Chapter 1

HALOGENATED ORGANIC COMPOUNDS -
A GLOBAL PERSPECTIVE

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1. INTRODUCTION

Halogenated organic compounds constitute one of the largest groups of environmental chemicals. Their use and misuse in industry and agriculture represent a large entry of these chemicals into the environment, resulting in widespread dissemination and oftentimes undesirable conditions, i.e., environmental contamination. It is important to recognize the beneficial aspects of halogenated organic compounds, as well as their potentially deleterious impact on the environment. While it is recognized that a large number of synthetic organohalides arise from anthropogenic activity, it is equally important to note that “naturally produced” organohalides abound in nature and have been present on earth for eons. In a discussion of the global cycling of halogenated organic compounds, it is necessary to consider all aspects of this diverse and biologically challenging group of compounds, including their production, biodegradation, assimilation, integration (e.g., sorption and coupling to organic matter), and also their persistence in the environment. Microorganisms impact each of these processes, and therefore play an essential role in the global cycling of organohalides. This chapter provides an overview of each of these aspects of global cycling, and the ultimate fate of organohalides in the environment.

In many respects, the chemistry of halogenated organic compounds is due to the unique physicochemical properties of their halogen substituent (F, Cl, Br, or I). At the start of the series, the carbon-fluorine bond is very strong with high polarity. With increasing molecular weight of the halogen, carbon-halogen bond energies decrease markedly, i.e., F > Cl > Br > I. Other characteristics, such as the electron-withdrawing effect of the halogen substituent impact chemical reactivity of the molecule and its heat transfer and dielectric characteristics (e.g., polychlorinated phenols; polychlorinated biphenyls, PCBs). The physical size and shape of the halogen substituent may also affect reactivity, due to steric constraints and may also hinder uptake into cells and enzymatic attack during biodegradation. In addition, the halogen moiety of an organic compound

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generally reduces its water solubility and conversely increases lipid solubility. The biological consequence of increased lipophilicity may be reduced biodegradation due to decreased bioavailability, and/or biomagnification in the food chain as the non-degraded haloorganic compounds sequester in the fatty tissues of higher animals. Finally, the halogen substituent and its potential organohalide metabolites may alter, oftentimes increasing, the inherent toxicity of the molecule. The latter characteristic is apparent both in synthetic, xenobiotic (foreign to the biosphere) compounds, such as toxic dibenzo-p-dioxins, chlorophenols, PCBs, and halogenated aliphatic compounds (tetrachloroethene, PCE; trichloroethene, TCE; vinyl chloride, VC), as well as in biologically produced natural products, such as antibiotics (e.g., chlortetracycline, chloramphenicol, drosophilin, bromopyrroles) and other antibiochemicals, produced by both micro- and macro-organisms for protection against competition and predation.

The discovery of chlorine and other halogens, and the elucidation of their unique chemistry was followed by their synthesis and large-scale industrial production and application (see 162). The scale of production (past and present) of these organohalide compounds has had direct implications for their occurrence and fate in the global environment. Organohalides are integral to a variety of applications, including use as solvents, degreasing agents, biocides, Pharmaceuticals, plasticizers, hydraulic and heat transfer fluids, intermediates for chemical synthesis, and numerous other industrial functions. Other halogenated compounds are produced as by-products during combustion, chlorine bleaching of pulp, or disinfection of water and wastewater. As a result, many halogenated organic compounds, including aliphatic, aromatic and heterocyclic derivatives, have been produced and used in vast quantities over the last 50 to 80 years. The majority of these compounds are chlorinated, but brominated, fluorinated and iodinated compounds also have industrial applications.

Historically, with increasing use, a number of the negative properties often associated with organohalide compounds had become widely evident in the 1960s. With the growing use of industrial chemicals, in particular organohalides, and their oftentimes indiscriminate dissemination in the environment, concern increased over the potential adverse effects of organohalides. This was brought to public attention in 1962 by Rachel Carson in her seminal work, “Silent Spring” (19). Further evidence for the widespread occurrence of organohalides has emerged from the development of improved sampling and analytical methods with greater sensitivity, in particular the invention of the electron capture detector for gas chromatography by James Lovelock in 1961 (104). With increased detection sensitivities, industrial organohalides have been increasingly found as trace contaminants broadly disseminated in the environment.

The initial recognition of the persistence and potential toxicity of different organohalides, and their propensity to bioaccumulate in the food chain, among other adverse effects, has led to extensive efforts to replace halogenated chemicals today. In cases where the unique physicochemical properties and/or economics of halogenated organic compounds are difficult or impossible to match with non-halogenated alternatives, greater care is exercised in their use and disposal. Current and improving regulatory guidelines and mandates will help to further control the potential adverse effects of organohalides in the environment.

Introduction of industrial halogenated compounds into the environment occurs through terrestrial, aquatic and atmospheric discharges. Therefore, their impact is on all