Contamination of environment in the road surroundings –
impact of road salting on Norway spruce (Picea abies) and
Scots pine (Pinus sylvestris)

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Abstract. A comprehensive overview of the influence of transport on the environment is
presented in this study. The complex analysis of soil and needle samples provides an extensive
set of data, which presents elemental contamination of the environment near roads. Traffic
pollution (including winter road treatment) has a significant negative influence on our
environment. Besides sodium and chlorine from winter maintenance many other elements are
emitted into the environment. Three possible sources of contamination are assumed for
environmental contamination evaluation: car emission, winter maintenance and abrasion from
breaks and clutches. The chemical analysis focused on the description of samples from
inorganic point of view. The influence of the contamination potential on the sodium and
chlorine content in the samples of 1st year-old and 2nd year-old needles of Norway spruce
(Picea abies) and Scots pine (Pinus sylvestris) is discussed. Additional soil samples were taken
from each sampling site and analyzed to get insight in the sodium and chlorine distribution.
Statistical evaluation was used for interpretation of complex interaction patterns between
element concentrations in different aged needles based on localities character including
distance from the road and element concentration in soils. This species of needles were chosen
because of its heightened sensitivity towards salinization. The study was conducted in different
parts of the Czech Republic. The resulting database is a source of valuable information about
the influence of transport on the environment.

1. Introduction
Traffic pollution (including winter road treatment) has a significant negative influence on our
environment. Besides sodium and chlorine from winter maintenance many other elements are emitted
into the environment. In the past lead was known as traffic marker. However, since it has been banned
as an anti-knocking additive other elements like platinum group elements (PGEs, from catalysts),
antimony (from brakes and clutches), vanadium and nickel (from fuel burning) are typical traffic
markers.

Different analytical methods are used for elemental determination of environmental samples. The
most common are methods of atomic spectrometry [1]. The used ICPQQQMS instrument has resulted
in successful method development to overcome several isobaric, polyatomic and doubly charged interferences in the analysis of environmental samples with complex matrices. The method is suitable for determination of elements at very low concentrations (Platinum group elements – PGE) and elements which are influenced by spectral interferences (PGE, S, P, As, Se).

To investigate a potential influence of traffic pollution (influence of road salting included) on the environment, samples of 1st year-old and 2nd year-old needles of Norway spruce - *Picea abies* and scots pine - *Pinus sylvestris* were collected from two sites differing in traffic loading. Spruce trees were selected because of their abundance and high sensitivity to salinity [2,3]. They are known to be good indicators for urban pollution [3,4]. The 1st and 2nd year old needles were analysed separately. Additionally soil samples were collected at each sampling site. Sodium chloride is the most commonly used de-icing material for road winter treatment. The applied sodium chloride is mobilized by melting snow or ice and rainfall, which leads to its distribution in the soil environment, surface water, geological environment, and groundwater [5].

The aim of this work was the preparation of data for risk assessment of environmental contamination in the vicinity of roads and highways. Soil is the final recipient of a wide range of contaminants and the source for entry into the food chain. The investigation of a potential influence of traffic pollution on the environment attention was focused on all components of the environment.

2. Results and discussion

2.1. Sampling and sample preparation

Sampling was carried out throughout the Czech Republic in the areas with high traffic impact (near the main roads and cities) and the areas with low traffic load (National parks, mountains,...) About one thousand samples of soil, one hundred samples of water and road dust, and three hundred samples of needles were collected during three years.

The study area to investigate the environmental impact of chemical winter road maintenance was chosen to be in the northern part of Czech Republic in the Liberec region. Pine needles were collected in metropolitan area of Prague and surrounding villages. The contaminated spruce needles and soil samples were collected in a distance of 5 m and the uncontaminated samples in a distance of 40 m from the road. The tree health was classified according to the physical appearance (crown density) and color of the needles. Also the contamination potential was estimated. Soil samples were collected over the years 2015 and 2016. Soil samples were collected across the entire country during the years 2013 – 2017.

The different age classes of needles were analyzed separately. The needles were crushed, milled and then extracted by pure water for Cl determination. For the analysis of other elements the samples were digested in Teflon vessels with HNO₃ and H₂O₂ at a temperature of 200°C for 30 min and a pressure of 30 bar using microwave system (SW-4+, Berghof, Germany). The soil samples were sieved, milled and digested in Teflon vessels with Aqua Regia at the same conditions. Samples were appropriately diluted before element analysis With ICPQQQMS. For comparison and Cl determination samples were extracted by pure water 24 hours, then filtered and analyzed. For PGE determination, of HCl was added to stabilize these elements.

2.2. Chemical Analysis

All samples were analyzed with ICPQQQMS (Agilent Technologies, Japan) in different tune modes (collision/reaction, He, H₂, O₂, NH₃). Especially for the detection of PGEs the reaction with NH₃ in MS/MS mode was necessary to achieve low detection limits. As, Se, S and P were analyzed in O₂ MS/MS mode with a mass shift of +16.

The quality of the analytical results was checked via frequent analyses of reference materials (NIST Pine Needles 1575a, QCM – Metranal-33 - Soil, NIST Trace elements in natural water 1640a, ERM – CZ120 – Fine Dust PM₁₀ - Like).
2.3. Results
To evaluate the environmental contamination in the vicinity of roads, the methodical scheme was selected:

- Sampling from small amount of selected areas (wider restricted area around the road, with chosen location) with the large number of sampling points (places for sampling in chosen location in different distances from the road).
- Sampling from more areas, with high amount of location
- Sampling high amount of location

Sampling was carried out near the main roads and the roads of 1st and 2nd category.

The results of the elements concentration in the soils were evaluated based on four factors:

- by the distance from the road
  V – road dust from the surface of the road
  K – the nearest sampling point from the road
  E – about five meters far from the road
  B – about twenty meters far from the road
  P – background, about one hundred meters from the road
- by the category of road
  main road
  road of 1st category
  road of 2nd category
- by the level of contamination potential
  1st class – lowest contamination potential, a tree with the lowest possibility of contamination
  2nd class – medium contamination potential, a transitional zone with minor contamination
  3rd class – highest contamination potential, the trees immediately next to the road

The results of the elements concentration in needles were evaluated based on four factors:

- the contamination potential:
  1st class – lowest contamination potential, a tree with the lowest possibility of contamination
  2nd class – medium contamination potential, a transitional zone with minor contamination
  3rd class – highest contamination potential, the trees immediately next to the road
- the health condition:
  1st class – healthy tree
  2nd class – slightly damaged tree
  3rd class – moderately damaged tree
  4th class – damaged tree
  5th class – severely damaged tree
- the distance from the road:
  1st category – samples collected from up to 5 m from the road
  2nd category – samples collected at least 40 m from the road
- the age of needles: first-/second-year

The concentrations for most of the traffic related elements (Na, Ca, S, V, Cr, Co, As, Sb and Pb) increased by 40 % to 60 % from first year needles to the second year needles. Concentration of K and Mg decrease in older needles, because these elements are displaced by Na and Ca from salt from winter maintenance (Figure 1).
Element concentrations found in control samples from “not contaminated area”, are typically lower than from all other areas (Figure 2). The antimony concentrations in roadside pine needles show the highest contamination compared to the control group. The behaviour of antimony as typical traffic related element and its interaction with the roadside trees is shown in the Figure 3. The antimony concentrations in roadside pine needles and the vanadium concentrations in urban soils show the highest contamination compared to the control group. The measured element concentrations in needles represent the combination of adsorbed particulate matter and trace elements taken up via the root system of the trees.
Figure 3. Antimony concentrations in 1st year and 2nd year pine needles and their corresponding soils.

If we compare concentrations of Na in soil samples from different road type side in different distance from the road, we can see a decreasing concentration with an increase of the distance to the road (Figure 4). This confirmed the low level of mobility in the soil and its retention in the vicinity of the road.

Figure 4. Concentration of sodium in soils near the three type of road in different distance from the roads.

The measured element concentrations in needles represent the combination of adsorbed particulate matter and trace elements taken up via the root system of the trees. The spruce needles and corresponding soil samples show elevated Na concentrations at locations close to the roads where chemical de-icing is performed. Trees from locations with a contamination potential (CP) of 1 show Na concentrations from 0.01 to 0.04 mg g\(^{-1}\), locations with CP 2 from 0.02 to 0.10 mg g\(^{-1}\) and CP 3 from 0.12 to 5.0 mg g\(^{-1}\). The Na concentrations in spruce needles directly correlate to the tree health as seen below. In contrast to the control group with comparable CP the Na concentrations in spruce needles close to the road are higher by a factor of 8-10 (Figure 5). In the case of other traffic related elements the trend is opposite. Position of the road in the monitored area has significant influence on
amount of elements concentration, in the case of 1st contamination potential, there is the largest accumulation effect (Figure 6).

In contrast to the study of Suoranta, T. et al. [6] the concentrations of Pt, Rh, and Pd were below the detection limits of 1 µg kg\(^{-1}\) for urban soil and pine needles.

2.4. Statistical evaluation of the analyses results
Data were evaluated for the two sites differing in traffic loading. Statistical evaluation was used for interpretation of complex interaction patterns between element concentrations in different age needles based on localities character including distance from the road and element concentration in soils. At the beginning, the data was summarized and the basic characteristics for visualization of element content in the needles and soil were calculated.

3. Conclusion
Comprehensive analysis of soil samples collected in the vicinity of roads provides an overview of the effect of transport on soil pollution. The result is an extensive set of data which presents the dependence of the contamination of the environment by selected elements. Results database provides a comprehensive overview of the contents of the traffic related element concentrations in the Czech Republic. Increasing concentrations of selected elements (e.g. Sb, V) in certain locations, where the natural content in soil is low, indicate transport contamination source. Sodium has a higher concentration in non-urban areas (mountains), because of longer winter maintenance. The research into the effects of winter road treatment on selected conifer confirmed the increased sodium and chlorine concentrations in trees growing in the areas with higher contamination potential. A deterioration of health condition of the trees depending on the increasing sodium and chlorine concentration in needles was also observed. The health condition of a tree is an important indicator of contamination. According to the study by Kayama at al. [4] it was also discovered that sodium contents are higher in damaged trees with worse health condition. The distinct sodium concentrations were confirmed in the soil samples. Concentration of PGEs in the monitored areas was below detection limit. The impact of traffic on the concentration of traffic related elements (Sb, V atc.) in soils and the needles is noticeable. The database is a source of valuable information about the impact of transport on the environment.

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