TERRESTRIAL POLLUTION IN THE PECHORA BASIN, NORTH-EASTERN EUROPEAN RUSSIA

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ABSTRACT

The chemical composition of snow, terricolous lichens and top-soil along with abundance and diversity of lichen communities were assessed in the Pechora and Usa basins, North-Eastern European Russia. Transects were established through the principal industrial towns of Vorkuta, Inta and Usinsk to assess the spatial extent of acid or alkaline and metal deposition. A further eight sites were selected to assess local impacts of oil and gas operations.

In the Usa basin decreases of nitrogen concentration in the lichen *Cladonia stellaris* and winter deposition of non-sea salt sulphate moving northward were attributed to long range transport of oxides of nitrogen and sulphur from lower latitudes. Increased ionic content and pH of snow, along with elevated nitrogen concentrations and modified cation ratios in lichens (*Cladonia arbuscula* and *Flavocetraria cucullata*) within 25-40 km of Vorkuta and Inta were attributed to local deposition of alkaline coal ash. Nitrate concentration in snow did not vary with proximity to perceived pollution sources. Trace metal composition of winter snowpack, snow-melt filter residues and top-soils indicated elevated concentrations of elements associated with alkaline combustion ash around coal mining operations in Vorkuta and Inta, adding significantly to the soil metal loading as a result of ash fallout. Around the petrochemical industry near Usinsk there was little evidence of trace metal deposition. Acid deposition was associated with pristine areas, whereas alkaline combustion ash near to emission sources more than compensated for the acidity due to SO_2 and NO_x. There were limited perturbations in the chemical signals in lichens, top-soils and lichen diversity close to an oil and gas industrial complex on the Kolva river. Here, there were elevations of lead and nitrogen concentrations in lichen apices and in the apical : basal nitrogen ratio in *Flavocetraria cucullata,* with lower lichen diversity of epigeal and epiphytic lichens. Elevated concentrations of Ba and Ca were found in soil-ash, probably as a result of local emissions from construction activity and gas flaring, rather than from long-range transport. Virtually all other sites remained unmodified and reflected background concentrations. The ecological impacts of the measured pollution loads are discussed.

CHAPTER 1. INTRODUCTION

1. 1. Arctic ecosystems

The Arctic is a fragile environment and is generally regarded as a vast sparsely populated wilderness (Cheng *et al.*, 1993). Arctic and Subarctic ecosystems possess landscapes that are amongst the most spectacular and least impacted in the world (Rapport *et al.*, 1997). They extend from extreme polar deserts of the Russian Arctic, northern Canada and Greenland to the closed canopy shrub tundra of the low Arctic, and the alpine tundra of mountain regions. They also exhibit much greater biological diversity than is commonly perceived (Wookey, 2002). The Arctic represents about 5.5% of the total landmass on earth (Jonasson *et al.*, 2000). Most of it is located in the northern parts of Russia and Canada, with smaller areas in Alaska and Scandinavia. The land is snow-covered for much of the year, with most of the ground remaining frozen as permafrost, a characteristic of the severe climate (Fitzpatrick, 1997). Plants and animals in these environments have to survive extremely low temperatures during winter, and have lower tolerances to additional man-induced stresses, such as pollution and climate change (Stanhill, 1995; Crawford, 1997; Huntley and Cramer, 1997; Oechel *et al.*, 1997; Press *et al.*, 1998; Lavrinenko and Lavrinenko, 1999; Molau *et al.*, 1999). Consequently, despite their daunting size and natural beauty, some Arctic and Subarctic regions are beginning to display signs of degradation as a consequence of economic development and resource-exploitation: e.g. Norilsk in Siberia (Vlasova *et al.*, 1991), the Kola Peninsula, Russia (Kapitsa and Golubeva, 1997; Reimann *et al.*, 1999), Prudhoe Bay, Alaska (Pelley, 2001) and northern Alberta, Canada (Strosher, 2000).

For centuries the Arctic has sustained traditional lifestyles, such as reindeer-herding, hunting and fishing (Forbes, 1999). Historically, the Arctic had experienced few effects of industrial development to the south until the middle of last century. However, the ever-increasing demand by the industrialised

world for energy, minerals, timber and other resources, has resulted in the search for, and the exploitation of, resources in Arctic regions and adjacent higher latitudes (Klein, 2000). In addition, long-range transport brings pollution to the Arctic from industrial regions at mid-latitudes driven by global atmospheric circulation patterns (Rahn, 1984; Dayon *et al.,* 1985; Dovland, 1987; Barrie, 1986a, b; Barrie *et al.,* 1992; Jaffe *et al.,* 1993; Ryaboshapko *et al.,* 1998; Reierson, 2000). Frequent 'Arctic haze', first described almost 50 years ago by Mitchell (1956), is now known to be caused by air pollution (Rahn, 1982; Barrie *et al.,* 1989; Heintzenberg, 1989; Tuovinen, 1990). Accordingly, pollution in the Arctic, particularly air pollution is well-documented (Ottar, 1989; Pacyna, 1995; Steinnes, 1997; Xie *et al.,* 1999a, b).

1.2. Industrial activity in the Russian Arctic and pollution

Exploitation of non-renewable resources such as minerals and hydrocarbons in Arctic and Subarctic regions has increased during recent decades (IUCN, 1993). This is part of a global trend of increasing industrialisation of the Arctic (Klein, 2000), which is especially prevalent in parts of Alaska (e.g. Prudhoe Bay Jaffe *et al.,* 1995b; Pelley, 2001), and northern Russia (Ziegler, 1987). The latter region has the most extensive industrial developments north of the Arctic Circle (Pryde, 1991). These include the mining and metallurgical industries in the Norilsk area of Taimyr and on the Kola Peninsula; both these areas are notorious sources of acid and metal emissions (e.g Vlasova *et al.,* 1991; Touvinen *et al.,* 1993; Shahgedanova and Burt, 1994; Tømmervik *et al.,* 1995; Rigina *et al.,* 1999).

Terrestrial pollution in Russian Arctic environments has, until recently, received little attention outside of Russia. Environmental data on the Russian Arctic (e.g. on atmospheric emissions and air quality) are limited (Spiro *et al.,* 1992; Tuovinen *et al.,* 1993; Ryaboshapko *et al.,* 1994, 1997; Rovinsky *et al.,* 1995; Benokovitz *et al.,* 1996; Äyräs *et al.,* 1997a, b; Pacyna, 1998). The opening up of the former Soviet Union has revealed major environmental

problems at high latitudes, some of which are in the vicinity of its western borders (Tuovinen *et al.*, 1993; Åsgeir-Almås *et al.*, 1995). A prominent example is the impact of air pollution around the metallurgical complexes on the Kola Peninsula (Feshbach, 1995). Several authors have classified the area as severely damaged and certain areas have frequently been described as an 'industrial desert' (Jaffe *et al.*, 1995a; Caritat *et al.*, 1996a,b; Reimann *et al.*, 1996, 1997a, 1999, 2000; Gregurek *et al.*, 1998a,b).

Globally, coal combustion remains the dominant anthropogenic source of sulphur emission, with Russia being one of the principal emitters (Lefohn *et al.*, 1999). Numerous studies have documented the release and effects of ecologically hazardous products of fossil fuel combustion (e.g. Dignon, 1992; Singh *et al.*, 1995; Vassilev and Vassileva, 1997; Larssen, *et al.*, 1998, 2000 a, b; Kizilshtein and Kholodkov, 1999; Jalkanen, *et al.*, 2000). Electricity is one of Russia's most polluting industries (Turnbull, 1990), accounting for approximately 25% of all industrial atmospheric emissions in Russia (Hill, 1997, 2000). This is partly because coal with a high sulphur content has traditionally been used for power generation, resulting in significant pollution from emissions of oxides of sulphur and nitrogen.

Exploitation of natural resources such as coal, oil and gas has been of paramount importance for the industrialisation of the far north of the former Soviet Union (Ziegler, 1987; Revich, 1995). More recently, gas and oil recovery has shown signs of major expansion in the Russian north (Forbes, 1999; Lausala and Valkonen, 1999; Locatelli, 1999; Wilson, 2000). Examples of this are gas exploration and development on the Yamal Peninsula (Klein, 2000) and oil and gas exploration of the Timan-Pechora province, which includes both the Nenets Autonomous Region and the Komi Republic (Lausala and Valkonen, 1999; Cottrell, 2002). Industrialisation at high latitudes has resulted in the development of many large Arctic and Subarctic towns, 34 of which are now inhabited by a total of 3.5 million people (Revich, 1995), adding to the risk of environmental pollution (Alexeeva-Popova *et al.*, 1995).

Industrialisation produces significant acid emissions deep into relatively pristine Arctic territory. Russia is the single largest contributor to SO_2 and NO_x emissions in Europe (Nriagu *et al.*, 1991; Barrie *et al.*, 1992; Hill, 1997; Ryaboshapko *et al.*, 1998) and about 6.7% of European and Eurasian emissions enter Arctic air masses (Barrie *et al.*, 1989). Norilsk has the highest atmospheric emissions of any city in Russia, with an SO_2 output in 1988 equivalent to about two thirds of the total UK emissions (Shahgedanova and Burt, 1993, 1994). The total SO_2 emissions on the Kola Peninsula alone exceed the total sum of those in Finland, Sweden and Norway, contributing 20% of global anthropogenic emissions north of latitude 60° (Tuovinen *et al.*, 1993; Kashulina, 1997a). While SO_2 emissions in Russia declined between 1980 and 1988 by 12-30%, NO_x emissions from stationary sources increased by 20% (Shahgedanova and Burt, 1994). At the same time it should be emphasised that vast areas of the Russian Arctic appear to remain in a condition close to pristine (Rovinsky *et al.*, 1995).

Analysis of ice cores taken from the Greenland ice sheet, has shown that there were marked increases in N and S deposition in the northern hemisphere during the last century (e.g. Brimblecombe and Stedman, 1982; Neftel *et al.*, 1985; Rodhe and Rood, 1986; Fischer *et al.*, 1998). For example, Laj *et al.* (1992) demonstrated an increase in S deposition of more than 300% since the beginning of the industrial revolution and an increase in N deposition of *c.* 100% since the middle of last century. The major impacts of acid pollution have been seen close to emission sources in industrialised regions where there have been many documented examples of environmental damage due to acidification and eutrophication (Jónsdóttir *et al.*, 1995). The ecological effects of increased acid deposition loads over remoter regions of the Arctic remain uncertain (Woodin, 1997). There is concern that enhanced N deposition could force ecological change in otherwise oligotrophic N-limited ecosystems (Chapin and Bledsoe, 1992; Nadelhoffer *et al.*, 1992; Tybirk *et al.*, 2000; Gordon *et al.*, 2001). Despite its remoteness, several processes in the Arctic

play a central role in regulating global climate (Weller, 1995), such as the hydrological cycle and albedo (van der Linden, 2002). Hence, any changes in the Russian Arctic environment due to climate change or pollution, (e.g. permafrost degradation or reduction of winter snow cover resulting in an 'albedo-reduction feedback') not only has local impacts on the Arctic, but also has consequences for the global climate (Krankina *et al.*, 1997).

1.3. The Pechora region

The Pechora region and the Usa river basin, (see Figures 2.1 and 2.2, Chapter 2) includes the north and east of the Komi Republic and a major portion of the Nenets Autonomous Region. It has abundant natural resources, both renewable (e.g. timber) and non-renewable (e.g. minerals, coal, oil and gas) (Lausala and Valkonen, 1999). Traditional livelihoods such as reindeer herding and fishing are important rural economic sectors for the indigenous population of the region (Gimardi, 2002). In terms of the environment, the region is unique in continental Europe in having extensive lowland tundra with permafrost in the north and large continuous tracts of 'old growth' taiga forest to the south in the pre-Polar Ural mountains. The extent of human impacts in the Pechora region varies from negligible effects in uninhabited pristine areas to high impacts in relatively densely populated industrial regions.

Coal combustion for electric power generation has historically been the principal source of SO_2 and heavy metal pollution in the Pechora and Usa basins. Other sources include: coal mining, gas and oil extraction, pulp and paper production, construction and oil refineries (State of the Environment of the Komi Republic, 1992-1998). At the same time, several authors have reported alkaline emissions in excess of acid output in the vicinity of Vorkuta, due in part, to the operation of a cement factory (Kuliyev, 1977, 1979; Kuliyev and Lobanov, 1979; Getsen *et al.*, 1994; Rusanova, 1995a, b). Coal is produced in the Pechora region from five principal deposits. Four of the deposits (Vorkuta, Halmer-Yu, Yunyaga and Vorgashor) produce coking coal, and the

fifth, Inta, produces coal suitable for combustion in heating and power plants. In all, there are 18 coal-mines in the Komi Republic, the majority being concentrated around Vorkuta. When coal combustion occurs in the absence of any pollution control measures, the resultant unmodified emissions include acidic gases (SO_2 and NO_x) and alkaline, metal-rich particulates (Vassilev and Vassileva, 1997; Kizililshtein and Kholodkov, 1999). For example, Shahgedanova and Burt (1994) presented data suggesting that annual mean atmospheric concentrations of NO_2 in Vorkuta are the highest of any town in the Russian Arctic. Although coal reserves remain in the region, many coal-mining communities are facing mine closures and growing emigration (Lausala and Valkonen, 1999). Gas flaring also occurs at locations 15-50 km north of Usinsk, as part of the gas and oil operations, the principal site being Golovnye Soorhuzheniya (Vilcheck and Tishkov, 1997).

According to Lausala and Valkonen (1999) and Pelley (2001) the Timan-Pechora Province is the third most important oil-producing region in Russia and is reputed to contain some of the World's richest deposits. The first evidence of oil deposits in the region was found in the 16th century and oil was produced and refined by primitive methods as early as 1745. The region attracted major interest in the 1930's, with several discoveries of oil near the town of Ukhta and production and further exploration began following the second world-war. Altogether, 180 oil and gas fields have been discovered in the Timan-Pechora province, but only 20 have been brought into production (Lausala and Valkonen, 1999). The Komi Republic is land-locked, bordered by the Arkhangelsk region in the west and the Nenets Autonomous region in the north. Its remoteness has thus far been responsible for the limited exploitation of its oil and gas reserves (Cottrell, 2002). The province is reported in the business press to have the capacity for considerable growth (International Herald Tribune, 4 October 2000). Furthermore, the gas reserves of the Barents Sea to the north are also of global significance. Thus, while the coal industry in the Usa basin and the larger Pechora region is in gradual decline it seems inevitable that polluting activities such as gas flaring, and heat and power

generation associated with gas hydrate recovery, will proliferate during the coming decades.

Future exploitation of these oil and gas reserves will necessitate improvements and developments of the present transport infrastructure. Current plans include construction of a road between Naryan-Mar and Usinsk by 2010; this will replace the temporary winter road which can only be used for 3-4 months each year and will require an estimated 950,000 tons of construction material. There are also plans for the modernisation of the existing 147 km inter-field oil pipeline from Haryaga to Usinsk and reconstruction of the Haryaga-Usa pipeline link.

It is possible that the Komi region will face considerable challenges both in terms of socio-economic development (Karjalainen and Habeck, *submitted*) and from global warming, as general circulation models predict that temperature increases over the coming decades will be especially pronounced at high latitudes (Krankina *et al.*, 1997; Wookey and Robinson, 1997). Briffa *et al.* (1995) has shown that the northern Urals in particular have experienced a pronounced warming trend (i.e. elevated summer temperatures) during the last 100 years. Warming will have positive consequences, such as longer growing seasons and reduced energy consumption for heating, but it could also have negative outcomes including loss of reindeer pasture in the tundra and infrastructure damage due to permafrost collapse. The latter effect may cause rupture of oil pipelines and thereby increase the risk of significant environmental pollution (Vilchek and Tishkov, 1997). Feshbach (1995) and Pelley (2001) estimate there are on average, two major oil and gas pipeline spills every day. Losses of oil account for up to 7-20 % of the total annual Russian output, equating to 15-20 million tonnes of oil lost through spills annually in Russia. A well-publicised recent spill occurred near Usinsk in September 1994, which disgorged upto 126,000 tonnes of oil and contaminated 68 km^2 of the surrounding area, with significant amounts entering the Kolva and Usa rivers (Vilchek and Tishkov, 1997).

As elsewhere in Russia, the Pechora region faces economic difficulties in its transition from a centralised system to a western style market economy (Locatelli, 1999). The conditions in the region are special due to its very rich renewable and non-renewable resources and its northern location (Lausala and Valkonen, 1999). Oil and gas production is of particular strategic importance to the region and to the European Union, and is expected to expand significantly. By contrast, mining is now in decline due to the poor quality of some coal deposits and high transport costs (Gimardi, 2002). The reserves of oil, gas, minerals, and forest resources of the region constitute a firm basis for economic growth, and future east-west co-operation; joint commercial activity is likely to be based on the exploitation of these reserves. For example the forestry sector has considerable potential for growth, but management practices need to safeguard biodiversity. However, both the booming oil and gas sector and the prospects of closing coal-mines bring about significant risks of environmental pollution.

1.4. Pollution monitoring in remote regions

The Pechora basin has already been identified as a significant source of acid emissions (Ottar, 1989; Nenonen, 1991; Vinogradova, 2000) mainly as a result of coal fired power stations in the towns of Vorkuta, Pechora and Inta, petrochemical operations in Ukhta and a gas-fired power station in Usinsk. However, prior to the present work there has been little supporting evidence.

Problems exist when monitoring pollution deposition in remote regions. There are usually few meteorological stations that can be used to monitor air and precipitation chemistry. Air and rain show very high temporal and spatial variation in chemical composition (e.g. Reimann *et al.*, 1999) and therefore require continuous sampling throughout the year. Furthermore, elemental concentrations in these media are usually low and so sample contamination is a significant problem. Alternative approaches include: (i) analysis of stored

water in snow-pack or glacial firn and ice, (ii) the analysis of ecological materials that accumulate contaminants (e.g. soils and plant tissues) and (iii) the use of bio-indicators, the physiology and/or the distribution of which become modified by exposure to pollution.

1.5. Pollution mapping based on analyses of ecological materials

1.5.1. Snow-pack chemistry

Analysis of the chemical composition of snow-pack has frequently been used to provide information on precipitation chemistry, including pollution loading (Jaffe *et al.,* 1993; Shaw *et al.,* 1993; Udisti *et al.,* 1994; Colin *et al.,* 1997; Tranter and Jones, 2001). Collecting snow is relatively easy and multi-element analysis of representative samples of the depth profile of the snow-pack is an expedient method of estimating wet deposition during the winter season. Snow-pack samples are well suited to fingerprinting local emission sources, even at low sampling density and to mapping spatial variation in pollution deposition (Reimann *et al.,* 1996). A useful property of snow sampling is that it measures the integrated wet and dry fallout of pollutants from the atmosphere during the period of snowpack accumulation and maintains natural preservation of this material (Shaw *et al.,* 1993). A potential pitfall in the use of snow chemistry to measure ion deposition is ion loss during any partial snowmelt that might occur prior to sample collection. Johannessen and Henriksen (1978) showed that when freshly fallen snow was allowed to melt under laboratory conditions, *c.* 60-70% of the total store of NO_3^-, and 50-60% of NH_4^+ was eluted in the first 30% of meltwater collected. Thus, periods of partial thaw can result in redistribution of ions within snow-pack and, if there is loss of water to surface run off, a decrease in ion concentrations in the remaining snow. Therefore, sampling during the spring, just before thawing occurs, ensures that most of the total solute load is not lost with the first melt (Tranter *et al.,* 1986, 1988). Snow cover in early spring is therefore an accumulation of the previous winter's precipitation, containing not only solid

snow with its solute components and co-deposited particles, but also blown dust of local natural and anthropogenic origin (Äyräs *et al.*, 1995). In addition to dissolved ions in snow there may be a significant quantity of elements associated with particulate matter. Quantification of these two fractions can provide a powerful tool for fingerprinting sources (Caritat, *et al.*, 1998). Moreover, total elemental loadings can be seriously underestimated if analysis of particulates (such as fly ash) is omitted (Reimann *et al.*, 1996; Gregurek *et al.*, 1998a).

Numerous studies of the spatial variation in rainwater and snow-pack chemistry have been used, for example, in the Scottish Highlands (Tranter *et al.*, 1988); in Alaska (Dayan *et al.*, 1985; Jaffe and Zukowski, 1993) and on the Kola Peninsula (Jaffe *et al.*, 1995a; Niskavaara *et al.*, 1996; Reimann *et al.*, 1996, 1997b; Caritat, *et al.*,1998; Gregurek *et al.*, 1998a). Jaffe and Zukowski (1993) found [NO_3^-] in snow-pack collected at 7 sites distributed along a transect parallel with the Dalton Highway, northern Alaska to be in the range 160 - 688 ng g^{-1}. These values were 1.5 times greater than those observed in Greenland, which the authors attribute to 'arctic front' activity over Alaska. Tranter *et al.* (1988) used snow-pack chemistry to monitor the impact of black snowfall on stream-water chemistry in the Scottish Highlands. They found that black acidic snowfalls occur under specific meteorological conditions and can increase [SO_4^{2-}] and [NO_3^-] in snowpack by an order of magnitude.

1.5.2. Analysis of accumulators

1.5.2.1. Lichen chemistry

Mat-forming terricolous lichens are important components of plant communities at high latitudes (Larsen, 1980; Ahti and Oksanen, 1990), where they contribute to nutrient cycling and hydrology as well as secondary production (e.g. grazing) (Chapin and Bledsoe, 1992; Longton, 1997). They are prominent in Arctic and alpine zones as well as in sub-arctic heaths and boreal forests. Habitats with extensive closed lichen mats, are mainly found on well

drained, moderately sloping grounds characterised by deep winter snow cover. In the arctic and boreal zones these habitats are called lichen heaths and in the boreal forests, lichen woodland (Longton, 1988).

Lichens are primarily dependant on atmospheric sources of nutrients and therefore readily accumulate atmospheric contaminants, such as metals and radioelements (Nash and Gries, 1995a,b; Seaward, 2002). In this sense they are therefore amongst the most pollution sensitive receptors in terrestrial ecosystems (Wielgolaski, 1975; Richardson, 1988). The high tolerance of lichens to most metal contaminants together with their slow growth are among the main factors that make them effective accumulators (Pakarinen *et al.,* 1978; Nieboer and Richardson, 1981; Puckett, 1988; Nash, 1989). Accordingly, lichens have been used widely to monitor environmental quality as a result of industrial activities (e.g. Nimis *et al.,* 1993); examples include fertiliser manufacturing plants (Kauppi, 1976), steel works (Pilegaard, 1978), the petrochemical industry (Addison and Puckett, 1980; Pakarinen *et al.,* 1983), zinc and nickel foundries (Nash, 1975; Nieboer *et al.,* 1972) and coal-fired power stations (Olmez *et al.,* 1985; Garty, 1988; Gonzalez and Pignata, 1997). Spatial variation in the chemical composition of lichens has been frequently used to map atmospheric deposits (Fahselt *et al.,* 1995; Nash and Gries, 1995a, b; Reimann *et al.,* 1997c, 2001; Takala *et al.,* 1998; Grodzinska *et al.,* 1999; Riget *et al.,* 2000); for example, Grodzinska *et al.* (1999) used *Cladonia stellaris* to monitor airborne pollution at 26 sites along transects on the Kola Peninsula and showed that element concentrations were higher closer to emission sources. Values of Pb in *C. stellaris* varied from 45.6 $\mu g\ g^{-1}$ close to smelters in Monchegorsk to 1.82 $\mu g\ g^{-1}$ at remote locations. Changes in the physiological status of lichens have also been used to monitor atmospheric pollution gradients on the Kola Peninsula (Tarhanen *et al.,* 1996).

The principal lichen species found in lichen-dominated ground cover in the Arctic are members of the genera *Cladonia* (sub-genus *Cladina*), *Cetraria, Flavocetraria, Alectoria* and *Stereocaulon.* A characteristic feature of mat-

forming lichens is that they grow acropetally (i.e. at their apices) and vertically upwards, while in mature mats the thallus bases die off. Thus the upper living parts of the mature mats are often supported physically by a deep layer of dead, structurally intact, thallus or necromass (Crittenden, 2000). Crittenden (1989) suggested that such carpets are largely ombrotrophic ('rain-fed'), and showed that *Cladonia stellaris* captured > 80% of wet-deposited inorganic nitrogen (NH_4^+ and NO_3^-). Key macronutrients for mat-forming lichens, such as N and P are probably derived largely from atmospheric deposits (Crittenden and Kershaw, 1978; Crittenden, 1983, 1996, 1998; Kytöviita, 1993). There is also evidence to suggest that N and P are conserved within thalli by, amongst other processes, internal recycling (Crittenden, 1989; Ellis *et al.*, 2003). Elevated concentrations of ions in polluted precipitation therefore, might be expected to have an impact on lichen growth (Crittenden *et al.*, 1994) and chemical composition (Kytöviita and Crittenden, 1994; Hyvärinen and Crittenden, 1998a).

Increased atmospheric N deposition has been recognised as a potential threat to plant communities (Pitcairn *et al.*, 1995). Nitrogen pollution is generally positively correlated with acid loads because nitrate is a component of acid deposition. The N content of lichen thalli is related to N deposition and has been used in several pollution monitoring exercises (Bruteig, 1993b; Halonen *et al.*, 1993; Søchting, 1995). Hyvärinen (1997) and Hyvärinen and Crittenden (1998b) argued that mat-forming lichens are particularly good bioindicators of air pollutant loads because they typically occur in open situations intercepting rainfall directly and largely unmodified by vascular plant canopies, which can confound relationships between the chemistry of epiphytic lichens and the atmosphere (Farmer *et al.*, 1991a, b). They are probably relatively independent of the chemical influence of the substratum owing to accumulation of basal necromass which tends to isolate the living parts of the thalli from underlying soil (Crittenden, 1991; Ellis *et al.*, 2003).

Hyvärinen and Crittenden (1996) also examined relationships between rainfall acidity and lichen chemistry. Kytöviita (1993) and Kytöviita and Crittenden (1994) had earlier conducted controlled experiments on the effects of simulated acid rainfall on the mat-forming lichens *Cladonia stellaris* and *Stereocaulon paschale.* Kytöviita (1993) observed that increased rainfall acidity promoted the migration of divalent cations (Ca^{2+} and Mg^{2+}) from the thallus apices downwards within the thalli, but had little affect on K^+ concentrations. This increased the ratio $K^+ : Mg^{2+}$ and $K^+ : Ca^{2+}$ in the thallus apices which she attributed to the different locations of these ions; K^+ is largely located with protoplasts which forms a major proportion of the thallus. Calcium and Mg^{2+} are located on cell wall exchange sites. Hyvärinen and Crittenden (1996) demonstrated that the $K^+ : Mg^{2+}$ ratio in the apices of *Cladonia portentosa* varied among heathland sites in the British Isles and that this variation was highly correlated with H^+ concentration in rainfall. The authors suggested that this ratio might provide a sensitive chemical marker for rainfall acidity in pollution surveys.

1.5.2.2. Soil chemistry

In Arctic areas, the topsoil is frozen for at least six months of the year (Niskavaara *et al.,* 1997). In spring, the still partly frozen soil is subjected to a sudden, intensive pulse of acidic snow-melt percolating through the uppermost soil layers; this is a phenomena observed even in pristine areas (Reimann *et al.,* 1996). For example Reimann *et al.* (1996) found that the most acidic snow-pack samples on the Kola Peninsula were found at background sites in northern Finland (pH 4.3-4.7). In contaminated areas, such as those around the roasting and smelting industries on the Kola Peninsula, melt-waters may contain additional amounts of acidifying components and heavy metals from the accumulation of winter deposition in snowpack (Niskavaara *et al.,* 1997). Analysis of the underlying soil, can be used to evaluate long term accumulation of conserved pollutants (e.g. Boyd *et al.,* 1997; Reimann *et al.,* 1997a, c, 1998, 2000). Soils act as a major sink for atmospheric deposits. In particular, the

topmost few cm of the soil profile become a sensitive accumulator in the terrestrial environment (Niskavaara *et al.,* 1997). In addition to the potential receipt of pollutants they are subject to the eroding effects of rain, wind and frost (Howells, 1995). Depending on the vegetation type, climatic conditions, soil formation conditions and extent of anthropogenic effects, topsoils contain varying amounts of organic and inorganic materials. Soil organic matter is one of the major factors controlling the physical and chemical properties of soils including metal binding capacity (Niskavaara *et al.,* 1997).

In highly polluted areas near industrial centres, the physical and chemical properties of topsoils can become radically modified. Soil contamination due to alkaline emissions from coal combustion has been widely reported (e.g. Singh *et al.,* 1995; Larssen *et al.,* 1998, 2000a, b; Kizililshtein and Kholodkov, 1999), including at several locations in Russia (e.g. Rusanova, 1995a, b; Hill, 1997; Jalkanen *et al.*, 2000; Haapala *et al.,* 2001). Deposition of alkaline fly ash particulates elevates both pH and total metal content of soils (Vassilev and Vassileva, 1997; Reimann *et al.,* 2000; Haapala *et al.*, 2001). Increased soil pH resulting from inputs of alkaline fly ash, may actually reduce the metal ion concentration in solution despite increasing the total metal loading to the soil (Robb and Young, 1999). Such effects are usually most pronounced close to emission sources where particulate fallout is maximal. Conversely, acidic deposition resulting in a progressive drop in soil pH, will raise the solubility and rate of leaching of even the most strongly bound metal elements (Reimann *et al.,* 1996).

Two approaches have been used to sample heavy metal contamination in soils. Either the uppermost, organic horizon is sampled, or soil is removed to a standard depth (Reimann *et al.,* 1997a). Both approaches have advantages and disadvantages. A depth-defined sample can be taken anywhere, independent of the soil type or the existence of an organic layer. In this case, element concentrations recorded will be characteristic for, e.g. 'the uppermost 5 cm of soil' throughout the sampling area. However, in podzolic soils in particular

problems can arise with depth-defined sampling due to inter-site differences in the depth of the organic horizon and hence the quantity of mineral material in samples. Heavy metals tend to accumulate in the organic fraction and thus, recorded metal concentrations might be considerably higher in samples consisting only of organic material compared to those samples taken from soils with a very thin organic layer for the same inputs (Reimann *et al.*, 1997a). Horizon orientated sampling, on the other hand, will result in substantial differences in the thickness of the final samples taken, with anthropogenic input accumulating in the top few cm of the soil profile. This can confound comparisons between sites that have O-horizons of very different thicknesses (Reimann *et al.*, 1998). Niskavaara *et al.* (1996) and Reimann *et al.* (1997a) used depth-defined sampling regimes (0-5 cm topsoil layer) for regional mapping of heavy metals on the Kola Peninsula. Analysis of soil samples allows for assessment of aerial deposition by comparison of concentrations per unit area, provided sampling is carried out to sufficient depth to audit all the analyte of interest. Also, assessments of aerial inputs of some elements can be used to compare concentrations in the mineral phase between topsoil and the underlying subsoil.

Numerous investigations have used variation in soil chemistry to map pollution deposition, particularly in the case of heavy metals (e.g. Balaganskaya, 1997; Kashulina, 1997b; Reimann *et al.*, 1997a, 1998; Haapala *et al.*, 2001). For example, Reimann *et al.* (1997a) collected top-soils at 174 sites from eight catchments on the Kola Peninsula, constituting an area of 188 000 km^2 and showed that soils close to smelters in Monchegorsk and Nikel were enriched with heavy metal concentrations up to 600 times greater than those at Finnish background sites (e.g. 2520 compared to 2.5 mg kg^{-1} Ni; 16400 compared to 745 mg kg^{-1} Fe).

1.5.3. Impacts on communities - lichen biodiversity

Due to their susceptibility to SO_2 and some other air pollutants, epiphytic lichens have been used for some decades to monitor air pollution (Hawksworth and Rose, 1970; Hawksworth, 1971, 1973; Nieboer *et al.*, 1977; Pirintsos *et al.*, 1993; van Dobben and ter Braak, 1999). In this respect the use of lichens as indicators of air pollution has been extensively reviewed (Ferry *et al.*, 1973, Hawksworth, 1974, 1975; Anderson and Treshow, 1984; Garty, 1993; Henderson, 1993; Gries, 1996; Conti and Cecchettib, 2001). In boreal forests, localised decline in abundance of the epiphytic lichens, *Alectoria, Usnea* and *Bryoria* has been attributed to increasing air pollution and acid rain (Helle *et al.*, 1990; Kauppi and Halonen, 1992; Aamlid and Venn, 1993; Thor, 1998). However, factors other than air pollution can modify epiphytic lichen abundance, such as changes in climate and stand age (Kuusinen *et al.*, 1990; Hyvärinen *et al.*, 1992).

Biodiversity is defined as 'Totality of hereditary variation in life forms, across all levels of biological organisation from genes and chromosomes within individual species to the array of species themselves and finally at the highest level to living communities of ecosystems, such as forests and lakes' (Wilson, 1988). Diversity is usually measured as species richness or the number of species in an area and varies with spatial scale. Alpha diversity is defined as, 'the number of species within a small area that is relatively uniform' (Wilson, 1988).

Methodologies for assessing diversity and abundance have been reviewed by Will-Wolf *et al,* (2002). Several studies of lichen diversity and abundance have been undertaken in boreal forests (Gorshkov, 1989a, b; Gorshkov and Lyanguzova, 1989; Oksanen *et al.*, 1990; Armleder *et al.*, 1992; Aamlid and Venn, 1993; Bruteig, 1993a; Kuusinen, 1994); for example, Bruteig (1993a) assessed epiphytic lichen species on *Pinus sylvestris* at 193 sites in Norway and

discovered that at sites in the southern parts of the country where air pollution was greater, *Bryoria* and *Usnea* species were largely absent.

1.6. The aims of the study

Until now there have been few detailed studies or audits of terrestrial pollution loads in the Pechora region. Those that have been conducted were in the immediate vicinity of towns, such as the Bolshezemel'skaya tundra around the city of Vorkuta (Getsen *et al.*, 1994, 1997; Rusanova, 1995a, b). The specific objectives of the current study were to assess the extent of acid (or alkali) and metal deposition in the Usa basin and the larger Pechora region by mapping spatial variation in the chemical composition of snow, lichens and top-soil. In addition, lichen biodiversity was investigated in order to yield further information on air pollution impacts at specific sites.

The principal industrial centres in the Usa basin are Vorkuta, Inta and Usinsk. The initial investigations involved taking measurments along transects through these towns. Subsequent studies examined industrial sites elsewhere in the Pechora basin, considered to be potential pollution 'hotspots'. Conditions at these industrial sites were compared with nearby undeveloped 'reference' sites of broadly similar community structure. The data produced will provide a baseline against which the extent of pollution in the future can be determined.

The specific objectives are detailed below:

1. To assess the extent of acid, alkaline and N deposition around Vorkuta, Inta and Usinsk as indicated by the spatial variation in the chemical composition of winter snow-pack and terricolous mat-forming lichens.

2. To provide information on the distribution and magnitude of trace metal composition in snow and soil resulting from fossil fuel combustion and petrochemical industrial processes within the Usa basin and extending to the larger Pechora region.

3. To seek evidence of environmental impacts of an expanding petrochemical industry in the Pechora region. This was achieved by quantifying the chemical status of terricolous mat-forming lichens and top-soil samples and by measuring the diversity of epigeal and epiphytic lichen communities in close proximity to perceived pollution 'hot spots' and in unpolluted 'reference' sites of broadly comparable community structure.

4. To further evaluate the use of terricolous lichens as indicators of nitrogen and acid deposition.

5. To assess, as a wider objective of the present work, the likely extent to which the Arctic ecosystem response to climate forcing in this region might be modified by pollution.

CHAPTER 2. MATERIALS AND METHODS

2.1. Study areas and sampling regimes

This study was part of two European Commission programmes: TUNDRA (TUNdra Degradation in the Russian Arctic) and SPICE (Sustainable development of the Pechora region In a Changing Environment and society). Both programmes were located in north-east European Russia. (see www.urova.fi/home/arktinen/tundra and www.urova.fi/home/arktinen/spice).

2.1.1. TUNDRA programme (TUNdra Degradation in the Russian Arctic)

The study sites are located in the Usa river basin lying between latitudes 64° and 68° N in the Komi Republic, north-east European Russia. This region has an area of 93,000 km^2. The Usa river is a major tributary of the Pechora river, which flows into the Barents Sea and is one of the largest rivers in Europe. The region is unique in continental Europe for having extensive lowland tundra with permafrost, together with an upland area (i.e. the Ural mountains) up to 1750 m.a.s.l. (Solovieva *et al.*, 2002). The Usa basin straddles the tree line with forest tundra and taiga in the south, dominated by spruce (*Picea obovata*) and birch (*Betula pubescens*) together with pine (*Pinus sylvestris*) and a small incidence of larch (*Larix sibirica*). The taiga zone is further sub-divided into northern taiga and extreme-northern taiga. The tundra zone encompasses forest-tundra in the south (Arctic tree line) and shrub tundra in the north. The shrub tundra is dominated by dwarf birch (*Betula nana*) found in well drained and slightly elevated sites. In addition the shrub tundra is characterised by *Vaccinium* spp. and *Empetrum* spp. as well as willow found in depressions.

Transects were established through the three principal towns of Vorkuta (67°30'N, 64°05'E; Transect 1), Inta (66°03'N, 60°10'E; Transects 2 and 3), and Usinsk (66°01'N, 57°30'E; Transect 4). The transects were approximately

130 km W-E, 240 km S-N (Transects 2 and 3 in combination) and 140 km SW-NE in length, respectively. It should be noted that, for logistical purposes, transects through Inta were assigned two numbers: Transect 2 to the north and Transect 3 to the south.

Coal mining is the main industry in both Vorkuta and Inta where there are 7 and 4 working mines, respectively. By contrast, Usinsk has developed in response to the recent emergence of the gas and oil industries. The Vorkuta region is the largest industrial centre in the North-European tundra. It consists of the main city and more than 10 sub-centres located near coal-mines and other industrial units (Virtanen *et al.*, 2002). Atmospheric pollution in the Vorkuta area is mainly caused by emissions from coal combustion at the nearby power plant, cement factory, dust from coal-mines and burning of waste rock near the coal-mines (Virtanen *et al.*, 2002). As Vorkuta is the largest industrial centre in the area, the total aerial emissions are about 8-9 times higher than in Inta and Usinsk. Quantities of pollutants emitted by the towns have been summarised by Solovieva *et al.* (2002). Coal mining is the main source of atmospheric contamination in the Usa basin (32.7% of total emissions), followed by gas (24.4%) and oil extraction (13.8%), power generation (10.8%) forestry, timber, pulp and paper production (3.5%), construction (3.0%) and oil refineries (2.7%). Briefly, annual emissions of SO_2 and NO_x (10^6 kg) in 1998 were, respectively, 37 and 7 (Vorkuta), 16 and 1.5 (Inta), and 6 and 2 (Usinsk).

The topography in the region is relatively smooth. Elevation varies from about 50 m above sea level (a.s.l.) in the deepest river valleys to about 250 m a.s.l. on the tops of smooth hills. The Ural mountains located east of the Usa basin have valley floors at 200 m a.s.l., whilst most of the mountains are 600-900 m a.s.l., with the highest points reaching over 1750 m a.s.l. (Virtanen *et al.*, 2002). The lowest point is 2 m a.s.l., while the highest point is 1,895 m (Narodnaya mountain). The Timan Ridge, with elevations of 200-500 m a.s.l., runs from the north-west to the south-east across the region. To the north of the Timan

Ridge, there is the Pechora Plain, and to the south the Mezen-Vychegda Plain. The climate in the region is mainly continental, although the Barents Sea influences the climate in the north. For the towns of Vorkuta, Inta and Usinsk mean temperatures are, respectively, -21, -20 and -18 °C in January, and 12.4, 13.8 and 14.1 °C in July. The long-term mean annual air temperatures for the towns are -6.0 (Vorkuta), -4.4 (Inta) and -3.2 °C (Usinsk). The mean number of days with snow cover for the 3 towns are: 237 (Vorkuta), 217 (Inta) and 213 (Usisnk). Average annual precipitation in the region is 625 mm, ranging from about 700 mm in the south to 500-550 mm in the north and 1,500 mm in the northern Urals. Mean annual precipitation levels for Vorkuta, Inta and Usinsk are 518, 473 and 495 mm, respectively (data supplied by the Institute of Biology, Komi Science Centre). The entire transect through Vorkuta is located in the permanent permafrost zone, whilst transects through Inta straddle the continuous and discontinuous permafrost zone. The transect through Usinsk is located in discontinuous permafrost. In the Vorkuta region the prevailing winds blow from the southwest and south from September to April. Prevailing winter winds blow from the north around Inta and are generally variable around Usinsk. Southwesterly winds generally prevail over the entire region (Taskaev, 1997).

Sampling sites (4-6) were selected along each transect. The sites were distributed at logarithmically increasing distances from the town centres (Figure 2.1, Table 2.1), although this ideal distribution was modified to meet the needs of other collaborating research groups. At each site, three sub-sites were selected, 500-1000 m apart, at which 6 replicate samples of ecological materials (see below) were collected at distances 10-20 m apart in open areas subject to minimal tree canopy effects (Derome, 1992; Reimann *et al.*, 1999). These were usually inter-tree positions in open forest, or in open tundra. Most sites were in wilderness areas remote from roads.

Due to the high costs and logistics involved with helicopter charter it was not always possible to visit all the sites along the transects. During spring 1998,

only eight sampling sites were visited along transects 2/3. Four sampling sites were visited along each transect, so that site 2.2 (Lake Tumbulovaty) to the north and site 3.2 (Mezhgornyye lakes) to the south were the transect extremes. During summer 1998 site 2.4 (Lake Lyz'vad) was not reached, therefore lichen and soil sampling was not possible here. Mean annual air temperature, precipitation data, vegetation type and industrial activity for Vorkuta, Inta and Usinsk are presented in Table 2.2.

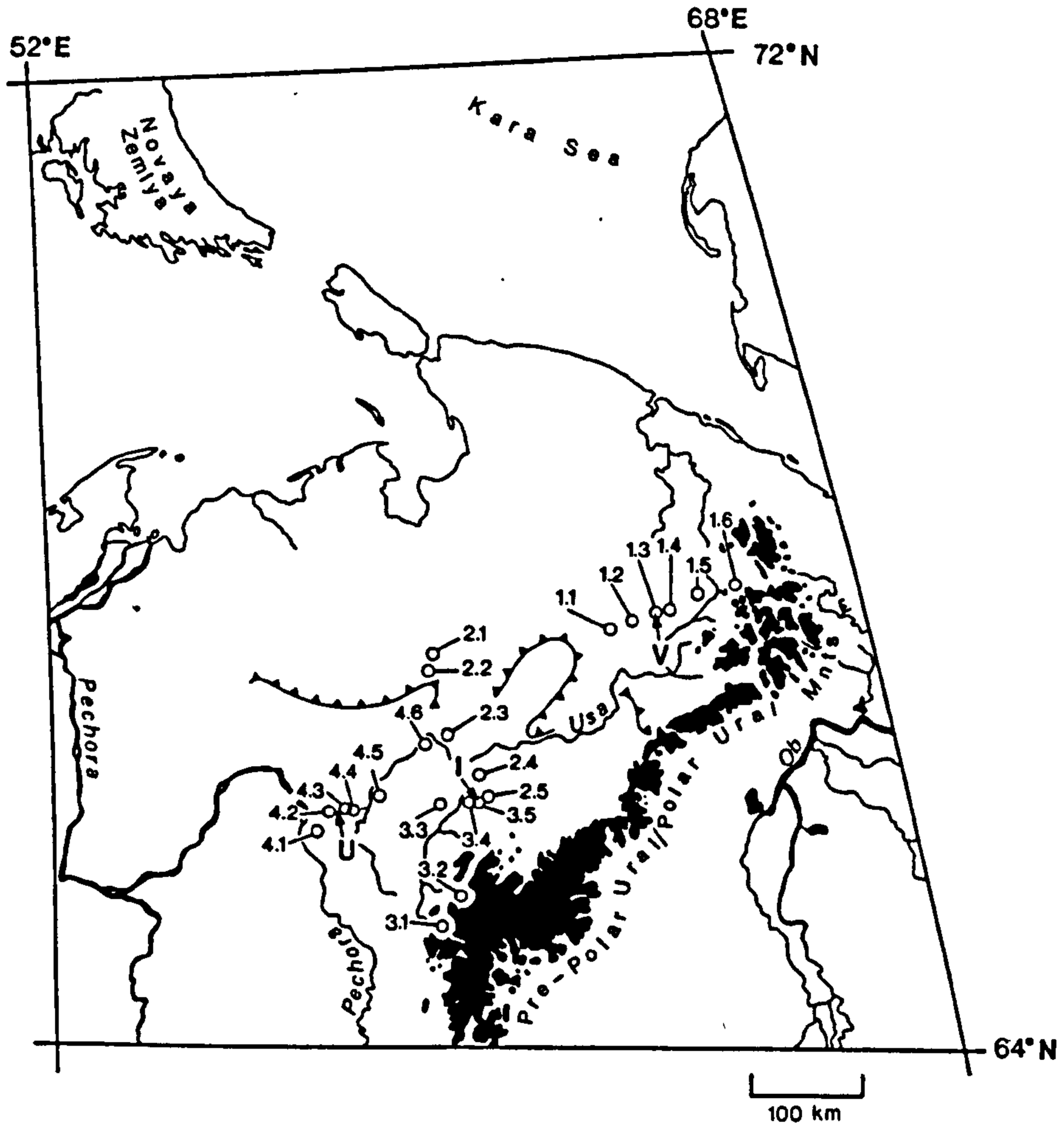


Figure 2.1. Map showing sampling sites on transects through the towns of Vorkuta (V), Inta (I), and Usinsk (U) in the Usa basin, Northeast European Russia. Linked triangles indicate the approximate position of the treeline across the Usa basin. Land above 500 m is also indicated. (Map reproduced from P. D. Crittenden with kind permission).

Table 2.1. Summary of main sampling sites along 4 transects within the Usa basin study area.

Site No.	Name of site	Co-ordinates	Elevation (m.a.s.l.)	Distance from nearest town
Transect 1				
1.1	Lake Padvaty	67°27'N 63°05'E	160	45 km W of Vorkuta
1.2	Malen'kiy arvozh	67°30'N 63°30'E	150	30 km SW of Vorkuta
1.3	Vorkuta	67°34'N 64°09'E	180	2 km NE of Vorkuta
1.4	Lake Ngayats'yakha	67°35'N 64°15'E	160	12 km NE of Vorkuta
1.5	Lake Mutnoye	67°44'N 64°52'E	260	40 km NE of Vorkuta
1.6	Lake Protochnoye	67°47'N 65°37'E	180	70 km NE of Vorkuta
Transect 2				
2.1	Khosedayu River	67°15'N 59°37'E	70	130 km N of Inta
2.2	Lake Tumbulovaty	67°07'N 59°34'E	110	110 km N of Inta
2.3	Two Lakes near Adak	66°35'N 59°45'E	75	62 km N of Inta
2.4	Lake Lyz'vad	66°16'N 60°13'E	52	20 km N of Inta
2.5	Lake Swan (Lebedinoye)	66°06'N 60°15'E	21	7 km N of Inta
Transect 3				
3.1	Vangyr river	64°59'N 59°12'E	270	110 km SW of Inta
3.2	Mezhgornyye lakes	65°15'N 59°40'E	510	90 km SSW of Inta
3.3	Lake Van'kavad	65°59'N 59°27'E	60	32 km SSW of Inta
3.4	'Fox Lake'	65°59'N 60°01'E	60	7 km SSW of Inta
3.5	Inta	66°03'N 60°10'E	60	2 km SSW of Inta
Transect 4				
4.1	Lake Bosmanvad	65°48'N 57°03'E	40	30 km SW of Usinsk
4.2	Lake Chakty	65°58'N 57°16'E	50	15 km W of Usinsk
4.3	Usinsk	65°59'N 57°35'E	60	2 km E of Usinsk
4.4	Lake Kankur'ya	65°57'N 57°42'E	40	10 km NE of Usinsk
4.5	Isaak-Ty/Shar'yu	66°07'N 58°18'E	50	35 km NE of Usinsk
4.6	Adz'vavom	66°33'N 59°16'E	50	100 km NE of Usinsk

Table 2.2. Principal industrial towns within study area.

Town	Co-ordinates	Mean Annual Precipitation (mm) (Temperature, °C)*	Principal industrial activity	Principle vegetation types on transects
Vorkuta	67°30'N, 64°05'E	518 (-6.0)	coal mining (7 mines), cement factory	open arctic tundra, alpine tundra
Inta	66°03'N, 60°10'E	473 (-4.4)	coal mining (4 mines)	Pine & birch forest, open tundra, alpine & arctic tree-lines
Usinsk	66°01'N, 57°30'E	495 (-3.2)	oil and gas extraction	Pine & birch forest

* Data supplied by the Institute of Biology, Komi Science Centre

2.1.2. SPICE programme (Sustainable development of the Pechora region In a Changing Environment and society)

The Pechora region (of which the Usa basin is a component), includes the north and east of the Komi Republic and a major portion of the Nenets Autonomous region. It is bounded by the Ural mountains to the east and by the Timan range to the west. The area has extensive natural resources, both renewable (e.g. forests) and non-renewable (e.g. minerals, coal, oil and gas). In terms of the environment, the region is unique in continental Europe with extensive lowland tundra and permafrost in the North and the largest continuous area of 'old growth' taiga to the south in the Urals. There are a variety of human impacts in the region with relatively uninhabited 'pristine' areas and a few densely populated regions, supported by indigenous economies and a few recent state-induced industries with attendant pollution.

Oil and gas production has strategic importance to the region and is expected to expand significantly (Lausala and Valkonen, 1999; Pelley, 2001). However,

some segments of the coal industry are in decline due to the poor quality of the coal and high transportation costs (Gimadi, 2002).

Sampling sites were chosen to quantify the chemical status of terricolous mat-forming lichens and top-soil samples and by measuring lichen biodiversity of epigeal and epiphytic lichens in close proximity to perceived pollution 'hot spots' and in unpolluted reference sites of broadly comparable community structure. Across the Pechora basin, 'industrial' sites (e.g. $F1_i$) and unpolluted 'reference' sites (e.g. $F2_r$), comprised of the following: Ukhta area ($F1_i$), Belaya Kedva river ($F2_r$), Ortina river ($F3_i$), Neruta river ($F4_r$), Svetly Vuktyl ($F5_i$), Maly Patok ($F6_r$), Upper Kolva ($F7_i$) and Moreyu river ($F8_r$) (see Figure 2.2; Table 2.3). Within the tundra zone the Ortina river site ($F3_i$) and Neruta river site ($F4_r$) were chosen to compare the effects of the 'industrial' petrochemical complex at $F3_i$ with the 'reference' site at F4r near to the Pechora delta. Additional tundra sites were chosen at Upper Kolva, $F7_i$, with its large oil industrial complex and compared with Moreyu river, $F8_r$, which is partly protected for reindeer herding, and is perceived as being 'pristine'. Within the taiga zone the site near Ukhta on the Izhma river at $F1_i$, was chosen due its petrochemical industry (oil processing at Ukhta and gas processing at nearby Sosnogorsk) and forestry, in order to compare with Belaya Kedva at site, $F2_r$, which is pristine. The site at $F5_i$ near Svetly Vuktyl was selected as a possible polluted area due the growing gas industry based there. The site at Maly Patok, $F6_r$ was chosen as a suitable comparison as it is situated in the protected Yugyd Va national park.

Fieldwork was carried out during the spring of 2000 ($F3_i$ and $F4_r$) and 2001 ($F1_i$, $F2_r$, $F5_i$, $F6_r$, $F7_i$ and $F8_r$) and began in early June at the southern-most sites until mid-July for the northern-most tundra site at $F8_r$. Each site was visited for approximately 6 days to allow members of other collaborative groups to complete their work.

Table 2.3. Summary of the main sampling sites within the Pechora region.

Site No.	Name of site	Co-ordinates	Type of industry and status of site
$F1_i$	Izhma river (near Suz'u river mouth), Ukhta area	63°44'10" N, 53°42'57" E,	Petrochemicals (oil and gas), forestry, fragmented lowland taiga
$F2_r$	Belaya Kedva river	64°19'27" N, 53°03'39' E,	Pristine lowland taiga
$F3_i$	Ortina river, Narjan-Mar area	67°55'59" N, 54°02'33" E,	Petrochemicals (oil and gas), tundra delta area
$F4_r$	Neruta river, Malozemelsk tundra	68°00'10" N, 52°24'16" E,	Reindeer herding, pristine tundra, partly protected, coastal
$F5_i$	Svetly Vuktyl river, Vuktyl area	63°47'42" N, 57°32'36" E,	Gas industry, fragmented lowland taiga
$F6_r$	Maly Patok river	64°18'54" N, 59°04'40" E,	Pristine taiga in Ural foothills, protected Yugyd Va national park
$F7_i$	Kolva river (near the Kharayaha river mouth)	67°08'22" N, 56°41'41" E,	Large oil industrial complex, tundra
$F8_r$	The Moreyu river (near the Syamayu river mouth)	67°52'51" N, 59°43'21" E,	Reindeer herding, pristine tundra, partly protected, coastal

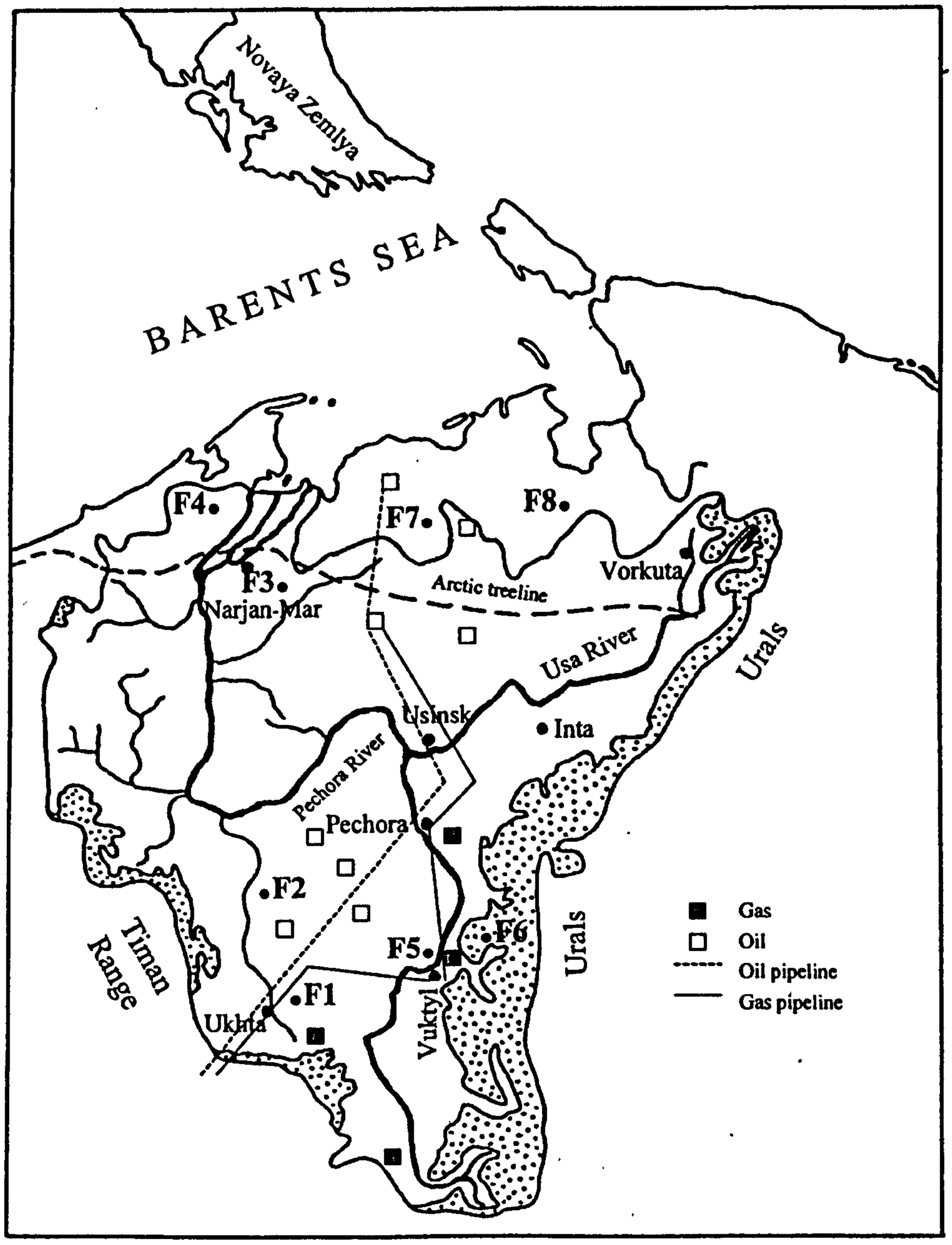


Figure 2.2. The Pechora region in northeastern European Russia, with major towns, industrial areas and natural ecotones.

2.2. Collection of ecological materials

2.2.1. Snow

Snow samples were collected between March and April in 1998 and 1999, on each occasion prior to the onset of seasonal snowmelt, as most of the total solute load can be lost from snow profiles with the first melt (Tranter *et al.*, 1986, 1988; Jaffe and Zukowski, 1993). On average, the mean dates for snowmelt commences on 9th, 15th and 26th of April at Inta, Usinsk and Vorkuta, respectively (Institute of Biology, Komi Science Centre Annual Reports, communicated by N. Solovieva). Sampling sites furthest away from towns were reached by helicopters (Mi-8), charted from Komiavia. Skidoos, overland tracked vehicles or skis were also used for travel and transportation. A snow pit was excavated at each collection point using a stainless steel spade, taking care not to disturb or contaminate surface snow at the top of the pit face to be sampled (Figures 2.3.a and 2.3.b). Care was taken to sample at least 500 m away from vehicles or helicopters.

(a)

Figure 2.3a. Snow sample collection using a 250 mL capacity low-density polyethylene (LDPE) bottle. Sampling involved repeatedly scraping the mouth of the bottle up the 'cleaned' face of the pit and compressing the loose snow into the sampling bottle.

(b)

Figure 2.3b. Snow sampling from shallow pits at the tundra site, Lake Protochnoye, 70 km NE of Vorkuta along Transect 1. (Photos a and b: P. D. Crittenden).

The face of the snow pit to be sampled was scraped downwards with a piece of PTFE sheet (after Tranter *et al.,* 1986) to prepare a clean surface; snow samples were collected in a 250 mL capacity low density polyethylene (LDPE) bottle. Collection was achieved by repeatedly scraping the mouth of the bottle up the 'cleaned' face of the pit (after Legrand and Delmas, 1985) with the snow being compressed into the bottle using a 35 mm diameter perspex rod. Snow was not collected from the lowermost 20 cm of the snowpack as a precaution against contamination from underlying surface soil (Shaw *et al.,* 1993). Samples were maintained frozen both during shipment and in the laboratory prior to analysis. For logistical purposes sample bottles were stored and transported in large aluminium boxes that had been fully insulated with polystyrene. Overnight these boxes were stored outside in the absence of any freezer facilities whilst staying in Russia. On average the overnight temperatures varied between -10 and -30 °C. The sample bottles, PTFE scraper, perspex rod and spade were all previously cleaned by rinsing in 2 hot washes of deionised (DI) water and finally by rinsing in ultra high purity water (Boutron, 1979). Low density polyethylene bottles were chosen for their low

cation content and the apparent absence of any leaching or ghost effects evident in collected snow samples (Gjessing, 1989). Powder-free LDPE gloves were worn during snow sampling both in the field and in the laboratory to minimise contamination.

2.2.2. Lichen sampling

Lichen samples were collected between July and August in 1998 and 1999 for TUNDRA and June and July in 2000 and 2001 for SPICE. At least one species of terricolous mat-forming lichen of the genera *Cladonia* [*C. stellaris* (Opiz) Pouzar and Vezda, *C. rangiferina* or *C. arbuscula* (Wallr.) Flot.] or *Flavocetraria* [*F. cucullata* (Bellardi) Kärnefelt and Thell] was collected at sub-sites during the snow-free season, subject to availability (Figure 2.4.). These species were chosen to provide biomarkers for atmospheric deposition and because of their ubiquity and abundance in forest tundra. At each site three sub-sites were selected, 500-1000 m apart, at which 6 replicate samples of lichen material were collected at distances 10-20 m apart in open areas subject to minimal tree canopy effects; these were usually inter-tree positions in open forest, or in open tundra.

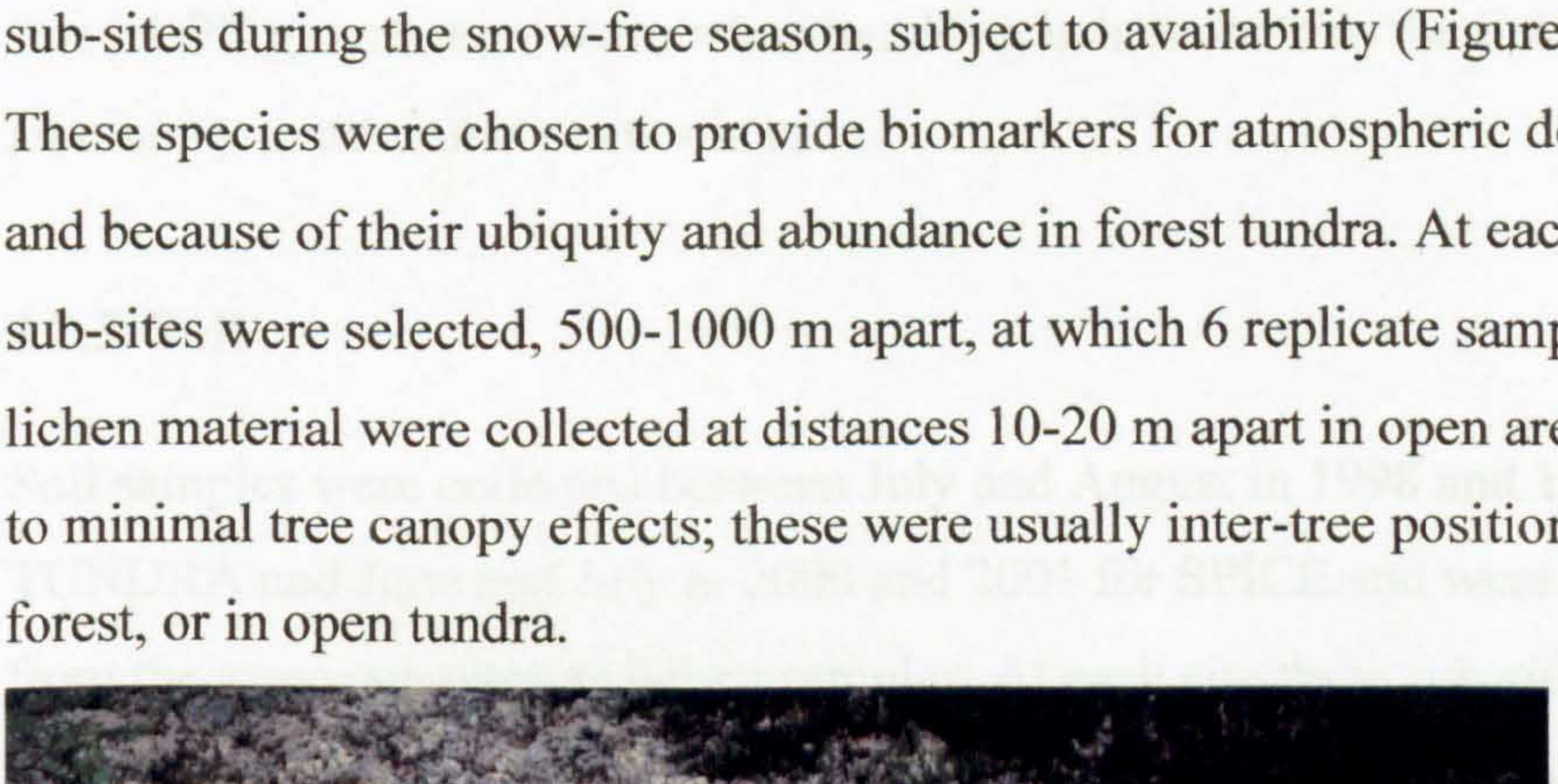


Figure 2.4. Lichen sampling using LDPE containers and powder-free LDPE gloves to minimise contamination. (Photo: P Kuhry).

Again, local Mi-8 helicopters were used to reach the most remote field sites and, when logistics allowed, other sites were reached by small boats and overland tracked vehicles. The majority of sub-sites were then reached on foot. Where sites were located close to towns some sites were accessed by car, although sub-sites were again reached on foot and chosen some distance away from the road to minimise road effects. Approximately 20 km beyond the northern-most site at Khosedayu river, 2.1, (see Figure 2.1, Table 2.1) on transect 2/3 additional lichen samples were collected along the Upper Kolva river during July 2000 by Dr Peter Kuhry, University of Lapland.

Lichen samples were air-dried, either under field conditions or in unheated rooms, sealed in LDPE containers and stored at 4 °C until analysis. Powder-free LDPE gloves were worn when handling lichens both in the field and in the laboratory to minimise contamination.

2.2.3. Soil

Soil samples were collected between July and August in 1998 and 1999 for TUNDRA and June and July in 2000 and 2001 for SPICE and were collected from the same sub-sites as lichen samples. At each site three sub-sites were selected, 500-1000 m apart, at which 6 replicate samples were collected at distances 10-20 m apart. The samples were collected 5 m from the base of trees, usually *Betula sp.* or *Sorbus sp.* in open areas subject to minimal tree canopy effects; these were usually inter-tree positions in open forest, or in open tundra. Approximately 20 km beyond the northern most site at Khosedayu river, 2.1, (see Figure 2.1, Table 2.1) on transect 2/3 an additional set of top-soil samples were collected along the Upper Kolva river during July 2000 by Dr. Peter Kuhry. Collection involved excavating organic and mineral topsoil from a 20 x 20 cm plastic quadrat with a stainless steel hand trowel, which was cleaned between samples to avoid cross contamination (Figure 2.5). Soil samples were passed through a 4 mm stainless steel sieve in the field, double-wrapped in polythene bags and, on return to the UK, were stored at -20 °C prior to analysis. The thickness of the surface organic and litter layers were recorded

for all quadrats. Because of variation in the depth of the organic layer (O-horizon) it was decided to sample to a standard depth of 5 cm following, for example, Niskavaara *et al.* (1997) and Reimann *et al.* (1997c). Powder-free polythene gloves were used at all times both in the field and in the laboratory to minimise the risk of contamination. Soil was imported into the UK in accordance with protocols established by MAFF (DEFRA) (licence number PHL 18/2351[08/97]).

(a)

(b)

Figure 2.5. (a) Soil sampling below terricolous lichen mats in an open area to minimise tree canopy effects. (b) Equipment used for soil sampling from left to right: double-wrapped polythene bags, plastic quadrat, stainless steel hand trowel, stainless steel sieve with base and stainless steel knife. (Photos: a, P. Kuhry; b, T. R. Walker).

2.3. Lichen biodiversity determinations

The purpose of this lichen biodiversity study was to determine differences in the lichen flora and in the percentage cover on trunks of *Picea obovata* and in selected sample plots in the tundra to explore the extent to which lichens serve as indicators of air purity.

2.3.1. Taiga sampling sites

Nine mature spruce trees (*Picea obovata*) were selected based on accessibility of trunks and representative nature of the stand from each forested study site: Ukhta area ($F1_i$), Belaya Kedva river ($F2_r$), Svetly Vuktyl ($F5_i$) and Maly Patok ($F6_r$). Trees were selected ≥ 100 m apart. An estimate of abundance and cover of each lichen species was made on trunks and branches, upto a height of 1.7 m. Many studies have used estimates of abundance of epiphytes (McCune, 1990; Halonen *et al.,* 1991; Aamlid and Venn, 1993). Estimates were made according to the scale used by Kauppi and Halonen (1992): 7 = >50%, 6 = 26-50%, 5 = 11-25%, 4 = 3-10%, 3 = poor cover, < 3%, 2 = little, many specimens, but not constituting any real cover, 1 = extremely little, only one or two specimens per trunk (Figure 2.6.a). After some training this scale proved easy and rapid to use. All the macrolichen and crustose lichen species were identified in the field according to Dobson (1979); Moberg and Holmåsen (1982); Goward *et al.* (1994); McCune and Geiser (1997). Where this was not possible, unidentified specimens were collected and returned to the Institute of Biology, Komi Science Centre, Syktyvkar and identifications made by Tatyana Prystina and Olga Lavrinenko.

2.3.2. Tundra sampling sites

Five quadrats (2 x 2 m), separated by > 100 m, were placed subjectively in lichen rich sub-sites which were dominated by dwarf birch (*Betula nana*) at each of the tundra study sites: Ortina river ($F3_i$), Neruta river ($F4_r$), Upper Kolva ($F7_i$) and Moreyu river ($F8_r$). The number and percentage cover of

epiphytic and epigeal lichen species were scored on Kauppi and Halonen's (1992) 1-7 point scale as above (Figure 2.6.b).

(a)

(b)

Figure 2.6. (a) Biodiversity determination on the trunk and branches of *Picea obovata* at Maly Patok, $F6_r$. (b) Biodiversity identifications in a *Betula nana* dominated heath tundra site at Upper Kolva, $F7_i$. (Photos: P. D. Crittenden).

2.4. Chemical analysis of snow

Thawed snow samples (110 mL) were filtered through 0.2 μm cellulose acetate membrane filters (Sartorius AG), which had been previously washed in 3 changes of DI water and not allowed to dry before use (Crittenden, 1983). The first 10 mL of filtrate was allowed to run to waste and the subsequent 100 mL was collected into two 50 mL metal-free, polypropylene centrifuge tubes (Elkay Products, Inc., Shrewsbury, MA, USA).

2.4.1. Anion analysis of snow

Anions (SO_4^{2-}, NO_3^- and Cl^-) were determined by means of ion chromatography using a Dionex DX 500 ion chromatograph fitted with a trace anion concentrator column (TAC-LP1). Confirmatory measurements of NO_3^- were made by HPLC using 5 μm amino Lichrosorb® as separator in a 250 mm long x 4.6 mm internal diameter column. The mobile phase (0.03 M KH_2PO_4 at pH 5) flowed at a rate of 1 mL. min^{-1} and ion detection was by UV absorption at 214 nm (Kratos Spectroflow® 757 Absorbance Detector) (Crittenden, 1998). Sea salt sulphate was estimated using the SO_4^{2-}: Na^+ molar ratio for seawater (0.0607), assuming that all Na^+ was of marine origin (Piccardi *et al.*, 2001).

2.4.2. Determination of pH and excess acidity/alkalinity in snow

Frozen snow samples were thawed overnight in a refrigerator and 20 mL aliquots were used for determination of pH and excess acidity or alkalinity. Standard protocols were used to measure pH (Tyree, 1981; Covington *et al.*, 1983) and initial pH drift was checked using a chart recorder REC80, Radiometer, Copenhagen. Hydrogen ion concentration was calculated from pH using the Davies equation to estimate the proton activity coefficient.

For acidity or alkalinity determinations a Gran titration method was used according to the method of Legrand *et al.* (1982). A research grade Orion 81

62sc electrode was used with a Radiometer pH meter, (PHM82). Titrant delivery was via an autoburette (Radiometer, ABU80) capable of delivery to an accuracy of ± 0.001 mL. To eliminate sample contamination from laboratory NH_3 and CO_2, the headspace of the titration vessel was continually flushed with N_2; care was taken to avoid bubbling N_2 directly into the filtered snowmelt. The sample was stirred using a Teflon coated stirring rod built into the titration assembly. A thermostatically controlled water bath (Grant; ± 0.5 °C) was used to maintain the titration solution at a constant temperature (24 °C) by circulating water around the titration vessel in an enclosing coil of plastic tubing. Test samples run without temperature control showed little difference to those with temperature control. All samples were stored in a test tube rack within the water bath to ensure that they had reached constant temperature before the titration began. Adjustable micropipettes (Finnpipettes and Gilson) and pre-cleaned accuvettes were used for dispensing solutions.

The acid titrant (1.00×10^{-3} M HCl) was prepared by diluting a sample of HCl (Analar, Fischer Chemicals, UK) stock solution with double-DI water. The same water was used to wash the electrode, stirrer and the glass microburette tip between each sample run. A small quantity of acid titrant was flushed out of the burette before each titration to avoid dilution from washing the delivery tip with DI water. The internal filling solution of the electrode (a saturated solution of KCl) was also used as the ionic strength adjuster (ISA) to control ionic strength in all Gran titration samples. Possible contamination from the ISA was checked by adding volumes of 0.5, 1.0 and 1.5 mL ISA to three DI water blanks. All three blanks showed no difference in total acidity and thus any background acidity in these blank samples was attributed to laboratory DI water and not contaminant in the ISA. The electrode was calibrated using pH buffers of 4.00 and 7.00. Calibration was always followed by two blank titrations using DI water to ensure that the electrode had stabilised and remove residual buffer from the electrode surface. At the end of each set of titrations the electrode was checked for drift by re-calibrating.

A 20 mL aliquot of thawed, filtered snow sample at 24 °C was pipetted into a sample container and 0.5 mL of ISA (saturated KCl solution) added. The sample container was then placed within the thermostatted water jacket and connected to the titration assembly. An initial pH measurement was taken after the electrode stabilised and temperature equilibrium was reached (usually less than 1 minute). The temperature of the sample was checked after titration, using a thermometer, and did not vary. An initial volume of titrant (0.001M HCl) was added until a pH of 4.75 was reached (unless the sample was already < pH 4.75). At this pH atmospheric CO_2 no longer contributes significantly to acidity. Following the Gran titration method of Legrand *et al.* (1982), the pH of the meltwater sample was gradually decreased by adding around six successive aliquots of dilute acid titrant. An example of which is shown in Table 2.3 for an alkaline sample (sample 3.4.3.6.) collected at site 3.4 along transect 3, south of Inta. The time interval between two successive additions was between 10-15 s. A linear regression of the 6 titration data was obtained and extrapolated to zero titrant (i.e. to intercept the 'y'-axis) to determine the value of acidity/alkalinity (Figure 2.7). Approximately 6-10 samples h^{-1} were measured. Determination of the acidity/alkalinity is described in the following section.

2.4.3. Gran plot determination of strong acid concentration in filtered thawed snow

Following Legrand *et al.* (1982), the concentration (normality) of strong acid in the sample (C_O) was derived from Equation 2.1 (see Table 2.4.; Figure 2.7).

$$Co = \frac{Y - Intercept}{Slope}\left(\frac{C}{Vo}\right) \qquad (2.1)$$

where:
C_o = Concentration (Normality) of strong acid in sample
V_o = Volume of water sample titrated
C = Concentration (Normality) of strong acid in titrant

This relationship is derived from an interpretation of the Nernst equation and the variation in measured electrode potential (E) with addition of strong acid. Concentration of strong acid (C_A) at each titration point is (Equation 2.2):

$$C_A = \frac{CoVo + CV}{Vo + V} \qquad (2.2)$$

where:

C_A = Concentration of strong acid during the course of the titration
V = Volume of titrant added

From equation (2.2), the Nernst equation may be written as (Equation 2.3):

$$E = Eo + \frac{\ln(10)\,RT}{F}\log\left[\frac{CoVo + CV}{Vo + V}\right] + \frac{\ln(10)\,RT}{F}\log(\gamma) + Ej \qquad (2.3)$$

where:

E = Measured potential (mV)
E_o = Potential for proton activity of unity – the 'standard' potential
E_j = The liquid junction potential
γ = Activity coefficient for the (H^+) ion
R = Gas constant
T = Thermodynamic temperature
F = Faraday constant

For convenience we can define the slope of the Nernst relation (S) as Equation 2.4):

(2.4)

$$S = \frac{\ln(10)\,RT}{F}$$

Dividing Equation 2.3 through by S, then removing logs and multiplying through by (V_O+ V) gives (Equation 2.5):

$$(Vo + V)10^{(E/S)} = 10^{\left(\frac{EO+Ej}{S}\right)}\gamma(CoVo + CV) \qquad (2.5)$$

Linear regression therefore gives (Equation 2.6):

(2.6)

$$Y = (Vo + V)10^{(E/S)};$$
$$X = V;$$
$$Slope = 10^{(EO+Ej/S)}C\gamma;$$
$$Y - axis\ Intercept = 10^{(EO+Ej/S)}CoVo\gamma$$

Measurements of pH were converted to values of potential, E (mV), in order to apply Equation 2.1. The value of the Nernst slope varied for each granplot, but was approximately 58-59 mV per pH unit.

(2.7)

$$E = Eo + \frac{\ln(10)\,RT}{F}\,pH$$

We used the measured E values at pH 7 (E = 0) and pH 4 to derive the slope of the Nernst equation.

Table 2.4. Example output from site 3.4 (sample 3.4.3.6.)

Cumulative Titrant (V) added (ml)	**pH measured**	**E (mV) calculated**	**Total Vol. ($V+V_O+Visa$) (ml)**	**Gran Parameter (Y)**	**G-Plot Slope**	**G-Plot Intercept**
0.873 1.000 1.250 1.500 2.002 2.500	4.75 4.65 4.50 4.39 4.23 4.12	131.250 137.083 145.833 152.250 161.583 168.000	21.373 21.500 21.750 22.000 22.502 23.000	3800.72 4813.25 6877.95 8962.37 13250.16 17447.28	8409.44	-3597.409
Sample Identification 3436	**Nernst Slope 58.333**	**Sample Volume (V_O) 20**	**ISA Volume (ml) 0.5**	**Conc. Titrant (M) 1.0×10^{-3}**	**Milli-volts At pH 4.00 175**	**Conc snow acid C_O (M) = -2.14×10^{-5}**
Start pH 6.36						

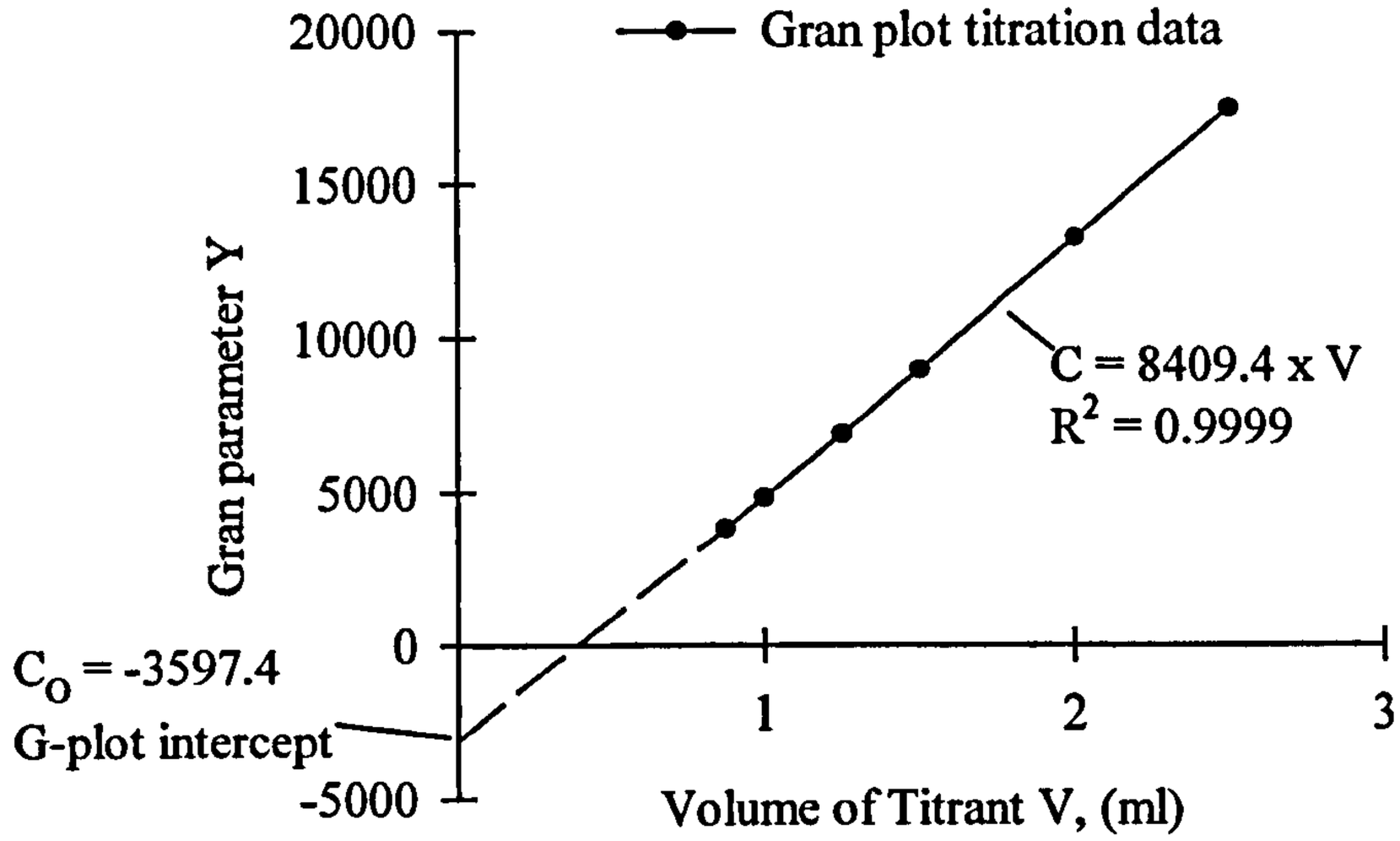


Figure 2.7. An example of a Gran Plot output for site 3.4 (Table 2.4; sample number 3.4.3.6.), showing alkaline snow.

2.4.4. Elemental analysis of snow

Analysis of trace metals was conducted on acidified liquid samples by inductively coupled plasma mass spectroscopy (ICP-MS) at the University of Lancaster by Dr. Hao Zhang. The trace metals Ag, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr and Zn were determined on pooled samples. These were composed of equal aliquots of 166 μL of filtered thawed snow taken from each of the six replicate samples from each site to make a combined sample volume of 1 mL. Filtered solutions were acidified with ultrapure HNO_3 to give 2 % HNO_3 prior to analysis of trace elements by ICP-MS. Cations (Na^+, Ca^{2+}, K^+) were determined by flame emission spectrometry (FES) with appropriate additions of CsC1 as ionisation suppressant (1000 mg Cs L^{-1}).

2.4.5. Elemental analysis of suspended solids in snow

Cellulose acetate membrane filters used to filter the thawed snow samples were oven dried at 80 °C overnight in glass petri-dishes and suspended solids were determined gravimetrically. The membrane filters from the Vorkuta and Usinsk transects were retained and photographed prior to digestion. Six cellulose acetate membrane filters from each sub-site were combined and digested together in 10 mL of conc. HNO_3 (Aristar, Fischer Chemicals, UK) (Reimann *et al.*, 1996). The digest was filtered through a Whatman No. 42 ashless filter and made up to 50 mL using ultra-pure water giving a final matrix of approximately 1 % HNO_3. Elemental analysis (Al, Ba, Ca, Cd, Cu, K, Mg, Mn, Ni, Pb, Sr and Zn) was undertaken by graphite furnace atomic absorption spectroscopy (GF-AAS) and flame atomic absorption spectroscopy (F-AAS); concentrations were recalculated in relation to the volume of filtered meltwater to allow direct comparison with the data for solute concentrations (Reimann *et al.*, 1996).

2.5. Chemical analysis of lichens

2.5.1. Preparation of material

Lichens were rehydrated overnight by exposure to water-saturated air (over DI water in a dessicator) at 4 °C, then fully saturated by spraying twice with DI water. The rehydrated material was cleaned of extraneous debris using forceps. The thalli were then cut horizontally (i.e. at right angles to the main axis of the thallus) at 5, 40 and 50 mm from the apex. The horizontal strata 0-5 mm (apices) and 40-50 mm (thallus base with respect to the apex) were retained for analysis and oven dried at 80 °C overnight. The analyses performed on each species is given in Table 3.1 (Chapter 3) and Table 5.1 (Chapter 5)

2.5.2. Total [Ca], [K], [Mg], [Zn] and [Pb] concentrations in lichen tissue

Approximately 100 mg of dried apical tissue was digested to dryness in 1 mL of concentrated HNO_3 (Aristar, Fisher Chemicals, UK) at 175 °C in 16 x 1.5 cm digestion tubes. The residue was dissolved in 10 mL 1 M HNO_3 and appropriate quantities of ionisation suppressant and releasing agent ($CsCl_2$, $LaCl_2$) added. Concentrations of $[Zn]_{lichen}$ were determined on the top 5 mm of apical thalli for *Cladonia stellaris* and *C. rangiferina* along transects 2/3 through Inta and for *C. arbuscula* along transect 1 through Vorkuta (see Chapter 3). Concentrations of $[Pb]_{lichen}$ were determined on the top 5 mm of apical thalli for *Cladonia stellaris* and *C. arbuscula* and *Flavocetraria cucullata* (see Chapter 5). Magnesium, Pb and Zn were determined by GF-AAS and Ca and K by FES.

2.5.3. Total nitrogen concentration ($[N]_{lichen}$) in lichen thalli

Total N concentration was measured in both apical (0-5 mm) and basal (40-50 mm) tissue. These strata were cut from thalli using a razor blade. Total $[N]_{lichen}$ was determined following the Kjeldahl digestion and distillation method of Bremmer and Breitenbeck (1983). Approximately 100 mg of dried apical thallus or 300 - 400 mg of dried basal thallus was digested in 3 mL of concentrated H_2SO_4 (Aristar, Merck UK Ltd) containing 1.0 g K_2SO_4, 0.1 g $CuSO_4.5H_2O$, 0.01 g Se and 3 anti-bumping granules. The digestion was performed in 100 mL (30 x 3 cm) digestion tubes, heated at 375 °C for 3 hours in an aluminium block digestor [Grant Instruments Ltd, Cambridge] (Bremmer, 1965; Bremmer and Breitenbeck, 1983). The cooled digest was diluted with 15 mL of DI water, then allowed to cool to room temperature. The steam distillation apparatus used to collect NH_3 from the digest is shown in Figure 2.8.

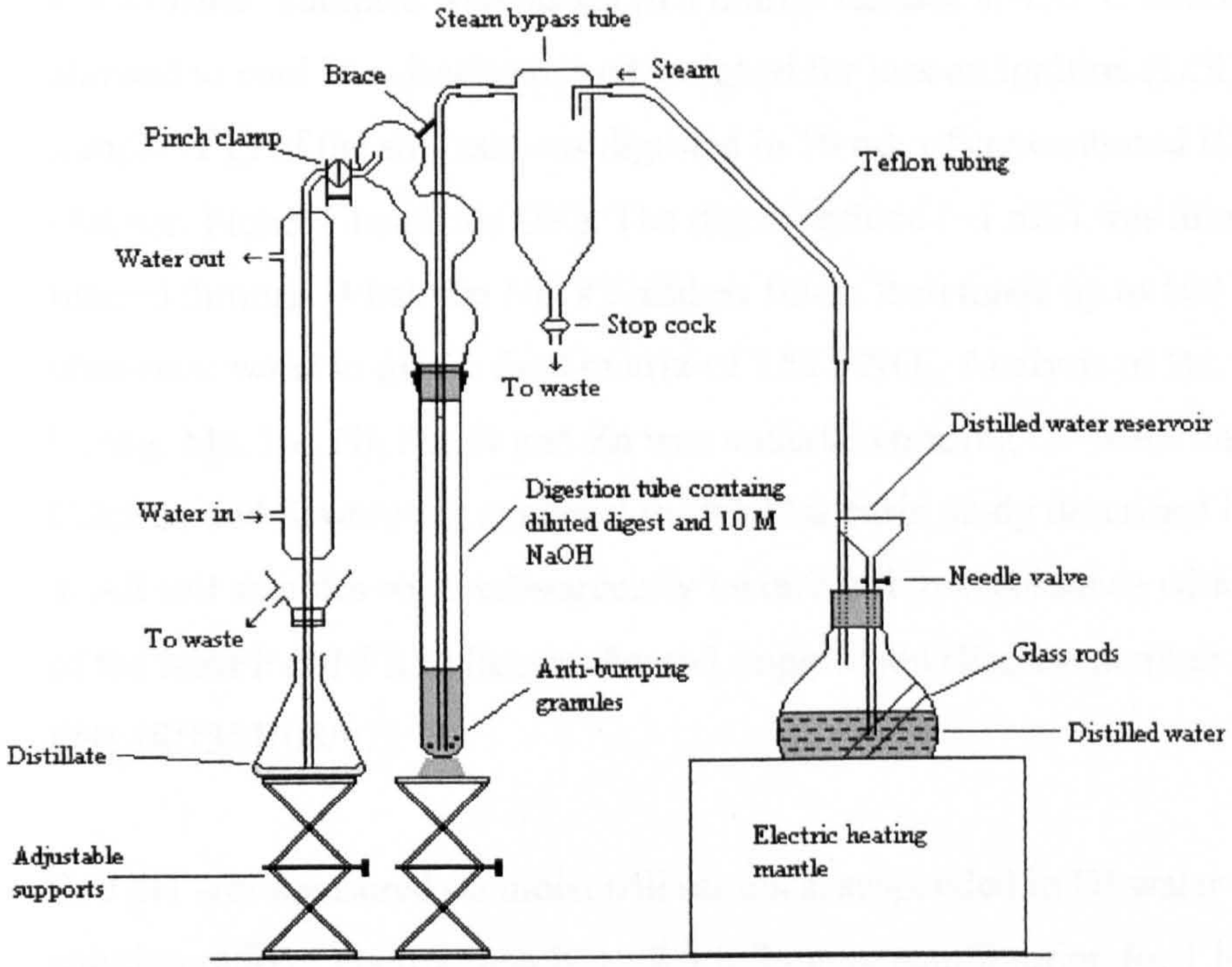


Figure 2.8. Steam distillation apparatus (after Bremmer and Breitenbeck, 1983).

Ammonium N was removed from the kjeldahl digests by steam distillation of NH_3 into boric acid indicator solution and determined by titration using an autotitrator (665 Dosimat, Metrohm, Switzerland) with 0.01 N H_2SO_4 (1 mL of 0.01 N H_2SO_4 = 0.14 mg of ammonium N). The colour change at the end point is from green to pink.

2.6. Soil analysis

Frozen soil samples were allowed to thaw overnight at room temperature and a representative sub-sample (5 - 10 g) was oven dried (105 °C) in acid washed

silica dishes. Samples were ashed in a muffle furnace at 450 °C overnight, allowed to cool in a dessicator and weighed for loss on ignition (LOI). A sub-sample (1 g) of the soil ash was digested in 10 mL of concentrated HNO_3 (Aristar, Ficher Chemicals UK). The digest residue (~1 mL) was diluted and filtered through Whatman No. 42 ashless filters then made up to 100 mL using ultra-pure water to give a final matrix of 1 % HNO_3. Analysis of Ba, Ca, Cu, K, Mg, Mn, Na, Ni, Pb, Sr and Zn was undertaken using GF-AAS and F-AAS. Calcium and K were not analysed for the Usa basin study described in Chapter 4. All soil samples were subsequently incinerated in accordance with the terms of the MAFF (DEFRA) licence for soil importation (licence number PHL18/2351[08/97].

Soil pH was measured on moist soil samples, suspended in DI water at a solid : solution ratio of approximately 1 : 2.5 following equilibration for 1 hour. Drift in pH was recorded to determine when equilibrium was reached.

2.7. Elemental deposition rates

Elemental concentrations in snow (including those associated with particulates) and soil were considered together in an attempt to explain the soil metal loadings found around emission sources in relation to current deposition rates. Sites affected by deposition were considered in relation to pristine sites. The time in years required to accumulate excess element concentration in soil (T_d) was determined by equation 2.8

$$T_d = \frac{(C_d - C_p) \times S_d}{A_d} \quad , \qquad (2.8)$$

where:

T_d = Time required to accumulate excess elemental concentration (y)

C_d = Concentration of element in soil within deposition area (g kg^{-1}).

C_p = Concentration of element in soil at background (pristine) site (g kg^{-1}).

S_d = Mass of soil in 5 cm slice in deposition area (kg m^{-2}).

A_d = Current element deposition rate (g m^{-2} y^{-1}).

This was estimated by combining measured elemental concentrations in thawed snow and filter residues (g m^{-3} liquid) then multiplying by the mean annual precipitation (m y^{-1}) for each town.

This approach assumes that:

(i) the lowest concentrations of elements found in soil (C_p) occur at sites at the transect extremes, furthest away from the emission sources (e.g. Transect 1 through Vorkuta - sites 1.1 and 1.6; Transects 2/3 through Inta - sites 2.1 and 3.1);

(ii) highest concentrations (C_d) occur close to emission sources (e.g. Vorkuta: sites 1.3 and 1.4, Inta: sites 2.5 and 3.5);

(iii) all historical deposition is contained within the top 5 cm of soil (S_d);

(iv) the mean annual precipitation is the same at all sites on a transect.

2.8. Statistical methods

Genstat and Minitab were used to perform standard statistical analyses (ANOVA, correlation analysis and linear regression). The extent of pollution at sites nearest to towns was assessed by comparing chemical data from these sites with those from sites at the extremities of transects using ANOVA with an appropriate contrast (Chapter 3). Tukey's tests were used for pairwise comparison of lichen biodiversity ANOVA-analysis.

CHAPTER 3. REGIONAL VARIATION IN THE CHEMICAL COMPOSITION OF WINTER SNOWPACK AND TERRICOLOUS LICHENS IN RELATION TO SOURCES OF ACID EMISSIONS IN THE USA RIVER BASIN, NORTHEASTERN EUROPEAN RUSSIA

3.1. Introduction

This Chapter reports on the geographical variation in the chemistry of winter snowpack and terricolous mat-forming lichens in the Usa basin, north-east European Russia. The research was a contribution to TUNDRA (TUNdra Degradation in the Russian Arctic), an interdisciplinary research project examining potential effects of environmental change in the Russian Arctic. As such, a wider objective of the work was to assess the likely extent to which the response of Arctic ecosystems to 'climate forcing' in this region might be modified by pollution. It also provided an opportunity to further evaluate the use of terricolous lichens as indicators of nitrogen and acid deposition. The objective was to provide information on the distribution and magnitude of acid deposition (and alkaline) resulting from industrial activity in the Usa river basin in the Komi Republic. This region has an area of 93,000 km^2 and spans the boreal forest-Arctic tundra ecotone (Figure 2.1). It has already been identified as a significant source of acid emissions (Ottar *et al.*, 1984; Ottar, 1989; Nenonen, 1991; Vinogradova, 2000) mainly as a result of coal fired power stations in the towns of Vorkuta and Inta and a gas-fired power station in Usinsk. Transects were established through the three principal towns of Vorkutá (67°30'N, 64°05'E; Transect 1), Inta (66°03'N, 60°10'E; Transects 2 and 3), and Usinsk (66°01'N, 57°30'E; Transect 4) (Figure 2.1, Table 2.1).

Reported here is an assessment of the extent of acid, alkaline and N deposition around Vorkuta, Inta and Usinsk as indicated by the spatial variation in the chemical composition of winter snowpack and terricolous mat-forming lichens. In part, these data will serve as a baseline against which contamination that might result from future industrial development of the area can be measured. The variables measured in snowpack were: anions (SO_4^{2-}, NO_3^- and Cl^-) by ion chromatography and HPLC; cations (Na^+, Ca^{2+}, K^+) by

flame emission spectrophotometry (FES); pH following standard protocols. The variables measured in lichens were: total N, determined by Kjeldahl digestion and distillation; cations (Mg^+ by F-AAS; Ca^{2+} and K^+ by FES); Zn by F-AAS.

The chemistry of snowpack and terricolous lichens was modified locally in the vicinity of the industrial towns, and also on a regional scale with respect to latitude. The probable underlying causal factors are discussed.

3.2. Materials and methods

3.2.1. Study area and sampling regime

The study sites are located in the Usa river basin between latitudes 64° and 68° N in the Komi Republic (east European Russia)(Figure 2.1, Chapter 2). Transects were established through the three principal towns of Vorkuta, Inta and Usinsk. On each Transect between 4-6 sampling sites were selected at roughly logarithmic intervals with respect to the town centres (Figure 2.1, Table 2.1). At each site three sub-sites were again selected, 500 - 1000 m apart, at which 6 replicate samples of snow and 6 of lichen (see below) were collected at distances 10 - 20 m apart in open areas subject to minimal tree canopy effects; these were usually inter-tree positions in open forest, or in open tundra. Most sites were in wilderness areas remote from roads. Note that snow samples were not collected at the most extreme sites on transects 2/3 (i.e. 2.1 and 3.1) and lichens were not collected at site 2.4.

3.2.2. Snow and lichen sampling

For further details of snow collection methods see Chapter 2. At least one species of terricolous mat-forming lichen of the genera *Cladonia* [*C. stellaris* (Opiz) Pouzar and Vezda, *C. rangiferina* or *C. arbuscula* (Wallr.) Flot.] or *Flavocetraria* [*F. cucullata* (Bellardi) Kärnefelt and Thell] was collected at sub-sites during the snow-free season. These species were chosen to provide

biomarkers for atmospheric deposition and because of their ubiquity and abundance in forest tundra. See Chapter 2 for details of collection.

3.2.3. Lichen biomarkers for nitrogen and acid deposition

The nitrogen concentration ([N]) in lichens is partially dependent on the amount of income of dry and wet deposited N (Kubin, 1990; Søchting, 1990; Bruteig, 1993b; Hyvärinen and Crittenden, 1998a). Hyvärinen and Crittenden (1998a) demonstrated a strong relationship between N deposition and [N] in the terricolous mat-forming lichen *Cladonia portentosa*. Mat-forming lichens include species of *Cladonia*, *Cetraria, Flavocetraria* and *Alectoria*, genera that are widespread and locally abundant in boreal-Arctic heathlands and open woodlands. Such species grow vertically upwards at the apices, and senesce and produce litter (necromass) at their bases (Crittenden, 1991). A gradient of decreasing [N] values exists from the thallus apices towards the bases. Hyvärinen and Crittenden (1998a) found that [N] in the apical 5mm of *C. portentosa* ($[N]_{apex}$) and in a deeper stratum 35 - 50 mm from the apices ($[N]_{base}$) were both significantly positively correlated, and the concentration ratio $[N]_{apex} : [N]_{base}$ was negatively correlated, with N deposition. Hyvärinen, 1997; Hyvärinen and Crittenden (1996) also showed that the concentration ratio of K^+:Mg^{2+} in the apices ($([K^+]:[Mg^{2+}])_{apex}$) of *C. portentosa* was positively correlated with precipitation acidity. Accordingly, concentrations of N, K^+, and divalent cations (Mg^{2+} and Ca^{2+}) in thallus apices, and [N] in the bases, were measured in lichens sampled in the present work.

Hyvärinen and Crittenden (1998a) consider that coupling between the chemical composition of mat-forming terricolous lichens and that of atmospheric deposits may be particularly close for three reasons. Mats typically develop in open situations and intercept precipitation directly, and hence relationships between lichen chemistry and atmospheric inputs are not compounded by nutrient exchanges between rainfall (or snow meltwater) and overlying vascular plant canopies (cf. Farmer *et al.*, 1991a,b; Søchting, 1995). Accumulation, below well-established lichen mats, of copious quantities of structurally intact necromass may partially isolate living thalli from the

chemical influence of the soil beneath (see Crittenden, 1991; Hyvärinen and Crittenden, 1996). Lichen mats are efficient scavengers of inorganic N and P in precipitation (Crittenden, 1983, 1989; Hyvärinen and Crittenden, 1998b, c) so that mats several cm deep become very strong sinks for ions such as NO_3^-, NH_4^+, and PO_4^{3-}.

3.2.4. Chemical analysis of snow

Full details of snow analysis are presented in Chapter 2 (2.4). Thawed snow samples (110 ml) were filtered through 0.2 μm cellulose acetate membrane filters, which had been previously washed in 3 changes of deionised water and not allowed to dry before use (Crittenden, 1983). Anions (SO_4^{2-}, NO_3^- and Cl^-) were analysed by ion chromatography and confirmatory measurements of NO_3^- were made by HPLC. Cations (Na^+, Ca^{2+}, K^+) were determined by flame emission spectrometry (FES) with appropriate additions of CsC1 (1000 mg Cs L^{-1}) as ionisation suppressant. Sea salt sulphate was estimated using the SO_4^{2-}: Na^+ molar ratio for seawater (0.0607) and assuming that all Na^+ was of marine origin. Snow meltwater pH was determined using standard protocols (Tyree, 1981; Covington *et al.*, 1983). Hydrogen ion concentration was calculated from pH using the Davies equation to estimate the proton activity coefficient. Acidity or alkalinity was measured by Granplot acid titrations (methods and data presented in Chapter 2 and Chapter 4).

3.2.5. Chemical analysis of lichens

Full details of lichen analysis are presented in Chapter 2 (2.5). Two horizontal strata were cut with a razor blade from each thallus: the apical 5 mm (analysed for total N and cations) and the stratum between 40 - 50 mm from the apices (analysed for total N). Magnesium and Zn was measured by flame atomic absorption spectrophotometry (F-AAS); Ca^{2+} and K^+ by FES. Zinc was selected as an additional analyte because it was one of several trace metals found to contaminate snow and soils locally in the survey region (Walker *et al.*, 2003). Total nitrogen concentration was determined by Kjeldahl digestion

and distillation following the methods of Bremmer (1965) and Bremmer and Breitenbeck (1983).

3.2.6. Data analysis

Genstat and Minitab were used to perform standard statistical analyses (ANOVA, correlation analysis and linear regression). The extent of pollution at sites nearest to towns was assessed by using ANOVA with an appropriate contrast by comparing chemical data from sites close to towns with those from sites at the extremities of transects.

3.3. Results

3.3.1. Snow chemistry

The depth of the snow pits ranged between 0.4 - 3.0 m and evidence of significant thawing, such as horizontal ice layers within the profiles, was not observed. However, at most sites on the Vorkuta Transect, and at sites close to Inta, dark horizontal bands were observed in many of the snow profiles.

Figure 3.1a,b and c gives the pH and concentrations of NO_3^- and SO_4^{2-} in snow samples (subsequently referred to as pH_{snow}, $[NO_3^-]_{snow}$ and $[SO_4^{2-}]_{snow}$, respectively, with logical extensions of this format to other ions) collected along the Transects through Vorkuta, Inta and Usinsk (Transects 1, 2/3 and 4, respectively). Values recorded at the extremities of the Transects are broadly similar, suggesting that the baseline pH_{snow}, $[NO_3^-]_{snow}$ and $[SO_4^{2-}]_{snow}$ values across the Usa basin were *c.* 4.9, 9.2 and 5.3 μmol L^{-1}, respectively. These approximate baseline values appear to be representative for each of the three Transects even though data for Transects 2 and 3 (Inta) were collected in the year prior to those for Transects 1 and 4 (Vorkuta and Usinsk). Note that site 4.6 sampled in 1999, is located near to site 2.3 (approx. 20 km apart) which was sampled in 1998, and that although $[NO_3^-]_{snow}$ and $[SO_4^{2-}]_{snow}$ values at these two sites are broadly comparable, concentrations of both ions are higher

at site 4.6. Acidity or alkalinity was also measured in all snow samples by Granplot acid titrations and the data are presented elsewhere (Chapter 4; Walker *et al.*, 2003).

Values of pH_{snow} and $[SO_4^{2-}]_{snow}$ were markedly elevated in the vicinities of Vorkuta and Inta; in each case the differences between the two sites closest to the towns and the two remotest sites were significant at the $P < 0.001$ level (one-way ANOVA)(Figure 3.1.a and 3.1.b). These perturbations were not detectable beyond a distance of *c.* 25 km from Inta (Figure 3.1.b) whereas around Vorkuta there was evidence of contamination even at the extremities of the Transect (sites 1.1 and 1.6) providing some evidence of spatially more extensive pollution around Vorkuta. Changes in pH_{snow} and $[SO_4^{2-}]_{snow}$ values along these Transects were positively correlated ($r = 0.822$, $P < 0.001$, $n = 144$; $r = 0.542$, $P < 0.001$, $n = 108$ [for Inta and Vorkuta, respectively]). By contrast, values of pH_{snow} and $[SO_4^{2-}]_{snow}$ were not modified significantly in the environs of Usinsk (Figure 3.1.c), and $[NO_3^-]_{snow}$ was invariant in the vicinity of any of the three towns. Nitrate concentrations measured by ion chromatography and by HPLC were in very close agreement ($r = 0.98$, $P < 0.001$, $n = 360$) (Figure 3.2).

Concentrations of organic N were also determined in a small subset of snow samples from Transects 1 and 4 by J.N. Cape (Centre for Ecology and Hydrology, Edinburgh) using an ANTEK model 8060 N-specific detector for HPLC. Molar concentrations of organic N were broadly similar to those of nitrate, except at sites close to Vorkuta where $[\text{organic N}]_{snow}$ values were greater than $[NO_3^-]_{snow}$ by a factor of 2 or 3 varying spatially in a manner similar to that of $[SO_4^{2-}]_{snow}$ values.

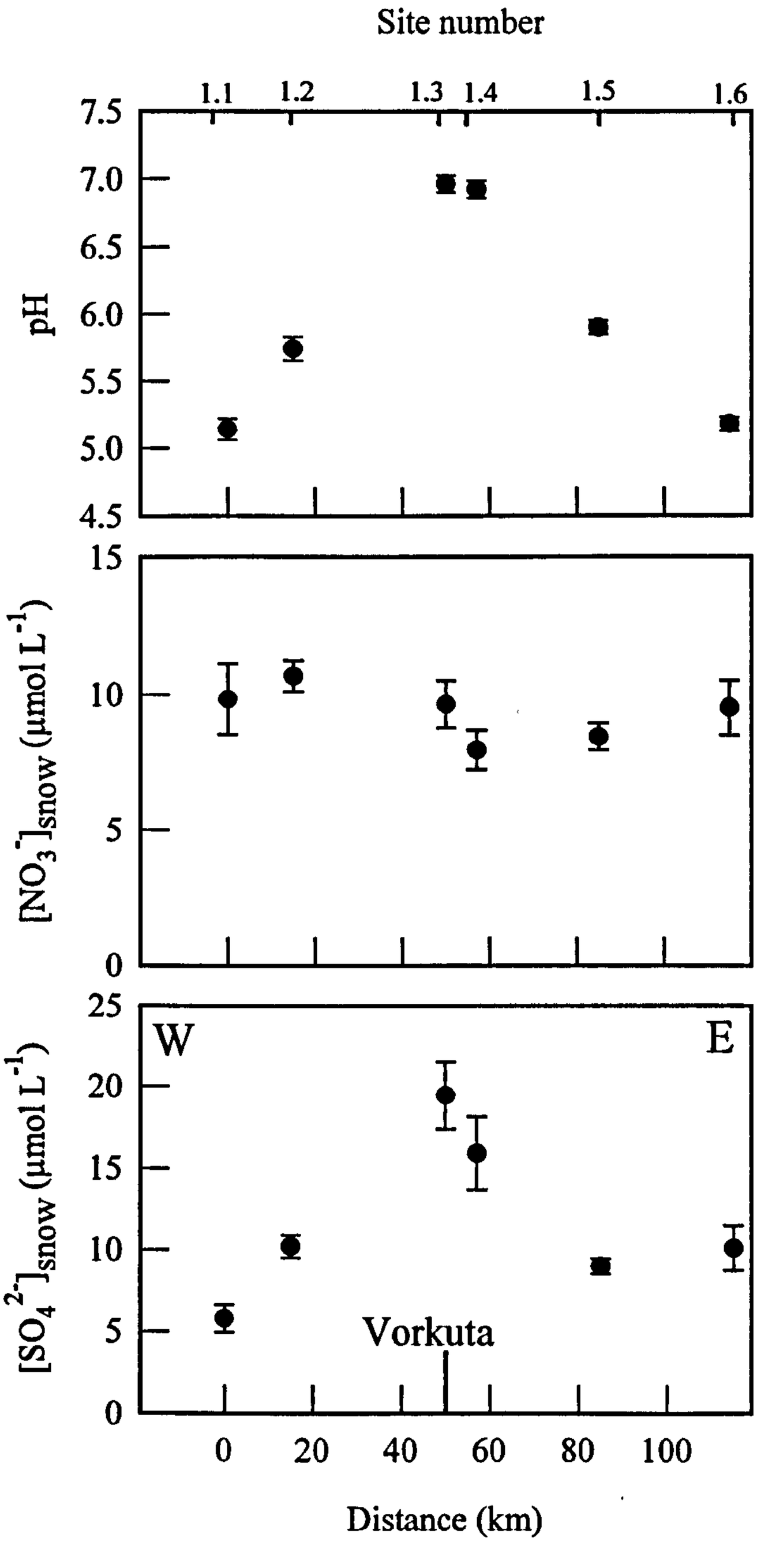


Figure 3.1.a. Variation in $[NO_3^-]_{snow}$, $[SO_4^{2-}]_{snow}$ and pH_{snow} on Transect 1 during Spring 1999. Plotted values are means ± 1 SE (n = 18).

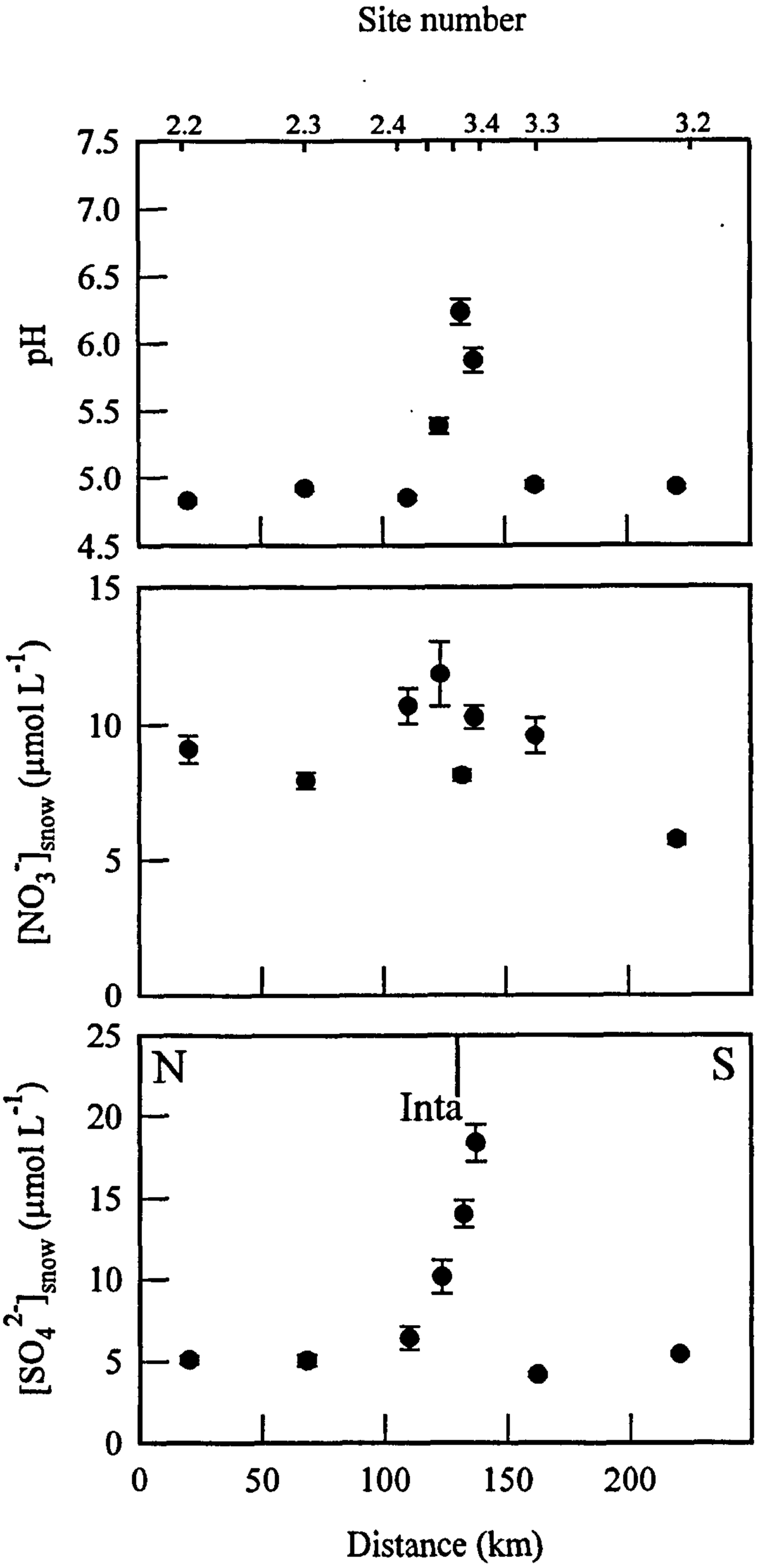


Figure 3.1.b. Variation $[NO_3^-]_{snow}$, $[SO_4^{2-}]_{snow}$ and pH_{snow} on Transects 2/3 during Spring 1998. Plotted values are means ± 1 SE (n = 18).

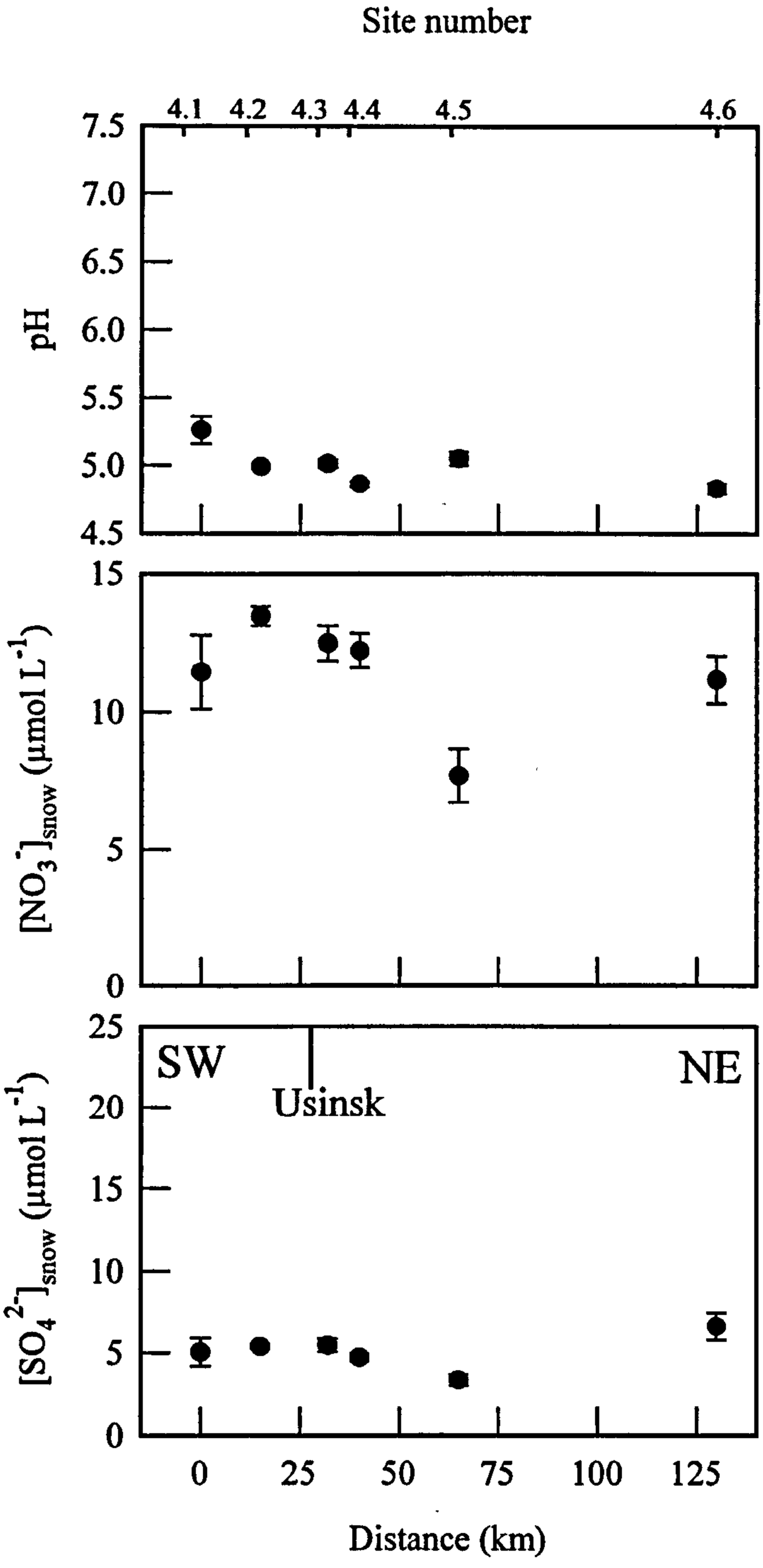


Figure 3.1.c. Variation in $[NO_3^-]_{snow}$, $[SO_4^{2-}]_{snow}$ and pH_{snow} on Transect 4 during Spring 1999. Plotted values are means ± 1 SE ($n = 18$).

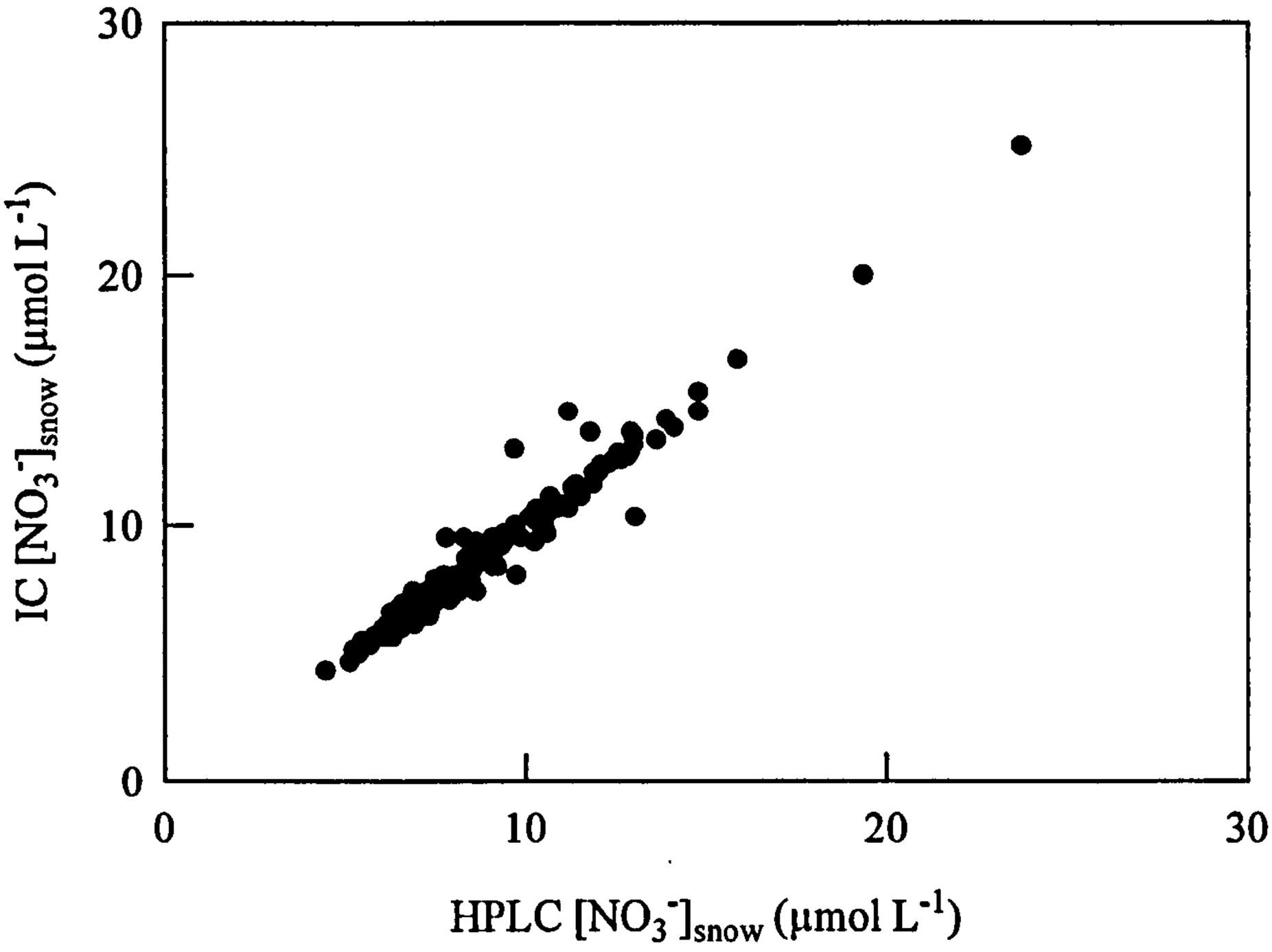


Figure 3.2. Agreement between $[NO_3^-]_{snow}$ measured by ion chromatography and HPLC ($r = 0.98$, $P < 0.001$, $n = 360$).

More general information on the sensitivity of snow pack chemistry, and the analytical methods employed, as tools to map pollution in this region is provided by data for Na^+ and Cl^- concentrations (Figure 3.3.a,b,c). Mean values of $[Na^+]_{snow}$ (measured by AAS) and $[Cl^-]_{snow}$ (measured by ion chromatography) along the Inta Transects (Figure 3.3.b) are both strongly related to latitude, used here as an analogue to distance from the coast ($[Na^+]_{snow}$: $r^2 = 0.76$, $P < 0.005$, $n = 8$; $[Cl^-]_{snow}$: $r^2 = 0.75$, $P < 0.01$, $n = 8$).

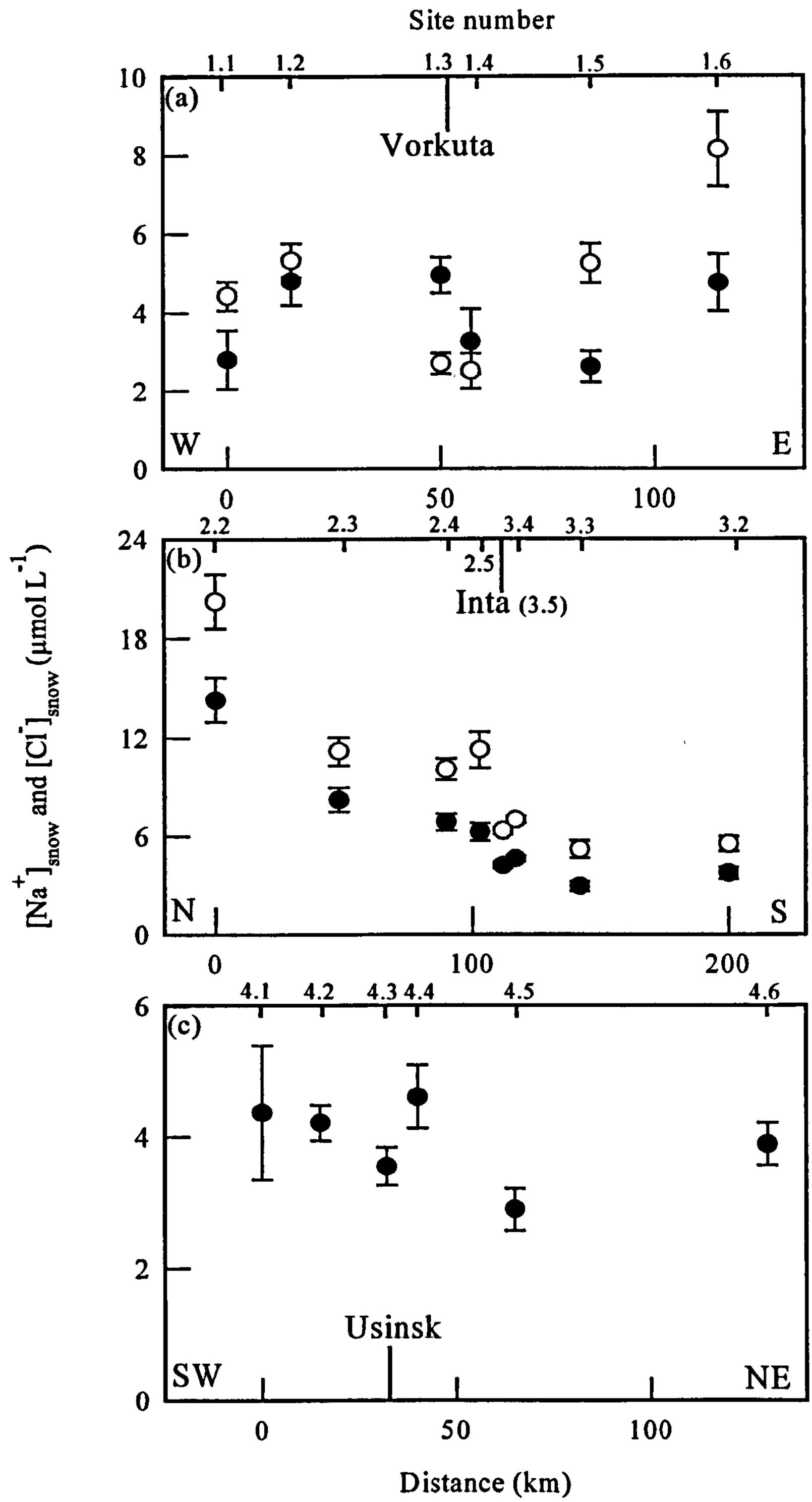


Figure 3.3. Variation in $[Na^+]_{snow}$ (○) and $[Cl^-]_{snow}$ (●) on Transects 1, (a); 2/3, (b) and 4, (c). Plotted values are means ± 1 SE (n = 18).

There was no apparent variation in $[Cl^-]_{snow}$ along the Transect 4 through Usinsk (Figure 3.3.c). Intra-site variation in absolute values of $[Na^+]_{snow}$ and $[Cl^-]_{snow}$ was most marked at the northernmost spring sampling site (2.2) whereas variation in the ratio $([Na^+]:[Cl^-])_{snow}$ was low with values approaching to the sea salt molar ratio of 0.85 (Figures 3.4 and 3.5b).

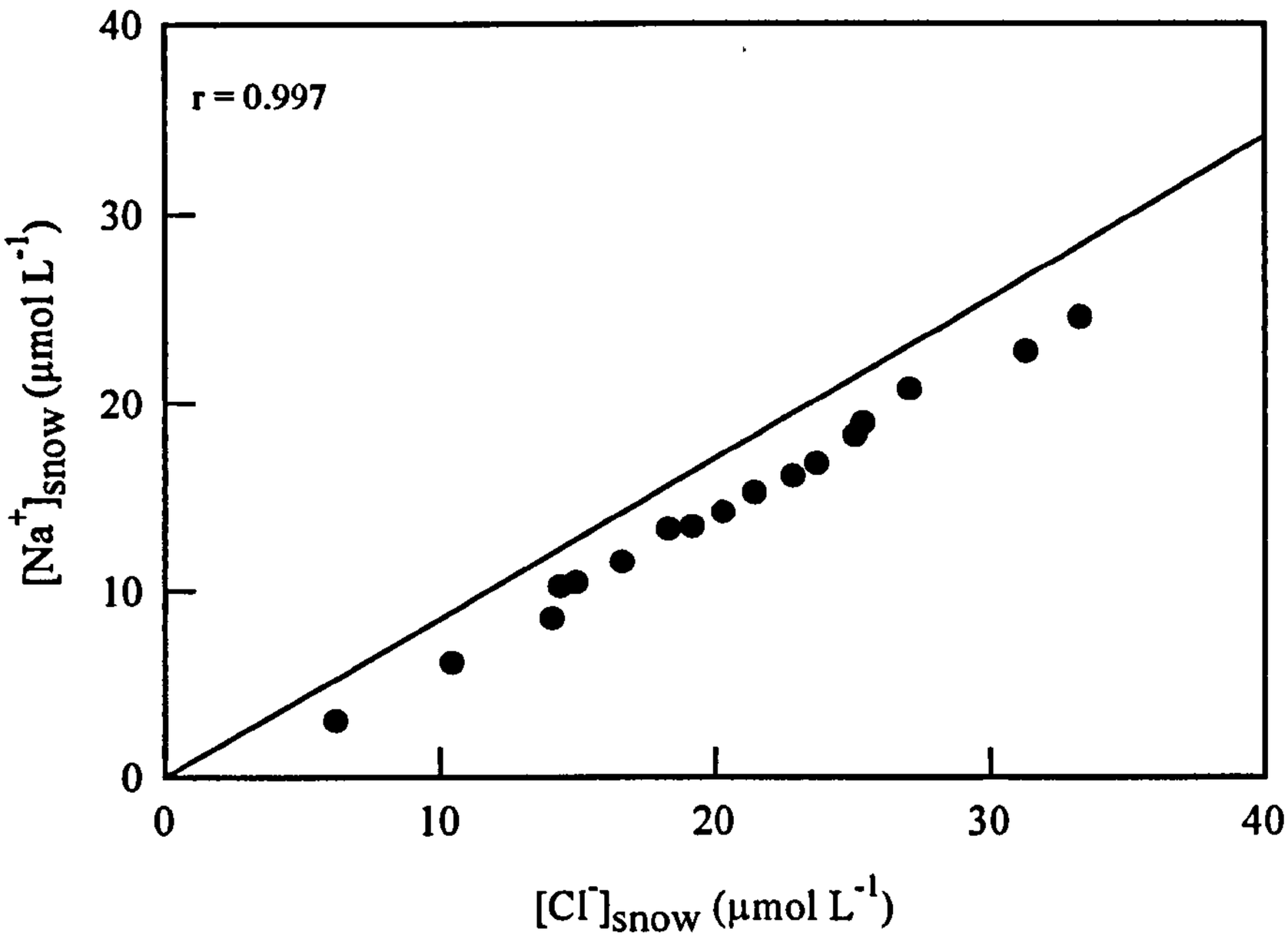


Figure 3.4. $[Na^+]_{snow}$ and $[Cl^-]_{snow}$ at Lake Tumbulovaty, (site 2.2), the northernmost tundra site on Transect 2 during spring 1998. The solid line indicates the molar ratio $[Na^+]:[Cl^-]$ in sea salt (0.85).

Variation in the absolute concentrations but stability in the ratio could be explained by the redistribution of snow by wind at this exposed tundra locality (site 2.2). The ratio was most variable at sites close to Inta (Figure 3.5b) while in the Vorkuta region there was pronounced intra and inter site variation in the ratio on the whole length of the Transect (Figure 3.3a and 3.5a) suggesting that the $[Na^+]_{snow}$ and $[Cl^-]_{snow}$ values were modified by pollution at all sites.

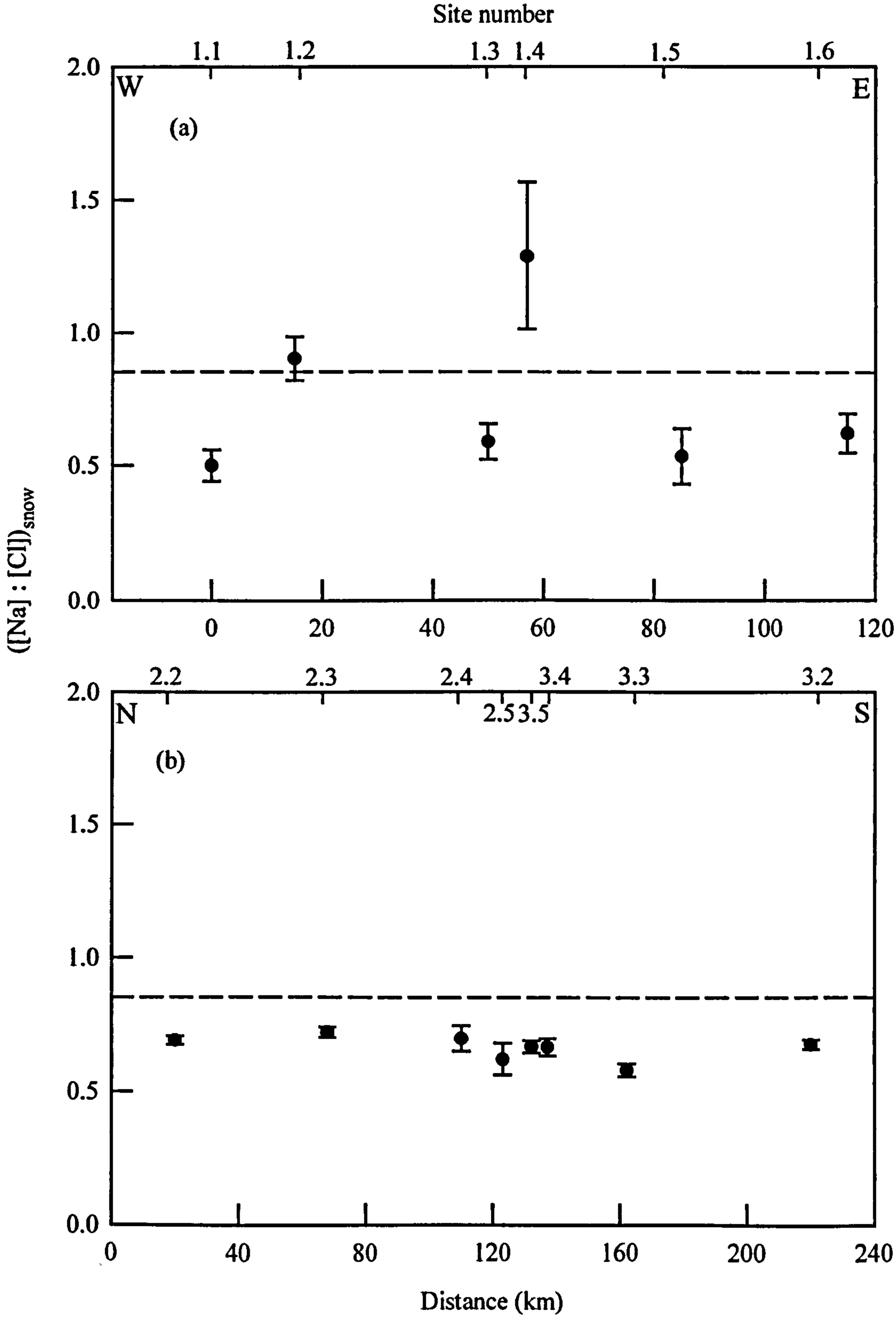


Figure 3.5. Variation in $([Na^+]:[Cl^-])_{snow}$ on Transect 1 (a) and Transect 2/3 (b). Broken lines indicate the molar ratio $[Na^+]:[Cl^-]$ in sea salt (0.85). Plotted values are means ± 1 SE ($n = 18$).

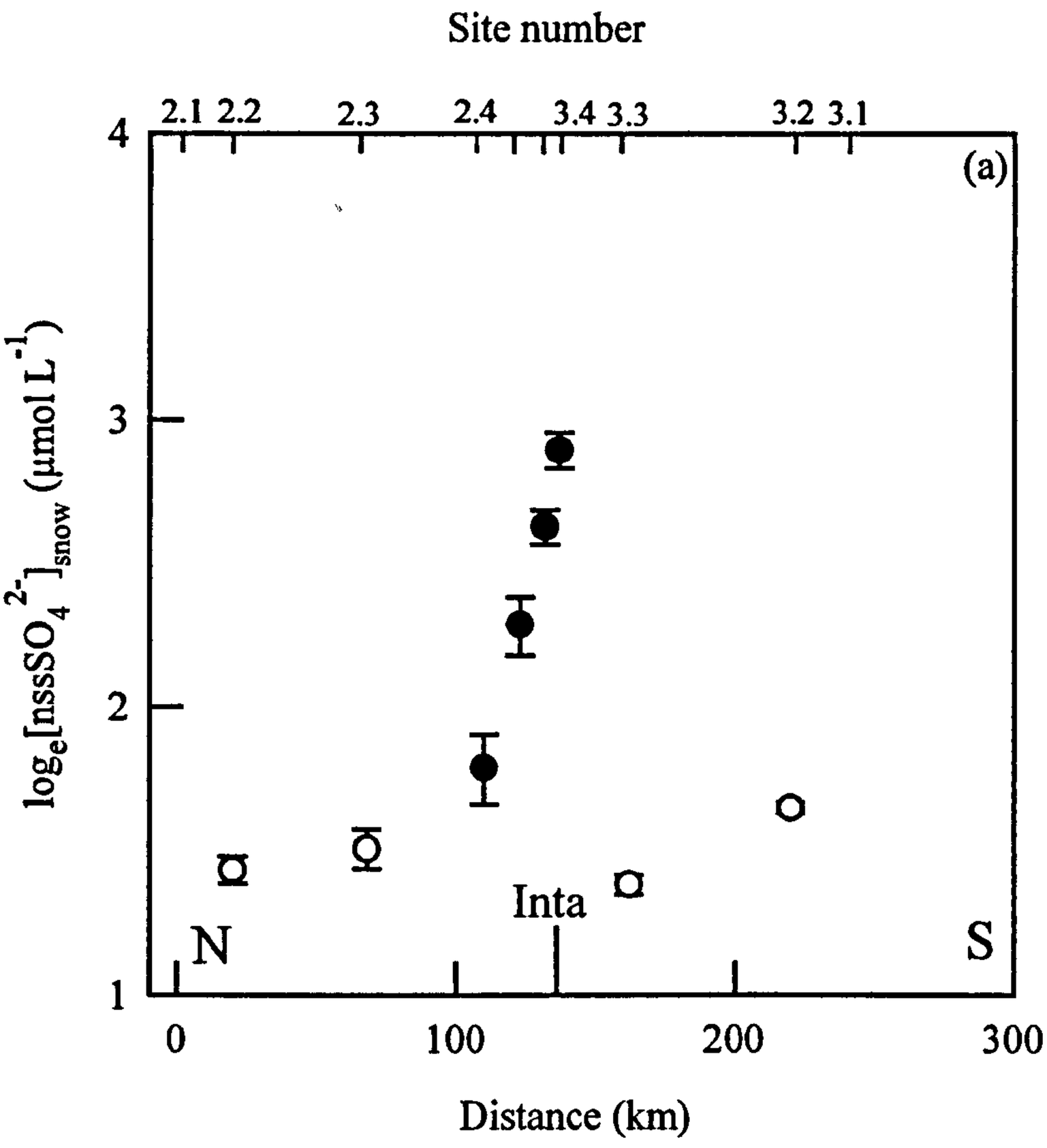


Figure 3.6.a. Variation on Transects 2 and 3 in $[nssSO_4^{2-}]_{snow}$ deposition at sites influenced by 'local' pollution effects (●) and at sites more remote from local pollution effects (○). Plotted values are means ± 1 SE (n = 18).

When non-sea salt sulphate ($nssSO_4^{2-}$) was calculated for sites on the Inta transects there was some evidence of a south to north trend in $[nssSO_4^{2-}]_{snow}$ at 'background' sites remote from Inta, although this trend was not statistically significant (Figure 3.6.a).

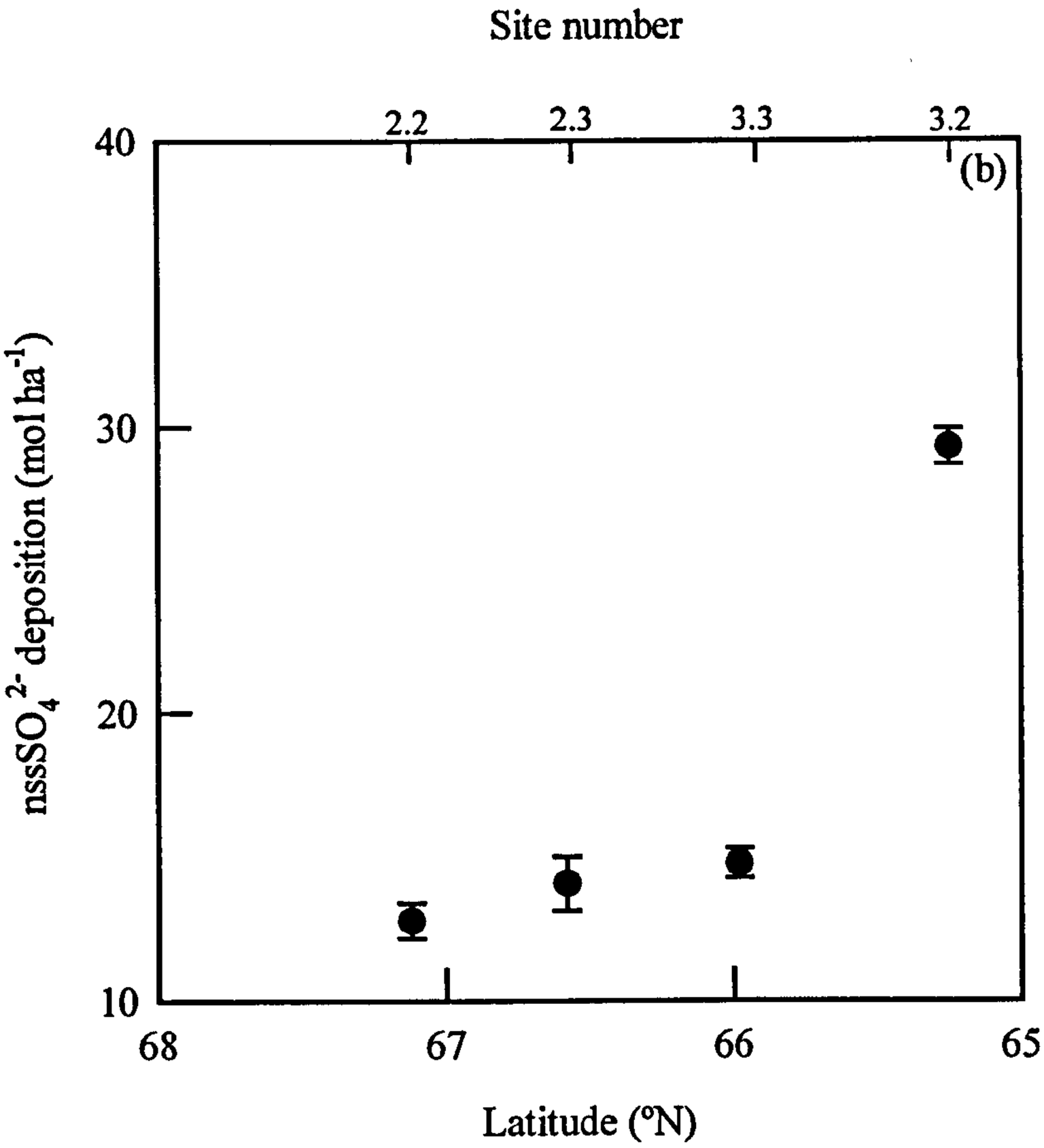


Figure 3.6.b. Variation on Transects 2 and 3 in total winter $nssSO_4^{2-}$ deposition at sites beyond the zone of 'local' pollution. Plotted values are means ± 1 SE ($n = 18$).

However, estimates of winter deposition of $nssSO_4^{2-}$, calculated as the product of $[nssSO_4^{2-}]_{snow}$ and modelled precipitation values from van der Linden and Christensen (*in press*), were negatively related to latitude (Figure 3.6b) (regression analysis after $1/x^2$ transformation: $r^2 = 0.91$, $P < 0.05$, $n = 4$). Concentrations of K^+ and Ca^{2+} in Vorkuta snow samples were also determined (Figure 3.7) in order to understand the basis of observed changes in lichen chemistry near the town. Both elements were present in higher concentrations in snow pack close to the town.

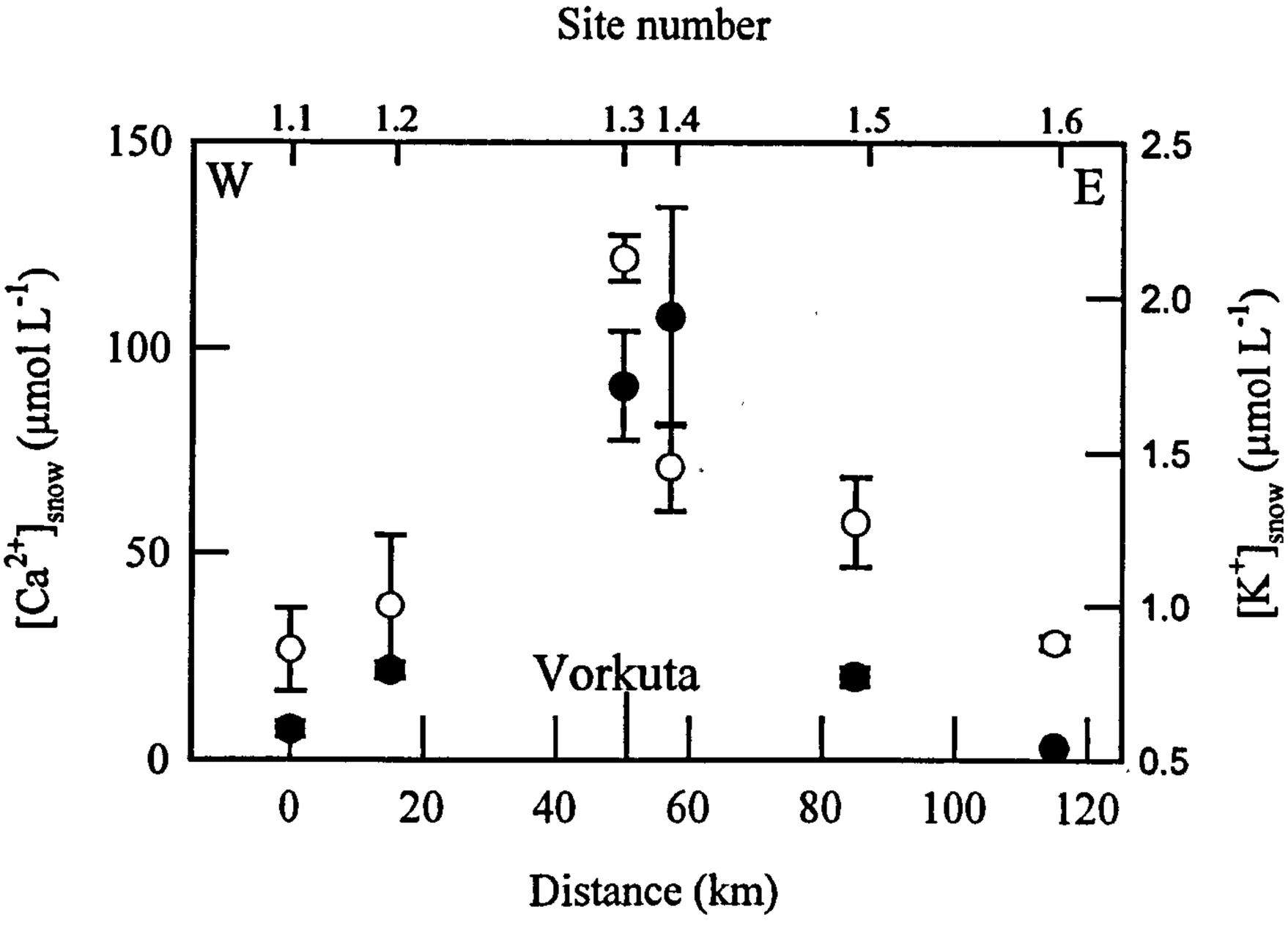


Figure 3.7. Variation in $[Ca^{+}]_{snow}$ (●) and $[K^{+}]_{snow}$ (○) on Transect 1. Plotted values are means ± 1 SE ($n = 18$).

Table 3.1. Summary of lichen species collected and elements analysed on four Transects in the Usa basin.

	Transect No.	Analysis					
		$[N]_{apex}$	$[N]_{base}$	$[Ca^{2+}]$	$[K^{+}]$	$[Mg^{2+}]$	$[Zn^{2+}]$
Cladonia stellaris	1	+	-	-	-	-	-
	2/3	+	+	+	+	+	+
	4	+	-	-	-	-	-
C. rangiferina	2/3	-	-	+	+	+	+
C. arbuscula	1	+	-	+	+	+	+
Flavocetraria cucullata	1	+	-	-	-	-	-

3.3.2. Lichen chemistry

The most complete data sets for lichen chemistry were obtained for *Cladonia stellaris* and *C. rangiferina* on the Inta and Usinsk Transects, and for *C. arbuscula* and *Flavocetraria cucullata* on the Vorkuta Transect (Table 3.1). Mat-forming lichen cover was generally poor in the Vorkuta region due to heavy grazing and trampling by reindeer; for example, *C. stellaris* was largely absent at most sites.

Nitrogen concentration in the apices ($[N]_{apex}$) of *C. stellaris* decreased northwards Transects 2/3 from a value of 0.57 ± 0.01 mmol g^{-1} at site 3.2 in the South to 0.43 ± 0.01 mmol g^{-1} at site 2.1 in the North (Figure 3.8b). The relationship between $[N]_{apex}$ and latitude being statistically significant (r^2 = 0.68, P<0.01, n = 9). There was no relationship between latitude and either $[N]_{base}$ (r^2 = 0.39, P < 0.1, n = 9) or the ratio $[N]_{apex}$:$[N]_{base}$ (r^2= 0.148, P > 1.0, n = 9) (Figure 3.9). Despite the clear spatial variation in $[N]_{apex}$, there was little evidence of N contamination ($[NO_3^-]_{snow}$ values, see Figure 3.1.b) from the town. Values of $[N]_{apex}$ for *C. stellaris* collected along transect 4 were higher than those in the Inta region and showed marked inter-site variation that did not accord with any clear spatial trend (Figure 3.8c). Again, where Transects 2 and 4 intersect, near to sites 2.3 and 4.6 (Figure 2.1, Chapter 2), values of $[N]_{apex}$ were in good agreement (0.55 and 0.57 mmol g^{-1}, respectively). Values of $[N]_{apex}$ in *C. arbuscula* and *F. cucullata* on Transect 1 were positively correlated (r = 0.863, P< 0.02, n = 6) and are significantly (P < 0.001) elevated in the vicinity of the town (Figure 3.8a) although, as in the Inta area, there was no evidence of a comparable trend in $[NO_3^-]_{snow}$ (Figure 3.1.a).

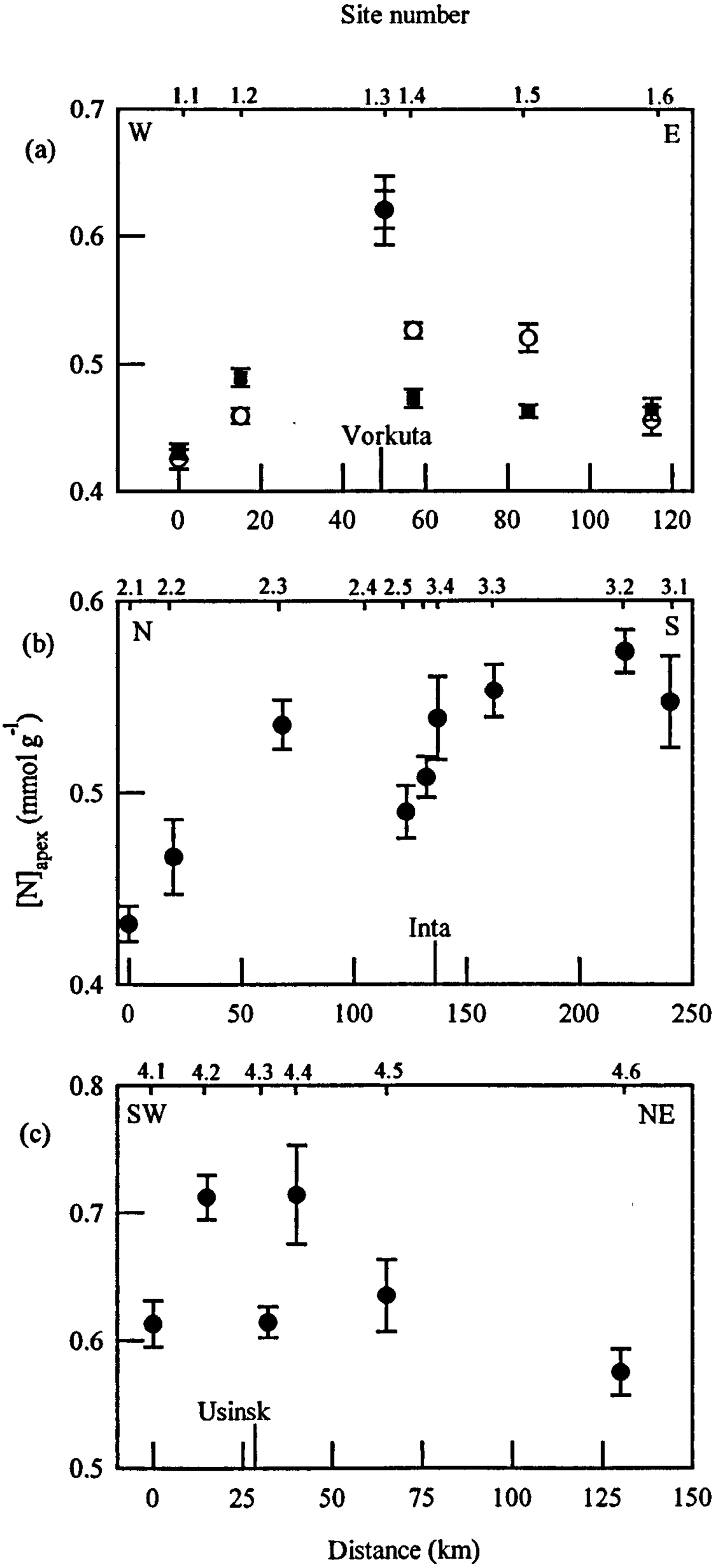


Figure 3.8. Values of $[N]_{apex}$ in *Cladonia arbuscula* (■), *C. stellaris* (●) and *Flavocetraria cucullata* (○) collected on Transects 1, (a), 2/3, (b) and 4, (c). Plotted values are means ± 1 SE (n = 18).

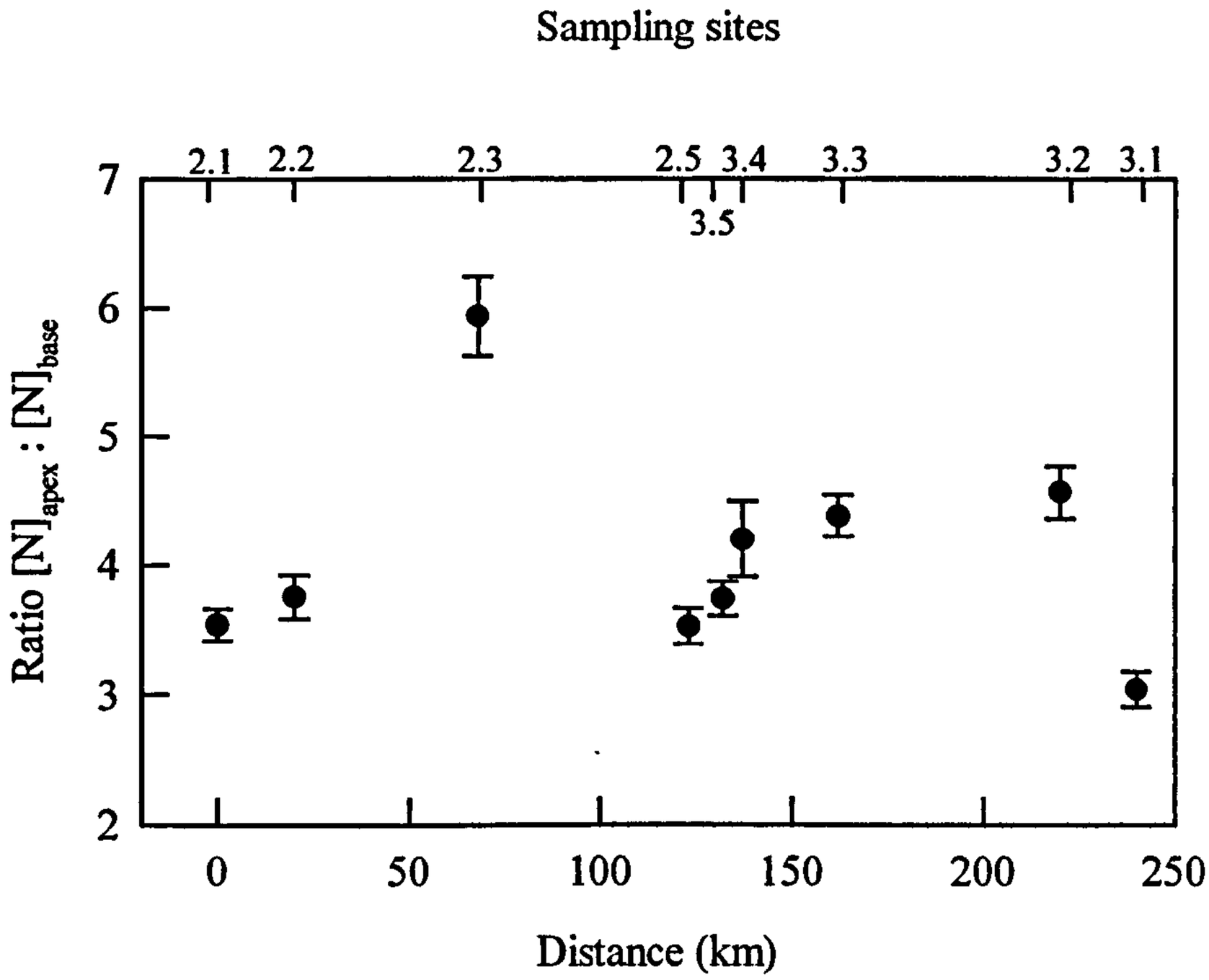


Figure 3.9. The relationship between distance along Transects 2 and 3 (latitude) and the ratio $[N]_{apex} : [N]_{base}$ ($r = 0.148$, $P > 1.0$, $n = 9$).

Zinc was selected as an additional analyte because it was one of several trace metals found to contaminate snow and soils locally in the survey region (Walker *et al.*, 2003). There was localised elevation of $[Zn^{2+}]_{apex}$ in *C. arbuscula* around Vorkuta particularly at sites, 1.3 and 1.4 (Figure 3.10.a). However there was no such elevation in $[Zn^{2+}]_{apex}$ in *C. stellaris* around Inta, but $[Zn^{2+}]_{apex}$ in *C. stellaris* was strongly related to latitude (Figure 3.10.b)($r^2 = 0.77$, $P < 0.005$, $n = 9$). Collections of *C. rangiferina* were incomplete at sampling sites around Inta (Figure 3.10.b), and there was no apparent relationship between $[Zn^{2+}]_{apex}$ and latitude.

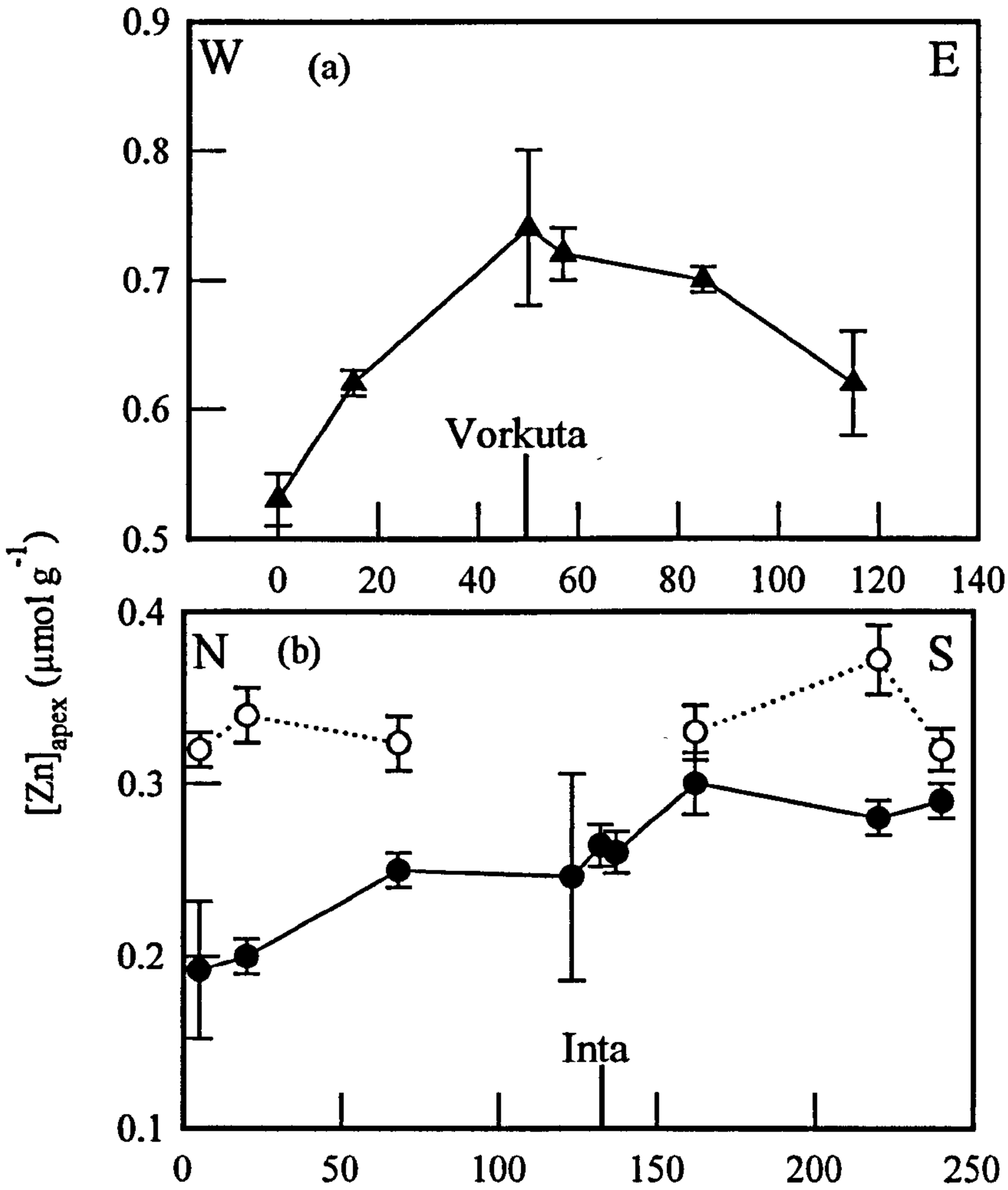


Figure 3.10. Variation in $[Zn^{2+}]_{apex}$ in *Cladonia arbuscula* (▲) along Transect 1 (a) and *C. stellaris* (●) and *C. rangiferina* (○) along Transect 2/3 (b). Plotted values are means ± 1 SE (n = 18).

Variation in $[Zn^{2+}]_{apex}$ in lichens on Transects 1 (Figure 3.11.a) and 2/3 (Figure 3.11.b) was strongly correlated with $[N]_{apex}$ (*C. arbuscula* on Transect 1: $r = 0.90$, $P < 0.01$, $n = 6$; *C. stellaris* on Transects 2/3: $r = 0.91$, $P < 0.001$, $n = 9$).

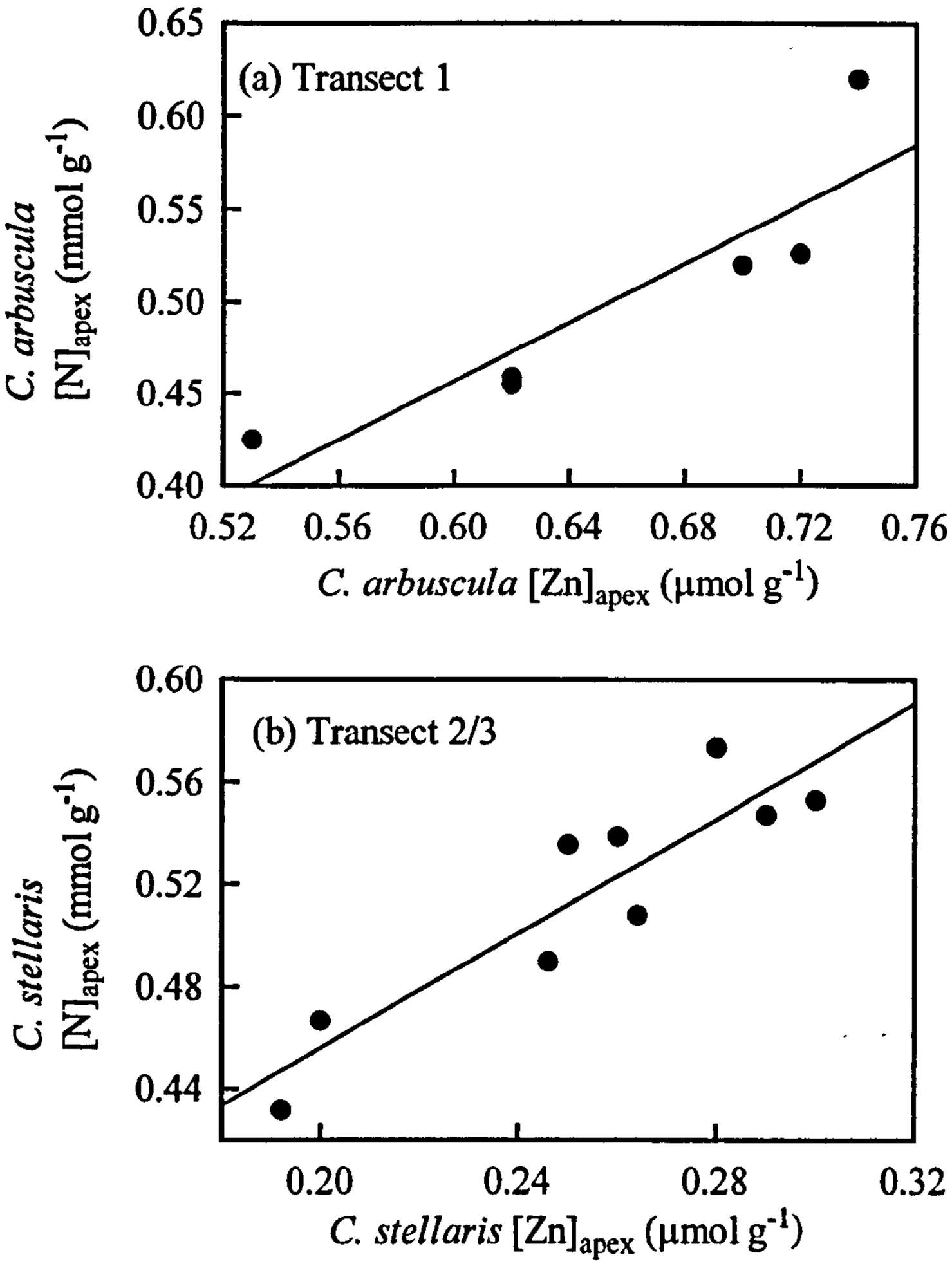


Figure 3.11. Variation in $[Zn^{2+}]_{apex}$ in lichens on Transects 1 (a), and 2/3 (b), with $[N]_{apex}$ (*C. arbuscula* on Transect 1; *C. stellaris* on Transects 2/3).

Figures 3.12a, b shows variation in the concentration of the principal cations in the apices of *C. arbuscula* and *C. stellaris* collected on Transects 1 and 2/3, respectively. The clearest evidence of perturbations in lichen cation content again was found in the close environs of Vorkuta. Concentrations of Ca^{2+} and K^+, and values of the ratio $[K^+]_{apex}$:$[Mg^{2+}]_{apex}$, in the thallus apices were significantly higher, and the ratio $[K^+]_{apex}$: $([Ca^{2+}]+[Mg^{2+}])_{apex}$ was significantly lower, in *C. arbuscula* growing near to the industrial areas, compared to material from the extremities of the Transect ($P < 0.001$). Values of $[K^+]_{apex}$ and $[Ca^{2+}]_{apex}$ and the ratio $[K^+]_{apex}$:$[Mg^{2+}]_{apex}$ were highly positively correlated with pH_{snow}, $[Ca^{2+}]_{snow}$ and $[K^+]_{snow}$ (Table 3.2, Figures 3.7 and 3.12a). A similar degree of inter-site variation in lichen cation ratios was evident along Transect 2/3 through Inta but it did not appear to be related to proximity to the town or latitude (Figure 3.12b). *C. rangiferina* was also collected at six sites on Transect 2/3 in addition to *C. stellaris* and chemical analysis revealed broadly similar inter-site variation in cation concentrations but the covariation between the two species was only significant in the case of $[Ca^{2+}]_{apex}$ ($[K^+]_{apex}$: $r = 0.610$, $P < 0.10$, $n = 6$; $[Ca^{2+}]_{apex}$: $r = 0.747$, $P < 0.05$, $n = 6$) (Figure 3.12c).

Table 3.2. Bivariate Pearson correlation coefficients (*r*) between chemical characteristics of the lichen *Cladonia arbuscula* and snow collected at sites on Transect 1.

	$[K^+]_{snow}$	$[Ca^{++}]_{snow}$	$[SO_4^{2-}]_{snow}$	pH_{snow}
$[N]_{apex}$	0.811***†	0.542*	0.841***	0.671**
$[K^+]_{lichen}$	0.637**	0.732***	0.628**	0.798***
$[Ca^{++}]_{lichen}$	0.655**	0.914***	0.851***	0.908***
$[Mg^{++}]_{lichen}$	-0.426	-0.607**	-0.415	-0.618**
$([K^+]:[Mg^{++}])_{lichen}$	0.480*	0.804***	0.738***	0.718***

† Two-tailed *P* levels are indicated as * < 0.05, ** < 0.01, *** < 0.002. (n = 18).

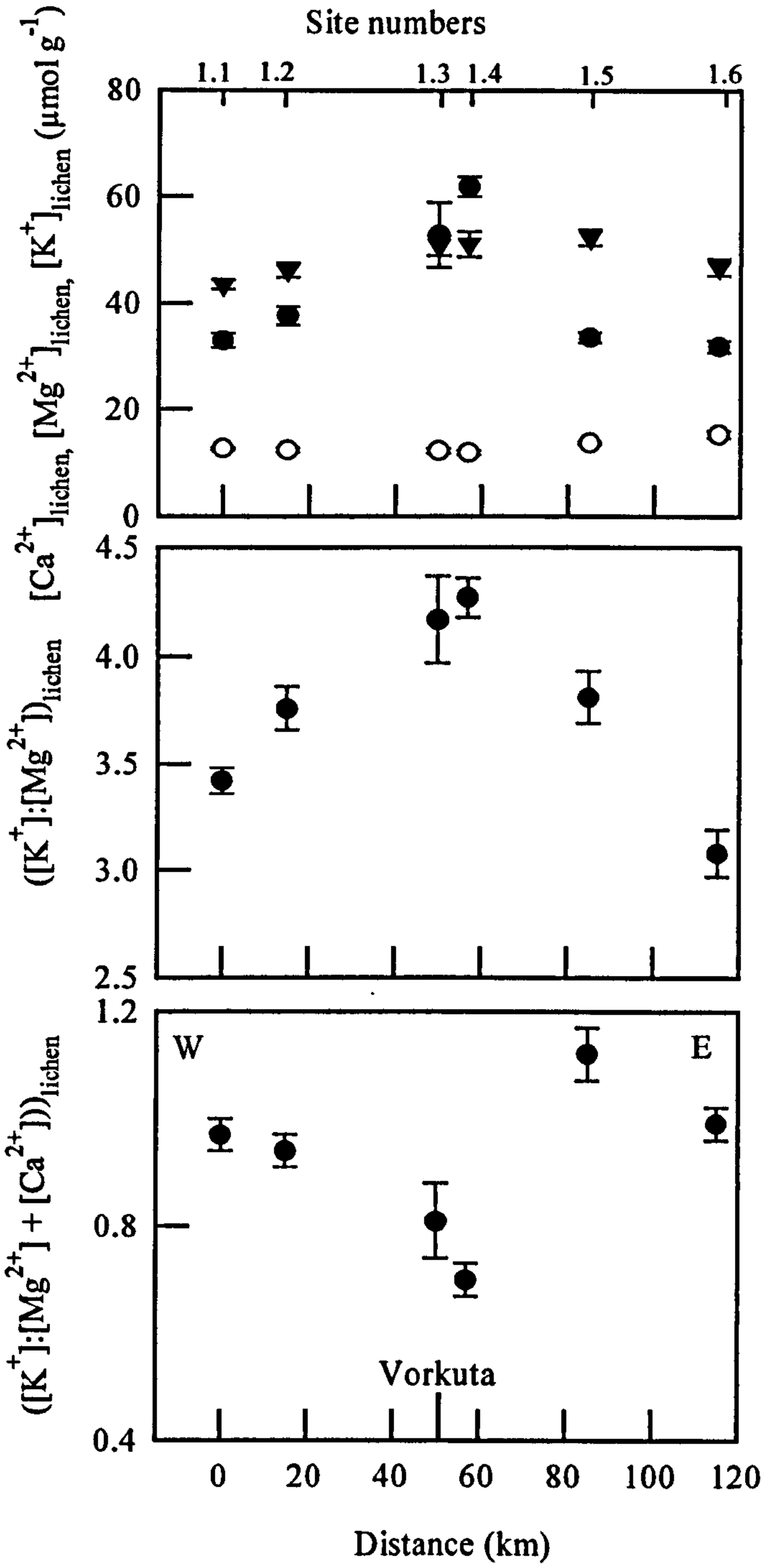


Figure 3.12.a. Variation in $[Ca^{2+}]$ (●), $[Mg^{2+}]$ (○), $[K^+]$ (▼) and ratios $[K^+]:[Mg^{2+}]$ and $([K^+]:([Ca^{2+}]+[Mg^{2+}]))$ in *Cladonia arbuscula* on Transect 1. Plotted values are means ± 1 SE (n = 18).

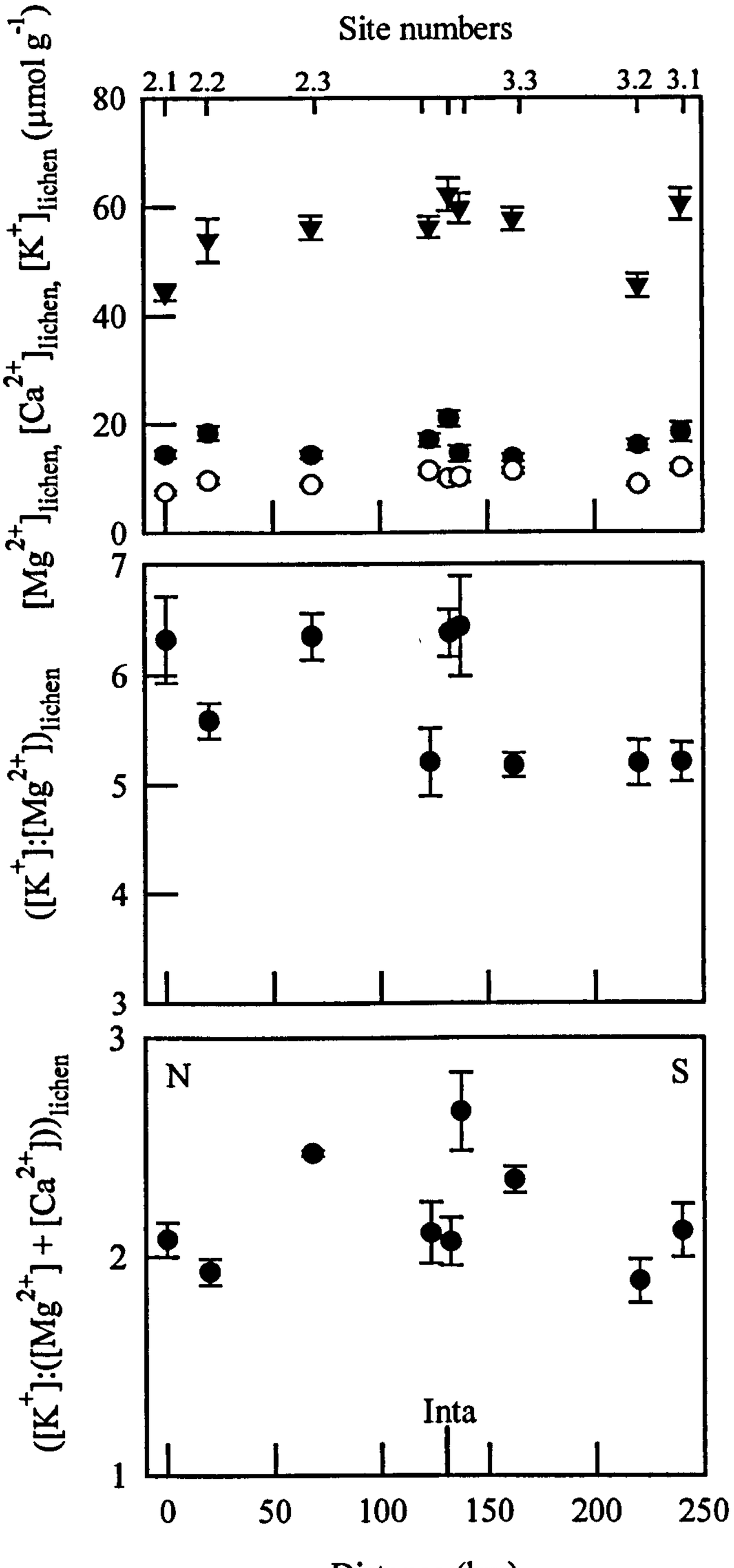


Figure 3.12.b. Variation in $[Ca^{2+}]$ (●), $[Mg^{2+}]$ (○), $[K^+]$ (▼) and ratios $[K^+]:[Mg^{2+}]$ and $([K^+]:([Ca^{2+}]+[Mg^{2+}]))$ in *Cladonia stellaris* on Transect 2/3. Plotted values are means ± 1 SE (n = 18).

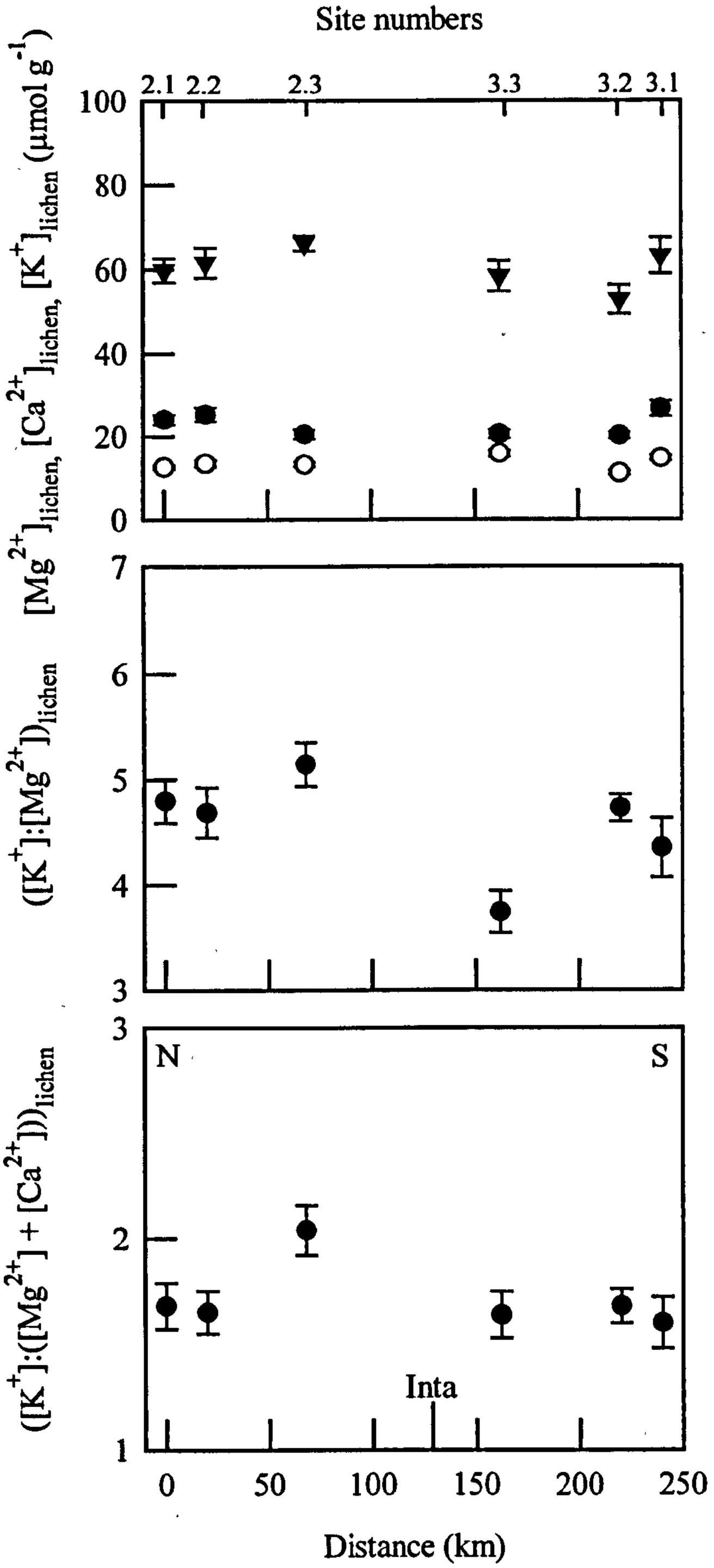


Figure 3.12.c. Variation in $[Ca^{2+}]$ (●), $[Mg^{2+}]$ (○), $[K^+]$ (▼) and ratios $[K^+]:[Mg^{2+}]$ and $([K^+]:([Ca^{2+}]+[Mg^{2+}]))$ in *Cladonia rangiferina* on Transect 2/3. Plotted values are means ± 1 SE (n = 18).

3.4. Discussion

3.4.1. Snow pack chemistry

Baseline SO_4^{2+} and NO_3^- concentrations in winter snowpack across the study area were *c.*5 and 9 μmol L^{-1}, respectively. Note that the low values (i.e. <1) of the ratio $([NO_3^-]:[SO_4^{2-}])_{snow}$ at remote sites are typical of snowpack (cf. Dasch, 1987; Moody and Samson, 1989) and are believed to be due to the low scavenging efficiency of ice (snow crystals) for SO_4^{2-} compared to NO_3^-. These concentrations are comparable with those reported by Jaffe *et al.* (1995a) for remote sites on the eastern Kola Peninsula, by Äyräs *et al.* (1995) for sites in Finnish Lapland (S only) and by Nickus *et al.* (1998), Winiwarter *et al.* (1998) and Puxbaum and Tscherwenka (1998) for the Austrian Alps. However, they are higher than at sites in Alaska and Greenland receiving relatively little pollution from lower latitudes (e.g. in the range *c.*1.2-4.5 and *c.*1.5-3.0 μmol L^{-1} for $[NO_3^-]_{snow}$ and $[SO_4^{2-}]_{snow}$, respectively [e.g. Osada *et al.,* 1996; Fischer *et al.,* 1998]). Simões and Zagorodnov (2001) estimated the true background value of $[nssSO_4^{2-}]_{snow}$ on Svalbard to be *c.*1 μmol L^{-1}. The results of studies around high latitude emission sources in Canada (Barrie and Walmsley, 1978; Barrie, 1980) and Russia (Jaffe *et al.,* 1995a) have shown that only < 2% of total S and N oxide outputs are deposited within 25 km of the sources. Therefore it is likely that the major part of the emissions from Vorkuta, Inta and Usinsk are dispersed over areas with dimensions very much greater than those of the transects studied here, contributing to the observed baseline $[SO_4^{2-}]_{snow}$ and $[NO_3^-]_{snow}$ values. There is evidence that the zone of local pollution around Vorkuta probably extends beyond the extremities of Transect 4 since values of $[SO_4^{2-}]_{snow}$ and pH_{snow}, and concentrations of spheroidal carbonaceous particles in surface lake sediments (Solovieva *et al.,* 2002) were greater at sites 4.1 and 4.6 than at remote sites elsewhere in the study area (e.g. sites 3.1 and 2.1).

In addition to local pollution sources in the Usa basin itself, major industrial regions and emission sources of SO_2 and NO_x exist in the Ural industrial

zone1000 km to the south (e.g. Ryaboshapko *et al.*, 1998). Furthermore, one of the major trajectories along which polluted air masses from Western Europe move into the Arctic passes over the Usa basin (Rahn, 1982; Polissar *et al.*, 1999; Simões and Zagorodnov, 2001). According to Barrie *et al.* (1989) and Xie *et al.* (1999a, b) the northwards pollution flux is probably greater in winter than during summer months. Accordingly, Ryaboshapko *et al.* (1998) have predicted a south to north gradient of decreasing deposition of pollution-derived N and S over the Komi Republic.

Analysis of snow and lichens collected from south to north on transects 2/3 provided an opportunity to seek evidence of such a gradient. Snow samples were collected at all sites between 3.2 and 2.2 at the extremes of the transects, which were located 200 km apart, approximately 20% of the distance between site 2.2 and the Ural industrial zone. While these analyses revealed clear gradients in $[Na^+]_{snow}$ and $[Cl^-]_{snow}$ consistent with varying proximity to the coast there was little evidence of gradients in concentrations of acid ions. However, there is a latitudinal gradient in precipitation (Taskaev, 1997), a recent climate model (van der Linden and Christensen, *in press*) yielding annual values of 1334 and 611 mm at sites 3.2 and 2.2, respectively. Total winter deposition of $nssSO_4^{2-}$ were negatively correlated to latitude (Figure 3.6b) but winter deposition of NO_3^-, H^+ and total SO_4^{2-} were not, although winter deposition of H^+ and total SO_4^{2-} were significantly greater at site 3.2 than at site 2.2 ($P < 0.05$, one-way ANOVA followed by Tukey's test, data not presented). However, a S to N gradient in $[N]_{apex}$ in *C. stellaris* is consistent with a concomitant gradient of decreasing total N deposition of total N. Note that total winter deposition of Na^+ and Cl^- increases northwards despite the counter gradient in precipitation (e.g. relationship between winter Na^+ deposition and latitude: $r^2 = 0.52$, $P = 0.042$, $n = 8$) and that transects 1 and 4 are not orientated along precipitation gradients according to van der Linden and Christensen's (*in press*) modelled data.

Elevated $[SO_4^{2-}]_{snow}$ values in close proximity to Vorkuta and Inta were associated with other changes in snow quality, probably resulting from the deposition of coal ash, including higher pH, and concentrations of K^+, Ca^{2+}

(Figures 3.1.a,b and 3.7), trace metals, particulates and alkalinity (Walker *et al.*, 2003). The link with coal ash is supported by (i) the absence of comparable contamination at sites close to Usinsk where power generation is gas-fired, (ii) the absence of concomitant elevations in $[NO_3^-]_{snow}$ values at all sites although the cluster of high values around Inta does not preclude some contamination at this site, and (iii) layers of black particulate matter visible in snow pits at sites close to Inta and quite widely around Vorkuta. A cement factory in Vorkuta contributes significantly to the snow Ca^{2+} load (Kuliyev, 1977, 1979; Kuliyev and Lobanov, 1979; Getsen *et al.*, 1994; Rusanova, 1995a; Walker *et al.*, 2003). Similarly, Reimann *et al.* (1996) noted that the highest snowpack pH and $[SO_4^{2-}]$ values recorded on the Kola Peninsula occurred close to emission sources, including mining sites, where dust is strongly believed to contaminate snow. Maximum values of $[SO_4^{2-}]_{snow}$ recorded in this study were comparable with the maximum values recorded on the Kola Peninsula and in northern Finland by Jaffe *et al.* (1995a); Äyräs *et al.* (1995); Reimann *et al.* (1996) and Caritat *et al.* (1998), and were only greater than background by a factor of about *c.* 4. The lengths of the transects were generally sufficient to characterize zones of local pollution around the towns although on transect 1 $[SO_4^{2-}]_{snow}$ values remained comparatively high at site 1.6, 60 km downwind of Vorkuta (Figure 3.1.a). Measurements of spheroidal carbonaceous particles made by Solovieva *et al.* (2002) in surface sediments of lakes on the same Transects as those studied here corroborate a wider extent of particulate fallout around Vorkuta. This class of particle, which is an emission product of coal combustion, was present at sites 1.1 and 1.6 at higher concentrations than at any of the other remote sites examined in the study area (e.g. sites 3.2 and 2.2).

3.4.2. Lichen chemistry

There are marked regional gradients in lichen nitrogen concentration in the Usa basin suggesting that there are concomitant gradients in N deposition. On the 240 km south to north transects through Inta (transects 2 and 3), values of $[N]_{apex}$ in *Cladonia stellaris* decrease from 0.57 ± 0.01 mmol g^{-1} at site 3.2, to 0.43 ± 0.01 mmol g^{-1} at site 2.1, a proportional change *c.* 25%. While we

consider that a gradient in N load is the most likely explanation for variation in $[N]_{apex}$ (see Hyvärinen and Crittenden, 1998a), other causal factors cannot be ruled out, thallus growth rate in particular. Higher growth rates might be expected in warmer and moister climates at lower latitudes where greater growth dilution would lower the value of $[N]_{apex}$, a predicted trend that is contrary to that observed. Data on NH_4^+ and organic N concentrations in snow pack and summer rainfall chemistry are required in order to further assess the trends in lichen N concentration.

Elevated $[N]_{apex}$ in *C. arbuscula*, and to a lesser extent in *Flavocetraria cucullata*, in the Vorkuta area suggest elevated N deposition due to local industrial pollution. Variation in $[N]_{apex}$ in *C. arbuscula* correlates well with other pollution signals in snow ($[SO_4^{2-}]_{snow}$, pH_{snow}) and metal contamination in soil (Walker *et al.*, 2003) as well as lichen thalli; for example, values of $[N]_{apex}$ and $[Zn^{2+}]_{apex}$ in *C. arbuscula* were strongly positively correlated along this transect ($r = 0.90$, $P = <0.01$, $n = 6$). As on the other transects, $[N]_{apex}$ was not correlated with $[NO_3^-]_{snow}$. Concentrations of organic N were also determined in a small subset of snow samples from transects 1 and 4 by J.N. Cape (Centre for Ecology and Hydrology, Edinburgh) using an ANTEK 8060 HPLC total N analyser. Molar concentrations of organic N were broadly similar to those of nitrate, except at sites close to Vorkuta where [organic $N]_{snow}$ values were greater than $[NO_3^-]_{snow}$ by a factor of 2 or 3 varying spatially in a manner similar to that of $[SO_4^{2-}]_{snow}$. Thus a higher deposition rate of organic N at sites close to Vorkuta might have contributed to elevated $[N]_{apex}$ in this area. In addition, the possibility cannot be excluded that impaired lichen growth at sites close to Vorkuta, perhaps due to phytotoxic air pollutants, might result in higher tissue N concentration.

Pollution emissions from Inta and Usinsk are considerably lower than from Vorkuta. This is the most likely explanation for the absence of a clear response in $[N]_{apex}$ in lichens close to Inta and Usinsk. However, even on transects 2/3 and 4 some of the higher $[N]_{apex}$ values were recorded in close proximity to the towns raising the possibility that the effects of N pollution here are close to detection limits. A lack of elevated $[NO_3^-]_{snow}$ around Vorkuta but elevated

$[N]_{apex}$ values in lichens may be explained by variation in elevated $[NO_3^-]_{soil}$ which may be governed by local site characteristics (Kashulina *et al.*, 1998). It should be emphasized that the data for snowpack chemistry provides data for a single winter period, whereas $[N]_{apex}$ values probably provide an indication of N deposition integrated over a period of at least 1 - 2 y. Furthermore, the above interpretations are made in the absence of commensurate data on $[NH_4^+]_{snow}$.

Terricolous mat-forming lichens are ubiquitous throughout the Subarctic and the present results are consistent with those of Søchting (1990) and Hyvärinen and Crittenden (1998a) in suggesting that they provide a useful reporter for N deposition. Hyvärinen and Crittenden (1998a) found that $[N]_{apex}$ in *C. portentosa* covaried with N deposition but not $[N]_{precipitation}$. Thus, in the present study the lack of covariation between $[NO_3^-]_{snow}$ and $[N]_{apex}$ in *C. stellaris, C. arbuscula* and *F. cucullata* does not vitiate a relationship between $[N]_{apex}$ and N deposition. Values of $[N]_{apex}$ in *C. arbuscula* and *C. stellaris* collected in the Usa basin varied between 0.4 - 0.7 mmol g^{-1}. These values can be compared with the range of 0.5 - 1.0 mmol g^{-1} for $[N]_{apex}$ in *C. portentosa* recorded in the British Isles at sites subject to a range of annual wet-deposited N loads varying from 71 - 1007 mol N ha^{-1} yr^{-1} ($NH_4^+ + NO_3^-$) (Hyvärinen and Crittenden, 1998a). The difference between these concentration ranges may reflect a physiological difference between species but more likely reflects higher N deposition rates in industrial Europe. In Hyvärinen and Crittenden's (1998a) survey of *C. portentosa* in the British Isles, $[N]_{base}$ (for the same thallus stratum as analysed in the present study) was found to fall in the range 0.1 - 0.5 mmol g^{-1}. This can be compared to $[N]_{base}$ values for *C. stellaris* on Transect 2/3 of 0.1 - 0.2 mmol g^{-1}. Hyvärinen and Crittenden (1998a) found that the relationship between $[N]_{apex}$ and annual total N deposition was significant but that $[N]_{base}$ was an even stronger correlate. It is not known why $[N]_{base}$ should correlate well with N deposition in one region and $[N]_{apex}$ to be apparently more responsive in another; here again, a species difference cannot be ruled out. It is also possible that $[N]_{apex}$ is a more coherent indicator of N deposition in highly oligotrophic regions while $[N]_{base}$ correlates better in regions with higher N loads.

Hyvärinen and Crittenden (1996) found that the ratio of $([K]:[Mg])_{apex}$ in the heathland lichen *C. portentosa* was a good index of $[H^+]$ in precipitation in the British Isles while the ratio $([K]:([Mg] + [Ca]))_{apex}$ was not. However, in the present study, $([K]:[Mg])_{apex}$ values in *C. arbuscula* were higher in the vicinity of Vorkuta but in this case it was apparently a response to deposition of alkaline ash. This change in lichen chemistry was associated with elevated concentrations in snow of a range of anions and cations, including heavy metals (Walker *et al.*, 2003), probably as a result of coal ash deposition. Thus in this region the $([K]:[Mg])_{apex}$ marker appears to have responded to elevated K deposition while the ratio $([K]:([Mg] + [Ca]))_{apex}$ has probably responded to emissions of Ca-rich particulates from coal burning at the power station and nearby cement factory (Figure 3.7)(cf. Jalkanen *et al.*, 2000). These findings demonstrate that these indirect lichen indices for acid deposition can be seriously confounded by enhanced deposition of alkali and alkaline-earth cations from pollution sources. Neither $([K]:[Mg])_{apex}$ nor $([K]:([Mg] + [Ca]))_{apex}$ in *C. stellaris* were higher at the southernmost sites on Transect 2/3 than at northernmost sites, suggesting that latitudinal differences in mean precipitation acidity, if any, were insufficient to modify lichen chemistry.

There was localised elevation of $[Zn^{2+}]_{apex}$ in *C. arbuscula* around Vorkuta and $[Zn^{2+}]_{apex}$ in *C. stellaris* around Inta, was strongly related to latitude. However, lowest concentrations of $[Zn^{2+}]_{apex}$ were comparable with other studies in pristine locations (Table 3.3) whilst elevated concentrations around Vorkuta are as high as concentrations found in *Cladonia* species around coal mining towns and zinc smelters. According to Folkeson and Andersson-Bringmark (1988) $[Zn]_{apex}$ measured in *C. rangiferina* sampled 6-7 km away from foundries in Gusun, Sweden were 55-75 $\mu g\ g^{-1}$ whilst the first sign of reduction of cover of *C. rangiferina* was observed when the $[Zn]_{apex}$ was 500 $\mu g\ g^{-1}$. Folkeson and Andersson-Bringmark (1988) suggested that a $[Zn]_{apex}$ limit of 600 $\mu g\ g^{-1}$ indicated the apparent threshold concentration for survival. The $[Zn]_{apex}$ observed in this study fall far below the threshold likely to cause damage to the lichen species sampled, even around the Vorkuta industrial complex where elevated concentrations were observed.

Table 3.3. Comparisons of $[Zn]_{apex}$ ($\mu g\ g^{-1}$) from high latitude industrial and pristine areas.

Location	Species	[Zn] ($\mu g\ g^{-1}$)	Study
Inta (Transects 2/3)	*C. rangiferina*	15-34	This study
	C. stellaris	9-32	
Vorkuta (Transect 1)	*C. arbuscula*	16-55	
Southern Finland	*C. stellaris*	38	Lounamaa (1965)
Delaware Gap, USA (zinc smelter)	*Cladonia* sp.	61-80	Nash (1975)
SE Ohio, USA (coal mining)	*Cladonia* sp.	27-42	Lawrey and Rudolf (1975)
Northwest Territories, Canada	*Cladonia* sp.	7-55	Puckett (1978)
	Cladonia sp.	16-25	Puckett and Finegan (1980)
Sudbury, Ontario, Canada (85-940 km from smelter)	*Cladonia* sp.	25-11	Glooschenko *et al.*, (1981)
Bellsund area, Spitzbergen	*Cladonia* sp.	29-39	Józwik (1990)
High Point Park, New Jersey, USA	*C. rangiferina*	7-16	Glenn *et al.*, (1991)
Ontario, Canada, Uranium mines (0.5-30 km)	*C. mittis*	13-22	Fahselt *et al.*, (1995)

3.5. Conclusions

Presented here is evidence of pollution gradients across the Usa basin on two geographical scales. The first is a latitudinal gradient in N and S deposition probably resulting from northward-moving air-masses originating from industrial regions of the Urals and Western Europe (Rahn, 1982; Ryaboshapko *et al.*, 1998) but with some contribution from more widely dispersed emissions from local sources. The second is local gradient in alkalisation extending to 25-40 km around the coal-burning centres of Vorkuta and Inta.

Baseline concentrations of NO_3^- in snowpack observed in this study were *c.* 9.2 μmol L^{-1}, and $[nssSO_4^{2-}]_{snow}$ values on Transects 2/3 were between 4.0 - 5.2 μmol L^{-1}. Using as a multiplier total annual precipitation values at each site modelled by van der Linden and Christensen (*in press*) yields annual depositions in the ranges of 56 - 123 mol N ha^{-1} y^{-1} and 29 - 65 mol nssS ha^{-1} y^{-1}. These values can be compared to published estimates of critical loads of N and S for Subarctic and Arctic ecosystems bearing in mind that nitrate deposition might be lower than total N deposition by a factor of at least two. Hornung *et al.* (1995) proposed that the critical load for N in Arctic and alpine heathlands was in the range 375 - 1071 mol N ha^{-1} y^{-1} while, on the basis of N fertilization experiments on Svalbard, Gordon *et al.* (2001) suggested that the critical load value is likely to be towards the lower end of this range. Bashkin *et al.* (1995) produced critical load maps for N and S over northern Siberia where the most sensitive ecosystems have critical load values <50 mol ha^{-1} y^{-1} for both N and S but with many areas with values in the range 51 - 100 mol ha^{-1} y^{-1}. Bashkin (1997) produced critical loads maps for European Russia suggesting that *c.* 50% of Subarctic and Arctic areas have critical loads for N in the range 0 - 200 mol ha^{-1} y^{-1}. While for S, only 2% of the region had a critical load in the 0 - 200 mol ha^{-1} y^{-1} range, and 31% of the region had values of 200 - 500 mol ha^{-1} y^{-1}. Lien *et al.* (1993) reports that the most sensitive surface waters on Svalbard have a critical load for nssS of between 59 - 309 mol ha^{-1} y^{-1}. Clearly there is still uncertainty about critical load values but current knowledge suggests that N deposition over the Usa basin could already exceed the critical load in some ecosystems.

There is now compelling evidence that tundra vegetation in the vicinity of Vorkuta has become modified due to alkaline dust pollution. Vegetation classification and mapping studies using satellite data suggest that the affected area is between 600 - 900 km^2 and is characterised by an increased abundance of willow and reduced abundance of dwarf birch and other dwarf shrubs (Virtanen *et al.*, 2002). Within this affected region a high impact zone is recognized in the immediate vicinity of the town and industrial complexes covering 150 - 200 km^2; here lichens are largely absent and mosses and grasses have a greater abundance. The causal agency may be complex

interactions between alkalisation, eutrophication, phytotoxic gases (e.g. SO_2) and heavy metal deposition (Walker *et al.*, 2003). In addition, deposition of black particulates in snow will accelerate spring snow melt due to reduction in albedo (average freezing point depression due to salts was <0.001 °C in all cases); evidence for such an effect again comes from satellite images (Virtanen *et al.*, 2002). Earlier spring thaw could have both positive and negative effects (e.g. longer growing season and increased exposure to frost, respectively). However, it is interesting to note that these vegetation changes in the Vorkuta area are similar to those observed to occur in response to N enrichment (Paal *et al.*, 1997). Data for [N] in lichen thalli and organic N concentrations in snow lend further support to an N enrichment hypothesis. Emissions from Vorkuta (currently 37 x 10^6 kg SO_2) have probably declined markedly since the 1980s when annual coal production peaked at 20 x 10^6 tonnes (Virtanen *et al.*, 2002). The results of a stratigraphical analysis of carbonaceous particles in two lake bottom sediments in two lakes in the Vortuka region corroborates this historical trend suggesting that maximum emissions of combustion products were probably reached several decades ago, since when output has declined (Solovieva *et al.*, 2002). It is not known to what extent the modified vegetation is a relic of a former and more severe pollution climate in this region. Such obvious impacts of local dust pollution were not evident around Inta (T. Virtanen, *pers. com.*) probably because (i) emissions from this source are considerably less than from Vortuka and (ii) Inta is in the forest-tundra zone where impacts may be less apparent from satellite data.

CHAPTER 4. ANTHROPOGENIC METAL ENRICHMENT OF SNOW AND SOIL IN NORTH-EASTERN EUROPEAN RUSSIA

4.1. Introduction

This Chapter reports the trace metal composition of winter snowpack, snow-melt filter residues and top-soil samples in the Usa Basin, north-east European Russia. The research was a contribution to TUNDRA (TUNdra Degradation in the Russian Arctic). The study area has a total surface area of 93,000 km^2. The region has been subject to a range of industrial impacts, producing variation in land use from pristine uninhabited areas to densely populated areas of industrialisation including oil and gas fields, coal and ore mining. The objective of the study was to provide information on the distribution and magnitude of trace metal composition in snow and soil resulting from fossil fuel combustion and petrochemical industrial processes within the Usa Basin.

Previous pollution studies in the region have been conducted in the immediate vicinity of towns such as in the Bolshezemel'skaya tundra around Vorkuta (Kuliyev, 1977, 1979; Kuliyev and Lobanov, 1979; Getsen *et al.*, 1994; Rusanova, 1995a, b). Heavy metal pollution within the Usa basin is associated with power generation (coal combustion), cement production, coal mining, gas and oil extraction, forestry, pulp and paper production, construction and oil refineries (State of the environment of the Komi Republic, 1992-1998). The region has already been identified as a significant source of acid and alkaline emissions (Ottar, 1989; Nenonen, 1991; Getsen *et al.*, 1994; Rusanova, 1995a, b; Vinogradova, 2000), mainly as a result of coal fired power stations in Vorkuta and Inta and a gas-fired power station in Usinsk.

The variables measured were, snow, which was analysed for Ag, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr and Zn using ICP-MS (Ca and K by F-AAS for Vorkuta only), pH and acidity/alkalinity. Filter residues were analysed for: Al, Ba, Ca, Cd, Cu, K, Mg, Mn, Ni, Pb, Sr and Zn using F-AAS and GF-AAS; top-soil samples were analysed for Ba, Cu, Mg, Mn, Na, Ni, Pb, Sr, Zn using

F-AAS. The analysis of the chemical composition of snow provides useful information on aerosol chemistry and long-range distribution patterns of anthropogenic substances emitted into the atmosphere (Tranter *et al.*, 1986, 1988; Jaffe and Zukowski, 1993; Shaw *et al.*, 1993; Colin *et al.*, 1997). Concentrations of dissolved elements in melted and filtered snow may be used to estimate deposition during winter. However, total deposition can be seriously underestimated if particulates within the snow are omitted and so analysis of filter residues was included in this study (Reimann *et al.*, 1996; Gregurek *et al.*, 1998a). Analysis of the underlying soil can be used to evaluate long term accumulation of conserved pollutants (Boyd *et al.*, 1997; Niskavaara *et al.*, 1997; Reimann *et al.*, 1997a,b, 1998, 2000).

The results presented here indicate elevated concentrations of elements associated with alkaline combustion ash around the coal mining towns of Vorkuta and Inta. There is little evidence of deposition around the gas and oil town of Usinsk. Atmospheric deposition in the vicinity of Vorkuta, and to a lesser extent Inta, added significantly to the soil contaminant loading as a result of ash fallout. Acid deposition was associated with pristine areas whereas alkaline combustion ash near to emission sources more than compensated for the acidity caused by SO_2. The probable underlying causal factors are discussed.

4.2. Materials and methods

4.2.1. Study area and sampling regime

For a more detailed description of the study area and sampling regimes see Chapter 2 (2.1.1; Figure 2.1; Table 2.1). Study sites were located in the Usa river basin between latitudes 64° and 68° N in the Komi Republic, north-east European Russia. Four transects through suspected point sources were undertaken to assess the distribution of pollutants from coal mining and burning in Vorkuta and Inta (Figure 4.1) and from oil and gas extraction and use in Usinsk. Thus, transects were established through the three principal

towns of Vorkuta (67°30'N, 64°05'E; Transect 1), Inta (66°03'N, 60°10'E; Transect 2 and 3) and Usinsk (66°01'N, 57°30'E; Transect 4) (see Figure 2.1; Tables 2.1 and 2.2).

4.2.2. Snow sampling

For further details of snow collection methods see Chapter 2 (2.2.1).

(a)

(b)

Figure 4.1. (a) Coal combustion at Inta and (b) Vorkuta. (Photos: T. R. Walker).

4.2.3. Soil sampling

Soil samples were collected between July and August in 1998 and 1999 from a 20 x 20 cm quadrat with a stainless steel hand trowel to a standard depth of 5 cm (Niskavaara *et al.*, 1997; Reimann *et al.*, 1997a). Powder-free polythene gloves were used at all times to minimise the risk of contamination. See Chapter 2 (2.2.3) for further details on soil collection.

Approximately 20 km beyond the northern most site at Khosedayu river, 2.1, (see Figure 2.1, Table 2.1) on transect 2/3 an additional set of top-soil samples were collected along the Upper Kolva river during July 2000.

4.2.4. Chemical analysis of snow

For further details on the chemical analysis of snow see Chapter 2 (2.4). Analysis of trace metals: Ag, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr and Zn were conducted on acidified liquid samples by inductively coupled plasma mass spectroscopy (ICP-MS) at the University of Lancaster by Dr Hao Zhang. Cations (Na^+, Ca^{2+}, K^+) were determined by flame emission spectrometry (FES) with appropriate additions of CsC1 as ionisation suppressant (1000 mg Cs L^{-1}).

4.2.5. Elemental analysis of suspended solids in snow

Details of elemental analysis of suspended solids in snow are given in Chapter 2 (2.4.5). Cellulose acetate membrane filters used to filter the snow-melt samples were oven dried at 80 °C overnight in glass petri-dishes and suspended solids were determined gravimetrically. Six cellulose acetate membrane filters from each site were digested and elemental analysis of Al, Ba, Ca, Cd, Cu, K, Mg, Mn, Ni, Pb, Sr and Zn was undertaken by GF-AAS and F-AAS. Concentrations were recalculated in relation to the volume of filtered meltwater to allow direct comparison with the solution data (Reimann

et al., 1996). Net acidity or alkalinity was determined by granplot acid titrations following the method of Legrand *et al.* (1982), see Chapter 2 (2.4.2).

4.2.6. Soil analysis

Details of soil analysis are given in Chapter 2 (2.6). Analysis of Ba, Cu, Mg, Mn, Na, Ni, Pb, Sr and Zn was undertaken using GF-AAS and F-AAS. Soil pH was measured on moist soil samples, suspended in DI water at a solid : solution ratio of 1 : 2.5 following equilibration for 1 hour. All soil samples were subsequently incinerated in accordance with the terms of the MAFF (DEFRA) licence for soil importation.

4.2.7. Elemental concentrations in snow and soil

Elemental concentrations in snow (including suspended solids) and soil were considered together in an attempt to explain the large concentrations found around the cities in relation to current deposition rates (see Chapter 2, 2.7; Equation 2.8).

4.3. Results and discussion

4.3.1. Acidity and alkalinity in filtered snow-melt

Results of Granplot titrations shown in Figure 4.2 illustrate pronounced alkalinity associated with ash deposition around Vorkuta. This was also reflected in the snow pH measurements (data shown in Chapter 3). Alkalinity values were greatest at site 1.4 (mean = 0.139 meq L^{-1}; ± 0.015). Only sites 1.1 and 1.6 at the transect extremes showed net acidity. By contrast, net acidity was recorded at all locations on the Usinsk transect. For the Inta transects (2/3) alkaline ash deposition around the city (sites; 2.4, 2.5, 3.5, 3.4) effectively neutralised any local acidity and the background acidity shown in pristine snow (approximately -0.01 meq L^{-1}).

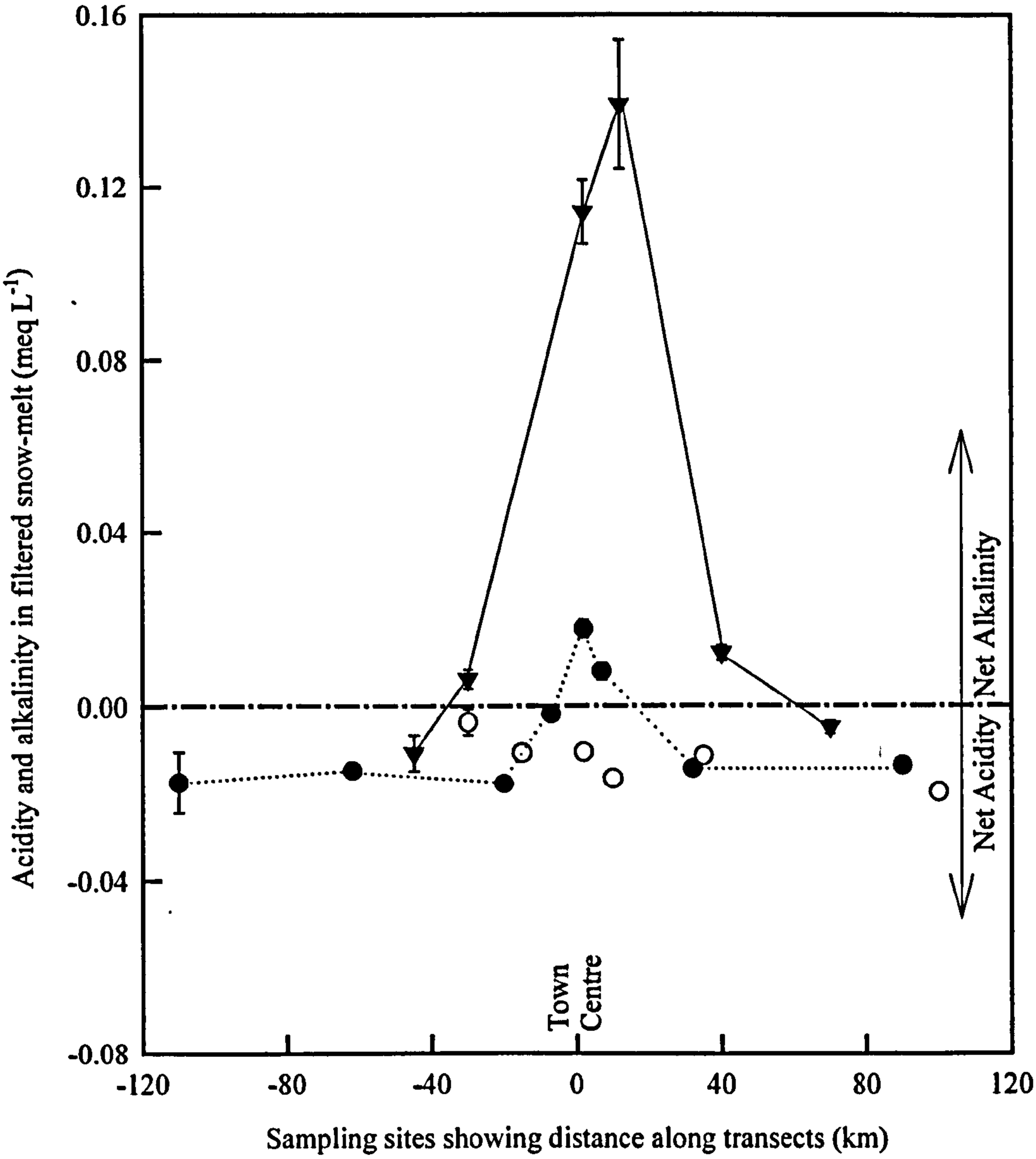


Figure 4.2. Values of granplot acid titrations determined for filtered snow-melt samples taken along transects through the industrial towns of Vorkuta (▼) , (running W - E), Inta (●), (running N - S) and Usinsk (○), (running SW - NE) during spring 1998 and 1999. Plotted values are means ± SE (n = 18).

4.3.2. Elemental analysis of filtered snow-melt (Figures 4.3.a. and 4.3.b.)

No evidence of previous snow-melt was observed in the snow profiles; characteristic horizontal ice layers were absent (Barrie and Walmsley, 1978; Shaw *et al.*, 1993). Along transects through Vorkuta and Inta snow collected at

sites closest to the towns contained elevated concentrations of As, Ba, Mn and Sr. In addition elevated concentrations of Ca and K in snow were found around Vorkuta (Figure 4.3.a), which may suggest that combustion ash was the source (Reimann *et al.,* 1996). Arsenic concentrations were greatest at the urban sites around Vorkuta (sites, 1.3 and 1.4) and lower, respectively, in Inta and Usinsk and concentrations of the trace metals Cd, Cu, Ni, Pb and Zn were uniformly low at all sites (Figure 4.3.b). However, the absence of a pronounced urban peak in solution concentration may have been a result of adsorption on alkaline ash. In addition, concentrations of Ba, Co, Cu, Sr and Zn were slightly greater in Inta than around Vorkuta, possibly because the town's coal-fired power plant was closer to those sampling sites. At the most southerly site on the Inta transect (site, 3.2) unusually large concentrations of Cu, Pb and Zn occurred in the vicinity of the Polar Ural Mountains, perhaps suggesting a local geogenic source or possibly even long-range transport from lower latitudes. Close to Usinsk (site, 4.3) there was minor elevation of Pb concentrations, compared to those of background values, but other metals were found at background concentrations around the town. Along all transects Co concentrations were uniformly low (< 0.10 $\mu g\ L^{-1}$) (Figure 4.3.b). For Ag (data not shown), Al and Cr urban peaks were not observed; concentrations ranged from 0.17 - 0.39, 3.3 - 18.3 and 0.03 - 0.3 $\mu g\ L^{-1}$ respectively.

4.3.3. Suspended solids in snow

At most sites on the Vorkuta transect, and at sites close to Inta, dark horizontal bands were observed in many of the snow profiles, probably the result of ash and soot deposition from coal combustion during periods of snow-fall. This was also evident when snow-melt was filtered through cellulose acetate filters (Figures 4.4.a, b).

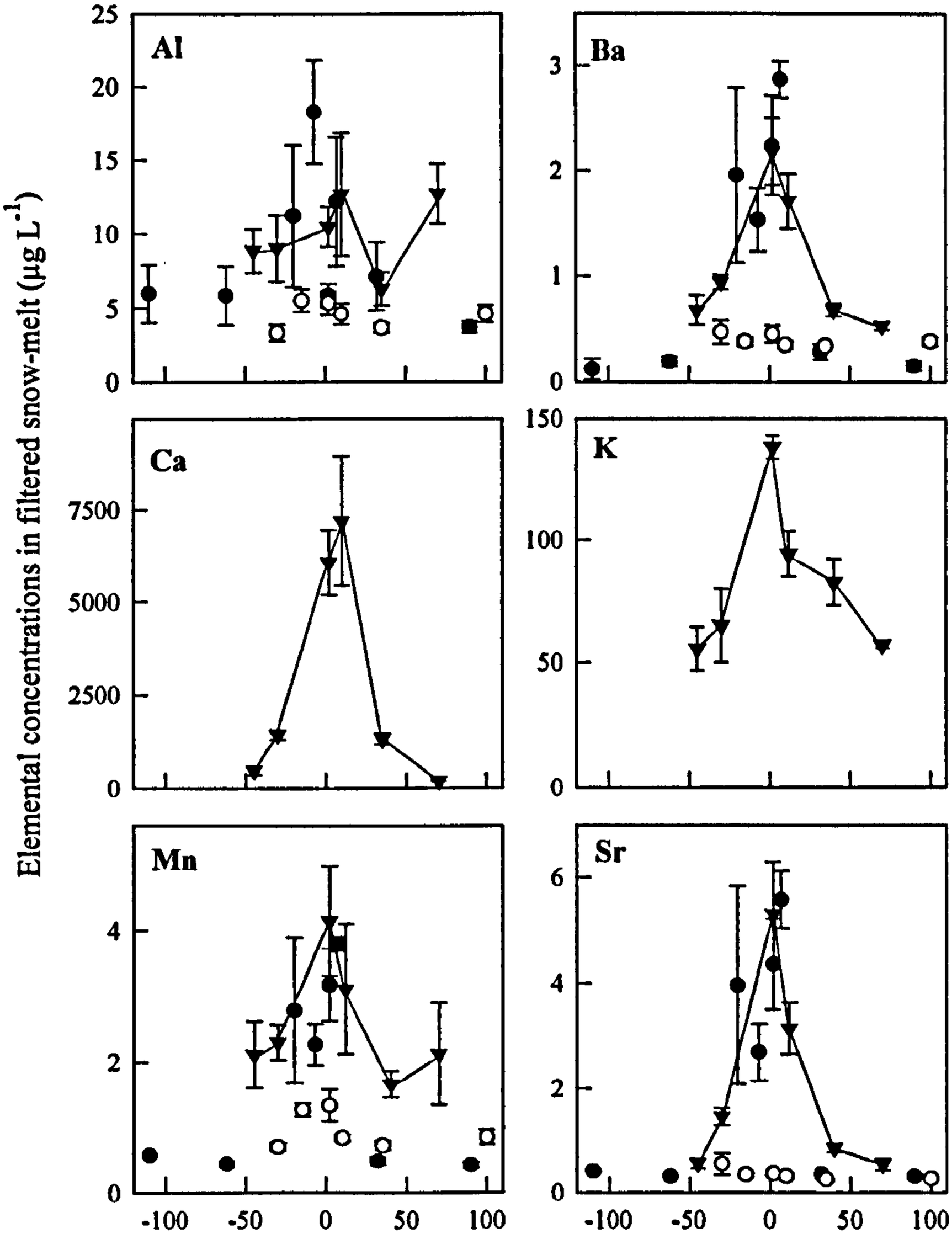


Figure 4.3.a. Concentrations of metal elements in filtered snow-melt, representing the principal soil and ash derived components, from transects through Vorkuta (▼) , Inta (●), and Usinsk (○), during spring 1998 and 1999. Trace elements were measured by ICP-MS; concentrations of Ca and K were measured by F-AAS along the Vorkuta transect only. Plotted values are means ± SE ($n = 3$).

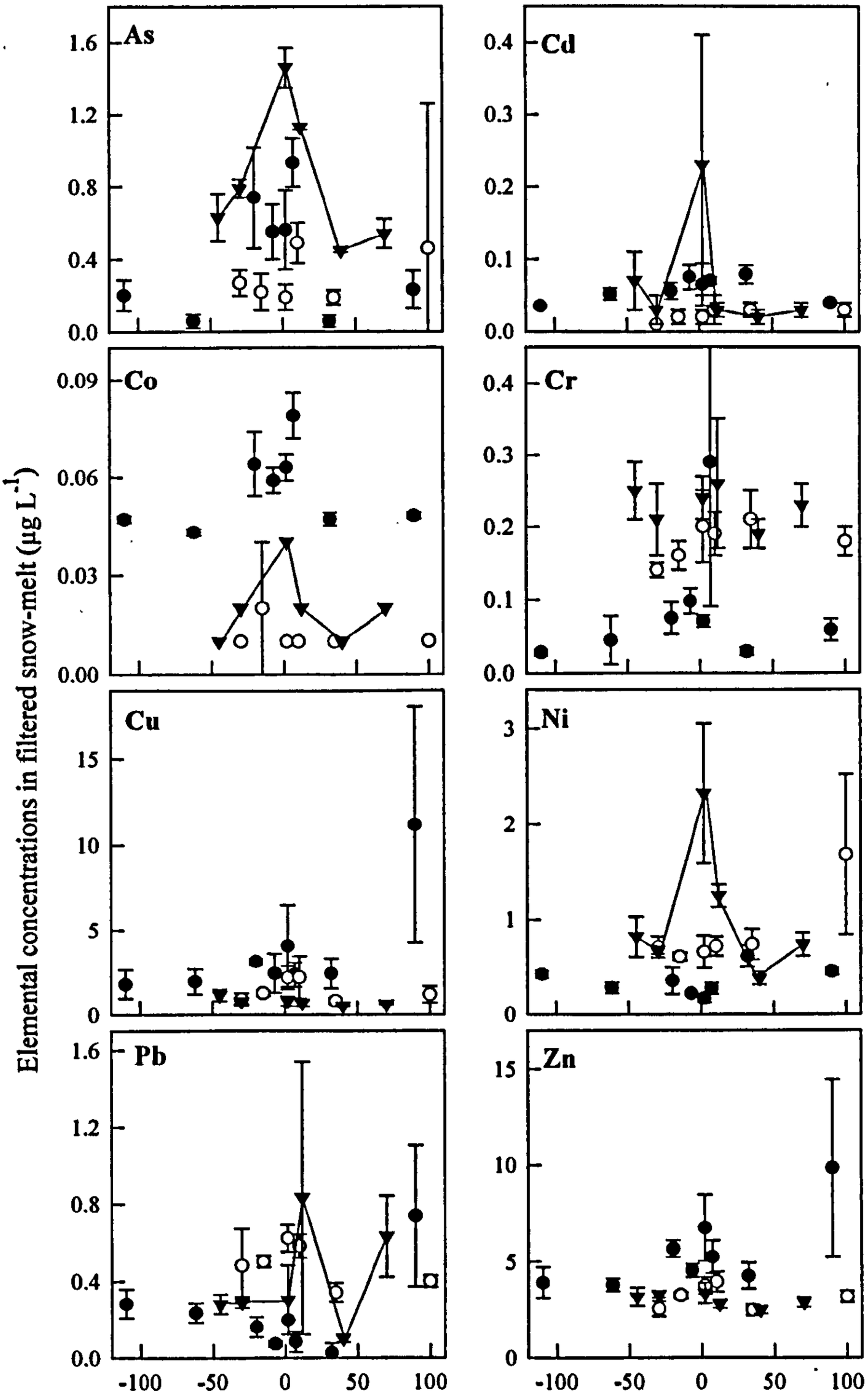
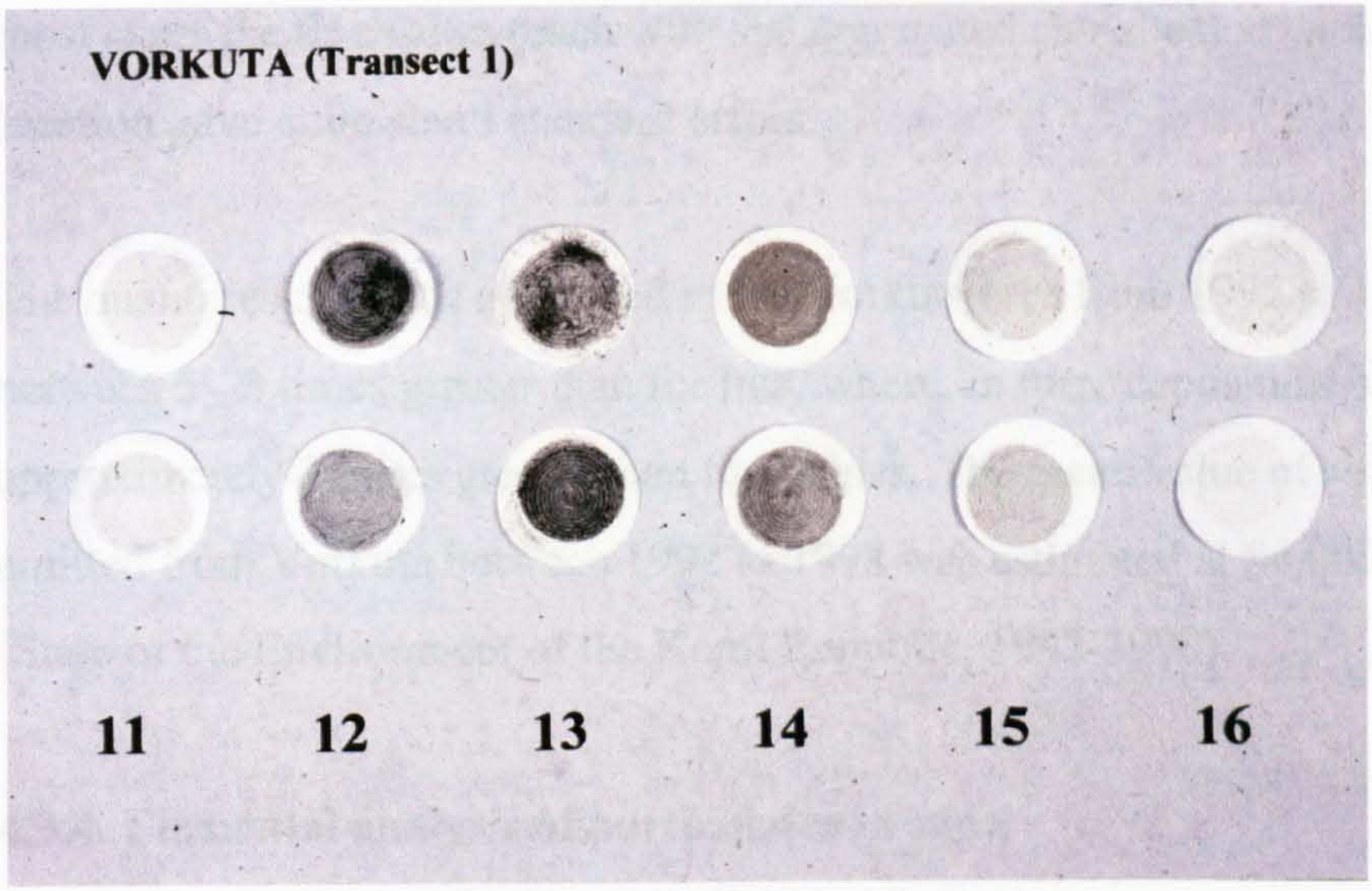
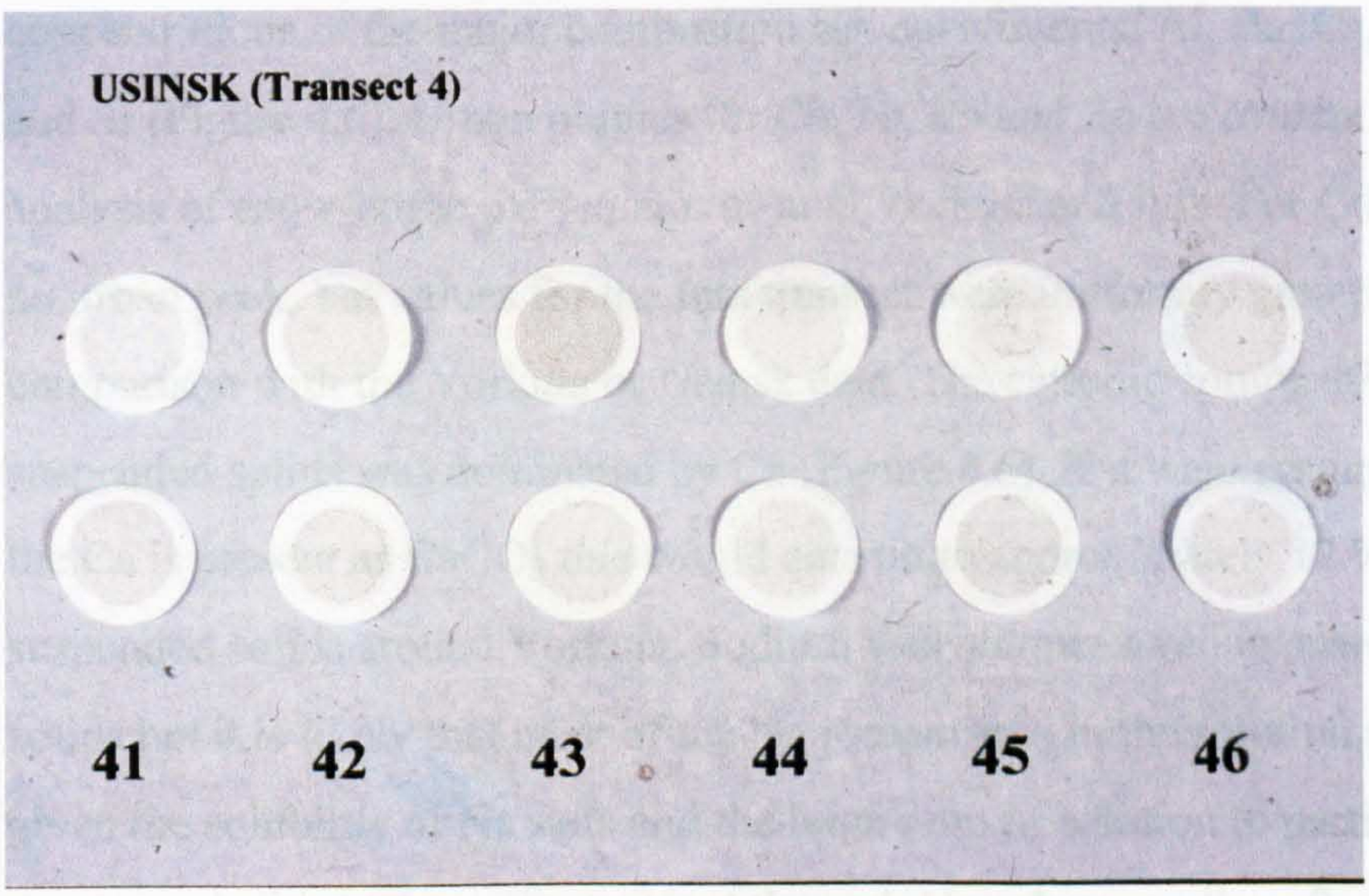


Figure 4.3.b. Concentrations of metal elements, representing industrial trace elements, in filtered snow-melt from transects through Vorkuta (▼), Inta (●), and Usinsk (○), during spring 1998 and 1999. Trace elements were measured by ICP-MS. Plotted values are means ± SE ($n = 3$).



(a)



(b)

Figure 4.4. Suspended solids collected on 2.5 cm diameter cellulose acetate filters after filtration of 110 mL of thawed snow samples collected along transects through Vorkuta (a) and Usinsk (b). (Photos: T. R. Walker).

Figure 4.5 shows the concentration of suspended solids collected on cellulose acetate filters following filtration of thawed snow. The trend along each transect strongly suggests a substantial contribution from coal combustion in Inta and Vorkuta, as the highest concentrations are found around the towns. In

most cases the three sites (each with six aggregated sub-sites) at each transect location gave quite small standard errors.

The quantities of solids deposited in the Vorkuta area from 1992 to 1998 were between 5 - 8 times greater than for Inta, where, in turn, deposition was approximately 3 times greater than for Usinsk. The mean value of solids emitted from Vorkuta between 1992 to 1998 was estimated at 84,000 t y^{-1} (State of the Environment of the Komi Republic, 1992-1998).

4.3.4. Elemental analysis of particulates in snow

In the immediate vicinity of Vorkuta and Inta there were elevated concentrations of the major combustion ash constituents: Al, Ba, Ca, K, Mg and Sr (Figure 4.6). Urban plumes for Cu, Ni, Pb and Zn are evident from analysis of snow-borne particulates around Vorkuta and Inta. For Cd there was no urban peak, but values for the Inta transect were uniformly greater in comparison with the Vorkuta or Usinsk data. The cationic composition of the suspended solids was dominated by Ca (Figure 4.6). If it were assumed that the Ca is present as $CaCO_3$ this would constitute approximately 12 % of the suspended solids around Vorkuta. Sodium was not measured in suspended solids but it is likely that most of the Na present was in the solution phase, given the solubility of Na salts and the large ratio of solution to particulates in the thawed snow. The entire transect through Usinsk generally reflected background concentrations similar to those observed in pristine areas at both ends of the Inta and Vorkuta transects.

Concentrations of ions associated with particulates and those in free solution were strongly related in snow collected on the Vorkuta transect e.g. Ca (r^2 = 0.97), Sr (r^2 = 0.97), Mn (r^2 = 0.91) and Ba (r^2 = 0.86). Combining the data for filter residues and snow meltwater gives the total concentration of these elements within the snow (Reimann *et al.*, 1996; Gregurek *et al.*, 1998b). The concentration ratio between elements in particulates and in the solution phase of thawed snow showed that the majority of the major constituents of

combustion ash were in particulate form. Mean solid : solution ratios for total concentration (mg L^{-1}) of Ca, Ba, Sr and Al were 12, 17, 10 and 9 respectively. This confirms that estimates of deposition from filtered thawed snow alone, can seriously underestimate deposition rates by up to 90 % for certain elements where there is significant particulate pollution (Äyräs *et al.*, 1995; Reimann *et al.*, 1996).

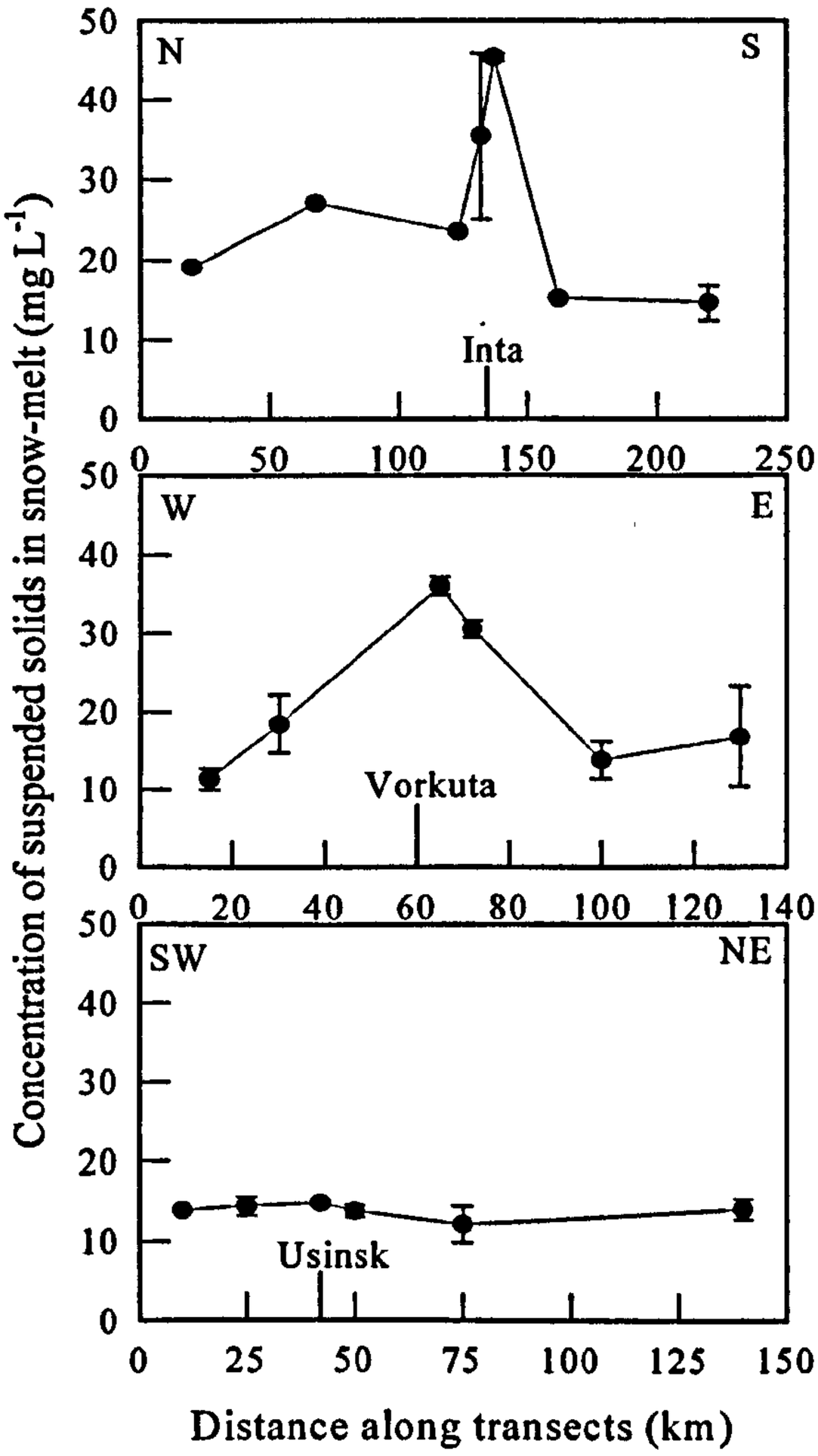


Figure 4.5. Concentration of suspended solids in filtered thawed snow samples taken along transects during spring 1998 and 1999. Plotted values are means ± SE (n = 3).

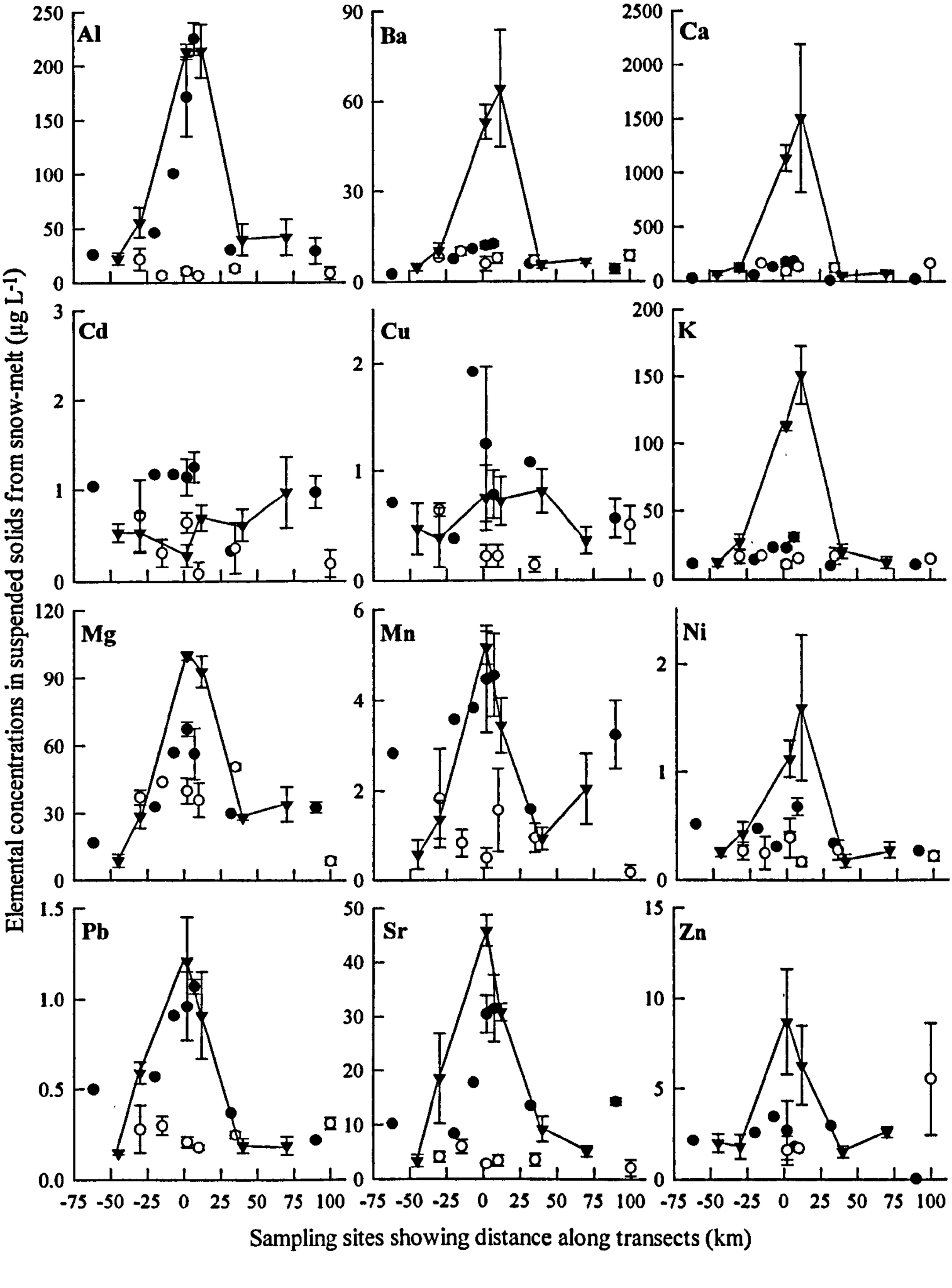


Figure 4.6. Concentrations of metal elements within filter residues from snow samples taken along transects through Vorkuta (▼), Inta (●), and Usinsk (○), during spring 1998 and 1999. Plotted values are means ± SE ($n = 3$). Note: element concentrations are expressed as µg L^{-1} snowmelt.

4.3.5. Soil analysis

The depth of the surface organic layer from each quadrat varied between 0.5 - > 5 cm (Figure 4.7).

Figure 4.7. Soil profile under pine-dominated lichen woodland at Shar'yu (site, 4.5; Figure 2.1). Note the shallow organic horizon (0-5 cm) and development of a bleached E_a horizon characteristic of podzol formation. (Photo: T. R. Walker).

Elevated soil pH, (mean pH 6.83; ± 0.08) was found only in the Vorkuta area at site 1.3 (Figure 4.8), possibly a result of local deposition of alkaline ash material from coal combustion and a cement factory. In mineral soil (0 - 5 cm depth) Rusanova (1995a) measured pH values of 7.2 within the town, whereas the pH fell to 4.8 at 15 km SW of the town limits; these figures compare favourably with the present data. Soil pH along transects through Inta and Usinsk were uniformly low. For transects 2/3 through Inta the lowest soil pH was recorded at the peatland site 3.3, (mean pH 3.51; ± 0.06) and the highest values were recorded at site 3.5 (mean pH 4.40; ± 0.09). Oksanen *et al.* (2001) measured pH values in the range, 3.8-5.0 at sites on the peat plateau along the Rogovaya river, a tributary of the Usa river. Along transect 4 through Usinsk, pH values varied between 3.90; ± 0.05 at site 4.1 and 4.93; ± 0.07 at site 4.3 similar to values recorded at the extremes of the Vorkuta transect.

For the less common soil constituents which are found in combustion ash (e.g. Ba and Sr) there was clear evidence of increased loading close to Vorkuta which compares well with another study of top soil close to combustion ash emissions (Vassilev and Vassileva, 1997). Mean concentrations of Ba and Sr in soil ash ($n = 18$) were 2780 μg g^{-1} (± 129) and 131 μg g^{-1} (± 6.1), respectively, at site 1.3 (see Fig. 4.9). By contrast, concentrations for the background site at the eastern end of the transect (site 1.6) were 309 μg g^{-1} (± 22) and 22.6 μg g^{-1} (± 1.9) respectively. There may also be soil enrichment of Ni, Zn and Cu around Vorkuta but the scatter in the data makes this conclusion difficult to sustain. According to Singh *et al.* (1995) elevated soil concentrations of Mn, Cu, Pb and Ni in soils can be found close to coal-fired power stations. There was no such enrichment around Inta, possibly due to the reduced quantities of solids emitted in Inta compared to Vorkuta (State of the environment of the Komi Republic, 1992-1998).

The spatial extent of the local alkalisation of top-soil at sites around Vorkuta corresponds with vegetation changes evident in satellite images which have been confirmed by ground plot field observations (Virtanen *et al.*, 2002). Similar observations were made on the Kola Peninsula where alkaline ash enrichment of the local area caused changes to the natural vegetation (Buznikov *et al.*, 1995; Reimann *et al.*, 2000).

The variation in top-soil pH shows the effects of the emission sources of Vorkuta and Inta; the most acidic samples were collected at the extremities of the transects. The higher soil pH values around Vorkuta correlate well with the Ca concentrations in snow and particulates. This indicates an important role for ash input from coal combustion and cement dust from the nearby cement factory in regulating snow and soil pH. Potentially, a reduction in fly ash and

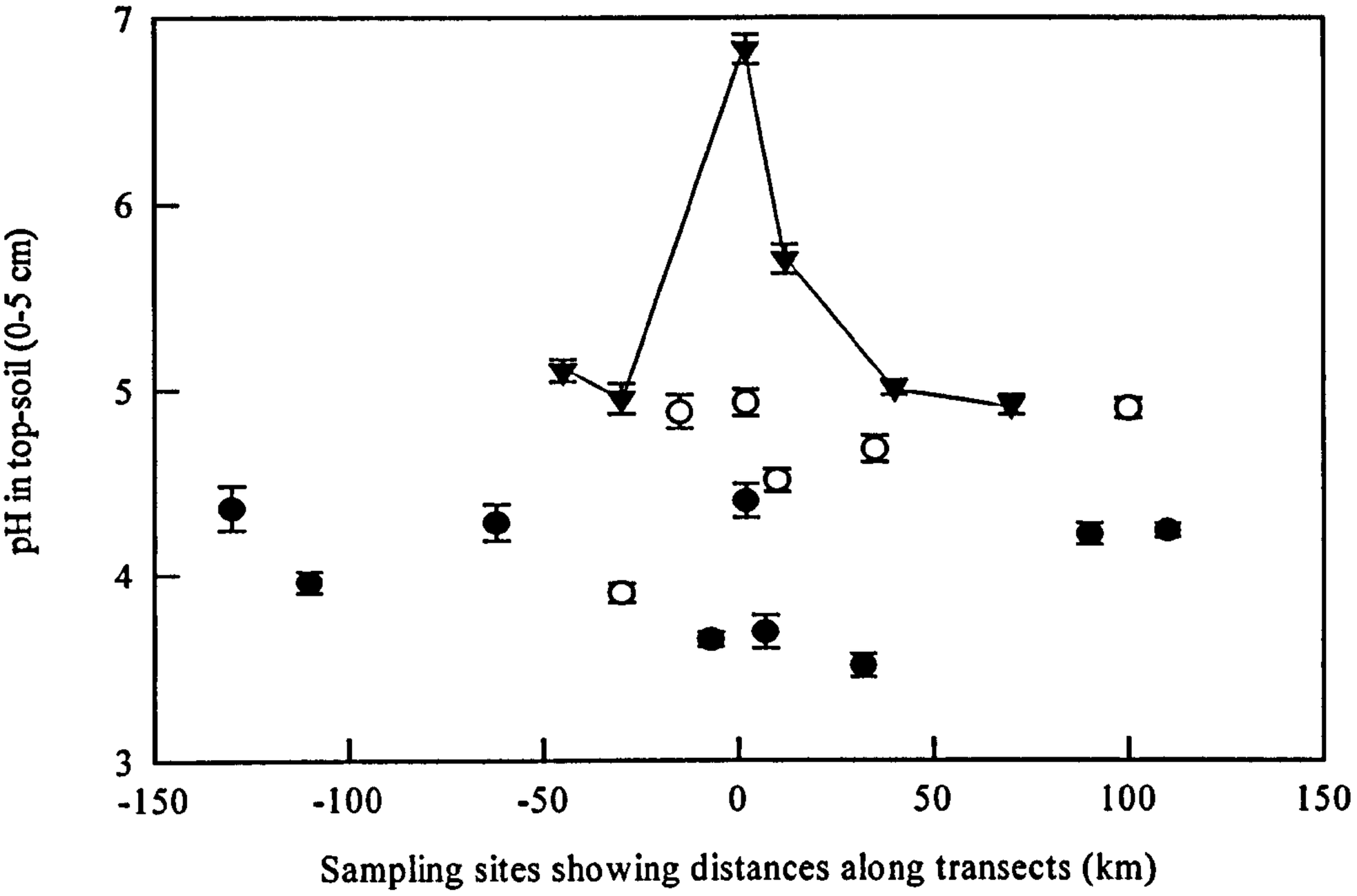


Figure 4.8. Measurements of pH in top-soil samples (0-5 cm) taken along transects through Vorkuta (▾), Inta (●), and Usinsk (○), during summer 1998 and 1999. Plotted values are means ± SE (n = 18).

cement dust emissions could mean solubilization of accumulated heavy metals due to a progressive drop in soil pH (Reimann *et al.*, 1996; Haapala *et al.*, 2001). Robb and Young (1999) found that large additions of calcareous, metal-rich, fly ash to acidic soils increased the soil pH, to the extent that the metal ion concentration in the soil solution was reduced despite the increased total metal loading to the soil from the ash. Approximately 20 km beyond the northern-most site at Khosedayu river, 2.1, (see Figure 2.1, Table 2.1) on transect 2/3 an additional set of top-soil samples were collected along the Upper Kolva river. Mean pH at this site was 4.26 (± 0.06, n = 6), which compares well with pH values found elsewhere along the transect extremes of transect 2/3. Analysis of additional soil samples collected from the Upper Kolva during summer 2000, are presented in Table 4.2. Mean concentrations of Ba, Cu, Mg, Pb, Sr and Zn in soil ash compare favorably with those concentrations recorded for the same elements along the entire 2/3 transect. As this was the northern most site along transect 2/3 elevated levels of Na and Ni were probably due to marine inputs

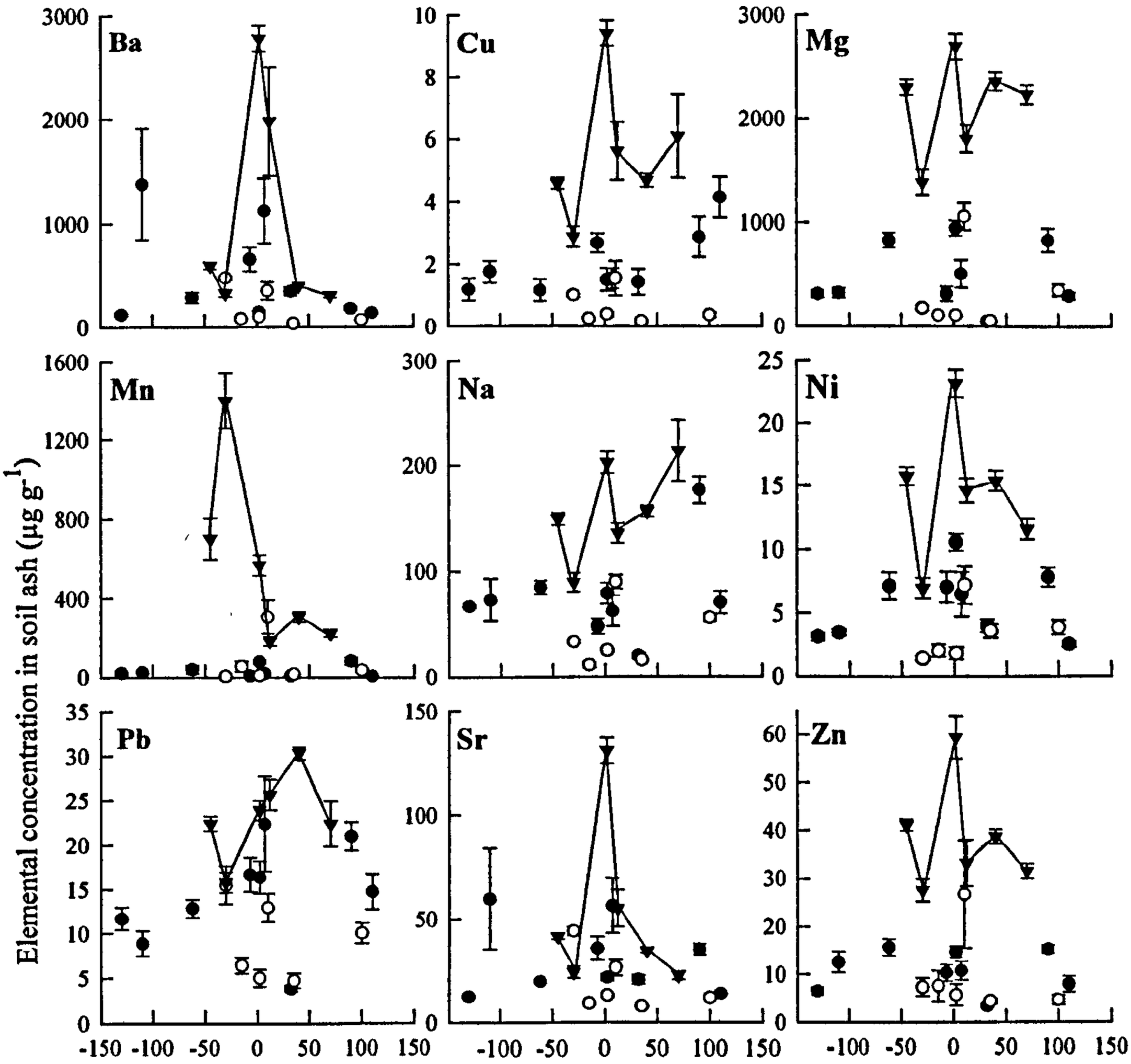


Figure 4.9. Concentrations of metallic elements within soil ash taken along transects through Vorkuta (▼), Inta (●), and Usinsk (○), during summer 1998 and 1999. Plotted values are means ± SE (n = 18).

from the Barents Sea. Concentrations of Ca, Cd and K ($n = 6$) were 171.9 μg g^{-1} (± 18.9), 0.09 μg g^{-1} (± 0.02) and 1325.5 μg g^{-1} (± 175.6), respectively, and could not be compared to other sites along transects as these elements were not previously analysed (see Table 4.1).

Table 4.1. Concentrations of metal elements within soil ash taken at the Upper Kolva.

Element analysed	Elemental concentrations in soil ash (μg g^{-1})	± SE ($n = 6$)
Ba	27.59	2.62
Ca	171.87	18.87
Cd	0.09	0.02
Cu	11.84	1.29
K	1325.50	175.51
Mg	1592.55	313.83
Na	199.78	36.14
Ni	102.68	30.67
Pb	35.20	1.21
Sr	1.59	0.30
Zn	39.66	1.25

4.3.6. Comparison of deposition rates with excess soil loading (Equation 4.1)

Tables 4.2.a and 4.2.b show the estimated times required for the accumulation of elements, in excess of pristine sites, at the current measured rates of element deposition in snow. For both major and minor elements T_d (equation 4.1) was considerably in excess of the life span of the city of Vorkuta, suggesting current rates of metal deposition in precipitation (A_d) cannot explain the apparent accumulation in soil. For example the values of T_d for the trace

elements Cu and Ni were 304 and 342 y respectively; for the alkali earth elements Ba and Sr T_d was 3250 and 154 y (Table 4.2.a and Table 4.2.b). The discrepancy between the duration of industrial development in the region and the amount of time required to accumulate apparent excess soil metal loadings from current deposition rates may arise for a number of reasons.

Firstly, there has been a substantial decline in coal mining in Vorkuta, since the peak of activity in the 1960s and 1970s. The 13 coal-mines operating in 1990 were reduced to just seven by 1999 (State of the environment of the Komi Republic, 1992-1998). Coal production at the largest mine, Vorgashorskaya, fell by 40% between 1991 and 1999, from nearly 21 x 10^6 tonnes to 13 x 10^6 tonnes (State of the environment of the Komi Republic, 1992-1998). This trend is consistent with data on spheroidal carbonaceous particles (SCPs, only produced from high temperature combustion) found in lake sediment profiles. Lake sediment profiles showed that a peak in SCP's was found at 1.5 cm below the sediment surface and suggest that SCP deposition rates has since been in sharp decline (Solovieva *et al.*, 2002). Secondly, Vorkuta has a total population of around 200 000 inhabitants housed mostly within concrete multi-storey flats. Urban development on this scale within the tundra ecosystem requires a great deal of construction activity, which would import considerable quantities of cement dust and other particles, resulting in elevated deposition of alkali-earth elements (Arslan and Boybay, 1990; Jalkanen *et al.*, 2000). It is therefore likely that elemental concentrations in soils within 20-30 km of Vorkuta do not reflect current deposition rates but are a historical legacy of greater construction and industrial activity in the recent past.

Table 4.2.a. Comparison between pristine and contaminated sites along transects showing measured element concentrations within soil and the amount of time required to accumulate these from current (apparent) deposition rates. The time in years required to accumulate excess element concentration in soil was determined by equation 2.8 (Chapter 2; 2.7).

Element	Transect	Site No.	Conc. in soil ash ($\mu g\ kg^{-1}$)	Mass of mineral ($kg\ m^{-2}$)	Expected conc. in ash ($\mu g\ kg^{-1}$)	Expected conc. m^{-2} ($g\ m^{-2}$)	Actual conc. m^{-2} ($g\ m^{-2}$)	Change ($g\ m^{-2}$)	Deposition rate ($g\ m^{-2}\ y^{-1}$)	Time required to accumulate (y)
Ba	1	1.6	3.1×10^5	35.70	3.1×10^5					
		1.3	2.8×10^6	37.60	3.1×10^5	11.630	104.500	92.870	2.9×10^{-2}	3247
	2/3	3.5	1.5×10^5	41.03	1.5×10^5					
		3.4	1.1×10^6	8.51	1.5×10^5	1.260	9.540	8.280	7.3×10^{-3}	1139
	4	4.5	3.6×10^4	47.77	3.6×10^4					
		4.4	3.5×10^5	45.13	3.6×10^4	1.610	1.700	0.090	4.0×10^{-3}	23
Cu	1	1.2	2.9×10^3	40.10	2.9×10^3					
		1.3	9.4×10^3	37.60	2.9×10^3	0.109	0.354	0.245	8.1×10^{-4}	304
	2/3	2.3	1.2×10^3	29.53	1.2×10^3					
		2.5	2.7×10^3	4.45	1.2×10^3	0.005	0.012	0.007	2.5×10^{-3}	3
	4	4.5	1.7×10^2	47.77	1.7×10^2					
		4.4	1.5×10^3	45.13	1.7×10^2	0.008	0.070	0.062	1.2×10^{-3}	51
Ni	1	1.2	6.9×10^3	40.10	6.9×10^3					
		1.3	2.3×10^4	37.60	6.9×10^3	0.261	0.870	0.609	1.8×10^{-3}	342
	2/3	3.3	4.0×10^3	2.33	4.0×10^3					
		3.5	1.1×10^4	41.03	4.0×10^3	0.164	0.432	0.268	2.7×10^{-4}	978
	4	4.1	1.4×10^3	2.45	1.4×10^3					
		4.4	7.2×10^3	45.13	1.4×10^3	0.063	0.323	0.260	4.4×10^{-4}	591

Table 4.2.b. Comparison between pristine and contaminated sites along transects showing measured element concentrations within soil and the amount of time required to accumulate these from current (apparent) deposition rates. The time in years required to accumulate excess element concentration in soil was determined by equation 2.8 (Chapter 2; 2.7).

Element	Transect	Site No.	Conc. in soil ash ($\mu g\ kg^{-1}$)	Mass of mineral ($kg\ m^{-2}$)	Expected conc. in ash ($\mu g\ kg^{-1}$)	Expected conc. m^{-2} ($g\ m^{-2}$)	Actual conc. m^{-2} ($g\ m^{-2}$)	Change ($g\ m^{-2}$)	Deposition rate ($g\ m^{-2}\ y^{-1}$)	Time required to accumulate (y)
Pb	1	1.2	1.6×10^4	40.10	1.6×10^4					
		1.4	2.6×10^4	37.60	1.6×10^4	0.579	0.940	0.361	9.0×10^{-4}	400
	2/3	2.3	1.3×10^4	12.89	1.3×10^4					
		3.4	2.2×10^4	8.51	1.3×10^4	0.110	0.191	0.081	5.4×10^{-4}	149
	4	4.5	4.7×10^3	47.77	4.7×10^3					
		4.4	1.3×10^4	45.13	4.7×10^3	0.214	0.586	0.372	3.7×10^{-4}	989
Sr	1	1.6	2.3×10^4	35.71	2.3×10^4					
		1.3	1.3×10^5	37.60	2.3×10^4	0.850	4.920	4.070	2.6×10^{-2}	154
	2/3	2.3	2.0×10^4	12.89	2.0×10^4					
		3.4	5.6×10^4	8.51	2.0×10^4	0.168	0.477	0.309	1.8×10^{-2}	18
	4	4.5	7.8×10^3	47.77	7.8×10^3					
		4.4	2.6×10^4	45.13	7.8×10^3	0.350	1.180	0.830	1.8×10^{-3}	450
Zn	1	1.2	2.8×10^4	40.10	2.8×10^4					
		1.3	6.0×10^4	37.60	2.8×10^4	1.034	2.230	1.196	6.2×10^{-3}	192
	2/3	3.3	3.4×10^3	2.33	3.4×10^3					
		3.5	1.5×10^4	41.03	3.4×10^3	0.140	0.599	0.459	4.5×10^{-3}	103
	4	4.5	4.4×10^3	47.77	4.4×10^3					
		4.4	2.7×10^4	45.13	4.4×10^3	0.199	1.200	1.001	2.8×10^{-3}	357

In the Vorkuta region the prevailing winds blow from the southwest and south from September to April (Virtanen *et al.*, 2002). In accordance with the prevailing winter winds around Vorkuta, the area with the greatest concentrations of elements within snow and soil was around at sites 1.3 and 1.4 which were located north-east of the main emission sources. It is clear that the sites most affected by pollution in the Vorkuta region are found around the main emission sources, i.e. the cement factory and the power plant (Kuliyev, 1977, 1979; Kuliyev and Lobanov, 1978; Getsen *et al.*, 1994; Solovieva *et al.*, 2002; Virtanen *et al.*, 2002).

4.4. Conclusions

Results show considerable local alkalisation in both the top-soil and snow-pack around Vorkuta; in the vicinity of Inta alkalisation was only apparent in the snow-pack. Deposition of coal ash around both towns is mainly responsible, with possible contributions from a cement factory located in Vorkuta and historical inputs from the major construction phase of the city. Near pristine areas located more than 30 km from Vorkuta and Inta appear to be unaffected by ash deposition and are characterised by acidity in both snow-pack and top-soils. Sites along the entire transect through the town of Usinsk, which is supplied by a gas-fired power station, were near pristine.

There were elevated concentrations of Al, Ba, Ca, K, Mg and Sr in suspended solids and snow-pack around Vorkuta and Inta. Most of the deposition of elements commonly associated with combustion ash, occurred in particulate form. There was evidence that the concentrations of soluble Pb, Cu and Zn in snow-pack were reduced around Vorkuta, due to adsorption onto alkaline ash particles.

Extremely high elemental concentrations of Ba and Sr in top-soils around Vorkuta could not be explained by current deposition rates. This discrepancy may be the result of greater coal mining and construction activity in previous decades.

CHAPTER 5. POLLUTION IMPACTS DUE TO THE OIL AND GAS INDUSTRIES IN THE PECHORA BASIN

5.1. Introduction

Reported here are the results of an investigation seeking evidence of environmental impact in the vicinity of a booming petrochemical industry in the Pechora region. This was achieved by quantifying the chemical status of terricolous mat-forming lichens and top-soil, and by measuring alpha (α) biodiversity of epigeal and epiphytic lichens in close proximity to both putative pollution 'hot spots' and unpolluted 'reference' sites with a broadly comparable community structures. The probable underlying causal factors are discussed.

The Pechora region, which includes the north and east of the Komi republic and a major portion of the Nenets autonomous region, faces considerable challenges both in terms of socio-economic development and environmental conditions (Lausala and Valkonen, 1999). The region is rich in non-renewable resources (e.g. minerals, coal, oil and gas), but the exploitation of coal is in decline due to its poor quality and high transportation costs (Gimardi, 2002). In recent decades the oil and gas industries have boomed and are expected to expand further, bringing about significant risks of environmental pollution.

Previously, the findings of the TUNDRA programme in the Usa basin, found evidence of pollution on two geographical scales. These were local emissions from coal combustion in Vorkuta and Inta, and long-range transport of pollutants from lower latitudes in Europe and industrial regions of the Urals. The work in this Chapter formed part of the SPICE project (Sustainable development of the Pechora region In a Changing Environment and society) which then looked at the environmental impact of emerging industries over a larger area of the Pechora basin. This investigation of potential terrestrial pollution was complimented by work carried out by other groups within the

project. This included studies on aquatic pollution based on analysis of surface waters and lake sediments, other indicators of biodiversity, including, avifauna, fish, invertebrates and cyanobacteria, and the genetic variability of spruce in tundra forest islands. Partners within SPICE were also examining the economy and society of the region by investigating socio-economic development, social perception of, and stakeholder involvement in the state of the environment and economic losses of infrastructure due to permafrost collapse. The impacts of global change formed an additional component of the programme. These ecological assessments were undertaken at eight sampling sites, four of which were selected close to industrial 'hot spots' ('industrial' sites, $F1_i$, $F5_i$, $F3_i$ and $F7_i$), and four were remote from industrial activity ('reference' sites, $F2_r$, $F6_r$, $F4_r$ and $F8_r$) (Figure 2.2, Table 2.2). Details of sampling sites, sampling regimes and subsequent chemical analysis are given in Chapter 2.

The variables measured in lichens were: total N, determined by Kjeldahl digestion and distillation following the method of Bremmer and Breitenbeck (1983); major cations (Mg^{2+} by F-AAS; Ca^{2+} and K^+ by FES) and Pb by GF-AAS. In addition, lichen abundance and species diversity was determined on epigeals in the tundra and epiphytes in the taiga. The variables measured in top-soil included elemental analysis of: Ba, Ca, Cu, K, Mg, Mn, Na, Ni, Pb, Sr and Zn, undertaken using GF-AAS and F-AAS and soil pH which was measured following standard protocols (see Chapter 2).

5.2. Statistical analysis

Unless otherwise indicated, significant differences between sites were determined by one-way-ANOVA followed by Tukey's test ($n = 18$).

5.3. Results

5.3.1. Lichen material collected

Terricolous mat-forming lichens in the genera *Cladonia* [*Cladonia arbuscula* or *C. stellaris*] or *Flavocetraria* [*F. cucullata*] were widespread and locally abundant in the Pechora basin. At least one species was collected at each site (Table 5.1). Cover was generally poor in the tundra due to grazing and trampling effects of reindeer, except for site $F7_i$. The most complete data set for lichen chemistry was obtained for *C. arbuscula,* which was collected at all sites in this study. However, only small thalli were found in the tundra, due to heavy grazing and it was only possible to measure [N] in the apical 5 mm. *Flavocetraria cucullata* was collected of sufficient length to measure [N] at different strata.

Table 5.1. Terricolous species of *Cladonia* and *Flavocetraria* sampled across the Pechora basin at 'industrial' sites (e.g. $F1_i$) and unpolluted 'reference' sites (e.g. $F2_r$), together with elemental analyses performed ($n = 18$).

Transect	Species sampled	$[N]_{apices}$	$[N]_{base}$	[Pb]	$[Ca^{2+}]$	$[K^+]$	$[Mg^{2+}]$
$F1_i$	*Cladonia arbuscula*	+	-	+	+	+	+
Izhma river	*C. stellaris*	+	-	+	+	+	+
$F2_r$	*C. arbuscula*	+	-	+	+	+	+
Kedva river	*C. stellaris*	+	-	+	+	+	+
$F3_i$	*C. arbuscula*	+	-	-	+	+	+
Ortina river	*Flavocetraria cucullata*	+	+	-	+	+	+
$F4_r$	*C. arbuscula*	+	-	-	+	+	+
Neruta river	*F. cucullata*	+	+	-	+	+	+
$F5_i$	*C. arbuscula*	+	-	+	+	+	+
Svetly Vuktyl							
$F6_r$	*C. arbuscula*	+	-	+	+	+	+
Malay Patok	*C. stellaris*	+	-	+	+	+	+
$F7_i$	*C. arbuscula*	+	-	+	+	+	+
Upper Kolva	*F. cucullata*	+	+	+	+	+	+
$F8_r$	*C. arbuscula*	+	-	+	+	+	+
Mareyu river	*F. cucullata*	+	+	+	+	+	+

+, analysis performed; -, no analysis

5.3.2. Total $[Ca^{2+}]$, $[K^{+}]$, $[Mg^{2+}]$ and [Pb] in lichen tissue

Figure 5.1 shows variation in the concentration and concentration ratios of cations in the apices of *Cladonia arbuscula, C. stellaris* and *Flavocetraria cucullata*. There were some marked and significant differences between comparable 'industrial' and 'reference' sites, e.g. site $F7_i$ compared to site $F8_r$ in both *C. arbuscula* and *F. cucullata,* and site $F5_i$ compared to site $F6_r$ in *C. arbuscula*. However, there was no consistent relatioship between differences in the cation values and proximity to perceived pollution sources. There was however, strong covariation in lichen chemistry among the three species (Figure 5.2.a-e), suggesting that differences among sites were due to different environmental circumstances as opposed to random variation with the data. Overall, potassium concentrations were generally higher in *F. cucullata* than *C. arbuscula* at all tundra sites.

Lead was selected as an additional analyte because it was one of several trace metals found to contaminate snow and soils locally in the tundra around the Vorkuta industrial complex (Chapter 4). Whilst absolute concentrations are low in all species there may be localised elevation of $[Pb]_{apices}$ in *C. arbuscula* and *F. cucullata* at site $F7_i$ (0.098 ± 0.008 and 0.143 ± 0.015 μmol g^{-1}, respectively) where concentrations were 3 - 4 times greater than at site $F8_r$ (0.025 ± 0.004 and 0.04 ± 0.005 μmol g^{-1}, respectively for *C. arbuscula* and *F. cucullata*) (Figure 5.3). There was a strong relationship between $[Pb]_{apices}$ in *C. arbuscula* and concentrations of Pb in soil ash ($[Pb]_{soil\ ash}$) ($r^2 = 0.834$, $n = 6$).

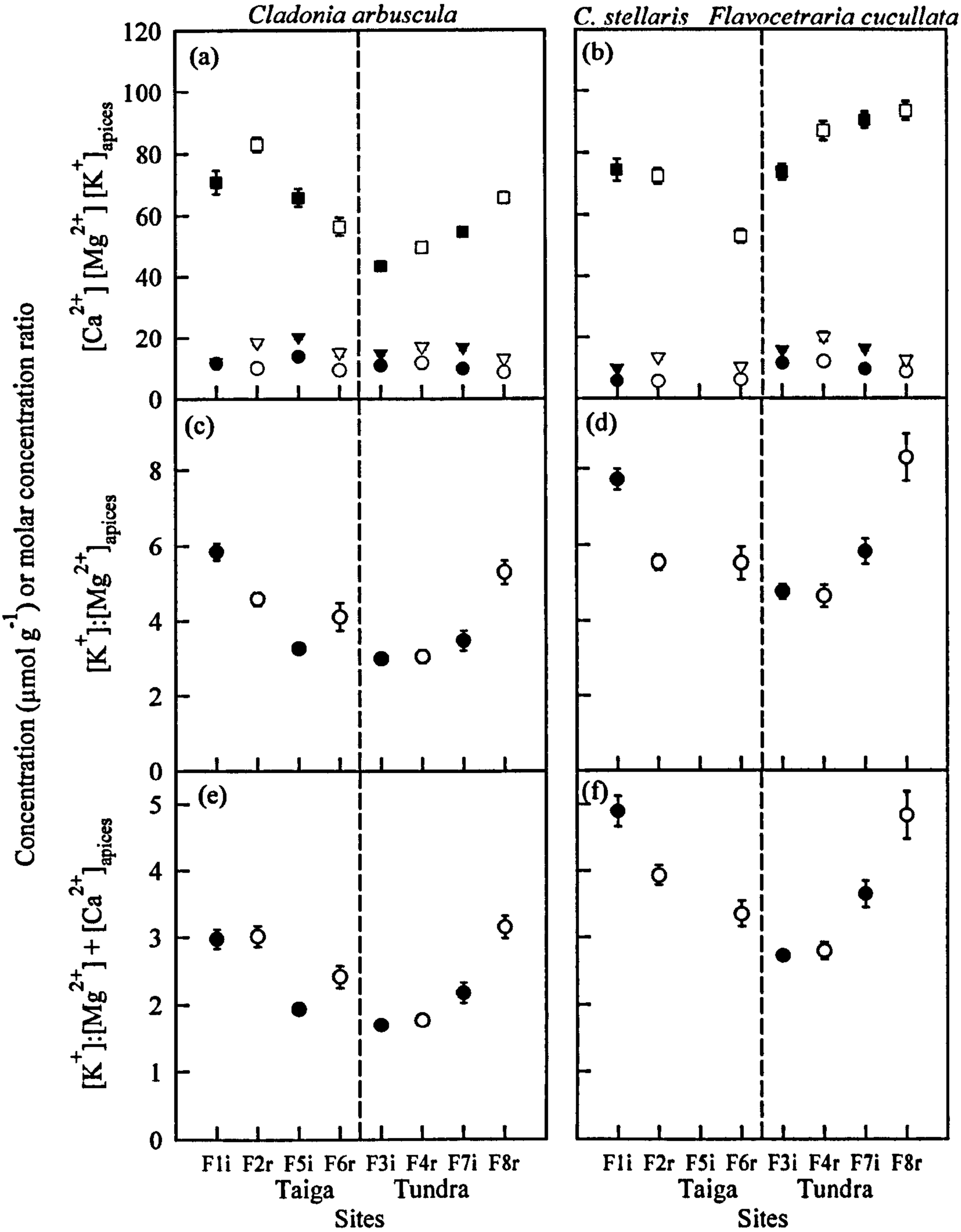


Figure 5.1. Variation in $[Ca^{2+}]_{apices}$ (●, ○), $[Mg^{2+}]_{apices}$ (▼, ▽) and $[K^{+}]_{apices}$ (■, □) (a, b) and the ratios $[K^{+}] : [Mg^{2+}]_{apices}$ (c, d) and $[K^{+}] : ([Ca^{2+}] + [Mg^{2+}])_{apices}$ (e, f) in *Cladonia arbuscula, C. stellaris* and *Flavocetraria cucullata*. Filled and open symbols indicate 'industrial' and 'reference' sites, respectively. Plotted values are means ± 1 SE, (n = 18).

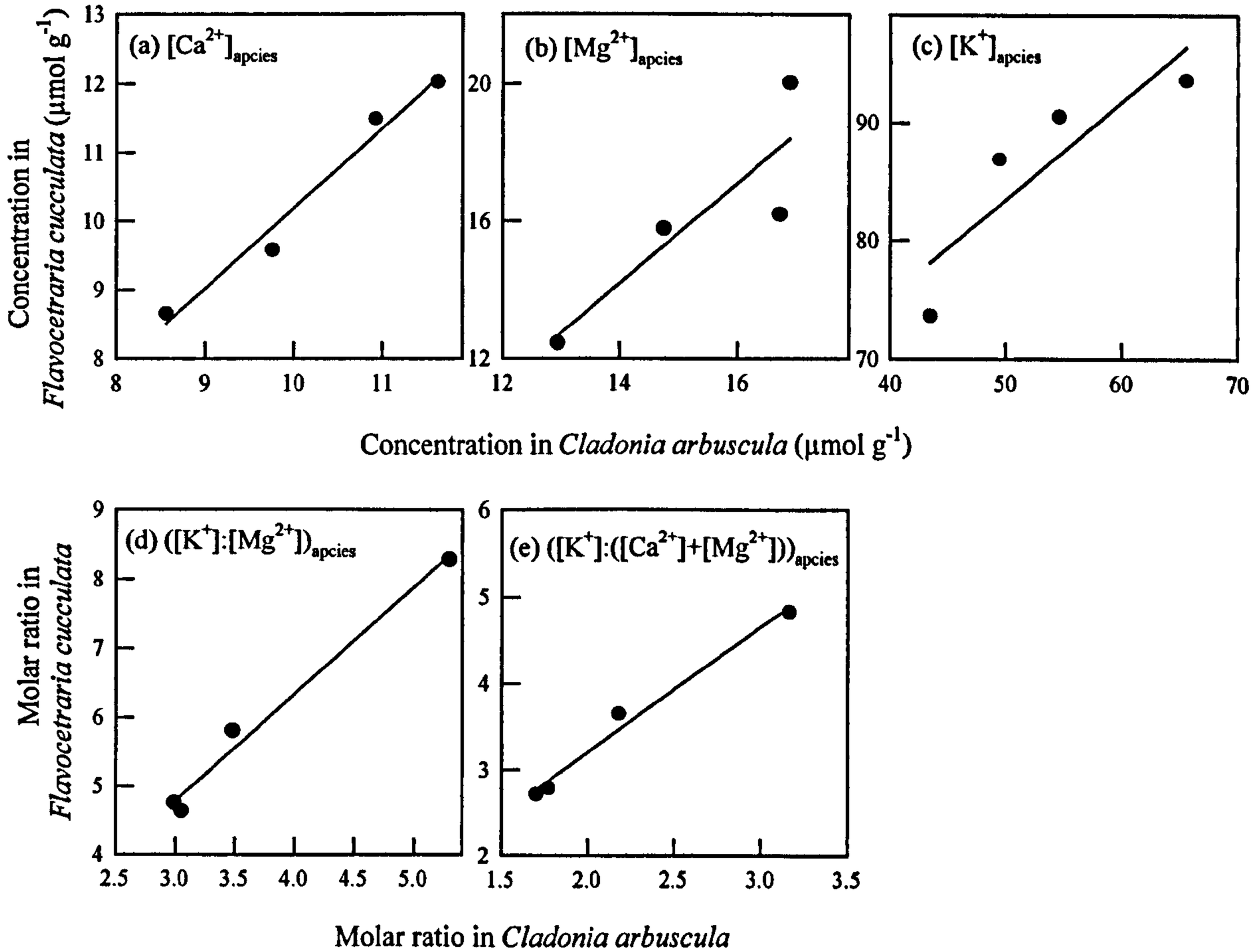


Figure 5.2. Relationships between *Cladonia arbuscula* and *Flavocetraria cucullata* in cation concentrations and molar ratios at tundra sampling sites: (a) $[Ca^{2+}]_{apices}$ ($r = 0.988$, $P<0.01$, $n = 4$); (b) $[Mg^{2+}]_{apices}$ ($r = 0.876$, $P<0.05$, $n = 4$); (c) $[K^{+}]_{apices}$ ($r = 0.877$, $P<0.05$, $n = 4$); (d) $([K^{+}]:[Mg^{2+}])_{apices}$ ($r = 0.992$, $P<0.005$, $n = 4$); (e) $([K^{+}]:([Ca^{2+}] + [Mg^{2+}]))_{apices}$ ($r = 0.992$, $P<0.005$, $n = 4$). Plotted values are means, ($n = 18$).

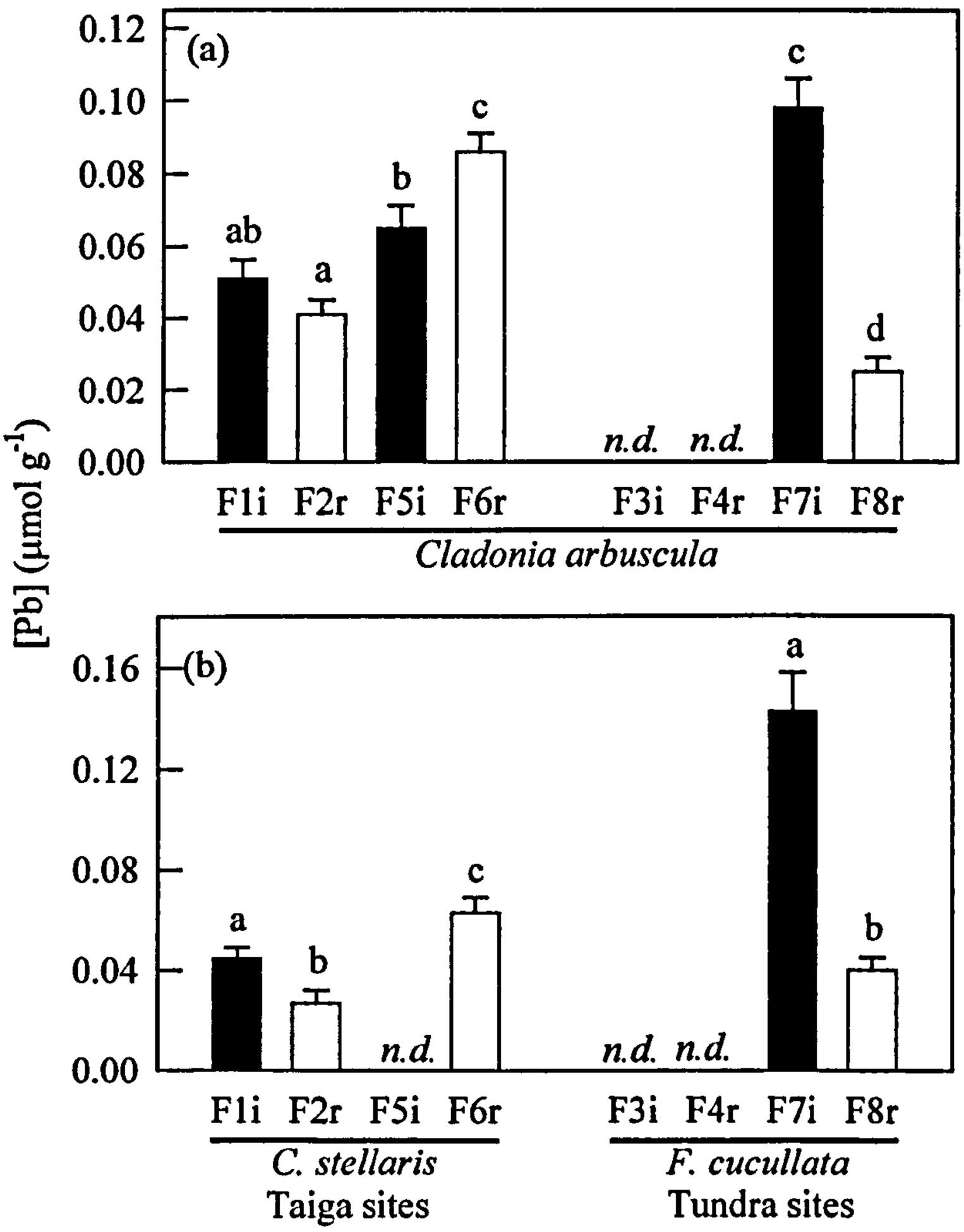


Figure 5.3. Mean concentrations of lead in lichen apices. (a) *Cladonia arbuscula*; (b) *C. stellaris* and *Flavocetraria cucullata*. Filled and open columns indicate 'industrial' and 'reference' sites, respectively. Plotted values are means ± 1 SE, (n = 18); *n.d.* = not determined. Significant differences were determined by one-way-ANOVA followed by Tukey's test, sites attributed with the same letters were not significant and sites with different letters were significantly different at the $P < 0.05$ level.

5.3.3. Total nitrogen concentration in lichen thalli

Values of $[N]_{apices}$ in *Cladonia arbuscula* varied from 0.39 ± 0.03 mmol g^{-1} (n = 18) at site $F3_i$ in the tundra, to 0.60 ± 0.07 mmol g^{-1} (n = 18) at site $F5_i$ in the taiga (Figure 5.4.a). Values were significantly higher at taiga than at tundra sites ($P < 0.001$). There was little evidence of elevated $[N]_{apices}$ in *C. arbuscula* at 'industrial' sites with the exception of site $F7_i$ which had the highest values for the tundra sites and significantly greater than the value for site $F8_r$. Nitrogen concentration in basal strata of *C. arbuscula* was not measured because thalli were generally of insufficient length.

Total N in the apices of *C. stellaris* was measured at three taiga sites (Figure 5.4.b) and found to be similar at each. Values ranged from 0.62 mmol g^{-1} (± 0.02) at site $F2_r$ to 0.65 mmol g^{-1} (± 0.01) at site $F6_r$ and were in the same range as those recorded at similar latitudes in the Usa basin (Chapter 3).

Values of total N in the apical (0 - 5 mm) and basal strata (35 - 40 mm) of *F. cucullata* are shown in Figure 5.5.a. While the highest value of $[N]_{apices}$ was recorded at site $F7_i$, the lowest value was also recorded at an industrial site ($F3_i$). There were significant differences in $[N]_{apices}$ and $[N]_{base}$ in *F. cucullata* between 'industrial' and 'reference' sites, but these did not provide any coherent evidence of pollution. Again the highest value of $[N]_{base}$ was recorded at $F4_r$ whilst the lowest value was recorded at site $F7_i$. Values of concentrations and ratios were in the same ranges as those recorded in *F. cucullata* at similar latitudes in the Usa basin (Chapter 3). There was a moderate degree of covariance between *F. cucullata* and *C. arbuscula* in $[N]_{apices}$ values (r^2 = 0.692, n = 4). The ratio of $[N]_{apices}$: $[N]_{base}$ in *F. cucullata* was significantly higher at site $F7_i$ than at the other tundra sites (Figure 5.5.b).

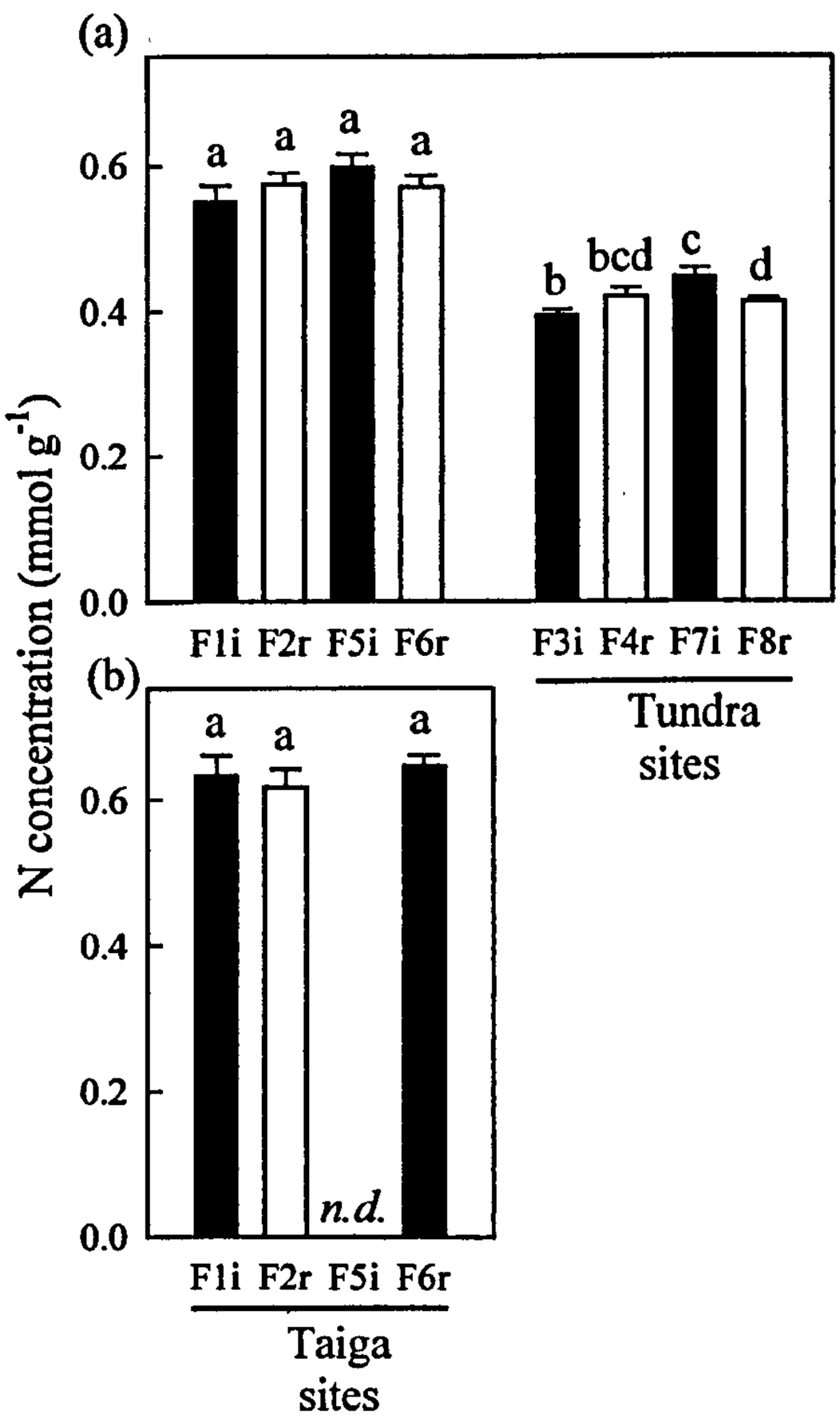


Figure 5.4. Mean values of $[N]_{apices}$ in *Cladonia arbuscula* (a) and *C. stellaris* (b). Filled and open columns indicate 'industrial' and 'reference' sites respectively. Plotted values are means ± 1 SE ($n = 18$); *n.d.* = not determined. Significant differences were determined by one-way-ANOVA followed by Tukey's test; values asigned the same letter were not significantly different at the $P < 0.05$ level.

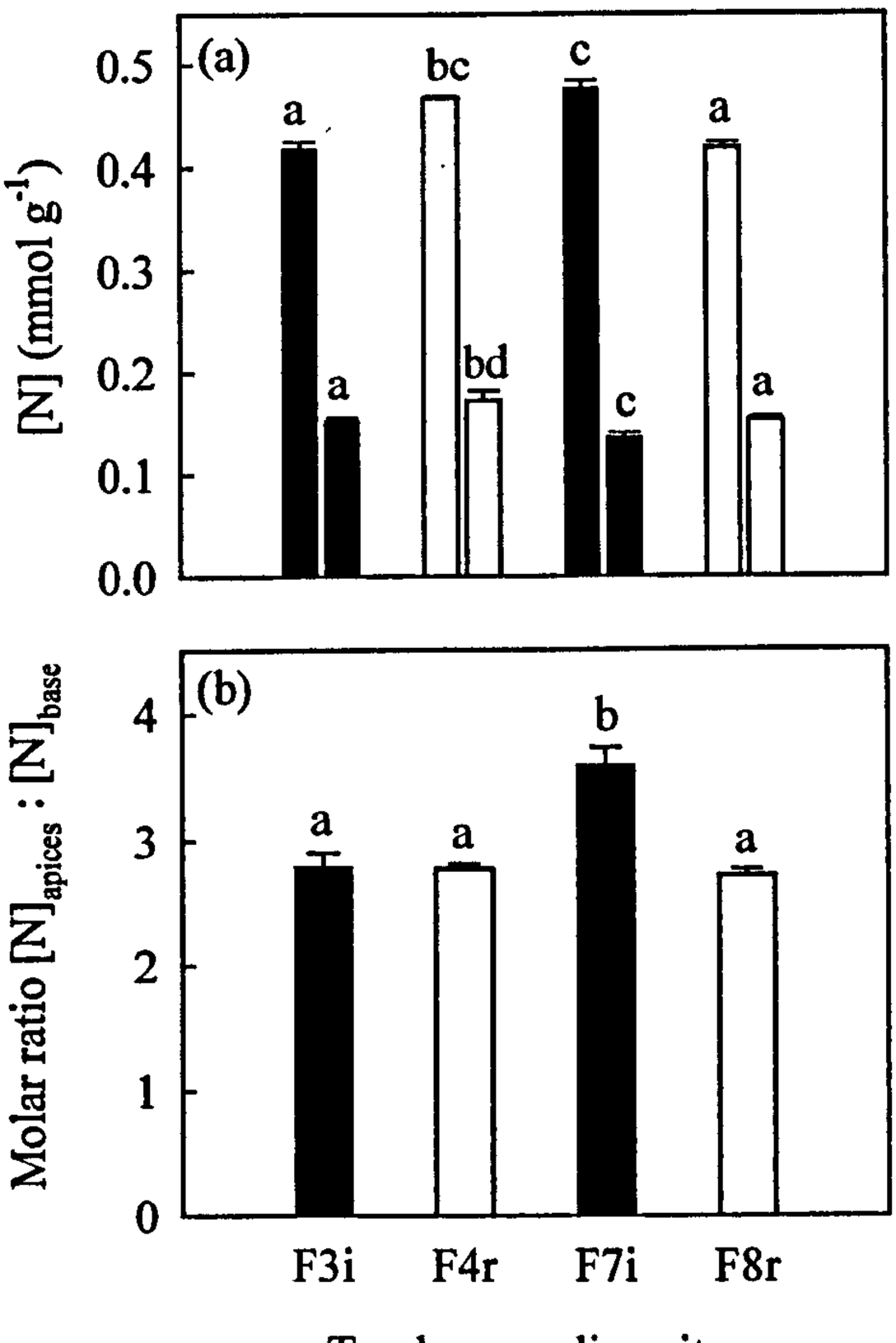


Figure 5.5. Nitrogen concentration in *Flavocetraria cucullata.* (a), values of $[N]_{apices}$ (0-0.5 cm, values > 0.4 mmol g^{-1}) and $[N]_{base}$ (3.5-4 cm, values < 0.2 mmol g^{-1}). (b), the molar ratio $[N]_{apices}$: $[N]_{base}$. Filled and open columns indicate 'industrial' and 'reference' sites, respectively. Plotted values are means ± 1 SE (n = 18). Columns with the same letters are not significantly different at the $P < 0.001$ level ($[N]_{apices}$ and the ratio $[N]_{apices}$:$[N]_{base}$) or $P <$ 0.05 level ($[N]_{base}$).

5.3.4. Soil analysis

The depth of the surface organic layer in sample quadrats varied between 0.5 and >5 cm. Top-soil pH (0-5 cm) at all sites was uniformly low, with mean values ranging from 4.03 (± 0.02), at site $F7_i$ (Kolva) to 4.88 (± 0.11) at site $F2_r$ (Kedva) (Figure 5.6). Generally, top-soils at tundra sites had lower pH values than those at taiga sites. The lowest recorded mean top-soil pH (0-5 cm) was 4.03 (± 0.02), at site $F7_i$; this value was significantly lower than the value of 4.48 (± 0.09) at site $F8_r$, (one-way-ANOVA, followed by Tukey's test, $P < 0.001$, $n = 18$).

Concentrations of metal elements in soil ash were generally low at all sites in the study (Figure 5.6). Values for several elements (Ba, Ca, K, Mg, Na, Pb and Zn) varied markedly between sites. However, only Ba, Ca and possibly Ni, were elevated at an industrial site: concentrations of these elements were significantly greater at site $F7_i$ than at site $F8_r$, (one-way-ANOVA, followed by Tukey's test; $P < 0.001$, $n = 18$). Mean concentrations of Ba, Ca and Ni in soil-ash were 459 (± 93), 4225 (± 1074) and 43 μg g^{-1} (± 3.1), respectively, at site $F7_i$, whereas, background concentrations for the 'reference' site $F8_r$ were 41 (± 4.6), 138 (± 16) and 21 μg g^{-1} (± 3.3), respectively. Figure 5.7 shows that concentrations of Ba and Ca in soil-ash, were highly positively correlated, whereas concentrations of Cu and Pb were only weakly correlated, perhaps as a result of a single outlying data point. Sodium occurred in high concentrations at sites $F3_i$ and $F4_r$, probably due to the close proximity of these sites to the Barents coast, resulting in marine inputs from sea-spray.

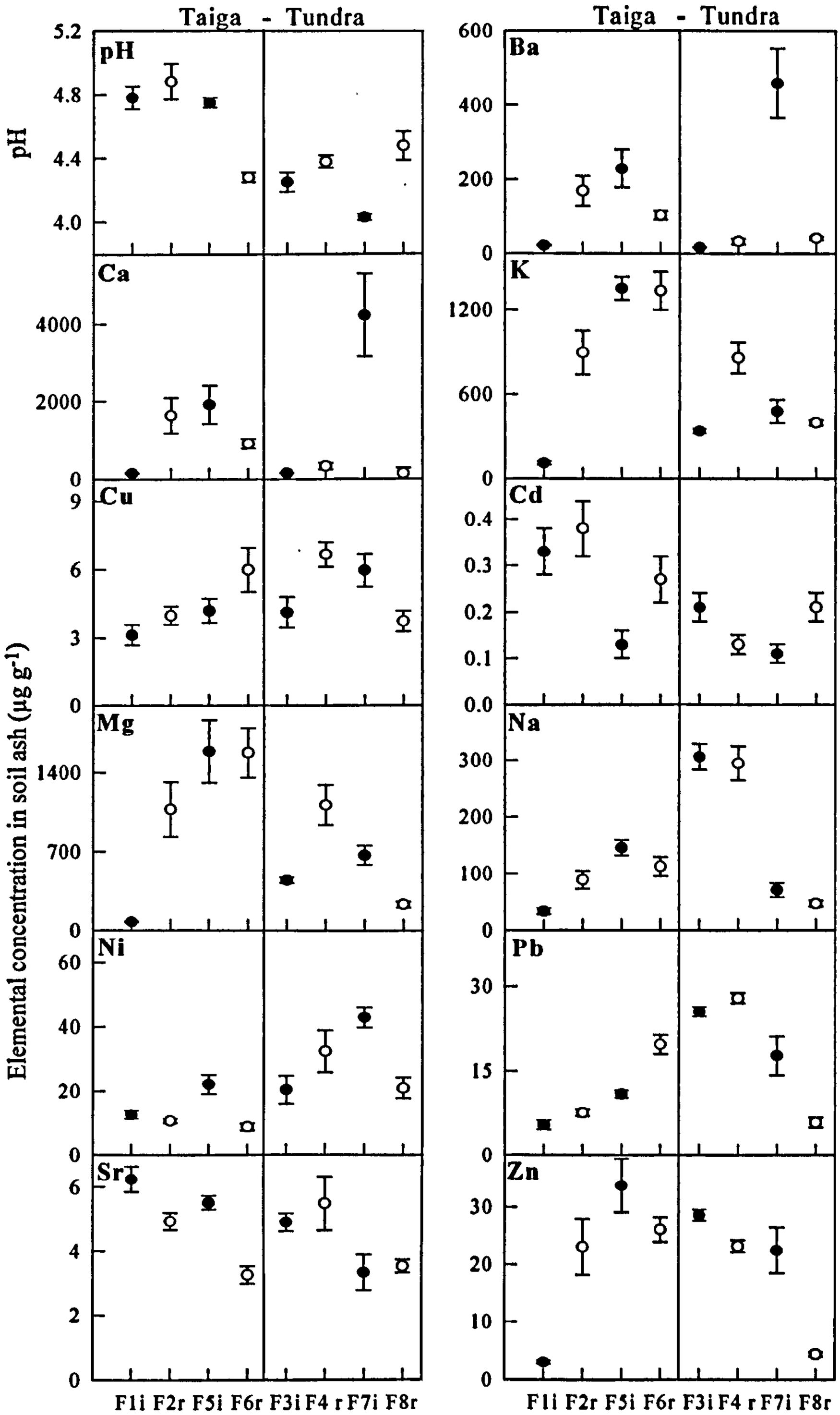


Figure 5.6. Values of pH in top-soil (0-5 cm) and concentrations of metallic elements in soil ash. Filled and open symbols indicate 'industrial' and 'reference' sites, respectively. Plotted values are means ± 1 SE (n = 18).

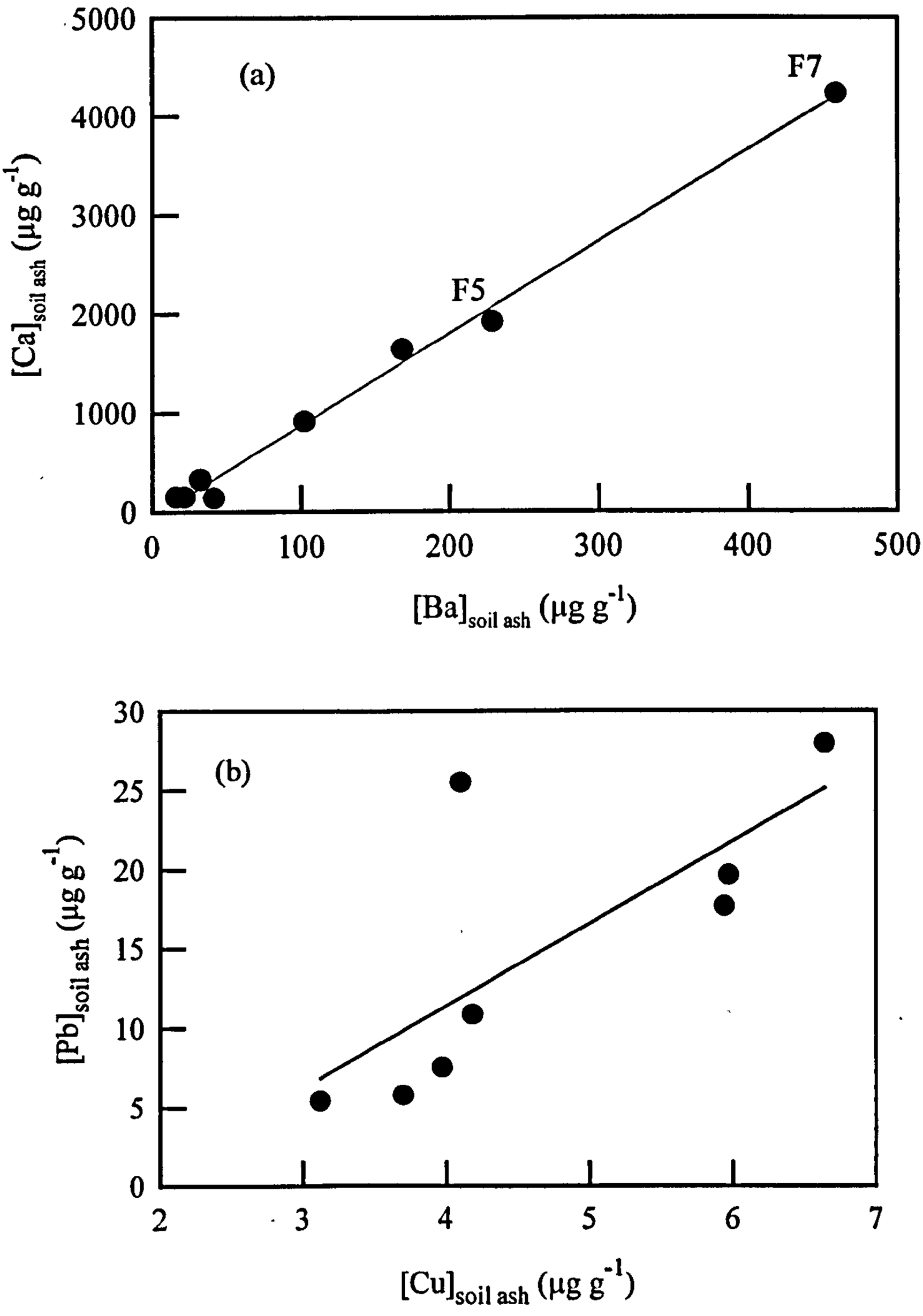


Figure 5.7. Elemental correlations in top-soil ash samples (0-5 cm): (a) [Ba] and [Ca] ($r = 0.997$, $P < 0.001$, $n = 8$), and (b) [Cu] and [Pb] ($r = 0.748$, $P > 0.01$, $n = 8$).

5.3.5. Lichen biodiversity

The abundance and diversity of lichens differed significantly between sites (Figure 5.8). Among the taiga sites differences were small, with 'reference' sites having the lower values. Complete listings of epiphytic lichen species assessed on the trunks and branches of *Picea obovata* up to a height of 1.7 m are given in Appendices 1.1 – 1.4. The first record of *Ramalina obtusata* in the Komi Republic was made at the Izhma river site ($F1_i$) during June 2001 (T. Prystina *pers. com.*).

Among the tundra sites, $F7_i$ had a markedly lower abundance and diversity of epigeals and lower abundance of epiphytes. Complete listings of epigeal lichen species and epiphytic lichen species recorded on *Betula nana* in each plot are given in Appendices 1.5 – 1.12. The effect of reindeer grazing and trampling were marked to severe at sites $F3_i$, $F4_r$ and $F8_r$, with $F8_r$ perhaps suffering the worst effects based on my own personal observations (see Figure 5.11).

Mean abundance of epigeal species at sites $F7_i$ and site $F8_r$ are compared in Figure 5.9 for the purpose of highlighting species with markedly different abundance values. *Alectoria nigricans*, *A. ochroleuca*, *Bryocaulon divergens* and *Sphaerophorus globosus* were common at site $F8_r$ but were poorly represented at site $F7_i$. With the exception of *Alectoria ochroleuca*, these species were also well represented at $F4_r$, although this site was not chosen as a comparable 'reference' site for $F7_i$. Similarly, mean abundance of epiphytic species at sites $F8_r$ and $F7_i$ are compared in Figure 5.10. *Cetraria nigricans* and *Ochrolechia frigida* were common at $F8_r$ but were poorly represented at $F7_i$. *Ochrolechia frigida* was also common at $F4_r$.

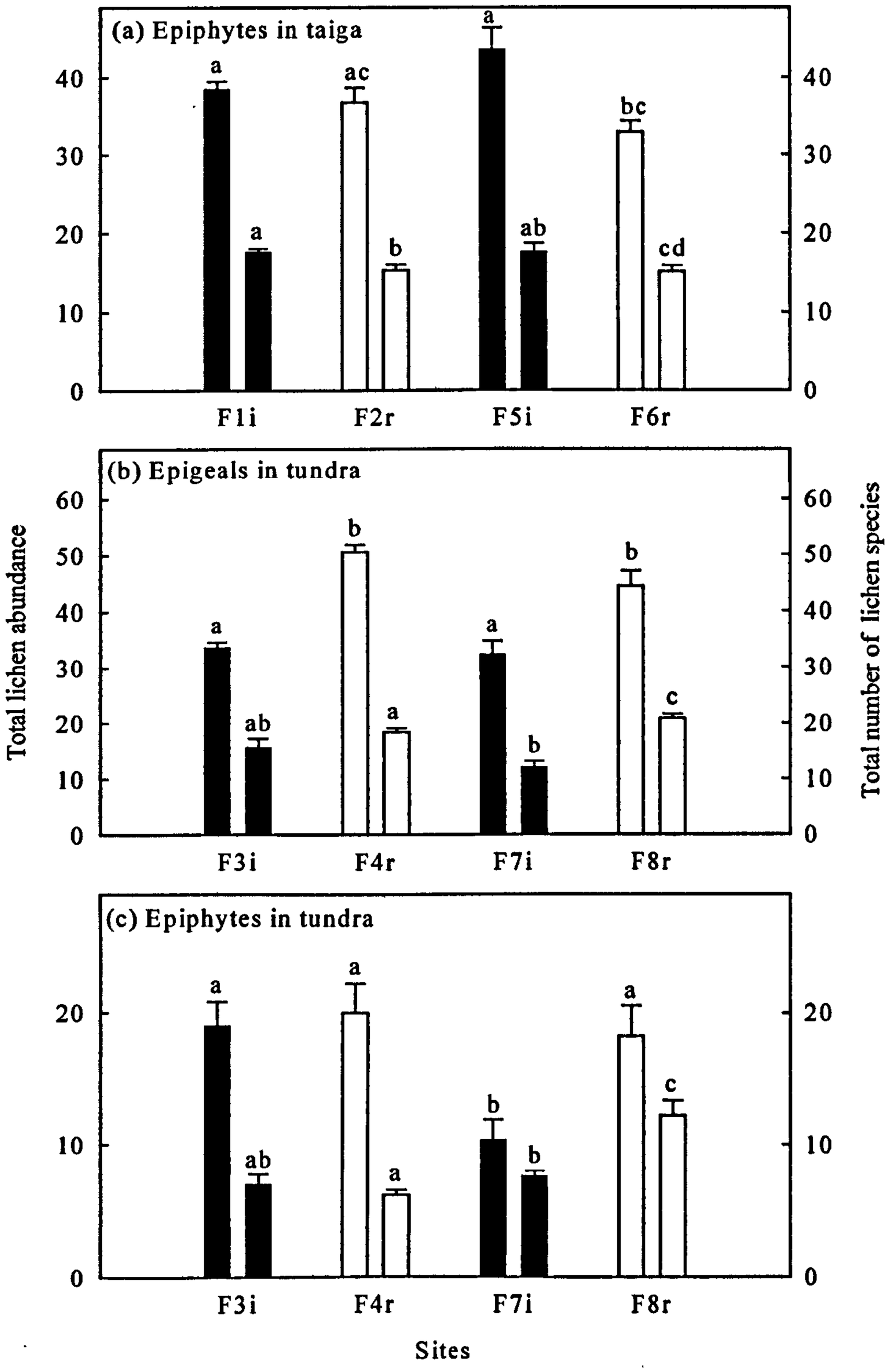


Figure 5.8. Mean values of total abundance (left hand column) and total number of lichen species (right hand column) at each sampling site. Filled and open columns indicate 'industrial' and 'reference' sites respectively. Plotted values are means ± 1 SE (n = 5-9). Significant differences were determined by one-way-ANOVA followed by Tukey's test; within each measured attribute sites with the same letters were not significantly different and sites with different letters were significantly different at the $P < 0.05$ level.

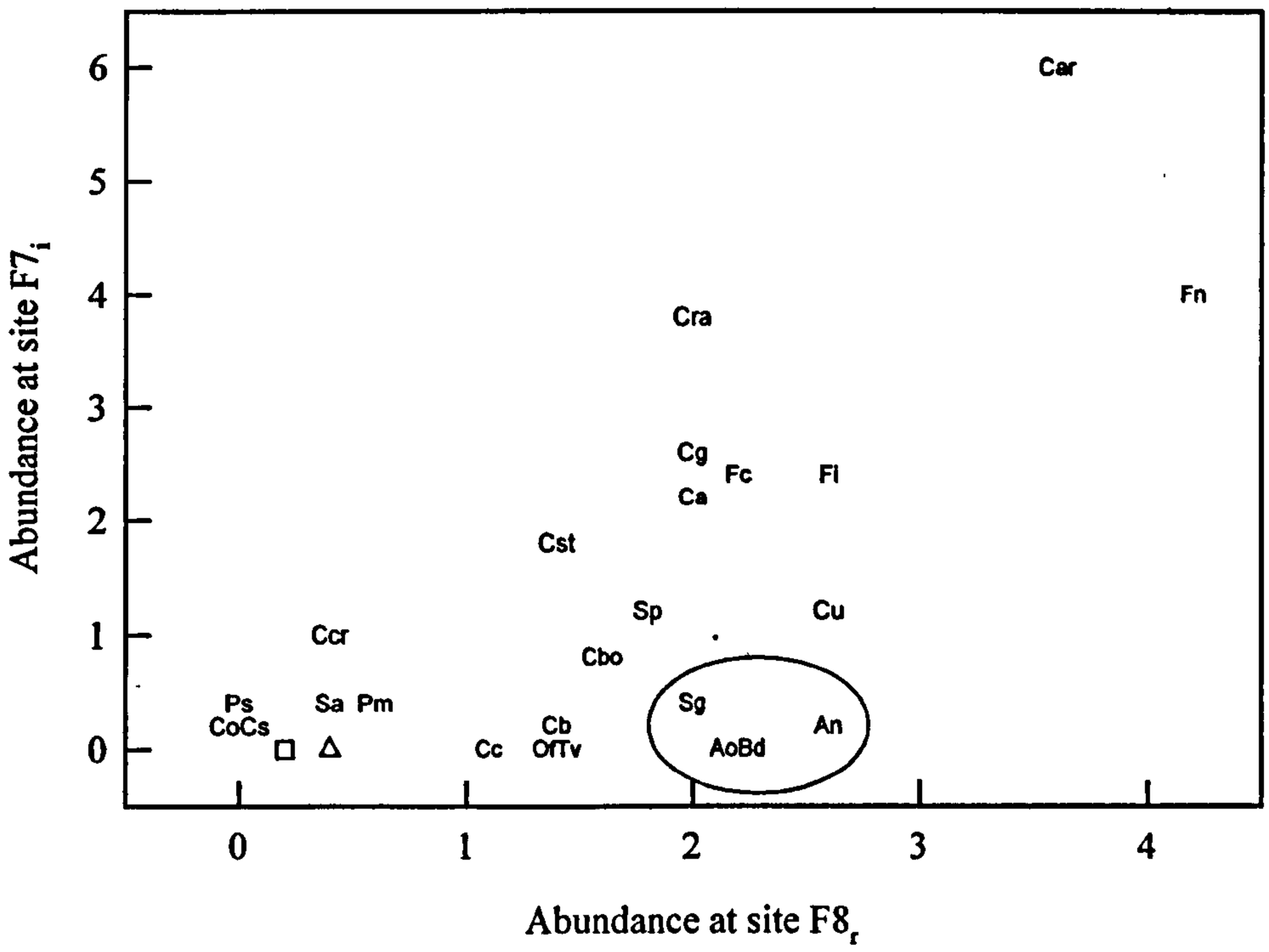


Figure 5.9. Comparisons of mean cover abundance of epigeal lichen species between sites $F7_i$ and $F8_r$. Species denoted as: (An), *Alectoria nigricans*; (Ao), *A. ochroleuca*; (Bd), *Bryocaulon divergens*; (Fn), *Flavocetraria nivalis*; (Fc), *F. cucullata*; (Fi), *Cetraria islandica*; (Ca), *Cladonia amaurocraea*; (Car), *C. arbuscula*; (Cb), *C. bellidiflora*; (Cbo), *C. borealis*; (Cc), *C. chlorophaea*; (Ccr), *C. crispata*; (Cg), *C. gracilis*; (Co), *C. coniocraea;* (Ccr), *C. cornuta*; (Cra), *C. rangiferina*; (Cst), *C. stellaris*; (Cs), *C. subfurcata*; (Cu), *C. uncialis*; (Ie), *Icmadophila ericetorum*; (Of), *Ochrolechia frigida*; (Pm), *Peltigera malacea*; (Ps), *P. scabrosa*; (Sg), *Sphaerophorus globosus*; (Sa), *Stereocaulon alpinum*; (Sp), *S. paschale*; (Tv), *Thamnolia vermicularis*; (□), *Cetraria nigricans, Cladonia cervicornis, Peltigera neckeri, Pertusaria correloides*; (Δ), *Cladonia pleurota, C. sulphurina, Hypogymnia physodes, Pertusaria panygra*. Circled species denotes those present at site $F8_r$ but were absent or rare at site $F7_i$. Estimates were made using the abundance scale of Kauppi and Halonen (1992): 7 = >50%, 6 = 26-50%, 5 = 11-25%, 4 = 3-10%, 3 = poor cover, < 3%, 2 = little, many specimens, but not constituting any real cover, 1 = extremely little, only one or two specimens.

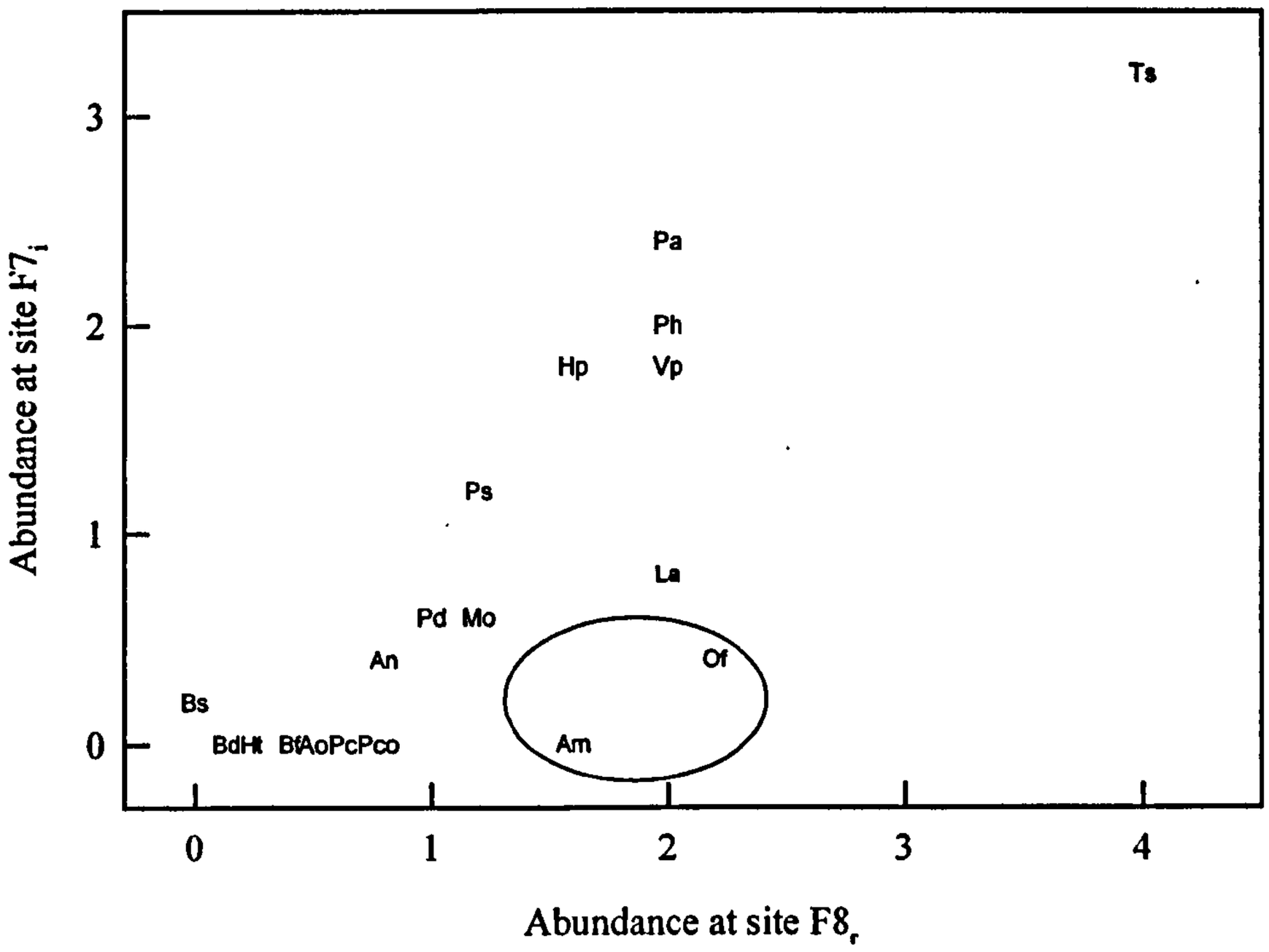


Figure 5.10. Comparisons of mean cover abundance of epiphytic lichen species between sites $F7_i$ and $F8_r$. Species denoted as: (An), *Alectoria nigricans*; (Ao), *A. ochroleuca*; (Am), *Cetraria nigricans*; (Bd), *Bryocaulon divergens*; (Bf), *Bryoria fuscescens*; (Hp), *Hypogymnia physodes*; (Ht), *H. tubulosa*; (La), *Lecanora argentata*; (Mo), *Melanelia olivacea*; (Of), *Ochrolechia frigida*; (Ps), *Parmelia sulcata*; (Pa), *Parmeliopsis ambigua*; (Ph), *P. hyperopta*; (Pc), *Pertusaria corallina*; (Pco), *P. coccodes*; (Pd), *P. dactylina*; (Ts), *Tuckermanopsis sepincola*; (Vp), *Vulpicida pinastri*. Circled species denotes those present at site $F8_r$ but were absent or rare at site $F7_i$. Estimates were made using the abundance scale of Kauppi and Halonen (1992): 7 = >50%, 6 = 26-50%, 5 = 11-25%, 4 = 3-10%, 3 = poor cover, < 3%, 2 = little, many specimens, but not constituting any real cover, 1 = extremely little, only one or two specimens.

5.4. Discussion

5.4.1. Chemical impacts on lichens and top-soil

The objective of the programme of chemical analysis of lichens was to perturbations in lichen chemistry at 'industrial' sites that might be caused by air pollution. In particular, increases in the ratios $[K^+]:[Mg^{2+}]_{apices}$ and $[K^+]:([Ca^{2+}]+[Mg^{2+}])_{apices}$ were sought as evidence of acid deposition and increased $[N]_{apices}$ values were sought as evidence of N deposition (see Chapter 3).

In general variation in lichen chemistry was either small or, if large, unrelated to industrial acitivity; for example the ratio $[K^+]:[Mg^{2+}]_{apices}$ in *C. arbuscula* varied across all eight sites by a factor of 1.9 and in *F. cucullata* amongst the four tundra sites by a factor of 1.8. Hyvärinen and Crittenden (1996) found that the ratio $[K^+]:[Mg^{2+}]_{apices}$ in *C. portentosa* varied by a factor of *c.* 4 amongst sites in the British Isles. In the present work the strong covariation in the chemical indices between species suggests that these differences in cation contents reflected inter-site differences in environmental circumstances, as opposed to random variation. However, there were examples of both high and low ratios at both 'industrial' and 'reference' sites suggesting that air pollution was not a factor contributing significantly to variation.

Amongst tundra sites, values of $[N]_{apices}$ were greatest at site $F7_i$ and the value of $[N]_{apices}$: $[N]_{base}$ in *F. cucullata* was significantly higher here than at other sites. Hyvärinen and Crittenden, (1998a), demonstrated a strong relationship between N deposition and [N] in the mat-forming terricolous lichen *Cladonia portentosa*. Their study of the common heathland lichen *C. portentosa* in the British Isles, found that [N] in the apical 5 mm of thalli ($[N]_{apices}$) and in a deeper stratum 35-50 mm from the apices ($[N]_{base}$) were both significantly positively correlated, and the concentration ratio $[N]_{apices}$: $[N]_{base}$ was negatively correlated, with N deposition. Since Hyvärinen and Crittenden (1998a) found the concentration ratio $[N]_{apices}$:$[N]_{base}$ to be negatively

correlated with N deposition in *C. portentosa*, the higher value of the ratio at site $F7_i$ is difficult to interpret; it may reflect a subtle physiological perturbation or simply random variation. Hyvärinen and Crittenden (1998a) reported that $[N]_{apices}$ in *C. portentosa* varied by a factor of 1.9 among sites in the British Isles and Sochting (1990) found [N] in unspecified strata of *Cladonia* sp. (sub-species *Cladina*) to vary by a factor of 3.4 among several European sites. In the present study, $[N]_{apices}$ varied by factors of 1.1 – 1.2 within biomes and 1.3 – 1.5 across all sites.

Coherent evidence of pollution was also generally absent in the soil metal concentration data across most sites. Elemental concentrations within soil ash were generally low. Exceptions were marked elevations by Ba and Ca, and a small elevation in Ni, at site $F7_i$. Contamination of Ba and Ca might arise from dust blown from gravel roads or building work where cement is handled. Concentrations of Ba in soil ash taken from sites close to Vorkuta were six times greater than those measured at site $F7_i$ (see Chapter 4). Other apparent chemical anomalies at site $F7_i$ include high $[Pb]_{apices}$ and low soil pH.

Nitrogen concentration in *C. arbuscula, C. stellaris* and *F. cucullata* at most sites were typical of background levels at comparable sites in the Usa basin (Chapter 3). For example values of $[N]_{apices}$ in *C. arbuscula* and *F. cucullata* at tundra sites were between 0.4 - 0.5 mmol g^{-1} which compares favourably with background sites at the extremes of the transect through Vorkuta. In *C. stellaris* values of $[N]_{apices}$ at site $F6_r$ were similar to values of $[N]_{apices}$ in this species at sites 3.2 and 3.1 at the southern extreme of the transect through Inta, e.g. 0.5 - 0.6 mmol g^{-1}. Values of $[N]_{apices}$ in *C. arbuscula* varied little within each of the tundra and taiga locations, but were consistently lower in the tundra. This reflects the trend observed in *C. stellaris* collected along the south to north transects (Transects 2/3) in the Usa basin where $[N]_{apices}$ decreased with increasing latitude and decreasing annual winter precipitation (Chapter 3). There are no data for N deposition around site $F7_i$, but gas flaring was observed at the industrial complex. Jaffe *et al.* (1995b) reported significant NO_x

emissions from gas flaring operations at Prudhoe Bay and accordingly elevated values of $[N]_{apices}$ in *C. arbuscula*, and *F. cucullata*, at $F7_i$ might result from local NO_x emissions due to waste gas combustion at this site.

Kytöviita (1993) observed that exposure of the mat-forming lichens *C. stellaris* and *Stereocaulon paschale* to simulated acid rain resulted in significant reductions in both $[Ca^{2+}]_{apices}$ and $[Mg^{2+}]_{apices}$ while $[K^+]_{apices}$ remained unchanged. Kytöviita (1993) suggested that the ratio $([K^+]:([Ca^{2+}]+[Mg^{2+}]))_{apices}$ in lichens might prove a sensitive index of acid exposure. Hyvärinen and Crittenden (1996) showed that $([K^+]:[Mg^{2+}])_{apices}$ in *C. portentosa* in the British Isles was positively correlated with precipitation acidity, while $([K^+]:([Ca^{2+}]+[Mg^{2+}]))_{apices}$ was not. Around the city of Vorkuta, I found $([K^+]:[Mg^{2+}])_{apices}$ to be elevated in *C. arbuscula*, while $([K^+]:([Ca^{2+}]+[Mg^{2+}]))_{apices}$ to be reduced. These trends were interpreted as responses to alkaline ash deposition (see Chapter 3). In the Pechora region $([K^+]:([Ca^{2+}]+[Mg^{2+}]))_{apices}$ at site $F7_i$ was lower than at $F8_r$ in both *C. arbuscula* and *F. cucullata*. Thus, at site $F7_i$, the marker ratio $([K^+]:([Ca^{2+}]+[Mg^{2+}]))_{apices}$ might have responded to emissions of Ca-rich particulates from construction activities. Potassium concentrations were higher in *F. cucullata* than *C. arbuscula* at tundra sites, comparing favourably with data from pristine sites in the Usa basin (see Chapter 3).

Lead concentrations in the apices of *C. arbuscula, C. stellaris* and *F. cucullata* were low and compare favourably with values recorded in terricolous mat-forming lichens at unpolluted tundra sites in the Usa basin (T. Prystina, *pers. com.*). They are below concentrations measured at background sites elsewhere in the Arctic (Puckett, 1978; Nash and Gries, 1995a; Riget *et al.*, 2000; Bargagli and Mikhailova, 2002). However, slightly elevated $[Pb]_{apices}$ and $[Pb]_{soil\ ash}$ values were recorded at site $F7_i$. It is noteworthy that Garty *et al.* (1998) found elevated concentrations of Pb in *Ramalina lacera* at a site close to an oil combustion plant.

The mean pH values of top-soil in this study were all uniformly low and were comparable with values reported at pristine sites in the Usa basin (Rusanova, 1995a; Chapter 4). At most sites metal concentrations in soil-ash were typical of those found at pristine sites in the Russian Arctic, measured by Walker *et al.* (2003) in the Usa basin and Alexeeva-Popova *et al.* (1995) on the Chukotka peninsula. One exception was Na, where concentrations were elevated at sites, $F3_i$ and $F4_r$, possibly as a result of marine inputs from the Barents coast as sea-spray. Concentrations of Ba, Ca and Ni in top-soil were highest at $F7_i$, but Ba measured at this locality was still lower than elevated concentrations measured at sites close to Vorkuta and Inta in the Usa basin (Chapter 4). Elevated concentrations of Ni in the vicinity of site $F7_i$ were probably the result of fuel oil combustion and gas flaring, which occurs around the Kolva site, (Vilcheck and Tishkov, 1997). In a study by Genoni *et al.* (2000), elevated concentrations of Ni were found in soil and moss samples taken close to oil-fired power plants. It is likely that soils from site $F7_i$, and those at other sites in this study, have not been significantly modified and remain close to pristine, although previous studies have documented contamination of soils from oil spills in the area (Rusanova, 1995b). It is doubtful that soils at these sites have been subject to an oil spill.

5.4.2. Lichen biodiversity

There was no evidence of deleterious industrial impacts on epiphytic lichens at taiga sites while values of lichen abundance and α-diversity were lower at industrial sites in the tundra, most notably at site $F7_i$. However, interpretation of these data must take into consideration the potential confounding effects of other man-made disturbances such as forestry around the industrial sites producing younger, more open forests and reindeer husbandry. Since little data exist on the pollution sensitivity of epigeal lichens, and the tundra sites were subject to reindeer grazing, greater emphasis was placed on data for epiphytic species for which more information exists on pollution sensitivity. In addition, it should be noted that the cover abundance scale used in this work was

subjective and non linear, potentially over emphasising the importance of species with low abundance scores.

The abundance and α-diversity of lichens varied significantly between sites. Among taiga sites differences were small, with 'reference' sites having the lower values. Site $F7_i$, appeared to be less disturbed by reindeer. This might be because roads and pipelines restrict the movement of reindeer herds, or because reindeer herdsmen avoid industrial sites where the occurrence of discarded debris on the tundra can injure animals (O. Harbeck *pers. com.*). The epigeal lichens here formed much deeper mats, and hence greater biomass but comprised fewer species (Figure 5.11b). By contrast, sites $F3_i$, $F4_r$ and $F8_r$ had more epigeal species, and hence greater diversity, but low biomass due to heavy grazing and trampling by reindeer (Figure 5.11a). Crittenden (2000) gives a detailed review of lichen growth and the impacts of trampling and grazing by reindeer. In the shrub tundra east of Vorkuta mat-forming lichens were largely eliminated from the ground cover, as Crittenden (2000) found *C. arbuscula* at most sites but usually only in trace quantities, possibly due a combination of efficient grazing as well as trampling. Manseau *et al.* (1996) also reported damage to epigeal lichen communities in tundra used by migratory caribou in northern Quebec and Moser *et al.* (1979) made similar observations at Anaktuvuk Pass in the Alaskan tundra. The problem of lichen cover depletion due to reindeer is widespread in the Russian tundra (Ahti and Oksanen, 1990; Vilchek and Tishkov, 1997; Forbes, 1999; Klein, 2000).

(a)

(b)

Figure 5.11. Reindeer impacted terrain at Mareyu River ($F8_r$) (a), in contrast to the lichen rich ground cover in tundra at upper Kolva River ($F7_i$) adjacent to the oil recovery site (b). (Photos: P. D. Crittenden).

It is not known why there were more epiphytic species at site $F1_i$ than at the 'reference' site $F2_r$, or why the sum of abundance of epiphytes was significantly higher at site $F5_i$ compared with site $F6_r$. All are lowland taiga sites, but $F1_i$ is situated at a distance of approximately 10 km from petrochemical operations, principally oil processing, located around Ukhta (Komi's third largest town) and the nearby gas processing operations in Sosnogorsk. Site $F1_i$ is also affected by forestry, which has left the taiga in this area fragmented, with forest stands of different ages. Svetly Vuktyl ($F5_i$) is almost exclusively characterised by its gas extraction industry which accounts for more than 95% of all industrial production in the area, and a small timber industry (Gimadi, 2002). However, lichens in the genera *Usnea* and *Bryoria* (see below) were present at this site, and site $F1_i$, presumably currently unaffected by emissions from the local oil and gas industries. If potential sources of pollution exist here, there may be a time lag before even the most sensitive species begin to decrease, possibly over several decades. These species are known to be pollution sensitive (Hawksworth and Rose, 1970; Kuusinen *et al.,* 1990; Oksanen *et al.,* 1990; Aamlid and Venn, 1993; Pirintsos *et al.,* 1993; van Dobben and ter Braak, 1999). For example Kauppi and Halonen (1992) found that the most SO_2 responsive epiphytic lichens around Oulu, northern Finland were, *Plastimatia glauca* and *Usnea filipendula,* together with *Bryoria fuscescens* and *B. capillaris*. Kuusinen *et al.* (1990) and Hyvärinen *et al.* (1992) found that these species also tended to favour older forest stands.

Factors other than air pollution affecting epiphytic lichen abundance include climate and stand age (Kuusinen *et al.,* 1990; Hyvärinen *et al.,* 1992). Site $F5_i$ comprises fragmented lowland taiga, whereas site $F6_r$ is pristine old growth taiga, protected in the Yugyd Va national park in the foothills of the pre-Polar Ural mountains. Furthermore, the annual precipitation in the Urals is higher than in lowland taiga (Christensen and Kuhry, 2000; van der Linden and Christensen, *in press*). The stand age of the forest at $F6_r$ is greater than parts of the fragmented forest of $F5_i$ (T. Virtanen, *pers. com.*). Trees of similar size

were selected to restrict sampling to lichen communities at broadly comparable successional stages (Stone, 1989). Hyvärinen *et al.* (1992) found that *Bryoria fuscescens* was common in all types of stand, whilst species such as, *B. capillaris* prefer older or denser stands. Both *B. capillaris* and *B. fuscescens* were abundant at site $F5_i$. Accordingly, differences in lichen abundance between the two sites could be due to regional variation in precipitation and impacts of forestry.

Epigeal lichen species which were present at sites $F8_r$ and $F4_r$, but were absent or poorly represented at site $F7_i$, included species that are known to be pollution-sensitive according to McCune and Geiser (1997) and Gilbert (2000) viz. *Alectoria nigricans, Bryocaulon divergens* and *Sphaerophorus globosus.*

5.5. Summary and the broader context

Data presented here for lichen and soil chemistry, and for lichen diversity suggest that the effects of pollution at the industrial sites examined were generally below detection limits. An exception is site $F7_i$ where a suite of minor shifts in environmental chemistry and lichen abundance might be an early signature of industrial activity.

Other aspects of environmental chemistry (Table 5.2), and components of biodiversity (Table 5.3) were examined at the same eight locations by other collaborating research groups in the SPICE programme. Data on environmental chemistry (Table 5.2), provide additional evidence that emissions at $F7_i$ can be detected in the environment. These include polycyclic aromatic hydrocarbons, Hg and As in lake sediments. Several signals were noted at $F3_i$ but mostly could be explained by global or natural sources. Table 5.3 summarises the results of a range of biodiversity assessments which again identifies site $F7_i$ as the most putatively impacted location.

Table 5.2. Occurrence of polluting substances in the Pechora region.

Indicators	Sites											References
	$F1_i$	$F2_r$	$F5_i$	$F6_r$	$F3_i$	$F4_r$	$F7_i$	$F8_r$	Pechora Delta	Usinsk	Vorkuta	
PAHs (lake sediments, (l.s.))	n.a.	n.a.	n.a.	+N	+L	n.a.	+L	-	+L	+L	+L	(V. Dauvalter, *pers. com.*)
OCCs (l.s.)	n.a.	n.a.	n.a.	-	-	n.a.	-	-	-	+L	+L	(V. Dauvalter, *pers. com.*)
SCPs (l.s.)	n.a.	+G	n.a.	+G	+G/L	-	+G	+G/R	n.a.	+G/L	+G/L	(Solovieva *et al.*, 2002)
Hg, As (l.s.)	n.a.	n.a.	n.a.	+G	+G/L	+G	+G/L	+G	+G/L	+G/L	+G/L	(V. Dauvalter, *pers. com.*)
Pb, Cd (l.s.)	n.a.	n.a.	n.a.	+G	+G/L	+G	+G	+G	+G	+G	+G	(Solovieva *et al.*, 2002)
Hydrocarbons (waters)	+N	+N	+N	+N	+N/L	+N	+N	+N	+N	+L	+N/L	(V. Jones, *pers. com.*)
Hg (waters)	-	-	-	-	-	-	-	-	-	-	-	(V. Dauvalter, *pers. com.*)
Fe, Cu (waters)	+N/L	+N	+N	-	+N	+N	+N	+N	+N	+N/L	+N/L	(V. Dauvalter, *pers. com.*)
Pb (lichens)	-	-	-	-	n.a.	n.a.	+L	-	n.a.	n.a.	n.a.	(This study)
Ca, Ba (soils)	-	-	-	-	-	-	+L	-	n.a.	-	+L	(Walker *et al.*, 2003)
N, P (lichens, sediments)	+G/L	+G	+G	+G	+G	+G	+G/L	+G	+G	n.a.	n.a.	(Solovieva *et al.*, 2002; Walker *et al., in press*; V. Dauvalter, *pers. com.*)
Localeffects/total effects	2/6	0/7	0/6	0/11	5/10	0/8	5/11	0/11	2/8	6/9	7/9	

+ = possible pollution detected; - = no detectable pollution

N = elevated values due to natural sources; G = elevated values due to global pollution sources

R = elevated values due to regional pollution; L = elevated values due to local pollution

PAHs = polycyclic aromatic hydrocarbons; OCCs = organic chloride compounds; SCPs = spheroidal carbonaceous particles

Table 5.3. Summary of putative impacts on biodiversity in the Pechora region.

Indicators	Sites								References
	$F1_i$	$F2_r$	$F5_i$	$F6_r$	$F3_i$	$F4_r$	$F7_i$	$F8_r$	
Birds	-	-	-	-	-	-	+D	-	O. Ratti (*pers. com.*)
Lichen biodiversity	-	-	-	-	+D	-	+P	-	This study
Fish biodiversity	-	-	-	-	-	-	+P	-	V. Pomonarev (*pers. com.*)
Fish populations	+O	+O	+O	+O	+O	+O	+O	-	V. Pomonarev (*pers. com.*)
Diatom biodiversity	-	-	-	-	-	-	-	-	E. Patova (*pers. com.*)
Diatom pollution indicators	+E	-	-	-	+E	-	+E	-	E. Patova (*pers. com.*)
Cyanobacteria biodiversity	-	-	-	-	-	-	-	-	E. Patova (*pers. com.*)
Cyanobacteria pollution indicators	+E	-	-	-	+E/H	-	+E/H	-	E. Patova (*pers. com.*)
Zoobenthos (1=Molluscs; 2=Oligochaeta)	+E	-	-	-	+H(1)	-	+H(2)	-	E. Patova (*pers. com.*)
Impact vs no impact	4/9	1/9	1/9	1/9	5/9	1/9	7/9	0/9	

+ = possible impact detected; - = no detectable impact
P = pollution; D = disturbance (hunting/reindeer grazing)
O = over fishing; E = eutrophication; H = hydrocarbons

CHAPTER 6. CONCLUSIONS

This work aimed to assess the extent of acid and alkaline and metal deposition initially in the Usa basin and then subsequently extending more widely over the Pechora region. The extent of contamination was assessed by mapping spatial variation in the chemical composition of snow, lichens and top-soil. In addition, differences in lichen biodiversity were sought between industrial and background sites in order to yield information on air pollution impacts.

The major findings of the chemical analyses of terrestrial ecological materials collected in this study, provided evidence that large areas of the Usa and Pechora basins remain in a condition close to 'pristine' (Chapters 3 and 4). Even when new industrial sites were compared alongside non-industrialised reference sites, there appeared to be little difference in the measured variables in both this study and those by other groups working within the SPICE programme. Any contamination that was found was largely confined to local sites, whereas, at sites remote from towns there was little supporting evidence of pollution; for example, around Vorkuta mean concentrations of Ba and Sr in soil ash were 2.78×10^3 μg g^{-1} and 1.31×10^2 μg g^{-1}, respectively. By contrast, concentrations for the background site were 3.09×10^2 μg g^{-1} and 22.6 μg g^{-1} respectively. This becomes particularly apparent when levels of contamination in the Pechora region are compared with those reported by Reimann *et al.* (2000) on the Kola Peninsula. Here, Ba and Sr in soil were 1.13×10^5 μg g^{-1} and 2.68×10^5 μg g^{-1} respectively at sites close to Monchegorsk. The background values of measured variables in this study were broadly comparable with those reported by Alexeeva-Popova *et al.* (1995) from the Chukotka Peninsula and by Rovinsky *et al.* (1995) in the Ust-Lena reserve, both considered uncontaminated areas of the Russian Arctic. From a chemical standpoint much of the Usa and Pechora region remains largely unmodified by pollution and reflects background conditions and concentrations, which further emphasises the need for environmental protection where future industrial exploitation is likely.

Over the Usa basin pollution gradients were found on two geographical scales. The first was a latitudinal gradient in the deposition of nitrogen (N) and sulphur (S), indicated by a northwards decline in $[N]_{apices}$ in mat-forming lichens and winter deposition of $nssSO_4^{2-}$. This probably results from long-range transport from outside the region by northward-moving air masses originating from industrial regions of the Urals and Western Europe (e.g. Rahn, 1982; Ryaboshapko *et al.*, 1998). Ryaboshapko *et al.* (1998) used NO_x emission data to model deposition loads over Russia. They predicted a gradient of N deposition over the Komi Republic varying very broadly from 500 to 200 mg N m^{-2} y^{-1}. The gradient in $[N]_{apices}$ reported here for *Cladonia stellaris* on the Inta transects is consistent with, although not proof of, such a deposition gradient. There may also be some contribution from more widely dispersed emissions from local sources; for example, Shahgedanova and Burt (1994) suggested that the annual mean atmospheric concentrations of NO_2 in Vorkuta are the highest of any town in the Russian Arctic. The second gradient is due to deposition of alkaline and metal-rich particulates extending to 25-40 km around the coal-burning centres of Vorkuta and Inta with associated changes in vegetation cover (Virtanen, *et al.*, 2002), lake chemistry (Solovieva *et al.*, 2002) and soil metal loading (Chapter 4).

Definitive evidence of increased N and S deposition rates over Arctic regions has come from the stratigraphic analysis of ice cores taken from the Greenland ice sheet; for example, NO_3^- and SO_4^{2-} concentrations in surface firn are twice as great as those in ice deposited prior to the industrial revolution (e.g. Brimblecombe and Stedman, 1982; Neftel *et al.*, 1985; Rodhe and Rood, 1986; Fischer *et al.*, 1998). The baseline $[NO_3^-]_{snow}$ values observed in the present survey were *c.*9.2 μmol L^{-1}, and $[nssSO_4^{2-}]_{snow}$ values on transects 2/3 were between 4.0-5.2 μmol L^{-1}. Using as a multiplier total annual precipitation values at each site modelled by van der Linden and Christensen (*in press*) yields annual depositions in the ranges of 56-123 mol N ha^{-1} y^{-1} and 29-65 mol nssS ha^{-1} y^{-1}. These values can be compared to published estimates of critical

loads for N and S in Subarctic and Arctic ecosystems bearing in mind that NO_3^- deposition might be lower than total N deposition by a factor of at least two. Hornung *et al.* (1995) proposed that the critical load for N in Arctic and alpine heathlands was in the range 375-1071 mol N ha^{-1} y^{-1} while, on the basis of N fertilization experiments on Svalbard, Gordon *et al.* (2001) suggested that the critical load value is likely to be towards the lower end of this range. Bashkin *et al.* (1995) produced critical load maps for N and S over northern Siberia where the most sensitive ecosystems have critical load values <50 mol ha^{-1} y^{-1} for both N and S but with many areas with values in the range 51-100 mol ha^{-1} y^{-1}. Bashkin (1997) produced critical loads maps for European Russia suggesting that *c.* 50% of Subarctic and Arctic areas have critical loads for N in the range 0-200 mol ha^{-1} y^{-1}. While for S, only 2% of the region had a critical load in the 0-200 mol ha^{-1} y^{-1} range, and 31% of the region had values of 200-500 mol ha^{-1} y^{-1}. Lien *et al.* (1993) reported that the most sensitive surface waters on Svalbard have a critical load for nssS of between 59-309 mol ha^{-1} y^{-1}.

The ecological effects of low acid deposition loads in the Arctic remain uncertain, but there is concern that enhanced N deposition in particular could force ecological change in otherwise oligotrophic N-limited ecosystems (Chapin and Bledsoe, 1992; Nadelhoffer *et al.*, 1992; Robinson and Wookey, 1997; Näsholm *et al.*, 1998; Tybirk *et al.*, 2000). The most pronounced impacts of 'acidification' have been seen closer to emission sources in industrialised regions where there have been many documented examples of environmental damage due to acidification and eutrophication (Jónsdóttir *et al.*, 1995; Woodin, 1997; Gordon *et al.*, 2001). Increases in N deposition in the Arctic may be particularly critical because there may be both direct and indirect effects (Walker *et al.*, 2001). Direct effects could change species composition and soil function, and indirect effects due to acidification, where this could significantly increase N concentrations in surface runoff waters, as soils and vegetation lose their buffering capacity over time (Williams *et al.*, 1998). Clearly there is still uncertainty about critical load values but current knowledge suggests that N deposition over the Usa basin could already exceed

the critical load in some ecosystems. Predicted ecological change due to N pollution is in the same direction as climate forcing e.g. it will promote expansion of shrub growth in tundra (e.g. Paal *et al.*, 1997) and a possible reduction in terricolous lichen biomass in high-latitude ecosystems due to competitive exclusion (Cornelissen *et al.*, 2001).

There is discussion in the literature as to whether N pollution is already increasing the productivity of boreal forests (Nadelhoffer *et al.*, 1999). D'Arrigo *et al.* (1987) and Myneni *et al.* (1997) observed an increase at high northern latitudes in the normalised difference vegetation index (NDVI), which is strongly correlated with photosynthetic canopies (i.e. leaf area index). Increased growth of boreal coniferous forests would contribute to feedbacks to global warming due to increased C storage (negative feedback) and reduced regional albedo (positive feedback) (Brooks *et al.*, 1997). Greenhouse gas induced global warming is predicted to be most pronounced at high latitudes (Keeling, 1996). This is possibly evidenced by marked increases in the late winter and early spring temperatures during the last 100 years in Siberia reported by Briffa *et al.* (1995). IPCC (2001) predicts a 6-10 °C warming over the next 50-100 years in this region, with consequences for infrastructure damage due to permafrost melting and collapse (N. Karstkarel *pers. com.*). Damage to permafrost might also increase due to the use of vehicles on tundra, and construction of roads, buildings and other installations. Therefore, extensive oil, gas and mining operations in the Arctic could potentially result in local effects on biodiversity and ecosystem functioning. Although, these disturbances might be small, their impacts can be far reaching because of the considerable length of roads and pipeline systems associated with them (Walker *et al.*, 1987).

Around Vorkuta there was pronounced local pollution associated with alkaline particulates and metal deposition and probably phytotoxic gases (e.g. NO_x and SO_2). This is the result of coal combustion which commenced on a large scale in the 1930's and is evident from increased soil metal loadings (Chapter 4), the

chemistry of lake sediments (Solovieva *et al.*, 2002) and changes in tundra vegetation (Virtanen, *et al.*, 2002).

Annual coal production peaked here at 20 x 10^6 tonnes several decades ago and there was a commensurate increase in coal combustion (Virtanen *et al.*, 2002). This suggestion is consistent with the stratigraphies of spheroidal carbonaceous particle (SCP) concentrations in lake sediments in the Vorkuta region described by Solovieva *et al.* (2002) which showed pronounced concentration maxima at a depth of *c.*5 cm below the sediment surface. The high soil metal loadings found locally around Vorkuta provide supporting evidence for such a historical change in Vorkuta's pollution climate because the quantities of metals present are too great to be explained by current deposition rates (Chapter 4). Sulphur dioxide emissions from Vorkuta (currently 37 x 10^6 kg) also declined markedly since the 1980s.

There is now compelling evidence that pollution has caused large scale ecological change in the vicinity of Vorkuta. Vegetation classification studies by Virtanen *et al.* (2002), using satellite data and ground truthing plots, concluded that there is an increased abundance of willow and reduced abundance of dwarf birch and other shrubs in tundra surrounding the city. Two impacted zones were recognised (Figure 6.1), defined as a 'polluted zone' (150-200 km^2) and a 'slight pollution or disturbance zone' (600-900 km^2). In the most severely impacted zone, lichens appear to have been largely replaced by mosses and grasses which were relatively abundant (Virtanen *et al.*, 2002).

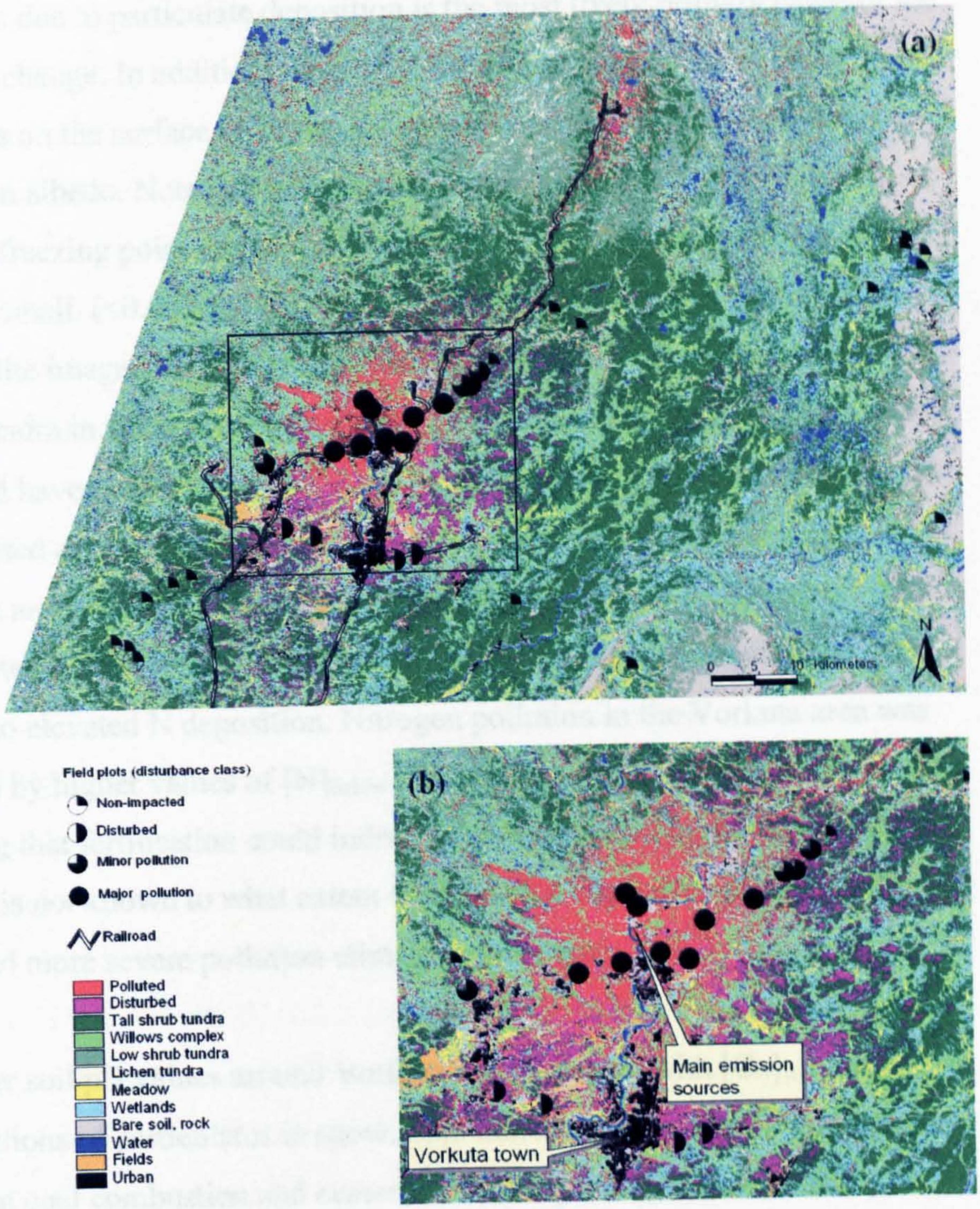


Figure 6.1. Landsat image classification for the whole Vorkuta region (a), classification around the main emission sources (b). Reproduced from Virtanen *et al.* (2002) with kind permission of the authors.

The causal agent(s) may be one or a combination of different components of the pollution climate (i.e. alkalisation, heavy metal deposition, eutrophication and phytotoxic gases) (see Chapter 4). Virtanen *et al.* (2002) consider that alkalisation due to particulate deposition is the most likely primary cause of the vegetation change. In addition, the deposition and accumulation of black particulates on the surface of snowpack accelerates spring snow-melt due to a reduction in albedo. Note that advanced snowmelt is unlikely to have been caused by freezing point depression due to pollutants since this was estimated to be very small, (<0.001 °C in all cases). Evidence for such an effect comes from satellite images, showing snow free areas around Vorkuta and snow covered tundra in remoter regions in June (Virtanen *et al.*, 2002). Earlier spring thaw could have both positive and negative effects (e.g. longer growing season and increased exposure to frost, respectively). However, the changes in vegetation around Vorkuta are similar to those observed by Paal *et al.* (1997), who reported a shift in the Norwegian alpine *Betula nana* community in response to elevated N deposition. Nitrogen pollution in the Vorkuta area was evidenced by higher values of $[N]_{lichen}$ and $[organic\ N]_{snow}$ (data not presented) suggesting that fertilisation could indeed have contributed to the 'Vorkuta effect'. It is not known to what extent the modified vegetation is a relic of a former and more severe pollution climate in this region.

The higher soil pH values around Vorkuta correlate well with $[Ca]_{snow}$ and concentrations of particulates in snow. This indicates an important role for ash input from coal combustion and cement dust in regulating snow and soil pH. Potentially, a reduction in fly ash and cement dust emissions, with a resultant progressive drop in pH, could mean solubilization of accumulated heavy metals (Reimann *et al.*, 1996; Haapala *et al.*, 2001). Increased heavy metal concentrations in solution would have wider implications, due to leaching into surface run-off water and other aquatic environments. Robb and Young (1999) found that large additions of calcareous, metal-rich, fly ash to acidic soils increased soil pH to the extent that metal ion concentrations in the soil solution were reduced despite an increased total metal loading to the soil from the ash.

Such a scenario is possible if the decline in the Vorkuta coal industry continues.

Chemical contamination around Inta was similar in type to that at Vorkuta, but on a smaller spatial scale. Near pristine areas were located *c.*20 km from the centre of Inta, where there was little evidence of ash deposition and where both snow-pack and top-soils were characterised by acidity. However, unlike Vorkuta, there was no evidence of vegetation changes, possibly because (i) emissions from this source are considerably smaller than those from Vortuka (State of the environment of the Komi Republic, 1992-98) and (ii) Inta is in the forest-tundra zone where impacts may be less apparent from satellite data. At the smaller industrial sites subsequently examined in the SPICE programme chemical contamination and modification to lichen communities were barely detectable. A small pollution signature was detected, however, at the Upper Kolva River site ($F7_i$) where oil and gas operations produce gas flares. Here, a suite of minor shifts in environmental chemistry and lichen abundance (which are in broad agreement) were recorded. These included marked elevations of $[Ba]_{soil}$ and $[Ca]_{soil}$ possibly arising from dust blown from gravel roads or building work where cement is handled. However, $[Ba]_{soil}$ values at site $F7_i$ constituted only 17% of those recorded around Vorkuta. Other apparent chemical anomalies at site $F7_i$ included high $[Pb]_{lichen}$ and low soil pH values. In other characteristics, soils at $F7_i$ and at the other industrial sites examined in SPICE ($F1_i$, $F3_i$ and $F5_i$) were close to pristine. Although Rusanova (1995b) documented contamination of soils from oil spills in the area, it is unlikely that sites examined in the present programme have been affected by spills. All sites along the transect through the town of Usinsk, which is supplied by a gas-fired power station, were near pristine, showing background concentrations of the majority of metals and anions measured.

An additional objective of this study was to produce a benchmark survey of chemical contamination in the Pechora region, against which effects of future developments can be assessed. Oil and gas reserves in the Timan-Pechora oil

province (currently the third most important oil producing region in Russia), are of global significance and have the capacity for considerable growth (Lausala and Valkonen, 1999; Pelley, 2001). Whilst the coal industry in the region is in gradual decline (Gimardi, 2002), it seems inevitable that activities such as gas flaring, and heat and power generation associated with gas hydrate recovery, will proliferate during the coming decades. These activities have the potential to increase atmospheric emissions, including those of NO_x which would contribute to background N deposition (Woodin, 1997) and eutrophication (Tybirk *et al.*, 2000).

Gas flaring is likely to increase at the Upper Kolva River industrial complex and increase NO_x emissions. Gas flaring is undertaken at oil and gas production facilities where there is no market for excess or waste gas and also for reasons of safety to avoid excessive pressure build up during temporary shutdowns. The importance of this activity as a source of NO_x is illustrated by the fact that, gas flaring at offshore platforms around the British Isles combusted 2.4 million m^3 of gas and emitted *c.*4% of the total UK NO_x emissions (Environment Agency, 1998). Also, flaring at the oil and gas operations at Prudhoe Bay, Alaska, has been estimated to emit annually between *c.*12 x 10^3 tonnes NO_x and *c.*14 x 10^3 tonnes CH_4 (Jaffe *et al.*, 1995b). Jaffe *et al.* (1995b) reported that, given appropriate wind directions at Point Barrow, Alaska, elevated concentrations of NO_x could be detected for up to 48h in air masses arriving from the oil development at Prudhoe Bay, located 300 km to the east. Improved technology and gas re-injection should be considered as an alternative to flaring.

Oil and gas recovery is associated with other environmental risks in addition to air pollution. Local impacts include an increased frequency of oil spills. For example it has been estimated that 7-20% of extracted oil is lost annually through accidents on oil pipelines in Russia (e.g. Vilchek and Tishkov, 1997). Improved technologies and maintenance will be necessary to reduce this loss (Pelley, 2001). Future oil and gas exploitation in this region could utilise

remote sensing techniques such as those used on the Kola Peninsula by Rigina *et al.* (1999), where it would be possible to assess biodiversity and ecosystem sensitivity to oil spills.

Oil and gas industries are not the only activities that are poised for development. Those proposed include a pulp and paper factory, a coal-burning power plant in Inta, an oil and titanium complex, an aluminium plant in Pechora, a sea terminal in Narjan-Mar, a manganese mine, expansion of eco-tourism in the Yugad-Va National Park and new tundra oil and gas fields. Oil and gas products in the region will supply the energy for a planned refinery near Ukhta to produce alumina using bauxite mined from the recently discovered Timan bauxite deposit (Cottrell, 2002). An aluminium plant proposed to be built at Pechora will require electricity for the electrolytic process. If hydroelectric power is used to operate the plant then this will result in minimal regional pollution. If, however, a gas driven power station is built then it will contribute to regional NO_x emissions. Aluminium refining also brings about new toxicity problems, such as fluoride contamination. An aluminium plant on the island of Anglesey (UK) has caused severe damage to lichen communities within a radius of 10 km (Perkins, 1992). Therefore, a restriction on reindeer grazing may be necessary within a local area around the new plant in Pechora. Fluoride pollution also reduces timber quality making it structurally weaker and less suitable for use in construction and pulping. However, it should be emphasised that inadequate pollution control measures could result in spatially more extensive pollution. The region therefore faces considerable challenges both in terms of socio-economic development and with it, the added risks of environmental pollution.

Another objective of the current research was to further evaluate the use of chemical markers in terricolous lichens as indicators of nitrogen and acid deposition. Hyvärinen and Crittenden (1998a) observed that N concentration (most notably, $[N]_{base}$) in *Cladonia portentosa* in British heathlands was positively correlated with N deposition. In the Pechora region there were

marked variation in $[N]_{lichen}$ which correlated with either measured or putative pollution gradients. In this case it was values of $[N]_{apices}$ that showed the strongest spatial relationships (e.g. with latitude). The lack of response of $[N]_{apices}$ at industrial sites examined in the SPICE programme (see Figures 5.4 and 5.5a, Chapter 5) was consistent with other pollution indicators examined both in this present work and in that of collaborating groups (see Tables 5.2 and 5.3, Chapter 5). These results demonstrate the potential of mat-forming lichens as coherent indicators of N deposition (Hyvärinen and Crittenden, 1998a). Ratios of $[K^+]$ to divalent cations in the apices of mat-forming lichens, proposed by Hyvärinen and Crittenden (1996) to indicate precipitation acidity, showed pronounced responses to the pollution climate of Vorkuta. However, these were interpreted as effects of enhanced deposition of cations and not a response to acidity. Clearly, measurements of cation ratios when used to seek evidence of acid precipitation must be interpreted with caution. Elsewhere in the Pechora region, remote from the confounding influence of particulate deposition, there were no spatial patterns evident consistent with gradients in acid deposition.

It is noteworthy that the search for pollution impacts using lichen abundance as an indicator was also confounded in the tundra, in this case due to de-vegetation by heavy reindeer grazing (see Figure 5.11, Chapter 5). The tundra regions examined in both the TUNDRA and SPICE programmes are known to be busy 'thoroughfares' for reindeer herds (O. Harbeck, *pers. com.*). Oksanen *et al.* (1995) suggest that the combined ecological effects of reindeer grazing and air borne pollution causes degradation of terricolous lichen pasture, which may influence soil temperature, moisture, microbial nutrient cycling, and frost hardiness of plant roots.

Data presented here for snow, lichen and soil chemistry, and for lichen diversity suggest that the effects of pollution at many sites examined were generally near to or below detection limits. Exceptions were Vorkuta and to a lesser extent Inta and the Upper Kolva site ($F7_i$). The semi-pristine nature of

much of the Pechora basin suggested by data documented in this thesis, will mean that increased pollution loads should be readily detected with a high degree of sensitivity, due to favourable signal to noise ratios. Therefore, future re-assessments of chemical contamination will be highly desirable since, as is clearly demonstrated by the 'Vorkuta effect', where changes in vegetation become visible only after profound damage has already occurred. Accordingly, the results in this thesis will help with future monitoring in the region and provides essential baseline data, against which future deterioration can be compared.

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APPENDICES

Appendix 1.1. Epiphytic lichen species and their cover abundance recorded on *Picea obovata* at site $F1_i$ (Izhma river).

Species	$F1_i$ Izhma river									
	1	2	3	4	5	6	7	8	mean	(sc)
Epiphytes										
Bryoria capillaris *	2	5	4	3	4	2	5	4	**3.6**	
B. furcellata *	2	2	0	1	1	1	1	0	**1.0**	
B. fuscescens *	6	4	4	3	3	5	5	6	**4.5**	
B. fremontii *	0	0	1	0	0	0	0	0	**0.1**	
B. nadvornikiana *	0	1	0	0	0	1	0	0	**0.3**	
Evernia mesomorpha	3	1	1	3	3	1	1	1	**1.8**	
E. prunastri	0	0	0	1	1	0	0	0	**0.3**	
Hypogymnia bitteri	0	0	0	0	0	2	1	1	**0.5**	
H. physodes	4	6	4	6	5	4	4	3	**4.5**	
H. tubulosa	3	2	2	1	1	3	2	2	**2.0**	
Imshaugia aleurites	1	1	0	0	0	0	1	0	**0.4**	
Melanelia exasperatula	0	0	1	2	0	1	0	0	**0.5**	
M. olivacea	2	1	2	2	3	2	0	1	**1.6**	
Parmelia sulcata	3	4	3	1	1	4	3	3	**2.8**	
Parmeliopsis ambigua	2	1	1	0	0	1	1	2	**1.0**	
P. hyperopta	2	0	1	1	1	0	1	2	**1.0**	
Platismatia glauca	2	2	0	0	0	2	1	1	**1.0**	
Ramalina dilacerata	1	2	2	3	0	1	1	1	**1.4**	
R. obtusata †	0	0	0	1	0	0	0	0	**0.1**	
R. roesleri	0	0	0	2	1	0	0	0	**0.4**	
R. thrausta	0	1	1	1	0	0	2	1	**0.8**	
Tuckermanopsis chlorophylla	0	3	3	2	0	3	2	1	**1.8**	
T. sepincola	3	0	0	0	0	0	0	0	**0.4**	
Usnea filipendula *	3	3	2	3	4	3	3	3	**3.0**	
U. glabrescens *	0	0	0	0	0	0	0	1	**0.1**	
U. lapponica *	0	0	0	1	3	0	1	2	**0.9**	
U. subfloridana *	2	2	2	1	5	2	0	2	**2.0**	
Vulpicida pinastri	2	1	1	1	1	1	1	0	**1.0**	
Sum of abundance	43	42	35	39	37	39	36	37	**38.5**	**(1.00)**
Number of species	17	18	17	20	15	18	18	18	**17.6**	**(0.50)**

† First record of this species in the Komi Republic
* Epiphytic species which are pollution sensitive according to Hawksworth and Rose (1970).

Appendix 1.2. Epiphytic lichen species and their cover abundance recorded on *Picea obovata* at site $F2_r$ (Belaya Kedva river).

Species	**$F2_r$ Belaya Kedva river**										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**mean**	**(sc)**
Epiphytes											
Alectoria sarmentosa *	0	0	0	0	1	0	0	0	0	**0.1**	
Bryoria capillaris *	2	1	1	0	3	6	3	1	5	**2.4**	
B. fuscescens *	2	2	4	5	1	6	3	3	2	**3.1**	
B. nadvornikiana *	0	0	0	0	0	0	1	1	2	**0.4**	
B. simplicior *	1	2	0	0	0	0	0	0	0	**0.3**	
Evernia mesomorpha	1	0	1	0	1	1	2	0	1	**0.8**	
Hypogymnia bitteri	0	0	0	1	1	0	0	2	0	**0.4**	
H. physodes	6	6	6	5	4	5	5	4	3	**4.9**	
H. tubulosa	2	2	3	2	2	4	4	2	1	**2.4**	
Melanelia exasperatula	0	0	0	0	1	0	0	0	0	**0.1**	
M. olivacea	4	5	4	2	3	3	3	0	3	**3.0**	
Parmelia sulcata	3	4	4	3	3	4	4	5	4	**3.8**	
Parmeliopsis ambigua	0	0	1	1	0	0	2	1	1	**0.7**	
P. hyperopta	0	0	0	1	0	0	0	1	1	**0.3**	
Physcia aipolia	0	1	0	0	0	0	0	0	0	**0.1**	
Platismatia glauca	0	0	0	1	0	0	1	0	0	**0.2**	
Ramalina dilacerata	5	5	4	2	3	2	2	0	1	**2.7**	
R. roesleri	1	1	1	0	1	1	1	1	1	**0.9**	
R. thrausta	0	0	0	1	1	0	0	0	0	**0.2**	
Tuckermanopsis chlorophylla	1	1	1	2	2	2	2	2	2	**1.7**	
T. sepincola	0	0	0	0	1	0	0	0	0	**0.1**	
Usnea filipendula *	0	0	0	2	1	4	5	5	3	**2.2**	
U. glabrescens *	0	0	0	0	0	0	2	5	0	**0.8**	
U. lapponica *	2	1	3	1	0	0	3	0	0	**1.1**	
U. subfloridana *	0	1	2	3	2	4	5	2	4	**2.6**	
Vulpicida pinastri	1	1	1	1	2	2	1	1	1	**1.2**	
Sum of abundance	31	33	36	33	33	44	49	36	35	**36.7**	**(1.98)**
Number of species	13	14	14	16	19	13	18	15	16	**15.3**	**(0.71)**

* Epiphytic species which are pollution sensitive according to Hawksworth and Rose (1970).

Appendix 1.3. Epiphytic lichen species and their cover abundance recorded on *Picea obovata* at site $F5_i$ (Svetly Vuktyl river).

Species	$F5_i$ Svetly Vuktyl river										
	1	2	3	4	5	6	7	8	9	mean	(se)
Epiphytes											
Bryoria capillaris *	5	4	4	6	3	2	4	3	2	**3.7**	
B. furcellata *	0	0	2	0	1	2	1	0	1	**0.8**	
B. fuscescens *	5	5	4	3	4	6	3	4	3	**4.1**	
B. nadvornikiana *	2	2	2	3	2	0	0	1	1	**1.4**	
Evernia mesomorpha	0	0	0	1	0	1	1	2	2	**0.8**	
Hypogymnia bitteri	0	1	0	0	0	0	1	1	0	**0.3**	
H. physodes	4	3	3	5	4	4	4	4	5	**4.0**	
H. tubulosa	2	0	1	4	0	3	2	2	3	**1.9**	
Imshaugia aleurites	0	0	0	1	0	0	0	0	0	**0.1**	
Melanelia exasperatula	0	0	0	2	0	0	2	1	1	**0.7**	
M. olivacea	2	0	3	3	2	3	4	4	4	**2.8**	
Parmelia sulcata	3	2	3	4	2	3	3	3	4	**3.0**	
Parmeliopsis ambigua	1	0	1	2	0	1	0	2	2	**1.0**	
P. hyperopta	1	0	1	2	0	0	0	2	2	**0.9**	
Platismatia glauca	0	0	2	1	0	1	1	1	1	**0.8**	
Ramalina dilacerata	1	1	1	3	0	2	3	3	2	**1.8**	
R. roesleri	0	0	0	0	0	0	1	1	0	**0.2**	
R. thrausta	1	2	2	0	0	1	0	1	0	**0.8**	
Tuckermanopsis chlorophylla	3	1	0	2	3	3	3	2	2	**2.1**	
Usnea filipendula *	4	6	4	4	6	5	3	4	2	**4.2**	
U. glabrescens *	0	2	3	2	2	4	2	2	4	**2.3**	
U. lapponica *	1	0	0	1	0	0	1	2	2	**0.8**	
U. scabrata *	0	0	0	0	1	0	0	0	0	**0.1**	
U. subfloridana *	4	2	4	4	2	4	4	5	4	**3.7**	
Vulpicida pinastri	1	0	1	2	0	1	2	2	3	**1.3**	
Sum of abundance	**40**	**31**	**41**	**55**	**32**	**46**	**45**	**52**	**50**	**43.6**	**(2.79)**
Number of species	**16**	**12**	**17**	**20**	**12**	**17**	**19**	**22**	**20**	**17.2**	**(1.16)**

* Epiphytic species which are pollution sensitive according to Hawksworth and Rose (1970).

Appendix 1.4. Epiphytic lichen species and their cover abundance recorded on *Picea obovata* at site $F6_r$ (Maly Patok river).

Species	$F6_r$ Maly Patok river										
	1	2	3	4	5	6	7	8	9	mean	(sc)
Epiphytes											
Alectoria sarmentosa *	0	0	0	0	0	0	0	1	0	**0.1**	
Bryoria capillaris *	0	0	2	3	2	3	3	3	2	**2.0**	
B. furcellata *	1	0	2	2	0	0	0	0	0	**0.6**	
B. fuscescens *	2	2	2	2	2	0	0	0	0	**1.1**	
B. nadvornikiana *	0	0	1	3	0	2	0	0	0	**0.7**	
Evernia divaricata	2	3	3	0	0	0	2	2	0	**1.3**	
E. mesomorpha	1	1	0	0	0	0	0	0	0	**0.2**	
Hypogymnia bitteri	1	1	0	0	2	1	1	0	0	**0.7**	
H. physodes	5	4	5	5	3	4	3	4	4	**4.1**	
H. tubulosa	4	3	4	4	3	4	3	3	3	**3.4**	
Melanelia olivacea	1	2	2	3	2	2	2	2	2	**2.0**	
Parmelia sulcata	2	2	2	2	2	2	2	2	2	**2.0**	
Parmeliopsis ambigua	3	3	2	2	2	4	2	2	2	**2.4**	
P. hyperopta	3	2	2	2	2	3	2	3	3	**2.4**	
Platismatia glauca	1	2	2	2	1	2	0	2	1	**1.4**	
Ramalina dilacerata	1	0	0	0	0	0	0	0	0	**0.1**	
Tuckermanopsis chlorophylla	2	2	2	2	2	2	2	2	2	**2.0**	
Usnea filipendula *	2	2	2	2	0	1	3	2	1	**1.7**	
U. lapponica *	0	1	2	0	0	0	2	0	0	**0.6**	
U. scabrata *	2	2	0	3	2	0	0	0	0	**1.0**	
U. subfloridana *	0	0	0	0	2	2	0	2	2	**0.9**	
Vulpicida pinastri	3	2	2	2	2	2	2	2	2	**2.1**	
Sum of abundance	**36**	**34**	**37**	**39**	**29**	**34**	**29**	**32**	**26**	**32.9**	**(1.42)**
Number of species	**17**	**16**	**16**	**15**	**19**	**14**	**13**	**14**	**12**	**15.1**	**(0.72)**

* Epiphytic species which are pollution sensitive according to Hawksworth and Rose (1970).

Appendix 1.5. Epigeal lichen species and their cover abundance recorded in plots at site $F3_i$ (Ortina river).

Species	$F3_i$ Ortina river						
	1	2	3	4	5	mean	(se)
Epigeal							
Alectoria nigricans *	3	2	0	2	0	**1.4**	
A. ochroleuca *	1	1	0	0	0	**0.4**	
Bryocaulon divergens *	3	0	0	2	0	**1.0**	
Cetraria islandica	1	1	6	4	2	**2.8**	
Cladonia amaurocraea	0	2	0	1	1	**0.8**	
C. arbuscula	4	3	6	5	5	**4.6**	
C. bellidiflora	1	0	1	1	0	**0.6**	
C. cervicornis	0	1	0	0	0	**0.2**	
C. coccifera	1	0	0	1	1	**0.6**	
C. crispata	1	1	0	0	0	**0.4**	
C. furcata	0	0	0	0	1	**0.2**	
C. gracilis	1	1	3	3	3	**2.2**	
C. pleurota	0	0	2	0	0	**0.4**	
C. rangiferina/stygia	1	1	5	3	4	**2.8**	
C. stellaris	1	0	1	0	0	**0.4**	
C. subfurcata	2	0	0	0	1	**0.6**	
C. sulphurina	0	0	1	0	0	**0.2**	
C. uncialis	1	2	3	1	3	**2.0**	
Flavocetraria nivalis	5	7	2	5	5	**4.8**	
F. cucullata	2	2	1	2	2	**1.8**	
F. nigricans	0	2	0	0	0	**0.4**	
Ochrolechia androgyna	0	1	0	0	0	**0.2**	
O. frigida	1	0	1	1	2	**1.0**	
Peltigera scabrosa *	1	0	0	0	0	**0.2**	
Sphaerophorus globosus	1	1	0	2	0	**0.8**	
Stereocaulon alpinum *	1	0	0	0	0	**0.2**	
S. paschale *	3	3	0	0	2	**1.6**	
Thamnolia vermicularis	2	2	0	1	0	**1.0**	
Sum of abundance	**37**	**33**	**32**	**34**	**32**	**33.6**	**(0.93)**
Number of species	**21**	**17**	**12**	**15**	**13**	**15.6**	**(1.60)**

* Epigeal species which are pollution sensitive according to McCune and Geiser (1997) and Gilbert (2000).

Appendix 1.6. Epigeal lichen species and their cover abundance recorded in plots at site $F4_r$ (Neruta river).

Species	$F4_r$ Neruta						
	1	2	3	4	5	mean	(sc)
Epigeal							
Alectoria nigricans *	3	3	3	2	2	**2.6**	
A. ochroleuca *	0	2	0	0	2	**0.8**	
Bryocaulon divergens *	2	2	0	0	1	**1.0**	
Cetraria islandica	3	3	3	4	3	**3.2**	
Cladonia amaurocraea	0	2	0	3	0	**1.0**	
C. arbuscula	5	5	5	5	6	**5.2**	
C. bellidiflora	1	0	0	1	0	**0.4**	
C. chlorophaea	2	0	0	0	0	**0.4**	
C. coccifera	1	2	1	1	2	**1.4**	
C. cornuta	2	0	0	0	0	**0.4**	
C. crispata	1	0	2	2	0	**1.0**	
C. furcata	0	1	0	0	0	**0.2**	
C. gracilis	3	2	3	3	4	**3.0**	
C. macrophylla	0	0	0	0	1	**0.2**	
C. rangiferina/stygia	4	4	4	4	4	**4.0**	
C. stellaris	2	1	1	1	1	**1.2**	
C. subfurcata	0	1	0	0	0	**0.2**	
C. uncialis	3	3	3	4	5	**3.6**	
Flavocetraria nivalis	5	6	7	6	7	**6.2**	
F. cucullata	4	3	3	3	4	**3.4**	
Nephroma arcticum *	2	0	2	2	2	**1.6**	
Ochrolechia frigida	1	0	0	1	0	**0.4**	
Peltigera scabrosa *	1	0	2	1	2	**1.2**	
Sphaerophorus globosus	3	2	2	0	0	**1.4**	
Stereocaulon alpinum *	0	0	3	3	0	**1.2**	
S. paschale *	4	2	4	3	4	**3.4**	
Thamnolia vermicularis	2	3	1	2	2	**2.0**	
Sum of abundance	**54**	**47**	**49**	**51**	**52**	**50.6**	**(1.21)**
Number of species	**21**	**18**	**17**	**19**	**17**	**18.4**	**(0.75)**

* Epigeal species which are pollution sensitive according to McCune and Geiser (1997) and Gilbert (2000).

Appendix 1.7. Epigeal lichen species and their cover abundance recorded in plots at site $F7_i$ (Kolva river).

Species	$F7_i$ Kolva river						
	1	2	3	4	5	mean	(se)
Epigeal							
Alectoria nigricans *	1	0	0	0	0	**0.2**	
Cetraria islandica	2	2	3	3	2	**2.4**	
Cladonia amaurocraea	2	2	2	2	3	**2.2**	
C. arbuscula	4	5	7	7	7	**6.0**	
C. bellidiflora	1	0	0	0	0	**0.2**	
C. borealis	0	1	0	1	2	**0.8**	
C. coniocraea	0	1	0	0	0	**0.2**	
C. cornuta	0	0	1	0	0	**0.2**	
C. crispata	1	0	1	2	1	**1.0**	
C. gracilis	3	3	2	3	2	**2.6**	
C. rangiferina/stygia	3	4	3	4	5	**3.8**	
C. stellaris	0	2	4	2	1	**1.8**	
C. subfurcata	0	0	1	0	0	**0.2**	
C. uncialis	2	2	2	0	0	**1.2**	
Flavocetraria nivalis	6	5	3	3	3	**4.0**	
F. cucullata	3	2	2	3	2	**2.4**	
Icmadophila ericetorum	0	1	0	0	0	**0.2**	
Peltigera malacea	2	0	0	0	0	**0.4**	
P. scabrosa *	2	0	0	0	0	**0.4**	
Sphaerophorus globosus	2	0	0	0	0	**0.4**	
Stereocaulon alpinum *	2	0	0	0	0	**0.4**	
S. paschale *	6	0	0	0	0	**1.2**	
Sum of abundance	**42**	**30**	**31**	**30**	**28**	**32.2**	**(2.50)**
Number of species	**16**	**12**	**12**	**10**	**10**	**12**	**(1.10)**

* Epigeal species which are pollution sensitive according to McCune and Geiser (1997) and Gilbert (2000).

Appendix 1.8. Epigeal lichen species and their cover abundance recorded in plots at site $F8_r$ (Mareyu river).

Species	$F8_r$ Mareyu river						
	1	2	3	4	5	mean	(sc)
Epigeal							
Alectoria nigricans *	2	3	2	2	4	**2.6**	
A. ochroleuca *	2	3	2	1	3	**2.2**	
Bryocaulon divergens *	2	3	2	1	3	**2.2**	
Cetraria islandica	2	3	3	3	2	**2.6**	
Cladonia amaurocraea	2	2	2	2	2	**2.0**	
C. arbuscula	3	4	3	4	4	**3.6**	
C. bellidiflora	1	2	1	2	1	**1.4**	
C. borealis	1	1	2	2	2	**1.6**	
C. cervicornis	0	0	0	1	0	**0.2**	
C. chlorophaea	0	2	1	1	2	**1.2**	
C. crispata	0	0	0	0	2	**0.4**	
C. gracilis	2	2	2	2	2	**2.0**	
C. pleurota	0	2	0	0	0	**0.4**	
C. rangiferina/stygia	2	2	2	2	2	**2.0**	
C. stellaris	1	2	0	2	2	**1.4**	
C. sulphurina	0	2	0	0	0	**0.4**	
C. uncialis	2	2	4	3	2	**2.6**	
Flavocetraria nivalis	4	4	3	5	5	**4.2**	
F. cucullata	2	3	2	2	2	**2.2**	
F. nigricans	0	1	0	0	0	**0.2**	
Hypogymnia physodes	2	0	0	0	0	**0.4**	
Icmadophila ericetorum	1	0	0	0	0	**0.2**	
Ochrolechia frigida	0	2	2	1	2	**1.4**	
P. malacea	0	0	3	0	0	**0.6**	
Peltigera neckeri	0	1	0	0	0	**0.2**	
Pertusaria coccodes	0	0	0	0	1	**0.2**	
P. panygra	0	1	0	1	0	**0.4**	
Sphaerophorus globosus	2	2	2	2	2	**2.0**	
Stereocaulon alpinum *	1	0	1	0	0	**0.4**	
S. paschale *	3	2	3	0	1	**1.8**	
Thamnolia vermicularis	2	2	1	0	2	**1.4**	
Sum of abundance	**39**	**53**	**43**	**39**	**48**	**44.4**	**(2.71)**
Number of species	**20**	**24**	**20**	**19**	**21**	**20.8**	**(0.86)**

* Epigeal species which are pollution sensitive according to McCune and Geiser (1997) and Gilbert (2000).

Appendix 1.9. Epiphytic lichen species and their cover abundance recorded growing on *Betula nana* in plots at site $F3_i$ (Ortina river).

Species	$F3_i$ Ortina river						
	1	2	3	4	5	mean	(sc)
Epiphytes							
Cetraria nigricans	0	1	0	0	0	**0.2**	
Hypogymnia physodes	4	5	4	2	1	**3.2**	
Lecanora argentata	1	1	0	0	0	**0.4**	
Melanelia olivacea	5	2	2	0	0	**1.8**	
Ochrolechia frigida	0	3	2	5	5	**3.0**	
Parmeliopsis ambigua	3	3	3	3	5	**3.4**	
P. hyperopta	0	2	3	3	5	**2.6**	
Pertusaria dactylina	0	3	0	0	0	**0.6**	
Tuckermanopsis sepincola	1	4	1	4	4	**2.8**	
Vulpicida pinastri	1	1	1	1	1	**1.0**	
Sum of abundance	**15**	**25**	**16**	**18**	**21**	**19**	**(1.82)**
Number of species	**6**	**10**	**7**	**6**	**6**	**7**	**(0.77)**

Appendix 1.10. Epiphytic lichen species and their cover abundance recorded growing on *Betula nana* in plots at site $F4_r$ (Neruta river).

Species	$F4_r$ Neruta river						
	1	2	3	4	5	mean	(sc)
Epiphytes							
Hypogymnia physodes	1	5	1	0	1	**1.6**	
Ochrolechia frigida	4	5	5	1	5	**4.0**	
Parmeliopsis ambigua	3	4	4	3	4	**3.6**	
P. hyperopta	3	4	4	3	4	**3.6**	
Pertusaria dactylina	1	0	4	0	0	**1.0**	
Tuckermanopsis sepincola	5	4	4	3	5	**4.2**	
Vulpicida pinastri	2	2	2	2	2	**2.0**	
Sum of abundance	**19**	**24**	**24**	**12**	**21**	**20**	**(2.21)**
Number of species	**7**	**6**	**7**	**5**	**6**	**6.2**	**(0.37)**

Appendix 1.11. Epiphytic lichen species and their cover abundance recorded growing on *Betula nana* in plots at site $F7_i$ (Kolva river).

Species	$F7_i$ Kolva river						
	1	2	3	4	5	mean	(se)
Epiphytes							
Alectoria nigricans *	0	0	0	0	2	0.4	
Bryoria simplicior *	0	0	1	0	0	0.2	
Hypogymnia physodes	3	1	0	2	3	1.8	
Lecanora argentata	2	0	2	0	0	0.8	
Melanelia olivacea	2	0	0	1	0	0.6	
Ochrolechia frigida	0	0	1	1	0	0.4	
Parmelia sulcata	2	1	0	1	2	1.2	
Parmeliopsis ambigua	3	2	3	2	2	2.4	
P. hyperopta	2	2	2	2	2	2.0	
Pertusaria dactylina	2	1	0	0	0	0.6	
Tuckermanopsis sepincola	3	2	4	4	3	3.2	
Vulpicida pinastri	2	1	2	2	2	1.8	
Sum of abundance	**16**	**7**	**9**	**9**	**11**	**10.4**	**(1.54)**
Number of species	**9**	**7**	**7**	**8**	**7**	**7.6**	**(0.40)**

Appendix 1.12. Epiphytic lichen species and their cover abundance recorded growing on *Betula nana* in plots at site $F8_r$ (Mareyu river).

Species	$F8_r$ Mareyu river						
	1	2	3	4	5	mean	(se)
Epiphytes							
Alectoria nigricans *	0	2	0	0	2	0.8	
A. ochroleuca *	0	1	0	0	2	0.6	
Cetraria nigricans	2	2	2	1	1	1.6	
Bryocaulon divergens *	0	1	0	0	0	0.2	
Bryoria fuscescens *	1	0	0	0	1	0.4	
Hypogymnia physodes	3	3	0	0	2	1.6	
H. tubulosa	1	0	0	0	0	0.2	
Lecanora argentata	2	2	2	2	2	2.0	
Melanelia olivacea	2	2	1	0	1	1.2	
Ochrolechia frigida	2	2	2	3	2	2.2	
Parmelia sulcata	2	2	0	1	1	1.2	
Parmeliopsis ambigua	2	2	2	2	2	2.0	
P. hyperopta	2	2	2	2	2	2.0	
Pertusaria corallina	0	0	0	1	2	0.6	
P. coccodes	0	2	1	0	0	0.6	
P. dactylina	2	0	1	0	2	1.0	
Tuckermanopsis sepincola	5	4	3	4	4	4.0	
Vulpicida pinastri	2	2	2	2	2	2.0	
Sum of abundance	**21**	**23**	**13**	**12**	**22**	**18.2**	**(2.35)**
Number of species	**13**	**14**	**10**	**9**	**15**	**12.2**	**(1.16)**

* Epiphytic species which are pollution sensitive according to Hawksworth and Rose (1970).