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Metal levels in an epiphytic lichen as indicators of air quality in a suburb of Helsinki, Finland

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The levels of Cd, Cu, Fe, Hg, Mn, Ni, Pb and Zn were measured in epiphytic lichens *Hypogymnia physodes* in a suburban area of Helsinki, Finland. The metal levels were near the background values or slightly higher. The concentrations of Cd, Fe and Zn were compared with results from a previous monitoring survey. The concentrations of Cd had increased significantly from 1980 to 2007 but were still at the background level. The levels of Fe and Zn had decreased during that period. The distribution of metals was in most cases rather even but land use explained partly the distribution of some of the metals studied.

Introduction

Epiphytic lichens have proved to be good indicators of airborne metal pollution. In most areas there are species occurring at both background and polluted sites. *Hypogymnia physodes* is a common species in Finland and it has been widely used for biomonitoring purposes (Lodenius 1981, Kubin 1990, Garty 2001, Takala *et al*. 1994). Biomonitoring that is based on lichens is strongly species dependent (Bennett and Wetmore 1999). Both the degree of damage in lichens and concentrations of pollutants have been used in monitoring studies (e.g. Garty 2001, Otnyukova 2007).

The nature of anthropogenic emissions has changed significantly during the last decades. Emissions from large industries and power plants have been reduced as a result of technological improvements and efficient treatment of flue gases. Traffic volumes have increased and are still increasing steadily. These changes as well as changes in local infrastructure accentuate the need for monitoring of pollutants and environment quality.

The aims of this investigation were (1) to study the distribution of metals in epiphytic lichens and to compare it with known emission sources and infrastructure in the area, and (2) to compare present concentrations with those reported earlier from the same area.

Study area, material and methods

The study area, Vuosaari (Fig. 1), is a suburb in eastern Helsinki, Finland. Here a biomonitoring survey was carried out in 1980 (Lodenius and Kumpulainen 1983). In that study Cd, Fe and Zn concentrations were measured from *Hypogymnia physodes*. Since that time the area has undergone a rapid and vast development. The number of inhabitants increased from approximately 14 000 in 1980 to approximately 34 000 in 2007. The traffic most probably more than doubled during that period. Formerly, small-scale oil heating was predominant in the area. Now remote heating — the energy being produced in large, centralized power plants — prevails. During the years 1974–1987, a medium-sized shipyard was located in north-eastern Vuosaari. Recently, this area has been converted into the main harbour of Helsinki, which became operational after the lichen sampling had started. A refuse dump in the north had been in active use between 1963 and 1988. Later this area was adapted for recreational purposes. Two power plants using natural gas constructed in the 1990s are situated between the harbour and the former refuse dump. They have a combined output of 630 MW electricity and 580 MW heat. The residential area is mainly in the middle of the suburb while forest areas are situated along the shores and in the north (Fig. 1). Land use within a radius of 400 m was determined for each site according to the following classification: residential areas, traffic and commercial areas, forests and parks, sea, industrial areas (including harbour and refuse dump).

Samples of *Hypogymnia physodes* growing at a height of 1–1.5 m on trunks of *Pinus sylvestris* were collected from 48 sites during January–February 2007. The weather was rather variable during the sampling period with temperatures ranging from +2.4 °C to –20.7 °C. Total precipitation (mainly snow) during the sampling period was 48 mm. Thirty-four of these sites were the same as in 1980 (Fig. 1). The distance between sampling points varied from 500 to 800 m depending on local conditions. At each site, samples were collected from at least three pine trees. These subsamples were pooled into one sample. The samples were cleaned manually, homogenised, dried and stored in paper bags before analyses. With one exception, two determinations were done from one sample and in the final calculation an average value was used.

The samples were weighed (0.1–0.3 g) and digested with 5 ml of 65% HNO_3 and 1 ml of 30% H_2O_2 in teflon vessels which were heated to approximately +200 °C for 10 minutes (Milestone Ethos 1600). The solutions were filtered (S&S Filter paper, 589[2]) and diluted to 25 ml with distilled water. The metals were determined by using flame (Fe, Cu, Mn, Zn) or electrothermal (Cd, Ni, Pb) atomic absorption spectrometry (Varian SpectrAA-400 equipped with GTA-96). In the graphite furnace measurements, a 1000 ppm solution of $(NH_4)H_2PO_4$ was used as a matrix modifier. Hg was analysed directly from solid samples (weight 0.2 g) using cold vapour AAS (Milestone DMA-80). "Tomato Leaves" (NIST SRM 1573a) was used as a reference material (Table 1).

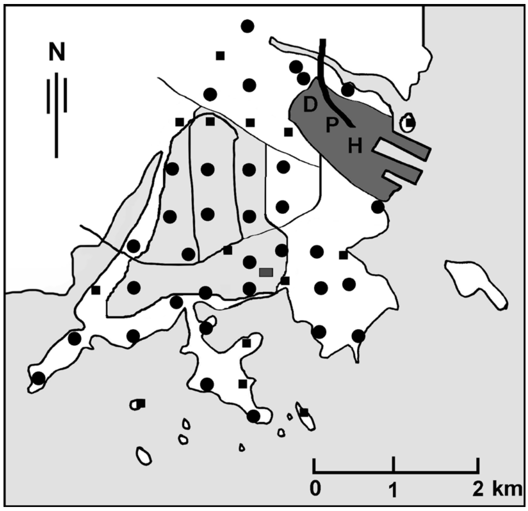

Fig. 1. Study area with sampling locations (dots and squares). Sampling sites common for 1980 and this study are indicated with dots. Main residential area is marked with grey and industrial areas with dark grey. D = former dumping ground, P = power plant, H = harbour (formerly shipyard).

Results

The concentrations of Cu, Hg, Ni and Zn were rather evenly distributed in Vuosaari while there

Table 1. Analytical results for a reference sample "Tomato leaves" NIST SRM 1573a (mg kg^{-1} dry wt).

	Obtained mean ± S.D. (n = 6)	Certified mean ± S.E.
Cd	1.66 ± 0.14	1.52 ± 0.04
Cu	4.9 ± 0.2	4.70 ± 0.14
Fe	374 ± 8	368 ± 7
Hg	0.033 ± 0.002	0.034 ± 0.004
Mn	220 ± 10	246 ± 8
Ni	1.78 ± 0.13	1.59 ± 0.07
Zn	31.3 ± 0.8	30.9 ± 0.7

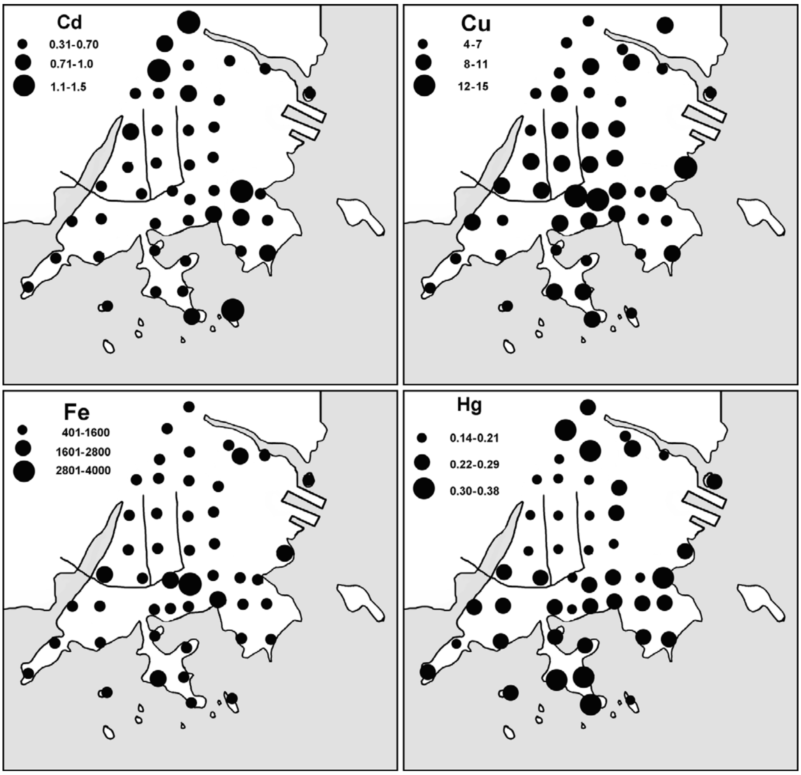

Fig. 2. Concentrations (mg kg^{-1} dry wt) of Cd, Cu, Fe and Hg in *Hypogymnia physodes*.

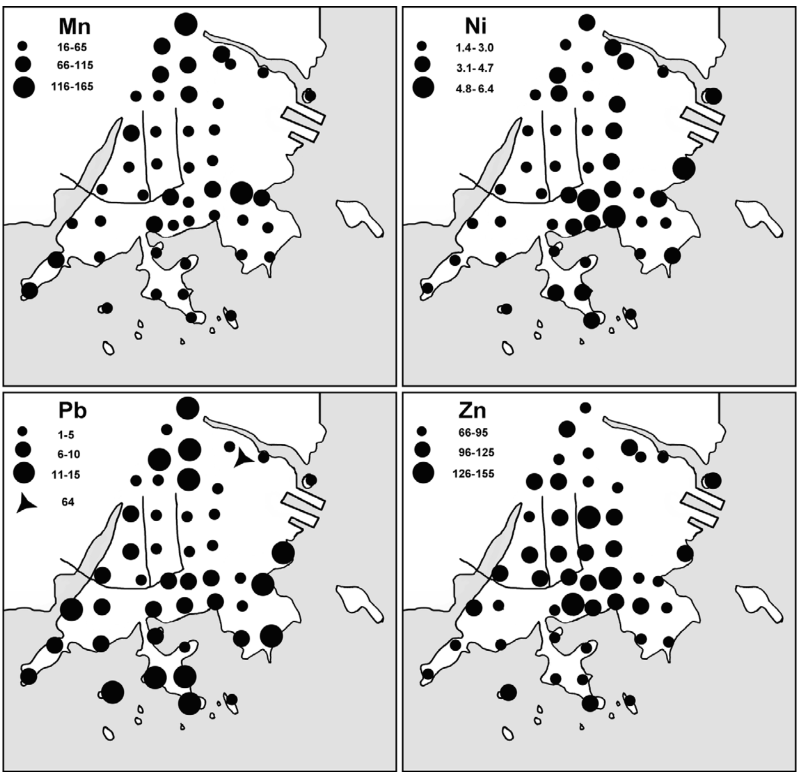

Fig. 3. Concentrations (mg kg^{-1} dry wt) of Mn, Ni, Pb and Zn in *Hypogymnia physodes*.

were larger variations in the concentrations of Cd, Mn and Fe (Figs. 2 and 3, Table 2). For Pb the distribution was even except one high concentration from a site near the construction of a railway to the harbour (Fig. 3). This exceptional result was excluded from statistical calculations. Very significant positive correlations were found between the pairs Cu/Fe, Cu/Ni, Cu/Zn, Fe/Ni, Fe/Zn and Hg/Pb. Significant negative correlations were found between Cu/Mn and Mn/Zn (Table 3).

Land use had affected the distribution of some metals. The strongest correlations were found for Cu, Zn and Mn: positive for traffic and negative for forest areas. Mn concentrations were higher in forest areas and lower near the sea (Table 3).

The concentrations of Cd had increased significantly (33%) from 1980 to 2007 while the concentrations of Fe and Zn had decreased significantly (29% and 24% respectively; Table 4). No significant correlations were found for Cd, Fe or Zn from corresponding samples of the years 1980 and 2007.

Discussion

As a whole, the metal concentrations in Vuosaari are near the background levels (Table 5) and land-use analysis explains part of the distribution of elements. Traffic explains partly the distribution of Cu, Fe, Ni and Zn which is in agreement with the results of Cicek *et al*. (2008) who found clearly elevated levels near roads. Variations in element concentrations are considerable for many

Table 2. Concentrations (mg kg^{-1} dry wt) of metals in *Hypogymnia physodes* in the suburb Vuosaari ($n = 48$).

	Mean ± S.D.	Range	C.V. (%)
Cd	0.65 ± 0.25	0.32–1.5	38
Cu	8.3 ± 2.0	5.1–15	24
Fe	1100 ± 610	440–4000	54
Hg	0.24 ± 0.06	0.14–0.38	25
Mn	57 ± 28	21–160	49
Ni	3.0 ± 0.91	1.3–6.1	30
Pb*	7.7 ± 3.4	2.8–16	44
Zn	99 ± 17	72–150	18

* one high value (64 mg kg^{-1}) excluded (*see* Fig. 3).

Table 3. Spearman rank correlations and significance levels (*p* values in parentheses) for relations between metals and land use categories (as defined in the text).

	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Cu	0.030 (0.843)							
Fe	−0.136 (0.361)	0.716 (0.000)						
Hg	−0.171 (0.251)	0.077 (0.608)	0.249 (0.092)					
Mn	−0.025 (0.869)	−0.432 (0.003)	−0.199 (0.179)	−0.041 (0.785)				
Ni	−0.106 (0.476)	0.608 (0.000)	0.736 (0.000)	0.283 (0.054)	−0.109 (0.466)			
Pb	0.182 (0.219)	0.145 (0.329)	0.180 (0.224)	0.529 (0.000)	−0.094 (0.528)	0.260 (0.077)		
Zn	0.156 (0.295)	0.758 (0.000)	0.421 (0.004)	−0.103 (0.490)	−0.398 (0.006)	0.323 (0.027)	−0.125 (0.401)	
Residential	0.009 (0.955)	0.378 (0.009)	0.268 (0.069)	−0.314 (0.032)	−0.081 (0.586)	−0.028 (0.854)	−0.278 (0.059)	0.252 (0.088)
Traffic	−0.142 (0.339)	0.514 (0.000)	0.540 (0.000)	−0.214 (0.149)	−0.069 (0.647)	0.256 (0.082)	−0.192 (0.197)	0.421 (0.003)
Forest	0.349 (0.017)	−0.499 (0.000)	−0.505 (0.000)	0.087 (0.561)	0.437 (0.002)	−0.329 (0.025)	0.130 (0.384)	−0.452 (0.002)
Sea	−0.230 (0.120)	−0.090 (0.548)	−0.190 (0.199)	0.360 (0.013)	−0.455 (0.002)	−0.019 (0.900)	0.360 (0.013)	−0.140 (0.348)
Industry	−0.391 (0.007)	0.111 (0.455)	0.312 (0.033)	−0.123 (0.411)	0.105 (0.480)	0.432 (0.003)	−0.186 (0.210)	0.186 (0.210)

metals, but still the use of epiphytic lichens can be seen as a good monitoring tool.

Yatkin and Bayram (2007) analysed element concentrations in particulate matter fractions ($PM_{2.5}$ and PM_{10}) at suburban and urban sites in Izmir, Turkey. At a suburban site they found significant correlations between Cd, Cu, Fe, Mn, Ni, Pb and Zn in the coarse fractions while fewer correlations were found in the finer particles (Hg was not analysed). They concluded that the metals originate from both terrestrial and anthropogenic sources including fossil fuel burning and traffic.

The Cd concentrations in Vuosaari are at the background level (Table 5) but 33% higher than those measured in 1980. The lack of positive correlation between samples from 1980 and 2007 indicate different sources of Cd pollution. Bennett and Wetmore (1999) found a significant increase in Cd in four lichen species including *Hypogymnia physodes* during the period 1986–1997 in Minnesota. However, the same authors found a decrease of approximately 30% in both *Parmelia sulcata* and *Xanthoparmelia chlorochroa* in North Dakota during the period 1982–1998. We found no significant correlations between Cd levels and those of other metals and a negative correlation with industrial areas (Table 3). Consequently, we found no signs of significant anthropogenic influence from local sources.

In Europe, the atmospheric anthropogenic emissions of Cd decreased from approximately 2300 t in 1975 to approximately 500 t in 2005 (Pacyna *et al*. 2009). Soil particles and forest fires contribute to the total Cd deposition (Richardson *et al*. 2001). In Finland, anthropogenic emissions decreased from 6.3 t in 1990 to 1.1 t in 2007 the most important emission source being energy production (*see* http://www.environment.fi/print.asp?contentid=315227&lan=en&clan=en). However, most of the anthropogenic Cd deposition in Finland originate from long-distance sources (Ilyin *et al*. 2008). Sources in the Baltic countries and eastern Europe possibly contribute to the total deposition in Finland. In a national moss monitoring survey the Cd deposition decreased by 67% between 1985 and 2000 (Poikolainen *et al*. 2004). The anthropogenic emissions of Cd decreased by 50% from 1990 in Europe, but in Belarus and Cyprus the emissions increased during the same period (Ilyin *et al*. 2008).

The concentrations of Cu were at the background level (Table 5). They were positively correlated with concentrations of Fe, Ni and Zn and negatively with those of Mn. They were also positively correlated with residential and traffic areas and negatively correlated with forest areas (Table 3). Soil particles are main natural causes of Cu in the atmosphere (Richardson *et al*. 2001) which means that dust raised by traffic may explain part of our results. In Finland, anthropogenic emissions of Cu decreased from 94 t in 1990 to 18 t in 2007 the main emission source being energy production (*see* http://www.environment.fi/print.asp?contentid=315227&lan=en&clan=en).

The concentrations of Fe were slightly higher than the background level (Table 5) but lower than those reported earlier from urban and industrial areas in Finland (Takala *et al*. 1994). This may be explained by a higher amount of forested areas and reduced dust emissions from traffic and other sources. The concentrations were now lower as compared with those measured during the previous investigation. There were positive correlations with Cu, Ni and Zn and with traffic areas (Table 3). Takala *et al*. (1994) found an increasing trend in Fe concentrations in

Table 4. Concentrations of three metals (mg kg^{-1} dry wt) in the lichen *Hypogymnia physodes* in pairs of samples (n = 34) from 1980 (Lodenius & Kumpulainen 1983) and 2007 (this study): Spearman rank correlations (r_s) and differences (sign test).

	Cd	Fe	Zn
1980 mean ± S.D. (range)	0.48 ± 0.25 (0.15–1.6)	1700 ± 600 (770–3600)	130 ± 31 (63–210)
2007 mean ± S.D. (range)	0.64 ± 0.25 (0.32–1.5)	1200 ± 660 (530–4000)	99 ± 19 (74–150)
r_s (p)	0.155 (0.38)	0.286 (0.10)	–0.005 (0.98)
Change 1980–2007 (p)	33% (0.009)	–29% (0.000)	–24% (0.001)

Hypogymnia physodes collected from 31 sites in Finland, some of them from industrial and urban areas. They also found a highly significant correlation with sulphur, indicating common occurrence of these elements in precipitation.

The concentrations of Hg were at the background level (Table 5). Globally, volcanic emissions and evasions from the soil are important sources of Hg which is transported over long distances (Richardson *et al*. 2001). We found a significant correlation with Pb and a slight correlation with sea areas (Table 3) which could possibly be explained by long-range transport and successive uptake by vegetation. In the early 1980s, higher Hg concentrations were found along the Finnish coasts as compared with those at the inland sites (Lodenius 1981). In Finland, anthropogenic emissions of Hg decreased from 1.1 t in 1990 to 0.8 t in 2007 the most important sources being energy production and industrial production processes (*see* http://www.environment.fi/print.asp?contentid=315227&lan=en&clan=en).

The Mn concentrations were slightly lower than the background level reported by Kubin (1990; Table 5). Mn concentrations correlated negatively with Cu and Mn and positively with occurrence of forest areas (Table 3). The concentrations of Mn in acidic bark is often high enough to limit the occurrence of *H. physodes* and the uptake of this metal is partly regulated by certain acetone-extractable substances (Hauck 2008). In moss, Mn is easily exchanged by neutral salt solutions (Rühling and Tyler 1970) and in *Hypogymnia physodes* a rapid absorption to extracellular cation exchange sites has been shown (Hauck *et al*. 2002). These phenomena could explain lower concentrations near the sea. The findings by Steinnes (1995) that Mn in moss is negatively related to marine conditions and strongly positively related to vegetation is in concordance with the distribution of Mn in the present study.

The Ni concentrations were at the background level (Table 5). They correlated positively with Cu and Fe and also with industrial areas (Table 3). In Finland, the emissions of Ni decreased from 67 t in 1990 to 22 t in 2007 the most important source being energy production (*see* http://www.environment.fi/print.asp?contentid=315227&lan=en&clan=en).

Table 5. Metal concentrations in *Hypogymnia physodes*: our results compared with those from reference areas and polluted (urban and industrial) areas. Means and ranges (mg kg^{-1} dry wt).

	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Vuosaari (this study)	0.65 (0.32–1.5), *n* = 48	8.3 (5–15), *n* = 48	1100 (440–4000), *n* = 48	0.23 (0.0–0.38), *n* = 48	57 (21–160), *n* = 48	3.0 (1.4–6.1), *n* = 48	7.7 (2.8–16), *n* = 48	99 (72–150), *n* = 48
Reference areas (Bennett 2000)	0.56 (0.0–1.0), *n* = 37	6.0 (0.8–6.7), *n* = 37	620 (110–950), *n* = 43	0.25 (0.07–0.6), *n* = 15	85 (13–158), *n* = 32	1.7 (0.0–2.4), *n* = 33	20 (0.05–31), *n* = 39	73 (7.0–95), *n* = 43
Polluted areas (Bennett 2000)	2.6 (1.0–22), *n* = 34	29 (6.7–37), *n* = 34	3100 (950–21000), *n* = 41	19 (0.6–190), *n* = 14	290 (158–690), *n* = 31	12 (2.4–150), *n* = 31	130 (31–1000), *n* = 37	439 (95–5600), *n* = 41
Rural areas (Kubin 1990)	0.70 (0.12–4.3), *n* = 2385	7.3 (3.5–200), *n* = 2385	540 (180–3800), *n* = 2385	–	130 (20–690), *n* = 2385	2.6 (0.0–51), *n* = 2385	18 (1–62), *n* = 2385	86 (38–220), *n* = 2385
Background (Lippo *et al.* 1995; except Hg)	0.69, *n* = 788	7.1, *n* = 788	540, *n* = 788	0.22 (0.07–0.48), *n* = 155 (Lodenius 1981)	–	2.5, *n* = 788	17, *n* = 788	84, *n* = 788

The Pb concentrations were lower than those in the 1990s (Table 5). A positive correlation was found with Hg but no significant correlations with land use (Table 3). The lower Pb level is obviously related to the decreased emissions in Finland and elsewhere in Europe (*see* http://www.environment.fi/print.asp?contentid=315227&lan=en&clan=en). The single high Pb concentration in northern Vuosaari (Fig. 3) is possibly related to local railway construction works. In Finland, emissions of Pb decreased from 326 t in 1990 to 21 t in 2007 and the most important emission source is energy production (*see* http://www.environment.fi/print.asp?contentid=315227&lan=en&clan=en).

The concentrations of Zn were slightly higher than the background level (Table 5). Zn correlated positively with Cu, Fe and negatively with Mn. The correlation with traffic areas was very significant and accentuated by the negative correlation with forest areas (Table 3). The observed decrease in concentrations is probably related to the decrease in emissions in Finland from 571 t in 1990 to 103 t in 2007. The most important sources are energy production (90%) and industrial production processes (10%) (*see* http://www.environment.fi/print.asp?contentid=315227&lan=en&clan=en). The Zn concentrations in this study were higher and the correlation between Fe and Zn (Table 3) much weaker than the values reported by Takala *et al*. (1998).

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