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1. Introduction

An abundance of trace metals in the environment is a characteristic property of only a few terrestrial ecosystems. Serpentine contains high concentrations of trace metals - especially Ni and Cr - that are released by weathering. Other natural sources of trace metals are volcanic eruptions and the deposition of marine aerosols. In the soil some trace metals are strongly adsorbed to the mineral matrix or fixed in stable complexes with soil organic matter, other ones are quite mobile. Trace metals show a high affinity to humic acids, iron oxides, clay minerals and carbonates in the soil.

Trace metals have gained in importance due to human activities that have fundamentally changed their biogeochemical cycling. They are emitted into the environment by numerous industrial processes and are dispersed by the application of sewage sludge, biogenic waste, pesticides and fertilizers.

Most trace metals play an ambivalent role in the environment: Depending on the concentration they are both essential micronutrients and toxic components for plants and soil organisms (VDI, 1984; Hock & Elstner, 1995; Weigl & Helal, 2001; Larcher, 2003; Alloway & Reimer, 1999; Ormrod, 1984; Elling et al., 2007). Therefore the emission and deposition of trace metals and their cycling in the environment are important issues in environmental research.

Naturally as well as artificially produced radionuclides can be found in all compartments of the environment. The interest in the content of radionuclides in *Picea abies* needle increased after the Chernobyl accident in 1986, because parts of the European forests were highly contaminated especially by Cs-137.

The role of trace metals in ecosystems depends on the degree and type of dispersion as gaseous compound or aerosols in the atmosphere and on their solubility and mobility in wet depositions. Some metals accumulate in plants and in soils. High local emission rates, e.g. by foundries, lead to acute damages of plants and to a long-lasting contamination of soils.
(Kazda & Glatzel, 1984) and are consequently found in game. In pristine areas, especially in the Alps, deposition rates of trace metals (e.g. of Pb) may be surprisingly high due to long-range transport of air masses (Herman et al., 2000; Smidt & Herman, 2003).

The goal of this chapter is to give an overview about the activities to monitor the input and distribution of trace metals and radionuclides in Austrian forest ecosystems and to describe temporal trends of the contamination of Austrian forests. For this purpose we use deposition measurements, bioindicators, and soil analyses.

1.1 Limit values, classification values and critical loads

A set of legal and effect-related limit values was established defining the trace metal concentrations that have adverse effects in terrestrial ecosystems:

1.1.1 Vegetation

Legal limit values for deposition rates and concentrations in the ambient air have been established in Austria, Switzerland and Germany (Table 1).

<table>
<thead>
<tr>
<th>Trace metal</th>
<th>Austria</th>
<th>Switzerland</th>
<th>Germany</th>
<th>EU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>2,500 g ha⁻¹ yr⁻¹</td>
<td>365 g ha⁻¹ yr⁻¹</td>
<td>365 g ha⁻¹ yr⁻¹</td>
<td>5 ng m⁻³</td>
</tr>
<tr>
<td>Cd</td>
<td>50 g ha⁻¹ yr⁻¹</td>
<td>7.3 g ha⁻¹ yr⁻¹</td>
<td>7.3 g ha⁻¹ yr⁻¹</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2,500 g ha⁻¹ yr⁻¹</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>10,000 g ha⁻¹ yr⁻¹</td>
<td>1,460 g ha⁻¹ yr⁻¹</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>-</td>
<td>7.3</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>54.8</td>
<td>20</td>
</tr>
<tr>
<td>As</td>
<td>-</td>
<td>-</td>
<td>14.6</td>
<td>6</td>
</tr>
<tr>
<td>Hg</td>
<td>-</td>
<td>-</td>
<td>3.65</td>
<td></td>
</tr>
</tbody>
</table>

*) Original limit value (annual mean value) transformed from µg m⁻² d⁻¹ into kg ha⁻¹ a⁻¹
Austria: Forstgesetz, Zweite Verordnung gegen forstschädliche Luftverunreinigungen, BGBl. 199/1984;
Switzerland: Schweizerische Luftreinhalteverordnung, 1985;
Germany: Technische Anleitung Luft (2002);

Table 1. Legal limit values for atmospheric deposition of trace metals established in Austria, Switzerland, Germany and for concentrations in the air by the European Union.

The limits vary in terms of the subject of protection. Limits for Hg, Pb and Cd concentrations in needles of Picea abies are based on the data of the Austrian Bio-Indicator Grid and long-term investigations. No established limits exist for the concentration of radionuclides in non-edible forest vegetation.

1.1.2 Soils

For the classification of soils typical ranges in the trace metal content and Critical Levels were established (Table 2).
Table 2. Evaluation of trace metal concentrations in the soil and Critical Loads.

<table>
<thead>
<tr>
<th>Trace Metal</th>
<th>Very low</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Very high</th>
<th>Critical Loads</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>As</td>
<td>mg kg(^{-1})</td>
<td>&lt; 5</td>
<td>5 - 10</td>
<td>10 - 15</td>
<td>15 - 20</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>Cd</td>
<td>mg kg(^{-1})</td>
<td>&lt; 0.10</td>
<td>0.10 - 0.25</td>
<td>0.25 - 0.50</td>
<td>0.50 - 1.00</td>
<td>&gt; 1.00</td>
</tr>
<tr>
<td>Cr</td>
<td>mg kg(^{-1})</td>
<td>&lt; 30</td>
<td>30 - 50</td>
<td>50 - 60</td>
<td>60 - 100</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>Co</td>
<td>mg kg(^{-1})</td>
<td>&lt; 7</td>
<td>7 - 12</td>
<td>12 - 20</td>
<td>20 - 50</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Cu</td>
<td>mg kg(^{-1})</td>
<td>&lt; 15</td>
<td>15 - 25</td>
<td>25 - 50</td>
<td>50 - 100</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>Hg</td>
<td>mg kg(^{-1})</td>
<td>&lt; 0.15</td>
<td>0.15 - 0.25</td>
<td>0.25 - 0.50</td>
<td>0.50 - 1.0</td>
<td>&gt; 1.0</td>
</tr>
<tr>
<td>Mo</td>
<td>mg kg(^{-1})</td>
<td>&lt; 0.3</td>
<td>0.3 - 0.6</td>
<td>0.6 - 2.0</td>
<td>2.0 - 5.0</td>
<td>&gt; 5.0</td>
</tr>
<tr>
<td>Ni</td>
<td>mg kg(^{-1})</td>
<td>&lt; 20</td>
<td>20 - 30</td>
<td>30 - 40</td>
<td>40 - 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>Pb</td>
<td>mg kg(^{-1})</td>
<td>&lt; 10</td>
<td>10 - 20</td>
<td>20 - 50</td>
<td>50 - 100</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>Zn</td>
<td>mg kg(^{-1})</td>
<td>&lt; 60</td>
<td>60 - 90</td>
<td>90 - 150</td>
<td>150 - 300</td>
<td>&gt; 300</td>
</tr>
</tbody>
</table>


A: agriculture, E: environment, EF: ecosystem function, F: forest, H: human health

1.2 The detection of heavy metals and radionuclides in the environment

The trace metal input into ecosystems can be determined by chemical analyses of aerosols, rain water, by means of bioindication and by plant and soil analyses, respectively. Bioindication is a low cost option for plants, fungi and animals accumulating trace metals (Markert et al., 2003). The anthropogenic impact on the soil can be detected by comparison of concentration levels of lower and upper horizons. If anthropogenic impacts of trace metals exist, higher concentrations in the “O-layers” and upper mineral soil layers (0-5 or 0-10 cm) than in deeper soil layers (deeper 30 or 50 cm) are observed. The relation between the concentrations in the upper and deeper layers is the enrichment factor (EF). An EF > 1 indicates accumulation of a specific trace element, an EF < 1 means a depletion. In general the EF should be at least > 1.5 for an indication of anthropogenic inputs (Walthert et al., 2004; Mutsch, 1998).

Radioactive elements are detectable by gamma-ray spectrometry in various compartments of the environment. It was described in the framework of the investigation programme “Artificial and natural radionuclides in spruce needles in Upper Austria from 1983 to 2008 – an application for radioecological monitoring” (Seidel, 2010). *Picea abies* needle samples of the Austrian Bio-Indicator Grid were analysed to investigate the geographical and temporal

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distribution of radionuclides in spruce needles during the last 25 years. While Cs-137 plant uptake has been widely studied in the last few decades, natural radionuclides have received less attention, despite ubiquitously occurring in the environment. Hence *Picea abies* needle samples were also analysed for the following natural radionuclides: K-40, Pb-210, Ra-226, Ra-228, U-238.

### 1.3 Effects of selected trace metals

Deficiency of essential trace metals, e.g. Cu, Fe, Mn, Mo, Ni, Zn, causes reduced growth of shoots and roots as well as visible symptoms (e.g. chlorosis). Excess concentrations in the soils and plant material, respectively, lead to numerous disturbances: Many trace metals inhibit enzymes due to the substitution of essential metals and/or reaction with SH-groups. Furthermore, they injure plasma membranes, promote the formation of reactive oxygen species and inhibit the stomatal function. General eco-toxicological risks are disturbances of microbial communities and reduced microbial biomass in the soil, decreasing litter decomposition, reduction of plant growth, damages of the roots and mycorrhiza, reduced species-diversity in the soil followed by inhibition of nutrients and water uptake, and accumulation of metals in the food chain (DeKok & Stulen, 1992; Hock & Elstner, 1995; Andre et al., 2006; Table 3). Plants provide several mechanisms to prevent heavy metal injuries (Larcher, 2003).

<table>
<thead>
<tr>
<th>Industrial use / production (examples)</th>
<th>Plant use</th>
<th>Uptake, role (1)</th>
<th>Symptoms (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Micronutrients</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>Alloys</td>
<td>Vitamine B_{12}, enzymes</td>
<td>Moderate transport from the roots to other plant parts</td>
</tr>
<tr>
<td>Cr</td>
<td>Alloys, surface protection of metals</td>
<td>Growth stimulation, formation of chlorophyll</td>
<td>Low translocation. Especially Cr(VI) is toxic</td>
</tr>
<tr>
<td>Cu</td>
<td>Electrical industry, alloys, pigments</td>
<td>Enzymes (e.g. of the nitrogen cycle)</td>
<td>Active and passive uptake and moderate translocation, organic chelates</td>
</tr>
<tr>
<td>Fe</td>
<td>Most important industrial metal</td>
<td>Enzymes (e.g. electron transport chain)</td>
<td>Negative effects of excess Fe in the soil/plants are of low relevance</td>
</tr>
<tr>
<td>Zn</td>
<td>Household and industrial instruments, alloys</td>
<td>Cell metabolism</td>
<td>Uptake as Zn^{2+} or organic chelates. Very mobile in acid soils, easily allocated to different plant parts</td>
</tr>
<tr>
<td>Ni</td>
<td>Alloys, catalysts</td>
<td>Part of enzymes, membranes and nucleic acids</td>
<td>Essential for plants with N-fixing symbionts</td>
</tr>
</tbody>
</table>

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Table 3. Use of micronutrients and non-micronutrients, uptake and symptoms caused by trace metal uptake by plants (Hock & Elstner, 1985). (1) Markert et al. (2003); (2) Weigel & Helal 2001.

<table>
<thead>
<tr>
<th>Non-nutrients</th>
<th>Uptake, role (1)</th>
<th>Symptoms (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Alloys, batteries, pigments</td>
<td>Very low mobility, uptake probably passive. Deposition and foliar uptake may contribute significantly to leaf concentrations.</td>
</tr>
<tr>
<td>Cd</td>
<td>Byproduct, pigment, semiconductors, batteries</td>
<td>Highly toxic, uptake passively or metabolically, inhibits enzymes. Very mobile within plants. In the soil it is easily adsorbed by clay minerals and organic matter.</td>
</tr>
<tr>
<td>Hg</td>
<td>Batteries, NaOH-production, Combustion, mining, sintering of ores</td>
<td>Inhibits enzymes. Retained in soils as organo-complex. Uptake elemental (Hg⁰), promoted by methylation and the formation of other methylated organo-compounds. In acid soils harmful for microbes and roots. Low Hg uptake from soil, roots are significant adsorption sites and a barrier for Hg transport to foliage; transported in the atmosphere as Hg⁰ and Methyl-Hg.</td>
</tr>
<tr>
<td>Radioactive isotopes</td>
<td>Cs-137: For humans hazardous, similar to K, slow downward migration in soil, accumulation in soil organic matter. K-40: Similar to Cs. Pb-210: Mainly deposited by natural fallout, transfer via roots is negligible. Ra-226, Ra-228: Similar to Ca, mobile, accumulation in the clay fraction, strong affinity to Fe- and Mn-hydroxides. U-238: Slow migration in soils.</td>
<td>Mutations in trees, light-brown leaves and needles (exclusively found near Chernobyl)</td>
</tr>
</tbody>
</table>

1.4 Metal cycles in forest ecosystems

Ecosystems are effective sinks for trace elements and radioactive isotopes such as Cs-137. The vegetation as well as the soil is able to accumulate and transfer trace elements within the ecosystems. The “rough surfaces” of forests are effective filters for atmospheric contaminations, dissolved substances and particles. Deposition, litterfall and stemflow affect soils by the transfer of trace elements in the surface soil layer and accumulate there.

Wash-off and leaching due to precipitation, litterfall, percolation in the soil and uptake by plants determine the internal cycle of trace elements. The input into the biogenic cycle takes place by wet, dry and occult deposition, output by harvesting, runoff into the groundwater and to a minor part by volatilisation (e.g. carbonyles and/or alkyles of Hg, Ni, Pb). Plants are able to take up trace metals as well as radionuclides actively via the roots and passively via the leaves.

The internal cycle is determined by the pH-dependent mobility of the respective element or radionuclide in the soil. The mobility in plants depends on the type of their chemical
bonding, e.g. as ion or ligand or bound to an organic molecule like citric acid, oxalic acid, amino acids or peptides. Some of the metals can be translocated through the xylem and phloem into other parts of the plant (Ziegler, 1988; Riederer, 1991). Because of high phosphate concentrations in the phloem the mobility of various elements (e.g. Ca, Sr, Pb, Po) is limited, whereas alkali metals, chlorine and phosphorus are rapidly translocated in plants via xylem and phloem (Gerzabek, 1992; Thiessen et al., 1999).

Most of the Chernobyl-derived Cs-137 is still fixed in the upper soil layers which is an indication for the low migration rates and discharge via drainage water. Forest soils act as a long-term sink for Cs-137 and as the main source for radioactive contamination of forest vegetation. The soil contamination by Cs-137 can only be reduced by physical decay, by the export of biomass that previously had adsorbed Cs-137, and by soil erosion (Seidel, 2010). The export in the biomass can be harvesting of fungi and fruits, the consumption by game, and timber harvest (Strebl et al., 2000; IAEA, 2002).

1.5 Objectives

Regarding the fate of selected metals and radioactive isotopes, the following questions arise:

- What is the current input into forest ecosystems?
- Can a risk for forest ecosystems be derived from the input data?
- Which trace metals are of special relevance and how is the feasibility for the use of spruce needles and mosses for environmental radioactive monitoring?
- Can trace metals from anthropogenic or geogenic origin in soils be distinguished?
- What are the patterns of pollution in scale and time within the last twenty years?
- How is the temporal distribution of Cs-137 in *Picea abies* needles in Upper Austria from 1983 – 2008 and what is the radioactive contamination of *Picea abies* needles due to natural radionuclides?
- How is the vertical distribution of artificial and natural radionuclides in soils?

2. Monitoring networks

Trace metals in Austrian forests are monitored within the scope of different programmes with different spatial and temporal resolution (Figure 1, Table 4).

3. Data sets, methods and results

Data sets of atmospheric depositions, forest soils and plant material enable the assessment of the input and the risk for forest ecosystems at a local and regional scale in Austria.

3.1 Deposition

Airborne trace metals and other components are removed from the atmosphere by wet, dry and occult deposition and enter the ecosystems. Wet deposition is the washout of components by rain and snow and is calculated by multiplying volume-weighted annual mean concentrations with the precipitation heights. Dry deposition comprises the settling of gases and particulate matter. The removal of airborne components via fog and hoarfrost (ice formation on cold surfaces) is the occult deposition. It is calculated by the deposition velocities and the average concentrations in the gas phase and fog phase, respectively.
Fig. 1. Distribution of plots where investigations were conducted.

<table>
<thead>
<tr>
<th>Project title</th>
<th>Deposition</th>
<th>Spruce needles (Hg)</th>
<th>Spruce needles (radioactive elements)</th>
<th>Mosses</th>
<th>Forest soils</th>
<th>Forest soils – (radioactive elements)</th>
</tr>
</thead>
<tbody>
<tr>
<td>National Monitoring Grid</td>
<td>Austrian Bio-Indicator Grid</td>
<td>Radio-nuclides in spruce needles</td>
<td>UNECE / ICP ²</td>
<td>Austrian Forest Soil Monitoring System; BioSoil (EU) ³</td>
<td>Radio-nuclides in forest soils ¹</td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Number of plots/samples</th>
<th>8</th>
<th>763 plots</th>
<th>71</th>
<th>220</th>
<th>511 (1987/89); 139 (2006/07)</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, Cd, Cu, Zn</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Co, Cr, Ni, Fe</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Cs-13 ⁴, K-40⁵, Pb-210 ⁶, Ra-226 ⁶, Ra-228⁶, U-238 ⁶</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

¹ Programme “Artificial and natural radionuclides in spruce needles in Upper Austria – an application for radioecological monitoring”
² Monitoring of atmospheric metal pollution by mosses in Austria within the UNECE ICP monitoring programme
³ Austrian Forest Soil Monitoring System
⁴ Artificial radionuclide; ⁵ natural radionuclides

Table 4. Trace metals and radionuclides measured in Austria.
According to meteorological conditions, geographical situation, type of vegetation, type of trace metal etc. different input pathways may be relatively more important for the deposition loads at a given site. In Austria wet deposition predominates at many sites. In an extensive field campaign covering a mountain and a valley site along an altitudinal gradient in western Austria, the total deposition of 10 trace metals was assessed for four seasons and at both sites. Wet deposition was the most important input pathway (Table 5; Bauer et al., 2008).

<table>
<thead>
<tr>
<th>Element, type of deposition</th>
<th>Christlumkopf (1786 m a.s.l.)</th>
<th>Mühleggerköpfl (920 m a.s.l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, wet deposition</td>
<td>14.07</td>
<td>9.32</td>
</tr>
<tr>
<td>Pb, dry deposition</td>
<td>0.35</td>
<td>0.12</td>
</tr>
<tr>
<td>Pb, occult deposition *)</td>
<td>4.20 (7.70 *)</td>
<td>0.04 (0.05 *)</td>
</tr>
<tr>
<td>Cd, wet deposition</td>
<td>1.42</td>
<td>0.94</td>
</tr>
<tr>
<td>Cd, dry deposition</td>
<td>0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>Cd, occult deposition</td>
<td>3.58 (6.80 *)</td>
<td>0.10 (0.12 *)</td>
</tr>
</tbody>
</table>

Table 5. Wet, dry and occult deposition rates (g ha⁻¹ yr⁻¹) of the analyzed heavy metals at the site Christlumkopf (1786 m a.s.l.) and Mühleggerkopfl (920 m a.s.l.), October 1997 - September 1998, also taking the “edge-effect” (*) into account (edge effect: increased deposition rates at forest margins).

A long-term study (1998-2008) carried out at the ICP-Forest site Zöbelboden (Upper Austria), showed that the relative importance of the various deposition pathways studied were quite variable for the most abundant metals (Al, Pb and Zn). Overall the relative importance of wet deposition was much higher for Al, equal for Pb and much lower for Zn compared to dry deposition (Offenthaler et al., 2008).

### 3.1.1 Wet deposition of Pb and Cd - Trends in Austria

Due to their hazardous effects on humans and ecosystems the deposition of Pb and Cd has been monitored for more than 20 years. In 1985 total Pb emissions in Austria amounted to 327 Mg and even to 219 Mg in 1990. Since then Pb emissions have decreased continuously to 15 Mg in 2008, which corresponds to a reduction of 93 % within 18 years. Cd emissions, however, were reduced by 51 % in the period 1985-1990, from 3.1 Mg to 1.58 Mg and since 1990 only by 27 % to 1.15 Mg in 2008 (Anderl et al., 2010). One reason for the strong decrease of Pb in rain and snow samples at rural and urban sites in Austria was the ban of leaded gasoline. This measure led to a decrease of Pb concentrations. Kalina et al. (1999) observed reductions in rural sites between 60 and 80 % within a period of 10 years (1984 - 1995) and around 90 % within 10 years in urban areas. Overall, an annual decline between 4.5 and 16 % was found (Table 6).

The reduction of the Pb concentration in precipitation is also reflected in the decrease of Pb loads by means of wet deposition. In Austria the wet deposition of Pb has been reduced by 80 % to 90 % at rural and 95 % at urban sites since 1990. At the European continental background station Mt. Sonnblick a decrease of 70 % since 1990 was observed (Figure 2).
According to the trend of Cd emissions, Cd loads by means of wet deposition did not decrease to the same extent as Pb loads. The reductions of Cd input by wet deposition since 1994 have been between 4 % and 10 % at rural sites and 20 % – 36 % at urban sites.

Table 6. Average inputs of Pb and Cd in Austria by means of wet deposition (means and mean annual changes) and statistical significances of the trends. Further data are reported in www.waldwissen.net/wald/klima/immissionen/
3.2 Bioindication

3.2.1 Hg in the needles of *Picea abies*

The atmosphere is in most cases the only source of Hg contamination in vegetation. Hg is transported in the atmosphere as Hg$_2$ and as Methyl-Hg. Its uptake from the soil is limited, with roots acting as a significant adsorption site and as a barrier for Hg transport to foliage (Grigal, 2002). These factors are the reason why Hg as a leading element for environmental pollution was selected. By means of a quick and easy analytical method (LECO-AMA 254) and the availability of archived samples it was possible for the first time to evaluate the situation throughout Austria. The analytical method is sensitive enough to determine naturally occurring Hg concentrations (Rea & Keeler, 1998; Rea et al., 2002). The analysed samples were collected within the framework of the Austrian Bio-Indicator Grid in the years 1986, 1996 and 2006 (Fürst et al., 2003).

A significant Hg impact can be found in the areas with iron- and steel production in the region around Linz (Upper Austria) and Leoben/Donawitz (Styria). Surprisingly the contamination is detectable in 100 km distance from Linz downstream the Danube (see maps 1986 and 1996; Figure 3). According to industry records VOEST-Alpine (Upper Austria), 720 kg Hg were emitted by the sintering plant in Linz in the year 2000 (Federal Environment Agency, 2004). Presently, the sintering of Hg-containing Austrian iron ore is a major Hg source in Austria (Fürst, 2007).

Of historical interest is the case of the elevated Hg levels in Brückl (Carinthia). Here amalgam electrodes were used in the chloralkali process of the chlorine plant in the late 1990ies. This source of Hg pollution was eliminated by a technological change. However there are still elevated Hg levels found in the surroundings. The second Austrian electrolysis plant in Hallein (Salzburg) was shut down at the end of the nineties and is shown in the maps from 1986 and 1996. In the Inn Valley (Tyrol) elevated Hg levels were detected in the areas around Schwaz (former silver mining) and Brixlegg (metal recycling by the Montanwerke).

In the vicinity of the capital cities Vienna and Graz (Styria) areas with Hg pollution were detected as well, however for the identification of the individual sources the density of the Bio-Indicator Grid is here not sufficient.

The Hg levels detected in Austria ranged from 0.006 to 0.174 mg kg$^{-1}$ in 1986, from 0.005 to 0.245 mg kg$^{-1}$ in 1996 and from 0.005 to 0.066 mg kg$^{-1}$ in the needles in 2006. The percentage of the plots in the lowest class increase from 27.0 % in 1986 and 49.2 % in 1996 to 73.7 % in 2006.

These concentrations correspond to the levels detected in the needles in other European countries. Around 90 % of the results obtained in different European studies (n = 63) were in the concentration range between 0.005-0.100 mg Hg kg$^{-1}$ (Grigal, 2002).

3.2.2 Radionuclides in the needles of *Picea abies*

In the period from 1986 to 2008, 782 *Picea abies* needle samples were analysed by gamma-ray spectrometry, being provided by the Austrian Bio-Indicator Grid to investigate the spatial and temporal distribution of radionuclides in needles with the main focus on the radioactive
contamination before and after the Chernobyl fallout in 1986. The samples were analysed for Cs-137, K-40, Pb-210, Ra-226, Ra-228 and U-238.

Fig. 3. Hg concentrations in the needle sets 1 of the sampling years 1986 (a), 1996 (b) and 2006 (c).

Due to the half-life time of 30.2 years and the high amount of deposition, Cs-137 can be well detected. The Cs-137 activity concentrations range from the detection limit (D.L.; approx.
2 Bq kg\(^{-1}\)) to 5150 Bq kg\(^{-1}\)) dry matter (D.M.) during the investigation period between 1986 and 2008 (1 Bq = 1 Becquerel = 1 decay per second). The maximum value was detected for needle samples of needle set 2 (sprout season to autumn of the subsequent year) in the year of the Chernobyl fallout. In the following years the Cs-137 activity concentrations in the younger sprouts of needle set 1 (sprout season to autumn) were higher than those in the older sprouts of needle set 2 (Figure 4).

![Cs-137 activity concentrations of Picea abies samples at a site in the Bohemian Massif (Upper Austria, 1983-2008).](image)

This observed age-dependency is in general agreement with former studies. The Cs-137 activity concentrations in *Picea abies* needles decreased at all measuring sites in the years after Chernobyl-derived contamination by various ecological half-live times. At several sites the Cs-137 activity concentrations decreased fast after the Chernobyl-derived contamination. Other sites are characterized by a low decrease of Cs-137 activity concentrations during the last 22 years which is exclusively due to the decay of Cs-137. Hence it can be assumed that these sampling sites are situated in closed forest ecosystems.

The process of Cs-137 recycling due to the needle fall to soil was detected at all measuring sites. The mean duration of Cs-137 cycles varies between 4-5 years depending on site and concentration. At some sites high Cs-137 activities were observed in the needle samples in the years before the Chernobyl accident occurred. These high contaminations could be attributed to the global fallout of nuclear weapon tests in the 1950ies and 1960ies.

With the knowledge of the current background radiation as well as temporal variations of Cs-137 activity concentrations in *Picea abies* needles over the last years, low percentages of Chernobyl-derived contamination (at some sites less than 1 %) are necessary to detect additional Cs-137 deposits in the youngest needles (Seidel, 2010).

K-40 activity concentrations are in the range of the D.L. (approx. 15 Bq kg\(^{-1}\) D.M.) and 294 Bq kg\(^{-1}\) D.M. as it could be observed that K-40 activity concentrations are strongly influenced
by the geological background and natural variations over the years. The trend for constantly increased activity concentrations in the younger sprouts, which was observed for series of Cs-137, was not found for K-40.

Pb-210 activity concentrations range from D.L. (approx. 5 Bq kg\(^{-1}\) D.M. to 45 Bq kg\(^{-1}\) D.M.). Pb-210 is generated by the decay of Ra-226, which is found in most soils and rocks and which produces short-lived gaseous Rn-222 as a daughter. Most of Rn-222 decays with several intermediate radioactive progenies to Pb-210 within the soil, producing supported Pb-210, which is essentially in equilibrium with the parent Ra-226. Some of the Rn-222 diffuses upwards into the atmosphere and decays to Pb-210. This Pb-210 is deposited by fallout, and since it is not in equilibrium with the parent Ra-226, it is commonly termed unsupported or excess Pb-210 (Pb-210\(_{ex}\)). Pb-210\(_{ex}\) was determined in spruce needles to quantify the atmospheric input. Up to 100 % of the Pb-210 content in *Picea abies* needles were of atmospheric origin. Significant higher Pb-210\(_{ex}\) activity concentrations were mostly detected in the older sprouts, which was interpreted as a result of longer atmospheric exposition.

Ra-226 activity concentrations range from the D.L. (1-4 Bq kg\(^{-1}\) D.M.) to 106 Bq kg\(^{-1}\) D.M. For needle set 1 significant higher Ra-226 activity concentrations were detected than for older sprouts of needle set 2. Due to the chemical similarity of Ra with the essential nutrient Ca, it is possible that the plant takes up Ra-226 from soil instead of Ca and transports it along with the transpiration stream to the newly developed sprouts.

All Ra-228 as well as U-238 activity concentrations in spruce needles are below D.L. (approx. 4-5 Bq kg\(^{-1}\) D.M.).

The total radioactivity in spruce needles is strongly influenced by the amount of the radionuclide Cs-137. A ranking list for the radionuclide content in spruce needles could be compiled: Cs-137 > K-40 > Pb-210 > Ra-226. It can be concluded that 52 % of the measured radioactivity was of artificial origin and 48 % of natural origin in the spruce needle samples from 1986-2008 (Seidel, 2010).

3.2.3 Heavy metals in mosses

The suitability of bryophytes for the quantification of trace metal deposition is based on their accumulation abilities derived from a series of morphological and physiological properties (e.g. cationic exchange properties). Since its introduction, the method has been tested and improved in many respects (e.g. sampling strategies, preparation of the samples, growth of indicator species, analyses and statistical tests), leading to a large number of papers supporting its applicability. Detailed literature reviews of methods and applications have been given e.g. by Onianwa (2001) and Zechmeister et al. (2003).

Beside trace metals listed in this article moss has been taken for the indication of a wide range of substances that has been analysed in many studies (Zechmeister et al., 2004; Zechmeister et al., 2005; Zechmeister et al., 2006), e.g. PAHs, dioxins, and trace metals originating mainly from traffic (e.g. Pt, Pd, Sb, Sn, Mo).

Mosses were used for bioindication of atmospheric trace metals in 1991, 1995, 2000, 2005, 2010 at 220 sites throughout Austria, where approximately 160 plots out of them are located in the Austrian Alps. Samples were taken within a Europe-wide project coordinated by the
UNECE ICP-Vegetation (e.g. Harmens et al., 2010) and according to respective guidelines (ICP Vegetation, 2005). Concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V, and Zn were determined in five moss species: *Hylocomium splendens*, *Pleurozium schreberi*, *Hypnum cupressiforme*, *Abietinella abientina* and *Scleropodium purum*.

Before analysis moss was dried and digested by the use of nitric and perchloric acid in a Kjeldatherm. Analysis was performed by inductively coupled plasma atomic emission spectrometry and by an atomic absorption spectrometer with a graphite furnace (for details see Zechmeister et al., 2008).

Mean values from all sampling sites decreased for most of the analysed metals in the overall investigation period (1991-2010). Nevertheless, some elements like Cu or Mo showed even increases and some elements did not show a clear trend for the overall period (e.g. Hg). Despite the general trend, local patterns varied strongly, according to local pollution sources like highways or major industries. Compared to other regions, the Northern Tyrolean Limestone Alps show the highest rates of metal deposition in Austria. Eastern parts of Austria are also influenced by major deposition rates which derive partly from long range transport from eastern countries as well as from agricultural sources.

Additionally, mosses were sampled across several transects in the Austrian Alps in 1991. By that time significant trends could be shown, among them an increase in the concentrations of Pb, Cd and Zn with increasing altitude (see the trend of Pb in Figure 5). Examples for deposition patterns in time and space are given in Figures 6 and 7.

![Figure 5. Pb-concentration in moss (μg Pb per g D.W. moss) within an altitudinal transect (numbers refer to m a.s.l.) at the Gasteiner Tal (Salzburg) and the respective regression line (modified from Zechmeister, 1995).](www.intechopen.com)
Fig. 6. Temporal trends of Hg, Mo, Ni, Pb, V and Zn concentrations (μg g⁻¹ D.W.) in mosses between 1991 and 2005 (n = 220).
3.3 Trace metals in forest soils

Trace metal data were obtained from the Austrian Forest Soil Monitoring System which is part of the Pan-European forest soil condition inventory. The first survey (organic surface layer; synon. ‘litter layer’, 0-10, 10-20, 20-30 and 30-50 cm) was conducted in 1987/89 at 511 plots describing the trace metal situation in Austrian forest soils (Mutsch 1992, 1998). A second investigation was conducted in 2006/2007 within the framework of the EU Project “BioSoil” with a reduced number of plots (139) of the former Austrian Forest Soil Monitoring System. At this time samples were taken from the litter layer and from the depth layers: 0-5, 5-10, 10-20, 20-40 and 40-80 cm. Data of both investigations were compared in order to detect temporal changes. Due to partly different sampling procedures of both investigations the following approach was necessary: the depth layer 0-10 cm of the first investigation was compared to the mean value of the depth layers 0-5 and 5-10 cm of the second one. In a similar way the depth layer 20-40 cm of the second investigation was compared to the mean value of the depth layers 20-30 and 30-50 cm of the first investigation. Thus it was possible to find out possible temporal changes within a period of about 20 years.

Depending on the concentrations in different soil depths the origin of the atmospheric trace metal input can be distinguished by the enrichment factor of the surface layer and upper mineral soil layer compared to the deepest investigated mineral soil layer (ratio of Pb- and Cd-content of the surface layer and of 0-10 cm compared to 30-50 cm). Within the frame of the first investigation (Austrian Forest Soil Monitoring System – 1987/89) the following mean enrichment factors for the surface layer were found: Zn (1.8 in carbonate influenced soils), Pb (3.5 in acidic soils) and Cd (5.6 in acidic soils). Moreover, the altitude of the plots showed an obvious elevation-dependent increase of Pb- and Cd-concentrations, especially in the upper mineral soil and thus an important influence of atmospheric deposition. This
relatively high accumulation occurs in regions where high flow of transboundary air masses and high precipitation amounts are characteristic (“Nordstaulagen” of the Alps; Mutsch, 1992; Herman et al., 2000).

For all investigated heavy metals and for nearly all depth layers a declining trend of concentrations was detectable within the time interval 1987/89 and 2006/07. The most pronounced decrease was observed in the litter layer. In carbonate soils the decrease seems to be more distinct (Table 7).

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Table 7. Mean values (mg kg⁻¹) of selected trace metals 1987/89 and 2006/07 of the BioSoil-plots.
The results proved the emission-reductions of Cu, Zn, Pb and Cd and consequently of deposition rates. The question was whether these reductions were also reflected by soils. For this purpose the differences of the element contents of approximately 130 plots (slightly different number of plots dependent on depth layer and element) were compared after the interval of about 20 years. Because the selected metals show a different behaviour of carbonate and silicate the evaluation is done separately for these two groups. The Figures 8a-e show the mean temporal changes between 1987/89 and 2006/07 for Cu, Zn, Pb, Cd and Hg for the litter layer and for the mineral soil layers 0-10 cm, 10-20 cm and 20-40 cm.

Fig. 8a. Differences (mg kg\(^{-1}\)) of the Cu-content 2006/07 – 1987/89 and standard deviations.

Fig. 8b. Differences (mg kg\(^{-1}\)) of the Zn-content 2006/07 – 1987/89 and standard deviations.
Fig. 8c. Differences (mg kg$^{-1}$) of the Pb-content 2006/07 – 1987/89 and standard deviations.

Fig. 8d. Differences (mg kg$^{-1}$) of the Cd-content 2006/07 – 1987/89 and standard deviations.
Cu: A decrease of Cu-contents is derived in both carbonate and silicate soils for all depth layers. The decrease in carbonate soils is more distinct than in silicate soils in terms of absolute values and relative changes. It can be hypothesised that in the acidic silicate soils the background contents of heavy metals are commonly higher and therefore the relative change by reduction of emitted Cu smaller (Figure 8a).

Zn: The decrease of Zn within 20 years in the litter layer of the carbonate soils is more distinct than in silicate soils. In the mineral soil layers no obvious changes could be detected: possible temporal changes are overlapped by local variation (Figure 8b).

Pb: A very clear decrease of Pb can be proved for the litter layers. It is the most distinct decrease found in this study. This tendency is weaker in carbonate mineral soils, whereas no change is detectable in acidic mineral soils. It seems that even the deposited but very immobile Pb disappears with time from the soil whereby a dynamic balance between input and output exists (Figure 8c).

Cd: Whereas for all the other discussed heavy metals the most obvious decrease can be found in the litter layers, for Cd also the decrease in the mineral soil layers is very clear. Cd is a very mobile element. Due to the current reduced Cd immissions the high Cd-levels measured in the past have not been maintained (Figure 8d).

Hg: Regarding Hg contents, the most distinct decrease is observed in the litter layers. For the mineral soils the tendency of changes is not as evident (Figure 8e).

Figure 9 gives an overview of the Hg contents in Austrian forest soils in different layers. In most cases the Hg contents are higher in the upper layers which indicates atmospheric import. Higher concentrations can be found nearby industrial regions.
**Fig. 9.** Concentrations of Hg in forest soils (mg kg$^{-1}$). FH-horizon: soil litter layer.

**Radionuclides:** A typical depth distribution of radionuclides from a forest site in the Bohemian Massif (Upper Austria) is given in Figure 10.

**Fig. 10.** Depth distribution of radionuclides in soil at a sample site in the Bohemian Massif, Upper Austria (2008).

The vertical depth distribution of Cs-137 showed that between 50% and 90% of the Chernobyl Cs-137 can be found in the uppermost soil layers with a peak in the organic rich layer of 0-10 cm depth. In a few soils, Cs-137 mass activity concentrations, which can be
attributed to the global fallout of the nuclear weapon tests in the 1950ies and 1960ies, were detected down to a depth of 50 cm. The vertical depth distribution of K-40 showed that the amount of K-40 contamination is strongly influenced by local geological situations. Generally the K-40 mass activities increase with depth, which gives a further indication for the geogenic origin of K-40. Lowest K-40 mass activities were detected for the litter layers, whereas these low amounts are probably caused by a very rapid K-40 uptake via fine roots. Thus, the measured low K-40 mass activities in litter layers can be an indication for a very efficient cycling-mechanism. The vertical depth distribution of Pb-210 is similar to Cs-137. The maximum values were detected in the litter layer as well in the uppermost soil layers. According to the determined Pb-210ex values, it was concluded that the Pb-210 detected in the uppermost soil layers is mostly of atmospheric origin and in deeper soil layers of geogenic origin. The natural radionuclides Ra-226, Ra-228 and U-238 were almost exclusively detected in the mineral soil horizons.

The Chernobyl-derived contamination is still present and well detectable in Austrian forest ecosystems. The vertical depth distribution of forest soils in Upper Austria showed that up to 90 % of the Chernobyl Cs-137 can be found in the litter and in the uppermost soil. In general, the amount of Cs-137 is decreasing exponentially with depth. In only a few soils, Cs-137 mass activities – which can be attributed to the global fallout of the nuclear weapon tests in the 1950ies and 1960ies - were detected down to a depth of 50 cm.

4. Conclusions

General statements

The evaluation of the relevance of trace metals in Austrian forest ecosystems can be achieved by comparing the deposition input and the pools in the soil with applicable threshold values. In addition, plants themselves are bioindicators. We used the needle chemistry of both Picea abies and mosses which are known for their ability to accumulate trace metals.

Deposition

The input of Pb and Cd by means of wet deposition remained far below legal limits established in Austria and Switzerland and decreased during the last 20 years. The reduction of Pb loads was significant. Nevertheless, considering the permanent input of Pb into soils especially at “hot spots” nearby metal industry may lead to negative effects on soil microbes after a long term input over decades.

Bioindication with Picea abies needles

The Hg levels in the needle samples of the Austrian Bio-Indicator Grid are mostly low and below the toxic range. Only in the proximity of specific pollution sources elevated levels could be detected. The results show a significant downward trend from 1986 to 2006. A decrease during an almost 30 year period (1963-1991) from approx. 3.5 ppm down to 0.1 ppm was also found in the content of Pb in spruce needles of six plots in Austria (Herman, 1998). The inclusion of legal limiting values for Hg in Norway spruce needles would be useful.

Bioindication with mosses

Compared to other bioindicators (e.g. fungi, needles), mosses have the main advantage in the accumulation and assessment of actual wet, occult and dry deposition only. The uptake
by mosses is a solely passive process and not interfered by any physiological activity of the moss. Another big advantage (e.g. compared to lichens) is the possibility to detect the annual increments of the monitoring species. The analysis of these increments provides information on the deposition within this period. There is no interference with deposits from previous periods because mosses gain the measured trace elements by atmospheric deposition only. Furthermore, aerogene soil particles deposited on the moss can be distinguished by a set of metals (e.g. Al, Fe).

A big task of current research will be the calibration of metal concentrations in mosses with data originating from time consuming and expensive established methods. Such investigations should enable to implement the bioindication method in legislation and to replace the established methods.

**Trace metals in forest soils**

Temporal decrease of Cu, Zn, Pb, Cd and Hg were proven between the first (Austrian Forest Soil Monitoring System – 1987/89) and the second soil inventory (BioSoil – 2006/07). The decrease is strong in the surface layer and applies to the mineral soil. Because emissions accumulate in (forest) soils these results are an indicator for the reduction of anthropogenic trace metal emissions in the last two decades and show that forest soils are a useful indicator for atmogenic pollution.

The presented results also demonstrate that temporal changes of selected parameters are detectable in soils. The obvious decrease of heavy metal concentration in the surface layer and no increase in deeper soil layers indicate that no accumulation takes place. Continuing decrease of heavy metal deposition will probably lead to distinct decreases in deeper layers in the future. The changes are explainable by cause-effect relationships (reduction of emissions) and support every effort in this direction. The success of environmental policy can be scrutinized by forest soil monitoring and forest soil investigations.

**Radionuclides in forest soils**

In Austrian forest ecosystems the Chernobyl-derived Cs-137 is still plant available due to the slow migration of the radionuclide, its retention in soil organic matter and the continuous Cs-137 cycling in forest ecosystems. Thus forest soils act as a long term sink for radio-caesium and as the main source for radioactive contamination of forest vegetation. Spruce needles are an appropriate indicator for radiation monitoring and integrated in environmental surveillance programmes, which are constructed for radiation protection of the public and the environment.


**5. References**


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In this book entitled “The Biosphere”, researchers from all regions of the world report on their findings to explore the origins, evolution, ecosystems and resource utilization patterns of the biosphere. Some describe the complexities and challenges that humanity faces in its efforts to experiment and establish a new partnership with nature in places designated as biosphere reserves by UNESCO under its Man and the Biosphere (MAB) Programme. At the dawn of the 21st century humanity is ever more aware and conscious of the adverse consequences that it has brought upon global climate change and biodiversity loss. We are at a critical moment of reflection and action to work out a new compact with the biosphere that sustains our own wellbeing and that of our planetary companions. This book is a modest attempt to enrich and enable that special moment and its march ahead in human history.

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