



## Zinc accumulation in lichens due to industrial emissions around Vorkuta, northeast European Russia

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**Abstract:** Zinc concentrations in apices  $[Zn^{2+}]_{apex}$  of the lichens, *Cladonia arbuscula* and *C. rangiferina* were determined along transects through two sub-Arctic towns in the Usa River Basin, northeast European Russia. One transect, which was 130 km long running in an east-west direction, passed through the town of Vorkuta and the other transect, which was 240 km long running in a southwest-northeast direction, passed through Inta. Zinc accumulation in lichens, which was detected 25–40 km within the vicinity of Vorkuta, was largely attributed to local emissions of alkaline coal ash from coal combustion. The present results using *C. arbuscula* around Vorkuta are consistent with those of previous studies suggesting that this lichen is a useful bioindicator for trace metals. There was no such elevation of  $[Zn^{2+}]_{apex}$  detected in *C. rangiferina* along the transect running through Inta.

**Key words:** Arctic, atmospheric deposition, zinc, lichens, bioindicators, *Cladonia arbuscula*, *Cladonia rangiferina*.

### Introduction

Russia is the principal contributor of metal emissions in Europe and has the most extensive industrial developments north of the Arctic Circle including the mining and metallurgical industries of Norilsk in Siberia and Monchegorsk on the Kola Peninsula (Toutoubalina and Rees 1999; Reimann *et al.* 2000). By comparison, north-eastern European Russia has suffered less from industrial pollution and large areas remain unpolluted, although some locations bear the signs of local environmental degradation, such as changes in community structure of vegetation around the coal mining town of Vorkuta (Virtanen *et al.* 2002). Exploitation of coal here began in the 1930s and intensified until the 1990s when extraction declined owing to increased transportation costs and poor combustion qualities of the coal (Hill 2000). Vorkuta is the centre of the coal industry with six mines operating during the period of this research in 1999 whereas Inta had fewer operating mines

in 1998 and a comparatively smaller coal mining industry. Coal mining and combustion for power generation have been the principal sources of heavy metal pollution in the region; with Vorkuta being the highest emitter and suffering a legacy of pollution impacts resulting from the deposition of alkaline fly ash (Solovieva *et al.* 2002; Walker *et al.* 2003a, b; Walker 2005). An inventory of pollutants emitted from both towns has been summarized by Solovieva *et al.* (2002).

Mat-forming terricolous lichens are important components of plant communities in high latitudes, where they contribute to nutrient cycling and secondary production, such as grazing (Longton 1997). Lichens are primarily dependant on atmospheric sources for nutrients and therefore readily accumulate atmospheric contaminants, such as metals (Nash and Gries 1995). Therefore, they are amongst the most pollution sensitive receptors in terrestrial ecosystems (Richardson 1988). Spatial variation in the chemical composition of lichens has been widely used to monitor environmental quality as a result of industrial activities including situated around coal-fired power stations (Gonzalez and Pignata 1997; Walker and Pystina 2006; Walker *et al.* 2006a). The principle source of electrical power used in the town in this study is generated by coal-fired power stations.

The present research aimed at assessing the extent of zinc deposition due to local sources around Vorkuta and Inta in the Komi Republic, northeast European Russia using the lichens *Cladonia arbuscula* and *C. rangiferina* along a transect passing through both towns. This region spans the sub-Arctic taiga forest and tundra ecotones and has already been identified as a significant source of metal emissions mainly as a result of coal fired power stations in the towns of Vorkuta and to a lesser extent Inta (Solovieva *et al.* 2002; Walker *et al.* 2003a, b; Walker 2005; Walker *et al.* 2006b). The study provided an opportunity to further evaluate the use of terricolous lichens as bioindicators of metal deposition (Walker *et al.* 2003b, 2006a).

## Materials and methods

Transects for sampling lichens were established that passed through the towns of Vorkuta (67°30'N, 64°05'E) and through Inta (66°03'N, 60°10'E). Inta was chosen for the second transect study because it also has a large coal industry and is currently the second most largest coal producing town in the region. These sampling locations and transects have been illustrated and described in greater detail elsewhere (see Fig. 1; Walker *et al.* 2003a, b). The transect passing through Vorkuta was approximately 130 km long and oriented west-east; characterized by *Betula nana* L. shrub tundra along its entire length. The transect passing through Inta was 240 km long and oriented southwest-northeast spanning taiga forest and tundra ecotones. Mean annual precipitation for Vorkuta and Inta is 518 and 473 mm respectively and south westerly winds prevail in the region.

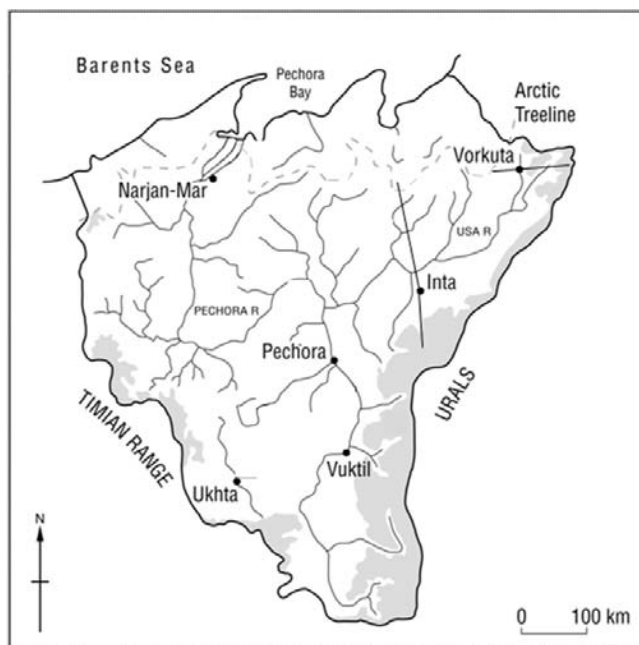


Fig. 1. Pechora region showing sampling transects through the towns of Vorkuta and Inta.

Six sampling sites were selected along each of the transects. Originally nine sampling sites had been chosen along the Inta transect (reflecting its greater length) but the availability of *C. rangiferina* along this transect was limited partly due to the lack of suitable lichen heath habitat in the area. At each site, three sub-sites were selected, 1 km apart, at which six replicate samples of lichen were collected at distances 10–20 m apart in open areas in order to minimize tree canopy effects; these were usually inter-tree positions in open forest, or in tundra. Most sites were in wilderness areas remote from roads. Terricolous mat-forming lichens *C. arbuscula* (Wallr.) Flot. and *C. rangiferina* (L.) F.H.Wigg. were collected at sub-sites to provide biomarkers for atmospheric deposition and because of their abundance in shrub tundra and taiga forest. Lichen samples were air-dried in the field, sealed in LDPE containers and stored at 4°C until analysis. Powder-free LDPE gloves were worn when handling lichens in the field and the laboratory to minimise contamination. Lichens were rehydrated overnight by exposure to water-saturated air (over water in a desiccator) at 4°C, then fully saturated by spraying lightly with deionised water and cleaned of extraneous debris using forceps. Samples were dried overnight at 80°C and then weighed, where c. 100 mg of apical (5 mm) tissue was digested to dryness in 1 mL of concentrated HNO<sub>3</sub> at 175°C. The residue was dissolved in 10 mL 1 M HNO<sub>3</sub> and appropriate quantities of ionisation suppressant and releasing agent (CsCl<sub>2</sub>, LaCl<sub>2</sub>) added. Zinc was selected because it was one of several trace metals found to contaminate snow and soils lo-

cally in the survey region (see Walker *et al.* 2003a; Walker 2005) and was measured by flame atomic absorption spectrophotometry (FAAS); concentrations were recalculated in relation to the mass of dried apical lichen tissue to allow direct comparison with the solution data (see Walker *et al.* 2003b).

Genstat and Minitab were used to perform standard statistical analyses (ANOVA, correlation analysis and linear regression).

## Results and discussion

Collections of *C. arbuscula* was complete at all six sites along the Vorkuta transect despite mat-forming lichen cover being generally poor in the region due to heavy grazing and trampling by reindeer (Crittenden 2000). Along the Inta transect collections of *C. rangiferina* were made as *C. arbuscula* was less abundant along this transect. Whilst no attempt was made to compare absolute concentrations between the two lichen species they were chosen based on their availability along each transect. Therefore the results of this study may be used as a proxy for indicating localized perturbations of Zn concentrations. There was significant localized higher  $[Zn^{2+}]_{apex}$  in *C. arbuscula* in the vicinity of Vorkuta ( $P < 0.001$ ). For example the highest concentration of  $[Zn^{2+}]_{apex}$  in *C. arbuscula* were found at the two sites closest to the town (see Fig. 2a). Previous studies found no such localized elevated concentrations in  $[Zn^{2+}]_{apex}$  in *C. stellaris* around Inta, but it was strongly related to latitude (Walker *et al.* 2003b). It is possible that the apparent lack of any Zn perturbation around Inta may be due to lower sampling density

Table 1  
Comparison of  $[Zn^{2+}]_{apex}$  ( $\mu g\ g^{-1}$ ) in *Cladonia* spp. from high latitude industrial and pristine areas. Grey shading indicates industrial areas

Location	Species	$[Zn]$ ( $\mu g\ g^{-1}$ )	Study
Vorkuta (Transect) (coal mining)	<i>C. arbuscula</i>	16–55	This study
Inta, NE European Russia (coal mining)	<i>C. rangiferina</i>	15–34	This study
Inta, NE European Russia (coal mining)	<i>C. stellaris</i>	9–32	Walker <i>et al.</i> (2003b)
Gusum, Sweden (steel foundry)	<i>C. rangiferina</i>	55–75	Folkesson and Andersson-Bringmark (1988)
SE Ohio, USA (coal mining)	<i>Cladonia</i> sp.	27–42	Lawrey and Rudolf (1975)
Ontario, Canada, Uranium mines (0.5–30 km)	<i>C. mitis</i>	13–22	Fahselt <i>et al.</i> (1995)
Delaware Gap, USA (zinc smelter)	<i>Cladonia</i> sp.	61–80	Nash (1975)
Northwest Territories, Canada	<i>Cladonia</i> sp.	7–55	Puckett (1978)
Northwest Territories, Canada	<i>Cladonia</i> sp.	16–25	Puckett and Finegan (1980)
Bellsund area, Spitsbergen	<i>Cladonia</i> sp.	29–39	Jóźwik (1990)
High Point Park, New Jersey, USA	<i>C. rangiferina</i>	7–16	Glenn <i>et al.</i> (1991)

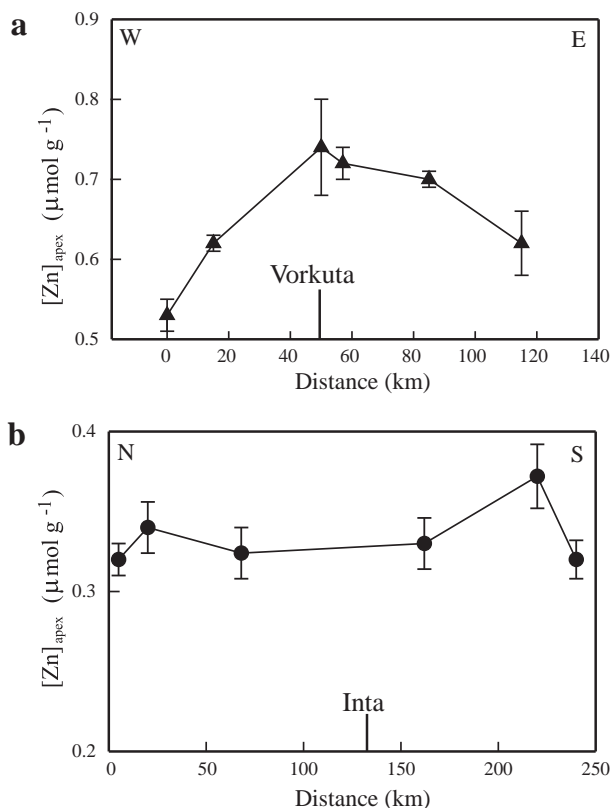


Fig. 2. Variation in  $[\text{Zn}^{2+}]_{\text{apex}}$  in *Cladonia arbuscula* ( $\blacktriangle$ ) along the transect passing through Vorkuta (a) and *C. rangiferina* ( $\bullet$ ) along the transect passing through Inta (b). Plotted values are means  $\pm$  1 SE ( $n = 18$ ). Note the different scales used for both plots.

along this transect, although local collections of *C. rangiferina* were attempted, their availability was scarce. Despite the lower sampling density along the Inta transect collections of *C. rangiferina* around Inta (Fig. 2b) did not show an apparent relationship between  $[\text{Zn}^{2+}]_{\text{apex}}$  and latitude unlike collections of *C. stellaris* in a previous study (Walker *et al.* 2003b). Variation in  $[\text{Zn}^{2+}]_{\text{apex}}$  in *C. arbuscula* around Vorkuta correlates well with other pollution signals from earlier work relating to snow ( $[\text{SO}_4^{2-}]_{\text{snow}}$ ,  $[\text{Ca}^{2+}]_{\text{snow}}$ ,  $[\text{K}^+]_{\text{snow}}$ , pH); metal contamination in soil and  $[\text{N}]_{\text{apex}}$  in lichens ( $r = 0.90$ ,  $P < 0.01$ ,  $n = 6$ ) (Walker *et al.* 2003a, b).

The concentration ranges presented in Table 1 are in broad agreement with previous studies but any discrepancies may reflect physiological differences between lichens or method of analyses. Therefore, it was not the intent of this study to make direct inter comparisons of Zn concentrations between different species but rather to use Zn concentrations in lichens as a proxy to detect elevated levels around industrial sites. The lowest concentrations of  $[\text{Zn}^{2+}]_{\text{apex}}$  were comparable with other studies in pristine locations (see Table 1), whilst elevated concentra-

tions around Vorkuta in this study were as high as concentrations found in other *Cladonia* spp. around coal mining towns (Walker *et al.* 2003b; Lawrey and Rudolf 1975). According to Folkesson and Andersson-Bringmark (1988),  $[Zn^{2+}]_{apex}$  measured in *C. rangiferina* sampled 6–7 km away from steel foundries in Gusum, Sweden were 55–75  $\mu\text{g g}^{-1}$  whilst the first indication of a reduced ground cover for this lichen species was only observed when the  $[Zn^{2+}]_{apex}$  exceeded 500  $\mu\text{g g}^{-1}$ . Therefore, they suggested that a  $[Zn^{2+}]_{apex}$  limit of 600  $\mu\text{g g}^{-1}$  would indicate the apparent critical threshold concentration (fatal concentration) for survival of *C. rangiferina*. The  $[Zn^{2+}]_{apex}$  observed around Vorkuta in this study fall far below the thresholds reported by Folkesson and Andersson-Bringmark (1988) and the concentrations reported here are therefore likely not to cause damage to these lichens.

Terricolous mat-forming lichens are abundant throughout the sub-Arctic tundra and taiga regions and are sentinel species that readily accumulate contaminants that reflect local environmental conditions due to their slow growth and physiology. The present results using *C. arbuscula* around Vorkuta are consistent with those of previous studies suggesting that they are useful bioindicators for trace metals. While there occurs a clear Zn peak in the town of Vorkuta, Inta is not marked by a Zn anomaly. The anthropogenic Zn peak in *C. arbuscula* around Vorkuta is attributed to local deposition of coal ash from coal combustion extending 25–40 km around Vorkuta.

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