Chlorinated Compounds in the Environment: An Interpretive Review

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Abstract
We present a comprehensive assessment of the potential adverse effects of past, present and expected future ambient concentrations of chlorine and chlorinated organic chemicals on the health of humans, and aquatic and terrestrial wildlife. The assessment is based on a comparison between exposure limits known not to cause adverse effects and rates of exposure resulting from estimated environmental concentrations of chlorinated organic chemicals, by integrating information on anthropogenic and natural sources, physical/chemical properties, environmental fate and toxicology/epidemiology. Evaluations were conducted on chlorinated organic chemicals representing eight product or process categories including: chlorine, polyvinyl chloride (PVC) and vinyl chloride monomer (VCM), pesticides, polychlorinated biphenyls (PCBs), pulp and paper products and effluents, drinking water and waste water, incineration and solvents.

Introduction
Since the beginning of this century, a number of useful, synthetic, halogenated hydrocarbons have been produced. Due to the fact that chlorine is the halogen in greatest, readily-available supply and the fact that chlorine is such a good "leaving group" in synthesis reactions, chlorinated hydrocarbons have been the dominant class of compounds used. Due to their unique and useful properties an number of these compounds have found their way into commerce. Some of these compounds were manufactured in great quantities and were released either intentionally or unintentionally to the environment where they have persisted and accumulated into biota. The results of field and laboratory studies with wildlife has indicated that, in at least some locations, the concentrations attained by the compounds, either singly or in combination would have been sufficient to cause observed adverse effects. Other than in cases of occupational exposure or spills effects on the general human population have not been demonstrated.

It has been suggested that future problems with chemicals in the environment can be avoided if all uses of chlorine technology were banned. Alternatively, we propose that by using sound scientific principles and conducting detailed risk assessments, it should be possible to use chlorine technology in a responsible, safe manner so that the beneficial uses of chlorine and chlorinated compounds can be maintained while avoiding adverse effects to either wildlife or humans.

Methods
Chlorinated chemicals used or produced in a number of product or process categories were initially identified and grouped by chemical class. From this comprehensive list, chemicals

and chemical groups, representing various degrees of hazard, persistence, bioaccumulation and exposure, as well as toxicological mechanisms were selected for detailed assessment (Delzell et al, 1994). The assessment concentrated on those compounds which, due to the quantity produced or measured in the environment or known to have great persistence or those thought to result in the greatest probable risk were examined in detail, even if their production has been stopped and their release to the environment greatly curtailed. In addition, compounds that are known to have additive effects in complex mixtures were also considered. Finally, those classes, which have been implicated as potentially hazardous by previous research were investigated in detail. A detailed review of the literature was conducted for these representative, exemplary or important chlorinated chemicals with emphasis on: Relative contributions of sources from activities or to natural production; to total concentrations in the environment; physical/chemical properties; environmental fate and bioaccumulation; toxicology in mammalian, aquatic and avian species; and human and wildlife epidemiology. Using temporal data on current or historical concentrations of these representative chemicals as well as those expected in the future, hazard/exposure analyses or risk assessments were conducted for aquatic and terrestrial wildlife and humans by comparing probable exposures to dose-response relationships. These assessments of potential adverse effects on humans or wildlife were based on the following fundamental scientific principles: **i)** dose-response relationships exist; the magnitude of the biological response is proportional to the dose in such a way that responses can be reported as probabilities of occurrence, and chemicals have exposure thresholds below which the probability of adverse effects is not quantifyable; **ii)** the biological significance of a response is related to the nature, degree and severity of the response, and the toxicological mechanisms involved; **iii)** inherent metabolic processes allow organisms to adapt to and thus tolerate measurable doses of chemicals; **iv)** dose is proportional to the rate of exposure and available fraction; **v)** chemical concentrations in environmental media represent the net difference between quantities and rates of release of chemicals into the environment from all sources (human activities and natural production) and the rates of elimination or degradation of the chemicals from the environment; **vi)** the environmental fate and bioaccumulative potential of organic chemicals are directly related to their physical/chemical properties; organic chemicals with high log K_{ow} values, low water solubilities, low vapor pressures and slow degradation characteristics tend to be more persistent in the environment and have a greater potential for bioaccumulation in food chains; vi) structure-activity relationships exist and can be useful for identifying chemicals for which further toxicological and environmental fate information should be gathered; and **vii)** statistical associations cannot be used in isolation to prove cause-effect relationships. The conclusions of the chapters on specific products or process categories were as follows:

Polyvinyl Chloride (PVC)/Vinyl Chloride Monomer (VCM): PVC is a solid, stable and environmentally inert polymer of VCM subunits. PVC is used in the production of numerous household and industrial products. Historically, the potential health concern regarding PVC polymer was residual VCM in PVC products. Today, residual concentrations of VCM in PVC products are extremely low and present no hazard to the general population. VCM exposures in manufacturing facilities, prior to the 1970s, resulted in hepatic angiosarcoma in some workers. Through improved technology and manufacturing practices, the concentrations of VCM in the workplace are now below those that cause adverse effects. At no time have ambient environmental concentrations of VCM been sufficiently great to cause adverse effects in humans or wildlife.

Pesticides: Whether natural or synthetic in origin, chlorinated or non-chlorinated, the toxicity of a pesticide depends on specific molecular configurations that affect the physical/chemical properties and reactivity, not on the presence of chlorine. Accordingly, certain chlorinated pesticides are less toxic than their non-chlorinated counterparts. Regulatory control of pesticides now involves comprehensive and effective risk/benefit analysis and risk management. New pesticides are being developed with the objective of increasing specificity to target organisms, and eliminating the potential for food chain accumulation.

Polychlorinated Biphenyls: PCBs are members of a sub-group of chlorinated organic chemicals that have high log K_{ow} values, low solubility in water, low vapor pressures and are slowly degraded and metabolized and thus can persist and bioaccumulate. Reports of possible adverse human health effects from ambient exposures to PCBs do not follow dose-responses, and may be confounded by exposures to other chemicals, and suffer from inadequate study design. The available data indicate that ambient concentrations of PCBs would not be expected to produce adverse effects in humans. Due to the extensive past use concentrations of PCBs as well as other persistent and bioaccumulative chemicals increased dramatically in fish and piscivorous wildlife during the 1960s. The concentrations of these compounds were cumulatively sufficient to cause adverse effects and subsequent declines in wildlife populations, notably among piscivorous birds. However, a direct link to specific chlorinated, organic chemicals can not be established. Changes in habitat quality may also have an impact on wildlife population density. Coincident with decreasing concentrations of PCBs and other chlorinated hydrocarbons during the 1970s and 1980s affected wildlife populations are recovering. Evidence of adverse effects remains in areas of continuing high concentrations of these compounds. Subtle biochemical effects considered to be associated with chlorinated hydrocarbons continue to be observed in piscivorous birds, but these effects do not seem to be limiting most populations except in specific areas.

Pulp and Paper: Chlorine and a variety of other agents may be used to bleach wood pulp used in the production of paper. Historically, effluents from mills using chlorine bleaching and from non-bleach mills often were untreated and were associated with adverse effects in fish and fish-eating wildlife. Concentrations of pentachlorophenol in fish near mill outfalls, measured during the 1970s, could have led to exposures, through fish consumption, that would have exceeded its human exposure limit. Today, improvements in pulping and bleaching technologies, and primary and secondary treatments of effluents by North American mills, result in much lower concentrations of chlorinated organic chemicals in receiving waters, such that exposures through consumption of fish do not exceed human exposure limits. Recent research efforts, focused on measuring enzyme activity in fish exposed to mill effluents, have demonstrated that increased enzyme induction is not restricted to mills that use chlorine.

Drinking Water and Waste Water: Chlorine is used to disinfect water for drinking and to treat waste water for release to the environment. Disinfection of drinking water and waste waters with chlorine continues to be the treatment method of choice. No other proposed method of disinfection is as effective as chlorine in achieving the main objectives of drinking water treatment: i) excellent biocidal activity; ii) improved taste and odor; and iii) residual disinfection within the distribution system. Greater knowledge of the chemistry of chlorine disinfection/oxidation has resulted in alterations in water treatment procedures that remove precursors of chlorinated organics prior to chlorination, minimize the chlorine contact time, and remove a significant proportion of the chlorinated by-products that are formed. Consequently, chlorination by-products in drinking water are generally several fold less than those reported for the 1960s and 1970s. No adverse human health effects are expected from consumption of drinking water disinfected with chlorine. Similarly, no adverse effects in aquatic or terrestrial wildlife are expected from the disinfection of waste waters with chlorine.

Incineration: Emissions of products of incomplete combustion (PICs), including chlorine and chlorinated chemicals, vary among incinerators, due in part to differences in waste feedstock composition, operating conditions, and emission control technologies. Operation of an incinerator at a high combustion efficiency with appropriate use of air emission control systems reduces the potential for the formation of PICs. The results of a case study assessment of a hazardous waste incinerator operating with the Best Available Technology (BAT) indicated that hazardous waste incinerators using such technologies will not produce adverse effects on human health.

Solvents: Chlorinated solvents are used to dissolve or disperse other chemicals and are common household and industrial chemicals. There are many natural sources of some of these chemicals that contribute to ambient environmental concentrations. Improvements in industrial containment, based on greater scientific understanding of potential environmental fate and effects, have substantially reduced total releases to the environment of chlorinated solvents from production and manufacturing facilities in the past decade. Current ambient concentrations of chlorinated solvents are not associated with adverse effects on human health or the environment.

Conclusions

The general conclusions of the report were: **i)** the presence of chlorine in a molecule does not necessarily confer unique toxic properties or bioaccumulative potential; **ii)** chlorinated chemicals span a wide range of physical/chemical properties and molecular structures, and consequently display a wide range of environmental fate characteristics and biological activities, and thus cannot be considered as a single group for the purposes of health or environmental risk assessment; **iii)** persistence and bioaccumulation are characteristic of certain highly chlorinated cyclic chemicals; however, these chemicals comprise only a small subset of the entire spectrum of chlorinated organic chemicals; **iv)** many chlorinated chemicals are produced from natural sources and in some cases, the proportional contribution to ambient concentrations from natural sources exceeds that from human activities; and **v)** technological improvements leading to reductions in the formation of chlorine-containing byproducts, decreased emissions and to reduced likelihood of accidental releases are expected to further reduce the already low probability of adverse effects to human and ecosystem health resulting from the presence of chlorinated organic chemicals in the ambient environment.

References

1) Delzell, E., J. Doull, J.P. Giesy, D. Mackay, I.C. Monro and G.M. Williams. 1994. Interpretive Review of the Potential Adverse Effects of Chlorinated Organic Chemicals on Human Health and the Environment: Polychlorinated PCBs. *Regulatory Toxicology & Pharmacology*. Special Supliment to Vol. 20 No. 1 Part 2 of 2 parts. Academic Press, Inc. New York, 1056 p.