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Estimation of amorphous organic carbon/water partition coefficients, subcooled liquid aqueous solubilities, and *n*-octanol/water partition coefficients of nonpolar chlorinated aromatic compounds from chlorine fragment constants

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ABSTRACT

This study aims to derive the relation between the number of chlorine atoms in chlorobenzenes, polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs) and $\log K_{oc}$ for linear partitioning between water and average amorphous organic carbon in soils or sediments. Because reliable determinations of $\log K_{oc}$ are relatively sparse for chlorobenzenes and PCBs, and are even absent for PCDDs and PCDFs, a work-around solution was developed: First, the relation of *n*-octanol/water partitioning (K_{ow}) and (subcooled) liquid solubility (S_l) to the number of chlorines was investigated. Slopes for the linear correlation of $\log K_{ow}$ with the number of chlorines (corrected for the number of *ortho*-chlorines in the case of PCBs) appeared identical for chlorobenzenes, PCBs, PCDDs, and PCDFs. Such was also the case for $\log S_l$. Slopes for the linear relation of chlorobenzenes and PCB $\log K_{oc}$ values with the number of chlorines were similar for the various soils and sediments, though intercepts were different. The *ortho*-chlorine correction factor for PCB $\log K_{oc}$ was equal to the *ortho*-chlorine correction factor for PCB $\log K_{ow}$ and $\log S_l$. For PCDDs and PCDFs, a relation between $\log K_{oc}$ and the number of chlorine atoms was derived by combining the chlorobenzenes/PCB $\log K_{oc} - \log K_{ow}$ and $\log K_{oc} - \log S_l$ relationships with $\log K_{ow}$ (or S_l)-chlorine number relations for PCDDs and PCDFs.

1. Introduction

In order to quantitatively estimate environmental fate and bioaccumulation for organic compounds in sediments and soils, their distribution over water and these geosorbents has to be known. At least for non-polar organic compounds, sorption is dominated by absorption into amorphous organic carbon as well as by adsorption onto hard carbon, such as kerogen, soot, or black carbon (Cornelissen et al., 2005; Koelmans et al., 2006). In the companion paper (van Noort, 2008), for PAHs and alkylbenzenes, a compound class-specific Quantitative Structure Property Relationship (QSPRs) has been derived for the estimation of $\log K_{oc}$ values for (linear) absorption into amorphous organic carbon from the number of aromatic, alkyl, and alicyclic carbons. The present study aims to derive compound class-specific $\log K_{oc}$ QSPRs for polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and chlorobenzenes, depending on the number of chlorine atoms.

Because of the relatively small number of useful $\log K_{oc}$ data from the literature for PCBs and chlorobenzenes and the absence of reliable $\log K_{oc}$ data for PCDDs and PCDFs, this study will try to close that gap. For that purpose, we start with the derivation of QSPRs for *n*-octanol/water partitioning coefficients (K_{ow}) and subcooled liquid solubility (S_l). Subsequently, findings from the derivations of these QSPRs are applied to the derivation of $\log K_{oc}$ QSPRs for PCBs and chlorobenzenes. Finally, $\log K_{oc}$ QSPRs for PCDDs and PCDFs are proposed, from a combination of $\log K_{oc} - \log K_{ow}$ linear free energy relationships for PCBs and chlorobenzenes with QSPRs for PCDDs and PCDFs $\log K_{ow}$ and $\log S_l$.

Recently, some studies appeared on the derivation of $\log K_{ow}$ and $\log S_l$ QSPRs for PCBs. For sixteen PCBs, Li et al. (2003) adjusted log mean values of literature experimental data for S_l, K_{ow}, vapor pressure, Henry's law constant, *n*-octanol/air partitioning and *n*-octanol solubility to yield an internally consistent set of data for each congener. For 16 PCBs they calculated $\log S_l$ values from (aqueous) solid solubilities using compound-specific fusion entropy values and melting temperatures if available. Otherwise, a default value of $56\ \mathrm{J\ K^{-1}\ mol^{-1}}$ was used for the entropy of fusion. For these 16 PCBs, both $\log K_{ow}$ and $\log S_l$ were linearly related to molecular mass. No statistically significant relation was found with the number of *ortho*-chlorines. Schenker et al. (2005) proposed a least-squares adjustment procedure for harmonizing physicochemical properties as an improvement to the adjustment procedure suggested by Li et al. (2003). They illustrated the procedure by applying it to the same 16 PCBs as used by Li et al. (2003) and calculated PCB $\log S_l$

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values accounting for differences in heat capacities between solid and liquid state, which is an additional significant improvement to the method used by Li et al. (2003), especially for higher-melting compounds (van Noort, 2004). Like Li et al. (2003), Schenker et al. (2005) found a linear relation of both $\log K_{ow}$ and $\log S_l$ with molecular mass without statistical need to include the number of *ortho*-chlorines. An analysis of Huang and Hong (2002), however, showed that the number of *ortho*-chlorines, together with the total number of chlorines, the number of adjacent chlorines and the melting temperature, was a relevant descriptor of the solid solubility for 58 PCBs. The relation with the melting temperature found by them can be considered an approximation for the conversion of solid solubilities to subcooled liquid solubilities. For PCB *n*-octanol/air coefficients, the number of *ortho*-chlorines was an important descriptor as well (Li et al., 2006). Qualitatively, K_{oc} values of 32 PCBs for 37 spiked North Sea sediments were inversely related to the number of *ortho*-chlorines (Booij et al., 1997). From a study on $\log K_{ow}$ values for 133 PCBs, Lü et al. (2007) found that $\log K_{ow}$ can be estimated from molecular descriptors such as molecular surface area, polarizability, and the maximum valency of a C-atom. The latter two parameters depend on the substitution pattern. This suggests that the number of *ortho*-chlorine atoms may determine $\log K_{ow}$, as well. It should be noted, however, that experimental $\log K_{ow}$ values for only 52 PCBs were found in the present study, in contrast to the 133 values used by Lü et al. (2007). Some of the PCB $\log K_{ow}$ values used by Lü et al. (2007) might therefore either be calculated values, or be obtained from a doubtful source. Recently, Razzaque and Grathwohl (2008) found that $\log K_{oc}$ for various compound classes is linearly related to the aqueous (subcooled) liquid solubility by a single equation for all classes together.

Some of the studies mentioned above were based on a relatively small data set for PCBs, while other studies suffer from a poor approximation of PCB fugacity ratios or a less critical use of experimental data from the literature. The present study will use experimental $\log K_{ow}$ and solubility data from the literature for a large number of PCBs combined with the most accurate up to date calculation or estimation of PCB fugacity ratios and a critical evaluation of data based on consistency between K_{ow} and solubility data.

2. Data selection and data conversion

Experimental $\log K_{ow}$ and aqueous solubility values from the literature are compiled in Tables S-1 to S-4 (Supplementary material). For each PCB, a Literature Derived Value (LDV) was obtained, equal to the average of all values. These LDVs were used to derive PCB QSPRs. No LDVs for chlorobenzenes, PCDDs, and PCDFs were calculated because of the small number of data. For these compound classes, the full data set was used to derive QSPRs.

The aqueous solubility of solid compounds reflects solid-state interactions, among others, while these interactions are not relevant for *n*-octanol/water distributions. Therefore, to relate $\log K_{ow}$ QSPRs to aqueous solubility QSPRs, solid-state interactions have to be removed from the latter. This can be achieved by using subcooled liquid solubilities instead of solid solubilities.

The subcooled liquid solubility (S_l) was calculated by dividing solid solubility (S_s) by the fugacity ratio F, defined in Eq. (1)

$$F = \frac{S_s}{S_l} = \exp(-\Delta G_{S \to L}/RT) \tag{1}$$

In Eq. (1), $\Delta G_{S \to L}$ denotes the change in Gibbs free energy on transformation of a solid into a (subcooled) liquid; R and T are the gas constant and the absolute system temperature, respectively. $\Delta G_{S \to L}$ can be obtained from the melting temperature, the fusion enthalpy, and the temperature dependent heat capacities of the solid and liquid state (Allen et al., 1999).

PCB fugacity ratios based on Eq. (1) were taken from van Noort (2006). For PCDDs and PCDFs, fugacity ratios either were from van Noort (2004), or were calculated using estimated fusion enthalpies from Iorish et al. (2001) taking into account differences in heat capacities between solid and liquid state by applying melting temperature dependent corrections given by van Noort (2004). No melting temperature data for 1,2,3,6,7,8-hexachlorodibenzofuran could be found in the literature. Therefore, it was estimated from the number of chlorines and the molecular symmetry according to van Noort (2002). For chlorobenzenes, melting temperature and fusion enthalpy were taken from Domalski and Hearing (2005); fugacity ratios were calculated using melting temperature corrections given by van Noort (2004).

3. PCB aqueous solubility and *n*-octanol/water partitioning

Experimental $\log K_{ow}$ and aqueous solubility data from the literature, along with LDVs, are listed in Table S-1 (Supplementary material). To avoid an unduly large influence of outlier values on QSPRs, some PCB LDVs were initially rejected. This rejection was based on the well-known linear relation between $\log K_{ow}$ and $\log S_l$ (Fig. S-3, Supplementary material). Fig. S-3 shows that $\log K_{ow}$ LDVs for most PCBs are equal, within 0.3 log units (arbitrarily chosen), to the predicted value from the $\log K_{ow} - \log S_l$ relationship. For 12 out of 43 PCBs for which aqueous solubility as well as $\log K_{ow}$ data were available (indicated by open symbols in Fig. S-3) the deviation was >0.3 log units. $\log K_{ow}$ and $\log S_l$ LDVs for these PCBs were not used to derive preliminary QSPRs.

$\log K_{ow}$ and $\log S_l$ PCB LDVs were fitted to equations of the general type:

$$\log K_{ow} \text{ or } \log S_l = a[N_{Cl} + bN_{\text{ortho}}] + c \tag{2}$$

where N_{Cl} and N_{ortho} denote the total number of chlorines and the number of *ortho*-chlorines, respectively. The factor a will be referred to later on as ‘chlorine fragment constant’. In Eq. (2), N_{ortho} is introduced as an independent variable because chlorines at *ortho*-positions may “feel” a smaller number of water molecules compared to chlorines at *meta* and *para* positions due to shielding of *ortho*-chlorines by an adjacent aromatic ring. It is reasonable to assume that the effect of *ortho*-chlorines on $\log K_{ow}$ is similar to $\log S_l$. In other words, the value of the coefficient b for the $\log K_{ow}$ QSPR may be assumed equal to that for $\log S_l$. Therefore, $\log K_{ow}$ and $\log S_l$ LDVs for the 31 PCBs remaining after the first selection were simultaneously fitted to Eq. (2) (data not shown). In this way, preliminary QSPRs for $\log K_{ow}$ and $\log S_l$ were obtained.

$\log K_{ow}$ and $\log S_l$ LDVs for all PCBs were tested against the preliminary QSPRs. LDVs for which the difference with estimated values from these preliminary QSPRs exceeded 0.3 log units were not used for the final derivation of QSPRs. After this selection, useful $\log S_l$ LDVs for 46 PCBs and $\log K_{ow}$ LDVs for 37 PCBs remained. The QSPRs (with standard deviations from the fit (Table 1) indicated) for this final data set were:

$$\log S_l\ (\text{mol/m}^3) = (-0.575 \pm 0.014)[N_{Cl} - (0.33 \pm 0.03)N_{\text{ortho}}] - (1.38 \pm 0.06) \tag{3}$$

$$\log K_{ow} = (0.448 \pm 0.013)[N_{Cl} - (0.33 \pm 0.03)N_{\text{ortho}}] + (4.40 \pm 0.06) \tag{4}$$

The median difference between LDV and model prediction was 0.11 and 0.12 for $\log S_l$ and $\log K_{ow}$, respectively. QSPR prediction versus LDV is shown in Figs. 1 and 2 for $\log S_l$ and $\log K_{ow}$, respectively.

For the LDVs not used for the derivation of QSPRs, Figs. 1 and 2 (closed symbols) show that most of these values do not substantially deviate from predicted values. For many of the PCBs for