Chirality: A challenge for the environmental scientists

Imran Ali, V. K. Gupta and Hassan Y. Aboul-Enein*

Most of the pollutants are present in the environment as a mixture of their chiral isomers. Studies have revealed that these isomers have an enantioselective distribution, metabolism, and toxicity of these pollutants, in the light of the toxicity of their individual chiral isomers. We describe here, the different chiral isomers of common pollutants, their metabolism and toxicity, and methods for their separation and quantification.

POLLUTION of the environment, one of the most pressing problems of our age, has now reached a level that it poses a potential threat not only to the health of people but also to entire populations. Among various environmental pollutants, organic contaminants, i.e. pesticides, phenols, plasticizers and polyaromatic hydrocarbons are the most toxic due to their carcinogenic nature[1–3]. The monitoring of these pollutants in the environment is essential and important. Many reports are available on the analysis of organic pollutants but these do not distinguish which mirror images of pollutants are present and which is harmful in the case of chiral pollutants. Scientists and other regulatory authorities are in demand for tackling associated problems in these areas.

Chirality and its occurrence

In 1883, Kelvin[4] used the term chirality, derived from the Greek word *kheir* for handedness. Any object lacking the three elements of symmetry, i.e. plane, centre and axis of symmetry, and exists in more than one form which are non-superimposable mirror images of each other, are called as chiral objects. From elementary particles to humans, chirality is found in a wide range of objects[5]. There are several examples of the chirality in our environment, i.e. burial chamber mural paintings in Egypt[4], the 540 galaxies listed in *Carnegie Atlas of Galaxies*[6], and helical structures of plants and animals. Briefly, chirality exists almost everywhere in this universe and is associated with the origin of the earth[7].

Chemical evolution of chirality

Knowledge of chemical evolution of chirality started in 1809 with the discovery of Haüy[8] who postulated that, from crystal cleavage observations, a crystal and each constituent space-filling molecule are images of each other in overall shape. Later in 1848, Pasteur reported the different destruction rates of *dextro* and *levo* ammonium tartarate by the mould *Penicillium glaucum*[9]. The tetrahedral arrangement of carbon valencies, having different groups, makes the whole pollutant (molecule) asymmetric in structure and such a carbon atom is called as asymmetric or the chiral centre. This type of pollutant differs in three-dimensional configurations and exists in two forms which are mirror images of each other (Figure 1). These mirror images are called optical isomers (having the capacity to rotate the plane polarized light) or stereoisomers or enantiomers or enantiomorphs or antipodes or chiral molecules. The phenomenon of the existence of the enantiomers is called as stereoisomerism or chirality. The 50 : 50 ratio of the enantiomers is called the racemic mixture, which does not rotate the plane-polarized light. The number of the enantiomers may be calculated by using 2^n, where n is the number of the chiral centres. In the beginning, the optical isomers were distinguished with (+) and (–) signs or *d* (*dextro*) and *l* (*levo*), indicating

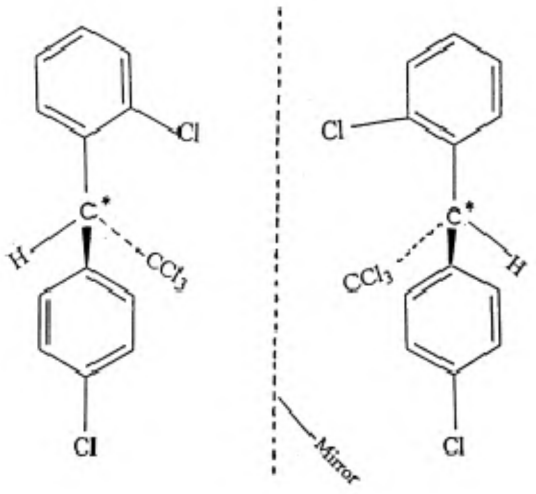

Figure 1. The enantiomers of *o,p*-DDT pesticide.

Imran Ali is in the National Institute of Hydrology, Roorkee 247 667, India; V. K. Gupta is in the Department of Chemistry, Indian Institute of Technology, Roorkee 247 667, India and Hassan Y. Aboul-Enein is in the Pharmaceutical Analysis Laboratory, Biological and Medical Research Department (MBC-03), King Faisal Specialist Hospital and Research Centre, PO Box 3354, Riyadh 11211, Saudi Arabia.
*For correspondence. (e-mail: drimran_ali@yahoo.com)

the direction in which the enantiomers rotate the plane polarized light. (+) or *d* stands for a rotation to the right (clockwise) whereas (–) or *l* indicates a rotation to the left (anticlockwise). The main drawback of such an assignment is that one cannot derive the number of chiral centres from it. This is possible when applying the well known *R*/*S* notation given by Cahn and Ingold, which describes the absolute configuration (the spatial arrangement of the substituents) around the asymmetric carbon atom of the pollutant (molecule).

Chirality and its consequence in the environment

Lewis *et al.*[10] reported that about one fourth of pesticides are chiral in nature. Many other xenobiotics such as polyaromatic hydrocarbons are also chiral pollutants. The example of the chirality in 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane, (*o*,*p*-DDT), a well-known chiral pollutant, is shown in Figure 1. Recently, it has been observed that one of the enantiomers of the chiral pollutant may be more toxic and hence the two enantiomers may have different toxicities[4,11]. This is important information to the environmental scientists when performing environmental analysis. Biological transformation of the chiral pollutants can be stereoselective. Uptake, metabolism, and excretion of enantiomers may thus be very different[11,12]. Therefore, the enantiomeric composition of the chiral pollutants may be changed in these processes. Metabolites of the chiral compounds often are chiral. Moreover, some of the achiral pollutants degrade into the chiral metabolites. For example, γ-hexachlorocyclohexane (γ-HCH) and atrazine degrade into γ-pentachlorocyclohexene and 2-chloro-4-ethylamino-6-(1-hydroxy-2-methylethyl-2-amino)-1, 3, 5-triazine racemic mixtures respectively. It has also been reported that the enantiomers may react at different rates with the achiral molecules in the presence of chiral catalyst[4]. Most of the identities and structures in nature are chiral and, therefore, there are greater chances of the chiral pollutants reacting at different rates. Therefore to predict the exact chiral pollution load, the determination of the toxicities (enantioselective toxicity) and concentrations of the enantiomers is required.

Enantioselective toxicities of the pollutants

Much work has been carried out towards different biological activities of drugs and other pharmaceuticals but, unfortunately, there is little information on the enantioselective toxicities of the chiral pollutants. Mostly pesticides and polyaromatic hydrocarbons are carcinogenic and toxic. They may damage certain body organs such as liver, kidney, bone marrow, etc. and also change the enzymatic activities.

Toxicities of pesticides

Polychlorinated biphenyls (PCBs) are carcinogenic compounds that are known for their persistence and bioaccumulation in the environment due to their physicochemical properties. 78 out of 209 congeners of PCBs have axial chirality in their non-planar conformation and 19 form stable enantiomers (atropisomers). The different toxicities of these PCBs include weight loss, porphyria, teratogenesis and endocrine and productive malfunctions in various organisms. Püttman *et al.*[13] reported PCB139 and PCB197 congeners as the drug metabolizing enzyme (cytochrom P-450, *N*-demethylase and aldrin epoxidase) inducers. The authors reported the (+)-enantiomer of PCB139 as the stronger inducer in comparison to the (–)-enantiomer. In contrast, the racemic mixture of PCB197 and its individual enantiomers were only weak inducers of these enzymes. Furthermore, the same group[14] reported concentrations-related induction of cytochrom P-450, ethoxyresorufin-*O*-deethylase (EROD) and benzphetamine-*N*-demethylase (BPDM). The authors also described that EROD activity was induced to a much greater extent by the (+)-enantiomers of all congeners studied with no activities of (–)-enantiomers of PCB88 and PCB197.

First of all, Möller *et al.*[15] observed the different cytotoxicities and growth stimulation of α-HCH enantiomers in primary rat hepatocyte by reporting 100% mortality in the presence of 3×10^{-4} M (+)-α-HCH while at the same concentration of (–)-α-HCH 75% mortality was reported. Using 5×10^{-5} M concentrations of both the enantiomers the significant mitosis occurred in the presence of (+)-α-HCH enantiomer (factor 2.4) as compared with the stimulation by (–)-α-HCH enantiomer (factor 1.7). Miyazaki *et al.*[16] studied the enantioselective toxicities of cyclodiene (chlordiene, chlordiene epoxide and heptachlor *exo*-epoxide) pesticides on male adults of German cockroach (*Blattella germanica*) and reported that (+)-chlordiene, (–)-chlordiene epoxide and (+)-heptachlor *exo*-epoxide enantiomers showed higher toxicity in comparison to their corresponding mirror images. In another study, the same group[17] reported that only (–)-enantiomer of chlordiene epoxide was insecticidal without any bioactivation whereas the (+)-enantiomer of chlordiene showed toxicity after its biochemical transformation. Again Miyazaki *et al.*[18] identified the different enantioselective toxicities of heptachlor and 2-chlorheptachlor pesticides on the same cockroach. (–)-*o*,*p*-DDT has been known as a more active estrogen-mimic than the (+)-enantiomer in rats[19]. Later on Hoekstra *et al.*[20] reported a yeast-based assay to assess the enantiomer specific transcriptional activity of DDT with the human estrogen receptor (hER). The (–)-enantiomer was the active estrogen mimic whereas the hER activity of (+)-*o*,*p*-DDT was negligible. Malathion is bio-transformed to a racemic malaxon that has anti-acetylcholinesterate (insecticidal)

activity with *R*-enantiomer 22 times stronger than the *S*-enantiomer for bovine erythrocyte cholinesterase[21]. The nerve agent, soman, has two chiral centres and the two (–)-diastereoisomers are more potent inhibitors than their corresponding (+)-counterparts for acetylcholinesterate and α-chymotrypsin. Miyazaki *et al.*[22] also reported the enantioselective toxicities of methamidophose (*O,S*-dimethyl phosphoramidothiodate) and acetaphate (*O,S*-dimethyl-*N*-acetylphosphoramidothiodate) to house flies.

Toxicities of polyaromatic hydrocarbons

Several chiral polyaromatic hydrocarbons (PAHs), including benzo(a)pyrene (BP) and anthracene derivatives, β-naphthoflavone and 3-methylcholanthrene have been reported to possess the enantioselective toxicities. The stereoselective metabolism of benzo(a)pyrene to an ultimate carcinogen follows the metabolic sequence BP → BP-7, 8-oxide → BP-7, 8-dihydrodiol → BP-7, 8-diol-9, 10-epoxide respectively. Wood *et al.*[23] reported that in strain TA98 of *Salmonella typhimurium*, (–)-chyresene-1,2-diol-3,4-epoxide 2 was 5 to 10 times toxic than the other three isomers. However, in strain TA100 of *S. typhimurium* and in Chinese hamster V79 cells, (+)-chyresene-1,2-diol-3,4-epoxide 2 was 5 to 40 times more toxic than the other three optical isomers. Similarly, the (–)-enantiomer of *trans*-3,4-dihydroxy-3,4-dihydrobenz(a)anthracene was found to be a stronger tumorigenic in newly-born Swiss-Webster mice[24].

Distribution of the chiral pollutants

Chiral pollutants enter the environment through point and non-point sources and are distributed in water, sediment, soil and biota. Marine water has been reported as polluted due to heptachlor, *exo*-epoxide (a metabolite of heptachlor), α-, β- and γ-HCHs, toxaphene and phenoxyalkanoic acid herbicides. There are many reports published on the groundwater contamination by pesticides and other toxic organic pollutants[3]. Weigel[25] reported the presence of several drugs in waste water. Later on Buser *et al.*[26] identified ibuprofen, a non-steroidal anti-inflammatory drug, in waste and river waters. Recently, Kümmerer[27] reviewed the presence of the several drugs in surface, ground and drinking water.

Vetter *et al.*[28] detected toxaphene in a Canadian lake sediment for the last 60 years and chlorborane congeners in the sediment from a toxaphene-treated Yukon lake[29]. Another study of the chiral pesticides in sediment was carried out by Rappe *et al.*[30] in the Baltic Sea sediment. Benicka *et al.*[31] also identified PCBs in the sediment of a river. Wong *et al.*[32] measured the enantiomeric ratios for eight PCB enantiomers in the sediment from selected sites throughout the United States. A most comprehensive study of the distribution of the chiral musks, in sediment obtained from wastewater plants, was carried out by Biselli *et al.*[33]. Moisey *et al.*[34] determined the concentrations of α-, β- and γ-HCHs structural isomers and enantiomers in the sediment obtained from North Sea. Aigner *et al.*[35] reported the enantiomeric ratio of chlordane pesticide in the soil of Midwestern United States. The pesticides detected in these samples were chlordane, heptachlor and heptachlor *exo*-epoxide. Wiberg *et al.*[36] reported the presence of organochlorine pesticide in 32 agricultural and 3 cemetery soils from Alabama. Lewis *et al.*[10] detected the presence of dichlorprop pesticide in Brazilian soils. Recently, White *et al.*[37] identified *cis*- and *trans*-chlordanes in the soil of a green house unit.

Some chiral pollutants have been detected in air with a variation in their concentrations from place to place. Aigner *et al.*[35] reported the different enantiomeric ratios of chlordane pesticide in the air of Midwestern United States. Similarly, Bidleman *et al.*[38] collected air samples from Cornbelt, South Carolina and Alabama areas. The authors reported the presence of *cis*-chlordane, *trans*-chlordane, heptachlor and heptachlor *exo*-epoxide in these samples. Ridal *et al.*[39] detected α-HCH in the air sample collected above the surface of Ontario lake. In one of the studies, Ulrich and Hites reported the existence of chlordane in the air sample near Great lake[40]. The other authors who described the presence of the chiral pesticides in the air samples are Wiberg *et al.*[41] (chlordane) and Buser and Müller[42] (heptachlor and chlordane). The enantiomeric ratios of the various pesticides have been detected in various organs of Eider duck[43]; seals[44]; whales[45]; polar bears[46]; fish, bivalves, crayfish, water snakes, barn swallows[47]; pelagic zooplankton, arctic cod, sea birds[34,48]; sheep[49]; roe deer[50] and human[51]. The enantiomeric distribution of various pesticides in the different components of the environment is summarized in Table 1.

Methods of the resolution of the chiral pollutants

Due to the similar physical and chemical properties of the enantiomers, their resolution is very difficult. Nowadays, the chromatographic, electrophoretic, spectroscopic, biosensor and membrane methods are available for the resolution of chiral pollutants[52]. Gas chromatography has been used for the determination of some chiral pesticides, which are volatile at the working temperature, into the environmental samples[53]. In view of the limitations of gas chromatography, high performance liquid chromatography is the only choice. Recently we[54] developed an HPLC system for the chiral resolution of *o,p*-DDT and *o,p*-DDD and the results are summarized in Table 2. The chromatograms of the resolved enantiomers are shown in Figure 2. For more extensive informations on the chiral liquid chromatography the book on the chiral liquid chromatography[52] is recommended. Besides chromato-

Table 1. Distribution of enantiomeric ratios of some chiral pollutants in different components of ecosystems

Chiral pollutants	Ecosystem component	Enantiomeric ratios	Ref.
α-HCH	Sea and rain water	0.79–1.08	55, 56
	Air and soil	0.86–1.10	45, 46
	Eider ducks	1.4	57
	Seals and cod	1.5–1.8	58
	Flounder and mussels	0.80–0.94	59
	Hare	0.80–1.50	60
HHCB	Rudd	0.66	4
PCCH	Sea water	0.97	56, 61
	Flounder	1.0	55
DCPP	Sea water	1.4	57
	Baltic sea	1.15	56
HEPX	Sea water	1.01–1.76	62
Chlordane and	Baltic herring	0.42	12
Octachlordane	Baltic salmon	1.19	12
	Baltic seal	0.60	12
	Air (above soil)	0.74	38, 63
	Plants	~0.50	64
Oxychlordane	Seagull's egg	1.5	55
	Roe deer	7.00–17.00	50
	Hare	1.00–1.5	60
Heptachlor	Air (ambient)	0.99	38, 63
Heptachlor *exo*-epoxide	Seagull's egg	1.6	55
	Roe deer	1.00–5.00	50
	Hare	2.5–3.7	60
	Air (ambient)	1.51	38, 63
Toxaphene	Air	1.00–0.71	28, 29

Table 2. Retention (k), separation (α) and resolution factors (R_s) for the chiral resolution of *o,p*-DDT and *o,p*-DDD pesticides on polysaccharides CSPs under reversed phase mode with 1.0 ml/min flow rate of mobile phase[52]

	k_1	k_2	α	R_s
Acetonitrile-water (50 : 50, v/v)				
Chiralpak AD-RH				
o,p-DDT	15.41	19.77	1.24	2.47
o,p-DDD	nr			
Chiralcel OD-RH				
o,p-DDT	4.54	10.28	2.27	2.03
o,p-DDD	nr			
Chiralcel OJ-R				
o,p-DDT	3.49	8.80	2.52	0.80
o,p-DDD	nr			
Acetonitrile-2-propanol (50 : 50, v/v)				
Chiralpak AD-RH				
o,p-DDT	4.74	8.00	1.69	1.00
o,p-DDD	3.26	4.11	1.26	0.60
Chiralcel OD-RH				
o,p-DDT	nr			
o,p-DDD	nr			
Chiralcel OJ-R				
o,p-DDT	nr			
o,p-DDD	nr			

nr, Not resolved; CSPs, Chiral stationary phases.
Source: Adapted from Ali and Aboul-Enein[54].

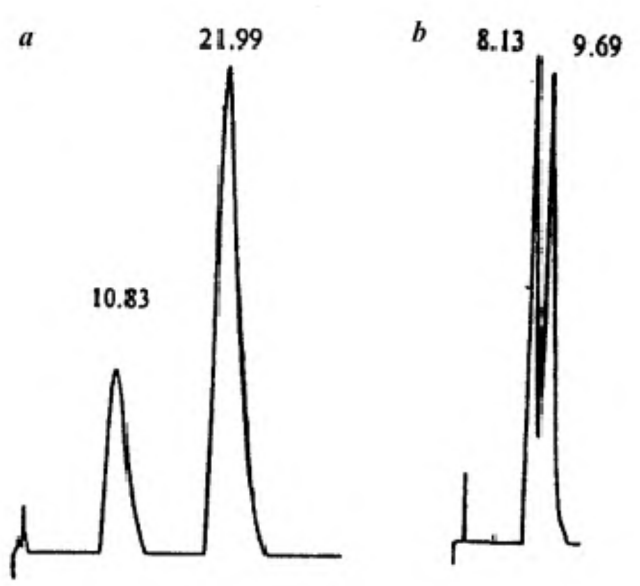

Figure 2. Chromatograms showing the enantiomeric resolution of (***a***) *o,p*-DDT on Chiralpak AD-RH column using acetonitrile-water (50:50, v/v); (***b***) *o,p*-DDD on Chiralpak AD-RD column using acetonitrile-2-propanol (50 : 50, v/v) as the mobile phases. Source: Adapted from Ali and Aboul-Enein[54].

graphy, some publications have appeared in recent years in the field of the chiral resolution using capillary electrophoresis (CE)[55].

Conclusion

As discussed above, the two enantiomers of any chiral pollutant may have different toxicities to the biota. Unfortunately, unlike in drugs and pharmaceuticals the enantioselective toxicities of the chiral pollutant have not been searched in detail. Therefore, there is an urgent need to explore the enantioselectiveness of the chiral pollutants. Existing data in the literature on the hazardous effects of the chiral pollutants should be modified in terms of the enantioselective toxicities. The chiral isomers of the pollutants are metabolized differentially in the biological systems and accordingly the stereoselective metabolism of the chiral pollutants is a demanding field. The knowledge of the stereoselective metabolism and enantioselective toxicities of the chiral pollutants will be useful for the treatment of the diseases caused by the chiral pollutants. Briefly, the studies on the distribution and the toxicities of the enantiomers of the chiral pollutants are an urgent and essential need of today which should be explored in detail.

1. Toxic Substance Control Act, US EPA, III, 1984, **344-III**, 348.
2. Hutson, D. H. and Roberts, T. R., *Environmental Fate of Pesticides*, John Wiley & Sons, New York, 1990, vol. 7.
3. Ali, I. and Jain, C. K., *Curr. Sci.*, 1998, **75**, 1011.

4. Kelvin, L., in *Chiral Environmental Pollutants: Trace Analysis and Ecotoxicology*, Springer Verlag, Berlin, 2000, p. 3.
5. Hegstrom, R. and Kondepudi D. K., *Sci. Am.*, 1990, **262**, 108.
6. Kondepudi, D. and Durand, D. J., *Chirality*, 2001, **13**, 351.
7. Bailey, J., Chrysostomou, A., Hough, J. H., Gledhill, T. M., McCall, A., Clark, S., Menard, F. and Tamura, M., *Science*, 1998, **281**, 672.
8. Haüy, R. J., *Tableaux Comparatif des Resultats de la Crystallographie et de L'analyse Chimique Relativement a la Classification des Mineraux*, Paris, 1809, p. XVII.
9. Pasteur, L., *Comptes Rendues de l'Acad des Sci.*, 1848, **26**, 535.
10. Lewis, D. L., Garrison, A. W., Wommack, K. E., Whittemore, A., Steudler, P. and Melillo, J., *Nature*, 1999, **401**, 898.
11. Ariens, E. J., van Rensen, J. J. S. and Welling, W. (eds), *Stereoselectivity of Pesticides, Biological and Chemical Problems, Chemicals in Agriculture*, Elsevier, Amsterdam, 1988, vol. 1.
12. Buser, H. R., Muller, M. D. and Rappe, C., *Environ. Sci. Technol.*, 1992, **26**, 1533.
13. Püttman, M., Mannschreck, A., Oesch, F. and Robertson, L, *Biochem. Biopharmacol.*, 1989, **38**, 1345.
14. Rodman, L. E., Shedlofsky, S. I., Mannschreck, A., Püttman, M., Swim, A. T. and Robertson, L., *Biochem. Pharmacol.*, 1991, **41**, 915.
15. Möller, K., Hühnerfuss, H. and Wölfle, D., *Organohalogen. Compd.*, 1996, **29**, 357.
16. Miyazaki, A., Hotta, T., Marumo, S. and Sakai, M., *J. Agric. Food Chem.*, 1978, **26**, 975.
17. Miyazaki, A., Sakai, M. and Marumo, S., *ibid*, 1979, **27**, 1403.
18. Miyazaki, A., Sakai, M. and Marumo, S., *ibid*, 1979, **27**, 1310.
19. McBlain, W. A., *Life Sci.*, 1987, **40**, 215.
20. Hoekstra, P. F., Burnison, B. K., Nehel, T. and Muir, D. C., *Toxicol. Lett.*, 2001, **125**, 75.
21. Rodriguez, O. P., Muth, G. W., Berkman, C. E., Kim, K. and Thompson, C. M., *Bull. Environ. Contam. Toxicol.*, 1997, **58**, 171.
22. Miyazaki, A., Nakamura, T. and Marumo, S., *Pestic. Biol. Chem. Physiol.*, 1989, **33**, 11.
23. Wood, A. W. *et al.*, *Cancer Res.*, 1982, **42**, 2972.
24. Wislocki, P. G., Buening, M. K., Levin, W., Lehr, R. E., Thakker, D. R., Jerina, D. M. and Conney, A. H., *J. Natl. Cancer Inst.*, 1979, **63**, 201.
25. Weigel, S., Master Thesis (Diplomarbeit), University of Humburg, 1998, p. 86.
26. Buser, H. R., Poiger, T. and Müller, M. D., *Environ. Sci. Technol.*, 1999, **33**, 2529.
27. Kümmerer, K., *Chemosphere*, 2001, **45**, 957.
28. Vetter, W., Bartha, R., Stern, G. and Tomy, G., *Organohalogen Compds.*, 1998, **35**, 343.
29. Vetter, W., Bartha, R., Stern, G. and Tomy, G., *Environ. Toxicol. Chem.*, 1999, **18**, 2775.
30. Rappe, C., Haglund, P., Buser, H. R. and Müller, M. D., *Organohalogen Compds.*, 1997, **31**, 233.
31. Benicka, E., Novakovski, R., Hrouzek, J. and Krupcik, J., *J. High Resolut. Chromatogr.*, 1996, **19**, 95.
32. Wong, C. S., Garrisson, A. W. and Foreman, W. T., *Environ. Sci. Technol.*, 2001, **35**, 33.
33. Biselli, S., Dittmer, H., Gatermann, R., Kallenborn, R., König, W. A. and Hühnerfuss, H., *Organohalogen Compds.*, 1999, **40**, 599.
34. Moisey, J., Fisk, A. T., Hobson, K. A. and Norstrom, R. J., *Environ. Sci. Technol.*, 2001, **35**, 1920.
35. Aigner, E., Leone, A. and Falconer, R., *Environ. Sci. Technol.*, 1998, **32**, 1162.
36. Wiberg, K., Harner, T., Wideman, J. L. and Bidleman, T. F., *Chemosphere*, 2001, **45**, 843.
37. White, J. C., Mattina, M. J. I., Eitzer, B. D. and Berger, W. I., *ibid*, 2002, **47**, 639.
38. Bidleman, T. F. *et al.*, *Environ. Sci. Technol.*, 1998, **32**, 1546.
39. Ridal, J. J., Bidleman, T. F., Kerman, B. R., Fox, M. E. and Strachan, W. M. J., *ibid*, 1997, **31**, 1940.
40. Ulrich, E. M. and Hites, R. A., *ibid*, 1998, **32**, 1870.
41. Wiberg, K. *et al.*, *Organohalogen Compds.*, 1997, **33**, 209.
42. Buser, H. R. and Müller, M. D., *Environ. Sci. Technol.*, 1993, **27**, 1211.
43. König, W. A., Icheln, D., Runge, T., Pfaffenberger, B., Ludwig, P. and Hühnerfuss, H., *J. High Resolut. Chromatogr.*, 1991, **14**, 530.
44. Möller, K., Bretzke, C., Hühnerfuss, H., Kallenborn, R., Kinkel, J. N., Kopf, J. and Rimkus, G., *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 882.
45. Müller, M. D., Schlabach, M. and Oehme, M., *Environ. Sci. Technol.*, 1992, **26**, 566.
46. Wiberg, K., Letcher, R., Sandau, C., Norstrom, R., Tysklind, M. and Bidleman, T., *Organohalogen Compds.*, 1998, **35**, 371.
47. Wong, C. S., Garrisson, A. W., Smith, P. D. and Foreman, W. T., *Environ. Sci. Technol.*, 2001, **35**, 2448.
48. Fisk, A. T., Moisey, J., Hobson, K. A., Karnovsky, N. J. and Norstrom, R. J., *Environ. Pollut.*, 2001, **113**, 225.
49. Möller, K., Hühnerfuss, H. and Rimkus, G., *J. High Resolut. Chromatogr.*, 1993, **16**, 672.
50. Pfaffenberger, B., Hardt, I., Hühnerfuss, H., König, W. A., Rimkus, G., Glausch, A. and Schurig, V., *Chemosphere,* 1994, **29**, 1543.
51. Alder, L., Palavinkas, R. and Andrews, P., *Organohalogen Compds.*, 1996, **28**, 410.
52. Aboul-Eneni, H. Y. and Ali, I., *Chiral Separations by Liquid Chromatography, Theory and Applications*, Marcel Dekker, Inc., New York, 2003.
53. Vetter, W. and Schurig, V., *J. Chromatogr.*, 1997, **774**, 143.
54. Ali, I. and Aboul-Enein, H. Y., *Environ. Toxicol.*, 2002, **17**, 329.
55. Altria, K. D., *J. Chromatogr.*, 1999, **856**, 443.
56. Hühnerfuss, H., Faller, J., König, W. A. and Ludwig, P., *Mar. Chem.*, 1992, **26**, 2127.
57. Hühnerfuss, H. and Kallenborn, R., *J. Chromatogr.*, 1992, **580**, 191.
58. Mössner, S., Spraker, T. R., Becker, P. R. and Ballschmiter, K., *Chemosphere*, 1992, **24**, 1171.
59. Kallenborn, R., Hühnerfuss, H. and König, W. A., *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 320.
60. Hühnerfuss, H., Pfaffenberger, B. and Rimkus, G., *Organohalogen Compds.*, 1996, **29**, 88.
61. Ludwig, P., Hühnerfuss, H., König, W. A. and Gunkel, W., *Mar. Chem.*, 1992, **38**, 13.
62. Jantunen, L. M. and Bidleman, T. F., *Arch. Environ. Contam. Toxicol.*, 1998, **35**, 218.
63. Falconer, R. L. *et al.*, *Organohalogen Compds.*, 1998, **35**, 331.
64. Mattina, M. J. I., White, J., Eitzer, B. and Berger, W. I., *Environ. Toxicol. Chem.*, 2002, **21**, 281.

Received 14 June 2002; revised accepted 21 October 2002