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EMERGING POPs. A SPECIAL SESSION AT “DIOXIN 2008”
IN BIRMINGHAM *

TRWAŁE ZANIECZYSZCZENIA ORGANICZNE (POPs) POJAWIAJĄCE
SIĘ W ŚRODOWISKU PRZYRODNICZYM. SESJA SPECJALNA PODCZAS
KONFERENCJI „DIOXIN 2008” W BIRMINGHAM

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This article discusses the topics and ideas presented at the Special Session of the conference Dioxin 2008 (28th International Symposium on Halogenated Environmental Organic Pollutants and POPs) titled: “Emerging POPs”. The session was devoted to emerging and re-emerging compounds or groups of compounds identified recently as environmental contaminants and classified as dioxin-like compounds or persistent organic pollutants.

Key words: biocides, brominated and chlorinated flame-retardants, environment, dioxins, dioxin-like compounds, food, perfluorinated compounds, synthetic musk, persistent organic pollutants.

Słowa kluczowe: biocydy, dioksyny, piżma syntetyczne, substancje dioksynopodobne, środowisko przyrodnicze, uniepalniacze bromoorganiczne i chloroorganiczne, związki perfluorowane, żywność.

The “Dioxin” series of symposia have been in existence now for 28 years and provide a major international forum for the presentation of scientific data and exchange of ideas on relatively persistent and highly toxic organohalogenated compounds. These contaminate the environment and food, migrate within the food chain and are accumulated in animal and human tissues. In recent years around 1000 people have typically attended this symposium. Presenters submit material as 4-page articles (short papers) – written in a concise style for publication

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in the conference periodical *Organohalogen Compounds*, which was published in printed format up until 2003 (volume 65) and electronically since 2004 (volumes 66-70). Volumes 40-65 are available in both printed and electronic formats. The University of Birmingham in England was host to the "Dioxin 2008" symposium (*28th International Symposium on Halogenated Environmental Organic Pollutants & POPs*) which took place in The International Convention Centre (ICC) in Birmingham from 17 to 22 August 2008.

The chemical compound which is the subject of most discussion during the symposium is, without doubt, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which is synonymous with the term "dioxin". The 'classical' understanding of the term 'dioxins' is for the most toxic and bioaccumulative compounds substituted with chlorine at least at positions 2, 3, 7 and 8, giving ten congeners of chlorodibenzo-*p*-dioxin (PCDDs; polychlorinated dibenzo-*p*-dioxins), the analogous fourteen congeners of chlorodibenzofuran (PCDFs; polychlorinated dibenzofurans), and four spatially planar congeners of chlorobiphenyl (PCBs; polychlorinated biphenyls). There are, however, a number of other compounds with spatial structure (stereo isomers) similar to TCDD, all likely to have a similar mechanism of toxic action, and could therefore be included into the group of dioxins for purposes of risk assessment.

There are even more compounds showing the typical characteristics of POPs. These mainly include a number of organohalogenated compounds (mainly organochlorinated, -brominated and -fluorinated), identified as relatively persistent under normal environmental conditions, and additionally with high predilection to accumulate in all biota, and these are frequently also highly toxic.

These 'other' chemicals, in addition to the 'dioxins', also exhibit the classical features of POPs such as similar toxicodynamic properties, which can result in their presence as environmental, food and human body contaminants. These include compounds such as: non-planar (or non-ortho) chlorobiphenyls; polychlorinated naphthalenes (PCNs); -terphenyls (PCTs); -dibenzotriphenyls (PCDTs); chlorinated polynuclear aromatic hydrocarbons (Cl-PAHs; e.g. polychlorinated anthracenes, -phenantrenes, -fluorenes, -fluoranthenes, -pyrenes); some organochlorine pesticides (e.g. DDT; constituents of Toxaphene or Melipax including polychlorinated bornanes, -bornenes, -bornandienes, -camphenes, -dihydrocamphenes; Chlordane compounds, and some other pesticides); polybrominated biphenyls (PBBs), -naphthalenes (PBNs); -dioxins (PBDDs); -furans (PBDFs); and several compounds belonging to the group of brominated and chlorinated flame retardants (e.g. polybrominated diphenyl ethers, PBDEs; Mirex). It also includes perfluorinated carboxylic acids (PFCAs), perfluorosulfonates (PF), and unsaturated fluorotelomer carboxylic acids (FTUCA).

An important aspect sometimes discussed but only rarely studied is the possibility that metabolites, such as the hydroxylated and sulfonated derivatives which can also be persistent and toxic – sometimes even more so than their precursor compounds, and impurities that are often found in technical formulations of some of the compounds.

Altogether there are at least several hundred individual or groups of chemicals identified as major or highly toxic constituents of particular technical formulations, that occur as contaminants in the environment and subsequently in body fluids and tissues of human and animals.

The number of individual compounds contained in all of the above mentioned groups of chemicals comes to several thousand. For example there are, theoretically 8149 congeners of *o*-, *m*- and *p*-chloroterphenyl (PCTs), and a total of 32768 congeners of the polychlorinated

camphenes (PCCs; including polychlorinated bornanes, -bornenes and -bornandienes but without -camphenes and -dihydrocamphenes). In addition, the toxic characteristics of dioxin and the way in which it behaves in the environment probably also feature in other compounds not yet identified as POPs. This may be predicatable by models or theory relating to their chemical structure and configuration in space (quantitative structure activity relationships, QSAR etc). Some compounds with highly similar properties to 2,3,7,8-TCDD, include e.g. polychlorinated thioanthrenes (PCTAs).

There was a special focus on emerging and re-emerging contaminants identified in the environment and food. The following section reviews the topics and ideas presented by the authors of the papers presented at Dioxin 2008 "Emerging POPs, Special Session", which was devoted to these chemicals. The session included eight oral and six poster presentations [7-8, 10-17, 19-21].

ORGANOCHLORINATED COMPOUNDS

Toxic organochlorine compounds with the characteristics that include persistence in the environment, bioaccumulation in animal tissues and biomagnification are substances which contaminate the environment and food. They were manufactured in relatively greater amounts compared to, organobrominated or -fluorinated compounds. The first organochlorinated compound synthesized industrially was hexachlorobenzene (HCB) which was manufactured from 1910.

The sites of adsorption of chlorobenzenes and analogues substituted at the *para* position with amino-, methoxy-, methyl-, chloro-, acetyl- and cyano- using palladium catalysts were studied *in silico* by Yoneda at al. [21]

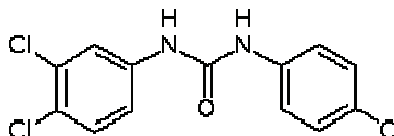
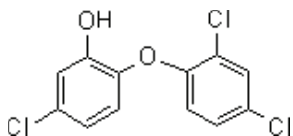
Industrial synthesis of chloronaphthalenes (CNs; polychlorinated naphthalenes, PCNs) commenced in Germany around the year 1914. PCNs as industrial compounds were precursors to PCBs [3]. Based on available experimental analytical data a chemometric analysis (principal components and cluster) was made on PCN congeners and compositional similarities and differences were investigated between the technical PCN formulations of the Halowax series (Halowax 1000, 1001 and 1031) and another technical PCN formulation (unknown name), of which 18 tons was imported unlawfully into Japan earlier this decade [7].

This unknown technical PCN formulation was similar in composition and content as regards PCN congeners found in Halowax 1031, but differs in other details from the Halowax series. There are indications that the formulation originated from a stockpile in the UK, of a formulation named Seekay wax 95. It is less probable that it was from another formulation similar to Seekay wax 95 that is thought to be still illegally synthesized or imported to the UK [7].

The sources of environmental contamination with PCNs to some extent originate from materials and products made with the use of technical PCN formulations. Minor sources include technical PCBs formulations contaminated with chloronaphthalenes (always contaminated; < 1 %), and also high temperature reactions (combustion, incineration, metal smelting etc.) [3]. Of the 75 chloronaphthalene congeners theoretically possible, up to 74 have been identified in technical PCN formulations of the Halowax series, and in fly ash from municipal solid waste incinerators. A majority of the 75 CN congeners have been identified as contaminants in

Triclosan and Triclocarbon

Triclosan [TCS; 5-chloro-2-(2,4-dichlorophenoxy)phenol, Fig 2] is used as an antimicrobial and conserving agent (for liquid soap, toothpastes etc.), and has sometimes been found to be contaminated with dioxins. Triclorocarbon [TCC; N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl)urea] has similar applications to TCS [11]. Both of these compounds are used in relatively large volumes. Both TCS and TCC have been found in untreated and treated sewage of the Savannah (USA). TCS and TCC are removed at the sewage treatment plant with an efficiency of 80-99 %. They are present in sewage either adsorbed on particulate matter or dissolved in solution. [11].



(a)

(b)

Fig. 2. Triclosan (a) and Triclocarbon (b).
Triclosan (a) and Triclocarbon (b).

ORGANOBROMINATED COMPOUNDS

The most diverse group of compounds discussed during the session were organobrominated compounds – mainly brominated flame-retardants but also compounds produced unintentionally e.g. polybrominated dibenzo-*p*-dioxins and –furans (PBDD/Fs). These can be formed during incineration of waste containing brominated chemicals [2]. The most widely discussed included: bromodiphenyl ethers (polybrominated diphenyl ethers, PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A).

Investigations have been carried on the degree of contamination of edible marine molluscs with 17 bromodiphenyl ethers, polybrominated biphenyls (PBBs; 10 congeners) and PBDD/Fs (10 compounds, from tetra- to heptaBDD and from tetra- to heptaBDF substituted with bromine at least at positions 2,3,7 and 8), as well as 2,3,7-triBDD (2,3,8-TrBDD) and 2,3,8-triBDF (2,3,7-TrBDF). The shellfish (mollusc) species examined included oysters (*Crassostera gigas* and *Ostrea edulis*), blue mussel (*Mytilus edulis*) and gastropods (*Cerastoderma edule* and *Pecten maximus*) from the coast of Scotland, England, Wales and Northern Ireland collected in 2006-2007 [8]. The edible part of the molluscs always contained measurable amounts of the compounds investigated but at varying concentrations. PBBs occurred at lowest concentration, i.e. *ortho*-substituted congeners found were on average at 0.001 µg/kg, and non-*ortho* congeners at 0.01 ng/kg. PBDD/Fs on average varied between 0.018 and 0.055 ng TEQ/kg (2,3,7-TrBDD and 2,3,8-TrBDF were also found), while PBDE dominated with 0.23 to 0.82 µg/kg.

With no toxic equivalency factor (TEF) values for brominated dioxins, the authors used TEF values of the chlorine-substituted analogues. The occurrence of these compounds in food did not seem to pose any health risk on their own, but they added to the contribution from all

contaminants with similar mechanism of action (e.g. also including PCDD/Fs, PCBs, PCNs), and the combined toxicity from all these compounds should be considered.

In the Republic of Ireland, statutory monitoring studies checked the content of PBDEs (nos. 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183 and 209), PBDDFs (2,3,7-TrBDD, 2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3(4/6)7,8-HxBDD, 1,2,3,7,8,9-HxBDD, 2,3,8-TrBDF, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF) and PBBs (nos. 15, 49, 52, 77, 80, 101, 126, 169, 153 and 209) in cow, pig, sheep and poultry fat and livers, as well as in milk and eggs [19]. The largest degree of contamination was with PBDEs, followed by PBDD/Fs and PBBs. Adipose fat of all species mentioned showed similar concentrations of PBDEs but cattle and sheep showed greater content in liver when compared with poultry or pigs. Food contained more PBDFs than PBDDs, and PBBs occurred in all eggs sampled at 0.1-2.8 $\mu\text{g}/\text{kg}$ lipid way, in a half of fat samples (0.03-0.26 $\mu\text{g}/\text{kg}$ lw) and in all samples of poultry, sheep and pig livers (0.15-0.30 $\mu\text{g}/\text{kg}$ lw) [19].

Increasing world usage of organobrominated flame-retardants (BFRs) and disposal of waste containing these compounds increases the risk of exposure of humans to these compounds and also to PBDFs and PBDDs. In adipose fat taken from individuals within the general population of Sweden (7 donors) 2,7/2,8-DiBDF, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF were found at concentrations from 0.12 to 2.24 pg/g , whilst 1-MoBDD, 2,7/2,8-DiBDD, 2,3,7-TrBDD, 2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 4-MoBDF and 2,3,8-TrBDF were not detected [1].

An analytical method for "new" brominated flame-retardants and for brominated diphenyl ethers, TBBP-A and DBDPE was presented and data for bottom sediments and particulate matter from the Western Scheldt river in the Netherlands was discussed [13]. The new flame-retardants included: pentabromocyclohexane (PBCCH; congeners A, B, C, D), 2,3,5,6-tetrabromo-*p*-xylene (*p*TBX), tetrabromo-*o*-chlorotoulene (TBoCT), 1,2-*bis*(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE), tetrabromophthalate anhydride (TBPhA), tris(2,3-dibromopropyl)phosphate (TTBPP) and pentabromotoluene (PBT). Apart from TBBP-A and TTBPP all of the other organobrominated compounds mentioned were found.

PERFLUORINATED COMPOUNDS (PFCs)

One of the highest profile groups of emerging contaminants where there is still much to learn, are the perfluorinated compounds (PFCs). These chemicals are manufactured intentionally and are not produced by natural processes. The group of perfluorinated compounds considered as possible environmental contaminants comprises almost 60 chemicals. Despite the fact that PFCs are or were manufactured for many years, the available database as regards which compounds were synthesized, by who, when, and in what quantities, and for what intended use is sparse. The questions regarding source and environmental fate of PFCs, and questions relating to the toxicity of these compounds to human and other biota, especially at low doses as found in cases of real exposure remains important.

Because of inadequate analytical methods and lack of available high purity analytical standards (including isotopically labelled standards), and scale of analytical problems, only

two compounds have been widely studied – perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA), and some other compounds have been studied to much less of an extent [6, 9]. During the last three years there has been a large advance with respect to analytical methods for these compounds [18].

Yeung et al. [20] could identify 11 of 21 PFCs tested in potable, riverine and sea water and in waste water (sewage) from India, with varying frequency and concentration. The authors cited [20] did indicate that the rivers in the south of India were on average less contaminated with PFOS and PFOA when compared to rivers in Korea, Japan, Germany or USA [20]. But the amount of published data on the degree of riverine water pollution with respect to PFOS and PFOA and possible sources of these compounds is small from all of these countries.

Nineteen perfluorinated carboxylic acids compounds, perfluorinated sulphonates, perfluorinated sulphonamidoacetic acids (perfluoro-N-ethylsulphonamido acetic acid; N-EtFOSA and perfluoro-N-ethylsulphonamidoacetic acid; N-EtFOSAA) and unsaturated fluorotelomer carboxylic acids were analysed in inland and coastal bottom sediments and biota at the sites near Savannah and New Brunswick (Georgia, USA). PFOS was the major compound noted in these materials (up to 320 ng/g wet weight), followed by one of several possible isomers of PFOS that have not been previously reported, at concentrations up to 75 ng/g [10].

Synthetic musk

Synthetic musks are fragrance compounds widely used in perfumes, cosmetics, detergents, fabric conditioners, shampoos etc., and these exhibit problems relating to persistency, bioaccumulative potential and estrogenic activity, in other words toxicity [4]. Due to their persistency and widespread use, these chemicals are commonly found contaminants in municipal sewage. Occurrence, fate and efficiency of removal of fragrance chemicals such as nitromusks (NMCs) – musk ketone (MK) and musk xylene (MX) or polycyclic musks – galaxolides (HHCB) and tonalides (AHTN) were investigated in various types of active sludge-based treatment processes.

Influent sewage at a municipal sewage treatment plant in Korea contained nitro- and polycyclic musks at a total concentration of between 3.7 and 7.3 $\mu\text{g}/\text{dm}^3$, and in treated effluent sewage (excluding musk xylene) concentrations were between 0.96 and 2.7 $\mu\text{g}/\text{dm}^3$ [12].

POPs in human milk in WHO studies

Results of the WHO coordinated activities from the third round (years 2001-2003; 26 countries participated) and fourth rounds (years 2005-2007; 14 countries participated and in 2008 a further 20 countries participated) of the international studies on human milk contamination with POPs in respect of possible impact on health were assessed [14]. 12 POPs covered by the Stockholm Convention were determined including PCDDs, PCDFs, planar PCBs, dieldrin (aldrin is rapidly metabolized to dieldrin), chlordane compounds, DDT and its analogues, hexachlorobenzene (HCB), heptachlor and heptachlor epoxide and Toxaphene. Human milk was not found to contain endrin, endrin ketone and Mirex. Dioxins were found at relatively greater concentration in material from Europe (median 8.9 pg/g lipid weight; WHO-PCDD/F-TEQ) and in one of the two African countries studied. In the case of PCBs, a greater concentration was found in human milk from Europe (median 9.4 pg/g lipid weight; WHO-PCB-TEQ), while in the case of DDT and its analogues, higher concentrations were found in tropical and subtropical countries (median between 848 and 1713 ng/g lipid weight).

When compared with DDT and its analogues, the degree of contamination of human milk by other pesticides was small.

As more knowledge about existing POPs is gathered, more compounds with persistent, bioaccumulative and toxic properties are uncovered. Some of these are easy to predict, such as the brominated dioxins, but there is little data or evidence that they are present in the environment and this is needed. Others such as the organo-fluorine are not as easy to predict because they are not lipophilic, but these compounds nevertheless display the same characteristics that can give rise to concern. There is still a need for more evidence and research into both exposure and characterisation of some of these emerging compounds, and also to be on the lookout for what will feature as emerging contaminants in the coming years.

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STRESZCZENIE

W artykule przedstawiono tematykę i idee zaprezentowane podczas specjalnej sesji zatytułowanej „Emerging POPs” na konferencji Dioxin 2008 (28th International Symposium on Halogenated Environmental Organic Pollutants and POPs). Sesja dotyczyła pojawiającym się w badaniach i publikacjach naukowych substancjom lub grupom substancji ostatnio identyfikowanych jako nowe zanieczyszczenia w środowisku przyrodniczym a zaliczanych do grupy substancji dioksynopodobnych lub trwałych zanieczyszczeń organicznych.

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