

PHOTOCHEMICAL DEGRADATION OF PCBs IN ARTIFICIAL SNOW

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Abstract

This work represents the first laboratory simulation of photochemical processes of organic contaminants in artificial snow at environmentally relevant concentrations. The study utilized a photochemical cold chamber reactor that allowed simultaneous monitoring the volatilization fluxes of organic compounds released to the gas phase. Two model PCBs (PCB-7 and PCB-153) with 100 ng L⁻¹ snow concentrations, were found to undergo reductive dehalogenation, which efficiently competed with a desorption process responsible for the pollutant loss from the snow samples. It is concluded that the snow quality, physico-chemical properties of compounds, their location in the matrix, and the presence of various trace contaminants are evidently the most important factors in evaluation, which of the two processes will prevail. In contrast, intermolecular reactions among organic contaminants were of negligible importance.

Introduction

The role of snow in distribution of organic contaminants¹⁻⁵ as well as in hosting their possible (photo)chemical transformations in regions of high altitude and latitude^{6, 7} has received growing attention. Many low-weight organic molecules, such as hydrocarbons or their halogenated derivatives, are present in snow at environmentally significant concentrations.⁷ Recent laboratory studies of photochemical transformations of some organic compounds in frozen aqueous solutions⁸⁻¹⁵ have raised the question whether compounds of anthropogenic origin, deposited in polar snowpacks or adsorbed on ice cloud crystals in the atmosphere, can afford products of a potentially high environmental risk and later be introduced into the environment via melting or evaporation processes.^{6, 15, 16} These experiments utilized frozen solutions with relative high reactant concentrations (freezing the solution causes a considerable local concentration enhancement¹⁷) and the phototransformations observed were very often intermolecular. In natural snow, concentrations are much lower; contaminants are deposited by scavenging processes, in which the concentration enhancement effect by freezing is absent.

In this work, artificial snow, containing approximately 100 ng L⁻¹ concentration of PCB-7 or PCB-153, was photolyzed in a cold chamber reactor, whilst the parent compounds and photoproducts mass distribution in snow and ambient air was followed. The main goal of the study was to estimate the scope of PCB photodegradation in natural snowpack. The work represents the first laboratory simulation of photochemical processes of organic contaminants in snow, occurring at relevant pollutant concentrations.

Materials and methods

Artificial snow used in photochemical experiments was prepared from aqueous solutions of either PCB-7 or PCB-153 according to the following procedure. The PCB solution in dichloromethane was evaporated to dryness and the crystalline material was dissolved in water. The whole amount was transferred into a stainless steel tank, pressurized with technical air to 4.3×10⁵ Pa and sprayed through 1-mm hollow cone brass nozzle into a large vessel containing liquid nitrogen. Careful and slow procedure afforded small and separated ice crystals.

Photochemical reactor was designed to carry out the irradiation of snow samples and, at the same time, to determine the fluxes of organic compounds released from snow to the gas phase during the irradiation or in dark. It is a steel box inside a freezer, equipped with a UV lamp in quartz-jacketed housing with inlet and outlet tubes for cooling medium (water) to remove an excess heat from the lamp and to filter off IR radiation. The snow sample was spread over the box bottom of the chamber and irradiated from a 50-cm distance. The air from the chamber was drawn through polyurethane foam filters using a low-volume pump (air flow rate ~ 0.32 m³ h⁻¹).

Irradiation experiments were performed with artificial snow in a photochemical cold chamber (-25 °C) described above. A multiwavelength UV irradiation filtered by Pyrex was used to simulate solar radiation.

Concentrations of the model compounds and their photoproducts were determined in non-irradiated and irradiated snow samples, as well as in sampled air. For the analyses, the snow samples were melted at room temperature. The corresponding liquid solutions were extracted by solid-phase extraction using disks with a C18 sorbent. Polyurethane foam filters were extracted with dichloromethane in an automatic extractor. GC-MS was used for the qualitative and quantitative analyses. The data reported are average results obtained from at least triplicate measurements.

Results and Discussion

Artificially prepared snow, containing $\sim 100 \text{ ng L}^{-1}$ concentration of either PCB-7 (2,4-dichloro-1,1'-biphenyl) or PCB-153 (2,2',4,4',5,5'-hexachloro-1,1'-biphenyl), in the absence or in the presence of H_2O_2 , was photolyzed in a photochemical cold chamber at $-25 \text{ }^\circ\text{C}$. During the photolysis, the starting material and photoproducts fluxes from the snow sample were evaluated by measuring the total amount of compounds released into the air.

The dehalogenated derivatives (PCBs and biphenyl) were identified as the major products in all cases although traces of many chloroquaterphenyls and hydroxychlorobiphenyls were also detected based on the corresponding mass fragments observed by SIM analyses. Unfortunately, the initial nM and sub-nM PCB concentrations implied that those of the photoproducts, which must be several orders of magnitude lower, approach the detection limitations of analytical techniques. As a result, we were unable to accomplish the quantitative analysis of all trace compounds.

Dechlorination is the major photochemical process observed when PCBs are irradiated in inert media.¹⁸ The mechanism of the reductive dehalogenation is straightforward: following the excitation and usually efficient intersystem crossing (*isc*), the triplet state dissociates and the radicals formed may abstract hydrogen from neighboring hydrogen donors (HS)¹⁸ or undergo radical aromatic substitution, in which the excessive hydrogen atom is simultaneously abstracted by another molecule.¹⁰

When water as a nucleophile¹⁹, or oxygen²⁰ are introduced, the corresponding hydroxy-substituted photoproducts are obtained. In contrast, photolysis of PCBs adsorbed on the surface of alumina and silica-alumina was found to produce radical cations as the major intermediates, which subsequently release the chlorine atoms.²¹

As previously reported, irradiation of aromatic halogen compounds in frozen aqueous solutions ($c > 10^{-7} \text{ M}$) below $-10 \text{ }^\circ\text{C}$ afforded dehalogenation, coupling, or rearrangement reactions only; no photosolvolysis photoproducts, that is products from intermolecular reactions between organic and nucleophilic water molecules, were formed.^{10,11} PCBs in artificial snow were also reductively dehalogenated but other major photodegradation mechanisms were absent. Upon photolysis of PCBs in snow matrix, the formation of the biphenyl radicals must precede hydrogen abstraction reaction from a hydrogen donor or minor arylation of a suitable aromatic reaction partner.⁹⁻¹¹ The coupling photoproducts (quaterphenyls derivatives) were identified in trace amounts but, with respect to their number and incomplete mass balance in all experiments, we believe that the radical arylation is a minor source of the hydrogen atom. However, this assumption cannot explain a predominant and extensive reductive dehalogenation observed.

Although water molecules cannot be a direct source of hydrogen (the O-H bond dissociation energy is too high), we still wanted to rule out any possible involvement of the water molecules in the reaction. The exhaustive photolysis of PCB-7 in deuterium oxide (97%) under the same conditions afforded no deuterated biphenyls, either formed within the solid matrix or released to the ambient air. Instead, a very similar product distribution of the same photoproducts was obtained. Therefore, the principle source of the hydrogen atom in our experiments remains unknown. We believe that trace amounts of various impurities, albeit undetected, originating from the air, entered the snow samples.

Hydroxylation reactions were obviously responsible for a more efficient PCB-7 degradation in the presence of H_2O_2 ¹¹ because traces of several hydroxylated photoproducts were identified. The presence of hydrogen peroxide enhanced the PCB-7 consumption by a factor of 4. In other experiments, such photoproducts (in significantly lower amounts) had to be produced only via addition of oxygen to form hydroperoxide/endoperoxide intermediates.¹²

Natural snow is expected to release organic contaminants, such as PCBs.^{2, 22} Therefore, we had to consider a partial evaporation of the starting PCBs as well as the photoproducts from artificial snow samples during irradiation and it was found that the mass loss due to the photochemical transformations competed with that occurring by vapor flux to the ambient air. PCB-153 concentration decreased in dark cold chamber by volatilization from snow under the same conditions as used in the photolysis experiments; the curve had an exponential character and seemed to level off to a plateau at more than 50% concentration reduction (> 12 days). This means that only less than 15% of the PCB-153 mass was released to the ambient air within the time required to accomplish a complete photochemical degradation in our experiments (2 days). Interestingly, only $\sim 1\%$ of the PCB-153 initial mass was detected in the air during the photochemical experiment but it is also possible that photodegradation of the parent molecule can still occur in the gas phase in a small extent. More volatile PCB-7 was found to be more susceptible to release; for example, $\sim 3\%$ of PCB-7 was found in air during 12-h Pyrex-filtered photolysis to a low conversion. This effect is well manifested in Figure 1, showing an increasing snow phase/air occurrence for 6 photoproducts upon irradiation of PCB-153 in artificial snow (the vapor pressure of least volatile PCB-101 and most volatile biphenyl is 1.6×10^{-3} and 104 Pa at $25 \text{ }^\circ\text{C}$ ²³, respectively).

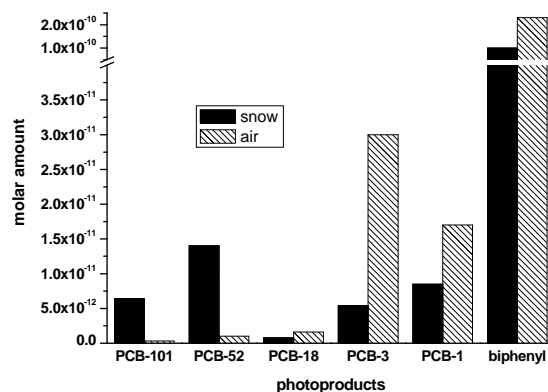


Figure 1. The formation of semi-volatile photoproducts during exhaustive irradiation of PCB-153. The molar amounts correspond to 1 L of the snow sample.

Freezing the aqueous solutions of organic molecules is known to be accompanied by their exclusion from the growing ice phase, resulting in increased local concentrations in a liquid layer covering ice crystals, which eventually freezes at low temperatures.^{17, 24, 25} Very low concentrations of impurities may allow some species to be incorporated in the ice crystals; however, semi-volatile organic molecules of low polarity interact with ice through van der Waals interactions only and are not considered to dissolve in ice.^{26, 27} The artificial snow production method utilized in this work (shock freezing in the liquid nitrogen) should provide a maximum distribution uniformity of the organic impurities within the crystals. Jacobi et al, however, observed that a large fraction of the inorganic nitrate is located close to the shock-frozen snow surface, enabling thus a quick mass exchange with the ambient air.²⁸ Since the volatilization of the starting compounds as well as products formed was considerable, it is highly possible that this sample preparation techniques produced ice crystals with hydrophobic organic impurities largely located on the surface, in the same way as they are located on ice crystals in natural snow.¹ In order to find if premelting²⁹ can have any effect on enhancing the efficiency of coupling reactions, the aged snow samples were irradiated at the same conditions as fresh snow samples. Since both conversion and photoproduct distribution were found comparable, we can conclude that even if any changes in impurity distribution within the matrix occurred, it had no impact on the scope of the reaction.

Conclusions

The PCB snow/air exchange is obviously a major competing process responsible for the pollutant loss from the snowpack², yet the question of the actual quantities of a chemical released back to the atmosphere is still open to debate.^{2, 30} The snow quality and the location of pollutant molecules in the matrix is evidently the most important factor in evaluation, whether the pollutants reside there sufficiently long to undergo phototransformations. The properties of artificial snow samples used in this work were different than those of natural snow, which, nevertheless, can also vary significantly.⁷ The release of PCBs from snow is strongly competing with its degradation upon irradiation with a solar simulator. However, the curve representing the volatilization loss levels off when the concentration is reduced below 50%, which possibly reflects a different location of organic molecules in snow matrix: those trapped within the crystals, unable to diffuse out, will have the greatest chance to react. In natural snowpacks, downward diffusion of desorbed vapors to deeper snow layers² will, furthermore, enhance the chance that photodegradation occurs if the molecules still reside in the photic layer.³¹

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