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Aspects of ecotoxicology of heavy metals in the Harz region – a guided excursion¹

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Abstract

The Harz Mountains are rich in metallic ores and show many remnants of former mining activities. Mining has caused extreme heavy metal pollution in the mountain area as well as in the valleys of rivers discharging from it. This is mirrored in the vegetation found here today. This excursion guide describes a route through the Harz mountain area along which remnants of mining activities and related vegetation can be studied. Near Bredelem, a Bronze Age smelting site is visited. On slag heaps, a poly-metallic soil has developed, which only allows for the growth of some specialised plant species. The area around Wildemann shows a typical heavy metal plant community (*Armerietum halleri*) on mine tailings, and gives insight into the impact of aerial emissions from the former lead smelter at Frankenscharrnhütte on the surrounding vegetation. At St. Andreasberg, the Samson silver mine displays the last original and fully functional "Fahrkunst" of the world. Around this area, there are fine examples of typical vegetation on arsenate-enriched soils. A stop at the river banks of the river Oker allows to study a well developed and quite diversified version of the *Armerietum halleri* on metal-enriched river sediments. West of Oker City, flotation waste ponds bear a permanent witness of high ecotoxicological relevance to the mining and ore processing activities.

Key words: Harz, mining, heavy metal contamination, vegetation, plant communities

Zusammenfassung

Aspekte der Ökotoxikologie von Schwermetallen in der Harzregion – eine geführte Exkursion

Der Harz ist reich an metallischen Erzen und zeigt zahlreiche Spuren ehemaliger Bergbauaktivitäten. Der Erzbergbau hat sowohl im Gebirge selbst als auch in den Flusstälern, deren Gewässer aus dem Harz gespeist werden, zu extremer Schwermetallkontamination geführt. Die heutige Vegetation der Gegend spiegelt dies wider. Dieser Exkursionsführer beschreibt eine Route durch die Harzregion, entlang derer Spuren des Bergbaus sowie dadurch geprägte Vegetation studiert werden können. In der Nähe von Bredelem wird eine bronzezeitliche Verhüttungsanlage besucht. Hier hat sich auf Schlackehalden ein poly-metallischer Boden herausgebildet, auf welchem nur einige spezialisierte Pflanzenarten wachsen können. In der Region rund um den Wildemann ist eine typische Schwermetallgesellschaft (*Armerietum halleri*) auf Bergwerksabraumhalden zu sehen; zudem wird hier der Einfluss von Emissionen der ehemaligen Bleihütte „Frankenscharrnhütte“ auf die Vegetation sichtbar. In St. Andreasberg kann in der Silbergrube Samson die letzte funktionstüchtige "Fahrkunst" der Welt besichtigt werden. In der Umgebung finden sich anschauliche Beispiele einer an arsenangereicherte Böden angepassten Vegetation. Ein Stop an den Flussufern der Oker gibt die Möglichkeit, eine gut entwickelte und sehr diverse Variante des *Armerietum halleri* auf schwermetallangereicherten Flusssedimenten zu studieren. Westlich von Oker legen ehemalige Absatzbecken ein dauerhaftes Zeugnis der Erzverarbeitung von hoher ökotoxikologischer Relevanz ab.

Schlüsselwörter: Harz, Erzbergbau, Schwermetallkontamination, Vegetation, Pflanzengesellschaften

¹ Prior and after the last COST Action 829 at Braunschweig, two excursions were guided into the Harz mountains and their surroundings to demonstrate the impact of the former mining and processing of sulphurous ores on ecosystems, the adaptation to heavy metal enriched substrates and gypsiferous soils, and the consequences of a lack of sulphur fertilization on oilseed crops and associated weed communities. The present report is part 1 of the excursion guide, which gives analytical data of materials collected during the first excursion on heavy metals to support the effects shown in the field and compares them to published data. Part 2 on the ecotoxicology of sulphur will be published in the following issue.

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Introduction

The Harz Mountains were folded in the late paleozoic Variscan orogeny and pushed up as a block from their geological surroundings since the Jurassic/Cretaceous age. The highest part with the Brocken (1142 m above sea level) consists of plutonites and metamorphic rocks (granite, hornfels, gabbro, gneiss). The western part visited during the two excursions described here and in the following issue is made up mainly from Devonian and Carboniferous schists and sandstones with an intensive mineralization, and shows many remnants of former mining and the related environmental problems (Figure 1). At the southwestern and southern part, layers of the Permian age come to the surface bringing up evaporites such as gypsum, anhydrite and dolomite. Mining of metals has caused extreme pollution in the Harz mountains, but also in the valleys of rivers discharging from the area. Topsoils in the valleys of Oker, Innerste, Leine and Aller are heavily loaded with As, Cd, Cu, Pb, Tl and Zn. Humans as well as animals have been subject to these intoxications for hundreds of years (Knolle and Knolle, 1983; Knolle, 1989).

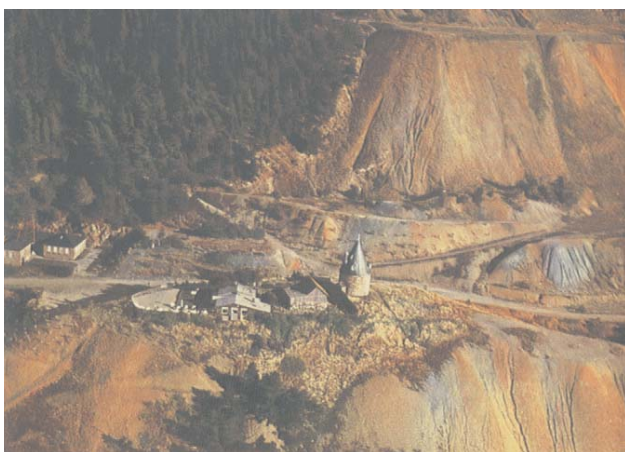


Figure 1: Aerial view on the former outcrop of the Rammelsberg ore bodies near Goslar and the related heavy metal contaminated soils (from a historical postcard)

1 Plants and soils with a surplus of heavy metals

1.1 The vegetation on soils naturally or/and anthropogenically enriched by heavy metals in the Harz mountains

Chemical components of the predominantly sulfidic ores of the Harz Mountains are arsenic, cadmium, cobalt, copper, gold, iron, lead, manganese, mercury, silver, tin, thallium, zinc and others, in various combinations and different concentrations. These cations often have more impact on the vegetation than the surplus of sulphur. With the disappearance of the ice (approx. 12000 years ago)



Figure 2: The metal-resistant ecotype of the glacial relict *Minuartia verna* is restricted to soils with an open vegetation due to its low competitive abilities (Photo: Ernst, 2003).



Figure 3: *Minuartia verna* flowering (Photo: Ernst, 2003)

and the sequence of climatic changes, woodlands and forests developed on nearly all soils in the temperate zone of Europe including the Harz mountains (Beug et al., 1999). Soils with high metal levels, however, were too toxic for the expanding populations of coniferous and broad-leaved trees, so a treeless vegetation with metal-resistant grasses and herbs established. The lack of trees and thus shadow allowed some of the periglacial, shadow-sensitive plant species to survive on these metal-enriched soils up to present times, but only if they had genes coding metal resistance in their genome. One of these species being considered as glacial relict is *Minuartia verna*. This non-mycorrhizal Caryophyllaceae is restricted nowadays to dolomitic, serpentine and heavy-metal soils in the lowland and mountainous regions of Central Europe (Verkleij et al., 1989). Its specific relation to metalliferous soils was already recognised in the Middle Ages by Thalius (1588), who described this plant species as a metal indicator for orogenic soils in the Harz Mountains. The plant species is not very strong in competition with other plant species. Therefore it is restricted to open sites (Figures 2 and 3).

Armeria halleri may also be considered as a glacial relict, although the debated taxonomy (Lefèbvre, 1974; Vekemans et al., 1996) does not exclude a more recent origin. Another plant species with glacial background may be *Silene vulgaris*, a Caryophyllaceae, with many highly specialised ecotypes in the temperate climate zone of Europe with resistance to high soil concentrations of cadmium, cobalt, copper, manganese, lead and zinc (Ernst, 2003). Many other plant species may have colonised heavy metal-enriched soils at later postglacial times. The contamination of soils by human activities far outside every natural metal-enrichment has shown that plant species can evolve metal-resistant ecotypes within a few years up to a decade if the selection pressure is high enough (Ernst, 1976; Bradshaw, 1976). Many plant species having a great ecological amplitude can evolve metal resistance, among them the herbs *Arabidopsis (Cardaminopsis) halleri*, *Achillea millefolium*, *Campanula rotundifolia*, *Plantago lanceolata*, *Rumex acetosa*, *Rumex acetosella*, *Thymus serpyllum*, and the grasses *Agrostis capillaris*, *Agrostis stolonifera*, *Deschampsia (Avenella) flexuosa*, *Festuca ovina*, *Festuca rubra*, and *Molinia caerulea* (Ernst, 1974). All metal-resistant plant species in the Harz Mountains make up the plant community “*Armerietum halleri*”, first described by Libbert (1930, 1937) from the Harz region (Figures 4 and 5).



Figure 4:
A view of the heavy metal vegetation of the *Armerietum halleri* with *Armeria halleri*, *Minuartia verna*, *Silene vulgaris* and the grasses *Agrostis capillaris* and *Festuca ovina* (Photo: Ernst, 2003)

Most sites with undisturbed heavy metal vegetation on natural ore outcrops were devastated by the mining industry from the late Bronze Age - ca. 1000 years B.P. – onwards (Anonymous, 2000). The remaining heavy metal vegetation is most strongly modified by human activities. The Bronze Age mining and smelting activities in the Harz Mountains demanded a lot of wood and brought about the first disturbance of Harz forests, which was intensified during the Middle Ages with the modernisation of mining, especially at the Rammelsberg sites. Roasting



Figure 5:
Armerietum halleri with *Plantago lanceolata*, *Festuca ovina* and *Armeria halleri* (Photo: Ernst, 2003)

of the sulfidic ores demanded 1.3 t wood per ton lead and copper ore, smelting of the ores a further 0.7 t wood. Already in the Middle Ages it was cheaper to transport the ores to wooded sites than vice versa.

Three different types of man-made metal-enriched soils can be found:

- a: Slags and other remnants of the smelting process were heaped up as slag tailings near the smelters at numerous sites in the Harz Mountains (Gundlach and Steinkamp, 1973) and bear a well-developed *Armerietum halleri* (Ernst, 1965, 1974). The re-use of mine tailings for road constructions made most of this heavy metal vegetation disappear since the mid of the 1960s.
- b: Up to the 19th century, ores were stamped and the metal separated by washing. Due to this procedure, rivers received metal-contaminated sediments (“Pochsande” = “sand of stamping mills”) which were transported to the lowland and were deposited on river banks up to more than 100 km downstream from the mining sites (Emmerling and Kolkwitz, 1914; Ernst, 1965, 1974; Baumann, 1984). The original heavy metal vegetation has been conserved best on these river banks. Springs being in contact with ore bodies were and are delivering metal-enriched water via small tributaries to the rivers Innerste, Oker and others (Nowak and Preul, 1971; Knolle, 1989). At periods of high water levels, the metal-contaminated sediments were deposited on the river banks together with seeds of metal-resistant plants,

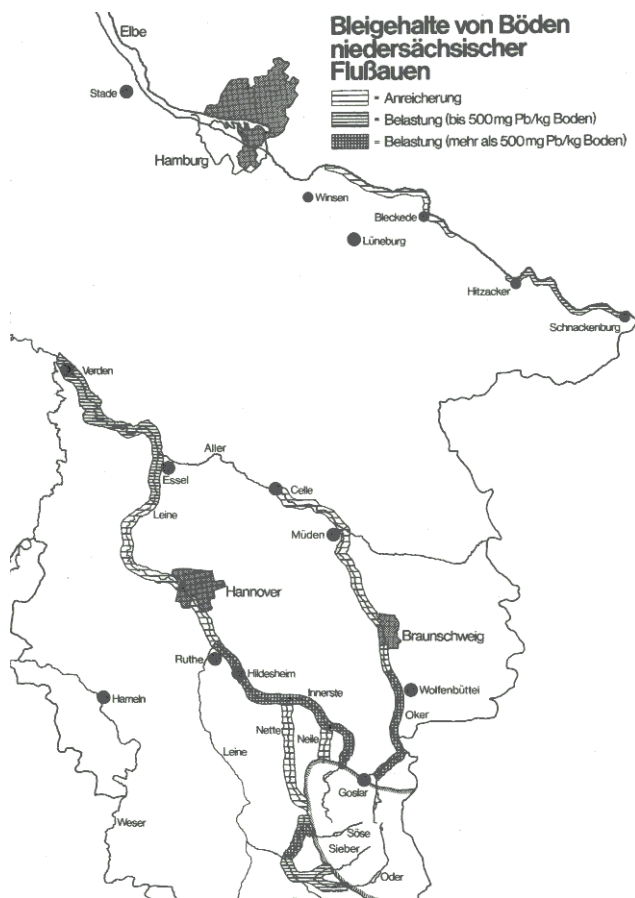


Figure 6: Lead contents of riverbank soils along the large stream valleys of Lower Saxony influenced by Harz mining and smelting effects over more than 200 km away from the Harz (legend from top to bottom: accumulation; pollution up to 500 mg kg⁻¹ Pb; pollution > 500 mg kg⁻¹ Pb) (from Köster and Merkel, 1985)

resulting in new sites of - in this case - anthropogenic heavy metal vegetation and, at the same time, intoxication of agricultural crops on arable land. The adverse impact of metal-loaded sediments on agriculture was already recognised by Meyer in 1822; it hampered agriculture up to the late 1960s (Emmerling and Kolkwitz, 1914; Ernst, 1974; von Hodenberg and Finck, 1975), when the construction of the Innerste and Oker dam was finished.

c: Although wood shortage was not the reason for the selection of the location of smelters in the 19th and 20th century, metal smelters and refineries were still constructed at the borderline of the Harz Mountains, e.g. at Langelsheim, Oker, and Harlingerode. Due to a lack of filters, metals and air pollutants (SO₂, NO_x) were emitted and affected vegetation up to several km distance, producing the so-called “Rauchschäden” (=“fumigation damage”), not only in the 19th century (Von Schroeder and Reuss, 1883), but also in the 20th century up to at least 1978, when the lead smelter at Frankenscharnhütte was closed. The smelter at Oker was technically

improved, but is still emitting considerable amounts of heavy metals from primary and secondary sources. According to the European register of emissions of harmful substances EPER (<http://www.eper.de/eper/2003/deutschlandkarte/karte.php?karte=m20200>), metal producing industry around Oker City emitted up to 222 kg Cd, 11500 kg Pb (Harz-Metall GmbH) and 4640 kg Zn (Metalleurop GmbH Niederlassung Harzer Zinkoxide) in 2001. The emitted metals consequently enriched the soils with cadmium, lead, and zinc (Anonymous, 1979). Some examples of the metal concentration of such soils will be given in the site descriptions.

Johannes and Krause (1985) found that ore deposits, mineralisations and anthropogenic influences in the north-western Harz Mountains were clearly indicated by Cu, Zn, Cd, Pb, Co, Ni, Mn, Fe, Mg, Ca, Sr, Ba, Rb, V and Mo contents in ashed needles from different spruce trees. Less known is the fact that animals in the Harz region, e.g. birds and mammals, also show enrichment of heavy metals (Knolle and Knolle, 1983). Koop (1989) discussed the high heavy metal contents in fishes of the Oker river north of the Oker smelter. Hartmann (2000) found that bats from the Harz region showed significantly higher lead concentrations in bones, livers and kidneys than bats from other parts of Lower Saxony.

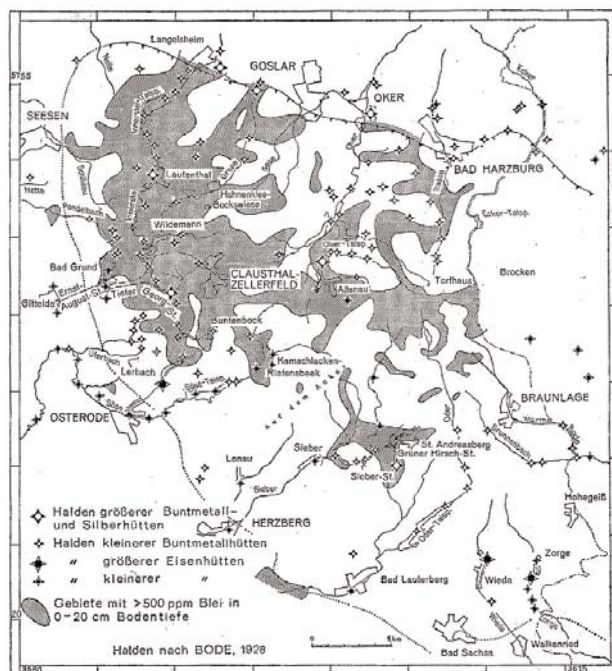


Figure 7: Regions of high lead concentration in the Upper Harz (from Nowak and Preul, 1971).

- Legend (from top to bottom):
- Slag heaps of large non-ferrous metal or silver smelters
 - Slag heaps of small non-ferrous metal smelters
 - Slag heaps of large iron smelters
 - Slag heaps of small iron smelters
 - Areas with > 500 mg kg⁻¹ Pb in 0-20 cm soil depth

1.2 Metal concentration in plants and their regulation

Plants growing on heavy metal-enriched soils are characterized by an enhanced metal level in all plant parts with the exception of the seeds (Ernst, 1974). At the whole-plant level, the transfer of metals from roots to shoots is specific for plant species and ecotype (Ernst, 1974; Macnair, 2002), resulting in different degrees of metal accumulation in the various plant tissues. The highest values are often found in roots, the lowest in seeds (Table 1).

Restriction of metal uptake, such as in the ecotype "Langelsheim" (Table 1), is one possible strategy to survive on heavy metal-enriched soils. Some plant species operate in an adverse way: They allow metal concentrations in the leaves to increase to extraordinarily high levels, a process termed "hyperaccumulation" by Brooks et al. (1977). The metal levels defining a hyperaccumulator were established specifically for each metal. The lower borderline of the metal level, however, was modified several times (Brooks, 1998) without any physiological reason. In the case of zinc, a hyperaccumulator contains more than 10 g Zn kg⁻¹ dry mass, as in *Arabidopsis halleri*. The Zn concentration can be strongly enhanced when an ecotype is grown on soils it is not adapted to. In such a situation the metal concentration of a plant can increase to a hyperaccumulator level, as shown for the ecotype "Plombières" of *Silene vulgaris* when grown on the soil of the Bredelem slag heap (Table 1). Plant species remaining below the hyperaccumulator level, but still accumulating considerable amounts of heavy metals, are called "accumulators", as many plant species given in Table 3.

Plant species sharing a symbiosis with arbuscular myc-

orrhizal fungi such as the perennial herb *Plantago lanceolata* and all grasses can restrict the metal uptake compared to non-mycorrhizal herbs such as *Arabidopsis halleri*, *Minuartia verna* and *Silene vulgaris* (Ietswaart et al., 1992). Other plant species can diminish their metal concentration by excretion. *Armeria halleri* exudates heavy metals by salt glands, but the efficiency is low (Ernst, 1974). *Minuartia verna* can dispose of heavy metals by excretion via hydathodes (Neumann et al., 1997).

All the various regulatory mechanisms can finally not prevent a high metal concentration in plant species growing on metal-enriched soils compared to ecotypes of the same species growing on soils with a "normal" metal concentration. Therefore, metal resistance in higher plants is not based on an exclusion of metals, but on a good regulation of a surplus of metals at the cellular and whole plant level. Uptake of heavy metals is steered by metal-specific genes responsible for the synthesis of metal transporters. Up to now only a few have been identified, such as the *ZNT1* and *ZNT2* for zinc in *Thlaspi caerulescens* (Assuncao et al., 2001). Compartmentation of heavy metals in the cytosol and the cell organelles is a very decisive process which avoids metal accumulation in the physiologically active parts of the cell, and makes them accumulate in vacuoles and cell walls. In this process, zinc and nickel will be complexed by organic acids (Mathys, 1977; Krämer et al., 2000; Sarret et al., 2002). Copper can be bound by metalloproteins of the MT-2b type (Van Hoof et al., 2001), and nickel by histidin (Krämer et al., 1996). In plants resistant to a surplus of arsenic and cadmium, an enhanced synthesis of phytochelatins takes place prior to the transfer of these chemical elements into vacuoles (De

Table 1:

Concentration of heavy metals (mean and standard error S.E.) in different plant parts of three ecotypes of *Silene vulgaris* with different degrees of metal-resistance

Ecotype	Plant part	Metal concentration in mg kg ⁻¹ dry matter							
		Cu		Fe		Mn		Zn	
		mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Langelsheim	Seeds	10.8	1.91	64.2	4.47	32.4	8.79	56.2	14.4
	Leaves	80.7	17.8	191	30.2	917	84.6	3361	96.8
	Stalk	38.1	9.53	88.2	10.6	73.6	15.9	5761	340
Plombières	Roots	374	43.2	2966	977	287	53.8	3438	879
	Leaves	259	75.6	994	324	898	168	9985	3073
	Roots	1640	613	8528	2044	961	269	26810	5300
Amsterdam	Leaves	941	257	6367	2670	1302	210	4028	1115
	Roots	2491	324	10053	2189	923	228	6029	987

In a pot experiment, three ecotypes were grown under controlled conditions from germination onwards in the soil of the Bronze Age smelting site south of Bredelem. The ecotype "Langelsheim", growing on its own soil, was resistant to a lot of heavy metals; the ecotype "Plombières" was resistant to Cd, Pb, and Zn, but its resistance was not high enough to survive to the reproductive phase. The ecotype "Amsterdam" was sensitive to a surplus of metals and died already 14 days after germination. The most metal-resistant ecotype "Langelsheim" can restrict the uptake of the heavy metals so that their concentration is relatively low in roots and leaves compared to the two other ecotypes. Data from Ernst et al. (2000) and Ernst (unpublished).

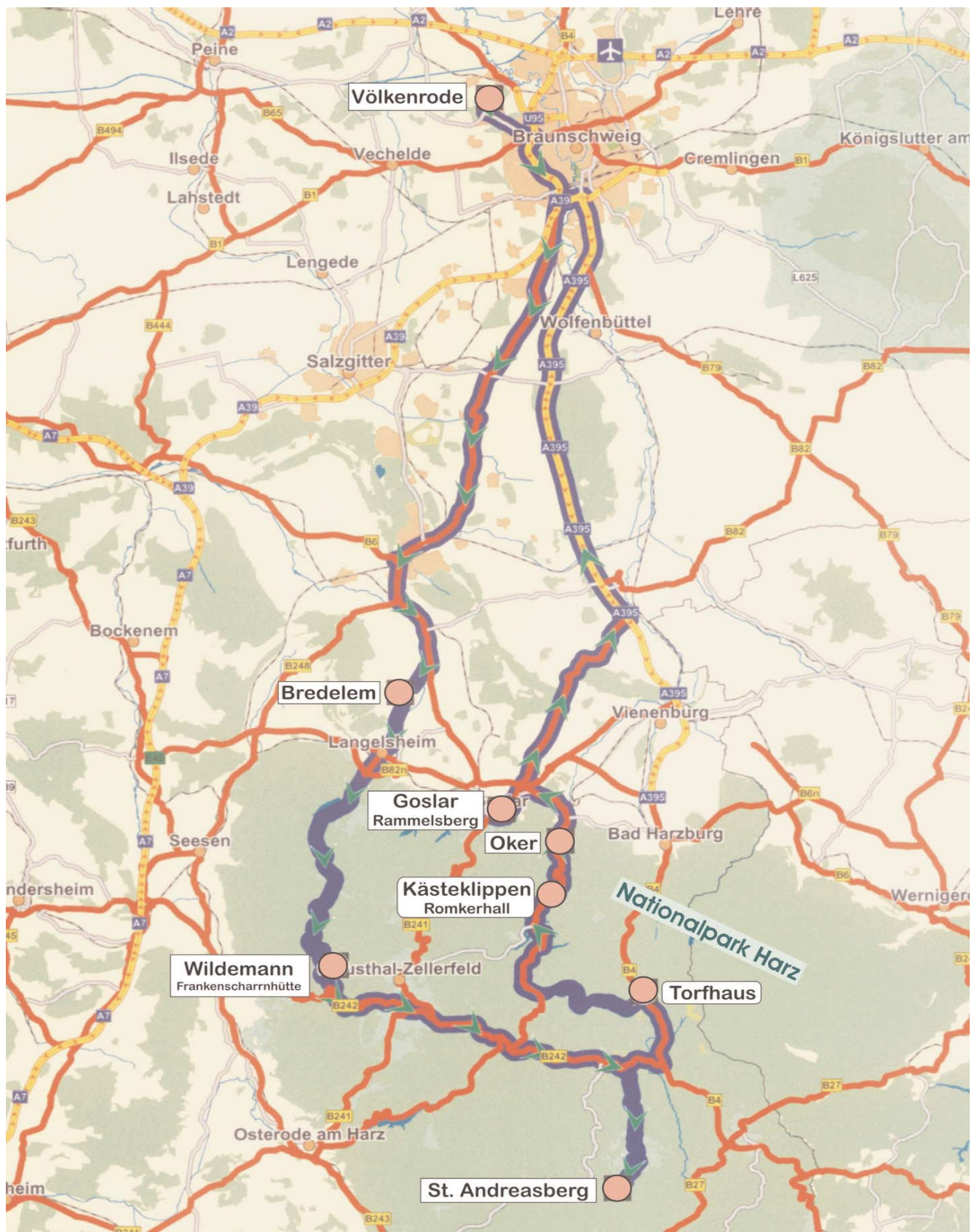


Figure 8:
Suggested excursion route on aspects of ecotoxicology of heavy metals in the Harz region (Note: Information on locations with rounded labels is given in part 2 of this excursion guide on aspects of ecotoxicology of sulphur, see next issue). Map produced with KlickRoute 2003©

Knecht et al., 1995; Hartley-Whitaker et al., 2001). One of the main differences between metal-resistant and non-resistant plants is a more rapid transfer into the vacuole in metal-resistant plants (Chardonens et al., 1999a). Within a leaf, the highest zinc and cadmium accumulation is found in the epidermal cells (Chardonens et al., 1999b). As soon as the metal concentrations in the cytosol, also in metal-resistant plants, exceed the regulatory level, plants become chlorotic, rich in anthocyanins, and can contain enhanced phytochelatin concentrations (Ernst, 1965, 1974, 1999; Ernst and Nelissen 2000). The chlorosis can be caused by different metabolic processes. Lead is blocking the activity of the delta-aminolevulinic acid, resulting in an insufficient amount of protochlorophyll. A surplus of cellular zinc, also in highly metal-resistant plants, hampers the transfer of magnesium into the chlorophyll molecule and lets the zinc concentration in the chloroplast increase, finally resulting in a reduction of photosynthesis by 90 % (Van Assche and Clijsters, 1986). Insufficient metal resistance can result in morphological changes such as dwarfed growth and small leaf size (Ernst, 1999).

The data presented below should emphasise that the concentration of heavy metals in plant species varies within species at a particular site and for the same species between different sites, depending on the metal concentrations in the soil.

Table 2:

Total concentration of heavy metals (HNO₃/HCl, 3:1) (mean and standard error S.E.) in the material of the slag heap at the Bronze Age smelting site south of Bredelem. The soil data of the pioneer site with *Armeria maritima* and with *Silene vulgaris* are those given by Ernst and Nelissen (2000) as sites no. 11 and 12, those of the site with dwarfed trees of *Betula pendula* by Ernst and Nelissen (2003)

Microsite	Heavy metal concentration in mg kg ⁻¹ dry matter											
	Cd		Cu		Fe		Mn		Pb		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
<i>Armeria halleri</i> site	18.0	1.12	6927	1017	126780	48478	8021	3626	18648	2694	36357	11182
<i>Silene vulgaris</i> site	16.9	1.12	5910	1462	63948	13907	5769	1758	16369	4144	28445	4773
<i>Betula pendula</i> site	7.42	1.46	1093	31.8	42614	559	8571	220	9324	1658	5950	327

Table 3:

Metal concentration (HNO₃/HCl extraction) (mean and standard error S.E.) in mature leaves of plant species growing on the slag heaps south of Bredelem (Ernst, 1974; Ernst, unpublished). nd = not determined

Plant species	Metal concentration in mg kg ⁻¹ dry matter											
	Cd		Cu		Fe		Mn		Pb		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
<i>Arabidopsis halleri</i>	157	4.50	6.99	1.91	251	20.7	1280	60.4	253	47.7	29229	8108
<i>Armeria halleri</i>	14.6	4.50	115	14.6	144	60.3	224	27.5	49.7	16.6	2021	307
<i>Minuartia verna</i>	49.5	3.37	574	62.3	1123	232	593	67.6	99.5	18.6	5427	1164
<i>Silene vulgaris</i>	23.6	4.50	80.7	17.8	191	30.2	917	84.6	180	45.6	3361	98.1
<i>Agrostis capillaris</i>	12.4	1.12	1.27	0.64	183	86.0	78.0	13.7	137	72.5	118	39.2
<i>Festuca ovina</i>	11.2	1.12	7.63	3.81	119	38.5	80.2	18.7	82.9	6.22	1144	255
<i>Molinia caerulea</i>	nd		13.3	3.18	329	92.2	76.4	14.8	nd		394	87.0

1.3 Visits to sites with heavy metal vegetation⁵

1.3.1 Slag heaps at the Bronze Age smelting site south of Bredelem⁶ (51°58'N, 10°21'E)

In the Bronze Age, production of bronze was realised by smelting of tin and copper of mostly hand-collected pieces of ores. The smelting of metals with charcoal was not very efficient, so that the slag heaps of such smelting sites are very rich in many heavy metals. From the Middle Ages onwards up to the 1960s, deposition of metal-contaminated sediments from mining activities added still more heavy metals to the soils along the river Innerste (Figures 9 and 10).

As a result, there is nowadays a polymetallic soil south of Bredelem very rich in several heavy metals (Table 2). Soil metal concentrations on this site show a very patchy distribution. At some microsites, the bio-available metal levels can increase to a degree which hampers all plant growth (Ernst et al., 2000; Ernst and Nelissen, 2000), whereas at other microsites the metal concentration is only moderate, enabling a lot of metal-resistant plant species to establish and grow.

⁵ Location of sites see Figure 8.

⁶ Please note that the Bredelem site is a protected area ("Naturschutzgebiet"). This implies that visitors may walk along the marked paths only. It is not allowed to pick plants or collect insects or other animals in this area.

1.3.1.1 Metal levels in higher plants

As a consequence of the high concentration of heavy metals in the soil at the Bronze Age smelting site, metal



Figure 9:

A view across the Innerste floodplain with remnants of the Bronze Age smelting site. The perennial herb *Armeria halleri* and the grasses *Agrostis capillaris* and *Festuca ovina* colonise the microsites with the highest metal concentration. The high demand for soil moisture restricts *Molinia caerulea* more to the river sites (the tussocks in the back). On soils without metal enrichment, willow, poplar, oak and Scotch pine can develop (Photo: Ernst, 2003)



Figure 10:

Armerietum halleri and metal-resistant woodland at the Bronze Age smelting site (Photo: Ernst, 2003)

Table 4:

Metal concentration (mean and standard error S.E., d.m. = dry matter) of bleeding sap in spring and of mature leaves of *Betula pendula* in autumn at the Bronze Age smelting site south of Bredelem (Ernst and Nelissen, 2003).

Betula pendula	Metal concentration											
	Cd		Cu		Fe		Mn		Pb		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Bleeding sap (mg L ⁻¹)	0.05	0.01	0.27	0.07	0.33	0.16	7.97	0.99	0.13	0.03	40.7	8.04
Leaves (mg kg ⁻¹ d.m.)	1.12	1.12	12.7	2.5	160	29.0	357	209	20.7		1975	333

concentrations in plants are also very high. With the exception of copper, the highest level of most other heavy metals occurs in the leaves of the Zn-hyperaccumulator *Arabidopsis halleri* (Table 3). The vitality of *Armeria halleri*, the plant species with the highest resistance to Cd, Cu, Pb, and Zn, is a good indicator of the bio-available metal concentration, which can be judged by the number of dead leaves in a rosette.

The growth pattern of the mycorrhizal grasses of *Agrostis capillaris* and *Avenella flexuosa* provides another option to evaluate the degree of bio-available metal levels of the soil with the naked eye. Very tiny tufts of the grasses indicate high soil metal levels, whereas a closed vegetation cover is characteristic for low soil metal levels (Figure 11). At moderate soil metal levels, some members of a population of *Betula pendula* can survive due to the evolution of metal resistance and the symbiosis with the ectomycorrhizal fungus *Paxillus involutus* (Ott et al., 2002) (Figure 12). The Zn concentration in bleeding sap in spring already gives a good indication for the Zn concentration of mature leaves in autumn (Table 4).

However, resistance to various heavy metals is not enough for colonising metal-contaminated river banks. Plant species on such sites also have to cope with drought in summer, explaining the mosaic vegetation pattern. Species with a deep rooting system (up to 3 m depth), such as *Armeria halleri* and *Silene vulgaris*, can penetrate down to the water level of the river (Figure 13). In addition, *Silene vulgaris* has a structurally increased level of proline on very dry metal soils (Schat et al., 1997). Superficially rooting species such as *Arabidopsis halleri* are restricted to those metal-enriched microsites which have a high water-holding capacity or a high soil compaction. Such sites are avoided by species with a high sensitivity to stagnant water, e.g. *Minuartia verna*.

1.3.1.2 Heavy metals and lichens

Open soils are colonised by epigeic lichens such as *Cladonia alpicornis*, *Cladonia arbuscula*, *Cladonia chlorophaea*, *Cladonia floerkeana*, *Cladonia furcata*, *Cladonia mitis*, *Cladonia pyxidata*, *Cladonia rangiformis*, *Cladonia verticillata*, *Cetraria aculeata*, *Stereocaulon dactylophyllum* and *Stereocaulon vesuvianum* (Ernst,

1964; Dierschke, 1969). Due to their limited soil contact they only contain moderate levels of heavy metals (Lange and Ziegler, 1963; Ernst, 1974). The regulation of metal concentration in epigeic lichens is not well known. In every case a surplus of cadmium is bound to phytochelatin (Pawlik-Skowronska et al., 2002).



Figure 11: The growth pattern of *Agrostis capillaris* and *Avenella flexuosa* provides an option to evaluate the degree of bio-available metal levels of the soil with the naked eye (Photo: Ernst, 2003)



Figure 12: At moderate soil metal levels, some members of a population of *Betula pendula* can survive (Photo: Ernst, 2003)



Figure 13: The more than two meter thick sediments of the river Innerste contain a lot of heavy metals from former mining activities in the Harz mountains. *Armeria maritima* can survive dry periods by penetrating with its roots down to the water level of the riverbed (Photo: Ernst, 2003)

Slags as remnants of the smelting process are characterised by a very specific epilithic community, the *Acarosporium sinopicae* (Figures 14 and 15). An analysis of *Lecidea fuscoatra* (L.) Ach. from the slag heaps at Bredelem demonstrates the accumulation of heavy metals by such orophilic lichens (Table 5). The crustaceous

Table 5:

Heavy metal concentration (mean and standard error S.E.) in the thallus of the lichen *Lecidea fuscoatra* growing on slags near Bredelem in comparison to the crustaceous lichens *Acarospora sinopica* and *Lecanora epanora* from the same site (Lange and Ziegler, 1963) and *Lecanora polytropa* from a copper ore outcrop in Greenland (Altrup and Hansen, 1977)

Species	Metal concentration in mg kg ⁻¹ dry matter											
	Cd		Cu		Fe		Mn		Pb		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
<i>Lecidea fuscoatra</i>	1.69	12.4	82.6		28148		155		41854		186	
<i>Acarospora sinopica</i>			1049	69.9	44345	12901						
<i>Lecanora epanora</i>			222		5808							
<i>Lecanora polytropa</i>			4900		26194		300		41.4		60.2	

lichen species *Lecidea fuscoatra* on some smelting remnants at the Bredelem site contains as much iron as *Lecanora polytropa* on an ore outcrop in Greenland



Figure 14:
The epilithic lichen community *Acarosporium sinopicae* with *Acarospora sinopica*, *Lecanora epanora* and *Lecidea fuscoatra* colonizes metal-enriched slags (Photo: Ernst, 2003)



Figure 15:
Lecidia spec. of the epilithic lichen community *Acarosporium sinopicae* (Photo: Ernst, 2003)



Figure 16:
The scrapes on a leaf of *Silene vulgaris* made by the herbivorous 24-spotted ladybird (Photo: Ernst, 2003)

(Alstrup and Hansen, 1977). It also has very high lead levels, but less copper than *Acarospora sinopica* and *Lecanora epanora* from the same site (Lange and Ziegler, 1963). In the lichen association of the *Acarosporium sinopicae*, *Acarospora montana*, *Acarospora sinopica*, and *Acarospora smaragdula* can contain up to 1144 mg kg⁻¹ Cu and 61435 mg kg⁻¹ Fe, mostly in the upper fungal part of the thallus. The copper is mostly restricted to the fungal partner in the lichen, where it is bound to oxalate (Purvis, 1984) or / and to norstictic acid, a specific lichen compound (Purvis et al., 1987). The metal binding may also occur for lead.

1.3.1.3 Metal-resistant plants and herbivores

Evolution of metal resistance in animals is quite scarce (Boyd and Martens, 1994; Martens and Boyd, 2002). Nevertheless, the high metal concentration of the plants does not prevent their consumption by some herbivores and semivivores. The only herbivorous insect on heavy metal sites in Central and Western Europe is a ladybird (*Subcoccinella vigintiquatuorpunctata* L.) consuming metal-loaded leaves of *Silene vulgaris* in all phases of its life-cycle, being the first time reported from *Silene vulgaris* from a mine site at Plombières (Jacquemart, 1958). By scraping some epidermal tissue in late April, the adult beetle can obviously “analyse” the metal concentration of a leaf prior to laying its 4-8 eggs on leaves with a moderate Zn level of 1635 to 3270 mg kg⁻¹ dry mass Zn. During development, the larva removes large parts of the upper epidermis and parenchyma of young leaves, and of the flower buds (Figure 16). Therefore, an infested plant cannot develop flowers and seeds.

Seeds are a metal-poor niche in a metal-enriched ecosystem in all metal-resistant plant species. Therefore, seeds are a preferred source for pre-dispersal seed-predators. On heavy metal sites, *Silene vulgaris* is suffering from a second group of predators concentrating on the developing seeds. Noctuid moths belonging to the genus *Hadena* are pollinators of *Silene vulgaris*. After pollination, the moth lays one egg in a flower of one raceme. The developing larva consumes the developing seeds of one capsule and moves to the next capsule up to pupation (Ernst, 1987). Larvae of *Hadena bicruris* are even able to consume the upper, less metal-loaded leaves of *Silene vulgaris* in the last larval phase. At heavy infestation, the diminished seed production affects the plant’s reproductive fitness.

Less damaging is the seed beetle *Sibinia viscaria* (Curculionidae), which lays one egg in one fertilised flower. The larva only consumes the seeds of one capsule. Similar seed predation by other insects was found in the infructescences of *Arabidopsis halleri* and *Armeria halleri*.

1.3.2 Mine tailings near Wildemann (51°50'N, 10°17'E)

The mining activities near Wildemann probably started in the early Middle Ages or before. However, the metal concentrations of the slag heaps are still comparable to those of the Bronze Age smelting site. The metal levels can increase up to 5.4 % Fe, 1 % Zn, 2.3 % Pb, 1.4 % Mn, 0.1 % Cu, and 0.06 % Cd (Ernst and Nelissen, 2000). The metal-rich microsites support a heavy metal vegetation of the *Armerietum halleri*, while a birch woodland is growing on moderately contaminated microsites. In contrast to the situation on river banks, the substrate on mine tailings is mobile and demands not only plant resistance to the various heavy metals, but also to mechanical damage (Figure 17).



Figure 17:

The substrate on mine tailings is not very stable and hampers a rapid colonisation by higher plants (Photo: Ernst, 2003)

Table 6:

Element concentration (mean and standard error S.E.) in the needles and the young twigs of *Picea abies* growing in a metal gradient near Wildemann, collected on May 15, 2003

		Element concentration in mg kg ⁻¹ dry matter							
Plant part	Colour	Cd		Cu		Fe		Mn	
		mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Needles	pale	1.35	0.11	11.8	1.97	263	30.7	183	25.3
	light green	1.57	0.45	9.28	2.99	79.9	1.12	137	4.94
	green	1.24	0.11	10.1	1.46	65.3	3.35	248	31.9
Twigs	pale	1.46	0.34	10.5	2.67	165	46.9	179	40.7
	light green	1.24	0.34	13.7	1.40	255	35.7	70.3	13.7
	green	1.24	0.11	13.3	1.33	141	30.2	177	13.7
		Pb		Zn		P		Mg	
		mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Needles	pale	18.4	2.28	592	92.2	777	68.1	425	70.5
	light green	14.7	6.84	318	6.54	712	49.6	260	4.86
	green	12.4	1.86	146	28.8	1183	46.5	545	70.5
Twigs	pale	74.8	3.73	512	88.9	622	92.9	399	38.9
	light green	88.5	10.2	252	24.2	938	130	382	43.8
	green	18.2	1.04	208	19.0	880	18.6	712	7.29

Only a few plant species have evolved this ability. Ecotypes of *Silene vulgaris* buried by soil can react with a rapid growth of the buried shoot (Ernst, 1965). Damage of the shoot can be repaired by a burst of dormant buds near the root crown or at undamaged parts higher up the shoot. Where the tailing is flat, seedlings of *Picea abies* and *Betula pendula* try to colonise the soil year by year. Despite their mycorrhization, however, they only succeed on soils with a very moderate to low metal content. On soils with higher metal levels, growth is stunted and needles are short and chlorotic (pale). These metal-affected needles have the highest concentration of Zn and Fe, but only a low concentration of phosphorus and magnesium. A similar chemical situation is found for the twigs supporting these needles (Table 6).

1.3.3 Impact of a former lead smelter on its surroundings

The smelter at Frankenscharrnhütte (south east of Wildemann) was established around 1355 to produce copper, silver and lead. It was in operation until December 1967. During the past 600 years, it has contaminated the surroundings predominantly with lead and emitted a lot of SO₂ into the air. The soil is still rich in lead, surpassing all lead levels caused by mining (Table 7), whereas the concentration of Zn, Cu, and Cd is moderate. Not only the total concentration of Pb is high, but also the CaCl₂- and H₂O-extractable fractions are dominated by lead.

Table 7:

Soil metal concentration (mean and standard error S.E.) in the surroundings of a former lead smelter at Frankenscharnhütte, collected on May 15, 2003

Extractant	Metal concentration in mg kg ⁻¹ dry matter											
	Cd		Cu		Fe		Mn		Pb		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
HCl / HNO ₃	8.21	1.01	288	34.4	46802	8489	442	29.7	64646	1865	1255	248
0.01M CaCl ₂	0.11	0.11	0.51	0.13	1.06	0.28	0.77	0.05	145	25.7	1.63	0.13
H ₂ O	0.11		0.25	0.06	0.56	0.17	0.55	0.05	85.6	29.4	1.24	0.07



Figure 18:

The lead-contaminated soil of the surroundings of the former lead smelter at Frankenscharnhütte is mainly colonized by *Calluna vulgaris* (Photo: Friedrich Balck, 2002)

The longterm SO₂-emission has resulted in a die-back of all trees. Only a heathland with *Calluna vulgaris*, *Avenella flexuosa*, *Festuca ovina* and *Silene vulgaris* was

able to resist the air pollution, mainly SO₂, and lead contamination in the past (Figure 18).

Heimhold (1987), who monitored 150 m² of this site for 16 years, found the lichens *Huilia (Lecidea) crustulata* (Ach.) Hertel, *Trapelia (Biatora) coarctata* (Sm. & Sowerby) Choisy, *Huilia macrocarpa* (DC.) Hertel fo. *tuberculosa*, *Huilia macrocarpa* fo. *contigua*, *Huilia* (DC.) Hertel cf. *cineroatra* and *Acarospora* cf. *scabrida*.

After smelter operation had been abandoned in 1967, only the contamination of the soil with lead and other heavy metals remained as environmental hazard, whereas the air pollution disappeared. Therefore, SO₂-sensitive but metal-resistant plant species such as *Minuartia verna* and others were able to colonise the site (Table 8). The vegetation of the surroundings of the former smelter is still dominated by *Calluna vulgaris*. It has relatively low metal concentrations in its stems and leaves compared to the herbs. Within the stem, there are significant differences in the Cu, Fe, and Mn contents between the lower, long-living part of the stem and the upper twigs and leaves.

Lead has a high affinity to carboxylic compounds in the cell walls (Ernst, 1974) and is therefore relatively immobile within the shoot, resulting in an enhanced accumula-

Table 8:

Metal concentration (mean and standard error S.E.) in plant species growing in the vicinity of the former lead smelter at Frankenscharnhütte

Plant species	Metal concentration in mg kg ⁻¹ dry matter									
	Cu		Fe		Mn		Pb		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
<i>Calluna vulgaris</i>										
Leaves	11.1	2.48	264	16.2	153	8.79	32.5	10.2	65.4	3.3
Twigs, above	11.2	2.10	324	69.3	136	15.4	38.7	1.7	62.8	7.2
Twigs, below	3.88	0.51	60.3	18.4	182	12.1	95.7	11.0	17.7	3.9
<i>Minuartia verna</i> , shoot	161		12734		681		3968		2106	
<i>Silene vulgaris</i> , leaves	18.2	4.77	221	65.9	291	69.8	224	35.2	994	181
<i>Rumex acetosa</i> , leaves	25.5		230		341		179		965	
<i>Viola tricolor</i> , leaves	11.4		247		124		259		218	
<i>Festuca ovina</i> , leaves	8.90	0.57	310	87.7	114	36.8	450	95.3	37.7	1.3

Collection of plant material on May 15, 2003. The Cd concentration in plant leaves was below the detection limit of 0.1 mg kg⁻¹ dry matter. The number of independent samples analysed was 3, except where due to insufficient specimens only a single analysis was made

tion in the lower part of the stem. Compared to lead, zinc is a more mobile element, resulting in a higher accumulation in leaves and young twigs.

In *Calluna vulgaris*, the uptake and accumulation of lead and zinc is lower by a factor of ten to thirty compared to the accumulation in herbal leaves. The lead resistance of heather is at least partly based on the symbiosis with an ericoid mycorrhizal fungus belonging to the ascomycota (Bradley et al., 1981). In grasses, a vesicular mycorrhizal fungus helps to withstand lead contamination (Hoiland and Oftedal, 1980). Violets also have a very effective association with arbuscular mycorrhizal fungi which diminishes the transfer of heavy metals to the roots, as shown for *Viola calaminaria* (Hildenbrandt et al., 1999).

1.3.4 The Samson mine at St. Andreasberg (51°43'N, 10°31'E) / Plants on As-enriched soils

The Samson silver mine was operational between 1521-1910. The deepest level of the mine is 810 m below surface. On this site, silver was found in very high concentrations, sometimes even solid. Accompanying ores contained among others high concentrations of arsenic minerals. A fine example for this is the so called "Scherbenkobalt" (Figure 19) which was used by the miners as "fly-stone": water was filled into a flat depression in the stone in order to kill flies drinking it. Remarkable technological features of the mining operations are the huge waterwheels (12 m diameter), which powered transport of ores and men, pumping of water and processing of ores. The Harz region is also the birthplace of the wire rope. In the Samson mine, the last original and fully functional "Fahrkunst" of the world is displayed (Figure 20). This wire rope elevator was installed in 1837 and allowed the miners to drive down into the mine within 45 minutes, which was twice as fast as before. It is still in operation today to transport servicemen to water driven power generators 190 m deep in the mountain.

In the surrounding area, plants on arsenate-enriched soils can be studied. Some plant species, especially the grasses *Agrostis capillaris*, *Deschampsia cespitosa* and *Holcus lanatus*, have the ability to evolve arsenate-resistance in populations growing on arsenate-enriched soils (Porter and Peterson 1975; Meharg and Macnair, 1991, 1992). A specific arsenate vegetation is not known. Arsenate is an analog of phosphate, competing for the same uptake carrier in the root plasma membrane (Meharg and Macnair, 1992). As a first step in the evolution of As-resistance in grasses, the high-affinity phosphate / arsenate uptake system is suppressed. Nevertheless, plants on arsenate-enriched soils accumulate a lot of arsenic in their leaves (Porter and Peterson, 1975), so that As-detoxification is necessary at the cellular level. As soon as arsenate has passed the plasma membrane, it is reduced by glutathione to arsenite which forms a very stable complex



Figure 19:
Scherbenkobalt (Photo: Schnug, 2003)



Figure 20:
Fahrkunst at Samson Mine, St. Andreasberg (from Klähn, no year)

(Scott et al., 1993). In addition, the activity of the phytochelatin synthase is stimulated by As resulting in stable phytochelatin-As-complexes (Schmöger et al., 2000; Hartley-Whitaker et al., 2001). It seems that As-phytochelatin complexes are essential in the As-resistance of grasses, and perhaps also herbs and As-hyperaccumulating ferns of the taxon *Pteris* (Schat et al., 2002; Zhao et al., 2003).

1.3.5 Metalliferous river banks of the Oker and surroundings (Oker City 51°54'N, 10°29'E)

In the past, the Oker river (Figure 21) has deposited a lot of metal-enriched sediments on its banks derived from the mining and smelting activities in the Harz Mountains. The most massive metal input comes from the Oker smelter site – up to now. In addition, slags from the mining industry were also dumped on this site so that there is a high heterogeneity in soil chemistry. The concentration of a particular metal can vary by a factor of 10 between microsites (Table 9).

Table 9:

Metal concentration (mean and standard error S.E.) in soil (aqua regia extract) and dumped materials on the river banks of the Oker at Oker City. Collected on May 15, 2003. nd = not determined

	Metal concentration in mg kg ⁻¹ dry matter							
	Cd		Cu		Fe		Mn	
Soil from	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Metal grassland	107	15.7	985	159	3021	408	1428	330
River bank	28.1		388				6098	
Deposit	13.5		4703				165	
Slag	1.12		3069				54.9	
	Pb		V		W		Zn	
Soil from ...	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Metal grassland	5284	787	nd	nd	6735	1504	5284	787
River bank	4227		122	99.3	3400		4227	
Deposit	6402		2501	1000	14974		6402	
Slag	2196		204	9.19	39692		2196	



Figure 21:
River Oker (Photo: Ernst, 2003)



Figure 23:
Cardaminopsis (Arabidopsis) halleri (Photo: Ernst, 2003)

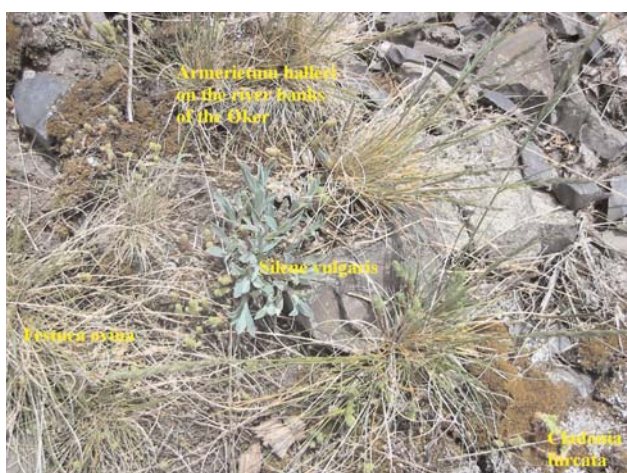


Figure 22:
Armerietum halleri with *Festuca ovina*, *Silene vulgaris* and *Cladonia furcata* on the river banks of the Oker (Photo: Ernst, 2003)

The low water capacity of the gravel only allowed deep-rooting plant species of the *Armerietum halleri*, e.g. *Armeria maritima* and *Silene vulgaris*, to establish on metal-enriched sites (Libbert, 1930; Ernst, 1965) (Figure 22). At microsites where fine sediments were deposited, shallow rooting species such as *Cardaminopsis (Arabidopsis) halleri* (Figure 23) and *Minuartia verna* have established. Plant species with an intermediate root length such as *Plantago lanceolata* and *Rumex acetosa* grow on a mixture of both soil components. At sites with tussocks of *Festuca ovina*, a soil profile has developed where the sediments are less rich in Cd, Mn and Zn, but contain higher concentrations of Cu and Fe than the Bredelem site. Due to the complexation of metals by humic compounds, the availability to plants is diminished. Therefore, more plant species with a moderate metal resistance such as *Plantago lanceolata* and *Rumex acetosa* can occur. *Festuca ovina* is the dominant grass in this heavy metal grassland (Table 10).

Table 10:

Metal concentration (mean and standard error S.E.) in mature leaves of plant species growing on the river banks of the Oker at Oker City. Collected on May 15, 2003

	Metal concentration in mg kg ⁻¹ dry matter											
	Cd		Cu		Fe		Mn		Pb		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
<i>Arabidopsis halleri</i>	138	6.74	27.3	4.45	1005	190	151	30.2	110	10.4	10986	2092
<i>Armeria maritima</i>	6.29	1.24	16.5	1.91	212	101	35.7	5.49	26.9	4.14	791	248
<i>Minuartia verna</i>	42.5	9.55	55.4	15.5	513	77.1	79.7	14.8	240	85.0	1988	333
<i>Plantago lanceolata</i>	3.37	0.56	25.4	5.21	100	25.1	44.5	7.14	70.4	18.6	1314	85.0
<i>Rumex acetosa</i>	21.6	6.41	14.8	4.51	237	102	57.1	15.4	141	22.8	2812	628
<i>Silene vulgaris</i>	8.66	0.90	20.3	0.64	391	65.9	61.5	7.14	143	78.7	2400	268
<i>Festuca ovina</i>	2.59	0.34	16.8	3.69	164	25.1	29.7	4.94	68.4	8.29	451	58.9



Figure 24:

When one part of a willow shrub is rooting in river sediments with a high metal concentration it becomes chlorotic whereas the other part rooting in non-contaminated sediments remains green (Photo: Ernst, 2003)

A willow shrub with *Salix alba*, *Salix fragilis*, and *Salix caprea* can develop at the border of the river banks (Brandes, 1992). The willow leaves show chlorosis when their roots are growing in metal-contaminated sediments (Figure 24).

Besides the rivers banks of the Oker, the whole agricultural region around Goslar-Oker and Bad Harzburg-Harlingerode is highly contaminated with heavy metals. The positions of the old large smelters at Langelsheim and Oker-Harlingerode show the highest metal concentration (Figure 25).

The rivers Oker and Innerste have a lot of tributaries which are not only passing old mining areas but are still fed from mineralised wells. Therefore the metal concentration of the river water is enhanced compared to rivers from non-mineralised areas (Table 11), but in general, the strongest heavy metal contaminations in the Harz Mountains are man-induced.

1.3.6 Flotation waste ponds west of Oker City

Some of the most problematical waste deposits in the Goslar/Rammelsberg mining district are the flotation waste ponds in the Gelmke Valley/Bollich area west of Oker city. The flotation method was used because the mineral components of the Rammelsberg ore were of extreme fine intergrowth. At Rammelsberg, the ore was crushed and milled to the required grain size of <0.04 mm. After comminution, sorting took place in various cleaner flotation phases. Copper concentrate was floated first, followed by lead bulk and zinc bulk concentrates. Following the zinc flotation, the remaining sulfides and especially pyrites were floated, however without a cleaner float, as this would have impaired the barite flotation, the last of the flotation processes. Then the final flotation concentrates were dewatered. The concentrate was sold in the form of filter cakes to different smelters. Barite was sold to the chemical industry as a raw material or, after calcining, as drilling mud additive. The quantities of run-of-mine ore processed at the Rammelsberg plant amounted to over 150000 t/a, of which about 75000 t were concentrates. The remainder, the so-called "tailings", were pumped to the settling ponds in the Gelmke Valley, where the solids settled out and the water was of accepted, but still highly contaminated quality. As the flotation process was run with fish toxic substances like xanthogenates, the ecotoxicological effects were always a problem. The settling ponds near Oker will remain a permanent environmental post-mining problem – 7 million t of tailings with 2.5 million t of Pb, Cu, Zn and Fe, and about 2 million t of barium sulfate were deposited here since 1937, when the ponds had been built in the NS rearmament period (for more technical information see <http://www.rammelsberg.de>).

Table 11:
 Mineral elements in the water of the rivulet Abzucht near Goslar and the river Oker at Oker city in comparison to the range of lead and zinc concentration of wells in mineralized area of the Harz Mountain. The data from Nowak and Preul (1971) are indicated by an asterisk (*).
 nd = not determined

	Element concentration in mg L ⁻¹						
	Ca	Mg	S	Cd	Mn	Pb	Zn
Abzucht	34	7	13	0.002	0.04	0.06	1
Oker	19	6	13	0.004	0.202	0.005	1
Wells, minimum*	nd	nd	nd	nd	nd	0.01	0.008
Wells, maximum*	nd	nd	nd	nd	nd	1.3	3.4

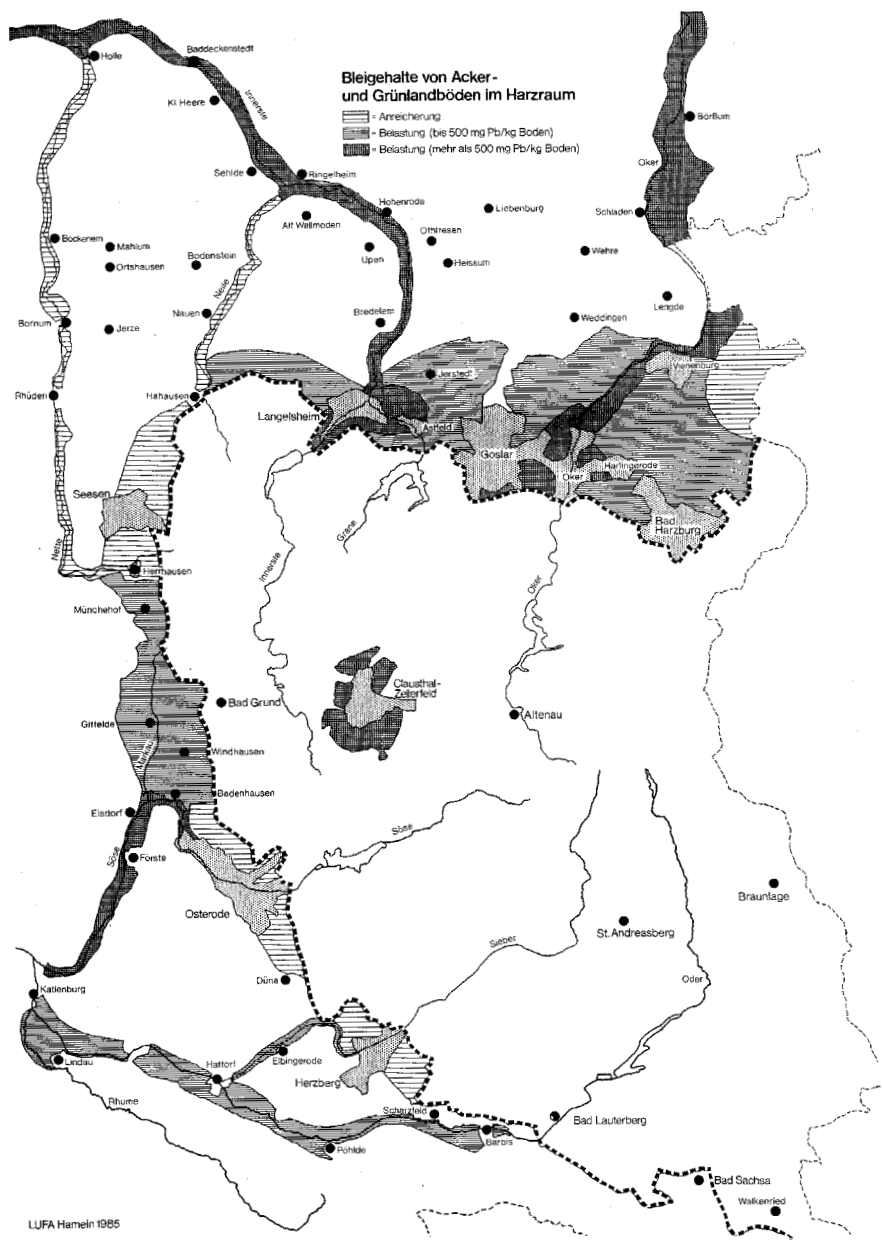


Figure 25:
 Lead contents of soils in the northern Harz foreland from Seesen to Bad Harzburg influenced by Harz mining and smelting effects (legend from top to bottom: accumulation; pollution up to 500 mg kg⁻¹ Pb; pollution > 500 mg kg⁻¹ Pb) (from Köster and Merkel, 1985)

2 Visit to Goslar and the Rammelsberg Mine (51°55'N, 10°25'E)

If there is enough time on this route, the imperial city of Goslar (see route map) is worth a visit. Goslar was officially founded by Henry I. in 922, but in fact mining in the Rammelsberg near Goslar is about 3000 years old and the first settlement was probably as old as that. Goslar gained its wealth mainly by silver from the Rammelsberg and even held an important place in the Hanseatic League because of these rich ore deposits. From the 10th to the 12th century it was one of the seats of the Holy Roman Empire of the German Nations. Goslar's well-preserved medieval historic centre has some 1500 half-timbered houses dating from the 15th to the 19th century, and many other monuments like old churches, chapels and monasteries, the Imperial Palace (Kaiserpfalz) built in the 11th century by the Emperors Henry II and III, or the City Hall.

The Rammelsberg Mine was exhausted after 3000 years and closed in 1988. Since 1989, this historically and technically important mining monument has been transformed into a mining museum below and above ground, conserving mining and processing technology in authentic form. The Rammelsberg Mine and the medieval town of Goslar were enrolled in the UNESCO World Heritage List in December 1992. Thus, Germany's first technical mining complex was declared a Cultural Heritage Monument. The Rammelsberg can, as the only mine worldwide, testify to more than 1000 years of continual working. The mine produced nearly 30 million t of ore - one of the most productive and richest deposits in the world, and can claim more mining technology "firsts" from the 1st to the 20th century than any other base metal mine in Central Europe.

Going underground into the mine is a must for the Harz visitor. For just a short visit, have a look into the bookshop of the mining museum and then drive or walk onto the Rammelsberg north slope to the Maltermeister Turm. Half way up on the road to the Maltermeister Turm, where a vegetation-free tailing heap shows up on the right side, we cross a zone of intensive morphology – historic narrow

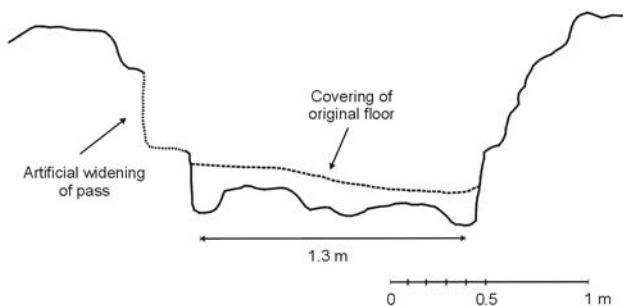


Figure 26: Cross section of a historic narrow pass ("Hohlweg") at the Rammelsberg slope to Goslar town (from Spier, 1988)

passes ("Hohlwege") showing how the metal ore was transported to the smelters in former times (Figure 26). For more information see <http://www.rammelsberg.de> and <http://www.goslar.de>.

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