Mineral nutrition of Scots pine (*Pinus sylvestris* L.)
on substrates contaminated with heavy metals

Scots pine is the primary forest-forming species in Poland, with a very high economic importance. It is also widely used in the reclamation of lands highly degraded by industry (including mining of metal ores). On such areas conditions for plants life are unfavorable, mainly due to the high content of heavy metals in the soil. Heavy metals in excess are a threat for proper plants functioning, because they disturb mineral nutrition, what cause nutrients deficits and lead to a reduction of plants growth. Despite of numerous studies carried over the Scots pine, knowledge about mineral nutrition of this species on post-mining areas is very limited.

The aim of this doctoral thesis was to characterize the mineral nutrition of Scots pine (*Pinus sylvestris* L.) growing on soils contaminated with heavy metals, originating from mining and processing of Zn-Pb ores, and to determine the effect of heavy metals on pine functioning.

The research was carried out in southern Poland, mainly in the Olkusz Ore-bearing Region (OOR), between towns Bolesław, Laski, Olkusz and Bukowno, in the area degraded and highly polluted, by centuries-old (since the 12^{th} to the 20^{th} cent.) open-cast mining and processing of Zn-Pb ores. Eight permanent study sites (0.05 ha each) were established: six of them were located in the OOR, the other two (control sites) were located outside of the OOR – near Trzebina and near Złoty Potok. The study sites in the OOR included pine monocultures planted in the 1990s., within the reclamation of areas degraded by mining. These sites represented two main types of substrates: stony (on mining wastes) and sandy.

From each study site 10 samples of the topsoil (to a depth of 10 cm), 15 samples of green pine needles (current year, one-year-old, two-year-old) and 5 samples of trunk wood from 5 cutted trees (in July) were collected. During the autumn fallen needles were collected as well (from September to November), using 10 collectors per study site. From all sample of needles, 150 pieces were taken to estimate the biometric parameters (the mass and length).

In the soil samples, the following parameters were measured: pH_{H20}, pH_{KCl}, CEC_E and the concentration of C, N, K, Ca, Mg, As, Tl (total forms) and P, Zn, Pb, Cd (total and bioavailable forms). In the pine needles (green and fallen) samples, the concentration of C, N, P, K, Ca, Mg, Zn, Pb, Cd were determined, and in the wood samples, the concentration of Zn, Pb, Cd. Standard methods of chemical analysis were used. All analyzes were carried out in the laboratory of the W. Szafer Institute of Botany PAS in Cracow.

The statistical analysis was performed for properties of soil (Kruskal-Wallis test), green needles (two-way analysis of variance, Tukey's test and multiple regression), fallen needles (three-way analysis of variance), wood (one-way analysis of variance and Tukey's test). Relationships between chemical properties of the soil, the chemical composition of pine needles and needle biometric parameters were examined by Spearman's rank correlation.

The intensity and direction of studied elements translocation was determined in the needles before their autumn fall and the above-ground biomass of pine stand and the pool of metals (Zn, Pb, Cd) were assessed for each study site.

The conducted studies show, that on the post-ming area of Zn and Pb ores pine monocultures were growing on mostly alkaline soils, poor in basic nutrients (C, N, P) and on some locations (on stony mining wastes) rich in basic cations (K, Ca, Mg). Soils in the OOR were differently contaminated by metals derived from mined ores. The concentrations of Zn, Pb and Cd were many times higher, than in soils of non-industrial regions of Poland, and the contents of As and Tl were low – mostly they were within ranges of typical values for uncontaminated soils.

It was found, that Scots pine can cope well in conditions of heavy metals excess, that are present in potentially toxic amounts (mainly Zn and Pb), both in stony and sandy substrates. No morphological damages were observed, which could be considered as specific for trees from metalliferous areas. However the following changes in the mineral composition of trees in the OOR were observed: N, P and Ca deficiency in the needles, and the excess of metals from the ores – Zn, Pb and Cd – in the living needles and trunk wood. The levels of K and Mg concentrations were within the range of optimal values for pine. Although from the analysis of individual concentration of nutrients in the needle, it follows that pines were poorly provided with basic biogens, N and P, the ratios of these elements in the needles seem to be correct and do not indicate on disharmony in their uptake. The patterns of concentration variation of the basic elements in pine needles related with their aging were also typical for this species – with the needle age, N, P and K concentration mostly gradually decreased and Ca, Zn, Pb and Cd concentration increased.

Based on the obtained results it can be found, that heavy metals from ores disturb the management of mineral nutrients in pines and influence on their growth limitation, which show in reduction of the length and mass of the needles. This was evidenced by the negative correlation between the content of N and P in needles (mainly two-year-old) and the concentration of metals in the soil – Ca, Mg, Zn, Pb, As, Tl – and by negative correlations between biometric parameters (mass, needle length) and concentration of metals in soil from ores – Zn, Pb, Cd, As, Tl. Moreover the multiple regression in the one-year-old needles confirmed negative infuence of Zn on the needle mass.

The needle fall in the OOR stands generally showed the concentration of the most important nutrients were similar to those observed on uncontaminated areas, whereas contents of Zn, Pb i Cd were many times higher. It found, that translocation directions during the autumn were mostly preserved – N, P and K were withdrawn from the senescing needles, while Ca, Zn, Pb and Cd were added to needle fall. However, in the context of literature data, it seems, that under conditions of nutrients deficiency and strong heavy metal contamination, as in OOR, the intensity of autumn translocation elements in pine was significantly reduced.

The metal concentration in trunk wood on all studied sites were lower, than those in green needles, as in pine trees from other areas; however; they were higher, than natural concentration of metals. Zinc reached the highest concentration; simultaneously it was the only element, which concentrations in wood and soil correlated with each other.

The pine stands accumulated significant quantities of metals in the aboveground biomass, and the amount of Zn, Pb, Cd pools and the share of wood and needles in it, varied depending on the metal and the degree of soil contamination. Pools of Zn in biomass of pine needles were similar or larger, than pools in trunks wood, especially in stands of highly contaminated study sites; Pb and Cd were accumulated mainly in wood. These results suggest,

that on contaminated sites large amounts of Zn are returned with falling needles and, as a consequence, the upper layer of soil may be enriched in this element.

The research has highlighted the factors, that can affect the availability of heavy metals to trees and can mitigate their toxicity. It seems, that in pine this toxicity is somewhat mitigated, and somewhat tolerated. This tolerance may be accompanied by a tolerance for deficiencies of the basic nutrients. The high plasticity of the studied pine stands proves their quite good condition, despite the revealed mineral disorders manifesting by: weak needles supply in nutrients and excess of metals from ores, reduced efficiency of biogenes retranslocation in autumn, production of litter rich in metals, high accumulation of ore metals in aboveground biomass. It seems, that the direction of nutrients movement is maintained, and their proportions in the needles are balanced. The study also found that heavy metals, which disturb mineral nutrition of pine trees, affect the reduction of their growth, presented in the decrease of length and weight of the needles.