 DOI: 10.2478/ctg-2014-0008

DOROTA ROŻEK

Faculty of Earth Science, University of Silesia,
Bedzinska Str. 60, 41-200 Sosnowiec
E-mail: dorota.rozek87@gmail.com

Metallophytes in biotopes polluted by waste dumps rich in Zn-Pb, Cd (Olkusz region) – review of previous and planned research

KEYWORDS:
metallophytes, heavy metals, zinc, lead, cadmium pollution, Zn-Pb, Olkusz mining region.

ABSTRACT.

The aim of that publication was the presentation of previous and planned research concerning selected vascular plants and soils near Olkusz (Southern Poland). The extremely high concentration of heavy metals in soils from that region was caused by the natural geochemical aureoles of dispersed metals (due to weathering of Zn-Pb-Fe ore sulphides) and mining and processing of shallowly occurring metalliferous deposits (containing Ag-Pb and Zn-Pb ores) since XII century. The condition of stress in metals, shortage of water and some plant nutrition led to formation of some adaptable vegetation features by plants growing in that region. Some species called metallophytes have been already detailed investigated. Moreover some geochemical and pedological research of soil have been already done. However the conditions of habitat of pioneering species such as *Koeleria glauca* and *Corynephorus canescens* are not still recognized.

Introduction

In the Silesia-Kraków region there are some areas of Zn-Pb ore exploitation and processing: Olkusz, Bytom and Tarnowskie Góry region. The soils, which neighbour Zn-Pb mines and foundries characterize by particularly high degree of contamination by lead, zinc and other elements: Cd, Tl, Fe, As, Sb, Mn. Those metals and metalloids derive from the minerals building ores and from Zn-Pb ore washing and flotation (Cabala et al. 2008; Chrastny et al. 2012; Verner et al. 1996). High concentration of heavy metals in soils is a problem for many regions of the historical Zn-Pb ore exploitation and foundry, inter alia in Belgium and Holland (Wilkens & Loch, 1997), France (Dahmani-Muller et al. 2000), Ireland (Good 1999), Portugal (Loureiro et al. 2006). It is distinguished two kind of contamination sources of heavy metal pollution: natural and anthropogenic. The first one contains shallow Zn-Pb mineral deposits and geochemical aureoles of Zn, Ob, Fe, Cd, As disperse. Anthropogenic pollution includes: historical (XII-XIX centuries) areas of Ag-Pb and Zn-Pb ore exploitation and contemporary (XX century): processing waste dump, flotation waste dump, washing plants areas and foundry emission.

Both dust from foundry emission and the different size fractions of waste contain even few percent of metalliferous minerals (Cabała 2009). The grains rich in metals are transported by the wind to soils and there, by the (bio)chemical alterations, they are transferred to steams, subterranean water and biota (Bauerek et al. 2009). Those conditions of environmental stress strongly influence on development of fungi, algae, microorganisms, plants, micro- and meso faun.

Because of such extreme conditions caused by extremely high concentration of metal compositions, that region consist very popular and interesting area for geochemical, botanic, ecological and pedological investigation. Many research had been already done, but some parts of that specific environmental are steel unrecognized. Therefore, in that publication author would present previous investigations done by other researchers and research that author is planning to do.

Localisation

The Olkusz region of Zn-Pb ore exploitation is situated in the Permian-Mesozoic Silesian-Cracowian monocline. The Permian and Mesozoic deposits are filled by Palaeogene and Holocene eolian and fluvioglacial deposits, mainly medium- and fine-grained quartz sands and silty sediments.

The Silesia-Kraków Zn-Pb ores were recognized as Mississippi Valley type ores (MVT). In that region metalliferous deposits occur shallowly or on the surface and their mineral composition includes sphalerite, galena, wurzite, pyrite and marcasite (Cabala 2000). Moreover, the hypergenic processes led to creation of secondary geochemical aureoles of metals and metalloids disperse.

Historical mining region



Fig. 1. The areas of historical mining in the Silesia-Kraków Zn-Pb ore region (Cabala et al. 2008)

The region of Olkusz – Bolesław – Bukowno is a part of Silesian-Cracowian Zn-Pb ore region (Fig. 1). Because of shallowly occurred metalliferous deposits the early development of Ag-Pb ore mining was possible. The exploitation has been starting in XII century and it was using only opencast methods with shallow mineshafts (Cabała 2009).

The further development of mining in that region was connected with new techniques of gravitational mine dewatering (Molenda 1963): five drift mine were built.

In the end of XVII and at the beginning of XVIII centuries the flotation and processing tailings, collected nearby former mineshafts and washing plants, have also been used as a source of lead (Molenda & Wołoszyński 1965).

The last period of development was in XIX-XX centuries. They were discovered the new, "silesian" technologies for receiving the metallic zinc from oxidized ores by J.Ch. Ruberg (Jamrozy & Rączka 1999). At the end of XIX century a modern method of oil flotation of sulphides zinc and lead ores was also applied. Because of that several mines were opened and the processing of Zn-Pb ore has stared. In the second part of XX century another mines were built and the zinc exploitation increased widely.

Actually, only one underground ore mine "Pomorzany" exploits Zn-Pb-Ag metals in Olkusz region. Except the mine a flotation processing plant and "Boleslaw" zinc smelting works also exist.

Because of rich mining history, in the vicinity of Olkusz there are many former washing plants, processing waste dumps and tailings derived from flotation. They and emission from foundry chimneys together are the source of soil and plant pollution.

Heavy metals in plants

The elements indispensable for plant workings (including toxical metals) are delivering mainly by root system. The roots absorb them in the ionic form from the soils solution, then they are transferred with the water and mineral salts through the over ground parts. Some metals (p. ex. cadmium, lead, zinc, copper, thallium) could disturb the proper workings of life-processes in the plant organisms. Plants have formed different defensive responses which prevent them from the penetration of noxious metals into the cells. Thanks to some complicated biochemical reactions, toxic metals are fixed in roots and intercellular spaces. The plants' detoxicative defensive mechanisms consist inter alia on synthetizing of proteins which fix heavy metals in the complex compound as chelates (Olko 2009). Those compounds are deposited in vacuoles with the dispensable metabolites, so they are not noxious any more for the life-processes. Metals could also be eliminated beyond cells. The places of metal concentration could be investigated by means of special methods, p. ex. usage of metallic chemical compounds transferring to roots. In the properly prepared samples from plant tissues the metal compound could be identified using the microscopic analysis (Olko et al. 2008). Plants could immobilize metals in their tissues, degrade them or transfer into their over ground parts. The complicated biochemical processes happen on the root level and into the plant tissues. Physical and (bio) chemical reactions lead to soil purification from toxic metals.

The metal transfer decline not only by plants. The role of micorhizal fungi (Turnau et al. 2002, Cabała 2009), algae (Cabala et al. 2011) and microorganisms (Stefanowicz et al. 2010) is also very important but still weakly recognized.

Previous research



Fig. 2. Metallophytes occurring in Olkusz region. A - Viola tricolor, B - Dianthus carthusianorum, C - Biscutella laevigata, D - Cardaminopsis arenosa, E - Armeria maritima, F - Silene vulgaris (Snowarski 2008)

5.1. Metallophytes

The metallophytes, as plants tolerating high levels of heavy metals, frequently occur in Zn-Pb Olkusz mining region. All those plants had to adapt themselves to extremely hard conditions which are not only caused by heavy metals pollution. The difficulties are also due to shortage of water and some plant nutrition (compounds of nitrogen, phosphorus, potassium), high insolation or strong winds (Siwek 2008). The metallophytes generally belong to association of xerothermic grasses from *Brassicaceae, Violaceae, Plantaginaceae* families (Grodzińska et al. 2001, Grodzińska & Szarek-Łukaszewska 2002, Jędrzejczyk-Korycińska 2006, Załęcka & Wierzbicka 2002, Szarek-Łukaszewska & Niklińska 2002). The most characteristic plants are inter alia: *Viola tricolor, Dianthus carthusianorum, Biscutella laevigata, Cardaminopsis arenosa, Armeria maritima, Silene vulgaris* (Fig. 2) and many other species of grasses and other vascular plants. There are many research of metallophytes from Olkusz region done by botanists and plant geneticists. All of them led to recognize the mechanisms of detoxification, adaptation strategies to heavy metal tolerance, changes in morphology etc. Some of processes is already known and described in detail (Baranowska-Morek 2003, Siwek 2008, Wierzbicka 2002).

There are two different strategies of adaptations: metal avoidance and tolerance (Siwek 2008). The stress avoidance (true exclusion) is based on the limitation of metal's uptake (on the root level) while the metal tolerance consist in metal detoxification in symplast. Some populations of metalliferous areas called shoot excluders can uptake and accumulate metals in roots restricting transport to shoots or called accumulators – can uptake and accumulate metals in shoots.

An uptake of metals from soil could be limited or controlled by some micro- and macroelements. The species tolerating heavy metals and a shortage of plant nutrition have also form a specific mineral management, mostly of calcium, phosphorus and potassium (Baranowska-Morek 2003).

Three of the most popular metallophytes have been investigated in detail: *S. vulgaris*, *D. carthusianorum* and *B. laevigata* (Siwek 2008, Wierzbicka 2002). They were compared the individuals derived from a galmei waste pile and individuals from non-contaminated habitats. In all three cases the pile population plants were visibly different from the "natural" ones (Godzik 1991, 1993, Siwek 2008, Wierzbicka & Panufnik 1998, Wierzbicka & Pielichowska 2002, Załęcka & Wierzbicka 2002).

The sprouts of galmei *S. vulgaris* were numerous, thin, trailing while the sprout of galmei *D. carthusianorum* were shortened and weak. The leaves of both were smaller and tighter. Those features have reduced the transpiration surface. Moreover their leaves were thicker, because of the increase of parenchyma, and the root hair were particularly plentiful. All of those features indicate the xeromorphic adaptation.

Both species had developed faster and characterised by much higher fecundity (numerous flowers and seeds) and they have produced a smaller biomass, so they are a r-selected organisms (reproductive strategy consisting on higher fecundity at the expense of biomass increase).

Simultaneously, they have had good resistance to dry weather periods, but *S. vulgaris* has had extra resistance to deficit of some plant nutrition as calcium, phosphorus and magnesium. It has also better adapted to high levels of heavy metals in soils.

B. laevigata is a herbaceous plant and the typical mountain species. In Poland it occurs only in Tatra mountains and in Olkusz region (Szafer & Zarzycki 1972).

The differences between galmei and natural individuals were smaller than in case of other two species. Both populations have been developing in the similar pace, have had similar size and the same size and habit of leaves. However the galmei *B. laevigta* has had light green, thin leaves covered by tomentose (flattened and matte plant hairs) in the opposite to natural one. It has also had better tolerance to lead. Generally, both populations of *B. laevigata* have adapted to xethermic conditions but in different ways. Nevertheless only galmei individual can tolerate the extremely high levels of heavy metals, particularly lead.

5.2. Other vascular plants

Another vascular plants are also using in research of heavy metals pollution.

The best example could be Scots pine (*Pinus sylvestris*). As a conifer, it enables to investigate the environmental pollution during several years (Ciepał 1999). The pine needles are really good samplers: they could be collected at any season and they are coated with a sticky epicuticular wax which readily traps even the smallest dust particles (Teper 2009). Using the atomic absorption spectroscopy and ESEM analysis it is possible to recognize the compounds linked to needles, determine their quantity and size of particles. The ways in which the particles appear on pine-needle surfaces are also interesting, inter alia: single particles, aggregate of particles, accumulations of mixed particles around stomata and particles inside a suprastomatal chamber (Teper 2009). The fungi hyphae occur frequently on the surface of pine needles. It is an extra surface which collect the dust particles.

Planned research

For detailed research a few areas had been chosen: in the vicinity of flotation processing plant in Olkusz, in the vicinity of foundry in Bolesław, the area without plant vegetation in the vicinity of Zn-Pb ore mine "Pomorzany", the area of former washing plant "Józef" near Olkusz and two comparable areas in the Silesian-Kraków Upland which are not under direct influence of Zn-Pb ore processing.

All those areas are covered by sand. There are not any soil cover or there are only initial soils. That kind of specific conditions influence on plants that could vegetate there.

It is observed the natural succession of some pioneer species. The detailed observation of habits led to choice two of them for further investigations: *Koeleria glauca* (Fig. 3) and *Corynephorus canescens* (Fig. 4). Both species are grasses which occur in all study areas. They have not been analysed yet the in regions polluted by heavy metals.



Fig. 3. Koeleria glauca (Snowarski 2008)



Fig. 4. Corynephorus canescens (Snowarski 2008)

From all those areas had been collected samples of both grasses and samples of soils and deposits in the basement. The laboratory analysis will concern epidermis of roots, their rhizosphere.

Those research let realize the following aims:

- the determination of degree of metal transfer into roots,
- the recognition of rhizospherical microenvironments of chosen plant species,
- the determination of contamination degree of soils and surrounding deposits, (all three problems will be analyzed for each area separately and together to show same changes with the increase of a distance).

Three kind of analysis are planned to do:

X-ray diffraction for determination of mineral composition of soils,

- chemical analysis:
  - atomic absorption spectroscopy (AAS) for determination of waste components in soils,
  - pH of soils,
  - content of organic carbon, N, Mg, Ca, P, K in soils,
- ESEM analysis of soils and plant roots using an Environmental Scanning Electron Microscope and semiquantitative microanalysis (EDS) using an EDAX analyzer.

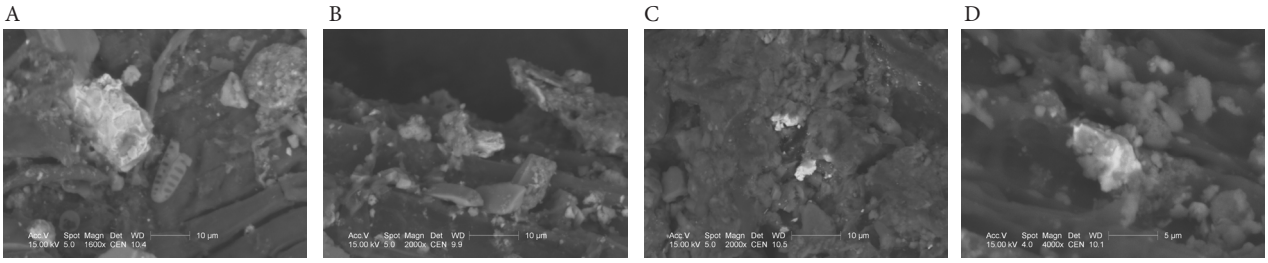


Fig. 5. SEM photography: A – Fe oxide on a K. glauca root, area in the vicinity of Bolesław foundry; B – Zn oxide on a C. canescens root, area in the vicinity of flotation processing plant in Olkusz; C – Pb-Cd carbonate on a K. glauca root, area without plants in the vicinity of "Pomorzany" mine, D – Zn-Pb carbonate/phosphate on the C. canescens root area in the vicinity of flotation processing plant in Olkusz.

Some ESEM analysis have been already done. A few SEM photography is presented below (Fig. 5). There were recognized following compounds: Zn, Pb, Cd, Cu, Fe, Mn, Al, Ti, As sulphates, sulphides, oxides, hydroxides and carbonates and many aluminosilicated aggregates containing numerous metals.

Conclusion

The galmei piles, Zn-Pb processing and flotation ponds are very interesting areas for study. The plants growing there had to adapt to extremely hard environmental conditions. The knowledge about plant vegetation and soils from there is not complete yet. It is valuable to recognize far more details about those specific habits. Some tailings derived from former Zn-Pb mining and foundry are not reclaimed still, some of them reclamation works were not effective. Therefore, the investigation of pioneering xerothermic plant, their rhizosphere, soils and natural spontaneous succession could be helpful in planned successful reclamation.

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