Identification and environmental significance of organic pollutants and heavy metal contaminants found in industrial wastewaters and soil collected from the vicinity of ATANOR and CLARIANT Chemical Companies, Lomas de Zamora, Argentina 1997-1998

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Summary

Two samples of effluent were collected from a pipe discharging to the Arroyo del Rey associated either with Atanor S.A. singly or jointly shared by Atanor and Clariant Chemicals. A single sample of soil was also collected from the point at which the effluent was discharged to the river. Analysis showed that the effluent contained fairly high levels of zinc and, more significantly, a wide range of organochlorine contaminants. The latter included a number of pesticides or pesticide precursors/intermediates, including isomers of HCH and DDT, 2,4-dichlorophenol, pentachloropropene and chlorinated benzenes. 2,4-Dichlorophenol is a known precursor in the manufacture of the herbicide 2,4-D, which is listed as being manufactured by Atanor. Clearly the Atanor/Clariant complex is acting as a significant source of these and other toxic and persistent chemicals to the river and the wider environment.

Introduction

Atanor S.A. and Clariant Chemicals are situated on the Arroyo del Rey in the district of Lomas de Zamora. Atanor S.A. produces a wide range of chemicals. According to the Guia de la Indusria Quimica y Petroquimica (1996), these include a number of pesticide intermediates and active ingredients such as 2,4-D, 2,4-DB, diuron, endosulphan, MCPA, urea, and trifluralin. In addition the company are listed as producing a wide range of phthalate esters. Although we do not know which of the Atanor plants in Argentina produce these organochlorine pesticides, we do know that this particular plant produces phthalate esters.

The Clariant Company manufactures pigments and colourants. Little further information is available.

Two samples of effluent were collected from a pipe arising on the sites of these chemical companies and discharging into the Arroyo del Rey. The pipe is known to discharge from the Atanor S.A. chemical plant. However it may also carry waste from the nearby Clariant plant. Sample AG7013 was collected from this pipe in November 1997, during the morning. Sample AG8004 was collected in March 1998, at night. In addition to these effluent samples, one sample of soil, AG7012, was also collected from directly beneath the pipe at the point of discharge, at the same time as sample AG7013.

Materials and Methods

1. Organic Screen Analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and cleaning up procedures was cleaned in detergent, rinsed with tap water and deionised water, dried in the oven overnight at 105^{0}C, and rinsed three times with low

haloform pentane.

Solid Samples

For each sample, approximately 30 g (wet weight) was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15 ml of pentane was added, followed by 5 ml of acetone. All samples were then sonicated for 2 hours.

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. They were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 20 ml pentane was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3 ml. The concentrated extract was cleaned through Florisil column, eluted with a 95:5 mixture of pentane:toluene, and evaporated down to a volume 2 ml under a stream of clean nitrogen. 1-bromonaphthalene was then added as a marker.

Aqueous Samples

Prior to the extraction, samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 150 ug/l. 20 ml of pentane was added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through a hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20 ml pentane was added and the extraction procedure repeated. The same clean up procedure, as described above, was employed.

Chromatographic Analysis

Samples were analysed using a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP Chem-Station data system, and linked to a HP 5972 Mass Selective Detector operated in scan mode. The identification of compounds was carried out by computer matching against a HP Wiley 275 library of 270,000 mass spectra combined with expert interpretation.

Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater are assumed to give reliable identifications; tentative identification refers to qualities between 51% and 90%. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

2. Heavy Metal Analysis

Solid Samples

Samples were dried in an oven until dry weight readings became constant (48 hours). They were then crushed using a pestle and mortar until homogenous and sieved through a 2 mm mesh. 0.5 g of sample was weighed into a 120 ml Teflon microwave vessel fitted with a screw cap and pressure relief valve. To this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The vessels were then sealed, placed on a rotating table in a microwave oven (model MDS-2000, CEM Corp.), and allowed to digest for one hour at full power (630 W).

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A Standard Reference Material, PACS-1 (trace elements in marine soil), certified by the National Research Council, Canada, and a blank sample, were prepared with each batch of 10 samples. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

Aqueous Samples

Water samples were preserved in 5% v/v nitric acid on arrival. 50 ml was transferred to a 120 ml Teflon microwave vessel and digested using the same procedure and programming conditions described above. After cooling to ambient temperature, samples were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A quality control standard (internally prepared at a concentration of 8.0 mg/l) and a blank sample were prepared with each batch of ten samples. Both were prepared in 5% v/v nitric acid.

ICP-AES Analysis

Following preparation, all samples were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese (Mn), chromium (Cr), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co) and cadmium (Cd). A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l (matrix matched to the samples). The calibration was validated using a quality control standard, prepared from different reagent stocks, at 8 mg/l. Samples exceeding the calibration range were diluted appropriately, in duplicate, and re-analysed. The spectrometer was re-calibrated after twenty samples to adjust for fluctuations in sensitivity. All other instrument and laboratory quality control procedures were adhered to.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (ii) was reduced to Hg (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 ug/l and 100 ug/l (matrix matched to the samples). Samples exceeding this range were diluted and re-analysed. The quality control standard was again prepared from a different reagent stock at 80% of the calibration range (i.e. 80 ug/l). The spectrometer was re-calibrated after every 10 samples.

Results

Groups of compounds identified to better than 90%	Number of samples	Sample codes
ORGANOHALOGEN COMPOUNDS		
Hexachlorocyclohexanes	2	AG7013, AG8004
DDT / DDD	1	AG8004
Trichlorobenzenes	1	AG8004
Dichlorobenzenes	2	AG7012, AG7013,
Dichlorophenols	1	AG8004
Chlorinated alkenes	1	AG7013
POLYCYCLIC AROMATIC HYDROCARBONS		
Naphthalene and derivatives	1	AG7013
OTHER AROMATICS		
Benzene derivatives (not already listed)	2	AG7012, AG7013
Biphenyl and alkyl derivatives	2	AG7013, AG8004
ALIPHATIC HYDROCARBONS	1	AG7012

Table 1 Groups of organic compounds reliably identified, ATANOR/CLARIANT, Argentina 1997-98

Sample Number	Compounds Isolated	Reliably Identified	Halogenated Compounds	PAHs	Other Aromatics	Aliphatics
AG7012	23	5 (22%)	1	0	2	2
AG7013	23	9 (39%)	5	1	3	0
AG8004	47	7 (15%)	6	0	1	0

Table 2 Results of organic screening analysis, ATANOR/CLARIANT, Argentina 1997-98

Sample Number	Mn (ppm)	Cr (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Ni (ppm)	Co (ppm)	Cd (ppm)	Hg (ppm)
AG7012	319	27	76	26	16	12	7	n/d	0.2
AG7013	0.19	<0.01	1.07	0.04	<0.03	<0.01	<0.01	<0.01	<0.002
AG8004	0.03	<0.01	0.28	<0.01	<0.03	<0.01	<0.01	<0.01	0.003

Table 3 Results of heavy metals analysis, ATANOR/CLARIANT, Argentina 1997-98

Discussion

Heavy metals analysis of sample AG7012 revealed detectable levels of Mn, Cr, Zn, Cu, Pb, Ni, Co, and Hg. However, none of these were present at levels which could be considered elevated above background (Salomons and Forstner 1984). Analysis of the effluent samples revealed detectable levels of Mn, Zn, Cu and Hg. Of these, Zn was present at significant concentrations (1.07 mg/l).

Zinc

Zn is most often employed in electroplating, smelting and ore processing, however it is also present in acidic mine drainage, and effluents from the chemical industry (organic synthesis, textiles, pigment and paint, fertiliser, and PVC production). Compounds of Zn can also be used as fungicides and herbicides, e.g. simple inorganic compounds such as zinc chloride, zinc sulphate and zinc phosphide, as well as more complex organic compounds such as the Zn containing fungicides Metirem, Mancozeb, Zineb and Ziram (Agrochemicals Handbook 1987, USPHS 1997).

Although Zn is not regarded as being especially toxic, it is sometimes released into the environment in appreciable quantities, and can thus have deleterious effects on certain

species at specific concentrations. For example, effects on fertilisation and embryonic development have been observed in species of fish and harpacticoid copepods (Ojaveer et al. 1980, Verriopoulos and Hardouvelis 1988).

Most of the studies relating to the human health effects of Zn concentrate on exposure via inhalation (which can cause a specific short-term disease called metal fume fever). Less is known about the long term effects of ingesting excess zinc, through food, water or dietary supplements but, although it is an essential trace element, it is recognised that ingestion of higher than recommended levels could have adverse effects on health. The recommended Dietary Allowances for Zn are 15 mg/day for men and 12 mg/day for women. If doses 10 –15 times higher than these recommendations are taken by mouth, even for a short time, stomach cramps, nausea and vomiting may occur (USPHS 1997). Ingesting high levels for several months may cause anaemia, damage to the pancreas, and decreased levels of high-density lipoprotein (HDL) cholesterol (USPHS 1997).

Clearly the two most direct potential routes of exposure to humans following discharge of zinc to the river would be consumption of the water or of fish or other food derived from the river. It is not, however, possible to estimate the magnitude of the hazard which may be presented by the discharge in question in this study.

Organic screening analysis of the two effluent samples revealed the presence of a large number of organochlorine compounds. Both samples contained isomers of hexachlorocyclohexane (HCH), and chlorinated benzenes. Sample AG8004 also contained DDT, its metabolite DDD and 2,4-dichlorophenol, with pentachloropropene reliably identified in sample AG7013. In addition, 1,1-biphenyl was reliably identified in both samples. Soil sample AG7012 contained 1,2-dichlorobenzene.

Hexachlorocyclohexane (HCH)

HCH was reliably identified in both samples of effluent, with the alpha, beta and gamma (lindane) isomers being the most likely chemical forms present. HCH is a synthetic chemical that can exist in eight chemical forms (called isomers), and whereas gamma-HCH (lindane) is the isomer most commonly used as an insecticide, technical grade HCH mixtures, containing alpha, beta, gamma, delta and epsilon isomers, are also manufactured, and utilised in the same way (USPHS 1997). Also, in addition to the specific uses of HCH, and therefore specific sources of HCH in the environment, HCH isomers also occur as unwanted by-products of other manufacturing processes. Most commonly the production of other chlorinated pesticides and chlorinated solvents (USPHS 1997).

The commercial applications of HCH rely on its toxicity to pest organisms. However, HCH isomers are also toxic to a wide range of other, non-target organisms, including humans. The toxicity of the isomers varies, and with respect to acute toxicity, gamma-HCH is the most toxic, followed by alpha, delta, and beta-HCH. In relation to chronic exposure, however, beta-HCH is the most toxic followed by alpha, gamma and delta-HCH. With chronic exposures, the increased toxicity of beta-HCH is probably due to its longer half-life in the body, and its accumulation in the body with time (USPHS 1997).

Acute toxic effects may include the death of animals, birds or fish, and death or reduced growth in plants (Bunton 1996, Smith 1991). Chronic toxic effects may include shortened life-span, reproductive problems, lower fertility, and changes in behaviour. Thus any HCH introduced to the environment from industrial discharges, insecticide applications or spills, has the potential to cause significant damage.

This damage can be more non-direct and therefore more widespread that initially obvious, due the bioaccumulation potential of these compounds, which has been widely reported (e.g. Strachan et al. 1994, Smith 1991, Junqueira et al. 1994, Larsen et al. 1994, Schlaud et al 1995, Schoula et al. 1996). In humans for example, gamma-HCH concentrates in adipose (fatty) tissues. Women chronically exposed, or living in areas of intense usage, have been found to accumulate residues of different organochlorines, including alpha, beta and gamma-HCH, in their breast milk (Larsen et al. 1994, Schlaud et al. 1995, Schoula et al. 1996, USPHS 1997).

Health effects associated with exposure can be summarised as follows (USPHS 1997):

In humans, blood disorders, dizziness, headaches, and changes in sex hormone levels, can all result following exposure to alpha, beta and gamma HCH vapours. Humans exposed to HCH isomers via ingestion have suffered seizures and have, in some cases, died. Similar effects have been observed in animals, with animals exposed to alpha and gamma HCH, suffering seizures; and animals exposed to beta HCH becoming comatose. In addition, exposed animals have developed liver and kidney problems, with long-term exposure to alpha, beta, gamma, or technical grade HCH reported to result in liver cancer. Reduced immunity i.e. reduced ability to fight infections, and reproductive effects such as injury to the ovaries and testes, have also been observed.

The International Agency for Research on Cancer (IARC) has classified HCH as a possible human carcinogen, with the US Department of Health and Human Services determining that HCH may reasonably be anticipated to be a carcinogen.

Dichlorodiphenyltrichloroethane (DDT) and Dichlorodiphenyldichloroethane (DDD)

DDT, and two isomers of its metabolite DDD, were identified with high match qualities in sample AG8004. DDT has been a widely used chemical to control insects on agricultural crops and insects that carry diseases such as malaria and typhus. DDD, one of the breakdown products of DDT, has also been employed as a pesticide (USPHS 1997). Use of both DDT and DDD is now banned in most of the world, except in cases of public health emergency. However use in a number of South American, African and Asian countries continues.

Both DDT and DDD are synthetically produced chemicals and are not known to occur naturally in the environment (WHO 1979). Therefore its presence is sample AG8004 is of concern. As their commercial applications and heavily restricted use suggest, DDT and DDD are extremely toxic, even at very low concentrations. They are also highly persistent and bioaccumulative. Studies on the toxicity of DDT and its primary metabolites are numerous, and major findings and conclusions of past and present research can be summarised as follows:

DDT is highly toxic to many aquatic invertebrates e.g. stoneflies, crayfish, daphnids and sea shrimp (USPHS 1997, WHO 1979), with early developmental stages being more susceptible to the toxic effects of DDT than adults (WHO 1979). It is also highly toxic to fish, with reported 96-hour LC50s less than 10 ug/l in some species of salmon, rainbow trout, pike, bullhead, sunfish and bass. Again developmental stages are more susceptible, and it has been reported that DDT levels of 1 ng/l in Lake Michigan, were sufficient to affect the hatching of coho salmon eggs (Matsumura et al. 1985).

It is known that DDT and DDD can bioaccumulate significantly in fish and other aquatic species, often at very low environmental concentrations. Thus leading to problems of long-

term (chronic), and potentially more in-direct and widespread contamination. If terrestrial organisms, including humans, consume contaminated food and / drinking water, deleterious health effects can result.

Eating food containing large amounts of DDT and its metabolites over a short period of time, will most notably effect the central nervous system. People who have accidentally swallowed large amounts of DDT became excitable and suffered from tremors and seizures. Humans exposed to DDT in smaller doses over a longer period of time have developed liver problems. Animal studies have confirmed the effects of DDT on the liver, with oral exposures particularly, linked to liver cancer. In addition, more recent research has implicated DDT and DDD as chemicals capable of interfering with the endocrine (hormone) system in animals (e.g. Colborn et al. 1993, Guillette et al. 1994) even at low body burden concentrations.

The Department of Health and Human Services has determined that DDT may reasonably be anticipated to be a human carcinogen. The International Agency for Research on Cancer (IARC) has determined that DDT, DDE and DDD are possibly carcinogenic in humans, and the EPA has determined that DDT, DDE and DDD are probable human carcinogens (USPHS 1997).

On account of its acute and chronic toxicity, and its persistence in the environment, HCB is one of the twelve priority POPs (persistent organic pollutants), intended for global action by the UN Environment Programme (UNEP) Governing Council. It is intended that DDT and its metabolites will be phased out worldwide under a convention currently being drawn up (UNEP 1995, 1997).

2,4-Dichlorophenol (2,4-DCP)

2,4-DCP was reliably identified in sample AG8004. It is widely used in the manufacture of a number of industrial and agricultural products such as pesticides, germicides, soil sterilants, seed disinfectants and antiseptics. It is also a key intermediate in the synthesis of the herbicide (2,4-dichlorophenoxy) acetic acid (2,4-D) (Merck 1989). 2,4-D and the related compound 4-(2,4-dichlorophenoxy) butanoic acid (2,4-DB) are both produced commercially by Atanor S.A. (Guia de la Industria Quimica y Petroquimica 1996).

Industrial wastes containing phenolic compounds are highly toxic and pose a direct threat to human (Veningerova et al. 1994) and aquatic life. They are compounds with a wide spectrum of toxic effects including teratogenic (Zhao et al. 1995) and carcinogenic actions (Nagyova & Ginter 1995, Mehmood et al. 1997). They are also relatively persistent in the environment (Narasimhan et al. 1992, Zhao et al. 1995).

2,4-Dichlorophenol is rapidly absorbed through the skin, either as a pure chemical or dissolved in water, where it can then enter the blood stream (USPHS 1991). Although a single dose may have a relatively short biological half-life in humans (2-3 days), long term or repeated exposure to significant doses may lead to permanent damage to the skin, eyes, liver and kidney. In addition, this compound is a suspected animal carcinogen, and a probable or possible human carcinogen (USPHS 1991).

Chlorinated Benzenes

1,2-Dichlorobenzene (o-DCB) was reliably identified in samples AG7012 (soil) and AG7013 (effluent). It is most commonly used as a solvent for waxes, tars, oils and resins; and as an insecticide to combat termites and locusts. It can also be used as a fumigant, a degreasing

agent and as a chemical intermediate in organic synthesis (Merck 1989).

Dichlorobenzenes are potent liver and, to a lesser extent, kidney toxins (Valentovic et al. 1993). Exposure to higher concentrations can result in central nervous system (CNS) depression. The toxicity of DCBs depends on their precise isomeric forms, with 1,2-dichlorobenzene (o-DCB) generally reported as more toxic in laboratory studies than the 1,3- (m-DCB) and 1,4- (p-DCB) substituted isomers. According to the U.S. EPA, o-DCB is toxic to animals, birds and fish, and can cause death or induce a low growth rate in plants (1988). Along with other isomers of dichlorobenzene, o-DCB is persistent in the environment, and has the potential to bioaccumulate (IUCLID 1996).

1,3,5-Trichlorobenzene was reliably identified in sample AG8004. Little specific toxicity data or information on production and use is available, however trichlorobenzenes are expected to induce similar toxic effects in aquatic and terrestrial organisms to those seen in organisms exposed to dichlorobenzenes. As with dichlorobenzenes, they tend to persist in the environment, and have a high tendency to bioaccumulate (IUCLID 1996). A commercial grade mixture of trichlorobenzenes, which would contain 1,3,5-trichlorobenzene, is used to combat termites, and has been found to cause irritation to eyes and mucous membranes (Merck 1989).

1,1,2,3,3-Pentachloro-1-propene

In addition to these organochlorine compounds, 1,1,2,3,3-pentachloro-1-propene was reliably identified in sample AG7013. Little specific toxicity data or information on production and use is available. Nevertheless, this compound has been detected in many effluents associated with industrial chlorination processes (Rosenberg et al. 1991).

1,1-Biphenyl

Relatively little is also known about the chronic toxicity of 1,1-biphenyl, although animal studies have linked exposure with increased respiratory rate, loss of appetite and weight, and muscular weakness. Workers involved in impregnating paper with biphenyl (it has been used as a pesticide) complained of headaches, diffuse pain, nausea and numbness and aching in the limbs (Edwards et al. 1991).

References

Agrochemicals Handbook Second Edition (1987). The Royal Society of Chemistry, UK. ISBN 0-85186-416-3

Bunton T.E. (1996). Experimental chemical carcinogenesis in fish. Toxicological Pathology, Vol.24 (5): 603-618

Colborn, T., vom Saal, F.S. and Soto, A.M. (1993). Developmental effects of endocrine-disrupting chemicals in wildlife and humans. Environmental Health Perspectives 101(5): 378-384

Edwards, I.R., Ferry, D.H., and Temple, W.A. (1991). Fungicides and related compounds. In: Handbook of pesticide toxicology. Volume 3. Classes of pesticides. [Eds] Hayes, W.J. and Laws, E.R. Academic Press Inc. 1409-1470

Guia de la Industria Quimica y Petroquimica, Argentina.8th Edition 1996

Guillette, L.J., Gross, T. S., Masson, G.R., Matter, J.M., Percival, H.F. and Woodward, A.W. (1994). Developmental abnormalities of the gonad and abnormal sex hormone concentrations in juvenile alligators from contaminated and control lakes in Florida. Environmental Health Perspectives 102(8): 680-688

IUCLID (1996). European Commission Database on Existing Chemicals (CD-ROM)

Junqueira V.B.C., Bainy A.C.D., Arisi A.C.M., Azzalis L.A., Simizu K., Pimentel R., Barros S.B.M., Videla L.A. (1994). Acute lindane intoxication - a study on lindane tissue concentration and oxidative stress-related parameters in liver and erythrocytes. Journal of biochemical Toxicology, Vol.9(1): 9-15

Larsen B.R., Turrio-Baldassari L., Nilsson T., Iacovella N., di Domenico A., Montagna M., Facchetti (1994). Toxic PCB congeners and organochlorine pesticides in Italian milk. Ecotoxicology and Environmental Safety 28: 1-13.

Matsumura, F. (1985). Toxicology of insecticides. New York, NY: Plenum Press

Mehmood, Z., Kelly, D.E., and Kelly, S.L. (1997). Cytochrome P450-3A4 mediated metabolism of 2,4-dichlorophenol. Chemosphere Vol. 34 (11): 2281-2291

Merck (1989) The Merck index: an encyclopaedia of chemicals, drugs and biologicals. 11th Edn.Budavari, S.M.J. O'Neil, A.Smith and P.E.Heckleman [Eds]. Merck and Co, Inc., New Jersey, USA

Nagyova, A. and Ginter, E. (1995). The influence of ascorbic acid on the hepatic cytochrome-p-450, and glutathione in guinea pigs exposed to 2,4-dichlorophenol. Physiological Research 44(5): 301-305

Narasimhan, T.R., Mayura, K., Clement, B.A., Safe, S.H. and Phillips, T.D. (1992). Effects of chlorinated phenols on rat embryonic and hepatic mitochondrial oxidative-phosphorylation. Environmental Toxicology and Chemistry 11(6): 805-814

Ojaveer, E., Annist, J., Jankowski, H., Palm, T. and Raid, T. (1980). Effects of copper, cadmium and zinc on the embryonic development of Baltic spring spawning herring. Marine Research 247, 135-140

Rosenberg C., Aalto T., Tornaeus J., Hesso A., Jappinen P., Vainio H. (1991). Identification by capillary gas-chromatography mass-spectrometry of volatile organohalogen compounds formed during bleaching of kraft pulp. Journal of Chromatography, Vol.552(1-2): 265-272

Salomons, W. and Forstner, U. (1984). Metals in the Hydrocycle. ISBN 3-540-12755-0, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo

Schlaud M., Seidler A., Salje A., Behrendt W., Achwartz F.W., Ende M., Knoll A., Grunel C., (1995). Organochlorine residues in human breast milk: analysis through a sentinel practice network. J. Epidemiol. Community Health, Vol. 49 (Suppl.1): 17-21

Schoula R., Hajslova J., Benko V., Holadova K., Vizek V. (1996). Occurrence of persistent contaminants in human milk collected in several regions of Czech republic. Chemosphere, Vol.33(8): 1485-1494

Smith A.G. (1991). Chlorinated Hydrocarbon Insecticides. In: Handbook of pesticide toxicology. Volume 2. Classes of pesticides. [Eds] Hayes W.J. and Laws E.R. Academic Press, Inc.: 731-860

Strachan W.M.J., Eriksson G., Kylin H., Jensen S. (1994).Organochlorine compounds in pine needles - methods and trends. Environmental toxicology and chemistry, Vol.13(3): 443-451

UNEP (1995) Decision 18/32 of the UNEP Governing Council: Persistent Organic Pollutants. UNEP Governing Council, 25th May 1995

UNEP (1997) Decisions adopted by the Governing Council at its nineteenth session: 13c. International action to protect human health and the environment through measures which will reduce and/or eliminate emissions and discharges of persistent organic pollutants, including the development of an international legally binding instrument. UNEP Governing Council, 7th February 1997

US Environmental Protection Agency (1988). Factsheets for regulated chemicals: 1,2-dichlorobenzene. Office of Environmental Health Hazard Assessment

USPHS (1991). Toxicological Profile for 2,4-Dichlorophenol. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service

USPHS (1997). Toxicological Profile for alpha, beta, gamma and delta Hexachlorocyclohexane. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

USPHS (1997). Toxicological Profile for DDT, DDE and DDD. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

USPHS (1997). Toxicological Profile for Zinc. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

Valentovic, M.A., Ball, J.G., Anestis, D. and Madan (1993). Acute hepatic and renal toxicity of dichlorobenzene isomers in Fischer-344 rats. Journal of Applied Toxicology 13(1): 1-7

Veningerova, M., Prachar, J., Uhnak, M., Lukacsova, M. and Trnovec, T. (1994). Determination of chlorinated phenols and cresols in human urine using solid-phase extraction and gas chromatography. Journal of Chromatography B-Biomedical Applications 657(1): 103-110

Verriopoulos, G. and Hardouvelis, D. (1988). Effects of sub-lethal concentrations of zinc on survival and fertility in four successive generations of Tisbe. Marine Pollution Bulletin 19, 162-166

World Health Organisation (1979). Environmental Health Criteria 9. DDT and its Derivatives. ISBN 92-4-154069-9

Zhao, F., Mayura K., Hutchinson, R.W., Lewis, R.P, Burghardt R.C., and Phillips, T.D. (1995). Developmental toxicity and structureactivity-relationships of chlorophenols using human embryonic palatal mesenchymal cells. Toxicology Letters 78 (1): 35-42