The variability of standard artificial soils: cadmium and phenanthrene sorption measured by a batch equilibrium method

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A B S T R A C T

Artificial soil (AS) is used in soil ecotoxicology as a test medium or reference matrix. AS is prepared according to standard OECD/ISO protocols and components of local sources are usually used by laboratories. This may result in significant inter-laboratory variations in AS properties and, consequently, in the fate and bioavailability of tested chemicals. In order to reveal the extent and sources of variations, the batch equilibrium method was applied to measure the sorption of 2 model compounds (phenanthrene and cadmium) to 21 artificial soils from different laboratories. The distribution coefficients (K_d) of phenanthrene and cadmium varied over one order of magnitude: from 5.3 to 61.5 L/kg for phenanthrene and from 17.9 to 190 L/kg for cadmium. Variations in phenanthrene sorption could not be reliably explained by measured soil properties; not even by the total organic carbon (TOC) content which was expected. Cadmium $\log K_d$ values significantly correlated with cation exchange capacity (CEC), pH_{H2O} and pH_{KCl}, with Pearson correlation coefficients of 0.62, 0.80, and 0.79, respectively. CEC and pH_{H2O} together were able to explain 72% of cadmium $\log K_d$ variability in the following model: $\log K_d = 0.29\, pH_{H2O} + 0.0032\, CEC - 0.53$. Similarly, 66% of cadmium $\log K_d$ variability could be explained by CEC and pH_{KCl} in the model: $\log K_d = 0.27\, pH_{KCl} + 0.0028\, CEC - 0.23$. Variable cadmium sorption in differing ASs could be partially treated with these models. However, considering the unpredictable variability of phenanthrene sorption, a more reliable solution for reducing the variability of ASs from different laboratories would be better harmonization of AS preparation and composition.

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1. Introduction

The distribution of a chemical between the soil and the aqueous phase at equilibrium is described as the soil sorption coefficient (K_d). Since the freely dissolved concentration is considered as mobile and potentially available for degradation, transformation, biological uptake, leaching, run-off as well as volatilization (Sauvé et al., 2000), K_d values are used for the estimation of potential fate, risks and toxicity of chemicals in soils (OECD, 2000). The K_d values gained for a respective chemical can substantially vary among soils (up to orders of magnitude, e.g. Degryse et al. (2009), Wauchope et al. (2002)) suggesting that substrate properties significantly influence partition of the chemical. This, in turn, implies that soil ecotoxicity data produced by various laboratories using different soils may also significantly vary as a result of varying substrate properties used for the toxicity evaluation. Since this variability would make results coming from different laboratories difficult to

compare, two attempts have been suggested to reduce it. The first recommends the usage of a standardized soil with well-defined properties, while the other allows various soils to be used with additional normalization of the data required before comparison.

The first approach resulted in the development of an artificial soil (AS) with a defined composition (Edwards, 1984; OECD, 1984, 2004; ISO, 1998a). According to OECD guidelines 207 and 222, and ISO norm 11268-2 (OECD, 1984, 2004; ISO, 1998a), the composition and properties of AS should be as follows: 10% Sphagnum peat (finely ground, as close to pH 5.5–6.0 as possible), 20% kaolinite clay (kaolinite content preferably > 30%), 70% industrial quartz sand (> 50% of particles between 50 and 200 μm), soil pH_{KCl} adjusted to 6.0 ± 0.5 by addition of $CaCO_3$. However, there is a reasonable doubt whether the specification is suitable for the preparation of soils with comparable properties and behaviour towards chemicals, largely because of variability in the sources of the AS components obtained locally (Bielská et al., 2012; Hofman et al., 2014; Römbke and Moser, 2002; Edwards, 1984).

An indirect indication of AS variability when prepared in different laboratories can be seen in the results of international

ringtests of soil bioassays (Edwards, 1984; Römbke and Moser, 2002; Krogh et al., 2008), where the span of toxicity values for a particular compound and organism tested ranged up to 2 or 3 orders of magnitude. The ringtests' organizers reasonably suspected that an important contribution to this variability was the variability of ASs prepared by individual laboratories from locally available components.

Direct indications of variability between ASs prepared in different laboratories were reported in our previous studies (Bielská et al., 2012; Hofman et al., 2014; Vašíčková et al., 2015). Twenty-five ASs varied in their properties such as total organic carbon (TOC) content (1.4–6.1%), organic matter composition (humic to fulvic acid ratio, 0.16–2.46), pH_{H2O} (4.5–7.2), pH_{KCl} (2.8–6.8), cation exchange capacity (68.2–215.8), particle size distribution and other parameters (Bielská et al., 2012). Furthermore, it was observed that differences between these ASs led to substantial variations in the environmental fate of organic pollutants: the phenanthrene fraction desorbable by supercritical fluid extraction fell in the range 3–89% (Bielská et al., 2012), lindane and phenanthrene fractions extractable by hydroxypropyl-β-cyclodextrin solution were in the range 10–44% and 57–70%, respectively (Hofman et al., 2014), and the phenanthrene fraction bioaccessible to degrading *Pseudomonas* sp. was in the range 17–53% (Hofman et al., 2014).

Variable properties of ASs prepared in different laboratories can also be expected to affect the environmental fate of inorganic pollutants, e.g. toxic metals, as indicated in the studies where AS properties (pH and/or organic matter content) were modified to determine the effects on metal behaviour, sorption, bioavailability and toxicity (Spurgeon and Hopkin, 1996; Crommentuijn et al., 1997; Van Gestel and Koolhaas, 2004; Van Gestel and Hoogerwerf, 2001; Lock and Janssen, 2001).

Another approach adopted in order to increase the inter-laboratory comparability of data was developed for hydrophobic organic compounds (HOCs). It assumes that organic carbon is the main factor responsible for sorption variations between soils and sediments and therefore, it can be used as a basis for normalization and extrapolation of sorption, bioavailability, toxicity and environmental quality standards over various soils or sediments (Di Toro et al., 1991; ECHA, 2008). However, this normalization concept has been questioned recently for soils with different characters of organic matter (Bielská et al., 2013, 2014; Bielská Hofman et al., 2008; Šmídová et al., 2012). As Wauchope et al. (2002) pointed out K_{oc} values for a large number of soils showed the coefficient of variation around 30–60% and the ratio of maximum to minimum K_{oc} values was around 6–10. They suggest that half of this variability can be ascribed to experimental errors, whereas the rest reflects differences in the nature of organic matter between soils (Wauchope et al., 2002). This might be the case for ASs, as the peat in them usually comes from very different sources (Bielská et al., 2012). For metals that do not have the hydrophobic and lipophilic characteristics of organic chemicals, a different approach than that based on organic carbon normalization is needed (Lee and Allen, 1998). Sauvé et al. (2000) reported that a large portion of variability in metal sorption and toxicity can be explained by soil pH suggesting that variations in binding capacity among natural soils are much smaller than the effect provoked by differences in pH. Therefore, for metals, soil pH may be suggested as an extrapolation basis between K_d values measured in different soils (Lee et al., 1996; Peijnenburg et al., 1997; Janssen et al., 1997). As shown by Lock and Janssen (2001); Butcher et al. (1989) or Christensen (1989) cation exchange capacity also was a good predictor of metal sorption.

To identify the possible sources and ranges of inter-laboratory variability among artificial soils, sorption of 2 model compounds (phenanthrene and cadmium) was measured using the standard batch equilibrium method defined by OECD guideline 106 (OECD,

2000) for 25 ASs collected from different ecotoxicological laboratories. In contrast to previous studies (Bonin and Simpson, 2007; Allen et al., 1995), both an organic and an inorganic compound were tested in our study to cover various sorption mechanisms and provide results relevant for the testing of a broader spectrum of chemicals. Phenanthrene and cadmium were selected as they are often used as model compounds in sorption studies (e.g. Khan et al., 2012; He et al., 2005; Shirvani et al., 2006; Zhang et al., 2011). However, in contrast to similar studies comparing K_d values in sets of natural soils, we were not attempting to refine the mechanistic understanding of metal and organic compound sorption to soils. This is most largely because the criterion for the AS selection was given by its routine usage in ecotoxicity testing rather than by component origin and properties. Our aim was to confirm/reject that differences in (albeit standardized) ASs from different laboratories and characterized by basic physico-chemical properties manifests in sorption coefficients and, if possible, provide recommendations in terms of reducing this variability.

2. Materials and methods

2.1. Artificial soils

The same set of soils as used in our previous studies (Bielská et al., 2012; Hofman et al., 2014; Vašíčková et al., 2015) was used in this study. These 25 soils were provided by laboratories in Europe and Canada that have considerable experience in soil ecotoxicology research. The laboratories were asked to prepare 2–3 kg of dry AS following their routine practice and the guidelines OECD 207 (OECD, 1984); OECD 222 (OECD, 2004) or ISO 11268-2 (ISO, 1998a) which describe AS preparation by the same way as: mixing the finely ground Sphagnum peat (10% of final mass), the kaolinite clay containing at least 30% kaolinite (20% of final mass), and the industrial quartz sand with at least a 50% fraction of 0.05–0.2 mm grains (70% of final mass, all contents based on dry mass) and adjusting soil pH_{KCl} to 6 ± 0.5 by adding $CaCO_3$. The laboratories utilized local sources for peat, sand and clay.

After delivery, it was apparent (see Graphical abstract) that the soils differed at the first sight. The soils were characterized in detail for physico-chemical properties: the total organic carbon (TOC) content (LiquiOC automatic analyzer, Elementar, Germany); the total nitrogen content (N_{tot}; ISO, 1995); pH in H_2O and KCl (ISO, 2005); the cation exchange capacity (CEC) calculated from Ca^{2+}, Mg^{2+}, and K^+ in Mehlich III extracts; humic compounds (HC), humic acids (HA) and fulvic acids (FA); $Q_{4/6}$ (the ratio of the absorbance of humic compounds measured at 400 and 600 nm); the maximum water holding capacity (WHC_{max}) (ISO, 1998a); and the contents of particles with defined sizes (ISO, 1998b): clay ($< 2\ \mu m$), fine silt ($2–10\ \mu m$), silt ($10–50\ \mu m$), fine sand ($50–100\ \mu m$), and sand ($0.1–2\ mm$). More details on the procedures used for the measurement of these parameters may be found in Bielská et al. (2012). Generally, the soils exhibited a wide range of physico-chemical properties, which were reported and discussed in detail in our previous study (Bielská et al., 2012).

The participants were also asked to compile the information on the sources and properties of components and to comment on any deviations from OECD/ISO guidelines. The information about components was of varying quality and no correlation was possible between soil properties and component data (Bielská et al., 2012). The reports from the laboratories revealed that soils 3, 4 and 7 were prepared from a reduced amount of peat (5%, as allowed by OECD guideline 222; OECD, 2004) and soil 3 from a reduced amount of clay (10%, for unspecified reasons). The very low pH_{KCl} value measured for soil 2 (2.8) implied that the step of $CaCO_3$ addition was omitted. Because of these apparent deviations