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Statistical uncertainty in hazardous terrestrial concentrations estimated with aquatic ecotoxicity data

Laura Golsteijn *, Rosalie van Zelm, A. Jan Hendriks, Mark A.J. Huijbregts

Radboud University Nijmegen, Institute for Water and Wetland Research, Department of Environmental Science, P.O. Box 9010, 6500 GL, Nijmegen, The Netherlands

HIGHLIGHTS

- We compared terrestrial and aquatic hazardous concentrations for 47 organic chemicals.
- We assessed uncertainty related to the sample size of species and the K_{oc}.
- For 81% of the chemicals, terrestrial and aquatic HC50s did not statistically differ.
- Uncertainty in the ratio HC50(soil)/HC50(aq) was typically 2.3 orders of magnitude.
- Regressions between aquatic and terrestrial HC50s differed per chemical class.

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ABSTRACT

Since chemicals' ecotoxic effects depend for most soil species on the dissolved concentration in pore water, the equilibrium partitioning (EP) method is generally used to estimate hazardous concentrations (HC50) in the soil from aquatic toxicity tests. The present study analyzes the statistical uncertainty in terrestrial HC50s derived by the EP-method. For 47 organic chemicals, we compared freshwater HC50s derived from standard aquatic ecotoxicity tests with porewater HC50s derived from terrestrial ecotoxicity tests. Statistical uncertainty in the HC50s due to limited species sample size and in organic carbon–water partitioning coefficients due to predictive error was treated with probability distributions propagated by Monte Carlo simulations. Particularly for specifically acting chemicals, it is very important to base the HC50 on a representative sample of species, composed of both target and non-target species. For most chemical groups, porewater HC50 values were approximately a factor of 3 higher than freshwater HC50 values. The ratio of the porewater HC50/freshwater HC50 was typically 3.0 for narcotic chemicals (2.8 for nonpolar and 3.4 for polar narcotics), 0.8 for reactive chemicals, 2.9 for neurotoxic chemicals (4.3 for AChE agents and 0.1 for the cyclodiene type), and 2.5 for herbicides–fungicides. However, the statistical uncertainty associated with this ratio was large (typically 2.3 orders of magnitude). For 81% of the organic chemicals studied, there was no statistical difference between the hazardous concentration of aquatic and terrestrial species. We conclude that possible systematic deviations between the HC50s of aquatic and terrestrial species appear to be less prominent than the overall statistical uncertainty.

1. Introduction

To protect terrestrial ecosystems against unacceptable risk from chemical exposure, several countries have established soil quality standards (Nortcliff, 2002). Yet, the risk assessment of contaminated soil is complex and terrestrial toxicity data are available to a limited extent only. Soil quality standards are derived from metrics describing the toxicity of chemicals. An important metric to describe the toxicity of chemical exposure and uptake is the environmental concentration of a chemical that is toxic to 50% of all species (Long and Chapman, 1985; Hauschild, 2005). This so-called hazardous concentration (HC50) is the average of all species-specific L(E)C50 values (i.e. the concentration with (lethal) effects in 50% of the individuals of a species). The HC50 is applied in life cycle impact assessment to express the toxic potency of a chemical (Hauschild, 2005; Rosenbaum et al., 2008). Furthermore, the HC50 can be applied in the Sediment Quality Triad concept, i.e. in the integrated use of site-specific chemical information (concerning contamination), bioassays (concerning several toxicological endpoints), and ecological information (concerning e.g. alterations in benthic community structure) (Long and Chapman, 1985; Chapman, 1990).

* Corresponding author. Tel.: +31 (0)24 365 20 66.
E-mail addresses: L.Golsteijn@science.ru.nl (L. Golsteijn), R.vanZelm@science.ru.nl (R. van Zelm), A.J.Hendriks@science.ru.nl (A.J. Hendriks), M.Huijbregts@science.ru.nl (M.A.J. Huijbregts).

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Ecotoxic effects of organic chemicals depend for most soil species on the concentration that is bioavailable via dissolution in pore water. Pavlou and Weston (1983) and Adams et al. (1985) suggested that pore water is the primary route of exposure for soil dwelling organisms, as later confirmed in several other studies (Belfroid et al., 1994a,b, 1996; Jager, 1998; Jager et al., 2003). Hence, exposure is controlled by both substance specific and soil specific properties, such as aqueous solubility, acid dissociation constant, pH, and organic matter content (Loibner et al., 2006). It should be noted that dermal contact with soil or ingestion of soil may also be important for assessments of soil toxicity of lipophilic substances (Jager et al., 2003). Porewater concentrations have been proven to be relevant determinants of the toxicity of polycyclic aromatic hydrocarbons (Swartz et al., 1990), heavy metals (Swartz et al., 1985; Kemp and Swartz, 1988), polychlorinated biphenyls (Pavlou and Weston, 1983), and pesticides (Ziegenfuss et al., 1986; Schuytema et al., 1989; Houx and Aben, 1993; Xu et al., 2007).

In the so-called equilibrium partitioning (EP) method (Pavlou and Weston, 1984; Shea, 1988), a chemical's concentration in water and sediment can be modeled on the basis of its sorption equilibrium. The EP-method allows estimation of terrestrial ecotoxicity from measured aquatic toxicity data (Pavlou and Weston, 1984; Shea, 1988; Van der Kooij et al., 1991). Since aquatic toxicity data are much more abundant than soil toxicity data, application of the EP-method facilitates the terrestrial ecotoxicity assessment in case of absent soil toxicity data. Terrestrial HC50s were more often extrapolated from aquatic HC50 for application in life cycle impact assessment (see e.g. Hauschild and Wenzel, 1998; Jolliet et al., 2003; Haye et al., 2007).

The applicability of the EP-method is dependent on the availability of soil–water partitioning coefficients and on the validity of the sorption equilibrium model (Van der Kooij et al., 1991). Large uncertainties are inherent in soil–water partitioning coefficients, and as a result, terrestrial HC50s that are estimated with aquatic ecotoxicity data can also be uncertain. Haye et al. (2007) found that the EP-method should not be used for metals, because the partition coefficient is highly variable due to soil pH, organic matter content, or cation exchange capacity. With regard to the validity of the sorption equilibrium model, it is important to note that possible changes over time in the bioavailability of chemicals are not taken into account (Ronday et al., 1997).

When applying the EP-method to aquatic toxicity data in order to estimate terrestrial toxicity, it is assumed that the sensitivity of the aquatic and terrestrial species is similar. Van Beelen et al. (2003) tested aquatic to terrestrial extrapolation for ten organic substances and eight metals and found that using the EP-method indeed led to an equal chance of underestimation or overestimation of terrestrial toxic concentrations. Occasionally, the toxicity of chemicals to different terrestrial and aquatic species has been determined within the same study (for instance, Siegfried, 1993). However, rigorous comparisons of terrestrial and aquatic toxicity for large sets of chemicals and species are lacking. Furthermore, to the best of our knowledge, an uncertainty assessment of the EP-method with a distinction between different chemical classes has not been performed up to now.

The goals of the present study were to analyze the statistical uncertainty in estimates of terrestrial HC50 values derived by the equilibrium partitioning method, and to make a comparison to the statistical uncertainty in freshwater HC50 values. Thereby, we aimed to answer the question whether there is a statistical difference between porewater HC50 values derived from terrestrial ecotoxicity tests by the EP-method, and freshwater HC50 values derived from standard aquatic tests. Statistical uncertainty in HC50 values due to limited species sample size, and in organic carbon–water partitioning coefficients due to predictive error, was treated with probability distributions propagated by Monte Carlo simulations. In our results we distinguished narcotic chemicals (nonpolar and polar), reactive chemicals, neurotoxic chemicals (acetylcholinesterase (AChE) agents and cyclodiene type), and herbicides-fungicides.

2. Materials and methods

2.1. Equilibrium partitioning method

The relationship between concentrations in water and solids is described by a partition coefficient (K_p in L water kg^{-1} solids). In case of equilibrium, K_p values for organic chemicals can be derived from chemical properties and soil characteristics (Van der Kooij et al., 1991). Specifically, the equilibrium partitioning between organic carbon and pore water is an important descriptor of terrestrial toxicity for organic chemicals (DiToro et al., 1991). Therefore, the partition coefficient is often normalized to the organic matter content in solids, called K_{oc} (L water kg^{-1} organic carbon), according to:

$$K_p = f_{oc} \cdot K_{oc} \quad (1)$$

where f_{oc} is the mass fraction of organic carbon in the soil (kg organic carbon kg^{-1} soil).

K_p values can be used in the EP-method, as described by Van Beelen et al. (2003), to derive terrestrial L(E)C50 values. We used the method the other way around to estimate toxic porewater concentrations from terrestrial L(E)C50 values:

$$\log \mathrm{L(E)C50}_{ep,pw} = \log \mathrm{L(E)C50}_{ex,soil} - \log K_p \quad (2)$$

The L(E)C50 value of a chemical is the environmental concentrations expected to cause an effect, e.g. mortality, in at least 50% of the individuals in a given population. In this equation $\mathrm{L(E)C50}_{ep,pw}$ is the toxic concentration in pore water derived by the EP-method ($mg\,L^{-1}$), and $\mathrm{L(E)C50}_{ex,soil}$ is the toxic concentration in soil derived from experimental data (mg per kg of soil dry weight; $mg\,kg_{dw}^{-1}$).

Subsequently, the hazardous porewater concentration ($\mathrm{HC50}_{ep,pw}$ in $mg\,L^{-1}$) was estimated by the geometric mean of all available species-specific log-normally distributed L(E)C50 values. Hence, log HC50 equals the arithmetic mean of the log-transformed L(E)C50 values:

$$\log \mathrm{HC50}_{ep,pw} = \frac{1}{n} \cdot \sum_{i=1}^{n} \log \mathrm{L(E)C50}_{ep,pw,i} \quad (3)$$

where n is the number of species i for which toxicity tests have been performed for chemical x. Similar to Eq. (3), a hazardous freshwater concentration ($\mathrm{HC50}_{ex,fw}$ in $mg\,L^{-1}$) was derived from all available experimental freshwater L(E)C50 values.

2.2. Statistical uncertainty

Several sources of uncertainty influence estimates of the HC50s for soil pore water and freshwater. Here, we focused on statistical uncertainties related to the chemical's properties. The uncertainty distributions of the HC50s depended on the number of species for which L(E)C50 values were available. We assigned a Student t-distribution with $n-1$ degrees of freedom to the log HC50s (Payet and Jolliet, 2004), with a standard error calculated directly from the individual L(E)C50 data. The K_{oc} values were predicted with a quantitative structure–activity relationship (QSAR) for organic compounds by Gramatica et al. (2007). We assigned a Student t-distribution to the predicted log K_{oc} values (Montgomery et al., 2001). The predictive errors in the QSAR predictions were calculated from the QSAR's residual error and the chemical-specific

leverage value. For details, we refer to the Supporting Information. The uncertainties in the predictive modeling output were propagated with Monte Carlo simulations using the spreadsheet-based application Crystal Ball (Oracle©, Release 11.1.2.0.00) in MS Excel with 10000 iterations per run.

The uncertainty in the HC50 was quantified by the 90% confidence interval (90% CI). The distribution of the log HC50 was defined by the predictive mean ($\overline{HC50}$); the value of the t-distribution for the log HC50 value (t_{90}), depending on the degrees of freedom; and the standard error of the log HC50 value ($SEM_{log(HC50)}$), which was based on the sample standard deviation (s) and the number of species tested (n) (Roelofs et al., 2003; Golsteijn et al., 2012), written as:

$$\log HC50 \sim \overline{\log HC50} + t_{90} \cdot SEM_{\log(HC50)} \quad \text{with } SEM_{\log(HC50)} = \frac{s}{\sqrt{n}} \tag{4}$$

We assessed the validity of the HC50 values derived by the EP-method by comparing $HC50_{ep,pw}$ values and $HC50_{ex,fw}$ values. This way, we tested the assumption underlying the EP-method that the average toxicities of chemicals to terrestrial and aquatic species are not statistically different from each other. The ratio of $HC50_{ep,pw}$ and $HC50_{ex,fw}$ functioned as an indicator of the similarity:

$$Ratio_{ter/aq} = \frac{HC50_{ep,pw}}{HC50_{ex,fw}} \tag{5}$$

In order to use standard aquatic ecotoxicity tests for the derivation of hazardous concentrations in soil, a value of 1 should be within the confidence interval of the $Ratio_{ter/aq}$.

2.3. Data collection and processing

Terrestrial toxicological data for organic chemicals were collected from the US Environmental Protection Agency TERRETOX Database (2011), and from the Dutch National Institute for Public Health and the Environment (Huijbregts, 1999; RIVM, 2011). We collected experimental L(E)C50 values per unit of soil dry weight from studies that reported the chemical name or CAS number, the species tested, toxic endpoint (i.e. LC50 or EC50), and the fraction of organic matter or carbon in the soil sample. For chemicals with more than one measurement for the same species, the geometric mean was used. For chemicals whose toxic concentration was expressed by a range, the midpoint value was used. If experimental studies reported the total fraction of organic matter rather than the fraction of organic carbon, we assumed that the fraction of organic carbon was a factor of 1.7 lower than the total fraction of organic matter (Verbruggen et al., 2001).

Aquatic toxicity data for freshwater were obtained from the Dutch National Institute for Public Health and the Environment (RIVM, 2008). Since Van Zelm et al. (2009) demonstrated that uncertainty in the HC50 drastically decreases when data on three instead of two test species are available, we used HC50 values based on toxicity data for at least three test species for porewater as well as for freshwater.

The input for the QSAR that was used to predict K_{oc}, i.e. the descriptor values, was taken from the Supporting Information of Gramatica et al. (2007) or, if not available, calculated with DRAGON software version 5.5 (Todeschini et al., 2007). For the log K_{oc} values and more details on the QSAR, we refer to the Supporting Information.

For the assessment of the validity and uncertainty of $HC50_{ep,pw}$ values, we distinguished different chemical classes. Chemicals were classified according to their toxic mode of action (TMoA) based on De Zwart (2002). Because of lacking information on TMoA, other literature was consulted for Tetrapropylene benzenesulphonic acid (Russom et al., 1997), Chlordane (Ecobichon, 2001), Trichloroacetic-acid (Wood, 1995–2013), and 2,4,5-T (Wood, 1995–2013). Subsequently, we grouped the narcotic (nonpolar and polar), reactive, and specifically acting chemicals. Narcotic chemicals induce a non-specific reversible state of arrested activity of protoplastic structures called 'narcosis' (Veith and Broderius, 1990). Reactive chemicals react unselectively with certain chemical structures and can thereby have all kinds of different modes of action (Verhaar et al., 1992). Specifically acting chemicals exhibit toxicity via specific interactions with certain receptor molecules (Verhaar et al., 1992). The latter group was divided into neurotoxic chemicals (acetylcholinesterase (AChE) agents and cyclodiene type), and herbicides-fungicides. There was one chemical, Pentachlorophenol, whose TMoA was classified as uncoupling of oxidative phosphorylation. For details, we refer to Table S1 (Supporting Information).

We used the Data Analysis Toolpak of Microsoft Excel to perform a regression analysis on the log-transformed HC50s of the different chemical classes and the complete dataset. This way we assessed the relationship between the log-transformed $HC50_{ep,pw}$ values and $HC50_{ex,fw}$ values. A significant positive value for the slope implies a positive relationship between the $HC50_{ep,pw}$ values and $HC50_{ex,fw}$ values. A significant positive value for the intercept means that, for a slope of 1, there is a systematic difference between $HC50_{ep,pw}$ values and $HC50_{ex,fw}$ values. The linear fit of the data was expressed by the R^2 value. The root mean square error (RMSE) expressed the spread of the $HC50_{ep,pw}$ values around the regression line.

3. Results

Porewater HC50s were estimated with the EP-method from soil toxicity tests for 47 organic chemicals, and compared to freshwater HC50s derived from aquatic toxicity tests. Median $HC50_{ep,pw}$ values ranged between 1.8×10^{-3} and 2.9×10^{4} mg L^{-1}, and median $HC50_{ex,fw}$ values between 8.1×10^{-3} and 7.3×10^{3} mg L^{-1} (see Figs. S1 and S2 in the Supporting Information). There was a positive correlation between the $HC50_{ep,pw}$ values and $HC50_{ex,fw}$ values (R^2 of 0.70), demonstrating that chemicals that were among the most

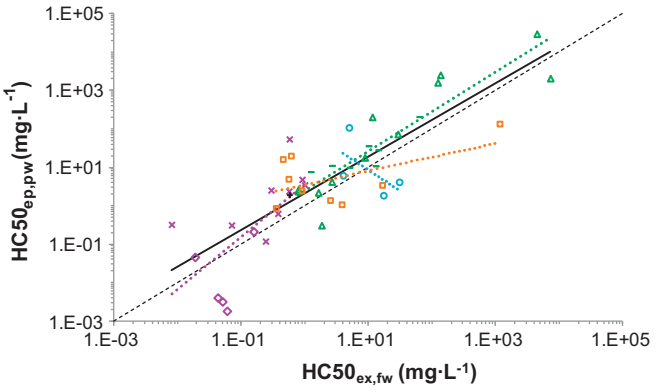

Fig. 1. Hazardous porewater concentrations ($HC50_{ep,pw}$) versus hazardous freshwater concentrations ($HC50_{ex,fw}$), for an oxidative uncoupler (black +), nonpolar narcotic chemicals (green Δ), polar narcotic chemicals (green –), reactive chemicals (blue ○), AChE agents (purple x), cyclodiene type neurotoxicants (purple ◇), and herbicides–fungicides (orange □). The dashed line indicates the 1:1 relation, the coloured dotted lines show the log-linear fits for narcotics, reactive chemicals, neurotoxicants and herbicides–fungicides, and the black line shows the log-linear fit for all data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

toxic for aquatic species were also among the most toxic for terrestrial species (see Fig. 1).

The regression lines between $HC50_{ep,pw}$ $HC50_{ex,fw}$ differed between the chemical classes (see Fig. 1). The regression lines of the reactive chemicals, the neurotoxicants, and the herbicides-fungicides crossed the 1:1 relation, but for narcotic chemicals higher $HC50_{ep,pw}$ values were found. Overall, for the complete dataset, also higher $HC50_{ep,pw}$ values were found. Significant p-values (i.e. <0.1) were found for the slopes of narcotic chemicals (for all narcotics, and also for nonpolar and polar narcotics separately), for all neurotoxicants grouped together, and for the regression for all data. No significant relationship between hazardous porewater and freshwater concentrations was found for reactive chemicals, for the separate groups of neurotoxicants (AChE agents and cyclodiene type), and for herbicides-fungicides. Furthermore, we found a significant p-value for the intercept of all narcotic chemicals grouped together, for polar narcotics separately, for herbicides-fungicides, and for the regression for all data. Table S2 (Supporting Information) gives more information about the slope and intercept of each chemical class.

For the $HC50_{ep,pw}$ values, 90% CIs ranged 1.8–5.2 orders of magnitude (typically 2.2), whereas for the $HC50_{ex,fw}$ values, 90% CIs ranged 0.2–2.1 orders of magnitude (typically 0.5). Table S1 (Supporting Information) gives the chemical-specific HC50 values for pore water and freshwater, the $Ratio_{ter/aq}$ values, and the accompanying uncertainty ranges.

Fig. 2 shows the uncertainty distribution of the $Ratio_{ter/aq}$ value per chemical. We found typical $Ratio_{ter/aq}$ values of 3.0 for narcotic chemicals (2.8 for nonpolar and 3.4 for polar narcotics), 0.8 for reactive chemicals, 2.9 for neurotoxic chemicals (4.3 for AChE agents and 0.1 for the cyclodiene type), and 2.5 for herbicides-fungicides. However, confidence intervals were typically 2.0 orders of magnitude for narcotic chemicals (2.0 for nonpolar and 2.1 for polar narcotics), 2.1 orders for reactive chemicals, 2.4 orders for neurotoxic chemicals (2.8 for AChE agents and 2.4 for the cyclodiene type), and 2.5 orders for herbicides-fungicides, respectively. For all data, the statistical uncertainty associated with the $Ratio_{ter/aq}$ was typically 2.3 orders of magnitude. A ratio of 1 was noted within the 90% CI for 81% of the chemicals (38 out of 47).

4. Discussion

In this study, we compared hazardous porewater concentrations, derived by the equilibrium partitioning method, with hazardous freshwater concentrations for various chemical classes. The reliability of the equilibrium partitioning calculations was a.o. dependent on: (I) the importance of chemical uptake by species via pore water, (II) the bioavailability of the chemical, and (III) the assumption underlying the EP-method that the average toxicities of chemicals to aquatic and terrestrial species are not statistically different from each other. We will elaborate more on these limitations in the next paragraphs. We will also discuss the interpretation of our findings and the practical implications.

4.1. Chemical uptake route

Besides chemical uptake from pore water, uptake of soil particles can be important for hydrophobic chemicals which sorb to these particles. Belfroid et al. (1996) showed that the difference between estimated and measured steady-state levels of chemicals in earthworms can be up to a factor of two for chemicals with a $\log K_{ow} > 5$. This may be the case for about 6 out of the 47 of the chemicals in this study. As a result, porewater concentrations that are toxic to terrestrial species may be lower than estimated here.

4.2. Bioavailability

The bioavailability of a chemical in the soil reduces with increasing organic matter content. Therefore, we used the organic matter content in the soil reported in the terrestrial toxicity test to estimate toxic porewater concentrations from terrestrial L(E)C50 values.

On a longer term, porewater concentrations calculated from chemical content measurements in soil and a partition coefficient obtained in short-term laboratory experiments may not give a good estimate for sorption or toxic effects (Ronday et al., 1997). This can be explained by the fact that a linear model based on K_{oc} may be insufficient to describe the phenomenon of time-related reduced bioavailability of pollutants in the soil. Cornelissen et al. (2005) explained how sorption to organic matter can be described by (I) linear and noncompetitive absorption in amorphous organic matter, e.g. partly degraded biopolymers, amino acids, and lipids; and (II) nonlinear, extensive and competitive adsorption to carbonaceous materials such as black carbon, coal, and kerogen. Therefore, when applying the linear EP-method, one should realize that time-related reduced bioavailability is not taken into account. Overestimating the bioavailability (i.e. underestimating the soil sorption), will lead to underestimating the hazardous terrestrial concentrations (mg kg_{dw}^{-1}). In other words, the substance's toxicity in the field will be overestimated.

The soil–water partitioning of chemicals is largely determined by their K_{oc}. Due to differences in test conditions (e.g. composition of the soil, temperature, etcetera), experimental K_{oc} values may differ from estimated K_{oc} values, resulting in uncertainty ranges that cannot be compared between chemicals. Therefore, we used solely K_{oc} QSAR estimates (Gramatica et al., 2007). The QSAR of Gramatica et al. (2007) has a smaller mean residual than e.g. the model K_{oc} WIN (EPI Suite). The availability of the underlying data of the QSAR made it possible to take into account the chemical-specific uncertainty (for details, see Supporting Information par. 1).

4.3. Sample uncertainty

The uncertainty in the HC50 that is related to the sample of species is multi-causal. To start with, it is a result of the number of test species. Numerous studies have shown that the number of species tested per chemical is a dominant factor in the uncertainty distributions of the HC50 for cold-blooded species (Kooijman, 1987; Aldenberg and Jaworska, 2000; Pennington, 2003; Harbers et al., 2006; Van Zelm et al., 2007, 2009), as well as for warm-blooded species (Luttik and Aldenberg, 1997; Golsteijn et al., 2012). Because of the additional uncertainty that is related to the small sample sizes of the test species, $Ratio_{ter/aq}$ values should be interpreted cautiously. However, we found no relationship between the number of species tested and the typical $Ratio_{ter/aq}$ values.

In addition, it is important to select a representative sample of species to determine a chemical's HC50 value. The chemical's activity may differ between species, and can be targeted at a specific species group, e.g. photosynthesis in plants (Escher and Hermens, 2002). Therefore, the types of species in the toxicity datasets may be an important determinant for the typical value of the $Ratio_{ter/aq}$. In particular for specifically acting chemicals, large differences between freshwater and hazardous porewater concentrations might be caused by differences in the dataset's species composition. For two neurotoxicants and three herbicides-fungicides, the target species (i.e. animal species or plant/fungi species, respectively) were not present in the terrestrial dataset. For four of these specifically acting chemicals a $Ratio_{ter/aq}$ of 1 was nevertheless noted within the 90% CI. However, for Captan, an inhibitor of sporulation, we found a high $Ratio_{ter/aq}$ value of typically 3.5×10^1 (90% CI: 4.0×10^0 to 3.2×10^2). Note that a

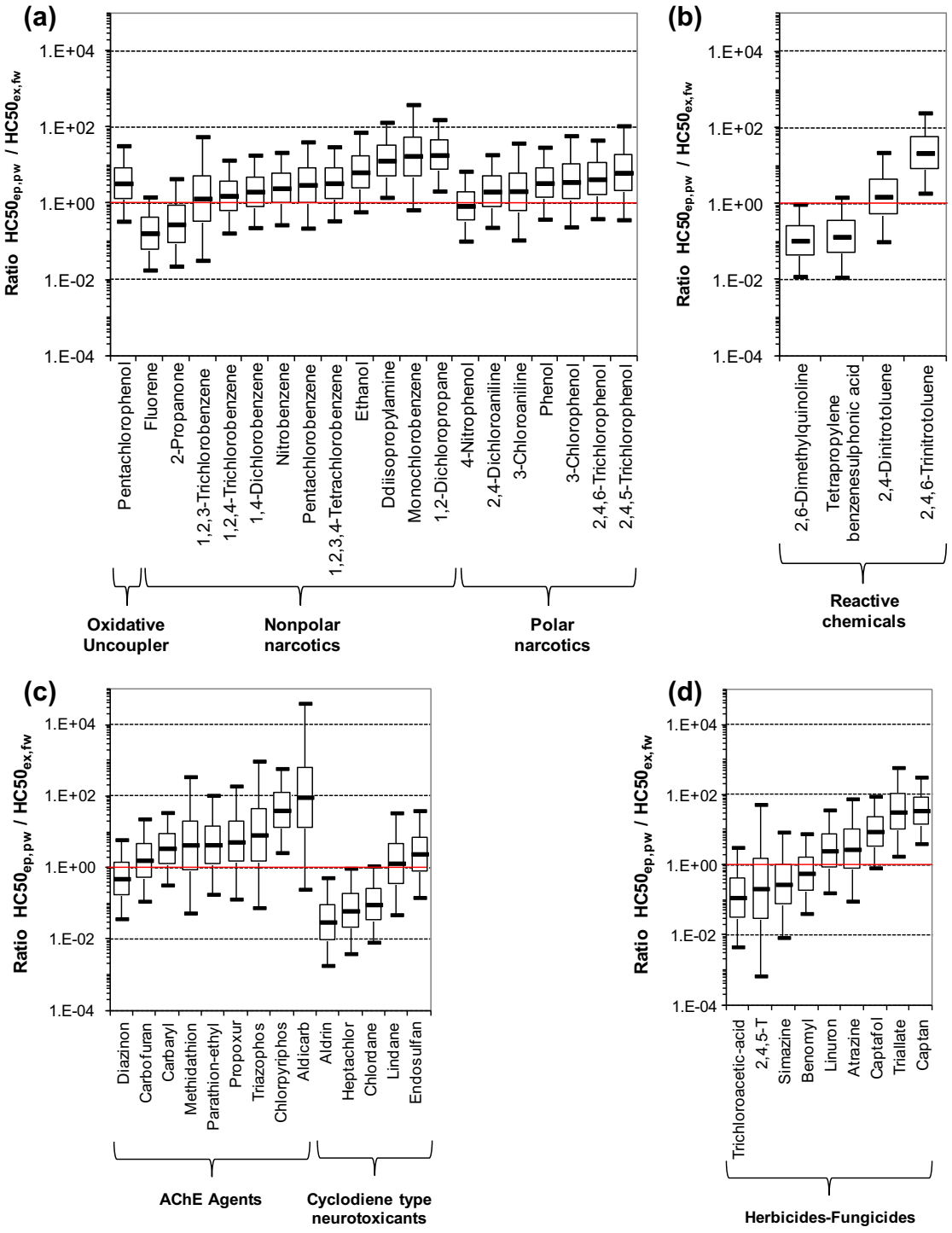

Fig. 2. Ratio of the hazardous porewater concentrations based on terrestrial ecotoxicity tests ($HC50_{ep,pw}$), and hazardous freshwater concentrations based on aquatic toxicity tests ($HC50_{ex,fw}$), for an oxidative uncoupler and narcotic chemicals (a), reactive chemicals (b), neurotoxic chemicals (c), and herbicides–fungicides (d). The center of each box equals the median, the edges of each box represent the 25th and 75th percentile, and the whiskers the 5th and 95th percentiles.

$Ratio_{ter/aq}$ of 1 was not within the 90% CI for this chemical. The specific mode of action of Captan could explain the lower HC50 for the aquatic dataset, since plants and fungi were present in the aquatic test set (8 out of 40 species were plants or fungi), but not present in the soil test set.

The variety in species sensitivity may be expressed using species groups. In the terrestrial ecotoxicity dataset, the number of species tested ranged from 3 to 9. When distinguishing producers (plants); consumers (insects, nematodes); and decomposers (earthworms), data were available for two or three species groups for over 57% of the chemicals (see Supporting Information Table S1). In the aquatic toxicity dataset, the number of species ranged from 4 to 224. When we distinguished single-celled organisms (bacteria, archaea, protista); plants and fungi; invertebrates; and cold-blooded vertebrates (a distinction similar to Van Zelm et al. (2009)), data were available for three or four species groups for almost 94% of the chemicals. For 6 out of the 9 chemicals for which a $Ratio_{ter/aq}$ of 1 was outside the 90% CI, experimental soil

toxicity data for only one species group were available. This indicates less representative samples of terrestrial species.

Variation in species sensitivity to specifically acting chemicals can also influence the uncertainty in the hazardous concentration, and consequently the uncertainty in the $Ratio_{ter/aq}$. Differences in sensitivities between species are much larger for specifically acting chemicals compared to narcotic chemicals, because the modes of action of specifically acting chemicals are much more complex and involve more intermediate steps (Escher and Hermens, 2002). In this study, the uncertainty in the ratio of $HC50_{ep,pw}$ and $HC50_{ex,fw}$ was relatively small for narcotic chemicals (typically 2.0 orders of magnitude). According to Vaal et al. (1997), narcotic chemicals have the smallest interspecies variation in sensitivity of all chemical classes. In addition Vaal et al. (1997) reported that variation in species sensitivity can be as large as 5 to 6 orders of magnitude for reactive and specifically acting chemicals. In this study, confidence intervals for the $Ratio_{ter/aq}$ values were typically 2.1 orders of magnitude for reactive chemicals, 2.4 orders for neurotoxic chemicals (2.8 for AChE agents and 2.4 for the cyclodiene type), and 2.5 orders for herbicides-fungicides, respectively. The number of species tested in soil was generally comparable between the different chemical classes (3–5 species). Also for freshwater, the number of species tested was generally comparable over the different chemical classes (18–25 species), except for AChE agents and cyclodiene type neurotoxicants which have been tested more extensively (typically 69 and 83 species, respectively). The large uncertainty in the $Ratio_{ter/aq}$ values for AChE agents can therefore not be explained by the number of species tested. It can, however, be explained by interspecies differences in the sensitivity for acetylcholine esterase (AChE), and in the biotransformation capacity for the parent compound (Escher and Hermens, 2002). Scheringer et al. (2002) demonstrated that the species sensitivity distribution of methyl parathion, which is an AChE agent, has several maxima representing sensitive subgroups of species. A similar observation was done by Solomon et al. (1996) for atrazine, a photosynthetically active chemical. Furthermore, these interspecies differences in the sensitivity for AChE agents may also explain the high typical $Ratio_{ter/aq}$ value of 4.3. The abovementioned examples illustrate the importance of a representative sample of species for the estimation of the HC50 of chemical.

4.4. Practical implications

In this study, we performed an uncertainty assessment of the EP-method with a distinction between different chemical classes. Despite the use of extensive databases, there were relatively few organic chemicals with terrestrial L(E)C50 values available for at least three different species. Nevertheless, our study gives valuable insights in the uncertainty of the hazardous concentrations derived by the EP-method.

Compared to narcotic chemicals, differences in species sensitivity are larger for specifically acting chemicals. So particularly for specifically acting chemicals, it is very important to base the HC50 on a representative sample of species, composed of both target and non-target species. In the case of lacking terrestrial toxicological data, the EP-method may be applied cautiously, for instance in the framework of life cycle impact assessment. With the method described in this paper, statistical uncertainty can also be taken into account.

For most chemical groups, $HC50_{ep,pw}$ values were approximately a factor of 3 higher than $HC50_{ex,fw}$ values. We found that the $Ratio_{ter/aq}$ was typically 3.0 for narcotic chemicals (2.8 for nonpolar and 3.4 for polar narcotics), 0.8 for reactive chemicals, 2.9 for neurotoxic chemicals (4.3 for AChE agents and 0.1 for the cyclodiene type), and 2.5 for herbicides-fungicides. However, the statistical uncertainty associated with the $Ratio_{ter/aq}$ was large (typically 2.3 orders of magnitude). For 81 percent of the organic chemicals assessed in this study, there was no statistical difference between the hazardous concentration of aquatic and terrestrial species. We conclude that possible systematic deviations between the HC50s of aquatic and terrestrial species appear to be less prominent than the overall statistical uncertainty.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.05.007.

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