
Occurrence and toxicology of natural and anthropogenic organohalogenes and relevance to environmental protection

R.L. Stringer and P.A. Johnston

Greenpeace Exeter Research Laboratory, Earth Resources Centre, University of Exeter,
Laver Building, North Park Road, Exeter EX4 4QE, United Kingdom

Introduction

The existence of natural organohalogenes has long been known and some fifteen hundred have now been identified. This number includes chlorinated, brominated, fluorinated and iodinated, as well as mixed halogenated compounds. They are of a very diverse nature both chemically and functionally and have over the last twenty years been the subject of considerable research. Also, since the recognition of the environmental hazards of anthropogenic organohalogenes, predominantly organochlorines, extraordinary efforts have been expended on environmental analysis of organochlorines. Consequently, attention has also been drawn to those which are biogenic or otherwise naturally occurring. The use of the AOX analytical parameter has allowed the determination of high molecular weight compounds poorly suited to chromatographic techniques. AOX has been widely applied as a regulatory parameter for complex and analytically intractable effluents although limitations in its utility are apparent. Critical areas of understanding of the identification and ecotoxicology of natural and anthropogenic organohalogenes and their relevance to environmental policy are discussed.

Occurrence and function of naturally produced organohalogenes

Since the 1960s, the number and variety of naturally produced organohalogenes known has increased tremendously. The greatest number are produced by algae, fungi and bacteria; organohalogenes are also produced by marine invertebrates such as the sponges, corals and molluscs, insects and higher plants (Gribble 1992, Engvild 1986, Neidleman and Geigert 1986). The phenomenon is comparatively rare amongst the higher animals, with only a few compounds other than the iodinated growth hormone thyroxine having been isolated in mammals. Organohalogenes are also released into the biosphere by natural combustion processes, though the quantification of these is unreliable and may have been enhanced by the

widespread use of organochlorines such as the herbicide 2,4-D and the insecticides DDT and dieldrin in forestry.

The marine environment is the largest source of volatile organohalogenes. Methyl chloride, methyl bromide and methyl iodide are all produced in significant quantities, with lesser amounts of dibromo- and tribromomethane (Penkett *et al.* 1985, Harper 1993). Lovelock (1975) postulated methyl chloride and methyl bromide to be natural regulators of the ozone layer prior to the introduction of artificial ozone depleting substances. He calculated the annual release of methyl chloride to be 28 million tonnes; subsequent calculations, however, indicate a much lower budget of between 2.5 and 5 million tonnes per annum (Singh *et al.* 1979, Rasmussen *et al.* 1980, Harper 1985 and 1993) including a possible contribution of approximately 12 to 20% from biomass burning (Rasmussen *et al.* 1980, Harper 1993) and an unquantified contribution from fungi (Herbert *et al.* 1986). The natural production of chloromethane is far in excess of man-made inputs (26kt/yr) (Harper 1985), but even so represents only a 20% contribution to total stratospheric chlorine budgets (Prather and Watson 1990). Ozone depletion resulting from anthropogenic emissions of methyl bromide will significantly exceed that from biogenic inputs. A global annual loading of 90,000 tonnes has been calculated of which 75,000 tonnes were emitted from use of methyl bromide as a fumigant in 1972 (Penkett *et al.* 1985). More recently, Khalil *et al.* (1993) have estimated total emissions at 100,000 tonnes per annum, in close agreement with Penkett *et al.* (1985). They also calculate the oceanic source to be only about 40% of the total flux. Although a complete source reconciliation calculation has not proved possible (cf Harper 1993), the dominance of anthropogenic emissions is emphasised by this work. CFC-11 and CFC-12 constitute the major ozone depleters and although some decreases in their emissions from Europe are evident, because of the extended atmospheric lifetime of these compounds, this trend is still not reflected in baseline concentrations (Simmonds *et al.* 1993).

Natural sources of volatile chlorohydrocarbons other than chloromethane appear to be quantitatively minor. Gribble (1992) cites examples of emissions of trichloroethylene and tetrachloroethylene from oceans and volcanoes and 1,1,1-trichloroethane from oceans. Similarly, carbon tetrachloride is reported as being released from marine algae, oceans, volcanoes and drill wells. However, these findings must be interpreted with considerable caution. Simmonds *et al.* (1988) concluded that there were probably no natural sources of carbon tetrachloride and that partitioning from the atmosphere into seawater accounted for the presence of carbon tetrachloride in the oceans. Similarly, Herbert *et al.* (1986) report substantially higher atmospheric concentrations of trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane in the atmosphere of the northern hemisphere than in the southern hemisphere, indicating the dominance of emissions from industrial sources concentrated in the northern hemisphere. Conversely, chloromethane showed no such interhemispheric variation (Rasmussen *et al.* 1980).

The haloperoxidase enzymes are responsible for both biosynthesis of halometabolites (Harper 1993) and transformation of pollutants. In mammals the haloperoxidases are active against pathogenic microorganisms by catalysing the production of toxins. Chlorinated antimicrobial compounds include hypohalous acids and chloramines. The reactions do not solely

utilise chloride, however; thiocyanates and oxygen can also be transformed into antimicrobial agents (Neidleman and Geigert 1986).

Organohalogenes are useful intermediates in chemical synthesis, a property which seems to have been frequently exploited biologically as well as industrially. In wood-rotting fungi, chloromethane is an intermediate in the synthesis of veratryl alcohol, of central importance in the catabolism of lignin (see eg Harper 1993). In experimental situations the addition of exogenous chloromethane can induce the manufacture of veratryl alcohol earlier in the growth cycle than would otherwise occur. In the Hymenochaetae synthesis and utilisation may become uncoupled in the final stages of growth, resulting in the release of chloromethane. In many species, however, the production and utilisation of chloromethane are tightly coupled, with little or no release of the intermediate. It is suggested that chloromethane has a role in other methylation systems in fungi and higher plants, though again, in many cases, it may remain tightly channelled into subsequent synthetic steps and thus not be freely available.

Where halometabolites are the final product of a synthetic pathway, they often have defensive or biocidal properties. Again, industrial development has exploited the toxicity of these compounds in the manufacture of herbicides and insecticides. The naturally produced antibiotics chloramphenicol, griseofulvin and aureomycin are chlorinated. Neidleman and Geigert (1986) point out that halogenation of compounds may significantly enhance their biological activity. This is evident in the number of both artificial and natural organohalogenes with biocidal properties. Increases of biological activity are dependent on degree and position of chlorination, and the chemical nature of the halogen, though the relative importance of these factors is highly variable. Toxicity of chlorophenols to yeast strains increases with degree of chlorination and toxicity increases of 500-fold over that of phenol itself have been recorded. In the case of the chloro-3-nitropyrroles, toxicity of the 2,4,5-trichloro-3-nitropyrrole is exceeded by several mono- and di-substituted congeners. In general, the 4,5-dichlorinated congener, which occurs naturally, has the greatest activity, but a single chlorine substituent at the 2-position is more active than several other di- and tri-substituted congeners. Effectiveness against different organisms can also be related to positioning of halogen atoms; 2-chloro-3-nitropyrrole has greater effect on gram positive and negative bacteria than does the 5-isomer. With respect to the yeast and fungi, the 2,5- and 4,5-isomers have greater inhibitory powers than the 2,4-isomer.

Hay and Fenical (1988) review the use of chemical deterrents in marine algae. 5-600 secondary compounds, including numerous halogenated acetogenins, terpenes and phenolics have been isolated. These are effective as defence against both microorganisms and invertebrate grazers. Neidleman and Geigert (1986), in reviewing marine halogenated defence compounds, report that a strong correlation between organohalogen content of extracts from microorganisms and the extracts' antimicrobial content has been found. The chlorobrominated monoterpene extracted from the red alga *Plocamium telfairiae* has strong insecticidal properties (Watanabe *et al.* 1989). Many defence compounds produced by marine organisms are brominated: bromoketones and brominated phenols are produced by the red algae; a

brominated diphenylamine derivative is found in the green algae; panacene, brucadene and isobrusadol come from the algae *Laurencia*, *Plocambium* and *Chondria* spp. These latter compounds are also utilised by the sea hare (*Aplysia* spp.) which accumulates them from the algae which synthesise them, and on which it feeds.

In the terrestrial environment, organohalogenes with identified deterrent function are less numerous, though the highly toxic fluoroacetic acid produced by some tropical plants (Vartiainen 1994) is thought to prevent attack by rodents. Grasshoppers synthesise 2,5-dichlorophenol to repel ants and it is thought that acorn worms utilise bromophenols in a similar antipredatory role (Gribble 1992).

Other organohalogenes function as messenger compounds; the female of some species of hard tick secrete 2,6-dichlorophenol as a sex pheromone. Iodinated thyroid growth hormones in humans are an example of an endogenous messenger, active at very low concentrations. Thus whilst the purpose of the majority of halometabolites remains to be elucidated, it is clear that many, and probably the majority, have evolved into finely balanced roles of biochemical and ecological importance.

Environmental determination of natural AOX

Recently, high levels of organically bound halogen, measured as the sum parameter AOX, have been found in terrestrial ecosystems not known to be industrially contaminated (see eg. Asplund *et al.* 1989, Asplund and Grimvall 1991, Asplund 1992, Enell and Wennberg 1989 and 1991). AOX levels measured in soils worldwide range from 4 $\mu\text{g Cl/g d.w.}$ (Botswana) to 348 $\mu\text{g Cl/g d.w.}$ (Sweden). Reasons for the wide variation are not immediately apparent, though in general organic soils contained higher levels. Furthermore, forest environments contained higher levels than grasslands and northern countries such as Sweden, the UK, Canada and Iceland demonstrated higher levels than Equatorial and southern nations (Botswana, Zimbabwe, Malaysia). Peat bogs also exhibited some of the most elevated concentrations (Asplund and Grimvall 1991). Mechanisms of production are unclear, though there is some evidence for halogenation of soil as well as biosynthesis and release of halometabolites. It is possible that low-molecular weight organohalogenes are produced by soil organisms and later become incorporated into humic matter. Halide ion could also be incorporated in the same way. Peroxidase enzymes, present in almost all organisms and excreted by saprophytes, could be responsible for such incorporation. Experimentation indicates that incorporation of chlorine proceeded best under acidic conditions (Asplund 1992, Asplund *et al.* 1993). This is consistent with *in vitro* experiments using chloroperoxidases and could partly explain the higher AOX levels in bogs, heaths and forest environments where acid soils are more prevalent.

The extent of enzyme-mediated incorporation of low molecular weight organohalogenes into soil organic matter has not yet been investigated in detail, nor has the potential anthropogenic influence on such a process. As discussed above, although wood-rotting fungi utilise chloromethane extensively in metabolic processes, the majority of production is tightly

coupled to subsequent synthetic steps and the release of chloromethane is limited to certain genera at restricted periods of the growth cycle (Harper 1993). Another potential source of low molecular weight organohalogenes is atmospheric deposition under both wet and dry conditions.

Atmospheric deposition is known to be a major source of input of many types of pollutants to environmental systems. Almost all organochlorine compounds investigated as environmental pollutants have been measured in precipitation. Dry deposition and fog are also quantitatively important. Fog is an important medium of deposition for some hydrophobic chemicals; it has been estimated that 100-fold more PCBs are deposited in urban fog than by dry deposition (Capel *et al.* 1991). Landsberger *et al.* (1988) analysed rainwater in Ontario using neutron activation analysis (NAA) which can distinguish between bromine, chlorine and iodine. Their results indicate that concentrations of chlorine and iodine had been subject to anthropogenic influence. High levels of C1 and C2 halocarbons have been found in the atmosphere, soil environment and biomass of seemingly remote European areas (Frank *et al.* 1989, Frank and Frank 1989, Frank *et al.* 1991, Frank 1991). Elevated concentrations of more labile organochlorine solvents over landmasses indicate their industrial origin (Frank *et al.* 1991) and transportation to remote sites has been demonstrated (Frank 1991). Some of these solvents have phytotoxic degradation products and so are suspected to be involved in forest decline in these remote areas (Frank 1991). It is also possible that atmospheric inputs of anthropogenic halogenated hydrocarbons may be incorporated into soil, contributing to soil AOX concentrations.

Enell and Wennberg (1991) estimated mass balances of AOX in Sweden. Wet deposition of AOX equated with riverine transport to the sea at 5,100 and 5,200 tonnes AOX per year respectively. The physical and chemical dynamics operating within this system are unknown. Some proportion of the atmospheric input could be subject to chemical or biological modifications while some could be leached into rivers without structural alterations. A range of factors could influence these dynamics, including nature of deposited chemicals, soil environment and microorganisms, pH, temperature and hydrological characteristics of catchments. A complex situation is thus to be expected, and one which will require extensive work to elucidate.

Interaction between natural systems and anthropogenic organohalogenes

The biological transformation of organochlorines is well known (see e.g. Neilson 1990), though in many cases the byproducts have not been identified. Peroxidase mediated dimerisation of chlorophenols to polychlorinated dibenzo-p-dioxins and dibenzofurans has been demonstrated in a number of studies, both *in vitro* (Öberg *et al.* 1990, Öberg and Rappe 1992) and in sewage sludge (Öberg and Rappe 1993). Chlorophenols have been recorded in U.K. sewage sludges at an average of 34.6 mg/kg d.w. (range 16.5-60.5 mg/kg d.w.) (Wild *et al.* 1993) indicating considerable potential for the biological formation of PCDD/Fs. Malloy *et al.* (1993) also postulate the biogenic formation of higher chlorinated dioxins and furans from pentachlorophenol in composting of yard waste. Thus the interaction of the chloro-

phenols with biological systems can both enhance their toxicity and increase their environmental persistence, strengthening arguments for ceasing their manufacture and use.

Oxidases also frequently have a role in the biochemical response to absorbed pollutants, and they can in some cases increase their toxicity (Buhler and Williams 1988). Anaerobic degradation of chlorinated solvents can lead to highly toxic products such as vinyl chloride in groundwater (Vogel and McCarty 1985). Transformation products of organochlorine pollutants have in many cases only recently been identified. In the case of the PCBs, metabolic methyl sulphone derivatives were first identified in seals in 1976, according to Haraguchi *et al.* (1990). Extractable organic chlorine (EOCl) analyses indicate that only 10-15% of EOCl in fish consists of identified pollutants (Wesén *et al.* 1990). After hydrolysis of cod liver fat, however, 70% of the total EOCl could be accounted for in acidic and neutral fractions. It appears that hydroxylated pollutants or pollutant degradation products had esterified with fatty acids. Similarly, chlorinated carboxylic acids could form esters with glycerol. Newsome *et al.* (1993), studying Great Lakes fish, found that concentrations of organic chlorine measured by neutron activation analysis were between 5 and 72 times higher than those attributable to PCBs and organochlorine pesticides. The unidentified organochlorine content was found to be associated with the high molecular weight lipid fraction, again suggesting the possibility of conjugation. The exact structure and individual toxicity of these conjugates has not yet been investigated, but when extracts from seal blubber were fractionated, the fraction containing the PCBs and DDTs exhibited less toxicity than the fractions containing the PCB methyl sulphones and other less persistent compounds (Ewald 1989). Other contaminants include the chlorinated paraffins which are neurotoxic in fish and bioaccumulate (Svanberg *et al.* 1978). After short-term toxicity tests it was found that much of the chlorinated paraffins were retained in the test organisms, though in an altered chemical form (Madely and Birtley 1980).

Tris(4-chlorophenyl)methanol has been found in the tissues of marine mammals and birds eggs from several global locations and in samples dating back to the 1950s (Walker *et al.* 1989, Jarman *et al.* 1992). It has subsequently also been determined in human milk (Rahman *et al.* 1993). This compound is structurally related to the pesticides dicofol and DDT, but analysis of formulations of these pesticides have so far proved negative. Dyes, antihelminthic drugs and a methyl methacrylate polymer could possibly be responsible for environmental inputs of this chemical, but the identity of its source or sources, has yet to be discovered (Walker *et al.* 1989).

Limitations and strengths of AOX as an analytical parameter

Unfortunately, use of a group parameter such as AOX does not allow accurate source identification without extensive further research. The non-specificity of the analytical method can also lead to a variety of inaccuracies if incorrectly carried out. The prepared sample is combusted at 950-1000 degrees centigrade and the released halide ions titrated against silver ions. Removal of inorganic halides prior to analysis is therefore required. Inorganic halides at concentrations found in brackish waters may adversely affect detection limits (Grøn 1990a).

Chloride content of aquatic microorganisms may cause interference in eutrophic waters (Asplund 1992), and the inclusion of soil animals could have a similar effect. The use of chlorinated reagents in isolation of humic and fulvic acid must be avoided to prevent overestimation (Grøn and Raben-Lange 1992). Nitrogen and sulphur compounds can also interfere with the standard combustion/titration methods. The importance of this interference has not been evaluated for all systems. It is estimated that where a washing step with concentrated sulphuric acid is employed between combustion and coulometry, up to 0.5 mg of organic nitrogen or the same amount of organic sulphur can be accommodated (Grøn 1990 a and b). Most importantly, although it is conventional to report AOX as organic chlorine, the titration method is unable to differentiate between bromine, iodine and chlorine. The strongly oxidising conditions of the German DIN Standard 38409 method (DIN 1985), will precipitate some, but not all, bromide as HOBr. The remaining bromine, as well as iodine, will be measured in the final titration. Iodine will also interfere with the ISO (1989) method; it is noted that inorganic iodine may interfere with absorption and titration and organic iodine can cause non-reproducibly high results. Wong (1991) reports approximately 3 ppm iodine in soils and 5 ppm in peats. It has been stated that "studies have shown that Br can be included in AOX analysis, probably in a comparatively small amount" (Enell *et al.* 1989) and "studies have shown that bromide (Br) can be included in AOX analyses, probably in a comparatively small amount", say, less than 10% (Enell and Wennberg 1991). No supporting data or citations are provided for these assertions. Contradictory evidence comes from Danish soil humic acid analyses, finding 0.15% chlorine, 0.08% bromine and 0.01% iodine by weight, of which 65% was in the organic form. This equates to a molecular Cl:Br ratio of 4.2:1 for the total halogen content, but the relative concentrations of organochlorine and organobromine in AOX was not ascertained (Grøn and Raben-Lange 1992). Thus it is evident that the absence of reliable data regarding the relative concentrations of the three species in the sample matrix may hamper interpretation of AOX results.

These considerations aside, AOX can be an invaluable tool in many research areas. It has allowed rapid identification of major reservoirs and fluxes of halogenated hydrocarbons, as discussed previously, identifying targets for analysis by more specific techniques. It can also be used to monitor chemical and biochemical reactions that are too complex to be investigated in any other way.

AOX as a regulatory tool; application and alternative strategies

AOX has been widely applied as a regulatory parameter, particularly for pulp and paper effluents, which, because of their high content of large, chlorinated biomolecules (MW > 1000), have proved extremely difficult to characterise. However, its inability to reliably predict effluent environmental toxicity is now well known. The Canadian Federal Government decided that there was no scientific basis for setting an AOX parameter for the control of pulp mill discharges after finding that it did not provide a reliable estimate of persistence, bioaccumulation or environmental toxicity (Carey *et al.* 1992).

The interferences from high inorganic halides discussed above preclude it from being used effectively in a marine setting, nor is it suitable for analysis of animal tissue. EOX (extractable organic halogen) has been used for both these types of sample (Grøn 1990), though it may not be directly comparable with AOX measurements. Finally, in the context of pollution control, the recently discovered pools of natural AOX in the soil environment must be regarded as an interference. No direct comparison of natural AOX with anthropogenic contamination can be considered valid. Enormous structural differences exist between the types of compounds under consideration. Degree of halogenation, often related to toxicity and resistance to biodegradation, is frequently orders of magnitude higher in industrial organohalogenes than natural ones. Polychlorinated halometabolites are comparatively rare; industrial chemicals generally contain far higher levels of chlorine. For example, the most widely used technical mix of PCBs contains 54% by weight of chlorine. There are also enormous structural differences between the majority of natural organohalogenes and their industrial counterparts. They have a higher carbon:chlorine ratio and far greater inclusion of other elements such as oxygen. This is likely to make the natural compounds much more amenable to degradation and prevent them bioaccumulating to the same degree as anthropogenics.

Although the difference in nature and ecotoxicology of the chlorinated biomolecules and chlorinated petrochemicals must be acknowledged, on the other hand it must not be assumed that the natural organohalogen content of soils is entirely non-toxic. No comprehensive appraisal of the toxicity of natural AOX has been carried out, though many of the organohalogenes produced by chlorination of naturally occurring organic matter in pulp bleaching and water chlorination are known to be toxic. The strong mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone (MX), for example, is reported to be the single largest contributor identified (Vartiainen *et al.* 1988) and is produced during chlorination of water with high humic content and in chlorinated pulp bleaching effluents (Backlund *et al.* 1988 and 1989, Holmbom 1990).

Yet if the group measures of halogens, or indeed non-halogenated pollutants, are ineffective as control measures, what tools are available to ensure that environmental discharges do not cause harm? The traditional approach requires calculation of a notional assimilative capacity of the environment for pollutants on a substance-by-substance basis. However, full characterisation of effluents is a tremendous task in analytical terms, even for the comparatively simple petrochemical effluents, as has been described by Johnston and Stringer (1991). Research of this nature is extremely slow and carries with it a comparable economic burden. Costs of effluent evaluation and routine monitoring at this level of complexity would be prohibitive. Even when substances emitted from a point source have been described, their persistence, behaviour and toxicity must be evaluated. Scientists from the U.K. Ministry of Agriculture, Fisheries and Food and the Natural Environment Research Council attempted to identify anthropogenic compounds, including phthalate esters and organohalogenes, in UK estuaries and the coastal North and Irish Seas (Law *et al.* 1990). These researchers were forced to conclude that amongst the limited subset of chemicals positively identified and quantitated, a reliable environmental impact dataset existed only for xylene. They state that imports of toluene, xylene and chlorobenzene via sea were a primary reason for concern, but

industrial inputs into the same waterways have been analysed by similar GC/MS techniques (Johnston and Stringer 1991, Johnston *et al.* 1991) and were frequently found to contain these same pollutants (Stringer, unpublished data). Nevertheless, diffuse or mobile sources are particularly difficult to evaluate, further complicating the task of assessing 'acceptable' rates of pollutant discharge. Ultimately, it must be recognised that this approach is not only technically and economically impossible, but it has also been repeatedly demonstrated as failing to protect the environment from harm. Each new environmental contamination issue, from Minamata Bay to ozone depletion, has been an example of the calculations and assumptions on which this permissive approach are based have been wrong.

The only feasible alternative strategy, and one which is being increasingly widely implemented at both the national and international level, is the precautionary approach. This employs a different philosophy in relation to releases of pollutants. Instead of allowing the discharge of compound unless (or in practical terms, until) damage to the environment has been proven, it requires that materials should not be discharged unless it can be established that they will not be deleterious. It also avoids problems deriving from the limitations of our understanding of toxicology by removing the assumption that a safe level of a particular compound or compounds can be estimated. Thus industry is often not just required to restrict emissions of environmental toxins, but to reduce them to zero. For example, the Contracting Parties to the Barcelona Convention agreed in October 1993 to phase out inputs from land-based sources to the Mediterranean of categories of known and suspected pollutants. Specifically, the following recommendations were passed (UNEP 1993):

'...the Contracting Parties reduce and phase out by the years 2005 inputs to the marine environment of toxic, persistent and bioaccumulative substances listed in the LBS Protocol, in particular organohalogen compounds having those characteristics....'

and:

'to promote measures to reduce inputs into the marine environment and to facilitate the progressive elimination by the year 2005 of substances having proven carcinogenic, teratogenic and/or mutagenic properties in or through the marine environment.'

Similarly, the Paris Convention agreed in September 1992 to the following commitment under Article 3 of Annex I on the Prevention and Elimination of Pollution from Land-based Sources:

'...it shall, inter alia, be the duty of the (Paris) Commission to draw up:

(a) plans for the reduction and phasing out of substances that are toxic, persistent and liable to bioaccumulate arising from land-based sources;'

In addition, the Paris Conference Ministers adopted a future action plan which calls for substantial reduction of inputs to the maritime area with the aim of their elimination, for sub-

stances that are toxic, persistent and liable to bioaccumulate, with priority given to the organohalogenes.

The Ministerial Declaration takes this approach one step further by agreeing, inter alia, to the following:

'Agree that, as a matter of principle for the whole Convention area, discharges and emissions of substances which are toxic, persistent and liable to bioaccumulate, in particular organohalogen substances, and which could reach the marine environment should, regardless of their anthropogenic source, be reduced, by the year 2000, to levels that are not harmful to man or nature -with the aim of their elimination; to this end to implement substantial reduction in those discharges and emissions and where appropriate, to supplement reduction measures with programmes to phase out the use of such substances; and instruct the Commissions to keep under review what timetables this would require;'

The phase out of the chemical family of organohalogenes despite the fact that is not solely of anthropogenic origin is in no way anomalous. Our understanding of the creation, structure and function of natural organohalogenes is still embryonic, but it is already apparent that they have considerable biological activity and functions that are essential to the survival not just of individual organisms, but of species and ecosystems. Indeed, in the light of these findings, there can be no possible justification for saturating natural organohalogen budgets with anthropogenically derived halogenated compounds.

References

- Asplund, G. (1992) On the origin of organohalogenes found in the environment, Linköping Studies in Arts and Science No. 77, Linköping: Linköping University
- Asplund, G., V. Christiansen and A. Grimvall (1993) 'A chloroperoxidase-like catalyst in soil: detection and characterization of some properties', *Soil Biol. Biochem.* **25**(1), 41-46
- Asplund, G. and A. Grimvall (1991) 'Organohalogenes in nature', *Sci. Tot. Environ.* **25**(8), 1346-1350
- Asplund, G., A. Grimvall. and C. Petersson (1989) 'Naturally produced adsorbable organic halogenes (AOX) in humic substances from soil and water', *Sci. Tot. Environ.* **81/82**, 239-248
- Backlund, P., L. Kronberg and L. Tikkanen (1988) 'Formation of Ames mutagenicity and of the strong bacterial mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone and other halogenated compounds during disinfection of water', *Chemosphere* **17**(7), 1329-1336
- Backlund, P., E. Wondergem, K. Voogd and A. de Jong (1989) 'Mutagenic activity and presence of the strong mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone in chlorinated raw and drinking waters in the Netherlands', *Sci. Tot. Environ.* **84**, 273-282
- Buhler, D.R. and D.E. Williams, (1988) 'The role of biotransformation in the toxicity of chemicals', *Aquatic Toxicology* **11**, 19-28
- Capel, P.D., C. Leuenberger and W. Giger (1991) 'Hydrophobic organic chemicals in urban fog', *Atmos. Environ.* **25A**(7), 1335-1346
- Carey, J.H., P.V. Hodson, K.R. Munkittrick and M.R. Servos (1992) Recent Canadian studies on the physiological effects of pulp mill effluent on fish, Burlington: Environment Canada
- DIN (1985) Bestimmung der adsorbieren organisch gebunden Halogene (AOX) (DIN 38409) Teil 14 Summarische Wirkungs- und Stoffkenngrößen (Gruppe H) Berlin: Beuth-Verlag
- Enell, M., L. Kaj, and L. Wennberg (1989) 'Long-distance distribution of halogenated organic compounds (AOX)', in Laikari, H., ed., River Basin Management Oxford: Pergamon

- Enell, M. and L. Wennberg (1991) 'Distribution of halogenated organic compounds (AOX)- Swedish transport to surrounding sea areas and mass balance studies in five drainage systems', *Wat. Sci. Tech.* **24**(3/4), 385-395
- Engvild, K.C. (1986) 'Chlorine-containing natural compounds in higher plants', *Phytochemistry* **25**(4), 781-791
- Ewald, G. (1989) *In vitro* toxicity testing of organic compounds extracted from seal blubber, Lund: University of Lund
- Frank, H. (1991) 'Airborne chlorocarbons, photooxidants, and forest decline', *Ambio* **20**(1), 13-18
- Frank, H. and W. Frank (1989) 'Uptake of airborne tetrachloroethene by spruce needles', *Environ. Sci. Technol.* **23**(5), 365-367
- Frank, H., W. Frank and D. Thiel (1989) 'C₁- and C₂- halocarbons in the soil-air of forests', *Atmos. Environ.* **23**(6), 1333-1335
- Frank, W., H.J.C. Neves, and H. Frank (1991) 'Levels of airborne halocarbons at urban and mountain sites and at the Atlantic coast', *Chemosphere* **23**(5), 609-626
- Gribble, G.W. (1992) 'Naturally occurring organohalogen compounds- a survey', *J. Nat. Prod.* **55**(10), 1353-1595
- Grøn, C. (1990a) Techniques in Marine Environmental Sciences No. 10. Organic halogens: determination in marine media of adsorbable, volatile or extractable total compounds, Copenhagen: International Council for the Exploration of the Sea
- Grøn, C. (1990b) 'Organic group parameters in ground water investigations. Part 3' *Chemosphere* **21**(1-2), 135-152
- Grøn, C. and B. Raben-Lange (1992) 'Isolation and characterization of a haloorganic soil humic acid', *Sci. Tot. Environ.* **113**, 281-286
- Haraguchi, K., A. Bergman, M. Athanasiadou, E. Jakobsson, M. Olsson, and Y. Masuda (1990) 'PCB methyl sulphones in grey seal and otter from Swedish environment' in O. Hutzinger and H. Fiedler, eds. Organohalogen Compounds Volume 1. Toxicology, Environment, Food, Exposure-Risk, Bayreuth, Eco-Infirma Press
- Harper, D.B. (1985) 'Halomethane from halide ion- a highly efficient fungal conversion of environmental significance', *Nature* **315**, 55-57
- Harper, D.B. (1993) 'Biogenesis and metabolic role of halomethanes in fungi and plants' in Sigel and Sigel (Eds.), Metal Ions in Biological Systems, Volume 29 Biological Properties of Metal Alkyl Derivatives, Marcel Dekker Inc
- Hay, M.E. and W. Fenical (1988) 'Marine plant-herbivore interactions: The ecology of chemical defense', *Ann. Rev. Ecol. Syst.* **19**, 111-145
- Herbert, P., P. Carbonnier, L. Rivolta, M. Servais, F. Van Mensch, and L. Campbell (1986) 'The occurrence of chlorinated solvents in the environment', *Chem. Ind.* 1986, 861-869
- Holmbom, B. (1990) 'Mutagenic compounds in chlorinated pulp bleaching waters and drinking waters', in Vainio, Sorsa and McMichael, eds. Complex Mixtures and Cancer Risk IARC
- ISO (1989) International Standard Organisation, Water Quality- Determination of Adsorbable Organic Halogens (AOX) ISO 9562
- Jarman, W.M., M. Simon, R.J. Norstrom, S.A. Burns, C.A. Bacon, B.R.T. Simoneit and R.W. Riseborough (1992) 'Global distribution of tris(4-chlorophenyl)methanol in high trophic level birds and mammals', *Environ. Sci. Technol.* **26**(9), 1770-1774
- Johnston, P.A. and R.L. Stringer (1991) 'Protecting the North Sea: the analytical challenge. Analytical difficulties in the full characterisation of industrial effluents', *Anal. Proc.* **28**, 249-250
- Johnston, P.A., M. MacGarvin and R.L. Stringer (1991) 'Regulation of effluents and implications for environmental policy', *Wat. Sci. Technol.* **24**(1), 19-27
- Khalil, M.A.K., R.A. Rasmussen and R. Gunawardena (1993) 'Atmospheric methyl bromide: trends and global mass balance', *J. Geophys. Res.* **98**(D2), 2887-2896
- Landsberger, S., J.J. Drake and S.J. Vermette (1988) 'Enriched concentration of bromine, chlorine and iodine in urban rainfall as determined by instrumental neutron activation analysis', *Chemosphere* **17**(2), 299-307

- Law, R.J., T.W. Fileman and P. Matthiessen (1991) 'Phthalate esters and other industrial organic chemicals in the North and Irish Seas', *Wat. Sci. Technol.* **24**(10), 127-134
- Lovelock, J.E. (1975) 'Natural Halocarbons in the air and in the sea', *Nature* **256**, 193-194
- Madely, J.R. and R.N. Birtley (1980) 'Chlorinated paraffins and the environment. 2. Aquatic and avian toxicity', *Environ. Sci. Technol.* **14**(10), 1215-1221
- Malloy, T.A., T.D. Goldfarb and M.T.J. Surico (1993) 'PCDDs, PCDFs, PCBs, chlorophenols (CPs) and chlorobenzenes in samples from various types of composting facilities in the United States', *Chemosphere* **27**(1-3), 325-334
- Neidleman, S.L. and J. Geigert (1986) *Biohalogenation: Principles, Basic Roles and Applications*, Chichester: Ellis-Horwood, 203pp
- Neilson, A.H. (1990) 'The biodegradation of halogenated organic compounds', *J. Appl. Bacteriol.* **69**, 445-470
- Newsome, W.H., P. Andrews, H.B.S. Conacher, R.R. Rao and A. Chatt (1993) 'Total organochlorine content of fish from the Great Lakes', *J. Ass. Off. Anal. Chem.* **76**(4), 703-706
- Öberg, L.G., B. Glas, S.E. Swanson, C. Rappe and K.G. Paul (1990) 'Peroxidase-catalyzed oxidation of chlorophenols to polychlorinated dibenzo-p-dioxins and dibenzofurans', *Arch. Environ. Contam. Toxicol.* **19**, 930-938
- Öberg, L.G. and C. Rappe (1992) 'Biochemical formation of PCDD/Fs from chlorophenols', *Chemosphere* **25**(1-2), 49-52
- Öberg, L.G. and C. Rappe (1993) Presented at International Conference on Naturally-Produced Organohalogenes, Delft, The Netherlands.
- Penkett, S.A., B.M.R. Jones, M.J. Rycroft and D.A. Simmons (1985) 'An interhemispheric comparison of the concentration of bromine compounds in the atmosphere', *Nature* **318**, 550-553
- Prather, M.J. and R.T. Watson (1990) 'Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine', *Nature* **344**, 729-734
- Rahman, M.S., L. Montanarella, B. Johansson and B.R. Larsen (1993) 'Trace levels of tris(4-chlorophenyl)-methanol and -methane in human milk', *Chemosphere* **27**(8), 1487-1498
- Rasmussen, R.A., M.A.K. Rasmussen, M.A.K. Khalil and R.W. Dalluge (1980) 'Concentration of distribution of methyl chloride in the atmosphere', *J. Geophys. Res.* **85**, 7350-7356
- Simmonds, P.G., D.M. Cunnold, F.N. Alyea, C.A. Cardelino, A.J. Crawford, R.G. Prinn, P.J. Fraser, R.A. Rasmussen and R.D. Rosen (1988) 'Carbon tetrachloride lifetimes and emissions determined from daily global measurements during 1978-1985', *J. Atmos. Chem.* **7**, 35-58
- Simmonds, P.G., D.M. Cunnold, G.J. Dollard, T.J. Davies, A. McCulloch and R.G. Derwent (1993) 'Evidence of the phase-out of CFC use in Europe over the period 1987-1990', *Atmos. Environ.* **27A**(9), 1397-1407
- Singh, H.B., L.J. Salas, H. Shigeishi and E. Scribner (1979) 'Atmospheric halocarbons, hydrocarbons and sulphur hexafluoride: global distribution sources and sinks', *Science* **203**, 899-903
- Svanberg, O., B-E. Begtsson, E. Linden, G. Lunde and E.B. Ofstad (1978) 'Chlorinated paraffins - a case of accumulation and toxicity in fish', *Ambio* **7**(2), 64-65
- UNEP (1993) Recommendations approved by the Contracting Parties UNEP/OCA/CRP.2 Athens: UNEP
- Vartiainen, T. (1994) Presented at International Conference on Naturally-Produced Organohalogenes, Delft, The Netherlands.
- Vartiainen, T., A. Liimatainen, P. Kauranen and L. Hiisvirta (1988) 'Relations between drinking water mutagenicity and water quality parameters', *Chemosphere*, **17**(1), 189-202
- Vogel, T.M. and P.L. McCarty, (1985) 'Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions', *Appl. Environ. Microbiol.* **49**(5), 1080-1083
- Walker, W., II., R.W. Riseborough, W.M. Jarman, B.W. de Lappe, J.A. Tefft and R.L. DeLong (1989) 'Identification of tris(chlorophenyl)methanol in blubber of harbour seals from Pudget Sound', *Chemosphere* **18**(9-10), 1799-1804
- Watanabe, K., M. Miyakado, N. Ohno, A. Okada, K. Yanagi and K. Moriguchi (1989) 'A polyhalogenated monoterpene from the red alga, *Plocamium telfairiae*', *Phytochemistry* **28**(1), 77-78

- Wesén, C., G.E. Carlberg and K. Martinsen (1990) 'On the identity of chlorinated organic substances in aquatic organisms and sediments', *Ambio* **19**(1), 36-38
- Wild, S.R., S.J. Harrad and K.C. Jones (1993) 'Chlorophenols in digested U.K. sewage sludges', *Wat. Res.* **27**(10), 1527-1534
- Wong, G.T.F. (1991) 'The marine geochemistry of iodine', *Rev. Aquat. Sci.* **4**(1), 45-73.