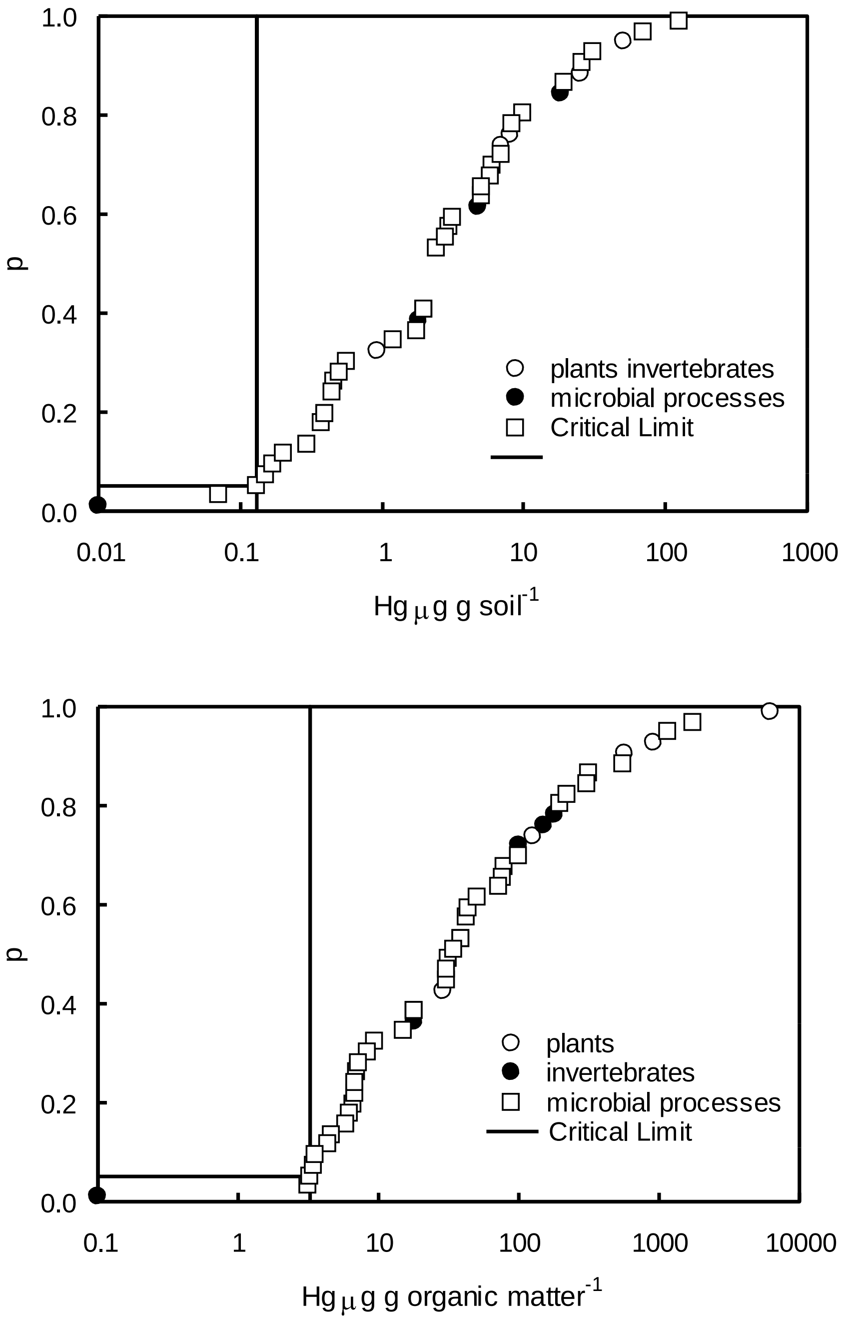
1.0
0.8
0.6
0.4
0.2
0.0
p
0.01
0.1
1
10
100
1000
Hg μg g soil^{-1}
○ plants invertebrates
● microbial processes
□ Critical Limit
1.0
0.8
0.6
0.4
0.2
0.0
p
0.1
1
10
100
1000
10000
Hg μg g organic matter^{-1}
○ plants
● invertebrates
□ microbial processes
Critical Limit

Figure 1

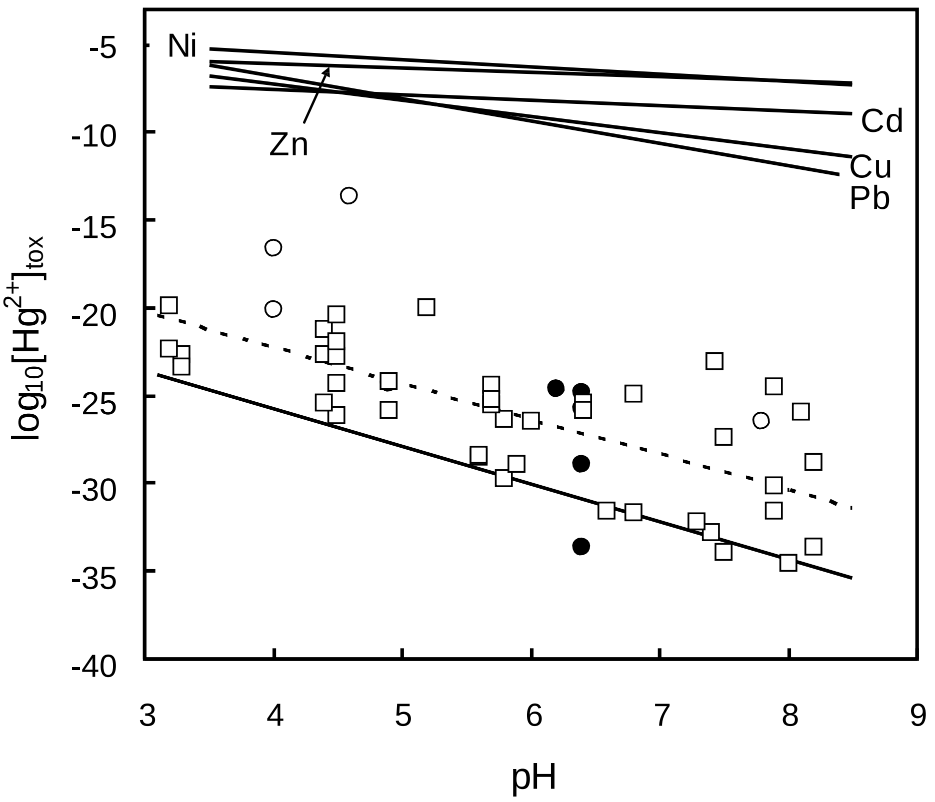

Figure 2