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Short Communication

Mercury Accumulation in *Picea abies* (L.) Karst. Needles with Regard to Needle Age

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Abstract

Our paper deals with mercury accumulation in Norway spruce needles (*Picea abies* (L.) Karst.) with regard to needle age. Samples of spruce branches from Slovakia were separated according to age. There were 85 samples of 1-yr-old needles, 85 samples of 2-yr-old ones, 82 and 61 samples of 3- and 4-year-old needles, respectively. Dried needles were homogenized by means of a ball mill. Mercury was determined by the Advanced Mercury Analyser AMA 254 (a single-purpose absorption spectrophotometer). The average concentration was 0.041 $mg \cdot kg^{-1}$, 0.048 $mg \cdot kg^{-1}$, 0.064 $mg \cdot kg^{-1}$, and 0.068 $mg \cdot kg^{-1}$ in dry matter of 1-, 2-, 3-, and 4-year-old needles, respectively. The variance analysis of mercury concentration in individual age classes shows statistically significant differences between average values on a 5% level of importance. The follow-up Duncan's test showed that there were significant differences between average values of non-adjacent age classes (first ↔ third and fourth; second ↔ fourth) of needles. The acquired data points out the falling tendency of mercury concentrations in Norway spruce needles as a reflection of improving environmental conditions.

Keywords: accumulation, mercury, needle age, Norway spruce (*Picea abies* (L.) Karst.)

Introduction

Elemental mercury (Hg^0) represents a dominant form of mercury in the atmosphere (>95%). It is characterized by resistancy and is considered a global pollutant [1]. According to data published by the Program for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) [2], there was a mercury deposition of 2.7 t/yr in Slovakia in 2007. Lesser amount of mercury deposition regarding the surrounding countries was registered only in Austria (1.1 t/yr).

Further study into mercury deposition extent can be done by means of plant bioindicators. Field studies [3, 4] and laboratory studies [5, 6] have determined atmospheric Hg as the major source of mercury in leaf tissues. Ericksen et al. [6] states that Hg content in forest foliage is a function of time and is independent of Hg concentration in the soil. Lodenius et al. [7] assumes that the increase in Hg concentration in foliage depends on a plant's ability to absorb deposition.

In general, coniferous species represent significant environmental bioindicators thanks to several age classes of needles. A potential sudden increase or decrease of Hg concentration in a particular needle age class can indicate a change of air quality or, ideally, that the source of Hg emissions has ceased to exist. A similar case has been described by Kindernajová [8] in northern Slovakia.

The Norway spruce (*Picea abies* (L.) Karst.) is an example of a good bioindicator plant. This species is easily identified, widely distributed, and widely used in bioindication studies [9-11]. We have used Norway spruce needles to examine and statistically evaluate increases in mercury concentration with regard to needle age.

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Methods

Samples (313) from 88 locations across Slovakia were collected during a non-growing period from September to January in 2003-07. Sampling locations included unpolluted sites (e.g. Low Tatras, Poľana Mts.) as well as areas polluted by anthropogenic activity (industrial and urban zones) or in areas with natural occurrence of mercury in the geological substrate (e.g. Banská Štiavnica Region, Slovenské rudohorie Mts.).

Spruce trees were sampled once by taking samples from two branches of the fifth whorl of five solitary trees aged 15-20 years from each location to obtain an average representative sample [12]. The samples were air-dried at about 20ºC. The needles were later separated from branches with respect to individual age classes according to Barták [13] (Fig. 1). One age class from each location was then treated as an individual sample.

The unwashed needles were milled into fine powder with the ball mill (RETSCH MM 301). Plant samples were analyzed with the use of the Advanced Mercury Analyser AMA 254 (a single-purpose absorption spectrophotometer; Altec Ltd., Praha); the detection limit was 0.01 ng Hg. Every sample was analyzed three times at least with rsd of 10 % and less. Quality of measurement was safeguarded by the use of certified materials of CMI 7003 (silty clay loam; Analytica Ltd., Czech Republic) and NIST-1575a (pine needles). Sample weights ranged from 40-60 mg. The parameters for drying, decomposing, and stabilizing (waiting) were 40 s, 150 s, and 45 s, respectively.

The results were compared with the normal Hg value of 0.12 mg·kg^{-1} in assimilatory organs according to Maňkovská [14]. The importance of the influence of needle age on Hg concentration in needles was evaluated by means of the analysis of variance of the Statistica 6.0 program. Four-year classes of Norway spruce needles represented four factor levels. Statistically significant differences were tested between the factor levels using Duncan's test. Tuckey's test could not be used due to various numbers of repetitions on single factor levels [15].

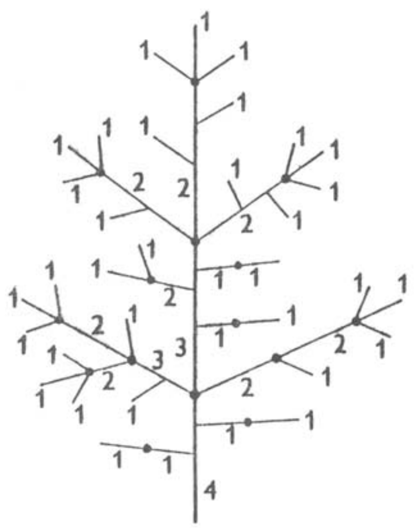

Fig. 1. Example of peripheral branch system [13]. Numbers represent needle age.

Table 1. Basic statistical data on total Hg content (mg·kg^{-1}) in assimilatory organs of *Picea abies* according to needle age.

Stats \ Age of needles	I.	II.	III.	IV.
count	85	85	82	61
average	0.041	0 .048	0.064	0.068
median	0.034	0.039	0.047	0.055
min	0.011	0.004	0.029	0.033
max	0.215	0.172	0.757	0.196
standard deviation	0.032	0.028	0.082	0.035

Results and Discussion

The analyses of four age classes of needles of *Picea abies* (Table 1) from 88 locations in Slovakia show that the most analyzed samples stem from 1- and 2-year-old needles (85 in each age class). The values ranged from 0.011 to 0.215 mg·kg^{-1} concerning 1-year-old needles. The average mercury concentration was 0.041 mg·kg^{-1}.

The normal value (0.12 mg·kg^{-1}), as defined by Maňkovská [14], was exceeded in four locations. The minimum value of Hg concentration regarding 2-year-old needles equals 0.004 and the maximum 0.172 mg·kg^{-1}.

The average value of second year concentrations increased in contrast to the first year, although only to 0.048 mg·kg^{-1}. Five samples exceeded the normal values. The lowest value from the data on 3-year-old needles (82 samples) was 0.029 mg·kg^{-1}, and the highest value reached 0.757 mg·kg^{-1}. The average value represents the concentration of 0.064 mg·kg^{-1}. The arithmetic mean of 61 samples of 4-year-old needles equaled 0.068 mg·kg^{-1}. The lowest measured value represents 0.033 mg·kg^{-1}; the highest value was 0.196 mg·kg^{-1}. The normal concentration was exceeded in six locations in cases of 3- and 4-year-old needles.

Median and average values (Table 1, Fig. 2) show a rise in Hg concentrations in individual needle age classes.

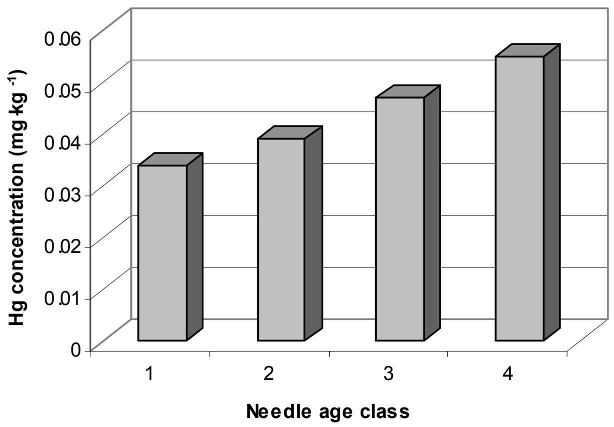

Fig. 2. Median values of Hg concentration in individual needle age classes.

Table 2. The variance analysis results of significant differences in Hg concentration according to needle age.

Variance	The sum of squared deviations	Degrees of freedom	Dispersion	F-value	p
Between needle age classes	0.026631	3	0.008877	8.9504	0.000010
Residual	0.310428	313	0.000992		

$F_{0.05}$=2.918, $F_{0.01}$=3.796

The presented data shows a falling tendency of Hg concentration in Norway spruce needles collected all across Slovakia. In 1984, normal Hg content in foliage was equal to 0.12 mg·kg^{-1} [14]. Consequently, in 1996 the average value in needles was defined as 0.1 mg·kg^{-1} [16] and the average of current 2-year-old needles is only 0.048 mg·kg^{-1}. This is a reflection of improving environmental conditions caused mainly by the closure of several industrial plants.

The importance of needles age influence on Hg concentration in needles is demonstrated in Table 2.

It is possible to reject hypothesis H_0 about the equality of the concentration averages, because of the calculated value of $F>F_{0.05}$ and $F_{0.01}$. Subsequently, hypothesis H_1 is acceptable with a 95% or 99% certainty. This gives evidence of statistical importance of the differences between Hg concentration averages in needles from individual year classes.

The importance of differences between averages of individual factor levels was tested in all combinations. Duncan's test showed significant differences between averages of non-adjacent age classes of needles; i.e. between the first and third years and between the second and fourth years. The differences in average mercury concentration between adjacent factor levels are statistically insignificant on a 5% level of importance.

Positive correlation between Hg concentration in assimilatory organs and the length of the growing period (especially considering the length of physiological activity) was substantiated by Fleck et al. [17]. Moreover, Rea et al. [4] note that mercury is the only metal of 9 monitored elements (Hg, V, Al, Zn, Cu, Rb, Sr, Ba, and Pb) that showed increasing concentration in leaves of deciduous species in the growing period. However, the differences were not statistically significant. An increasing trend was also not confirmed in cases of herbs and bushes (*Vaccinium myrtillus*, *Calamagrostis villosa*, *Deschampsia flexulosa*) [18].

Table 3. Results of Duncan's test concerning assessment of significance of differences between concentration averages in each combination.

Age of needles	(1)	(2)	(3)	(4)
1		0.141107	**0.002591**	**0.000003**
2	0.141107		0.099623	**0.000514**
3	**0.002591**	0.099623		0.053677
4	**0.000003**	**0.000514**	0.053677	

Statistically significant differences between averages are bold.

On the other hand, Kuang et al. [19] confirm the increased concentration (by 33-120%) of Ca, Mn, Zn, Fe, and Pb in 2-year-old needles. The authors also state that there are no significant differences in Mg, Ni, Cd, Cr, and Cu concentrations. Fleck et al. [17] compared Hg concentrations in needles of 24 specimens of red pine (*Pinus resinosa* Ait.). Based on the analyses, they concluded that Hg concentration in 2-year-old needles was approximately twice as high as in 1-year-old needles (r=0.77). Grigal [20] also described the increasing trend in various coniferous species such as the Norway spruce, the Douglas fir, the black pine, and the red pine. Wyttenbach et al. [21] describes a steady increase in Hg (as well as Fe, Al, As, Ba, and I) concentration in relation to age. They also provide a function of increase but the extrapolated line does not pass through the origin.

Although all mentioned authors depict the increase in Hg concentration relating to needle age, this trend was not statistically proven in most cases. Therefore, the concentration of mercury is not primarily dependent on needle age. Of course age influences Hg concentrations in assimilatory organs, but the mercury amount in foliage depends on other factors such as weather conditions, morphologic character of species, and resources of Hg [4, 22].

The majority of studies dealing with the issues of element concentrations in needles were based on analyses of 1-year-old needles; only a few authors determined Hg pollution by means of analysis of 2-year-old needles [e.g. 10]. However, this approach does not take advantage of the needles' potential as bioindicators. Mercury absorbed by needles of multiple age classes could be used for better evaluation of environmental threats. On the other hand, the analysis of four or more age classes of needles requires a lot of time and is also not always economically efficient. According to the acquired data (Table 1), it seems possible to analyse only the second or third age class or, ideally, a mixed sample of them, because the average value of all age classes is close to the average of the second and third age class. This procedure could be introduced into monitoring practice after further examination and discussion.

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