



QSPR-based estimation of the atmospheric persistence for chloronaphthalene congeners

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ABSTRACT

Gas phase reaction with OH[•] radicals is the major atmospheric loss process for the aromatic hydrocarbons. Thus, we used the half-live values ($t_{1/2}$) derived based on this mechanism for characterization of environmental persistence and long-range atmospheric transport (LRAT) potential of all 75 chloronaphthalene congeners (CNs). We applied the single-media LRAT criterion from the Stockholm Convention ($t_{1/2}$ in air > 2 days and vapor pressure < 1000 Pa). The values of $t_{1/2}$ were estimated from a robust and predictive quantitative structure–property relationship (QPSR) model. The average half-lives for particular homologue groups of CNs were as following: 2 days for mono-CNs, 5 days for di-CNs, 10 days for tri-CNs, 19 days for tetra-CNs, 39 days for penta-CNs, 79 days for hexa-CNs, 163 days for hepta-CNs, and 343 days for octa-CN. Main factors affecting the persistence of chloronaphthalenes were the degree of chlorination and the substitution pattern. The congeners having the $-\text{C}(\beta)\text{Cl}-\text{C}(\alpha)\text{H}-\text{C}(\alpha)\text{Cl}-$ fragment, in which relatively low electron density was observed on the α hydrogen and carbon atoms, were characterized by significantly lower half-lives than the rest of the compounds within the individual homologue groups.

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1. Introduction

Chloronaphthalenes (CNs) and polychlorinated naphthalenes (PCNs) are two synonyms defining a group of 75 similar compounds based on the same (naphthalene) skeleton, but differ by a number of chlorine atoms and the substitution pattern. Chlorine substituents (between one and eight Cl atoms) occur either in α (1, 4, 5, and 8) or β (2, 3, 6, and 7) positions on the naphthalene nuclei (Falandysz et al., 2001).

There are two most important anthropogenic sources of PCNs in the environment: (i) intentional synthesis of technical formulations and (ii) unintentional formation in various thermal processes, when the organic matter is buried.

The formulations were manufactured in several countries between 1910s and 1970s and introduced into the market under various trade names (i.e., Halowax, Nibren wax, Seekay wax etc.). They have found many applications in a wide range of the electro-energetic equipment (i.e., as transformers and capacitors fluids), oil and plastic additives, impregnates and synthetic rubbers (Falandysz, 1998; Lukaszewicz et al., 2007). The estimated worldwide production of the CN formulations in 1920s was approximately 9000 tons per year (Weem, 2007).

Although the CN mixtures seemed to be very usable, their toxicity to animals and human (i.e. skin irritation, genotoxicity, carcinogenicity, endocrine disruption, negative effects on fertility, induction of microsomal enzymes) has been reported quite early (IPCS, 2001). Moreover, because of their high lipophilicity, chloronaphthalenes have been bioaccumulated and biomagnified along many food chains (Falandysz, 2003). In consequence, the synthesis was formally abandoned.

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Nowadays, even if some commercial products (i.e., sealants, putty, shock absorbing materials, adhesive materials, insulating materials, rubber belts and neoprene) containing chloronaphthalenes can be still available (Yamashita et al., 2003), the thermal-related synthesis (i.e. medical, municipal and industrial waste incineration as well as domestic heating) seems to be the main source of CNs in the environment (Lee et al., 2007). The emission of PCNs to the atmosphere (only by the European countries) is estimated at 1.03 tons per year (Weem, 2007).

Currently PCNs are being considered as new candidates for the list of priority persistent organic pollutants (POPs), managed by the *Stockholm Convention* (UNEP, 2001) and the *UN-ECE protocol to the Convention on Long-range Transboundary Air Pollution* (UNECE, 1998). Both documents establish strict criteria for including new compounds in the list. Besides them, there are atmospheric persistence and long-range atmospheric transport ability. The persistence of a compound is described by its half-life values ($t_{1/2}$) and a screening threshold for the atmospheric persistence enabling the long-range transport (if the vapor pressure is lower than 1000 Pa) is $t_{1/2} > 2$ days (IPCS, 2001; Lerche et al., 2002; Weem, 2007).

There is no detailed and quantitative data on the half-lives available for the individual congeners, and the experimental studies for all congeners seem to be very expensive and time-consuming (Lerche et al., 2002; Mackay et al., 2007; Weem, 2007). However, some existing examples show that various types of computational techniques, involving the quantitative structure–property relationship (QSPR) approach, can be successfully employed instead of the experiment (Gramatica et al., 2004; Öberg, 2005; Gramatica and Papa, 2007).

Thus, the aims of this study were to (i) fulfill the mentioned data gaps, predicting atmospheric persistence of all chloronaphthalene congeners by means of the QSPR methodology; and (ii) classify all PCNs along with the criteria of persistence specified by the Stockholm Convention.

2. Methodology

The QSPR approach is based on the axiom that the variation of a given physical or chemical property in a group of compounds (ΔY) strictly depends on the variation in their molecular structures (ΔX). Therefore, if the experimental data (Y) are available only for some chemicals in the group, it is possible to predict lacking data from molecular descriptors (X) calculated for the whole group and an appropriate regression model (Karcher and Devillers, 1990; Cronin and Livingstone, 2004).

2.1. Experimental data

A common problem, widely discussed in the QSPR literature, is how to define this “group of compounds”, called as the applicability domain of the model (AD) (Netzeva et al., 2005). Ideally, the AD in this study should be restricted only to polychlorinated naphthalenes to give the most precise results of the prediction. However, because there were no enough experimentally measured data available for CNs, it

was necessary to extend the AD on the other similar POPs, for which the data had not existed. We have used data for polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) initially assuming that PCNs should be located within the domain defined in such a way. We verified this initial assumption providing a validation of the applicability domain (Eriksson et al., 2003; Netzeva et al., 2005).

Since the gas phase reaction with OH^\bullet radicals is the major atmospheric loss process for the aromatic hydrocarbons (Atkinson, 1986), we used the half-lives ($0.95 < \log t_{1/2} < 3.90$) derived based on this mechanism (Table 1). It should be emphasized that the half-lives in the environmental media are not measured directly. They are calculated according to the pseudo first-order kinetics from the corresponding reaction rate constants, assuming that the concentration of the hydroxyl radicals is constant. In our study we applied data calculated with this method taken from the previous contribution by Hirai et al. (2004). As we noticed, the authors had derived the values of $\log t_{1/2}$ from the previously published rate constants and the time-averaged (1978–2000) concentration of the OH^\bullet radicals, $[\text{OH}^\bullet] = 9.4 \times 10^5 \text{ radicals cm}^{-3}$, reported by Prinn et al. (2001). To have a wider range of the half-life values in the database, we included additional data calculated in the same way from the rate constants experimentally measured by Kwok et al. (1995) and Brubaker and Hites (1997, 1998b).

Unfortunately, since the data were unique, it was very hard to judge their quality. However, when the data are taken from more than only one source, the influence of the uncertainties relative to the particular laboratories (systematic errors) on the QSPR model decreases. Such a procedure helps to avoid the situation when the model describes not only the endpoint (i.e., the half-life value), but also the endpoint measured by a single operator (i.e., the half-life values measured by Smith). In addition, we have assumed that the data used in this study met basic criteria of quality, because they were accepted and published in the leading peer-reviewed scientific journals.

Because only QSPRs validated externally (after the initial internal validation) can be considered as reliable and applicable for predictions (Gramatica, 2007), we split the compounds from our database into a training ($n = 29$) and a validation set ($k = 10$). We applied the following algorithm of splitting: the compounds were ranked in line with the values of $\log t_{1/2}$, and then every fourth compound was moved to the validation set (V). Remaining compounds formed the training set (T). This is a method producing the training and validation sets fairly represented the data (Hewitt et al., 2007). In addition, the first and the last compound were arbitrarily selected for the training set, while the second and the penultimate one were included in the validation set (Table 1). This additional selection was based on our experience that some of the first and last compounds in such ranking have usually high influence on the model (high leverage values, for details please refer to the Section 2.2.). Therefore, it was possible to extend maximally the applicability domain of the model and to investigate better the prediction error for the most influential compounds.

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