THE DEPOSITION OF PESTICIDES INTO ALPINE FOREST ECOSYSTEMS

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Riassunto
Lo strato di humus e gli aghi di conifera di circa 50 siti remoti distribuiti lungo tutto l’arco alpino di Austria, Svizzera, Baviera, Veneto, Lombardia e Slovenia sono stati studiati per la determinazione del loro contenuto di pesticidi. Nonostante le influenze dovute alle caratteristiche orografiche, vegetazionali e pedologiche e alle differenze meteorologiche, è stato possibile misurare i gradienti regionali della contaminazione del suolo con pesticidi i quali presentano un andamento decrescente dall’estremità nord agli Alpi Centrali. Si osserva inoltre che gli aghi e l’humus si comportano in modo leggermente diverso. Per ultimo è stato riscontrato che alcuni pesticidi mostrano un incremento delle concentrazioni con la quota.

Abstract
Humus layer and spruce needles of approximately 50 remote forest sites spread all over the Alpine regions of Austria, Switzerland, Bavaria, Veneto, Lombardy and Slovenia were investigated for their concentrations of pesticides. Despite the numerous influences regarding orographic aspects, forest and soil characteristics and meteorological differences we measured regional gradients of soil contamination with pesticides with increasing concentrations from the Northern fringe to Central Alps. Slightly different features can be observed if the content in spruce needles are considered. For some pesticides a vertical increase from valley to higher is evident.
**Introduction**

Remote areas like the Arctic and the Alps are likely to serve as a sink of organic persistent contaminants. As a consequence of the lipophilic characteristics organochlorine compounds are attracted by plant stands and tend to be retained in the organic material of their leaves and needles. Due to their high persistence they can be stored in humus layer and mineral soil for many years. Furthermore forests are effective filters for all pollutants for their roughness (Table 1). In the framework of the MONARPOP project humus and needles investigations deliver the basis information of ecosystem contamination by POPs in Alpine Ecosystems. Whereas spruce forest humus layer content of pesticides delivers the information about the last decades’ deposition, spruce needles as a part of living organisms comprise the information about recent contamination.

**Materials e Methods**

The different sites and vertical profiles were chosen carefully in the way that the high number of possible natural and anthropogenic interfering factors could be minimized. In the case of the soil sampling 10 sub-samples of the humus layer were taken at each of the sites with a frame and composited to one sample. The needle sampling was performed by a tree climber; current year Norway spruce needles were taken from the range of the seventh branch whorl from the top of the trees. As main organochlorine substances have been chosen DDX, HCH’s, HCB, aldrin, dieldrin and mirex to be analyzed in soil and spruce needles. Sampling and analytical procedures have been described in Kirchner et al. (2007); the description of different statistical tests to identify differences between the regional groups can be found at Weiss et al. (2000).
Results and discussion

Figure 1 shows the distribution of p,p’-DDT as measured at the singular sites. As the statistical tests reveal, the concentrations of some pesticides in humus layers differ from one to another regional latitudinally and longitudinally defined sub-group. Mainly p,p’DDE and γ-HCH decrease from Northern to Central Alps, longitudinal differences between eastern group and western group could not be identified with statistical significance. Adopting a grouping which considers more climatological aspects the differences between Alpine fringe regions and the more protected centre of the Alps, where precipitation is lower and insolation is higher, may result in steeper gradients.

Table 2: Literature values for humus and needles

<table>
<thead>
<tr>
<th>Region</th>
<th>Time</th>
<th>γ-HCH µg/kg</th>
<th>p,p’-DDT µg/kg</th>
<th>Dieldrin µg/kg</th>
<th>HCB µg/kg</th>
<th>Author</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maine (USA)</td>
<td>1967</td>
<td>900 - 3000</td>
<td>0 - 1000</td>
<td>0 - 300</td>
<td></td>
<td>Diamond, Owen</td>
<td>forest after DDT application</td>
</tr>
<tr>
<td>Main (USA)</td>
<td>1993</td>
<td>0 - 300</td>
<td></td>
<td>0 - 1000</td>
<td></td>
<td>Diamond, Owen</td>
<td>forest late after DDT application</td>
</tr>
<tr>
<td>Bavaria (D)</td>
<td>1990</td>
<td>&lt; 1 - 252</td>
<td></td>
<td></td>
<td></td>
<td>LFU Bavaria</td>
<td>forest (background - urban)</td>
</tr>
<tr>
<td>Sweden</td>
<td>1990s</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>forest (urban)</td>
</tr>
<tr>
<td>Linz (A)</td>
<td>1990s</td>
<td>0 - 32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>forest</td>
</tr>
<tr>
<td>Tianjin (China)</td>
<td>2004</td>
<td>1.0 - 5.0</td>
<td>0.5 - 30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leipzig-Halle (D)</td>
<td>1995 - 96</td>
<td>1.5 - 5.6</td>
<td>14 - 87</td>
<td>0.6 - 3.8</td>
<td></td>
<td>Wang</td>
<td>agric. soil after appl. of pesticides</td>
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<td>Eastern-Alps (A)</td>
<td>1990s</td>
<td>0.6 - 3.4</td>
<td>0 - 12</td>
<td>&lt; 1 - 36</td>
<td></td>
<td>Manz</td>
<td>field near industry</td>
</tr>
<tr>
<td>Bavaria Forest (D) / Sumava (CR)</td>
<td>2003</td>
<td>2.1 - 7.5</td>
<td>19 - 35.5</td>
<td>2.7 - 4.3</td>
<td>1.7 - 3.4</td>
<td>Kirchner, Schramm</td>
<td></td>
</tr>
<tr>
<td>Alps (A, D, CH, SL, I)</td>
<td>2004 - 06</td>
<td>0.3 - 8.8</td>
<td>0.4 - 28.8</td>
<td>0.4 - 6.0</td>
<td>0.7 - 4.4</td>
<td>MONARPOP</td>
<td>spruce</td>
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<tr>
<td>Dutch list, exposure limits (Optimum)</td>
<td>1994</td>
<td>HCH: 1</td>
<td>DDX: 2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Dutch list, intervention value</td>
<td>1994</td>
<td>HCH: 200</td>
<td>DDX: 4000</td>
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<td></td>
<td></td>
<td></td>
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</table>

NEEDLES

<table>
<thead>
<tr>
<th>Region</th>
<th>Time</th>
<th>γ-HCH µg/kg</th>
<th>p,p’-DDT µg/kg</th>
<th>Dieldrin µg/kg</th>
<th>HCB µg/kg</th>
<th>Author</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milan (I)</td>
<td>1990s</td>
<td>3.0 - 5.0</td>
<td>12.0 - 15.0</td>
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<td></td>
<td>Calamari</td>
<td>pine</td>
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<tr>
<td>Koestice (CZ)</td>
<td>1990s</td>
<td>1.0 - 2.0</td>
<td>0.1</td>
<td></td>
<td></td>
<td>Holoubek</td>
<td>pine</td>
</tr>
<tr>
<td>Bratislava (SK)</td>
<td>1990s</td>
<td>25.0 - 35.0</td>
<td>6.0 - 8.0</td>
<td></td>
<td></td>
<td>Holoubek</td>
<td>pine</td>
</tr>
<tr>
<td>Finland</td>
<td>1990s</td>
<td>2.0 - 4.0</td>
<td>0.1</td>
<td></td>
<td></td>
<td>Holoubek</td>
<td>pine</td>
</tr>
<tr>
<td>Holland</td>
<td>1990s</td>
<td>10.0 - 15.0</td>
<td>0.5 - 1.5</td>
<td></td>
<td></td>
<td>Holoubek</td>
<td>pine</td>
</tr>
<tr>
<td>Nürnberg (D)</td>
<td>1990s</td>
<td>0.1 - 0.5</td>
<td>2.0 - 8.0</td>
<td></td>
<td></td>
<td>LFU Bavaria</td>
<td>spruce (urban)</td>
</tr>
<tr>
<td>Himalaya (China)</td>
<td>2006</td>
<td>0.1 - 0.3</td>
<td>0.1 - 0.3</td>
<td>0.5 - 3.8</td>
<td>0.1 - 0.2</td>
<td>Wang</td>
<td>pine</td>
</tr>
<tr>
<td>Eastern-Alps (A)</td>
<td>1990s</td>
<td>1.9 - 7.9</td>
<td>0.0 - 0.8</td>
<td>0.3 - 1.1</td>
<td></td>
<td>Weiß</td>
<td>spruce</td>
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<tr>
<td>Bavaria Forest (D) / Sumava (CR)</td>
<td>2002 - 05</td>
<td>0.1 - 0.3</td>
<td>0.1 - 0.3</td>
<td>0.5 - 3.8</td>
<td>0.1 - 0.2</td>
<td>Kirchner, Schramm</td>
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<tr>
<td>Alps (A, D, CH, SL, I)</td>
<td>2004 - 06</td>
<td>0.0 - 0.2</td>
<td>0.0 - 0.1</td>
<td>0.4 - 72</td>
<td>0 - 0.2</td>
<td>MONARPOP</td>
<td>spruce</td>
</tr>
</tbody>
</table>
On behalf of the needle’s concentrations there are tendentially higher concentrations of some DDX in the Southern Alps. It seems that current contamination in Southern Alps may be higher than in Northern Alpine regions. There is a marked increase of some substance, which are transported into the Alps by long-range transport, from bottom of valleys to higher slope levels where input is higher and degradation is lower. The increase is frequent for Bavarian, Austrian and Swiss high profiles. Italian and slovenian high profile do not show this increase. The reasons for that are unknown; the remote situation, the complex orographic terrain, different height of inversion layers and possible local sources may be responsible. Generally the lower number of sites in the Southern Alps – only Lombardy, Veneto and Slovenia participated – lead to the result that the representativity of results related to Southern Alps is reduced.

A first conclusion of the project regarding the contamination of pesticides is that the content in needles of organo-chlorine compounds may have been reduced in the last decades, which is parallel to the reduction of emissions in Europe, whereas many substances are still stored in the humus layer and possibly present for food chains (table 2).

**Literature**


NOVEL DIAGNOSTIC TOOLS FOR POPs
IN ALPINE AREAS

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\(^8\)WSL-Swiss Federal Institute for Forest, Snow and Landscape Research
\(^9\)Federal Environment Agency Ltd. - Austria
\(^10\)Slovenian Forestry Institute

RIASSUNTO

Il presente articolo illustra due nuove metodologie che sono state applicate nell’ambito del Progetto MONARPOP per il monitoraggio degli inquinanti organici persistenti (POPs) nelle aree alpine.

ABSTRACT

Two novel methodologies have been applied for environmental monitoring of persistent organic pollutants (POP) in alpine areas. First a modern passive sampling

Figure 1: Experimental setup for deployment of the SPMD at remote field sites containing 25 SPMD subsequently sampled and renewed twice a year.

Figure 2: Scheme of the bioassay for the determination of dioxin-like compounds in soil and other complex matrices by determination of CYP1A1 expression.
CYP1A synthesis which then can cause excess oxidative stress in living organisms. In air and spruce needles the biological activity of dioxin-like activities is currently low, but soil exhibits prominent activities and also show some altitude related features.

In order to monitor persistent organic pollutants in a forested mountainous area, humus, mineral soil, spruce needles and air were sampled and analysed by analytical and bio-analytical methods. Quantitative determinations of organic persistent pollutants were performed by HRGC-HRMS (El-Kady et al. 2007). Then, a total toxic equivalent value for each sample was calculated using relative potency factors and the concentration value for each sample was calculated using 7-Ethoxyresorufin O-deethylase (EROD) bioassay (Hofmaier 1999, Schwirzer et al. 1996). The ability to elicit response when the cytochrome CYP1A is induced makes this bioassay suitable as a screening tool of dioxin-like chemicals capable of AhR binding. This micro-bioassay evaluates the overall potency as AhR modulators of the sample constituents and consequently is related to the potential toxicity of such chemicals in a complex mixture when an organism is exposed to them. In air and spruce needles the biological activity of dioxin-like activities is currently low, but soil exhibits prominent activities and also show some altitude related features.

Figure 3: EROD response of the altitude profile Rauris in Austria

Figure 4: EROD response of the altitude profile Wechsel in Austria

Figure 5: TE-EROD values after 72 hours incubation and WHO-TEQ values (WHO, 1998) calculated as the sum of PCDD/F and PCB WHO-TEQ from the analytical determinations of humus samples from Norway spruce forest sites. EROD values are the mean of 3 replicates.
analysed by analytical and bio-analytical methods. Quantitative determinations of organic persistent pollutants were performed by HRGC-HRMS (El-Kady et al. 2007). Then, a total toxic equivalent value for each sample was calculated using relative potency factors and the concentration of the single compounds. These calculated values from chemical analysis were then compared to the bioassay results. In this

![Graph](image)

**Fig. 6:** Phenanthrene concentrations at an altitude profile for SPMDs ½ year and 1 year exposure

![Graph](image)

**Figure 7:** 4,4´DDT concentration at altitude profiles for SPMD ½ and 1 year exposure. Period 1: ½ year exposure, Period 2: ½ year exposure and Period 3: 1 year exposure.
way, we determined similarities and differences between both methods. Based on this, a better data interpretation is achieved in order to obtain a sound environmental assessment of the samples and to exclude or confirm the presence of unknown toxic dioxin-like compounds.

Passive sampler, so called ‘semi-permeable membrane devices’ (SPMD), were deployed simultaneously at remote mountain areas for $\frac{1}{2}$ and 1 $\frac{1}{2}$ years (Levy et al. 2006, Levy et al. 2007). Active sampling measurements were also performed at the end of the passive sampling periods. Concentrations in passive samplers obtained by HRGC-HRMS were compared with the atmospheric concentrations for some PAH, PCB and chlorinated pesticides. From the compounds analysed, those with the lowest affinity to the gas phase were still being sequestered without reaching an equilibrium state between the atmosphere and the SPMD. Key findings with these technique was the increase of selected pesticides such as DDT with altitude (Fig. 6) as a result of long range transport and a decrease of PAH (Fig. 7) with altitude in consequence of the emissions due to traffic and domestic heating at the bottom of the alpine valleys.

**Biobliography**


**Acknowledgements**

MONARPOP is funded by the EU Interreg III B Alpine Space Programme (Alpine Space) and by the participating national partners. Additionally, we would like to thank the Swiss Federal Office for the Environment (FOEN - BAFU) for financial support.
NOVEL AMBIENT AIR SAMPLING TECHNIQUES
ADAPTED FOR THE NEEDS OF PROJECT MONARPOP

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Abstract
A novel ambient air sampling technique has been developed within the project MONARPOP, which affords the opportunity to attribute measured concentrations of different POPs to four predefined source regions important for the alpine area. Such
ambient air samplers and in addition bulk deposition samplers have been installed at three high altitude sampling sites Weissfluhjoch (CH; 2663 m), Zugspitze (D; 2650 m) and Sonnblick (A; 3106 m). Since the start of the project sampling was done for five trimonthly periods. For most of the analysed POPs no predominant source region could be detected so far, but clear seasonal differences are obvious. The concentration levels for ambient air and deposition as well are in the same range as those measured in the rural lowlands indicating long-range transport of PCDD/F and PCBs to these sites.

**Introduction**

The evaluation of the influence of long range transport of POPs to the alpine region was one of the main issues of Interreg III B Project MONARPOP. An additional question in this context was to detect which source regions are possibly responsible for POPs immissions in the alpine region.

To answer these questions it was planned to carry out ambient air measurements for various POPs with the additional requirement to attribute the measured concentrations to source regions. This meant relating the sampled air masses to their way to the sampling sites and possible influences by POP emissions during this way.

**Material and Methods**

Ambient air measurements for POPs are a two stage process, a long-time sampling with durations from days to weeks at the sampling site and a more or less complicated chemical analysis in a well equipped laboratory. Therefore in contrast to the onsite and online monitoring of gaseous pollutants like \( \text{NO}_x \) the attribution of POP concentrations to air masses is not possible after the measurement in most of the cases due to changing weather situations during the long sampling periods.

A solution is the predefinition of possible source regions followed by the source region specific sampling of air masses arriving at the sampling site. The region specific sampling allows to correlate between measured concentrations and source regions. Three high altitude measurement sites have been installed at three mountain summits which provide well equipped infrastructures of meteorological stations necessary for the operation of POP samplers. The three sites are Weissfluhjoch (CH; 2663 m), Zugspitze (D; 2650 m) and Sonnblick (A; 3106 m) which are shown in pictures 1, 2 and 3. All these three sites are well-staffed all year round to ensure daily checkup of the sampling equipment and prompt maintenance in the case of malfunctions.

Existing sampling techniques for POP had to be modified for the planned investigations. Ambient air samplers have been equipped with four filter cartridges each attributed to one source region. The selection of the corresponding filter cartridge was done by remote control based on meteorological trajectory forecasts. All filter
cartridges and moving parts had to be heated due to the rough weather conditions at the selected sites. Only 50 days per year show temperatures above 0 °C.

In addition to the ambient air samplers deposition samplers for bulk deposition have been installed at the three high altitude sites. The samplers are built according to DIN 19739-1, “Measurement of atmospheric deposition of organic trace substances – funnel adsorber method”, but necessarily in a heated version, due to the above mentioned weather conditions.

At all three sites the following equipment has been installed:

1. a low volume sampler for the collection of organochloropesticides (OCP) and polyaromatic hydrocarbons (PAH)
2. a high volume sampler for the collection of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) and polybrominated diphenylethers (PBDE)
3. 7 identical deposition samplers, each used for the collection of one of these four groups of pollutants completed by chlorinated paraffins (CP), Nitrophenols and trichloroacetic acid.
4. A meteorological cabin for SPMD sampling.
Results and Discussion

Since the start of the project sampling was done for five trimonthly periods. For most of the analysed POPs no source region which was predominant in all sampling periods could be detected so far, but clear seasonal differences are obvious. Whether these detected seasonal differences are periodical will be clarified in an intended prolongation of these measurements.

The concentration levels both for ambient air and deposition are in the same range as those measured in the rural lowlands, clearly indicating a long-range transport of POPs to these sites and the whole alpine region.