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Review

Environmental analysis of chlorinated aromatic thioethers, sulphoxides and sulphones

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ABSTRACT

Chlorinated aromatic thioethers discussed here are polychlorinated dibenzothiophenes, thianthrenes and diphenylsulphides. Relatively little is known about their occurrence, behaviour and fate in the environment. Polychlorinated dibenzothiophenes and diphenylsulphides have recently been found to be formed in waste combustion and analysed in pulp mill effluents. Chlorinated sulphoxides and sulphones are usually metabolites or oxidation products of different chlorinated aromatic compounds. Different gas chromatographic–mass spectrometric techniques are used in the analysis of the chlorinated thioethers. The sulphoxides and sulphones, because of their higher polarity, can be isolated from other compounds by liquid chromatography.

CONTENTS

1. INTRODUCTION

Polycyclic aromatic sulphur heterocycles (PASHs) and polycyclic aromatic hydrocarbons (PAHs) occur widely in the environment [1–5]. Dibenzothiophene (DBT) and some methyl-substituted dibenzothiophenes are persistent residues in the marine environment after oil accidents. Dibenzothiophene and its alkyl derivatives have been found to accumulate in eels, clams, short-necked clams, oysters and mussels [6–15]. These compounds in biota are supposed to originate mainly from crude oil pollution. Different crude oils contain 1–10% sulphur, of which about half is organically bound, mostly in aromatic structures [16]. The most important compound is dibenzothiophene [17].

The occurrence of polychlorinated polycyclic aromatic sulphur heterocycles (PCPASHs) in the envi-

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ronment has been reported recently. Polychlorinated dibenzothiophenes (PCDBTs) have been found in stack gases, bleached pulp mill effluents and aquatic organisms [18–21]. PCDBTs and polychlorinated thianthrenes (PCTAs) are environmentally and toxicologically interesting compounds because of their structural similarity to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The structures of the compounds reviewed are described in Fig. 1. PCDBTs are sulphur analogues of PCDFs, and PCTAs are sulphur analogues of PCDDs. PCTAs and PCDBTs can in theory be formed analogously to PCDDs and PCDFs in different ways. Polychlorinated diphenylsulphides (PCDPSs) are sulphur analogues of the polychlorinated diphenylethers (PCDEs), which are common residues in the environment. There is no considerable knowledge about the potential toxicity of these kind of compounds. However, 2,3,7,8-tetrachlorothianthrene is suspected to possess dioxin-like activity [22], and recently preliminary toxicological studies have shown that the toxicity of PCDBTs is less than that of the most toxic co-planar PCBs [23].

Chlorinated aromatic methylsulphides, sulphoxides and sulphones are metabolites or oxidation products of different compounds [24–31]. Methylsulphonylation of xenobiotics leads to the formation of mercapto (–SH), methylthio ($-SCH_3$), methylsulphinyl ($-SOCH_3$) and methylsulphonyl ($-SO_2CH_3$) thioether derivative metabolites [32]. The formation of xenobiotic thioether derivatives is considered to be a pathway for the detoxification of reactive intermediates [32,33]. The metabolic pathway of halogenated aromatic hydrocarbons consists of three stages: oxygenation, glutathione thioether disposition and sulphoxidation [32–35]. The intestinal microflora is involved in the formation of these metabolites [36]. Many of these compounds possess some kind of biological activity [37–39].

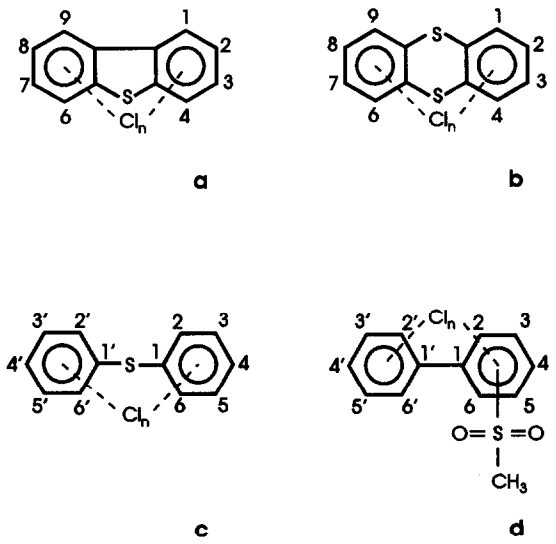

Fig. 1. Structures of the compounds reviewed: (a) polychlorinated dibenzothiophenes (PCDBTs); (b) polychlorinated thianthrenes (PCTAs); (c) polychlorinated diphenylsulphides (PCDPSs); (d) methylsulphones of PCBs.

2. EXTRACTION AND CLEAN-UP PROCEDURES

2.1. Chlorinated thioethers

PCDBTs have been analysed in stack gas, fly ash, bleached pulp mill effluent and aquatic biota samples [18–21,40].

The water samples were filtered twice, and the filters dried, weighed and Soxhlet-extracted with toluene for 48 h. The stack gas samples were extracted with toluene and washed with sulphuric acid. Column chromatography with basic aluminium oxide and activated carbon was used to separate the dioxin fraction from the sample extracts [41]. PCDBTs, PCDPSs and PCTAs behave during purification and fractionation with basic aluminium oxide and activated carbon in the same way as PCDFs and PCDDs [41,42].

2.2. Sulphoxides and sulphones

Fatty materials from lung, liver and adipose tissue were extracted with *n*-hexane after homogenizing with anhydrous sodium sulphate [43–45] and saponified with 2 *M* alcoholic sodium hydroxide or 1 *M* alcoholic potassium hydroxide solution [43,46] or extracted with 95% (v/v) dimethyl sulphoxide–water solution by shaking. Purification was done by silica gel column chromatography. The PCBs and other non-polar compounds were eluted with *n*-hexane, and sulphones, sulphoxides and other compounds with *n*-hexane–diethylether mixtures [43].

The sulphone-containing fraction could be extracted with concentrated sulphuric acid. The solu-

tion was then diluted with water and subsequently re-extracted with hexane, producing a pure sulphone fraction without any interfering compounds [47].

The methylsulphones and methylsulphoxides could also be extracted with dichloromethane and purified by gel permeation chromatography followed by alumina column chromatography [48].

2.3. TLC and HPLC of PCPASHs

In environmental samples, PCPASH compounds occur in a complex matrix of thousands of different organic compounds. The separation of the PCPASHs from interfering compounds in GC–MS and in GC proved to be difficult. Several different liquid chromatographic fractionations have to be applied to obtain a fraction with minimum amounts of interfering compounds [49,50]. Normally the first step is to separate the non-polar aromatic compound fraction, which contains a lot of halogenated and alkylated low-polarity compounds. This is usually done by silica gel or alumina column chromatography using hexane and hexane–dichloromethane as eluents. There does not exist any unambiguous method of separating PCPASHs from other compounds.

Reversed-phase (RP) TLC with RP-18 plates and acetonitrile–water eluents can separate PCDBTs from many interfering compounds but not completely from complex environmental samples [49]. In normal-phase NH_2-TLC with hexane the PCDBTs elute faster than the corresponding non-chlorinated compounds [49]. By oxidizing these compounds to the corresponding sulphones, they can be separated by RP-TLC or by RP-HPLC because of the difference in their polarity, but this makes the GC analysis more difficult [50,51].

The sulphones and sulphoxides, because of their different polarity, can be separated as a group from other non-polar compounds. In clean-up procedures used to prepare samples for the analysis of non-polar chlorinated compounds these are retained in the columns [52]. They also have longer retention times in GC columns usually used for residue determination [53]. From alumina or silica columns the sulphoxide–sulphone fraction can be eluted with more polar eluents, *e.g.*, ethyl acetate, after the PCBs and other non-polar compounds have been eluted with hexane or diethyl ether [44,46,54]. From Florisil columns these compounds can be eluted separately as a group using different diethyl ether–light petroleum mixtures [52].

In silica gel TLC when methylene chloride–hexane (50:50) is used as eluent, all compounds with a similar oxidation level (methylthio, methylsulphinyl and methylsulphonyl compounds) have similar R_F values [52].

Sometimes the methylthio and methylsulphinyl compounds are oxidized to sulphones to simplify the analysis [46,52]. These sulphones can further be desulphurized to facilitate normal GC analysis using non-polar columns [46].

The sulphones can be derivatized before analysis by preparing trimethylsilyl derivatives, methyl esters or different acetates [54,55].

Sulphoxides and sulphones, owing to their higher polarity, can easily be separated from other compounds by RP-HPLC. In RP-HPLC using a μBondapak C_{18} column and acetonitrile–water eluents the methylsulphone-PCBs elute before the methylthio-PCBs and PCBs [43].

3. GC AND GC–MS OF ENVIRONMENTAL SAMPLES

3.1. Chlorinated thioethers

Tetrachlorinated dibenzothiophenes (TeCDBTs) and tetrachlorinated dibenzo-*p*-dioxins (TeCDDs) have in low-resolution MS the same values of M^+, $[M+2]^+$ and $[M+4]^+$ ions. A resolution of about 20 000 is needed to separate TeCDBTs (MW=319.87880) from TCDDs (MW=319.89650). The retention times of the congeneric PCDBTs in GC with unpolar SE-30 and HP-5 columns are longer than those of the PCDDs; however, in many environmental samples there are several interfering peaks eluting in the same window as the PCDBTs if low resolution in GC–MS is used [42].

Several PCDBTs are available as model compounds in environmental analysis. The compounds are prepared by direct chlorination of the parent compound, DBT, when a mixture of different congeners is obtained, or by reacting PCBs with sulphur, when in some cases it is possible to obtain one isomer, although usually a mixture of a few isomers is obtained [19,20,41,56,57].

Buser and co-workers [19,20] have used different

GC–MS techniques to determine PCDBTs in fly ash samples and aquatic organisms. In electron impact (EI) mass spectra the PCDBTs show a strong molecular M^+ ion and the expected clustering due to chlorine and sulphur isotopes. The major difference in the EI mass spectra of the PCDDs and PCDBTs is the formation of a strong $M^+ - COCl$ in the former and a strong $M^+ - 2Cl$ in the latter compounds. QUAD MS–MS was found to be highly sensitive for detecting PCDDs and PCDFs via the reaction $M^+ \rightarrow [M - COCl]^+$, and mass-analysed ion kinetic energy (MIKE) MS–MS was found suitable for detecting the PCDBTs via the reaction $M^+ \rightarrow [M - 2Cl]^+$ [19].

Stack gas samples and bleached pulp mill effluent samples have been analysed for PCDBTs and PCDPSs with high-resolution GC–MS with a resolution of 20 000. Only particles in the effluent waters were studied, and it was assumed that PCDBTs are mostly particle-bound. Selected-ion monitoring was done with the values of M^+ and $[M + 2]^+$ ions of the TeCDBTs and pentachlorinated dibenzothiophenes (penta-CDBTs) (319.8788, 321.8758, 353.8398 and 355.8369). When the resolution was increased to 20 000, disappearance of the PCDDs was nearly complete [18,21].

3.2. Sulphones and sulphoxides

In MS fragmentation of methylsulphones the loss of CH_3 yields the $[M - 15]^+$ ion. The 1,2-phenyl migrates from sulphur to oxygen and the aryl methane sulphinate thus formed is fragmented to a phenolate ion, $[M - 63]^+$, by the loss of $SO–CH_3$. One of the major fragments, $[M - 114]^+$, is produced by the loss of the methylsulphone group and one chlorine atom [55,58,59].

Haraguchi *et al.* [48] have used selected-ion monitoring GC–MS with the values of M^+ and $[M + 2]^+$ ions for di- to tetrachlorophenylmethylsulphones, di- to hexachlorobiphenylmethylsulphones, tetra- to hexachloroterphenylmethylsulphones and dichloro-(diphenyl)dichloroethene (DDE)-methylsulphone. The values of the ions $[M - 16]^+$, $[M - 14]^+$ and $[M - 12]^+$ were used in the analysis of di- and trichlorophenylmethylsulphoxides and di- to pentachlorobiphenylmethylsulphoxides in human liver, lung and adipose tissues, human milk, human blood, blubber of blue whale, sardine, rainbow trout, Yaname, oyster and baby clam [48]. A 25 m × 0.25 mm I.D. fused-silica MPS-50 capillary column (Quadrex) in a JEOL JMS-DX300 mass spectrometer with a JMA-DA5000 data system was used [48].

In GC analysis electron-capture detection (ECD) and/or flame photometric detection (FPD) are normally used in the analysis of Cl–S compounds [43–46,52,59,60].

4. OCCURRENCE AND ENVIRONMENTAL CONCENTRATIONS OF PCPASHs

Stack gas samples contain several TeCDBT and penta-CDBT isomers that elute within the retention window of the prepared model compounds and have the typical $M^+/[M + 2]^+$ ion ratios for tetra- and pentachlorinated compounds. The concentrations of the TeCDBTs in stack gas samples are very high compared with the concentrations in bleached pulp mill effluents.

The isomer profiles observed in selected-ion monitoring chromatograms of TeCDBTs in stack gas samples and in pulp mill effluents are quite different [21]. The stack emissions contain faster-eluting (column HP-5) isomers [21]. This probably indicates a different route of formation of these compounds in waste combustion and in pulp bleaching.

Buser *et al.* [20] estimated the concentrations of PCDBTs in fly ash to be up to 55 ng/g, which is one order of magnitude below the concentrations of the PCDDs and PCDFs in these samples [20]. The PCDBTs detected were TeCDBTs and penta-CDBTs, including the 2,3,7,8-TeCDBT [20]. Aquatic organisms such as crabs, lobsters and worms from New York Bight/Newark Bay contain high levels of some PCDBTs. The main isomer found in aquatic organisms was the 2,4,6,8-TeCDBT. 2,3,7,8-TeCDBT was not found [19,40].

In pulp mill effluents analysed the concentrations of the TeCDBTs were <1–60 pg/l. In the pulp mill effluent samples the 2,3,7,8-TeCDBT isomer was the dominating TeCDBT isomer [21]. The ^{13}C-12-labelled 2,3,7,8-TeCDBT was used as a tentative internal standard in the quantitative determinations of the TeCDBTs in the pulp mill effluent samples, supposing that the MS response of the TeCDBTs is almost the same as that of the TeCDDs [21]. Penta-CDBTs and higher chlorinated PCDBTs were not found from the pulp mill effluent samples [21].

Hilker *et al.* [22] have reported on the finding of 2,3,7,8-tetrachlorinated thianthrene (TeCTA) in sediment from a sanitary sewer near a chemical plant that patented this compound. Recently, the determination of trichlorinated diphenylsulphides (tri-CDPSs) and tetrachlorinated diphenylsulphides (TeCDPSs) in stack gas and bleached pulp mill effluent samples has been reported [61]. 2,4,4',5-TeCDPS (Tetrasul) has been used as pesticide and has been analysed by GC–ECD–FPD from food samples [62,63].

PCB methylsulphones are persistent and lipophilic compounds. Methylsulphones are accumulated in adipose tissue. Methylsulphone and methylsulphoxide metabolites of chlorinated benzenes (CPs), polychlorinated biphenyls (PCBs) and DDE have been detected in environmental samples and human tissues and milk [43–45,48,60,64–66].

These were identified as mainly tri-, tetra-, penta-, hexa- and heptachlorinated methylsulphones [44,67]. For example, in lung tissue obtained from a Yoshu victim about 60 different isomers of methylsulphone-PCBs were still present more than 15 years after intoxication [45]. The levels of methylsulphones were estimated at one twentieth of those of PCBs in the corresponding samples [60]. Seals from the Baltic have been found to contain at least 30 different methylsulphone-PCBs [53]. The major sulphone metabolites contain the methylsulphonyl group in the 4-position and the minor ones in the 3-position [33,47,60,68–70,71]. Tissue-specific, structure- and species-dependent high-affinity bindings and long retentions in lung, kidney and brain have been demonstrated [33,43,54,64,69–73].

From fish samples (striped bass, catfish, goldfish, carp, sucker) that contained high levels of chlorobenzenes and PCBs the metabolite sulphoxides and sulphones could not be found [52]. It is possible that these metabolites are not formed in fish or are not stored in the edible parts as are the parent compounds.

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