DO ORGANOCHLORINE PESTICIDES IN ALPINE SOILS INCREASE WITH ALTITUDE?

Manfred Kirchner¹, Gert Jakobi¹, Theresa Faus-Kessler¹, Walkiria Levy¹, Bernd Henkelmann¹, Silke Bernhöft¹, Jarmila Kotalik¹, Rodolfo Bassan², Claudio Belis³, Saverio Iozza⁴, Wilhelm Knoth⁵, Norbert Kräuchi⁶, Wolfgang. Moche⁷, Peter Schröder¹, Primož Simončič⁸, Maria Uhl⁷, P., <u>Peter Weiss⁷</u>, Karl-Werner Schramm¹

¹Helmholtz Zentrum München, GmbH, Institutes of Ecological Chemistry, Developmental Genetics and Soil Ecology, Ingolstädter Landstraße 1, D-85764 Neuherberg - Germany

- ²ARPA Veneto, Via F. Tomea 5, I-32100 Belluno, Italy
- ³ARPA Lombardia, Via Stelvio 35, I-23100 Sondrio, Italy

⁴EMPA - Materials Science & Technology, Überlandstr. 129, CH-8600 Dübendorf, Switzerland

⁵Umweltbundesamt, Paul-Ehrlich-Strasse 29, 63225 Langen, Germany

⁶WSL, Abt. Waldökosysteme und ökologische Risiken, Zürcherstrasse 111, CH-8903 Birmensdorf, Switzerland

⁷Umweltbundesamt GmbH, Spittelauer Lände 5, 1090 Vienna, Austria

⁸Slovenian Forestry Institute, Dept. for Forest Ecology, Vecna pot 2, SL-1000 Ljubjana, Slovenia

Introduction

In atmosphere persistent organic pollutants (POPs) are exposed to various processes, like adsorption to aerosols, transformation by ozone and radicals, photolysis and finally deposition on earth surfaces. Generally, such processes depend on the properties of the singular compounds like phase partitioning, volatility and water solubility ¹. In addition, the meteorological conditions have a strong impact on them. Surface characteristics have a further dominant influence on depositional processes. As a result of the lipophilic properties of POPs and the high organic content of forests, such terrestrial systems act as a sink for organochlorine compounds.

On their way semi-volatile organic compounds are re-emitted from several reservoirs like soils and intercepted by forests, before they will reach higher latitudes where colder temperatures favour their condensation and deposition ²; this behaviour is denominated as cold condensation and occurs not only in fluxes towards high latitudes but also towards high altitudes ^{3,4,5,6}. But not all studies, particularly if related to snow or needles which integrate over shorter periods, confirm these findings ⁷. Organochlorines can also be degraded on their pathway in air, soils and plant tissues by a number of factors, like UV-B radiation ^{8,9}. In cold climates degradation can be assumed to be low or negligible.

For this study, which was performed in the framework of the MONARPOP project, humus from forest sites, located along several vertical profiles in different parts of the Alps, were investigated for their concentrations of organochlorine pesticides (OCPs) like dichlorodiphenyltrichloroethanes (DDTs), hexachlorobenzene (HCB), hexachloro-cyclohexanes (HCH), heptachlor, aldrin, dieldrin and mirex.

Materials and methods

The selection of transect was performed in a standardized way, with restriction to sites stocked almost completely by Norway spruce (*Picea Abies*) forests reaching from valley ground to upper tree limit and with avoidance of known local sources in the vicinity. Differences in forest stands between Northern and Southern Alps, complex orography and the restricted accessibility had to be taken into account.

Nevertheless, the seven altitude profiles were characterized by some particularities, which have to be considered interpreting the results. Based on the geographical location of the individual valleys, there are two groups of profiles, the first starting with sites below 900 m a.s.l., the second above 1100 m a.s.l.. In fig. 1 the location of the seven profiles is shown.

The humus sampling is described by Knoth et al. (this volume); detection and quantification of OCP were carried out by high resolution gas chromatography (HRGC) on a Rtx-Dioxin2 column (Restek, Germany) followed by HRMS (MAT 95, Thermo Electron GmbH, Germany); the spectrometer was operated in single ion monitoring mode ^{10,11}. For the climatological characterization of the 7 vertical profiles we used data from surrounding meteorological stations for regression analyses. As the altitude profiles are grouped data, they were analyzed with mixed-effects models ¹².

Results and discussion:

Meteorology

All climate regions are characterized by temperature decrease and precipitation increase with altitude. On the basis of annual values, the vertical temperature decrease is similar in all Alpine regions and ranges between - 0.6 and -0.4 °C/100 m. This range depends on the frequency of temperature inversions occurring particularly during night and winter. The Central Alps receive less precipitation than the Northern and Eastern Alps; the Slovenian Alps, which are strongly influenced by the Adriatic Sea, belong to the wettest parts of Central Europe.

Due to barrier effects, the altitudinal increase of precipitation is stronger at the Alpine fringes than in the Central Alps. The low number of sites and the specific climate of inner-alpine dry valleys are responsible that the positive correlation between precipitation and sea level was not always significant.

Vertical distribution of pesticides

The concentration ranges of organochlorines in the Alpine humus layers were 0.4-28.8 μ g/kg d.m. for p,p'-DDT, 0.3-8.8 μ g/kg d.m. for γ -HCH or 0.4-6.0 μ g/kg d.m. for dieldrin. The ranges of mean carbon content and humus depth are 15-45 % respectively 2-24 cm.

Comparing the different regions in which the profiles are located, the altitude profiles with the highest concentrations of pesticides in humus are those in the northern Alpine fringe in Bavaria (particularly with the Eschenlohe profile) and the Pokljuka profile in the Slovenian Alps. The humus concentrations seem to decrease markedly from the most exposed northern Alpine fringe, where Eschenlohe is located, to the following Alpine mountain chain (such as Berchtesgaden), which is already protected to some extent from external effects, and to the Central Alps, for instance to Rauris, Davos and Valvisdende.

There is a marked concentration increase with altitude for some of the studied pesticides. Particularly for p,p'-DDT (figure 2), δ -HCH, endrin and dieldrin we found a pronounced increase along five of the seven vertical profiles, whereas the concentrations of β -HCH, γ -HCH, mirex and HCB show this trend only for three or four profiles. Aldrin and heptachlor do not show any increase with elevation.

At the vertical profiles of Rauris and Wechsel we noticed a marked increase for quite all organochlorines with altitude. Along the profiles of Klosters-Davos, Berchtesgaden and Eschenlohe a concentration increase with altitude can be found for more than half of the compounds. Only Pokljuka and Valvisdende do not show any increase with elevation. We assume for Valvisdende influences from a different transversal valley and for Pokljuka an influence of past local sources close to single sites of the profile.

We calculated the correlation of the pesticide concentrations with temperature, precipitation, humus depth and carbon content as covariables. A model with temperature alone as significant variable was found for dieldrin, β -HCH, δ -HCH, ϵ -HCH, o,p'-DDT, p,p'-DDE, and p,p'-DDT. Complementary to the effect of altitude, slopes were always negative. Precipitation and humus depth had a joint significant influence with positive coefficients on the α -HCH, γ -HCH, and hexachlorobenzene concentration. For modelling the mirex concentration, both temperature and precipitation were significant, temperature with a negative and precipitation with a positive sign.

For all profiles, but particularly for Rauris and Berchtesgaden, the occurrence of low inversion layers on valley ground in combination with the existence of so-called warm slope zones may be responsible for the initial decrease in concentrations with height. Another explanation may be historic emissions at the valley ground.

Despite our findings that temperature and precipitation may play an important role on humus concentration along altitudinal gradients, it cannot be quantified to which extent these meteorological parameters interfere with major processes like deposition, degradation and re-volatilization ^{1,2}.

Acknowledgments

MONARPOP is funded by the EU Interreg III B Alpine Space Programme and by the participating national partners. The authors wish to express particular thanks to the Bavarian State Ministry for Environmental, Health and Consumer Care for supporting the study in Bavaria.

References:

1. Mackay D. and Wania F. Science of the Total Environment 1995; 160/161: 25.

2. Wegmann F., Scheringer M. and Hungerbühler K. Ecotoxicology and Environmental Safety 2006; 63: 42.

3. Daly G.L. and Wania F. Environmental Science & Technology 2005; 39: 385.

4. MacDonald R.W., Harner T.and Fyfe J. Science of the Total Environment 2005; 342: 5.

5. McLachlan M and Horstmann M. Environ Sci Technol 1998; 32: 413.

6. Davidson D.A., Wilkinson A.C., Kimpe L.E.and Blais J.M. Environmental Toxicology and Chemistry 2003; 23: 540.

7. Carrera G., Fernandez P., Vilanova R.M. and Grimalt J.O. Atmospheric Environment 2001; 35: 245.

8. Niu J., Chen J., Henkelmann B., Quan X., Yang F., Kettrup A. and Schramm K.-W. *Chemosphere* 2003; 50: 1217.

9. Dolinova J., Klanova J., Klan P.and Holoubek I. Chemosphere 2004; 57: 1399.

10. Gawlik B.M., Martens D., Henkelmann B., Schramm K.-W., Kettrup A. and Muntau H. Fresenius J Anal Chem 2000; 367: 232.

11. Levy Lopez W. PhD Thesis, Technischen Universität München, Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt, 2008.

12. Pinheiro J. C. and Bates D. M. Springer, New York, Mixed-Effects Models in S and S-Plus, 2000.



Figure 1: MONARPOP sites and altitudinal profiles in the Alps



Figure 2: Variations of p,p'-DDT concentrations with altitude