SHORT-CHAIN ALIPHATIC HALOCARBONS: ENVIRONMENTAL LEVELS AND ECOTOXICOLOGICAL PROPERTIES

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Introduction

Short-chain aliphatic hydrocarbons (SCAH's) are produced at a total amount of about fifteen million tons annually; some are used in emissive applications as solvents and propellants, but most are employed in closed systems as monomers for polymer production and as intermediates in chemical syntheses. The mammalian toxicological properties of most technically important SCAH's are well studied; since air levels at work places will continue to decline due to increasingly automated production, the health risks for humans associated with occupational exposure have diminished over the last decade.

On the other hand, the growth of global chemical production may entail rising environmental levels. For ecotoxicological considerations, mammalian toxicological data can only be applied with great caution, because the effects of xenobiotics upon any organism depend upon many features characteristic of the respective species, its anatomy, physiology, enzymology, etc. In addition, the parent compounds as well as their major abiotic and biotic degradation products must be taken into account, another reason why occupational risk assessments have little relevance to ecotoxicological considerations.

Compounds

The technically most important and environmentally most abundant SCAH's are:
- the tropospherically and metabolically inert anthropogenic chlorofluorocarbons (CFC's);
- the C_1- and C_2-chlorocarbon solvents dichloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene with long to intermediate environmental stability and intermediate metabolic reactivity;
- the polychloromethanes tetrachloromethane and trichloromethane, emitted inadvertantly or formed as secondary chlorination products;
- the carcinogenic C_2-halocarbons 1,2-dichloroethane and vinylchloride which may occur locally in ambient air at levels up to several $\mu g/m^3$;
- the natural methylhalides methylchloride, methylbromide, and methyliodide;
- and, since recently, various partially halogenated chlorofluorocarbons (HCFC's), mostly C_2-halocarbons with atmospheric lifetimes in the range of a few years.

SCAH

Ecotoxicological relevance and environmental levels

Analytical monitoring of SCAH's is possible with high selectivity and, thus, high sensitivity. Most SCAH's are predominantly or exclusively anthropogenic. These are the main reasons why some of them serve as "benchmark chemicals", i.e. model compounds for predicting and tracing the fate of anthropogenic organic compounds in the environment. For the same reasons, they recommend themselves for exemplary studies on the environmental impact of organic xenobiotics. Ecotoxicological properties are of interest because metabolic activation and abiotic reactions of several SCAH's entail reactive secondary pollutants of considerable reactivity and potentially elevated toxicity; chloroethenes are known to be oxidatively metabolized to epoxides and reductively to vinyl chloride, while atmospheric oxidations of SCAH's entail numerous reactive carbonyl chlorides, acyl chlorides and haloaliphatic acids.

The importance of the availability of requisite analytical methods for testing mechanistic hypotheses and for comparison of model calculations with real-world conditions cannot be overemphasized. The atmospheric levels of the short- and medium-lived SCAH's fluctuate over two orders of magnitude, so large numbers of single analytical values must be collected in order to arrive at representative data. Advances in automation and miniaturization of separation (chromatographic) methods have been a prerequisite for the progress in environmental research which is well illustrated in the gradual elucidation of atmospheric accumulation and the ozone-depleting potential of volatile halocarbons over the last two decades. As the electron-capture detector became available for gas chromatographic monitoring of halocarbon trace levels, a prime prerequisite for establishing the global network for monitoring tropospheric halocarbon levels (Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment) was fulfilled; this ultimately led to the formulation of the hypothesis of the ozone-depleting potential of CFC's - and its analytical verification in recent years.

A need for further development of analytical capabilities also exists for monitoring their environmental fate, for identification of potentially problematic secondary products, and for assessment of the ecotoxicological properties of the latter. This, however, meets considerable difficulties as many of the latter are polar, highly reactive, and present at low steady-state levels; since they are chemically reactive, they tend to decompose during the requisite sampling and enrichment steps. Due to this fact, airborne haloacetic acids have only recently been recognized as ecotoxicologically relevant, although they are amongst the most potent algal toxicants.

Chemical and Toxicological Properties

SCAH's are often treated collectively because:

- most (not all!) halocarbons are predominantly or exclusively anthropogenic;
- they are relatively non-polar, volatile and lipophilic;
- they are detectable with high selectivity and, hence, sensitivity.

The chemical stability, i.e. metabolic and environmental persistence, and the peculiar toxicological properties of some members have advanced a common regard of a particularly problematic class of compounds. On the other hand, the chemical, toxicological and environmental properties of SCAH's vary as for any other class of organic compounds, depending upon chemical structure, in particular upon the respective halogen atoms (F, Cl, Br,I). Physico-chemical properties and the chemical and metabolic reactivities of organohalides range from chemically stable to highly reactive, from metabolically inert to highly toxic.

However, there are also chemical features common to all organohalogens:
- the atomic volumes of halogens are similar to the related noble gases;
- the outer p-electron shells are filled in the bonded state;
- halogens have high electron affinity;
- C-Hal bond strengths are high, decreasing from F to I;
- C-Hal bonds are polarized, increasing from F to I.

The first two features entail moderate to weak interactions with water dipoles, high lipophilicity, and small Henry constants. Their biotic or abiotic reactivities are governed mainly by the latter three features which determine the synthetic usefulness of alkyl halides as electrophilic chemical intermediates. This is also the reason for increasing carcinogenicity of alkyl halides (e.g.: methyl fluoride, non-carcinogenic; methyl chloride, weakly carcinogenic; methyl bromide, strong evidence of carcinogenicity; methyl iodide, established carcinogen). Vicinal or geminal electronegative substituents (Hal, O, S) increase electrophilicity and - hence - carcinogenicity (e.g. 1,2-dibromoethane, chlorooxirane, bischloromethyl ether, mustard gas, haloketones). On the other hand, further crowding of halogens (especially F and Cl) decreases oxidative reactivity, both towards abiotic and metabolic oxidations (cf. 1,1-dichloroethane vs. 1,1,1-trichloroethane), the main reason for non-inflammability, low toxicity, and practical usefulness of halocarbons in technical applications. Polyhalogenated alkanes tend to participate in reductive metabolism to toxic radical intermediates. In vinylic position, halogens first activate double bonds (vinylchloride), at higher substitution double bond reactivity decreases (tetrachloroethene), especially when d-electron shell participation is possible (Cl, Br). Correspondingly, biotic and abiotic oxidation rates decrease with increasing halogen substitution.

Ecotoxicological Relevance

Assessments of the ecotoxicological relevance of various SCAH's require knowledge of the thermodynamic parameters of precursors and products, of kinetic constants of degradation/formation, determination of transfer coefficients between compartments, of toxicokinetic and toxicodynamic parameters in the relevant organisms, and indirect effects upon populations and coenoses. Some of these parameters can be predicted by computer model calculations from basic physical and chemical properties but these are at best semi-quantitative and must be backed by actual experiments in appropriate microcosms, mesocosms, and by field oberservations. An assessment of the ecotoxicological impact of pollutants on the total environment is conceptually similar to the toxicokinetic and toxicodynamic analysis of a xenobiotic upon an organisms, although a much larger number of compartments, transfer-processes and reaction pathways must be taken into consideration and quantitatively weighted. Reactive and/or toxic secondary products are formed by metabolic or abiotic/photochemical processes at minute steady-state concentrations which are often impossible to determine directly.

Several studies in aquatic and soil ecosystems have shown that some SCAH's elicit ecotoxicological effects at concentrations several orders of magnitude lower than the thresholds considered as safe for human exposure. The phytotoxicity of haloaliphatic acids is a typical example of selective toxicity: while some higher plants are resistant to fluoroacetate or even synthesize it from inorganic fluoride, other photoautotrophic organisms are highly sensitive. A similarly high variability over several orders of magnitude has been found for vertebrate toxicity of fluoroacetate. The same is true for other haloacetates which arise from atmospheric degradation C_2-halocarbons, although their mechanism of toxic action is not yet as well elucidated as of fluoroacetate. The high reactivity of chloro-, bromo-, and iodoacetate (e.g. for carboxymethylations) suggests them as potent alkylating agents; exposure studies with whole plants and suspension cell cultures have shown that the toxicity thresholds of monochloroacetate, but also of several trichloroacetate derivatives are in a similar range as the levels in plant tissue and rain water. Whether haloacetates in the environment may be formed by biotic processes, e.g. haloperoxidase catalysis, remains to be investigated.

Conclusions

Mammalian toxicological data are of limited value for ecotoxicological risk assessments of C_2-halocarbons. Reactive, usually more toxic secondary pollutants may turn out to be more relevant than the parent compound. One of the major requirements in addressing the environmental impact of a chemical is the problem-oriented development of analytical methods, enabling the reliable determination of parent compounds, major secondary products, and their cellular reaction products in small absolute (not relative!) quantities in numerous (several hundred) samples of high matrix complexity.

The widespread occurrence of haloaliphatic acids on the northern hemisphere is now well established; their considerable ecotoxicological relevance has been shown in several in-vitro and in-vivo experiments as well as in field studies.