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

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28 “Capsule”

29 *Published laboratory toxicity data and chemical speciation modelling are used to derive*
30 *Critical Limits expressed as either soil Hg(II) content or Hg²⁺ concentration.*

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34

35 **Abstract**

36

37 Published chronic toxicity data for Hg(II) added to soils were assembled and evaluated to
38 produce a data set comprising 52 chronic endpoints, five each for plants and invertebrates and
39 42 for microbes. With endpoints expressed in terms of added soil Hg(II) contents, Critical
40 Limits were derived from the 5th percentiles of species sensitivity distributions, values of 0.13
41 $\mu\text{g (g soil)}^{-1}$ and $3.3 \mu\text{g (g soil organic matter)}^{-1}$ being obtained. The latter value exceeds the
42 currently-recommended Critical Limit, used to determine Hg(II) Critical Loads in Europe, of
43 $0.5 \mu\text{g (g soil organic matter)}^{-1}$. We also applied the WHAM/Model VI chemical speciation
44 model to estimate concentrations of Hg^{2+} in soil solution, and derived **an approximate** Critical
45 Limit Function (CLF) that includes pH; $\log [\text{Hg}^{2+}]_{\text{crit}} = -2.15 \text{ pH} - 17.10$. Because they take
46 soil properties into account, the soil organic matter-based limit and the CLF provide the best
47 assessment of toxic threat for different soils. For differing representative soils, each predicts a
48 range of up to 100-fold in the dry weight-based content of mercury that corresponds to the
49 Critical Limit.

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

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56 1. Introduction

57

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

70 The Critical Limit for Hg(II) used by De Vries et al. (2007) was derived differently
71 from limits for other metals (Cu, Zn, Cd, Pb), for which experimental chronic (NOEC, EC₁₀)
72 toxicity data have been assembled and analysed using the Species Sensitivity Distribution
73 (SSD) concept (e.g. Crommentuijn et al., 1997). The work described here was performed in
74 order to derive SSD-based limits from published laboratory toxicity data for Hg(II). We
75 assembled all available and acceptable published soil toxicity data for Hg(II) and analysed
76 them to derive Critical Limits based on the maximum information. The limit values were set
77 at the 5% level, i.e. protective of 95% of soil organisms (see e.g. Posthuma et al., 2003; Van
78 Straalen and Denneman, 1989). Our main purpose in conducting this work was to obtain
79 Critical Limits that can be used to quantify the possible effects of atmospherically-deposited
80 Hg on natural and semi-natural ecosystems. However, the values should be generally
81 applicable.

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

89 The third approach followed that of Lofts et al. (2004), who described toxic effects not
90 in terms of the total metal added to the soil, but the metal free ion concentration in soil
91 solution. They derived Critical Limit Functions, in which the logarithm of the critical free ion
92 concentration was expressed as a linear function of pH. Although this does not involve an
93 explicit mechanism of toxicity, it is consistent with the idea that toxic response is elicited by a
94 quasi-complexation mechanism in which the reactivity of the metal, expressed through the
95 free ion concentration, is a pH-dependent measure of toxicity. This takes bioavailability into
96 account in a simple way, as is thought desirable (Peijnenburg et al., 2002; Janssen et al.,
97 2003); there is much current interest in relating metal toxic effects to the chemistry of the
98 metals in the solution phase by which exposure occurs. Lofts et al. (2004) used pedotransfer
99 functions to estimate free metal ion concentrations in soil solution for published toxicity
100 experiments. These functions were multiple regression equations that were derived from
101 analysis of metal concentrations in the solutions of soils of differing pH, organic matter
102 content and heavy metal content (Tipping et al., 2003). Because such pedotransfer functions
103 are not currently available for Hg(II), we used the WHAM chemical speciation model
104 (Tipping, 1994; 1998) to estimate Hg²⁺ concentrations, denoted by [Hg²⁺].

105

106

107 2. Methods

108

109 2.1 Toxicity data

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

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

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

117 (iii) The metal was added singly to the soil in a soluble form. In all the tests accepted, the
118 form of mercury added was HgCl₂.

119 (iv) The pH and organic carbon or organic matter content of the soil were quoted or
120 referenced. Where organic carbon alone was quoted it was converted to organic matter by
121 multiplying by 2.0. Measured pH values were converted from values obtained by soil
122 extraction (using H₂O, KCl or CaCl₂) to soil solution pH using the equations given by de
123 Vries et al. (2005).

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

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

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

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

143

144 2.2 Chemical speciation modelling

145 Calculations of soil and water chemical speciation were performed using WHAM (Tipping,
146 1994) incorporating Humic Ion-Binding Model VI (Tipping, 1998). Model VI uses a
147 structured formulation of discrete, chemically-plausible, binding sites for protons, in order to
148 allow the creation of regular arrays of bidentate and tridentate binding sites for metals. Metal
149 aquo ions (Al^{3+} , Fe^{3+} , Hg^{2+} etc.) and their first hydrolysis products (AlOH^{2+} , FeOH^{2+} , HgOH^{+}
150 etc.) compete with each other, and with protons, for binding. The same intrinsic equilibrium
151 constant (K_{MA}) for binding to carboxyl or type A groups is assumed to apply to the aquo ion
152 and its first hydrolysis product. The constant (K_{MB}) for binding to weaker acid groups is
153 related to K_{MA} , and the contribution of rarer “soft” ligand atoms is factored in. The intrinsic
154 equilibrium constants are modified by empirical electrostatic terms that take into account the
155 attractive or repulsive interactions between ions and the charged macromolecule. More
156 information and parameter values are given in Table S1. The humic ion-binding model is
157 combined with an inorganic speciation model, the species list and constants for which were
158 given by Tipping (1994). The inorganic reactions in this database are restricted to monomeric
159 complexes of metals. The effects of ionic strength on the inorganic reactions are taken into
160 account using the extended Debye-Hückel equation. Temperature effects on reactions
161 between inorganic species are taken into account using published or estimated enthalpy data,
162 but in the absence of experimental information, reactions involving humic substances are
163 assumed to be independent of temperature. Tipping (1998, 2002) showed that the model can
164 account for the great majority of published data sets describing either proton binding by
165 humic matter or the binding of individual metals. Results from laboratory experiments
166 involving competition for binding between metal ions and protons, and between different
167 metal ions, have also been described successfully.

168 Soil organic matter is considered to comprise humic and fulvic acids (HA and FA),
169 together with “inert” organic matter. The solution phase contains FA and inert organic
170 matter. Therefore to apply the model the amounts of the humic substances (active with
171 respect to cation binding) have to be determined or assumed. Information relevant to the
172 present study has been reported by Tipping (2002) and Tipping et al. (2003). Tipping et al.
173 (2003) showed that the active organic matter could be represented by a combination of humic

174 and fulvic acids, but their combined contribution to the total organic matter varied. If the soil
175 contained less than 45% SOM, the active binding compounds accounted on average for 0.386
176 of the total SOM, but for soils with SOM contents of greater than 45 %, their combined
177 amount was 0.174 of the total soil mass (i.e. SOM and mineral matter). These values were
178 used in the present work to estimate the concentrations of soil humic substances. For soil
179 water, 65% of the dissolved organic matter was assumed to be active FA (Tipping et al.,
180 2003).

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183

184 3. Results and discussion

185

186 3.1 Chemical speciation modelling of Hg(II) in soil

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

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

206 The model should also provide reasonable estimates of soil solution $[Hg^{2+}]$. However
207 estimates of this variable are scarce, reflecting the extremely low values and absence of
208 reliable direct methodologies. The only relevant study is that of Skyllberg et al. (2000), who
209 measured total dissolved Hg(II) concentrations in suspensions of peat in 0.5 M NaBr, which
210 permitted estimation of $[Hg^{2+}]$ using equilibrium constants for Hg(II)-Br complexation. We
211 applied WHAM / Model VI to the same data, and compared the predicted and experimentally
212 estimated $[Hg^{2+}]$. The model outputs were insensitive to the value of $\log K_{MA}$ for FA; thus,
213 increasing the $\log K_{MA}$ for FA from 2.9 to 3.5, as applied above to match Hg:OC ratios, made
214 little difference to the simulated values because binding is dominated by solid phase HA.
215 Therefore for consistency we used the value of 3.5. Agreement between the measured and
216 calculated values of $[Hg^{2+}]$ is only approximate (Table 1). The model predicts higher
217 concentrations at low pH, with better agreement at higher pH. We examined competition due

218 to Al and Fe(III) by varying their assumed soil contents. There was little dependence on the
219 Al concentration for typical soil levels. Relatively large effects of Fe(III) were found. The
220 results in Table 1 are based on a solubility product ($\log K_{so}$) for the reaction $\text{Fe}(\text{OH})_3 + 3\text{H}^+ =$
221 $\text{Fe}^{3+} + 3\text{H}_2\text{O}$ ($\log K_{so}$) of 2.7 at 25°C. If a $\log K_{so}$ of 0.0 was assumed, agreement with the
222 observations was good at low pH, but simulated $[\text{Hg}^{2+}]$ became too low at higher pH.

223 The observations and simulations are both consistent with strong binding of Hg(II) by
224 organic matter and very low Hg^{2+} concentrations in soil solution. However the validation
225 attempt is clearly not fully successful, in particular with respect to the pH dependence of
226 Hg(II) binding. The stronger pH dependence predicted by WHAM is consistent with
227 observations of Hg binding by isolated dissolved organic matter fractions covering the pH
228 range 4.9 to 7.0 (Haitzer et al. 2002, 2003). It can also be argued that modification of the
229 model on the basis of indirect estimates based on results obtained from experiments under
230 unnatural chemical conditions (i.e. 0.5 M NaBr) is inappropriate. Furthermore, adjustment of
231 the pH dependence of binding would require a major change to WHAM, the model assumes
232 competition between metal ions and protons, the binding of which is determined separately.
233 Therefore we decided not to make further model amendments, and it is applied to estimate
234 $[\text{Hg}^{2+}]$ in the soils used for toxicity experiments with caution.

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

248

249 3.2 Critical Limits expressed in terms of Hg(II) soil contents

250 Fifty-two toxicity end-points were obtained from published data, and these are summarised in
251 Table 2. The results refer to five studies each with plants and invertebrates, and 42 studies of

252 microbial processes. For this analysis we used the published end-points for all studies except
253 those of Semu et al. (1985), Gudbrandsen et al. (2007), Son et al. (2007), van Faassen (1973)
254 and Landa and Fang (1978), and the new data reported here (see Supplementary Content), for
255 which we estimated endpoints using the log–logistic dose response model used by Lofts et al.
256 (2004). The data set of Table 2 represents a substantial increase in the number of data points
257 (18) assembled by Slooff et al (1995), and is an up-to-date compilation providing the best
258 current basis for assessing Hg(II) toxic effects in soils. The number of end-points is
259 comparable to those used for other heavy metals (Table 3).

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

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

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

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

291

292 3.3 Critical Limit Function in terms of $[\text{Hg}^{2+}]$ and pH

293 We applied WHAM / Model VI to estimate $[\text{Hg}^{2+}]$ from added Hg(II), pH and SOM content.
294 The calculation required assumptions about the background electrolyte, and each soil had to
295 be “titrated” with either strong acid or strong base to achieve the measured pH. The $[\text{Hg}^{2+}]$
296 values finally used were obtained assuming all soils to contain 0.5 mM $\text{Ca}(\text{NO}_3)_2$ as
297 background electrolyte, with calculated additions of either Na or Cl to adjust pH. However,
298 very similar results were obtained if NaCl was used as background, and adjustments were
299 made with Ca or NO_3 . As discussed in Section 3.1, we set $\log K_{\text{MA}}$ to 3.5 for both HA and
300 FA, and assumed $\log K_{\text{so}} = 2.7$ for $\text{Fe}(\text{OH})_3$ solubility. Since the toxicity data refer to added
301 metal in laboratory toxicity experiments, we assume that all the metal is “reactive” or
302 “geochemically active”, i.e. able to participate in solid-solution partitioning, chemical
303 speciation in solution, and to be bioavailable. The estimated free ion concentrations are
304 included in Table 2, and plotted against pH in Figure 2. The calculated values of $[\text{Hg}^{2+}]$ fall
305 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
306 linear regression ($p < 0.001$ by bootstrapping).

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

- 313 (i) The toxicity dataset (comprising pairs of soil solution pH and $\log [\text{Hg}^{2+}]$ concentrations)
314 was sampled 10,000 times with replacement and slope (α) and intercept (γ) values
315 calculated using median linear regression.
- 316 (ii) For each sample, a sensitivity distribution of the regression residuals was calculated and
317 the 95–percentile (δ) of this distribution calculated. A value of γ corresponding to the

318 critical concentration of $[\text{Hg}^{2+}]$, was calculated as $\gamma_{\text{crit}} = \gamma + \delta$. The critical concentration
319 of $[\text{Hg}^{2+}]$ is given by $\log [\text{Hg}^{2+}]_{\text{crit}} = \alpha \cdot \text{pH} + \gamma_{\text{crit}}$.

320 (iii) Using the sampled slope and intercept parameters α and γ_{crit} , 10,000 values of \log
321 $[\text{Hg}^{2+}]_{\text{crit}}$ were calculated at each of a series of pH values spanning the range found in the
322 toxicological tests. The CLF was derived by linear regression of the median $\log [\text{Hg}^{2+}]_{\text{crit}}$
323 against pH. The solid line in Figure 2 represents the CLF, with $\alpha = -2.15$ and $\gamma_{\text{crit}} = -$
324 17.10.

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

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

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

350

351 3.4 Application of the Critical Limits for Hg(II)

352 For four hypothetical but representative soils differing in pH and OM content, we calculated
353 the active Hg content corresponding to the three types of Critical Limit derived in the present
354 work (Table 4). For the soil-based Hg content limit of $0.13 \mu\text{g g}^{-1}$ the value is the same in all
355 cases, and variation in soil properties cannot be taken into account. The SOM-based limit of
356 $3.3 \mu\text{g g}^{-1}$ yields a variation of 100-fold, from 0.03 to $3.3 \mu\text{g g}^{-1}$. The CLF gives similar
357 results but a slightly smaller range, from 0.04 to $1.2 \mu\text{g g}^{-1}$. The differences between the
358 SOM- and CLF-based values arise because the pH dependence of Hg(II) binding by soil
359 differs from the pH-dependence of the CLF. These results demonstrate the superiority of
360 approaches that take soil properties into account; the purely soil-based Critical Limit would
361 be over-protective at low pH / high SOM and under-protective at high pH / low SOM.

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

373

374

375

376 **4. Conclusions**

377

378 (a) Critical Limits for Hg expressed as added metal content of soil are $0.13 \mu\text{g (g soil)}^{-1}$ and
379 $3.30 \mu\text{g (g SOM)}^{-1}$. These are substantially lower than values derived by the same method
380 for other bivalent cationic metals (Ni, Cu, Zn, Cd, Pb).

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

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

386 (d) The SOM-based Critical Limit and the CLF provide the best assessments of permissible
387 soil levels of reactive Hg(II), which vary from *c.* $2 \mu\text{g (g soil)}^{-1}$ for acid organic soil to *c.*
388 $0.05 \mu\text{g (g soil)}^{-1}$ for neutral soil low in organic matter.

389

390

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396 (in Northern Ireland).

397

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526 volatilization. *Chemosphere* 19, 1721-1727.
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- 528

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

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 532

| 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 |

533
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 535

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

538

| Toxicity variable | pH | OM % | added Hg μg gsoil ⁻¹ | log [Hg ²⁺] mol l ⁻¹ | Reference |
|---|-----|---------|------------------------------------|--|-------------------------|
| <u>Plants</u> | | | | | |
| <i>Cynodon dactylon</i> leaf dry weight | 7.8 | 1.4 | 8.0 | -26.5 | Weaver 1984 |
| <i>Cynodon dactylon</i> stem dry weight | 4.6 | 0.4 | 25.0 | -13.7 | Weaver 1984 |
| <i>Lactuca sativa</i> seed emergence | 4.0 | 5.6 | 7.0 | -20.1 | Environment Canada 1995 |
| <i>Raphanus sativa</i> seed emergence | 4.0 | 5.6 | 51.0 | -16.7 | Environment Canada 1995 |
| <i>Phaseolus vulgaris</i> straw yield | 4.9 | 3.2 | 0.9 | -24.3 | Semu 1985 |
| <u>Invertebrates</u> | | | | | |
| <i>Eisenia fetida</i> reproduction | 6.4 | 10.0 | 10.0 | -25.7 | Lock & Janssen 2001 |
| <i>Eisenia fetida</i> reproduction | 6.2 | 3.2 | 4.8 | -24.7 | Gudbrandsen et al 2007 |
| <i>Enchytraeus albidus</i> reproduction | 6.4 | 10.0 | 18.0 | -24.9 | Lock & Janssen 2001 |
| <i>Folsomia candida</i> reproduction | 6.4 | 10.0 | 1.8 | -28.9 | Lock & Janssen 2001 |
| <i>Paronychiurus kimi</i> progeny | 6.4 | 10.0 | 0.0 | -33.7 | Son et al 2007 |

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541

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

544

| Toxicity variable | pH | OM | added Hg | log [Hg ²⁺] | Reference |
|--|-----|------|-----------------------|-------------------------|---------------------|
| | | % | µg gsoil ¹ | mol l ¹ | |
| ammonification | 7.9 | 1.5 | 26.0 | -24.5 | van Faassen 1973 |
| amylase activity | 7.4 | 3.8 | 70 | -23.1 | Tu 1998 |
| ATP content | 5.9 | 24.0 | 2.0 | -29.0 | Zelles 1989 |
| ATP content | 6.4 | 3.2 | 3 | -25.8 | Zelles et al. 1985 |
| dehydrogenase activity | 7.5 | 2.2 | 0.1 | -33.9 | Welp 1999 |
| Fe(III) reduction | 5.8 | 4.0 | 0.1 | -29.8 | Welp & Brummer 1997 |
| Fe(III) reduction | 5.6 | 2.4 | 0.2 | -28.5 | Welp & Brummer 1997 |
| Fe(III) reduction | 5.6 | 2.4 | 0.2 | -28.4 | Welp & Brummer 1997 |
| Fe(III) reduction | 8.0 | 3.4 | 0.2 | -34.6 | Welp & Brummer 1997 |
| Fe(III) reduction | 7.3 | 3.2 | 0.3 | -32.2 | Welp & Brummer 1997 |
| Fe(III) reduction | 8.2 | 2.2 | 0.4 | -33.7 | Welp & Brummer 1997 |
| Fe(III) reduction | 5.8 | 6.6 | 2.0 | -26.4 | Welp & Brummer 1997 |
| Fe(III) reduction | 6.0 | 5.2 | 2.0 | -26.5 | Welp & Brummer 1997 |
| Fe(III) reduction | 4.5 | 11.0 | 2.0 | -24.4 | Welp & Brummer 1997 |
| Fe(III) reduction | 7.9 | 9.6 | 3.0 | -31.6 | Welp & Brummer 1997 |
| Fe(III) reduction | 5.7 | 6.6 | 5.0 | -24.4 | Welp & Brummer 1997 |
| Fe(III) reduction | 4.4 | 15.6 | 6.0 | -22.7 | Welp & Brummer 1997 |
| Fe(III) reduction | 5.2 | 22.8 | 125.0 | -20.0 | Welp & Brummer 1997 |
| 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 | van Faassen 1973 |
| nitrification | 7.9 | 1.5 | 1.2 | -30.2 | van Faassen 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 |

545

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

548

| Metal | no. of data | $\mu\text{g (gsoil)}^{-1}$ | $\mu\text{g (gSOM)}^{-1}$ | 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 |

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551

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

554

| pH | %OM | log [Hg ²⁺] | soil Hg $\mu\text{g g}^{-1}$ | | |
|-----|-----|-------------------------|------------------------------|--------|-------|
| | | | 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 |

555

556 **Figure captions**

557

558 **Figure 1**

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

562

563 **Figure 2**

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

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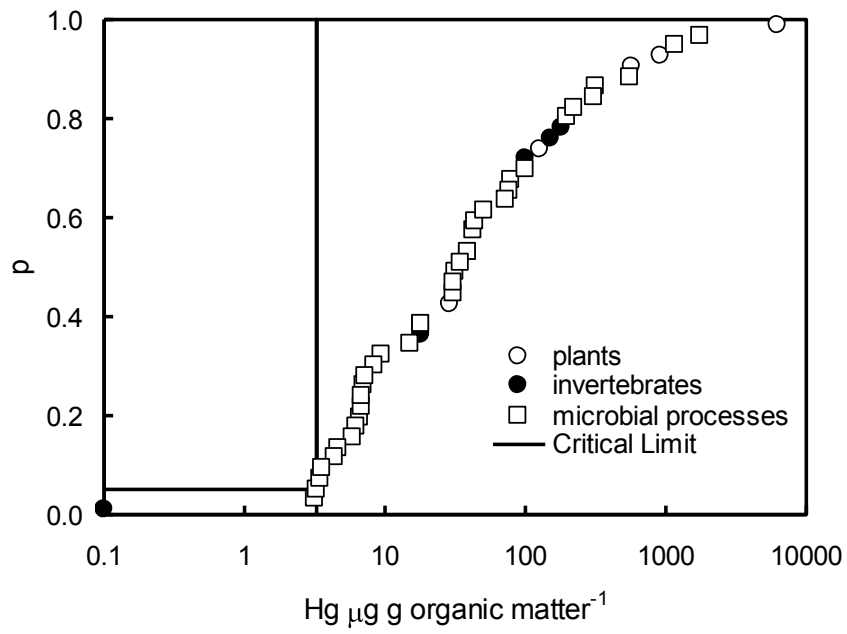
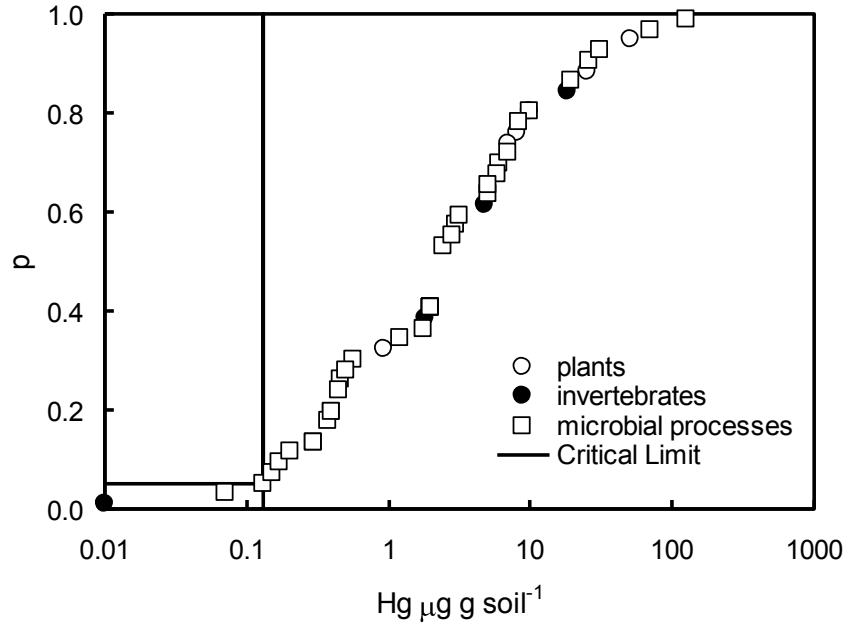


Figure 1

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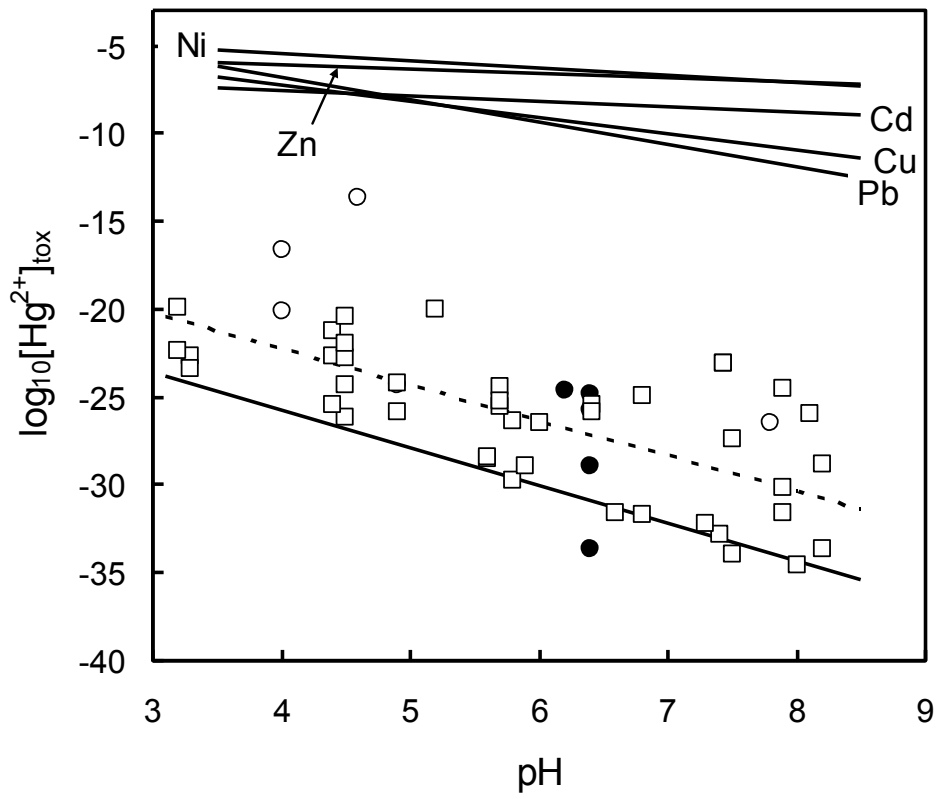


Figure 2