PHOTODEGRADATION OF ORGANOPHOSPHORUS PESTICIDES IN WATER, ICE AND SNOW

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Introduction

Semivolatile compounds as pesticides are a subject to the regional and long-range atmospheric transport to remote and polar regions[1]. As snow is known as a very good scavenger of atmospheric pollutants, these compounds can be scavenged from air upon their arrival to the cold environments, deposited on the ground, and accumulated in the seasonal snowpack. Consequently, they can be re-volatilized or released with meltwater during the periods of temporal or global warming[2].

Organophosphorus pesticides (OPs) represent more polar compounds with better water solubility and higher degradation rates than organochlorine pesticides which made them attractive for a wide application in agriculture. OPs can be degraded both in abiotic and biotic compartments[3] but they still belong to the group of compounds capable of the long-range transport.

Snow and ice cores taken recently in the Austfonna ice cap in Svalbard revealed concentrations of the individual compounds ranging up to 87 ng L^{-1} for dimethoate, 7.4 ng L^{-1} for methyl-parathion and 32.9 ng L^{-1} for fenitrothion[4] indicating a significant historical contamination of the atmosphere with OPs. Similar concentration levels were observed in snow from the national parks to the west of the United States (US). Reported sum of chlorpyrifos (including oxon) ranged from 0.02 ng L^{-1} to 2.3 ng L^{-1} of meltwater[5]. Chlorpyrifos and terbufos were found also in fog (maximum of 5 ng L^{-1} for chlorpyrifos and 20 ng L^{-1} for terbufos) and in marine ice (170 ng L^{-1} for chlorpyrifos) in the Bering and Chukchi[6].

In the cold regions, snow and ice affect the processes of OPs deposition, accumulation and transformation and they can significantly alter their life times, degradation and elimination rates. However, our knowledge on photodegradation processes of OPs in the matrices of ice and snow is still very limited. Filling this gap is crucial for an enhancement of our understanding to the fate of the organic compounds in pristine arctic environments.

This study is focused on the photochemical behaviour of fenitrothion and methyl-parathion as two currently used organophosphorus pesticides in the cold environments. Methyl-parathion is one of the most extensively used pesticides in the US and Russia[7,8]. Both, methyl-parathion and fenitrothion are susceptible to a direct photolysis, and photodegradation is considered to be an important transformation process in natural waters[9,10].

Material and methods

Instruments
A GC-MS system consisting of a HP 6890 gas chromatograph (Agilent) and a J&W Scientific DB-5MS fused silica column (60 m × 0.25 mm with 0.25 μm stationary-phase film (5% phenyl / 95% methyl-polysiloxane) combined with a HP 5972 mass selective detector (Agilent) was used; the carrier gas was helium at a flow of 1.5 mL min^{-1}. Injector and transfer line temperature were 280 ºC. Samples (1 μL) were injected in split mode (1:20) for a full-scan analysis and split-less in SIM mode. Initial temperature was 80 ºC, held for 1 min, the temperature was raised by 15 ºC min^{-1} to 180 ºC, then by 5 ºC min^{-1} to 310 ºC, and the final temperature was held for 20 min.

UV-Vis spectra of the liquid aqueous solutions were measured against a Milli-Q water sample in 1 cm-quartz cuvettes on a Varian Cary 50 Bio UV-Vis spectrophotometer.

HPLC analyses were performed on a HP 1100 Agilent (Hewlett Packard) equipped with photodiode array detector ($\lambda = 220$ nm) and a reverse-phase column (Gemini C-18, 5 μm; 250 × 4.6 mm, Phenomenex; acetonitrile/water (75:25%); runtime = 15 min at 1 mL min^{-1}; 30 ºC).

Irradiation in water and ice
Liquid (20 ℃) or ice (–15 ℃) samples (c ~3×10^{-5} mol L^{-1}) in 13×100-mm quartz vessels, sealed with septa, were irradiated simultaneously at >290 nm (Pyrex filter) using a medium-pressure mercury discharge lamp (125 W; Teslamp Co.) in a merry-go-round apparatus; the ice samples were kept at –15 ℃ by immersion in an ethanol cooling-bath. The irradiated samples were analyzed directly on HPLC-DAD to obtain the degradation dependencies.

Snow preparation
Fenitrothion and methyl-parathion solutions were prepared by direct dissolving in Mili-Q water without using any organic co-solvents. The concentration (5 mg L^{-1}) for both compounds was achieved by evaporating the solvent (acetonitrile) of the stock solution under a stream of nitrogen to dryness. The residue was dissolved in water (4 Litres) and sonicated for 5 min. The whole volume was transferred into a stainless steel tank (Alto Liquid Sprayer 20S, Switzerland), pressurized with technical air and sprayed through a thin 1-mm hollow cone brass nozzle into a container filled with liquid nitrogen. After preparing artificial snow in liquid nitrogen, snow sample was divided to three parts of the same homogeneity. The first part of this artificial snow was analyzed directly using solid phase extraction (SPE), the rest were irradiated or studied for plausible volatilization of compounds in dark at -25°C.

Irradiation and dark study in freezer
Experiment took place in a freezer, which contained a stainless steel vessel inside, and was equipped with a UV 125-W medium-pressure mercury lamp (Teslamp Co.) in Pyrex filter (λ_{irr} > 290 nm) with water as a cooling medium for simulating solar radiation in the environment. Snow sample (around 1 Litre) was spread on thin aluminium foil with maximum 1 cm depth on the bottom of vessel. The lamp was situated 50 cm above the snow sample. Low-volume devices drew the air inside steel vessel through polyurethane foam filters (PUFs) to adsorb volatilized and possibly transformed product compounds during irradiation.

Sample extraction
Samples of irradiated, non-irradiated and control snow were melted at room temperature and extracted by solid phase extraction on the Bakerbond Speedisk C18, Ø 47 mm (JT Baker, USA), pre-conditioned by methanol (50 mL) and Mili-Q water (25 mL). The elution was performed using 40 mL of dichlormethane. Recoveries ranged between 80-95 %. PUFs were extracted with dichloromethane for one hour and 20 minutes using a Büchi B-811 automatic exctraction system (Büchi, Switzerland). The extracts were blown down under a stream of nitrogen to 10 mL, dried with 5 g anhydrous sodium sulphate, filtered through a glass wool, concentrated to 1 mL under a gentle stream of nitrogen and measured directly on GC-MS.

Results and discussion

Fenitrothion and methyl-parathion absorb light of wavelength greater than 290 nm and their UV-VIS aqueous spectra are presented in Figure 1. Both of them have considerable tail absorption within solar light region of 310-400 nm and are suitable for direct photolysis.
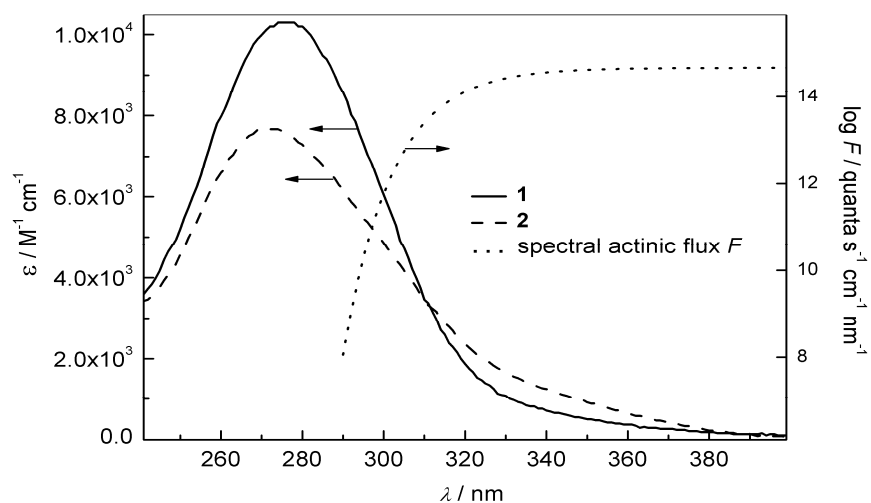
Figure 1. Absorption spectra of methyl parathion (**1**; ———) and fenitrothion (**2**; − − −) in aqueous (liquid) solutions ($c \sim 3 \times 10^{-5}$ mol L^{-1}), compared to the calculated solar spectral actinic flux (F) at the Earth's surface for cloud-free skies and solar 45° zenith angle (• • •)[11].

Water and ice experiments

Fenitrothion and methyl-parathion are photodegradable in aqueous solutions natural soils[9] or using photocatalytic sensitisation with TiO$_2$ [12]. During the irradiation in water, photoproducts could be formed by the three major phototransformation pathways going through oxons (methyl-paraoxon and fenitrooxon) and S-methyl isomer of fenitrothion to phenolic compounds (4-nitrophenol and 3-methyl-4-nitrophenol)[13].

The water (20 ℃) and ice samples (−15 ℃) of methyl parathion and fenitrothion in the absence of any organic co-solvents were UV-irradiated through a Pyrex filter in the ethanol bath of a cryostat box. The use of Pyrex resulted in >300 nm multi-wavelength radiation that approximately simulated natural solar radiation. The initial pesticide concentrations were as low as $\sim 10^{-5}$ mol L^{-1}. Figure 2 compares a time-dependent consumption of methyl-parathion and fenitrothion by photolysis in liquid water and ice. Methyl parathion degradation was more efficient in ice than in water in the course of irradiation experiments. While the degradation profile obtained for the liquid solutions was fitted with mono-exponential curve, the one for ice samples corresponded to an exponential dependence of the third order suggesting that different and complex photodegradation pathways must be responsible for photoinduced degradation. In contrast, the degradation efficiencies of fenitrothion were comparable in both phases. The most interesting finding was an enhanced initial photodegradation efficiency of both compounds in ice compared to the liquid solutions.

Identification of all the photoproducts was not possible due to the low initial pesticide concentrations, although these were still considerably higher than those observed in remote polar or mountainous environments. Oxons and nitrophenols were formed in ice and water in higher chemical yields. Traces of other photoproducts were also detected.
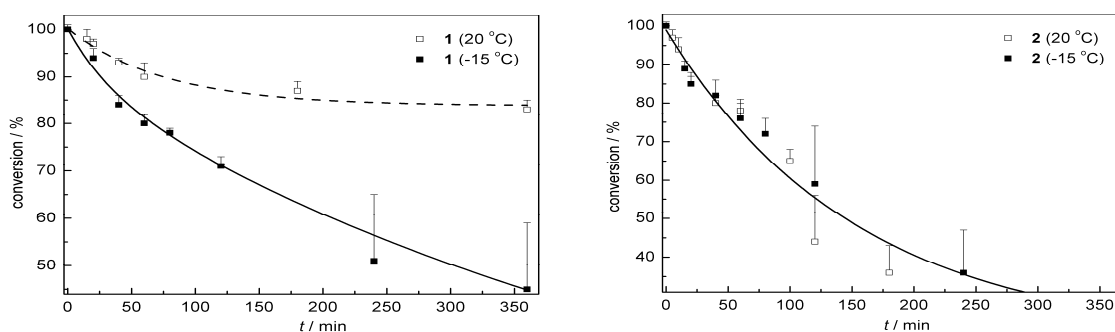
Figure 2. Photodegradation of 1 (methyl-parathion) and 2 (fenitrothion) in aerated liquid solution (20 ℃) and ice (–15 ℃) by multi-wavelength radiation >290nm. The curves for 1 represent the exponential fit of the first (─ ─ ─) and third (──) order and for 2 only the first order. The bars represent the relative standard deviations from triplicate measurements conducted at each time step.

Snow experiment
Due to the different experimental set-up, snow data are not directly comparable to water and ice experiments and they have to be viewed as a pilot study only. Fenitrothion concentration decreased to 60 % and methyl-parathion to 71 % of the original concentrations upon 8 hours of irradiation in the snow matrix. As expected, a photodegradation of fenitrothion was more efficient than the one of methyl-parathion which corresponds to the results of previous experiments. Neither parent compounds nor their photoproducts were found in the polyurethane filter of the low volume air sampler indicating that re-volatilization from the snow was not a major elimination pathway of these pesticides from snow.

Acknowledgments

References

1. Daly G. L. and Wania F. *Environ. Sci. Technol.* 2004; 38: 4176
2. Burniston D. A., Strachan W. J. M., Hoff J. T. and Wania F. *Environ. Sci. Techno*l. 2007; 41: 4932
3. Barcelo D., Sole M., Durand G. and Albaiges J. *Fresenius J. Anal. Chem.* 1991; 339: 676
4. Hermanson M. H., Isaksson E.H., Teixeira C., Muir D. C. G., Compher K. M., Li Y. F., Igarashi I. and Kamiyama K. *Environ. Sci. Technol.* 2005; 39: 8163
5. Hageman K. J., Simonich S.L., Campbell D. H., Wilson G. R. and Landers D. H. *Environ. Sci. Technol.* 2006; 40: 3174
6. Chernyak S. M., Rice C.P. and McConnell L. L. *Mar. Poll. Bull.* 1996; 32: 410
7. Orme S., Kegley S. PAN PesticideDatabase, Pesticide Action Network, 2004
8. Kiely T., Donaldson D. and Grube A. Pesticides Industry Sales and Usage Report, US-EPA, 2004
9. Sakellarides T. M., Siskos M.G. and Albanis T. A. *Intern. J. Environ. Anal. Chem.* 2003; 83: 33
10. Lacorte S. and Barcelo D. *Environ. Sci. Technol.* 1994; 28: 1159
11. Hutzinger O. The Handbook of Environmental Chemistry, Springer-Verlag, 1982
12. Topalov A., Molnar-Gabor D., Abramovic B., Korom S. and Pericin D. *J. Photochem. Photobiol. A: Chem.* 2003; 160: 195
13. Castillo M., Domingues R., Alpendurada M. F. and Barcelo D. *Anal. Chim. Acta* 1997; 353: 133