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ORGANOHALOGEN COMPOUNDS IN THE MARINE ENVIRONMENT:

A REVIEW

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INTRODUCTION

The Mediterranean States meeting in Barcelona in 1975 adopted an Action Plan for the Protection of the Mediterranean Sea against pollution. The legal framework for this co-operative regional programme is the Convention for the Protection of the Mediterranean Sea against pollution (also known as Barcelona Convention) and its related protocols which has been ratified by 18 Mediterranean States and the European Economic Community. So far, four protocols have been adopted and entered into force, one of them being the Protocol for the Protection of the Mediterranean Sea against pollution from Land-based Sources (LBS protocol).

The MEDPOL programme is the scientific/technical component of the Mediterranean Action Plan and is concerned with assessing and evaluating environmental problems. The environmental assessment undertaken, provides a basis for assisting national policy makers to manage their natural resources in a more effective and sustainable manner.

The specific objectives of the MEDPOL programme are designed to provide the Contracting Parties to the Barcelona Convention, inter alia, with:

- information required for the implementation of the Convention and protocols;
- indicators and evaluation of the effectiveness of the pollution prevention measures taken under the Convention and the protocols;
- scientific information which may lead to eventual revisions and amendments of the relevant provisions of the Convention and the protocols and for the formulation of additional protocols;
- information which could be used in formulating environmentally sound national, bilateral and multilateral management decisions essential for the continuous socio-economic development of the Mediterranean region on a sustainable basis.

One of the basic components of the MEDPOL programme is the implementation of the LBS protocol according to which Contracting Parties undertake to eliminate pollution from land-based sources by the substances listed in Annex I to the Protocol. Assessment documents have already been prepared and recommendations adopted for mercury and mercury compounds, cadmium and cadmium compounds, used lubricating oils, organohalogen compounds, organotin compounds, organophosphorus compounds, radioactive substances, persistent synthetic materials which may float, sink or remain in suspension, and organophosphorus compounds.

Organohalogen compounds are included within the substances listed in Annex I and for this reason an expert meeting was convened at IAEA-MEL in Monaco (24 to 28 October 1988) to compile information relating to the distribution, possible impacts and analytical protocols necessary to evaluate contamination from the many diverse compounds included within this group and especially those not routinely considered within monitoring programmes. This volume in the MAP Technical Reports Series is the report of the above mentioned meeting and presents a review on organohalogen compounds in the marine environment.

The present report was edited by James Readman and Sabine Lutz of the Marine Environmental Studies Laboratory of IAEA-MEL, Monaco on the basis of the documents drawn up during the meeting.

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BACKGROUND

A primary aim of the Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MEDPOL) is to provide information on the quality of the Mediterranean environment. This data can then be used to advise on legal measures for the protection and development of marine and coastal environments in the Mediterranean Region.

Organohalogen compounds, and substances which may form such compounds in the marine environment (with the exception of those which are biologically harmless or which are rapidly converted into biologically harmless substances) are identified within the protocols of the Barcelona Convention as pollutants of environmental concern.

During the last decade, substantial information has been compiled on organohalogen compounds (UNEP/FAO/WHO/IAEA, 1990). Attention has been focussed on a suite of compounds which include pp'DDT, opDDT, pp'DDE, pp'DDD, aldrin, dieldrin, endrin, hexachlorobenzene, heptachlor, heptachlor epoxide, HCH isomers and PCBs. These represent only a small proportion of the total organohalogens in the environment, and it was the purpose of this workshop to discuss and evaluate the possible environmental significance of organohalogens not usually measured as part of the "routine protocols". In addition, analytical chemistry guidelines for the identification and determination of organohalogen contaminants other than "PCBs and DDTs" were discussed and are presented.

Organohalogen priority pollutants defined by other Agencies

Several lists of dangerous substances, also termed "chemical priority pollutants" have been drawn up by different National and International bodies, such as the EPA (United States), the EEC (Europe) and the World Health Organization (WHO).

The EPA list was established using several criteria such as toxicity, persistence, bioaccumulation capacity and actual identification in environmental samples (especially in urban and industrial effluents). 129 chemical substances were selected as priority chemical pollutants. In this list, there are 114 organic chemical compounds and 15 inorganic compounds. A classification of organic substances was proposed and relates to the analytical methods which can be used to detect them. They include: 31 volatile compounds which can be extracted by gas stripping, and mainly comprise halogenated C_1/C_2 compounds; 11 phenol compounds extracted from water at acid pH; 26 compounds extracted from water at neutral or basic pH which are analysed by GC/ECD (chlorinated insecticides and PCBs); and 46 other compounds extracted from water at neutral or basic pH, which are quantified using GC/FID (including polyaromatic hydrocarbons and phthalates).

The EEC list also selects 129 chemical substances. The aim is to eliminate these chemicals from effluents, especially from industrial effluents discharged into aquatic environments. In this list, there are 118 organic substances. In spite of the same number of substances selected by the EEC and EPA, comparison between the two lists is difficult because the EEC list includes names of "substances" which are mixtures of chemicals [eg. chloro-nitrotoluenes; DDT (which includes DDE and DDD); hexachlorocyclohexane, which includes all isomers; etc.].

WHO has established a list of 17 inorganic chemicals and 23 organic chemicals which are considered as dangerous to human health. Criteria used in their selection were toxicity and actual identification in drinking water and/or ground waters.

Organohalogens feature prominently in all three lists. Compounds specified include low molecular weight/volatile solvents and propellants, chlorinated aromatics, chloro-anilines, chloro-phenols, halogenated ethers, PCBs and pesticides. The wide range of listed compounds are further definied and discussed in Appendix 1.

1. ORGANOHALOGENATED COMPOUNDS OF ENVIRONMENTAL CONCERN; GROUPS AND SOURCES

"Organohalogens" are an extremely diverse group of compounds with respect to molecular structure and physical/chemical properties. Discussion of the compounds is simplified by dividing them into sub-groups. Many features can be used to delineate groups, for example, molecular structures, physical and chemical properties, sources, toxicological properties or their analytical chemistry. Choice of division can never satisfy discussion of all properties of the compounds and the divisions listed below represent only an attempt to categorize the compounds.

1. low molecular weight "volatile" compounds
2. chlorinated paraffins
3. halogenated mono-aromatic compounds
4. halogenated phenolic compounds
5. halogenated polyaromatic compounds
6. organohalogen pesticides
7. "other" halogenated compounds.

1.1. Low molecular weight "volatile" compounds

1.1.1 Tetrachloromethane (CCl_4) and trichloromethane ($CHCl_3$) are volatile organic solvents which are widely used. The annual production rate of trichloromethane has been estimated (on a global basis) as 250,000t (Class and Ballschmiter, 1986).

To this industrial production, an unintentional production of more than 10,000 t/a, originating from water chlorination processes, must also be considered. Natural sources of tetra- and trichlomethane have not as yet been quantified, but probably represent a minor role. Tetra-, and to a lesser extent, trichloromethane have been found in air samples in remote areas. Class and Ballschmiter (1986) recorded a concentration of 140 pptv for CCl_4 in air from remote Atlantic Ocean Stations, with no significant differences between the Northern and Southern hemispheres. Levels of trichloromethane in the same samples were 20-50 pptv and 10-20 pptv for the Northern and Southern hemispheres respectively.

1.1.2 Polyhalomethanes. The principal polyhalomethanes are:

CH_2Br_2; $CHBr_3$; $CHBrCl_2$ and $CHBr_2Cl$.

Bromo-methanes and bromo-chloro-methanes have both natural and anthropogenic origins. Present knowledge on natural sources indicate that various species of macro-algae can synthesize organobromine compounds (e.g. bromoform). Anthropogenic sources include the industrial production of flame retardants and the use of bromomethane as a fumigant. Other anthropogenic environmental inputs of bromo-chloro-methanes and bromoform originate from water chlorination, especially when seawater is chlorinated (as in anti-fouling treatments of the cooling water pipes of coastal power plants).

Polyhalomethanes have been found in remote areas of the Atlantic Ocean at levels of the order of 1 pptv in the air and of 1 ng/l in seawater and rainwater samples (Class et al., 1986).

1.1.3 1,2-dichloroethane, CH_2ClCH_2Cl (ethylene dichloride). This is one of the most important products for the chemical industry, being an intermediate for vinyl chloride (VC) synthesis. The annual world production of ethylene dichloride in 1981 was estimated to be 23,130 kilotonnes (Gold, 1980), 10% of which, it has been assumed, reaches the environment by losses

during production. It is also used as a petrol/gasoline additive. Ethylene dichloride is also produced during combustion processes (e.g. in engines and municipal solid waste incinerators). Levels of the compound in air at remote stations in the Atlantic Ocean were found to approximate 15-30 pptv in the Northern hemisphere and lower then 4 in the Southern hemisphere (Class and Ballschmiter, 1986), indicating the anthropogenic origin and also little resistance to degradation.

1.1.4 1,1,1-trichloroethane, CH_3CCl_3 (methyl-chloroform). This compound is largely used in industrial degreasing and in dry-cleaning. The annual global release was estimated to be approximately 600,000 t in 1980 (Class and Ballschmiter, 1986). Baseline levels of methyl-chloroform in air samples from remote regions of the Atlantic Ocean were 200 and 140 pptv for the Northern and Southern hemisphere, respectively (Class and Ballschmiter, 1986).

1.1.5 1,1,2-trichloroethene, $CHCl=CCl_2$ is mainly used as a solvent. The annual production is around 500,000 t (Pearson, 1982). It is rapidly degraded in the air and hence long range contamination problems do not occur. Contamination of ground water by improper waste dumping or from losses of urban used waters have been reported (Class and Ballschmiter, 1986).

1.1.6 Tetrachloroethene, $CCl_2=CCl_2$. More than 1,000,000 t/a are produced (Pearson, 1982). The environmental behaviour is similar to that of 1,1,2-trichloroethene, with a little higher resistance to degradation.

1.1.7 Hexachlorobutadiene, $CCl_2=CCl-CCl=CCl_2$.
Hexachlorobutadiene is a by-product in aliphatic compound synthesis. The annual environmental load is estimated to be around 10,000 t (Pearson, 1982). The baseline level of this compound in remote air samples has been indicated as 0.3 and 0.1 pptv for the Northern and the Southern hemispheres, respectively (Class and Ballschmiter, 1986).

1.2. Chlorinated Paraffins

Chlorinated-n-paraffins (CP) are currently produced industrially by chlorination of straight chain paraffin oils and waxes (C_{10}-C_{30} range). The degree of chlorination may vary from 40 to 70% and the final products are employed as fire retardants, plasticizers, varnishes, sealants and as extreme pressure additives in lubricants and metal cutting oils. Present world consumption of CP can be estimated at more than 300,000 t/a. (Campbell and McConnell, 1980). Of major environmental concern is probably the use of CP in oils, which accounts for about 20% of production (i.e. 60,000 t/a) (Campbell and McConnell, 1980). The improper disposal of these used oils represents an important source of CP to the environment.

1.3. Chlorobenzenes

Chlorobenzenes (CBs) are widely used for an extensive range of applications. For example, hexachlorobenzene (HCB) is applied as an organochlorine pesticide, whereas domestic usage of CBs includes their presence in perfume blocks for lavatories. Production of CBs in the USA in 1978 was about 200,000 t (EPA, 1980) and the present global production rate is probably in excess of 600,000 t/a. CBs have been found extensively in waste waters, rivers, lake waters and in fish from many locations around the world. CBs (and especially HCB) can be considered as ubiquitous environmental contaminants.

1.4. Halogenated phenolic compounds

1.4.1 Chlorophenols

Chlorophenols(CPs) include mono-, di-, tri-, tetra-, and penta-chlorinated phenols (CP, DCP, TCP, TTCP, PCP). Of the 19 possible isomers, eight have commercial utility:

mono- : 2-CP, 3-CP, 4-CP.
di : 2,4-DCP.
tri : 2,4,5-TCP, 2,4,6-TCP.
tetra : 2,3,4,6-TTCP.
penta : PCP.

CPs are broad spectrum pesticides, primarily used as preservatives in woods, paints, leathers and textiles, as anti-microbial agents in industrial cooling systems and in the manufacture of pulp and paper. They are also intermediates in the manufacture of herbicides.

Monochlorophenols are synthesised by chlorinating phenol. Their main use is as a chemical intermediate in the synthesis of the higher chlorophenols, phenolic resins, dyes, and drugs. Monochlorophenol production in Europe is about 4,500 t/a (Krijgsheld and van der Gen, 1986).

"Unintentional" sources of chlorophenols to the environment include their production during chlorination processes eg. of potable waters, of municipal sewage, and especially during bleaching in pulp mills and textile plants. Degradation of the phenoxy-herbicides (2,4-D and related compounds) also produces CPs (especially 2,4-dichlorophenol).

1.4.2 Pentachlorophenol (PCP). Of the CPs, PCP is of most environmental concern owing to its widespread use and high toxicity. PCP and its sodium salt were introduced in the 1930s as wood preservatives. The present annual production rate is probably in the order of 100,000 t. It is a widely used biocide with both agricultural and industrial applications. PCP occurs in effluents from pulp mills at the (µg/l) range (Leuenberger et al., 1985).

Technical PCP has been shown to contain trace amounts of polychlorodibenzo-p-dioxins (PCDDs) and polychloro-dibenzofurans (PCDFs) (Miles et al., 1985) (see Section 1.5).

1.5. Halogenated polyaromatic compounds

1.5.1 Polychlorinated biphenyls (PCBs). PCBs are widely used in electronic capacitors and transformers, in heat transfer systems, and as plasticizers. The world-wide production of PCBs, since their introduction in the late 1920's, was estimated in 1971 to be 1,000,000 t (Bacci and Gaggi, 1985). In the seventies, some governments of technically advanced countries regulated or banned the production and use of PCBs. However, production of these compounds continues in several countries. At present, the global load of PCBs probably exceeds 2,000,000 t.

1.5.2 Polychlorinated dibenzodioxins (PCDD,"dioxins") and Polychlorinated dibenzofurans (PCDF)

These compounds are produced as by-products during a variety of processes preparing industrial chemicals and also by thermal processes such as waste incineration. They can also be "liberated" from reservoirs such as hazardous waste dumps.

Production processes which inadvertently produce PCDD/PCDF include:

(a) Chlorophenol production, eg. 2,4,5-trichlorophenol manufactured until 1988 contained up to 3mg/g of PCDD and PCDF, mainly as hexa-, hepta- and octa-CDD, and including the highly toxic 2,3,7,8- substituted congeners;

(b) substituted benzenes production, eg hexachlorobenzene has been reported to contain octa-CDD;

(c) chloranol, an intermediate product for dyes, contains high concentrations (>1mg/g) of octa-CDD;

(d) production of inorganic chlorides (eg. $FeCl_3$ and $AlCl_3$) liberates PCDD and PCDF;

(e) processes involving chlorine containing catalysts;

(f) paper/pulp industry effluents (and some paper products) contain PCDD and PCDF; and finally:

(g) the production of high purity Ni, Co and Mg via the corresponding metal chlorides produces dioxins.

Incomplete incineration of waste chloro-aromatics and other organochlorines liberates PCDD and PCDF. For example, PCBs burned at temperatures up to 600-750 EC, chloro-benzenes burned at below 600-750 EC and chlorophenols at below 350 EC, all produce PCDD and PCDF (PCBs: Buser and Rappe, 1979; chlorobenzenes: Buser, 1979; chlorophenols: Rappe, 1978b). Incomplete incineration of non-chlorine containing organic compounds in the presence of a chlorine source (de novo synthesis) also produces PCDD/PCDF (Milnes, 1971). This de novo formation of PCDD/PCDF and other chlorinated aromatic compounds (chlorobenzenes, PCBs, chloronaphthalenes) has been shown to be a catalytic process of particulate matter starting with the formation of chlorine from copper and/or other metal chlorides in the presence of oxygen (analogous to the Deacon-process) in the temperature range of 250 E - 400 EC. PCDD/PCDF have indeed been shown to be formed in the cooling zones of waste incinerators. Due to this de novo synthesis, PCDD/PCDF have been found in nearly all thermal processes in which chlorine (independent of form ie. inorganic or organic) is involved. PCDD/PCDF have been shown to be emitted from: municipal waste incineration (filter ash and exhaust gas; Buser and Bosshardt, 1978); hospital waste incineration (Hagenmaier et al., 1986); hazardous waste incineration (Rappe et al., 1983); metal reclamation (especially copper smelters; Marklund et al., 1986); and motor vehicle exhaust (gasoline and diesel; Marklund et al., 1987).

Of special relevance to aquatic environments are the atmospheric inputs from combustion processes, the use of chlorophenols (especially pentachlorophenol), chlorination processes (in particular effluents from paper/pulp production) and, on a local scale, production of high purity Ni, Co and Mg.

1.5.3 Polychlorinated naphthalenes

Polychlorinated naphthalenes (PCNs) are used as dielectric fluids, flame retardants and fungicides. Their commercial names are Halowax (Halowax 1000 with an average of 26% chlorine; Halowax 1001; Halowax 1013; Halowax 1014; etc.).

PCN molecules contain from 1 to 8 chlorine atoms with up to 75 possible isomers/congeners. Properties of PCNs are similar to those of PCBs.

1.5.4 Polychlorinated terphenyls (PCTs) and quaterphenyls (PCQs)

PCTs have been manufactured since the 1930s, with the production being a few percent of, say, the PCBs. Their main uses are as resins in adhesive products and also as plasticizers. The compounds have not been studied intensively.

PCQs are dimers of PCBs.

1.6. Organohalogen pesticides

Division of this class is not by structure but by usage. Consequently overlaps will occur with other sub-divisions e.g., pentachlorophenol is a "general" pesticide which has been previously discussed in the section on halogenated phenolic compounds.

Halogenated pesticide molecules are hydrocarbon skeletons with varying degrees of halogen substitution. Other pesticide groups, however, also contain halogen atoms, for example the triazines (e.g. simazine); organophosphorus pesticides (e.g. bromophos and profenophos); benzamides (e.g. propiconazole); imidazoles (e.g. prochoraz); carbamates (e.g. propamocarb hydrochloride) and even the bipyridyliums-diquat dibromide and paraquat dichloride. These are not, however, usually considered as organochlorine pesticides. They are generally not as persistent in aquatic systems as the "organohalogens" and are, on the whole, less lipophilic. In addition, analytical techniques of choice for these compounds do not generally involve GC-ECD.

In addition to the standard series of organohalogen pesticides currently monitored, other compounds should also be considered. These compounds include: chlordane (insecticide), endosulfan or thiodan (insecticide/acaricide), toxaphene or campheclor (insecticide), mirex (insecticide), captan (fungicide), dicofol or kelthane (acaricide), 2,4-D (herbicide), and dichlorophen (general biocide). It is stressed that these compounds represent an extremely small proportion of the organochlorine pesticides and are used only as examples. These selected products are, however, extensively used in the Mediterranean region.

1.7. Other halogenated compounds

The occurrence of unknown halogenated compounds ("unknown peaks") during analyses of the 'standard suite' of organochlorine pesticides and PCBs (see 'Background' and Section 4) indicates that chemicals not previously considered, may have a wide distribution in the environment. It was recently demonstrated that the amount of organic-bound chlorine associated with known chlorinated compounds in some marine organisms, accounted for only 1-20% of the total organic-bound chlorine in the samples (Watanabe et al., 1987a).

1.7.1 Brominated flame retardants. Polybrominated biphenyls (PBBs) and polybrominated biphenyl ethers (PBBEs) are widely used as flame retardants. Watanabe et al., (1987b), reported that the annual usage of PBBEs in 1984 exceeded 3,000 t in Japan , mainly as deca-brominated products.

PBBs and PBBEs have been found at ng/g levels in marine organisms from hot spots in Japan (Watanabe et al., 1987b). Higher concentrations (3-370 ng/g) have been found in seals and marine birds from both anthropogenically influenced and remote areas (Jansson et al., 1987). In these samples the PBBs are lower than PCBs. However, the PBB pattern is generally dominated by one compound containing six bromine atoms. The concentration of this hexabromobiphenyl may be higher than that of any single PCB isomer.

1.7.2 Brominated phenols and anisoles. The origin of these brominated compounds may be attributed to water chlorination processes. According to Watanabe et al. (1985), halogenated anisoles can be produced by biological methylation of halogenated phenols.

1.7.3 Polychlorinated styrenes (PCSs)

Penta-to octachlorostyrenes are formed as by-products in technical processes where chlorine is used (eg. electrolytic production of magnesium from its oxide, or chlorine production where graphite electrodes are used). A total of 159 isomers/congeners are possible.

1.7.4 Halogenated alkylphenol polyethoxylate residues.

Brominated and chlorinated alkylphenol polyethoxylated residues originating from non-ionic surfactants (which constitute 30% of the surfactant market in the EEC) have been identified in the chlorinated effluent from a municipal advanced waste water treatment plant and in chlorinated secondary waste water (Stephanou et al., 1987).

2. DISTRIBUTION AND FATE OF ORGANOHALOGEN POLLUTANTS IN AQUATIC SYSTEMS

The wide variety of possible molecular structures and hence physical and chemical properties render distribution patterns for organohalogen compounds highly diverse, eg. volatile chlorinated solvents behave very differently to chlorinated humics. Selection of sampling strategy must account for differences in physico-chemical properties. These properties, such as solubility, vapour pressure (Henry's law constant), and the octanol/water partition coefficient will be controlled by characteristics including molecular weight and polarity. Environmental conditions, such as salinity, dissolved oxygen, pH, and turbidity will also control the environmental behaviour of the compounds.

Introduction and origins of the compounds will also dictate sampling strategy. Point source inputs, such as sewage outfalls, industrial discharges and accidental spillages afford well defined environmental distributions. Non-point sources and diffuse patterns such as agriculture and atmospheric inputs are more difficult to evaluate. Environmental conditions, including weather, precipitations, aerosol productions and wave action directly influence these inputs.

Compartmental exchange between the atmosphere, water column and sediment can be estimated from the physical and chemical properties of the compounds using simple linear free-energy models. These can thermodynamically predict distribution under equilibrium conditions. Such models are primarily used for hydrophobic compounds. Increased polarity (such as for chlorinated phenols) involve ionic chemical speciation which complicates modelling. Often aqueous solubility for these compounds is increased, although volatility is also an important property. The charge characteristics of suspended particulates such as clays, also play an increasingly important role with prediction of sorption of these components.

For hydrophobic organohalogens (such as PCBs, dioxins, dibenzofurans and many of the pesticides) simple relationships can be used to study transfer of compounds between water and suspended particulates, for example:

$\log K_{oc} = 0.96 \log K_{ow}$ (Mackay and Shiu, 1984)
or $\log K_p = 0.72 \log K_{ow} + \log f_{oc} + 0.49$ (Schwarzenbach & Westall, 1981)

Similarly, Henry's law constants (H) and vapour pressure data (when available) can be used to investigate exchange between the water column and the atmosphere. For example, Liss and Slater (1974) have developed a model which is based on the knowledge of the Henry's law constant. The application of this model enabled MacKay et al. (1979) to establish a volatility scale of hydrophobic substances according to the H value (Atm m^3 $mole^{-1}$).:

- volatile substances : $H > 5x10^{-3}$
- non volatile substances : $H < 5x10^{-6}$
- moderately volatile substances : $5x10^{-3} < H < 5x10^{-6}$

Adsorption and absorption of halogenated organics by biota occurs and is of special concern when there is the potential for bioaccumulation and biomagnification. Toxicity of the compounds within the environment is controlled by the compartmental exchange. The toxic action is discussed further in a later Section.

Transformation Processes

Degradation of organohalogens occurs in the environment via processes such as microbial heterotrophic degradation, metabolism by organisms, chemical degradation and photo-oxidation. Such processes are highly compound specific and generalisations are difficult. In accord with their periodic distribution, however, reactivity generally increases from Cl to Br to F. For example, the photo-oxidation half-lives of brominated organics are generally shorter than those of the equivalent chlorinated compounds.

The environmental behaviour and effects of degradation products from parent compounds further complicates discussion of this group of contaminants. These are of particular importance when considering toxic action.

For each group of organohalogen contaminants defined in the previous chapter, a presentation of general physical and chemical properties is given. The properties taken into consideration are solubility, vapour pressure, Henry's law constants and octanol/water partition coefficients (K_{ow}). These directly control the environmental behaviour of the compounds. Most of the properties can be found in the review: "Handbook of Chemical Properties. Examination, Methods, Environmental Behaviour of Organic Chemicals"(W. Lyman et al., 1981). Another very important aspect is the persistence of compounds in the aquatic environment, which is related to biotic and abiotic transformation processes.

Using the information available within the literature on various organohalogens (including any environmental measurements) generalised distributions within the environment are modelled, proposed and discussed. Special reference is made to the marine environment.

2.1. Low molecular weight 'volatile' compounds

Chloromethanes, chloroethanes, chloroethenes, polyhalomethanes, freons and chlorinated-dienes are all included within this group. In general, these are non-polar substances which are relatively insoluble in water. Their Henry's law constants are high and most of the compounds can be defined as 'volatile'. Low K_{ow} values for these organohalogens indicate only weak lipophilicity. Thus, bioconcentration factors are low, ranging from 20 for CCl_4 to 40 for CCl_2=CCl_2. The compounds are only weakly adsorbed onto suspended particulates, partition coefficients (K_p) range from 20-70. Sedimentation of these substances therefore appears to be of minor importance as an environmental fate.

Laboratory experiments have shown that trihalomethanes (THM) and C_2-halocarbons are not significantly degraded under aerobic conditions by bacteria inocula from sewage effluents. Half-lives calculated for abiotic hydrolysis range from 1 to more than 100 years for C_1-halomethanes, 0,01 to 5 years for haloethanes and 0.1 to 6 years for haloethenes. According to studies carried out in Narragansett Bay, volatilization is apparently the major removal process for all halogenated volatile C_1- and C_2-hydrocarbons. Calculations suggest water column residence times with respect to volatilization of approximately 150 to 300 hours in this bay (Wakeham et al., 1983).

Chemical properties

	Solubility	Henry's law constant	$LogK_{ow}$
	(mole/l)	(atm m^3/mole)	
Chlorinated solvents	10^{-2} to 10^{-3}	10^{-2} to 10^{-4}	2 to 3
Trihalomethanes	1 to $6x10^{-2}$	10^{-3} to 10^{-4}	
Freons	2 to $8x10^{-3}$	10^{-1} to 10^{-2}	
Hexachlorobutadiene	10^{-5}	$2.5x10^{-2}$	about 5
Hexachlorocyclopentadiene	-	-	5.5

These compounds have been detected in many aquatic environments including rivers, lakes, groundwaters and marine coastal waters. In several European rivers, the following approximate concentrations have been reported:

$CHCl_3$	:	40 ng/l
CCl_4	:	20 - 4300 ng/l
CCl_3-CH_3	:	10 - 100 ng/l
$CHCl=CCl_2$	:	5 - 750 ng/l
$CCl_2=CCl_2$	:	100 - 1200 ng/l

Urban sewage, which contains the following concentrations of volatile organohalogens, is also a source of contamination for the marine environment (Marchand et al., 1989):

$CHCl_3$	:	5 - 13 µg/l
CCl_3-CH_3	:	1 - 100 µg/l
$CHCl=CCl_2$	:	3 - 80 µg/l
$CCl_2=CCl_2$	:	1 - 50 µg/l

Chlorinated seawater, used to cool power plants, is also a source of contamination. For example, bromoform has been found at concentrations of up to 60,000 ng/l in Sweden (Dyrssen and Fogelquist, 1981).

All of these inputs can potentially contaminate marine waters, especially in coastal locations. The following concentrations of volatile organohalogens have been reported for marine environments:

Trihalomethanes

Coastal and open sea	:	less than 1 to 20 ng/l
Swedish coastal waters ($CHBr_3$)	:	5 - 200 ng/l (Dyrssen and Fogelquist, 1981)
Chesapeake bay	:	nd to 45,000 ng/l
French Mediterranean ($CHBr_3$)		
open sea	:	less than 1 to 12 ng/l
Rhone delta	:	8 - 11 ng/l
Sewage outfall (Marseille)	:	about 400 ng/l (Marchand et al., 1988)

C_2-halocarbons

Chesapeake bay	:	up to 50,000 ng/l
Liverpool bay	:	up to 3,600 ng/l
Rhode Island Sound	:	1 - 10 ng/l
Gulf of Mexico	:	10 - 50 ng/l
French Mediterranean, open sea	:	less than 1 ng/l
Rhône delta	:	60 - 250 ng/l
Sewage outfall	:	up to 10,000 ng/l
Coastal waters	:	about 1 ng/l
(Marchand et al., 1988)		

Narraganssett bay (Wakeham et al., 1983):

Near sewage outfall	:	200 - 19,000 ng/l ($CCl_2=CCl_2$)
Estuary	:	5 to more than 1000 ng/l ($CCl_2=CCl_2$)

2.2. Halogenated paraffins

These compounds are resistant to degradation and, especially those in the C_{10}-C_{20} chain length range, are sufficiently mobile to become global contaminants. Vapour pressures of 1-2x10^{-6}mm Hg (20 EC) have been reported for C_{14-17} paraffins with 52% chlorine (Campbell and McConnell, 1980). Water solubility is in the ppb range (4 and 10 µg/l for a C_{16} paraffin with 52% chlorine, at 20 EC in sea and fresh water, respectively). Very few data on the environmental levels of halogenated paraffins are available from the literature (Campbell and McConnel, 1980). However, the presence of these compounds, at ppb or sub-ppb levels in waters and sediments have been demonstrated far away from known sources. Concentrations of 0.2 µg/g have been found in eggs of marine birds for the C_{10}-C_{20} CP, while the C_{21}-C_{30} CP were not detected.

2.3. Halogenated mono-aromatic compounds

There are 12 chlorobenzenes (CBs) from mono-(CB) to hexachloro- (HCB). The chemical properties of these non-polar compounds are directly related to the number of chlorine atoms.

Chemical properties of Chlorobenzenes

		Solubility (mole/l)	Henry's law constant (Atm m^3/mole)	log K_{ow}
Mono-	CB	4x10^{-3}	2x10^{-3}	2.8
Di-	DCB	10^{-3} to 5x10^{-4}	1 to 3x10^{-3}	3.4 - 3.5
Tri-	TCB	1 to 2x10^{-4}	1 to 5x10^{-3}	4.0 - 4.3
Tetra-	TTCB	2 to 6x10^{-5}	0.9 to 3x10^{-3}	4.5 - 4.7
Penta-	PeCB	5x10^{-6}	-	5.2
Hexa-	HCB	2x10^{-6}	-	5.5

These data suggest that CBs from CB to TTCB are volatile compounds, poorly adsorbed onto suspended particulates and are weakly bioconcentrated in biota. Conversely PeCB and HCB have low solubilities and relatively high K_{ow} values; thus these two compounds will partition onto sediments and into biota from water. Bioconcentration factors of 60 for DCB to 20,000 for HCB have been reported (Oliver and Nicol, 1982). Partition coefficients (K_p) increase with increasing chlorine content. This is illustrated by data from an estuarine environment at Narraganssett Bay (Wakeham et al., 1983):

CB: Kp=17,; 1,4-DCB: Kp=36,; 1,2,4-TCB: Kp=74

MERL experiments suggest that under natural conditions in marine coastal ecosystems, rapid biodegradation of mono-chlorobenzene (CB) will occur. Concentrations of CB could be reduced by 2 - 4 orders of magnitude in 12 to 24 hours.

More than one halogen atom on the aromatic nucleus greatly reduces biodegradation rates, although soil microbes can still slowly degrade DCBs and TCBs. Conversely, HCB is well known to be a highly persistent compound in aquatic environments.

Municipal waste waters discharged into coastal waters contain relatively high concentrations of CBs. According to studies carried out in California, levels of total CBs in waste waters are typically an order of magnitude above those of PCBs (Brown et al., 1986) and mass emission rates (expressed as Kg/year) from the JWPCP Californian waste water treatment plant were estimated to be:

1,3-DCB	:	4,680
1,2-DCB	:	4,000
1,2,4-TCB	:	1,320
1,3,5-TCB	:	20
HCB	:	150
total CBs	:	10,170

(for comparison, total PCBs = 1,310/Kg/year)

In Narraganssett bay, high concentrations of CBs were found near an urban sewage outfall (CB = 60 - 350 ng/l ; 1,2,4-TCB = 180 - 540 ng/l) indicating the sewage effluent to be an important source of contamination for the marine environment (Wakeham et al., 1983). In the vicinity of the Marseilles sewage outfall in the Mediterranean, similar observations have also been reported (1,2-DCB = 180-2,200 ng/l ; 1,2,4-TCB = less than 20 to 80 ng/l; Marchand, pers. comm.).

River inputs must also be considered as a source of contamination. In the Pawtuxet river which flows into Narraganssett Bay, CB concentrations of 2,200 ng/l have been reported (Wakeham et al., 1983). A similar range of concentrations was also observed for 1,2-dichlorotoluene in this river. Other data on CBs in continental waters are also available :

CBs in rivers and lakes (ng/l):

	DCB	TCB	TTCB	PeCB	HCB
USA (Niagara river) (Oliver and Nicol, 1982)	70	20	7	1.3	1.1
Canada (rivers & lakes) (Oliver and Nicol, 1982)	4-50	0.2-2	0.05-0.2	0.5-0.2	0.04-0.6
Europe (rivers & lakes) (Germany, Holland, Switzerland)	7-2,800	4-12	-	0.35	0.2

Comparatively little data is available for marine waters. In Narraganssett bay, a suite of CBs from CB to TCB were recovered from most water samples. The dominant CB compound was usually 1,2,4-TCB (0.3-50 ng/l). Chlorotoluenes were also detected, of which, 1,2-chlorotoluene dominated (Wakeham et al., 1983). In French Mediterranean waters, 1,2-DCB and 1,2,4-TCB have been detected at the mouth of the Rhone river (200-300 ng/l). A concentration gradient was observed in the dispersal zone of the Rhone waters (DCB:207 to less than 2 ng/l; TCB: 23 to less than 2 ng/l). Off the coast, levels were below the detection limit (less than 2 ng/l). Chlorobenzene (CB) was identified in only one sample collected in the Rhone delta (20 ng/1); elsewhere it was not detected.

HCB (which is used as fungicide) has also been detected in Mediterranean waters:

France :	Estuary zone of the Var river	:	nd - 0.05 ng/l
	Coastal zone, Monaco	:	0.71 - 1.05 ng/l
	Open sea (Gulf of Lion) (Marchand, pers. comm.)	:	nd - 0.01 ng/l
Spain :	Alfaques estuary	:	0.084 ng/l
	Transect east of Tarragona	:	0.054 ng/l

HCB is strongly adsorbed onto suspended particulates and has been detected in marine sediment collected from: the Rhone delta (32 ng/g), the dilution area of the Rhone river (average 3 ng/g), in the coastal zone (less than 0.1 - 0.5 ng/g), but was not detected in the open sea (less than 0.1 ng/g) (Marchand, pers. comm.).

Concentrations of CBs in biota increase with increasing chlorine content and octanol/water partition coefficients (K_{ow}). This is exemplified by data reported from Ontario Lake, Canada (Oliver and Nicol, 1982):

	Log K_{ow}	Concentrations reported in:	
		water (ng/l)	fish (µg/kg)
1,2,4-TCB	4.08	0.6	0.6
1,2,4,5-TTCB	4.70	1.1	0.5
1,2,3,4-TTCB	4.6	0.1	1.0
PeCB	5.2	0.2	3.4
HCB	6.2	0.05	33

2.4. Halogenated phenolic compounds

Selected chemical properties of chlorinated phenols (CPs) are listed below:

Chemical properties of commercial chlorophenols:

	Boiling point (EC)	Solubility (mole/l)	constant (25 EC) (Ka)	Log K_{ow}
CP	175-220	about $9x10^{-2}$	$0.6\text{-}1.4x10^{-9}$	2.2-2.4
DCP	210	-	$2.1x10^{-8}$	3.1
TCP	246-275	-	$3.7\text{-}3.8x10^{-8}$	3.7-4.2
TTCP	-	-	$4.2x10^{-6}$	4.4
PCP	310	$5.3x10^{-5}$	$1.2x10^{-5}$	5.1

Both the solubility and polarity decrease as the level of chlorine substition increases. Relatively high values of K_{ow} for pentachlorophenol (PCP) supports the high concentrations of this compound which have been found in some sediments and biota.

Although degradation of CPs in the environment can occur through abiotic and biotic processes, the rates of these processes are insufficiently high to prevent the widespread occurrence of some CPs in effluents, natural waters and biota.

CPs enter the environment at points of use, disposal and especially manufacture. PCP is found at relatively high concentrations in sewage effluents:

PCP in urban sewage (concentrations expressed as µg/l):

USA (Los Angeles)	:	2.3 (Gossett et al., 1983)
Canada (Vancouver)	:	1.3-12 (Garrett, 1980)
Denmark	:	0.17-0.67 (Folke and Lund, 1983)
Switzerland (Zurich)	:	0.72 (Giger and Schaffner, 1981)
Netherlands	:	0.46-0.76 (Van Luin and Van Starkenburk, 1984)

CPs can also be formed as a result of the interaction of aqueous chlorine with organic molecules in process waters and in waste water chlorination processes.

CP concentrations (ng/l) have been reported for rivers, lakes and coastal waters:

		TCP (2,4,5)	TCP (2,4,6)	TTCP (2,3,5,6)	TTCP (2,3,4,6)	PCP
(Rivers)						
Holland	<20-150	<20-180	<10-60	<10-110	320-1,100	
Germany		1-5	3-10	-	11-86	100-400
Switzerland		-	-	-	40	170-240
France		<10	<10	<10	<10	120-200

(Wegman and Hofstee, 1979; Weber and Ernst, 1978; Ahel et al., 1984; Marchand, pers. comm.)

(Lakes)

Holland	-	-	-	70	410	
Japan		-	-	-	-	180

(Wegman and Hofstee, 1979; Matsumoto, 1982)

(Marine coastal waters)

Baltic (German Bight)	Trace	0.01	total tetra- : 0.08-0.14		0.4-1.3
Denmark(Holbaek fjord)	-	-	-	6-8	2-3
France (Mediterranean)	<10	<10	<10	<10	10-25

(Weber and Ernst, 1978; Folke et al., 1984; Marchand, pers. comm.)

2.5. Halogenated polyaromatic compounds

2.5.1 Polychlorodibenzodioxins (PCDDs)

The PCDD compounds exist as a series of 75 isomers/congeners. Among these, the most toxic is the 2,3,7,8-tetrachlorodibenzodioxin (TCDD). This compound is thermally very stable, melts at 307 EC, has a vapour pressure of 1.7×10^{-6} mm Hg at 25 EC and is practically insoluble in water.

As identified in Section 1.5.2. the sources of PCDDs in the environment are rather wide. They are found, for example, in the exhaust of incinerators (eg. 0.2 µg/g in fly ash of a municipal incinerator; Buser and Bosshardt, 1978) and are also present in commercial products such as

phenoxy-herbicides (Rappe, 1978a), hexachlorophene (Baughman, 1974) and chlorophenols (Buser and Bosshardt, 1976).

PCDDs bioaccumulate in organisms. Concentrations of TCDD in commercial fish from Lake Ontario were reported by Ryan et al., (1984) to range from 2.0 to 32.9 ng/Kg. PCDD concentrations (ng/Kg) in River Rhine fish samples have been recorded by Hagenmaier to be:

2,3,7,8	tetra-CDD	: 1.3
1,2,3,7,8	penta-CDD	: 1.6
1,2,3,4,7,8	hexa-CDD	: 1.1
1,2,3,6,7,8	hexa-CDD	: 3.2
1,2,3,7,8,9	hexa-CDD	: 1.6
1,2,3,4,6,7,8	hepta-CDD	: 4.6
	octa-CDD	: 395

2.5.2 Polychlorinated dibenzofurans (PCDFs)

These compounds are also formed during incineration (0.1 µg/g in fly ash; Buser and Bosshardt, 1978) and are present in commercial mixtures of chlorophenols, PCBs, diphenyl-ether, herbicides (WHO, 1989). Rappe et al. (1981) reported total concentrations of TCDF to OCDFs in fat samples of snapping turtle from Hudson River and Grey seals from the Baltic sea to be 3 ng/g and 40 ng/Kg respectively.

The most toxic PCDFs are the 2,3,7,8-tetra, 2,3,4,7,8-penta and 1,2,3,4,7,8-hexa-CDF, isomers/congeners. Hagenmaier has recorded concentrations of PCDFs in fish (ng/Kg) from the River Rhine to be:

2,3,7,8	tetra-CDF	: 15.6
1,2,3,7,8	penta-CDF	: 1.4
2,3,4,7,8	penta-CDF	: 4.6
1,2,3,4,7,8	hexa-CDF	: 2.6
1,2,3,6,7,8	hexa-CDF	: 1.1
1,2,3,7,8,9	hexa-CDF	: 0.4

2.5.3 Polychlorinated naphthalenes (PCNs)

Crump-Weisner et al. (1973) have reported concentrations of 1250 to 5000 ng PCNs/g in sediment samples from Florida, USA, with 5.7 µg/l in the overlying waters.

Concentrations reported in marine fish from Japan are generally <1ng PCNs/g, although Takeshita and Yoshida (1979) have reported concentrations in fish of up to several hundred ng PCNs/g and 3-17 ng PCNs/g for adipose tissues.

For the Mediterranean area, Vannucchi et al. (1978) reported values of 700 and 62500 ng/g wet weight for seagulls' livers from Italy.

2.5.4 Polychlorinated-terphenyls (PCTs) and -quaterphenyls (PCQTs)

Physical and chemical properties of the PCTs and PCQTs are generally similar to those of the most highly chlorinated PCBs. PCT vapour pressures (Aroclor 5460) however, range from $2x10^{-7}$ to $8x10^{-11}$ mm Hg at 38 EC, substantially lower than those of PCBs. Hence atmospheric transport of "gaseous" PCTs is unlikely to be important.

PCTs have been detected in aquatic species, birds, cows' milk and human tissues. Precipitation samples collected in 1980 were shown by Wingender and Williams (1984) to contain 3.4 to 960 ng PCTs/Kg. Stratton and Sosebee (1976) reported concentrations of 0.17-13 µg/g in soils from the vicinity of a casting facility in Chicago.

PCQTs have been identified in Yusho patients blood and in the contaminated rice oil responsible for their condition (Mochiike et al.,1986).

2.6. Organohalogen Pesticides

As described in Section 1.6, "organohalogen (typically organochlorine) pesticides" incorporates a multitude of products with diverse physical/chemical properties and hence environmental distribution patterns. Description of their individual distributions and fates in aquatic systems was considered beyond the scope of this current document.

2.7. Other halogenated compounds.

Of the compounds discussed in Section 1.7, information on environmental distribution is only available for the polychlorinated styrenes (PCSs). These compounds are environmentally ubiquitous, especially in industrialised areas. They have been identified in birds from the vicinity of the River Rhine and from the Netherlands Coast (Koeman et al., 1969; Noever de Brauw and Koeman, 1972), in fish from Saginaw Bay, Lake Huron, the Detroit River, Lake Ontario and the River Rhine at concentrations from 20 to 3700 ng/g lipid (Kuehl et al., 1976; Steinwandter and Zimmer, 1983; Reichel et al., 1977; Kaminsky and Hites, 1984). PCSs were not, however, detected in fish livers from the North Atlantic (Greenland and Tenerife), the Eastern Mediterranean (Greece) or the Red Sea (Ernst et al., 1984).

Partition ratios between sediments and water range approximately from 10^3 to 10^4 and between fish and water from 10^4 to 10^6 (Ernst et al., 1984). Bioconcentration of octachlorostyrenes is of the same order of magnitude as for highly chlorinated PCBs.

3. TOXIC POTENTIAL AND EFFECTS OF ORGANOHALOGENATED COMPOUNDS

3.1 General Considerations

To evaluate the toxic potential of environmental contaminants, an ecotoxicological approach is preferable. Ecotoxicology has been defined as a science "concerned with the toxic effects of chemical and physical agents on living organisms, especially in populations and communities within defined ecosystems; it includes the transfer pathways of those agents and their interactions with the environment" (Butler, 1978). The basic objective of applied ecotoxicology is to develop workable, systematic programmes to enable an early, cost-effective prediction of hazards at an acceptable level of certainty to guide regulatory and industrial decision making.

Such a programme must be planned in order to assist in answering various basic questions:

- what is the fate of the chemical in each compartment?
- what are the possible environmental concentrations?
- which are the biological effects of the chemical and what factors affect them?
- is the chemical harmful at the possible environmental levels?

Answers to these questions are needed for hazard assessment. Environmental concentrations can be obtained through monitoring programmes, and ecological effects can be determined through laboratory experiments or field observations.

However, with the enormous numbers and variety of anthropogenic organic compounds, both the scientific community and administrative authorities have recognized the importance of predictive modelling of the potential hazard of a chemical before it is marketed or introduced into the environment, and also to forecast the benefits of possible regulatory remedies in order to be able to choose the most cost-effective control measures.

Predictive techniques are evolving rapidly to enable ecotoxicologists to assess both exposure and effects. The biological activity of a molecule can be evaluated, at least as a rough approximation, by means of Quantitative Structure Activity Relationships (QSARs). Trends in environmental distribution and fate can also be estimated by means of evaluative models or through integrated approaches based on theoretical models, laboratory and field experiments (Calamari and Vighi, 1988). Thus, predictive hazard assessment for potentially harmful chemical substances must take into account several factors, both intrinsic with the substance (such as the biological activity and physico-chemical characteristics which affect environmental distribution and fate) and extrinsic conditions which depend on emission features (loads, discharge patterns etc.) or from environmental properties (biological systems, characteristics of the ecosystems, etc.).

An example of such an approach applied to the marine environment, is schematically presented in Fig. 1 (Vighi and Bacci, 1988).

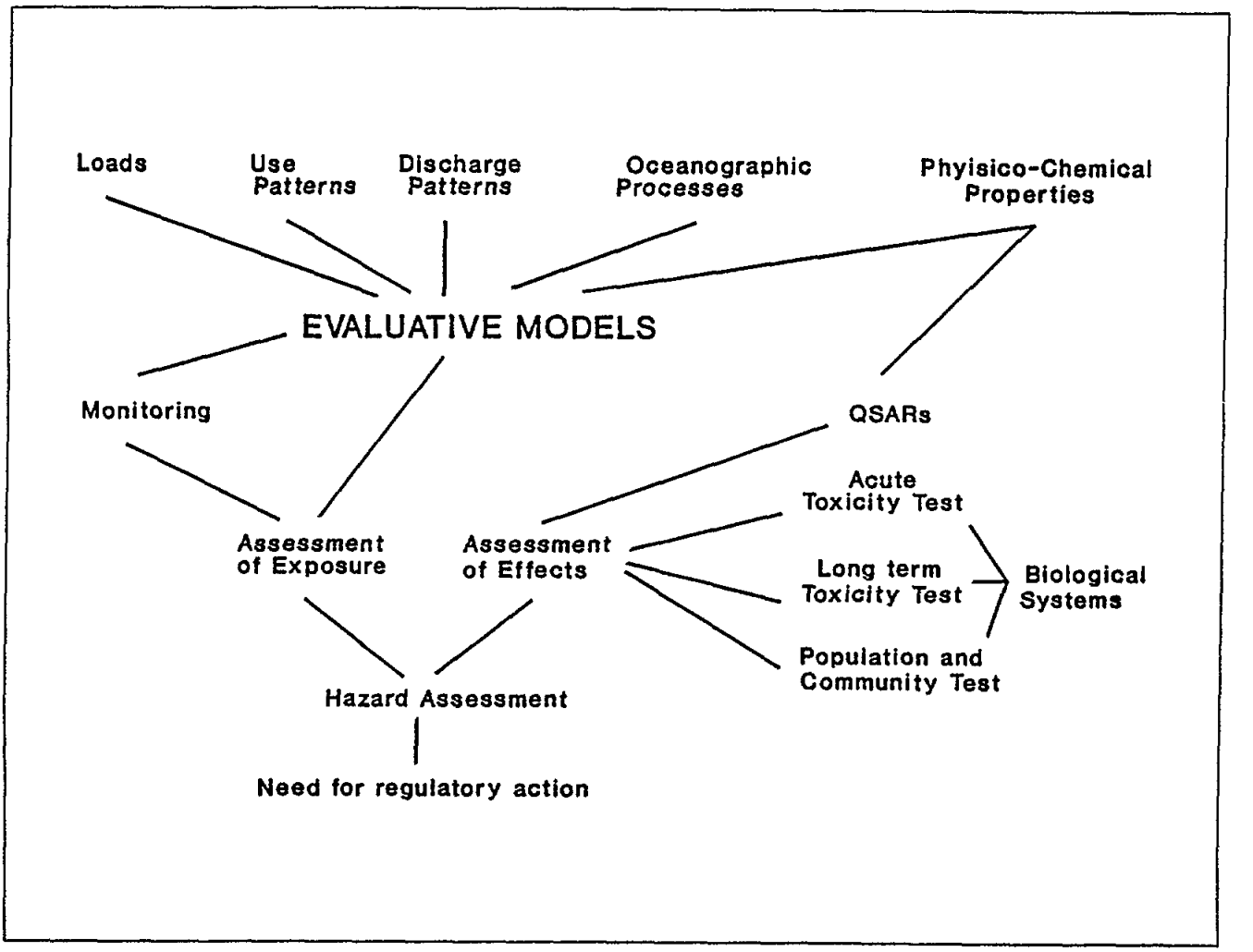

Fig. 1 - An ecotoxicological approach for the study of marine contaminants.

3.2. Organohalogenated compounds

Information available to construct such schemes is, of course, largely insufficient in the case of the organohalogen compounds being considered. An ecotoxicological approach such as that described does, however, identify areas requiring research in logical sequence. The data available on sources, and that on distribution/physico-chemical properties has been summarised in Sections 1 and 2 respectively. Information available specifically on the toxicity of the compounds is, however, very limited and negligible data relates to marine environments.

The low molecular weight "volatile" compounds have short residence times in aquatic systems and toxicological impact is only likely to occur where high and continuous inputs are present.

Chlorinated paraffins are resistant to degradation and are lipophilic. Although the little data that is available indicates relatively low acute toxicity, the characteristics noted render the compounds of concern.

Chlorobenzenes are, in general, highly toxic but are rapidly degraded in aquatic environments. Impact will therefore be localised. Hexachlorobenzene, however, contrasts by being both lipophilic and resistant to transformation processes. It is considered a "global" pollutant but information available on its acute toxicity to mammalian and aquatic organisms indicates that HCB could be considered as a low toxicity contaminant. More research is, however, required to evaluate its environmental impact.

Although mono-and di-chlorophenols have "moderate" acute toxicity, they show low resistance to biological degradation. Tetra- and penta- chlorophenols are more resistant to degradation. Concentrations of these compounds reported in highly contaminated pulp-mill effluents are well below experimentally derived LC_{50} values (Sundstroem and Remberg, 1985).

Comparatively more information is available on polychlorinated dibenzo-dioxins and -furans (PCDDs and PCDFs). There are significant differences between the toxicities of the various PCDD and PCDF congeners. For example, the "no-observed effect levels" (NOEL) reported by Karasek and Hutzinger (1986) in ng/Kg/day for PCDDs were:

2,3,7,8 - TCDD	:	0.003
1,2,3,4 - TCDD	:	800
2 - MCDD	:	2000
2,7 - DCDD	:	100000
OCDD	:	500000
1,3,6,8 - TCDD	:	3000000

The most toxic PCDDs are 2,3,7,8 TCDD; 1,2,3,7,8 PCDD; 1,2,3,6,7,8 HCDD; 1,2,3,7,8,9 HCDD and 1,2,3,4,7,8 HCDD; ie. laterally substituted PCDDs. Compared with these compounds, the other congeners exhibit much lower toxicity. For example, with 2,3,7-triCDD or 2,8-diCDD the LD_{50} values were in the range 1,000 to 100,000 times higher than with 2,3,7,8-TCDD (WHO, 1989). Dioxins with a low proportion of chlorination are readily taken up by fish, but are rapidly eliminated. Conversely, OCDD appears not to be taken up by fish. The same is true of dioxins with 1,4 or 1,6 chlorine substitution, probably because of their large cross-sectional molecular area. Thus, toxic effects are dependant on uptake mechanisms (and hence physical/chemical speciation) as well as biological activity (Sijm and Opperhuyzen, 1988). Of the PCDFs, the most toxic are 2,3,7,8 TCDF; 1,2,3,7,8 PCDF; 2,3,4,7,8 PCDF; 1,2,3,6,7,8 HCDF and 1,2,3,7,8,9 HCDF. The only toxicity data found for PCDFs relates to Guinea pigs and reports LD_{50} concentrations of below 10 µg/Kg for 2,3,7,8 TCDF and 2,3,4,7,8 PCDF (Moore et al., 1979).

4. ANALYTICAL CHEMISTRY OF ORGANOHALOGENS

4.1. Methods of Analysis

Techniques for analysis of selected organohalogens have been included within the series of Reference Methods for Marine Pollution Studies by the United Nations Environment Programme (UNEP). They include: NE 14 - "UNEP/FAO/IOC/IAEA, Determination of DDTs and PCBs in selected marine organisms by packed column gas chromatography". A revision of this method which develops the technique reported by Burns and Villeneuve (1983) with the modifications of Risebrough et al.,(1983) using capillary gas chromatography has also been issued as Reference Method NE 40 - "UNEP/FAO/IOC/IAEA, Determination of DDTs and PCBs in selected marine organisms by capillary gas chromatography". Other relevant methods which are proposed include NE 16: "UNEP/IAEA, Determination of DDTs, PCBs, PCCs and other hydrocarbons in sea water by gas chromatography" and NE 17: "UNEP/IAEA, Determination of DDTs, PCBs, PCCs and other hydrocarbons in marine sediments". These reference methods are/will be available from IAEA - Marine Environment Laboratory.

4.1.1 Extraction Techniques

Extraction is generally achieved by partitioning the organohalogens into suitable organic solvents (eg. hexane/dichloromethane etc.). This can be either direct, as in the case of water analysis, or, as with sediments and organisms, can be achieved using soxhlet apparatus, prolonged boiling solvent extraction followed by selective partitioning, or by steam distillation.

Extraction of volatile halogenated compounds requires a technique such as 'closed loop stripping' (CLSA) (Grob and Zurcher, 1976).

4.1.2 Fractionation

Organic extracts should be fractionated prior to capillary GC-ECD analysis to minimize interferences between the analytes and other co-extracted materials. Amongst the great variety of fractionation procedures described in the literature, compatibility with multi-residue analysis should be considered. Hence, clean-up procedures based on acid or basic treatments are usually discarded. Validation of the selected analytical method using standard reference compounds is essential prior to analysis of environmental samples. Standardisation of adsorbent (eg. silica,alumina and florisil) activity is necessary to obtain reproducible results. Adsorbents and eluents are a source of possible interferences, therefore their quality must be assessed by analysing reagent blanks.

Florisil is probably the most used adsorbent in column chromatographic fractionation of pesticides (eg. Erickson, 1986; Aceves et al., 1988) because it affords pesticide fractionation without PCB interferences.

Low resolution Gel Permeation Chromatography (GPC) is an attractive clean-up procedure for multi-residue analysis, but should preferably be combined with other clean-up procedures, dependant on the environmental sample being analysed (Roos et al., 1987; Fernandez et al., 1988). Normal phase semi-preparative HPLC provides an alternative fractionation protocol (Petrick et al., 1988). Tong et al.,(1984) have obtained excellent recoveries of dioxins using semi-prep normal-phase LC. Other multi-step fractionations procedures have been used for various environmental samples (eg. Smith et al.,1984; Ryan et al.,1984, etc).

4.1.3 Capillary gas chromatography-electron capture detection (GC-ECD)

Gas chromatography is the most frequently used method for the analysis of organochlorine compounds (including pesticides and PCBs). In the past, residues of organochlorine pesticides and PCBs in environmental samples have been determined by GC-ECD with packed glass columns according to the previously described (Section 4.1) UNEP Reference Method NE 14.

During the last decade, high resolution capillary columns (glass and fused silica coated with stationary phases such as methyl-, phenyl-, fluoropropyl- and cyanopropyl substituted polysiloxanes) have become commercially available and provide dramatically higher resolution than packed columns. Capillary GC-ECD is now used routinely in many laboratories for quantitative analysis of organohalogen compounds in environmental samples (Cooper et al.,1985; Mullin et al., 1984; Dunn et al., 1984; Hall et al., 1986; Eklund et al., 1978; Duinker et al., 1983).

Identification of peaks associated with organohalogens in GC-ECD chromatograms is usually achieved using retention time comparisons with authentic standards separated on at least two different polarity columns.

If dedicated capillary column (approximately 0.3 mm i.d.) gas chromatographs are not available, packed column GC equipment can be converted, most easily to use "megabore" (approximately 0.53 mm i.d.) open tubular columns. This provides a substantial increase in resolution.

4.1.4 Computerised gas chromatography-Mass spectrometry (CGC-MS)

Computerised GC-MS analysis of halogenated compounds has become the instrumental technique of choice in many environmental laboratories. It provides a clear distinction between halogenated compound classes (eg. between pesticides and PCBs) which are not achieved using cGC-ECD. This is especially useful when, as in the case of many halogenated groups of compounds, they cannot be easily separated using simple clean-up/fractionation techniques and for the positive identification of compounds that coelute in the GC with the same m/z, like dioxins and PCBs (Clement and Tosine, 1988).

GC-MS in the selective ion monitoring mode (Slivon et al.,1985; Duinker and Hillebrand, 1983) with electron impact (EI) and negative ion chemical ionisation (NICI) (Swackhamer et al.,1987; Stemmler and Hites, 1988) provides high specificity and high sensitivity (NICI can yield equivalent sensitivity to ECD). NICI using mixtures of reactant gases can also exhibit selectivity for some chemical classes (Oehme et al.,1986).

4.1.5 Liquid chromatography-Mass spectrometry (LC-MS)

LC-MS is the analytical technique of choice for the identification of polar or thermally labile biocides because no analyte derivatives are required. Thus, compounds that cannot be analyzed by GC-MS because of their restricted volatility, are amenable to LC-MS. However, because of the lower resolution of LC when compared to capillary GC, extended fractionation techniques should be considered for environmental samples. The sensitivity and ionisation processes are dependant on the type of interface used. Several have been described in the literature (Arpino and Guiochon, 1979; Blakely and Vestal, 1983; Covey et al., 1986; Barcelo, 1988; Geerdink et al., 1987; Levsen, 1988) but thermospray (TSP) is the most commonly used on a routine basis. In addition, it is compatible with the flow rates used for packed 3-4 mm id.columns (1 ml/min.). Typical mass spectra obtained are characteristic of chemical ionisation, exhibiting ionic adducts of the molecular ion and the buffer solution used in the mobile phase, depending on the detection mode (positive or negative). Isotopic distributions provide information on halogen composition, but usually because of plasma interferences, data acquisition is only reliable above m/z 150. Detection limits depend on the specific compound, but are usually in the pg and ng ranges for selected ion monitoring (SIM) and multiple ion detection techniques respectively. Typical applications of LC-thermospray-MS are the chlorophenoxyacetic acids, triazines and halogenated carbamates (Barcelo, 1988; Levsen, 1988).

4.2. The identification of "unknown" peaks in cGC-ECD chromatograms

General characteristics of compounds contained within a residue can be estimated from the sample treatment used to prepare the residue. For example, the solvent "strength" required to elute the residue from a chromatographic column will indicate polarity; also the pH of the sample during solvent extraction will dictate recovery of certain compounds. These factors must be considered when investigating residues analysed by cGC-ECD. During most cGC-ECD analyses of environmental samples, peaks appear which do not correspond to the retention times of known compounds used to standardise the system. These peaks are defined in this context as "unknown" compounds.

It is useful to outline parameters to consider when selecting whether or not identification of an unknown peak should be attempted. The following suggestions are proposed:

a) The peak should be a prominent peak in the chromatogram. The peak should, at least, be comparable in height to the peaks routinely determined. An unknown peak in the chromatogram of a PCB-fraction worth identification should therefore have at least the height of the PCB-congener 153.

b) It has to be ascertained that the "unknown peak" is indeed a constituent of the sample analysed and not an artifact. To test this, the analysis should be repeated, starting with a fresh sample aliquot. A blank run has to be carried through the extraction and clean-up procedure in parallel to ensure that contamination from reagents and/or apparatus is not occurring.

c) If identification of the unknown peak is not possible with reasonable effort, the importance of compound identification has to be evaluated. For this purpose several samples from the same sampling site should be analysed. Only if the "unknown peak" turns up in all samples further effort in identification is indicated.

On deciding to attempt identification of a peak, there are various protocols which can be used (usually in combination with each other). These techniques are described in the following sections:

4.2.1 Retention Time Indices

Using specified chromatographic conditions, it is possible to compile a library of retention times of authentic standard compounds which are frequently encountered in environmental samples. To enhance accuracy of the measurement, retention times are usually measured relative to standards. To identify (or more precisely to "commence" identification of) a peak in an environmental extract, the chosen retention time-standards are added to the extract and relative retention times of unknown peaks are calculated for comparison with the library. An example using di-alkyl-phthalates is appended (Appendix 2). An index of 100 is given to di-methyl-phthalate, 200 to di-ethyl-phthalate, etc. A listing of retention times of numerous electron capture sensitive compounds relative to these phthalates is included.

4.2.2 Multiple Column Analyses

Speculative identification of a peak from retention time data is supported if the retention times of both the peak in the environmental extract chromatogram and that of the standard compound remain the same when they are chromatographed on different polarity columns.

An elegant "multi-dimensional" GC system has been described by Duinker et al.,(1988) which utilises two capillary columns in series, the second of which receives only a small preselected fraction from the first. This has proven particularly useful in the separation and identification of PCB congeners.

4.2.3 Other Selective Detectors

It must be realised that the electron capture detector is not exclusively selective to halogenated compounds. Thus, non-halogenated organics might be responsible for "unknown" peaks. Equivalent chromatographic analyses using other selective detectors such as the nitrogen/phosphorus detector (NPD) or the flame photometric detector (FPD) can determine whether or not the molecule responsible for the peak contains N,P or S. A microwave plasma detector (MPD) attached to the GC affords multi-element analyses. Possibly the most useful selective detector is, however, the mass spectrometer.

4.2.4 Gas chromatography-mass spectrometry (GC-MS)

Unknown peaks in GC-ECD chromatograms can sometimes be identified using GC-electron impact ionisation mass spectrometry. Often, however, the peak contains insufficient material to provide a good mass spectrum. This can be overcome by sample concentration, but frequently this has deleterious effects on the chromatography. In these instances, chemical ionisation (CI) or negative ion chemical ionisation (NICI) techniques can be attempted. These techniques are often adequately sensitive to provide information on the molecular weight of the compound and the isotope pattern of the molecular ion provides information on the elemental composition (especially if chlorine and/or bromine atoms are present in the molecule).

4.3. Screening for unknown compounds

For the screening of unknown compounds, no generally applicable approach can be given. The following are examples of previously applied approaches and no attempt is made to provide a complete list.

(a) Negative ion chemical ionisation mass spectrometry can be used to screen for chlorinated (m/z 35-chloride ion) and brominated (m/z 79/81-bromide ion) compounds in GC separations (Richter and Schwarz, 1978).

(b) Total organic chlorine and total organic bromine can be determined in environmental matrices (Stephanou et al.,1987).

(c) Preparation of samples can be designed to isolate compounds with specific chemical properties. For example, the solvent strength used in elution of LC columns selects polarity of the eluents. The more pre-fractionation steps which are used, the more clearly defined are the contents of the extract.

(d) Compounds can be isolated according to their molecular weight (for example by using ultrafiltration).

(e) Biologically active substances can be screened in HPLC eluents by testing for biological activity (eg. mutagenicity, immunotoxicity, enzyme induction etc.). Fractions exhibiting high activity can then be further processed to identify the compounds responsible (Reinhard et al.,1982).

5. CONCLUSIONS

1. This document represents a preliminary and brief investigation/discussion of organohalogen compounds. Although many compounds and products are identified, these represent only a portion of the total. In addition, environmental transformations of original compounds will generate halogenated metabolites which are not discussed and for which the behaviour and toxicity are unknown.

2. The group contains an extremely diverse suite of compounds with very wide differences in physical and chemical properties. This means that approaches to sampling, analytical chemistry, toxicity investigations, etc. differ substantially.

3. Although the "standard suite" compounds remain of interest, certain of the compounds identified within this document are undoubtedly of environmental concern (eg. dioxins, dibenzofurans, halogenated paraffins, toxaphene etc.) and require investigation. For others, the information available is insufficient to make judgement.

4. It is useful to distinguish coastal areas with "localised" pollution from open-sea areas which are subject to "global" scale pollution. Organohalogen contamination/persistence and investigative strategies differ substantially - both areas are of concern.

5. Analytical approaches to identify and quantify organohalogen compounds are summarised.

6. RECOMMENDATIONS

Further work would be required to compile a definitive review document.

It is necessary to identify sources of the organohalogens in the Mediterranean Region. Investigation of production/uses of compounds in conjunction with considerations of source (eg. point and/or diffusive; riverine; atmospheric etc.) can then be used to estimate environmental loads (both spatially and temporally).

Transport and transformations of the compounds should be assessed. Initial modelling studies using physical and chemical constants (such as those reported in Section 2) can provide good, albeit broad, estimates of biogeochemical behaviour. Major "outputs" should be investigated to afford estimation of losses from the environment.

The information compiled from the above recommendations can then direct strategies for initial environmental surveys to investigate contamination.

The environmental significance of the contaminants can be further assessed by questioning: (1) is there an increasing trend of levels with time in different media? (2) is the molecule highly biologically active? (eg. toxic, mutagenic, carcinogenic etc.) (3) are there any observed ecological/field effects? Mass balance models for "hot-spots" and reference areas should be compiled.

Concerning analytical strategies, measurement and identification should be attempted (see Section 4), of non-DDT or PCB peaks within cGC-ECD chromatograms of environmental samples. Protocols to enable identification of these peaks are described in Section 4.2. It is also recommended that rapid analytical techniques suitable for screening samples for high organohalogen content should be investigated.

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IAEA/UNEP/IOC/FAO, MEDPOL Organohalogen Workshop
(IAEA, Monaco - 24-28 October 1988)

List of Participants

Dr M. Azzouz
ISMAL
1er Novembre
Algiers, ALGERIA

Dr E. Bacci
Dipartimento di Biologica Ambientale
University of Siena
Via delle Cherchia 3
53100 Siena, ITALY

Dr J. Bayona
C.I.D.-C.S.I.C.
Environmental Chemistry Department
Jorge Girona Salgado, 18-26
08034 - Barcelona, SPAIN

Dr L. Graboletta
Instituto di Biologia del Mare
Riva 7 Martiri 1364/A
Boizz Venezia, ITALY

Prof. H. Hagenmaier
Institute of Organic Chemistry
University of Tubingen
D-7400 Tubingen, F.R.G.

Dr M. Marchand
IFREMER
Centre de Brest
BP 2029263
Plouzané, FRANCE

Dr L.D. Mee
International Atomic Energy Agency
Marine Environment Laboratory
P.O. Box 800
MC 98012 Monaco, PRINCIPALITY OF MONACO

Dr M. Picer
Center for Marine Research
Ruder Boskovic Institute
P.O. Box 1016
41001 Zagreb, CROATIA

Dr J.W. Readman
International Atomic Energy Agency
Marine Environment Laboratory
P.O. Box 800
MC 98012 Monaco, PRINCIPALITY OF MONACO

Dr E. Stephanou
Laboratory of Environmental Chemistry
Department of Chemistry
University of Crete
711 10 Iraklion, GREECE

Dr J.P. Villeneuve
International Atomic Energy Agency
Marine Environment Laboratory
P.O. box 800
MC 98012 Monaco, PRINCIPALITY OF MONACO

Dr T. Wechsler
Swiss Federal Institute for Water Resources
and Water Pollution Control (EAWAG)
CH 8600 Dubendorf, SWITZERLAND

Appendix I

Priority pollutants identified by the EPA, the EEC and the WHO

1. Halogenated aliphatic compounds C1 to C5

EPA : 26
EEC : 24
WHO : 6

This group mainly contains: Chlorinated solvents
freons
trihalomethanes
chloro-propane,-propene
hexachlorobutadiene, hexachlorocyclopentadiene

2. Mono-aromatic hydrocarbons

EPA : 3
EEC : 5
WHO : 1

This group contains benzene and some alkylated benzenes

3. Polyaromatic hydrocarbons

EPA : 16
EEC : 4
WHO : 1

4. Chlorinated and nitrated aromatic compounds

	Cl	N	Cl & N	Total
EPA :	7	3	0	10
EEC :	15	0	7	22
WHO :	4	0	0	4

This group can be divided:
chlorinated compounds : chlorobenzenes and chloronaphthalenes
nitrated compounds : nitrobenzenes
chloro-nitro-compounds : chloro-nitro-benzenes (or toluene)

5. Organochlorine compounds

EPA : 26
EEC : 9
WHO : 8

This group contains : chlorinated insecticides
PCB's
tetrachlorodibenzodioxin

6. Phenolic compounds

	Phenols	chloro-	nitro-	total
EPA :	2	5	4	11
EEC :	0	7	0	7
WHO :	0	2	0	2

This group can be divided in subgroups:
phenol compounds : phenol and dimethyl-phenol
chlorophenols : from mono- to penta- chlorophenols
nitrophenols : nitrophenol, dinitro-phenol (or cresol)

7. Halogenated ethers (R-O-R')

EPA : 7
EEC : 1
WHO : 0

This group contains : halogenated aliphatic ethers
halogenated aromatic ethers

8. Phthalates

EPA : 6
EEC : 0
WHO : 0

9. Amine compounds

	Amines	Nitrosamines	Chloroanalines	total
EPA :	0	3	0	3
EEC :	2	0	8	10
WHO :	0	0	0	0

10. Organophosphorus insecticides

EPA : 0
EEC : 18
WHO : 0

11. Herbicides

	Aryloxyacids	triazines	urea compounds	Amides	total
EPA :	0	0	0	0	0
EEC :	5	2	2	1	10
WHO :	1	0	0	0	1

12. Miscellaneous

EPA : 6
EEC : 8
WHO : 0

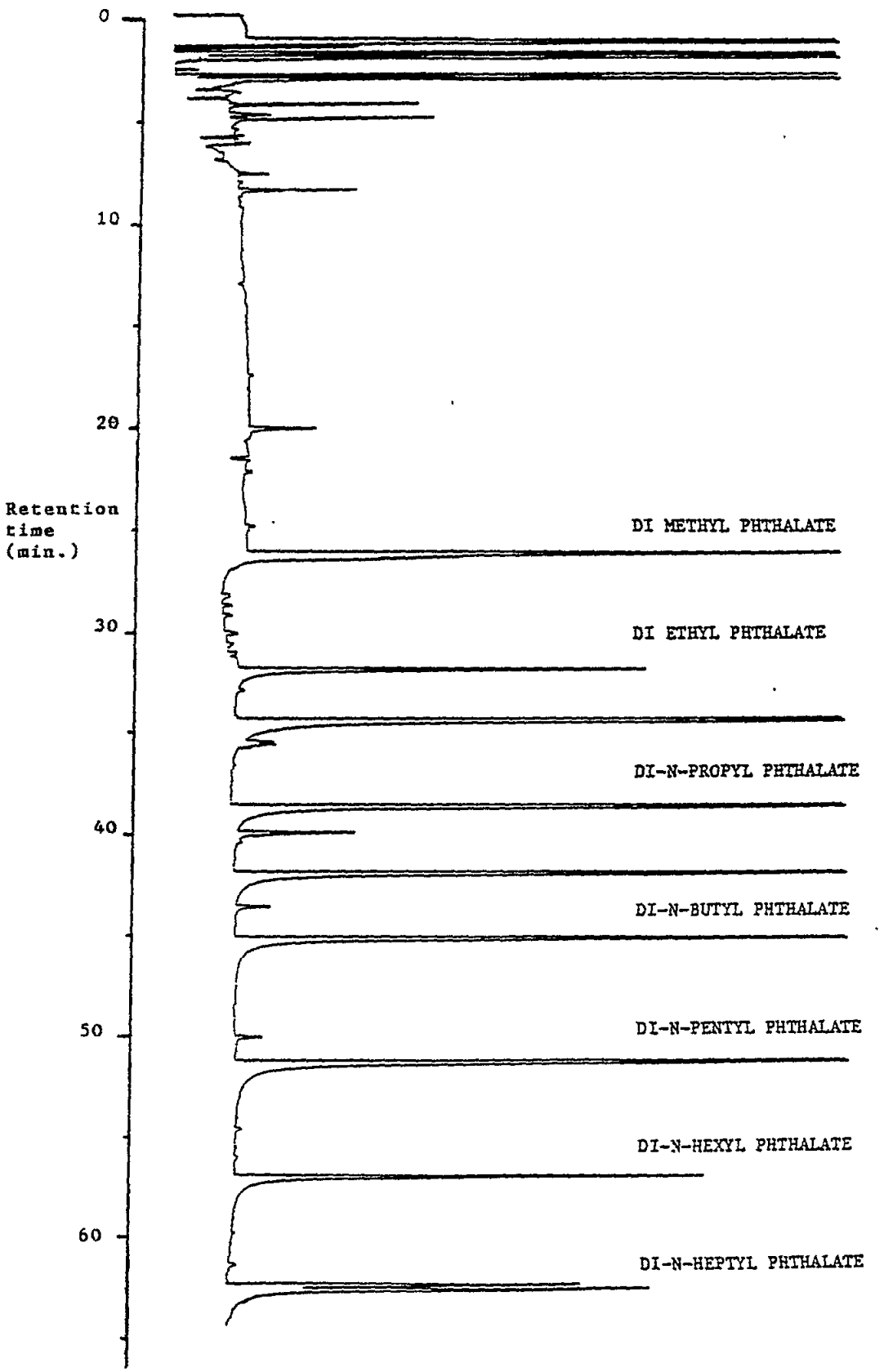
The organohalogen pollutants which appear in these lists can be divided into several groups:

1 - Halogenated aliphatic compounds (EPA/EEC/WHO)
2 - Chlorinated mono-, di-aromatic compounds (EPA/EEC/WHO)
3 - Chloro-nitro-monoaromatic compounds (EEC)
4 - Organochlorine compounds (EPA/EEC/WHO)
5 - Chloro-phenols (EPA/EEC/WHO)
6 - Halogenated ethers (EPA/EEC)
7 - Chloro-anilines (EEC)
8 - Herbicides (aryloxyacid compounds) (EEC)

Appendix II

Relative Retention Time Indices for various organohalogen compounds calculated relative to di-alkyl phthalates

cGC-ECD chromatogram of phthalate standards



Name of Compounds	Retention Times (min.)	Retention Indexes phthalates	Response Factor pg/unit Ar.	Fraction	Acid Stable	Base Stable
1,3 Dichloropropane	2.77	006.5	1.71	1	+	-
1 Chlorohexane	3.76	010.5	162	1	+	+
1,4 Dichlorobutane	4.71	014.3	6.02	1	+	+
1,2,3 Trichloropropane	4.97	015.3	0.05	1	+	-
o-Chlorotoluene	5.91	019.1	190	1	+	+
2 Chlorophenol	6.82	022.7	5.79	4	-	-
m-Chlorotoluene	7.33	024.8	21.14	1	+	+
p-Dichlorobenzene	7.53	025.6	3.15	1	+	+
1,5 Dichloropentane	7.94	027.2	4.70	2	+	+
o-Dichlorobenzene	8.29	028.6	0.07	1	+	+
1 Chlorooctane	9.34	032.8	600	1	+	+
p-Chlorotoluene	11.59	041.8	0.08	1	+	+
1 Chlorononane	13.23	048.4	34.10	1	+	+
2,4 Dichlorophenol	13.33	048.8	0.25	4	+	-
2,5 Dichlorophenol	13.43	049.2	0.28	4	+	-
Chlorobenzene	13.83	050.8	27.72	1	+	+
3 Chlorophenol	14.66	054.1	9.71	4	-	-
4 Chlorophenol	14.67	054.2	15.29	4	-	-
2,6 Dichlorophenol	14.85	054.9	0.16	4	+	-
1 Chlorodecane	17.72	066.4	47.00	1	+	+
1,2,3,5 Tetrachlorobenzene	20.36	077.0	0.02	1	+	+
2,3,5 Trichlorophenol	20.55	077.7	0.009	4	+	-
2,4,6 Trichlorophenol	21.41	081.2	0.02	4	+	-
2,4,5 Trichlorophenol	21.62	082.0	0.02	4	+	-
2,3 Dichlorophenol	22.05	083.7	0.009	4	+	-
2,3,6 Trichlorophenol	22.77	086.6	0.01	4	+	-
3,5 Dichlorophenol	23.20	088.3	0.47	4	-	-
3,4 Dichlorophenol	24.23	092.5	0.57	4	-	-
DI METHYL PHTHALATE	26.11	100.0	5.32	4	-	-
2,3,5,6 Tetrachlorophenol	29.57	161.6	0.08	4	+	-
2,3,4,5 Tetrachlorophenol	29.73	164.4	0.08	4	+	-
2,3,4 Trichlorophenol	29.93	168.0	0.007	4	+	-
DI ETHYL PHTHALATE	31.73	200.0	2.67	4	-	-
Ramrod	32.40	209.7	0.13	4	-	-
2,2'Dichlorobiphenyl	32.65	213.4	0.07	1	+	+
3,4,5 Trichlorophenol	32.89	216.9	0.05	4	-	-
2,4 D Methyl ester	33.37	223.8	0.09	4	-	-
CIPC	34.09	234.3	5.24	4	-	+
Di iso propyl phthalate	34.32	237.6	0.98	4	-	-
2,5 Dichlorobiphenyl	34.55	241.0	0.03	1	+	+
Alpha-HCH	35.66	257.1	0.01	2	+	-
2,4'Dichlorobiphenyl	35.70	257.7	0.08	1	+	+
2,3 Dichlorobiphenyl	35.81	259.3	0.05	1	+	+
HCB	36.09	263.4	0.009	1	+	-
3,5 Dichlorobiphenyl	36.78	273.4	0.09	1	+	+
2,3,4,6 Tetrachlorophenol	37.75	287.5	0.15	4	+	-
Pentachlorophenol	37.75	287.5	0.05	4	+	-

Name of Compounds	Retention Times (min.)	Retention Indexes phthalates	Response Factor pg/unit Ar.	Fraction	Acid Stable	Base Stable
Silvex methyl ester	38.00	291.1	0.003	4	-	-
Lindane (gamma-HCH)	38.08	292.3	0.01	2	+	-
3,3'Dichlorobiphenyl	38.21	294.2	0.05	1	+	+
3,4 Dichlorobiphenyl	38.59	299.7	0.07	1	+	+
DI-N-PROPYL PHTHALATE	38.61	300.0	1.94	4	-	-
Beta-HCH	38.69	301.2	0.01	2	+	-
4,4'Dichlorobiphenyl	39.01	306.1	0.05	1	+	+
2,4,5 T Methyl ester	39.05	306.7	0.006	4	-	-
2,3,6 Trichlorobiphenyl	39.64	315.7	0.03	1	+	+
Delta-HCH	39.91	319.8	0.01	2	+	-
2,4,5 Trichlorobiphenyl	41.09	337.7	0.02	1	+	+
2,4 DB Methyl ester	41.39	342.3	0.06	4	-	-
2,5,3'Trichlorobiphenyl	41.51	344.1	0.05	1	+	+
Di iso butyl phthalate	41.95	350.8	1.20	4	-	-
2,5,4'Trichlorobiphenyl	42.08	352.8	0.02	1	+	+
2,3,4 Trichlorobiphenyl	42.69	362.1	0.03	1	+	+
3,4,2'Trichlorobiphenyl	42.83	364.2	0.04	1	+	+
Heptachlor	43.01	367.0	0.01	1	+	+
2,3,2',6'Tetrachlorobiphenyl	44.19	384.9	qual.	1	+	+
2,5,2',5'Tetrachlorobiphenyl	44.58	390.9	0.03	1	+	+
2,5,2',3'Tetrachlorobiphenyl	44.85	395.0	0.02	1	+	+
2,4,2',4'Tetrachlorobiphenyl	45.04	397.9	0.06	1	+	+
DI-N-BUTYL PHTHALATE	45.18	400.0	1.44	4	-	-
2,3,5,6 Tetrachlorobiphenyl	45.28	401.6	0.02	1	+	+
2,3,4,6 Tetrachlorobiphenyl	45.32	402.3	qual.	1	+	+
Aldrin	45.33	402.4	0.04	1	+	+
2,3,2',4'Tetrachlorobiphenyl	46.12	415.3	qual.	1	+	+
2,3,3',4'Tetrachlorobiphenyl	47.24	433.5	qual.	1	+	+
2,4,6,2',5'Pentachlorobiphenyl	47.26	433.8	0.02	1	+	+
2,4,2',5'Tetrachlorobiphenyl	47.31	434.6	0.02	1	+	+
2,3,3',5'Tetrachlorobiphenyl	47.87	443.7	qual.	1	+	+
Heptachlor epoxide	48.09	447.3	0.01	3	+	+
2,5,3',4'Tetrachlorobiphenyl	48.56	455.0	0.03	1	+	+
2,4,6,2',3'Pentachlorobiphenyl	48.64	456.3	qual.	1	+	+
2,4,6,2',4',6'Hexachlorobiphenyl	49.68	473.2	0.02	1	+	+
2,6,3',4'Tetrachlorobiphenyl	49.86	476.1	qual.	1	+	+
DDMU	49.88	476.4		1	+	+
2,3,5,2',5'Pentachlorobiphenyl	49.98	478.0	0.05	1	+	+
op'-DDE	50.26		qual.			
2,4,5,2',5'Pentachlorobiphenyl	50.37	484.4	qual.	1	+	+
Ovex	51.23	498.4	0.07			
DI-N-PENTYL PHTHALATE	51.33	500.0	2.35	4	-	-
2,3,5,2',3'Pentachlorobiphenyl	51.36	500.5	qual.	1	+	+
2,4,5,2',3'Pentachlorobiphenyl	51.70	506.5	0.02	1	+	+
2,3,4,2',5'Pentachlorobiphenyl	51.76	507.5	0.02	1	+	+
2,3,4,5,6 Pentachlorobiphenyl	52.02	512.0	0.03	1	+	+
Dieldrin	52.14	514.1	0.01	3	-	+
2,4,5,3',5'Pentachlorobiphenyl	52.26	516.2	qual.	1	+	+
pp'DDE	52.26	616.2	0.01	1	+	+
DEF	52.40	518.7	0.002	4	-	-
2,3,6,2',3',6'Hexachlorobiphenyl	52.52	520.8	0.03	1	+	+

Name of Compounds	Retention Times (min.)	Retention Indexes phthalates	Response Factor pg/unit Ar.	Fraction	Acid Stable	Base Stable
Silvex PBEE	52.69	523.7	0.27	4	-	-
3,4,3',4'Tetrachlorobiphenyl	52.71	524.1	0.06	1	+	+
op'-DDD	52.85					+
2,3,4,2',3'Pentachlorobiphenyl	53.40	536.1	qual.	1	+	+
Endrin	53.51	538.0	0.02	3	-	+
2,3,5,3',4'Pentachlorobiphenyl	54.02	546.9	qual.	1	+	-
2,4 D iso octyl ester	54.09	548.2	2.84	4	-	+
3,4,5,2',4'Pentachlorobiphenyl	54.22	550.4	qual.	1	+	-
pp'DDD	54.91	562.5	0.02	2	+	-
Silvex iso octyl ester	55.03	564.6	0.29	4	-	+
op'-DDT	55.18					
2,4,5,2',4',5'Hexachlorobiphenyl	55.83	578.5	0.01	1	+	+
2,3,5,6,2',3',6'Heptachlorobiphenyl	56.69	593.5	qual.	1	+	-
DI-N-HEXYL PHTHALATE	57.06	600.0	1.66	4	-	+
1,2,3,4 Tetrachlorodibenzo-p-dioxin	57.14	601.5	0.05	2	+	+
2,3,4,5,2',3',6'Heptachlorobiphenyl	57.15	601.7	qual.	1	+	-
pp'DDT	57.29	604.2	0.05	2	+	+
2,3,4,2',4',5'Hexachlorobiphenyl	57.49	607.9	0.02	1	+	-
2,4,5 T iso octyl ester	57.77	613.1	0.16	4	-	+
2,3,5,6,2',4',5'Heptachlorobiphenyl	58.58	628.0	qual.	1	+	+
2,3,4,6,2',4',5'Heptachlorobiphenyl	58.92	634.3	qual.	1	+	+
2,3,4,2',3',4'Hexachlorobiphenyl	59.27	640.7	0.03	1	+	+
3,4,5,3',4',5'Hexachlorobiphenyl	59.30	641.3	qual.	1	+	+
2,3,4,5,2',3',6'Heptachlorobiphenyl	60.01	654.3	qual.	1	+	+
2,3,5,6,2',3',4'Heptachlorobiphenyl	60.36	660.8	qual.	1	+	+
2,3,5,6,2',3',5',6'Octachlorobiphenyl	60.60	665.2	0.01	1	+	+
2,3,4,6,2',3',4'Heptachlorobiphenyl	60.64	665.9	qual.	1	+	-
Methoxychlor	61.00	672.6	0.04	3	-	+
2,3,4,5,3',4'Hexachlorobiphenyl	61.32	678.5	qual.	1	+	-
DI-N-HEPTYL PHTHALATE	62.49	700.0	8.53	4	-	

Gas chromatographic conditions:

Varian 3700 (Detector Erba-Science) Att. 512
Temperature injector: 210 EC
Temperature Detector: 300 EC
Oven progr. 70 EC for 2 min., 3 EC/min. up to 260 EC
Carrier: N_2 Flow: 2 ml/min.
Make-up: 200 ml/min.

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Unité de coordination du Plan d'action pour la Méditerranée
Programme des Nations Unies pour l'Environnement
Leoforos Vassileos Konstantinou, 48
B.P. 18019
11610 Athènes
GRECE