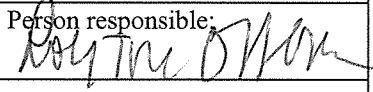


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Title: Temporal variations 1995 - 2005 for heavy metals, arsenic and PAH in the humus layer in Pasvik and Jarfjord, Finnmark County, Norway.			
Authors: Jensen H. K. B. and Finne T. E.		Client: Miljøverndepartementet	
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<p>Summary:</p> <p>The project presented in this report has been supported financially by the Ministry of the Environment. The report summarizes geochemical analyses of humus samples from Pasvik and Jarfjord in Sør-Varanger in Eastern Finnmark sampled in 1995, 2000 and 2005 together with locations in Karasjok sampled in 1995 and 2005. Pasvik and Jarfjord have been exposed to the emissions of several metals and arsenic from the smelter in Nikel and ore roasting factory in Zapoljarnyi. The Karasjok area 200 km further to the west in central Finnmark functions as an area, which has not been exposed to deposition from the smelter in Nikel. The selected humus samples from 1995 and 2000 sampling campaigns have been reanalysed together with the 2005 samples. Temporal variations for selected heavy metals and arsenic are presented together with PAH concentrations for the three selected areas.</p> <p>The results presented in this report are transferred to the ongoing Norwegian – Finnish - Russian trilateral Pasvik Environmental Monitoring Project (2003 - 2006).</p> <p>Temporal variations in copper and nickel show minor increasing trends in Jarfjord. However, these changes are not statistically significant. The increases in median-values for copper and nickel are more pronounced in Jarfjord than in Pasvik. Deposition data 1995 to 2004 from Svanvik for copper and nickel show that the annual deposition constitutes less than 1 % of the concentrations observed in the upper 3 cm of humus layer in the Pasvik area. Therefore one cannot expect dramatic changes in levels of these heavy metals in the humus layer over a 10 years period. Levels of PAH are low in all three areas. Most PAH contributions to the humus layer are believed to be of local origin, i.e. open fires, local traffic etc. There is an increasing temporal trend in all three areas.</p> <p>The humus layer in Pasvik and Jarfjord seem to be able to absorb the deposited heavy metals and arsenic after more than 50 years of deposition.</p> <p>Gaps of knowledge include lack of knowledge concerning downward fluxes of heavy metals and arsenic deeper into the ground and the groundwater. Although there is no apparent major threat to the groundwater in Pasvik or Jarfjord, this situation might change, if conditions change. Changes in weather and climate leading to increased precipitation as rain and thereby increased infiltration might be one such scenario. Another scenario is erosion of the soil surface which might lead to reduced retention of deposited heavy metals due to lack or reduced thickness of the humus layer. Another gap of knowledge is that a ten year period from 1995 to 2005 is too short to give statistically reliable evaluations of for the loads of heavy metals, arsenic and PAH in the humus layer. Therefore sampling and analysis of humus samples should be repeated on a 5-year regular basis.</p>			
Keywords: soil pollution		heavy metals	Arsenic
PAH		humus	Temporal variations

CONTENTS	page
1. INTRODUCTION.....	4
2. CONTRIBUTION OF HEAVY METALS, ARSENIC AND PAH TO THE HUMUS LAYER.....	5
3. METHODS.....	6
4. RESULTS.....	9
4.1 Loss of ignition (LOI)	10
4.2 Copper	11
4.3 Nickel	12
4.4 Arsenic	13
4.5 Cadmium	14
4.6 Lead.....	15
4.7 Mercury	16
4.8 Zinc.....	17
4.9 Cobalt	18
4.10 Polycyclic aromatic hydrocarbons	19
5. SUMMARY	20
6. RECOMMENDATIONS	20
7. REFERENCES.....	22

1. INTRODUCTION

The Geological Survey of Norway has conducted regional mapping of soil chemistry in Northern Norway since the 1980-ies. Data from these investigations show that both natural and anthropogenic processes influence the soil geochemistry. Particularly the humus layer at the top of the soil profiles reveals anthropogenic influence. Humus from the Eastern Finnmark region including Pasvik and Jarfjord is clearly affected by emissions of metals from the smelter in Nikel and an ore roasting plant in Zapolyarniy, NW-Russia. Emission of heavy metals and arsenic from these facilities has been deposited on the soil surface in Eastern Finnmark for decades. The Karasjok area some 200 km further to the west in Finnmark is considered to represent natural conditions, i.e. the main contribution is from the geology within this area and not from the Russian nickel industry. Pasvik and Karasjok both have greenstone bedrock geology, which makes these two areas comparable, whereas the Jarfjord area has a gneissic bedrock. The Karasjok area constitutes a natural background area compared to Pasvik and Jarfjord. Reimann et al. (1998) give a regional overview of the distribution of several metals, arsenic and PAH in humus as well as deeper levels in the soils. Figure 1 shows the studied areas in Finnmark.

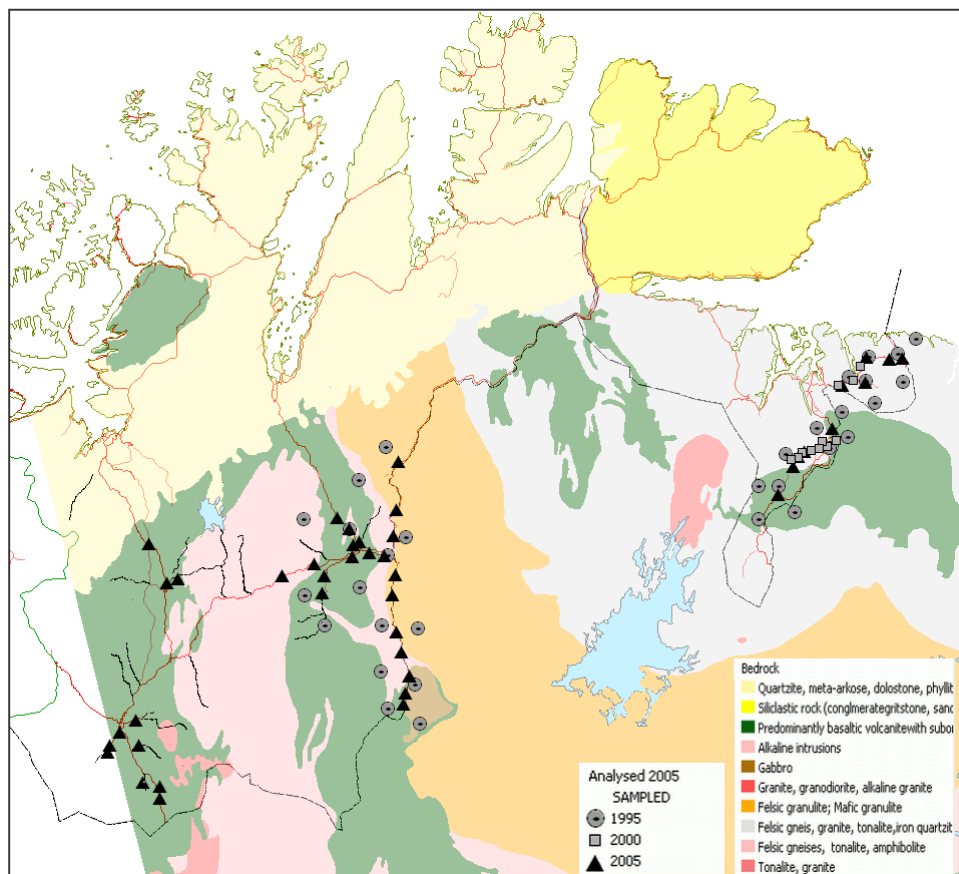


Figure 1. The bedrock of the studied areas in Finnmark, including Pasvik, Jarfjord and Karasjok. Sample locations for the different sampling campaigns 1995, 2000 and 2005 are presented. From Reimann et al. (1998).

Re-analysis of stored humus samples from 1995 and 2000 together with new samples from 2005 has made it possible to establish a temporal dataset for heavy metals, arsenic and PAH in Jarfjord and Pasvik, as well as for Karasjok for 1995 and 2005. This provides an opportunity to compare the temporal changes in Eastern Finnmark with natural development as seen in Karasjok within the decade 1995 – 2005. When looking at the metal, arsenic and PAH data in humus it is important to keep in mind various processes and sources including contribution from bedrock and Quarternary deposits in the different areas, emission from industry, forest fires contributing to PAH, long-range transport of compounds such as lead and mercury, as well as sea spray. Greenstone bedrock is present in both Pasvik and Karasjok. Statistical data treatment including Mann-Whitney U-test has been applied in order to determine whether changes in concentrations of metals in Pasvik, Jarfjord and Karasjok in the period from 1995 to 2005 are statistically significant or not.

2. CONTRIBUTION OF HEAVY METALS, ARSENIC AND PAH TO THE HUMUS LAYER.

Deposition of heavy metals in precipitation including copper and nickel together with arsenic and SO₂ measured in air has been recorded at Svanvik in Pasvik since 1989. The average figures for summer and winter season as reported by Hagen et al. (2004) are shown in Figure 2. The deposition data for copper, nickel and arsenic from Svanvik constitute important information, when compared with the levels of the same compounds in the upper 3 cm of the humus layer.

Contribution of heavy metals and arsenic from sources such as bedrock is an important factor when the levels of e.g. copper, nickel and arsenic in the humus layer are considered. Deeper in the podsol soil profiles the natural minerogenic soil forming material is present. This horizon, which is a few or several tens of centimetres below the humus-layer, is called the C-horizon in soil terminology. Soil and humus formation has taken place since termination of the last ice age approx. 9.000 years ago on soil forming materials such as the C-horizon. C-horizon values for heavy metals and arsenic are presented together with the humus layer heavy metal and arsenic values. At least, some of the heavy metals and arsenic present in the humus layer originate from natural occurrence in the soil forming minerogenic material.

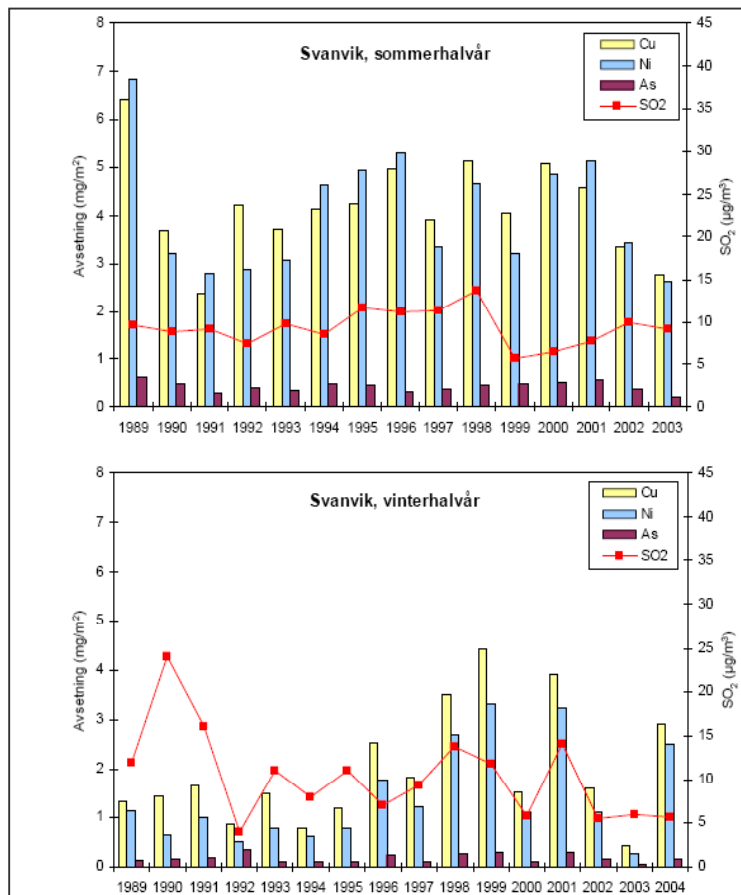


Figure 2. Deposition data for copper, nickel and arsenic in precipitation and SO₂ in air at Svanvik. From Hagen et al. (2004).

The humus layer is the top layer in the soil horizon comprising of decayed organic matter. This layer within the soil profile is called the A-horizon. Ideally, the humus layer consists of only decayed organic material, but due to several physical processes, there is often a quite substantial mineralogical component in the organic layer and possibly decaying organic matter in the upper part. Additionally, the humus layer has also taken up nutrient elements from deeper in the soil profiles and thereby enriched the humus layer with inorganic elements. Hence, a sample of the humus-layer will to a varying degree reflect local geology, atmospheric deposition and up-take of element from deeper in the soil horizon.

3. METHODS

Selection of sample sites was governed by two major rules: On the local scale, samples were taken a minimum of 50 m from public roads, and in well drained sites mid-slope or in flat terrain, avoiding positions underneath trees. On the regional scale, sites were chosen to give the best regular area cover (1995), and along a transect away from Nikel (2000). In 2005 the sites were chosen to give the best available replication of the previous campaigns. The humus samples consisted of a minimum of five subsamples taken within an area of 15 m x 15 m to

ensure good representativity and sufficient sample volume. Each subsample was collected by pushing a sharpened, paintfree steel cylinder through the uppermost part of the soil profile, taking the top 3 cm of the humus layer as the sample. A photo of the extracted core and the sampling tool is shown in Figure 3.



Figure 3. Sampling tool with captured humus on top of upper part of mineral soil horizons.

Samples were wrapped in fiber glass bags, and about 1,5 kg (moist) material was taken to the laboratory. Drying was done below 40°C, and the dry sample was sieved through a 2 mm nylon sieve. Sieved material was stored below 25°C in airtight polyethylene or polycarbonate containers. For analysis of inorganic compounds, 0,500 g of the homogenized sample was extracted by autoclave in HNO₃ according to NS 4770. The solutions were analysed at NGU's accredited lab by ICP-AES (Perkin Elmer Optima 4300 Dual View) for 31 elements, and by AAS (Perkin Elmer SIMAA 6000) for As and Cd, and (CETAC M-6000A Hg Analyzer) for Hg. Concentrations are reported as mg/kg dry matter; the notation ppm (parts per million) is used throughout this article. To ensure uniform extraction and analytical conditions for the inorganic analysis, all samples were treated in one batch regardless of sampling year. Samples

for PAH analysis were collected in pre-treated 0,2 l glasses and shipped in humid condition without any pre-treatment to accredited laboratories during the field campaigns in 1995, 2000 and 2005.

To ensure geographically and statistically comparable selections of samples from the three field campaigns involved, the least wide-spread campaign (2000) set the limits in Sør-Varanger, allowing two subsets: Pasvik and Jarfjord affected by emissions from the smelter in Nikel, whereas Karasjok serves as a natural background area underlain by a similar geology as Pasvik. In Karasjok, where no samples were collected in 2000, collation of samples was done to best reflect the area of the regional survey of 1995 and the 2005-campaign.

Figure 4 shows the Pasvik and Jarfjord areas and locations for the various sampling campaigns 1995, 2000 and 2005. The Norwegian locations from 1995, 2000 and 2005 included in this study are within the framed areas for Pasvik and Jarfjord. Locations outside the boxed areas were not included because of the need for looking at geographically uniform areas.

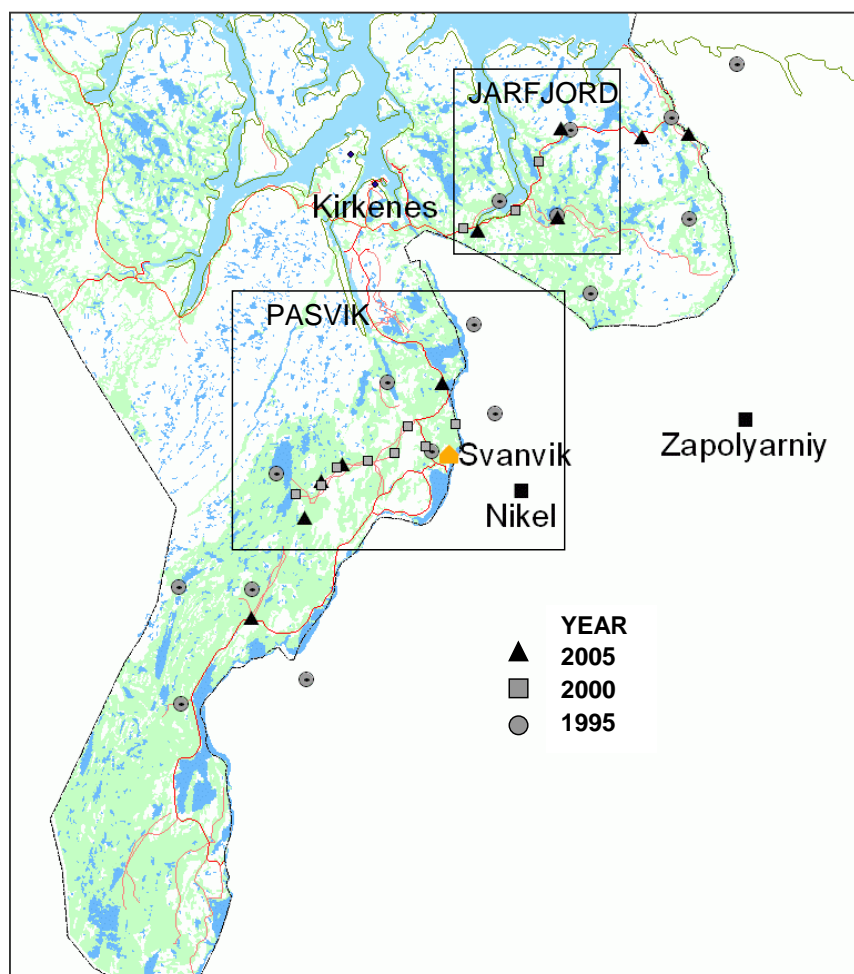


Figure 4. Pasvik and Jarfjord areas in Eastern Finnmark with sampling locations in 1995, 2000 and 2005.

4. RESULTS

When assessing possible change of chemical composition of the humus with time, applying statistical techniques, it is vital to recognize the fact that our data does not show normal distribution, and that the number of observations for some areas/years are as small as 3.

The most recommended choice for a statistical method in such cases (Statsoft 2006), where one group of observations is to be compared with a different group for the same variable, is the Mann-Whitney U-Test. It assumes no knowledge of the (range) distribution of the involved data, as it employs rank statistics. To some extent it is similar to a common t-test of significance, and the U-test yields a p-level as a measure of significance level for the hypothesis that the median has changed from one group of observations to the other.

Results for heavy metals and arsenic are presented in eight one-page descriptions and summary statistics, including group-wise box-plots. For each of the Area/Year groups, number of observations, minimum, 25 percentile, median, 75 percentile and maximum values are listed in the first rows of the table. Below are key figures of the statistical test for significant change of metal level between the two groups, i.e. 1995-2000, 2000-2005, and 1995-2005. The "p-level" directly translates as the significance level for the hypothesis that there is a change in median value. Significance levels better than 0,05 are marked with **red, bold figures**. The Z value is a measure of the difference in rank score between the two groups considered, similar to the t-value of a classical t-test. At the bottom of each area column, the median value of the C-horizon (viz. the local subsoil) as determined in 1995 is given. Finally, the box-plot is presented, in which the box represents the range between the 25- and 75-percentiles, the lines extending includes minimum and maximum values, and the median value is marked with a small square. We have chosen $p < 0,05$ as a limit for significance (less than 5% chance that the observed change of value is a mere statistical coincidence).

4.1 Loss of ignition (LOI)

Loss of ignition data show that the humus samples in all three areas Pasvik, Jarfjord and Karasjok have median values in 80 – 90 % range within the 1995 – 2005 decade. The one exemption is the Jarfjord samples from 2000, which have a LOI median value less than 80 %, suggesting a higher content of mineral material in the humus samples. However, the main impression from the figure is, that the humus material is relatively uniform, when the three areas are compared

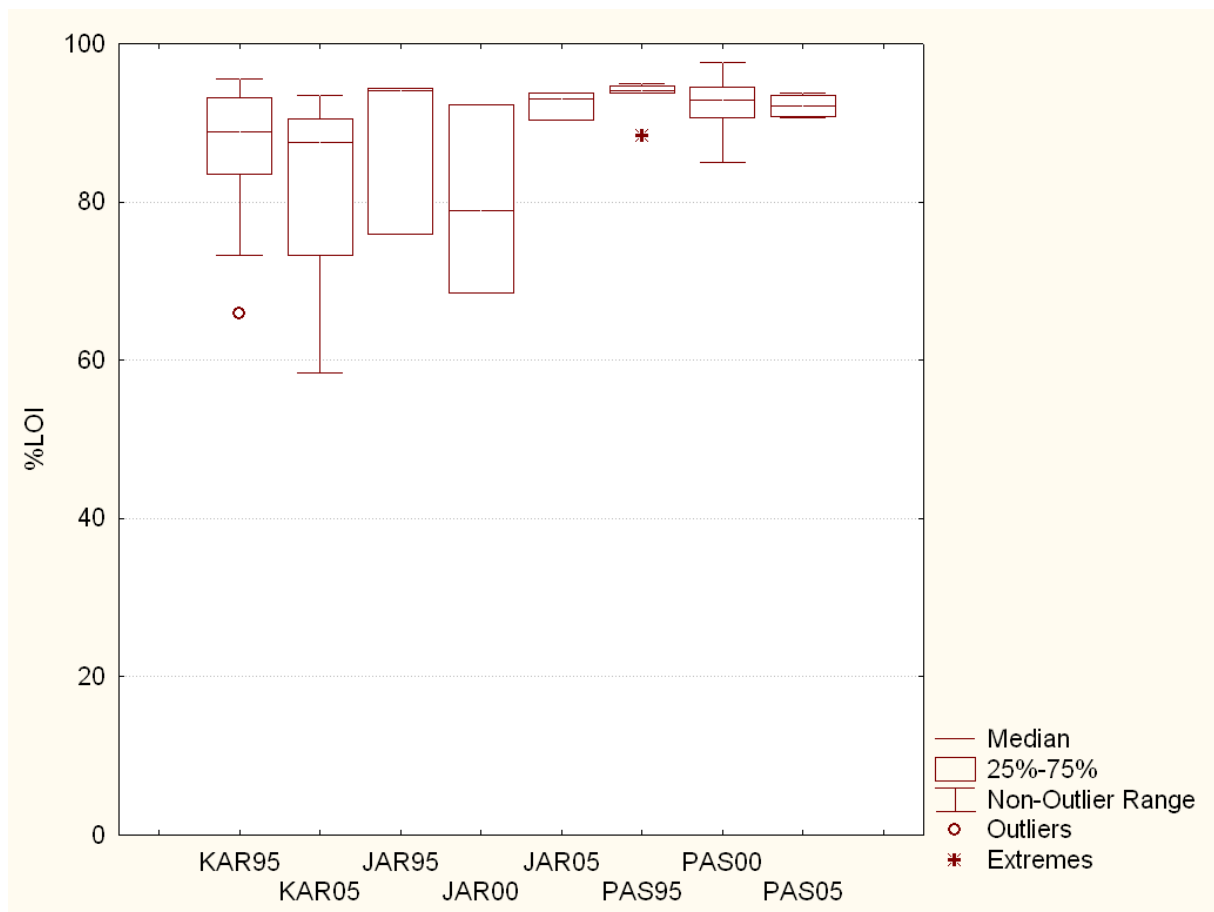


Figure 5. Loss of ignition (LOI) for Pasvik, Jarfjord and Karasjok samples.

4.2 Copper

Figure 6 shows that the Pasvik median values show an increasing trend from 1995 to 2000, maintained in 2005. The Jarfjord samples have a clear indication of an increase over the entire time span. However, neither of these increases is statistically significant, and the small number of samples makes the increase somewhat uncertain for the Jarfjord area. Karasjok, represented by 15 samples in 1995 and 21 samples in 2005, have much lower values, even though Ni-levels of the C-horizon are comparable in all three areas. The 1989 – 2003 annual deposition data from Svanvik extracted from Hagen et al. (2004) show, that the accumulation of copper constitutes less than 1 % of the copper in the upper 3 cm of the humus layer concentrations in Pasvik.

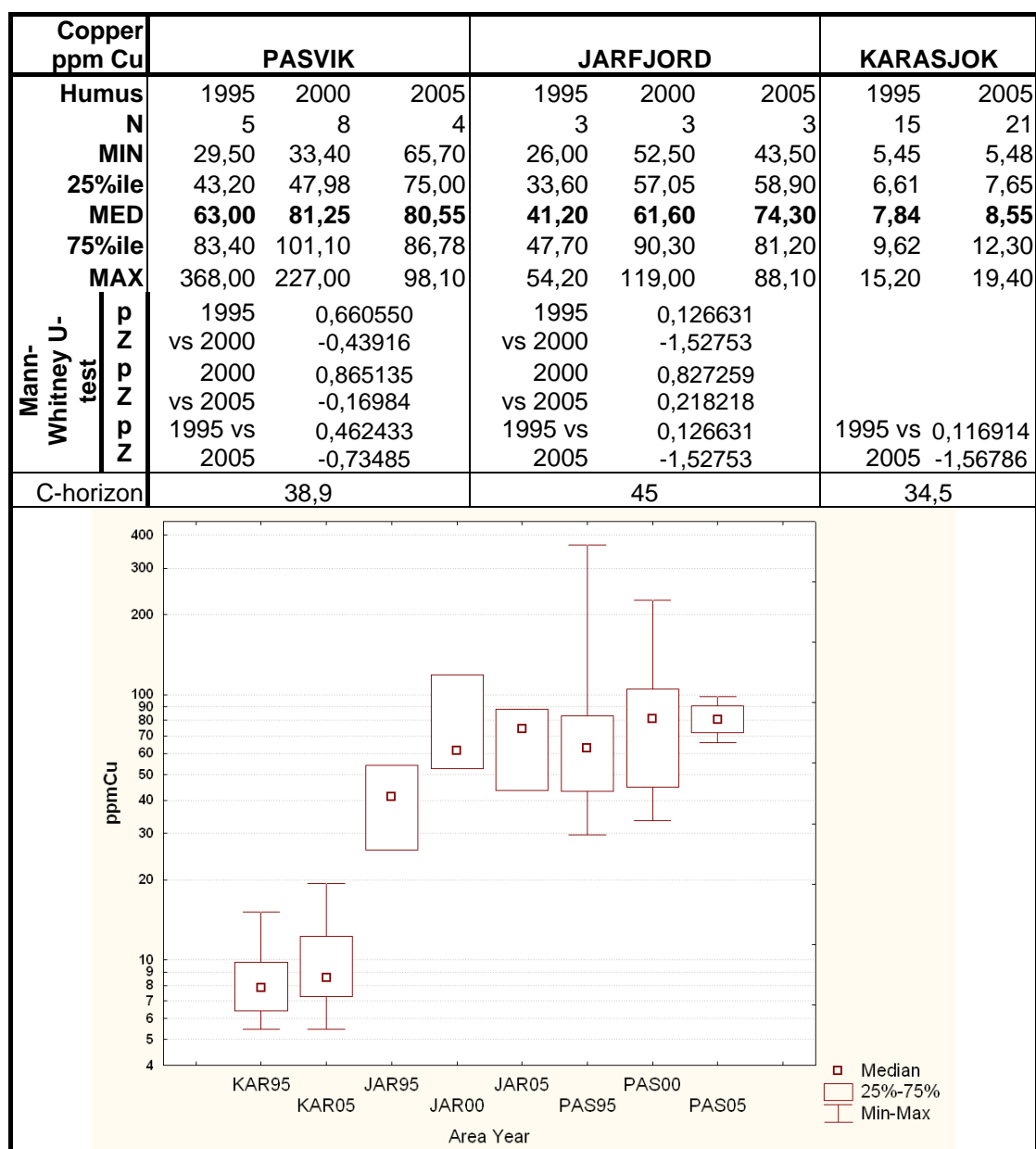


Figure 6. Copper: Descriptive statistics and results of statistical comparison between time groups.

4.3 Nickel

Key values for Ni are presented in Figure 6 with associated table. The Pasvik median values fluctuate between 102 and 92,45 ppm. The nickel median values increase in Jarfjord from 61,3 ppm in 1995 to 64,9 ppm in 2000 and 89,4 ppm in 2005. However, the Mann-Whitney U-test indicates that the change is not statistically significant. Karasjok median values are considerably lower compared with Pasvik and Jarfjord. The slight increase of the Karasjok median value from 1995 to 2005 is not significant. The C-horizon median values are distinctly higher in Jarfjord and Karasjok compared to Pasvik. This suggests that nickel deposition plays a larger role in Pasvik compared to Jarfjord. This can partly be explained by the shorter the distance from Nickel to Pasvik than to Jarfjord.

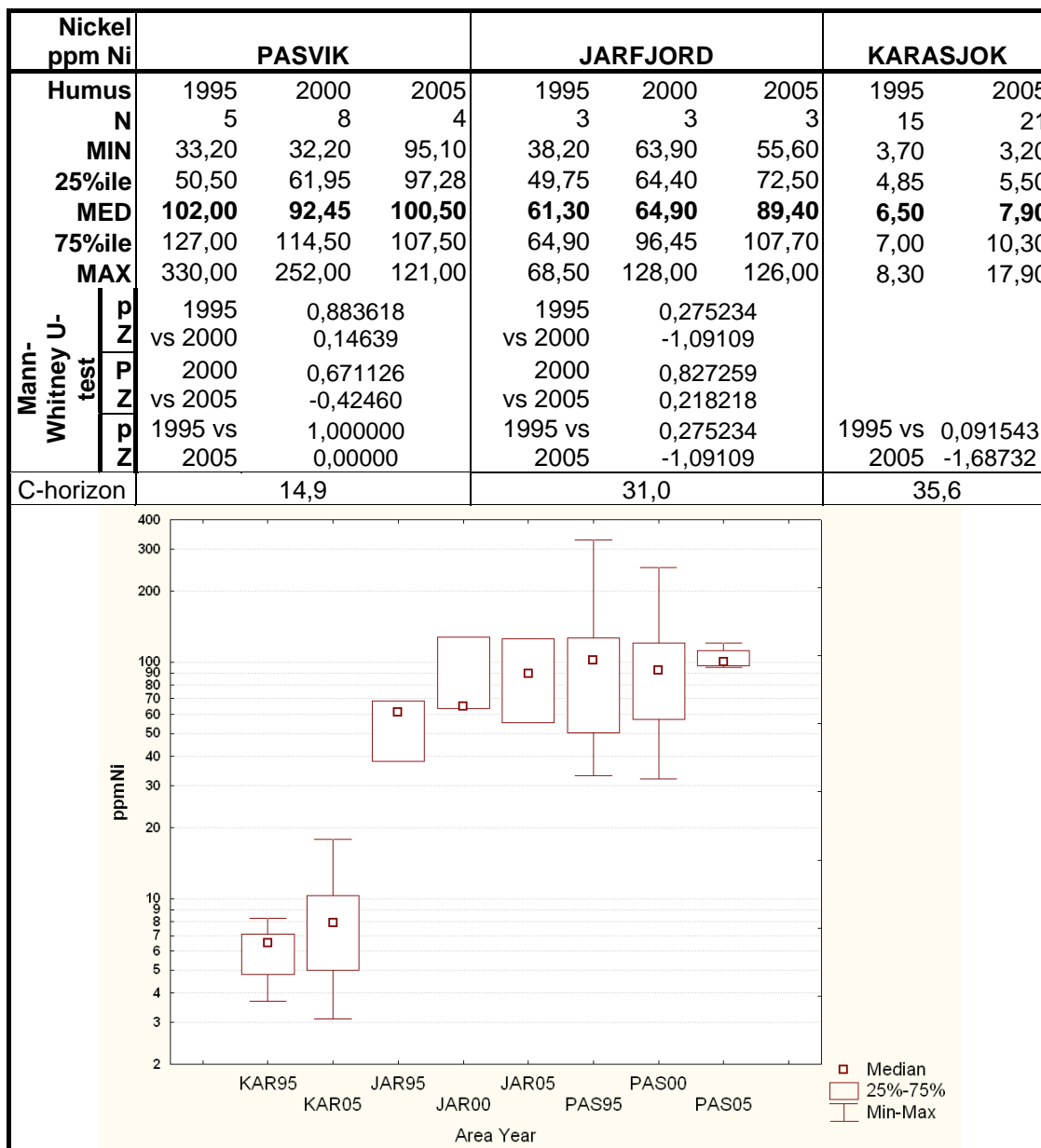


Figure 6. Nickel: Descriptive statistics and results of statistical comparison between time groups.

4.4 Arsenic

Arsenic values are shown in Figure 7. The median values show decreasing trends in all three areas, and there are only minor differences between the Pasvik and Jarfjord. This opposite temporal trends compared to copper and nickel suggests either decreasing emissions of arsenic and/or higher mobility of arsenic in the humus layer. The data presented by Hagen et al. (2004) indicate reduced deposition of arsenic in Svanvik in the last years. Arsenic deposition is obvious in both Pasvik and Jarfjord compared with Karasjok, which has distinctly lower levels in both 1995 and 2005, and shows a statistically significant reduction over the decade. Comparison of the humus median values and C-horizon values in the table shows that there is relatively small enrichment of arsenic in Jarfjord and Pasvik.

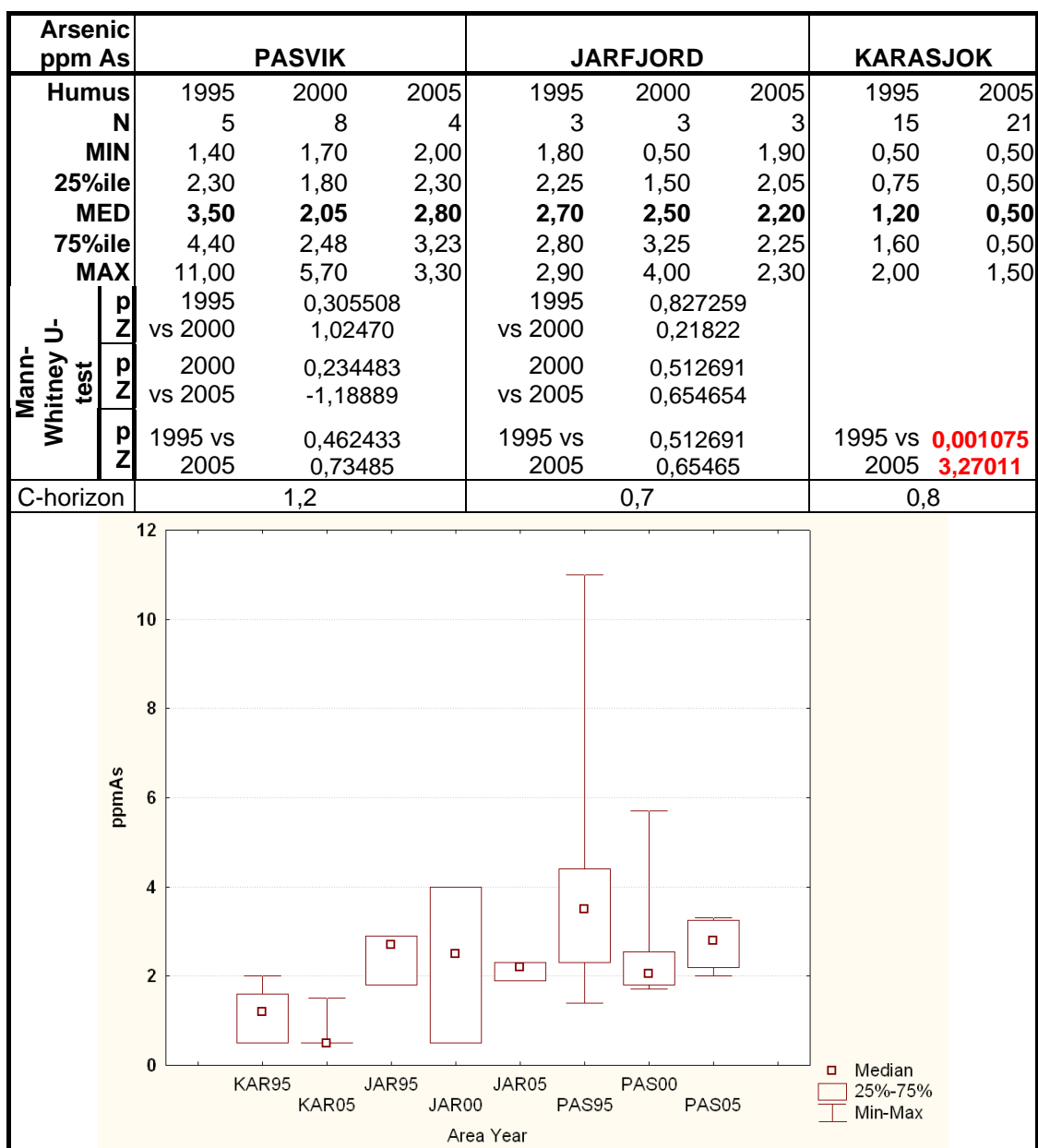


Figure 7. Arsenic: Descriptive statistics and results of statistical comparison between time groups.

4.5 Cadmium

The cadmium values in Figure 8 show that Pasvik and Jarfjord have somewhat higher median values than Karasjok, and the Jarfjord values appear to be slightly higher than the Pasvik values. There are no clear trends from 1995 to 2000 and 2005 in Pasvik and Jarfjord. Since the concentrations in the humus layer in Pasvik and Jarfjord are approx. 10 times higher than the C-horizon values, and only 5 times in Karasjok, it suggests a contribution from deposition from airborne cadmium. The smelter in Nikel is a source for cadmium in Pasvik and Jarfjord (Reimann et al., 1998). Another important human source for cadmium is waste incineration according to AMAP (1998), which might add to cadmium in humus in all three areas.

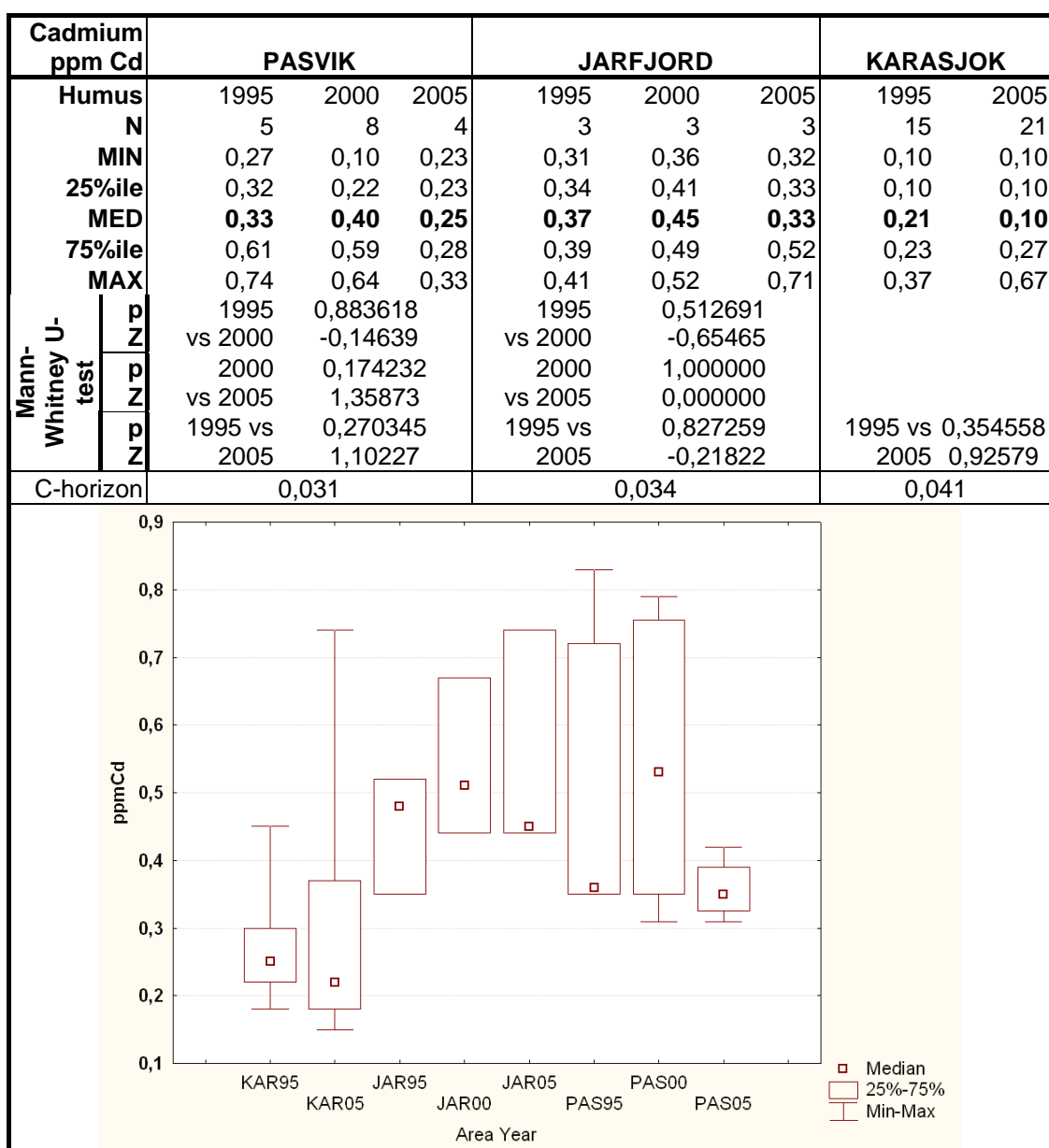


Figure 8. Cadmium: Descriptive statistics and results of statistical comparison between time groups.

4.6 Lead

Lead presented in Figure 9 shows different temporal and geographical variations compared to copper, nickel and arsenic. There is a minor, statistically insignificant increase for the Pasvik median value, whereas the Jarfjord median value has a more fluctuating variation. In Karasjok there is a statistically significant decrease from 1995 to 2005; nevertheless the levels are relatively similar in Pasvik, Jarfjord and Karasjok. Humus lead values are 5-10 times higher than the C-horizon values. Lead from human activity appears to be present in all three areas, partly a result of long-distance transport. The reduction in Karasjok from 1995 to 2005 might well be due to a shift from leaded to unleaded gasoline in the early 1990-ies, thereby removing a (local and distant) human lead source. At the same time, a similar reduction is not seen in the area influenced by the nickel industry.

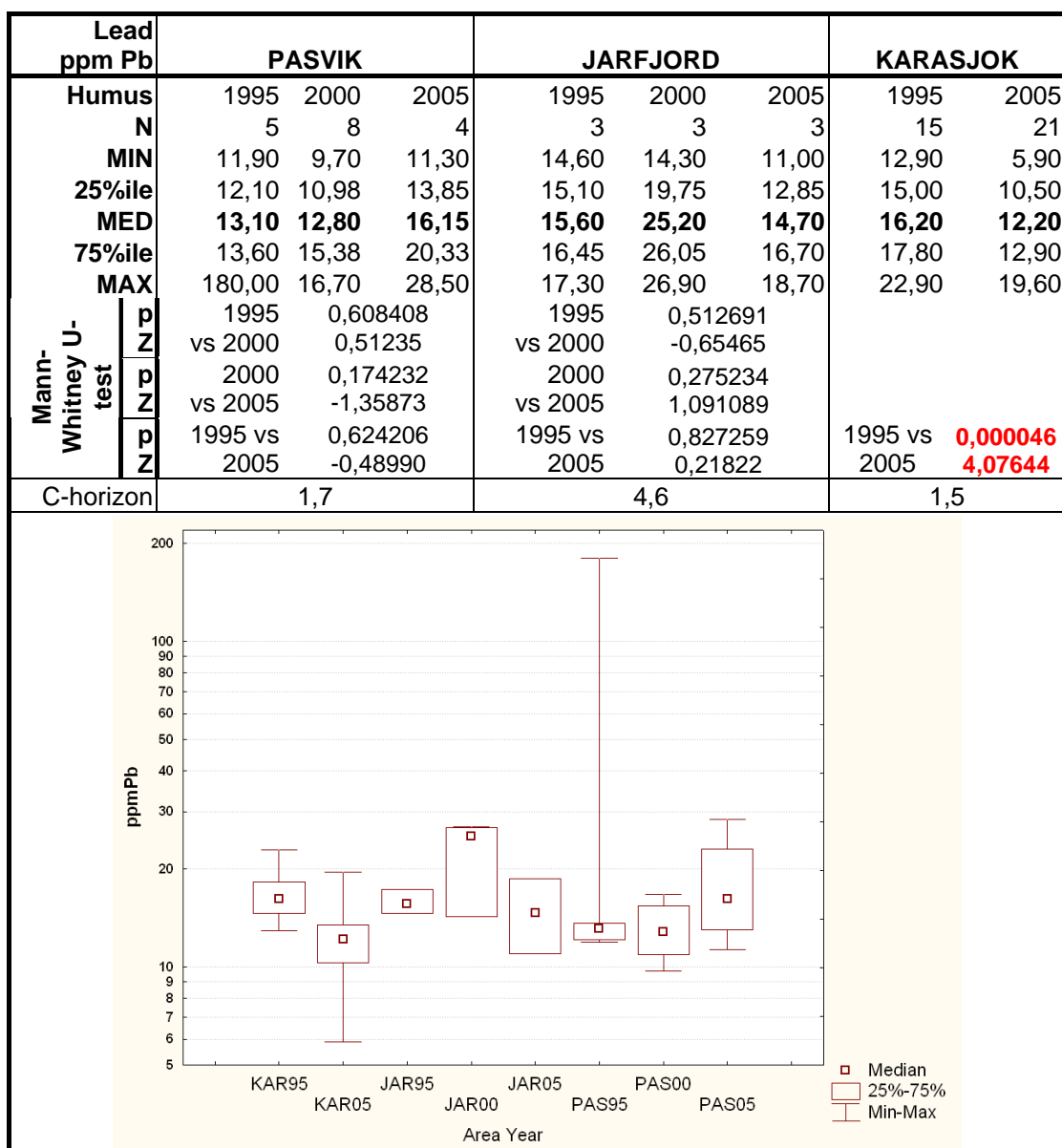


Figure 9. Lead: Descriptive statistics and results of statistical comparison between time groups.

4.7 Mercury

Mercury presented in Figure 10 shows relatively uniform median values in Pasvik. In Jarfjord, a significant increase followed by a significant decrease for the periods 1995-2000 and 2000-2005 respectively is ruled out by the significance test for the 1995-2005 comparison; a reminder that statistical procedures always should be accompanied by insight in their requirements and limitations. In Karasjok, a significant decrease from 1995 to 2005 is seen. As for lead, the relatively uniform median concentrations might suggest long-range transport, i.e. sources outside Finnmark. AMAP (1997) show that mercury is transported over long distances from the European and North-American continents into the arctic. Coal-fired power plants are important for emission of mercury into the atmosphere.

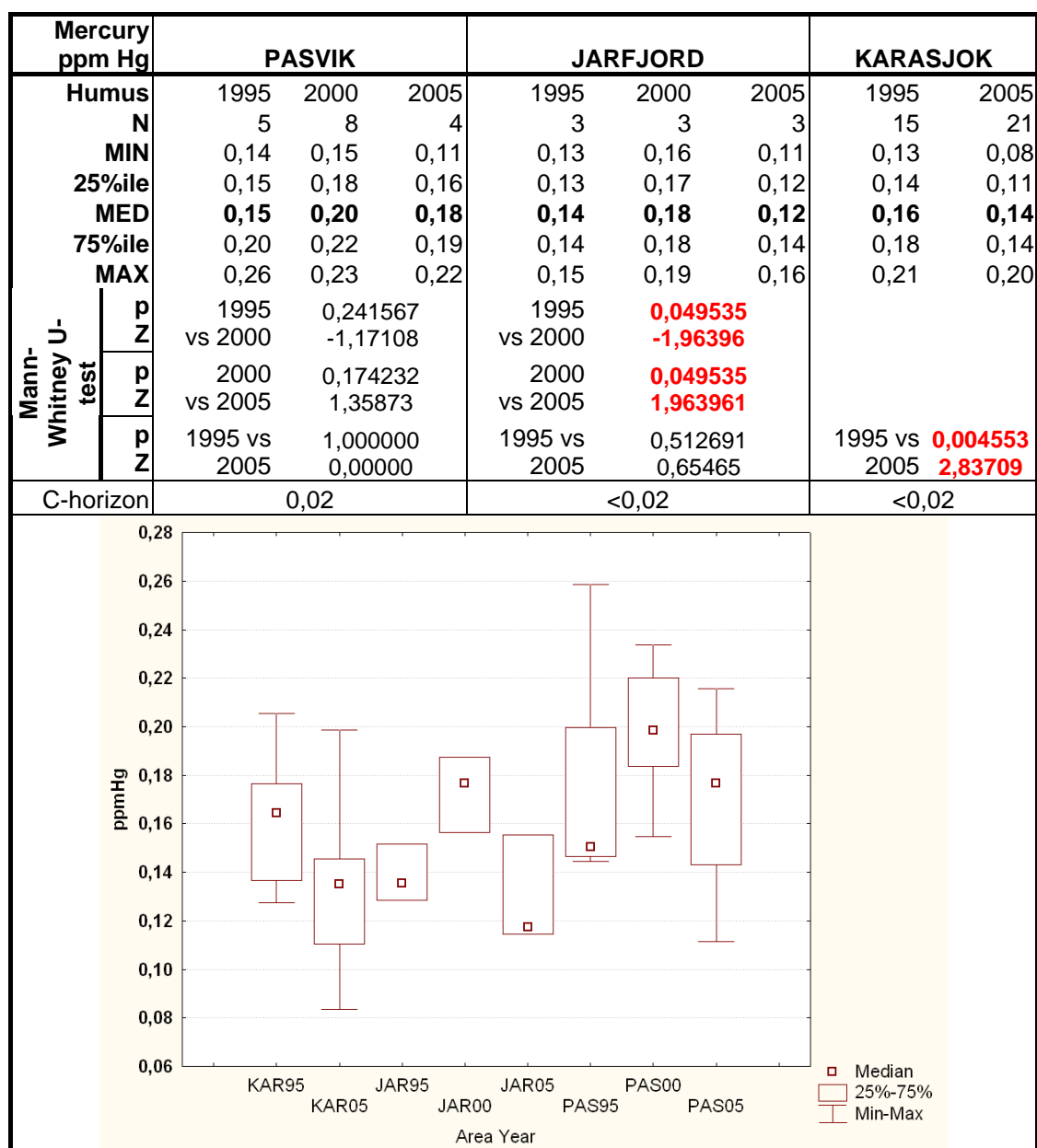


Figure 10. Mercury: Descriptive statistics and results of statistical comparison between time groups.

4.8 Zinc

Zinc median values in Figure 11 show an increasing, but not statistically significant trend in Pasvik from 1995 through 2000 and 2005. There is a less clear trend in Jarfjord within the same decade. Karasjok has an statistically significant increasing trend from 1995 to 2005. Nevertheless, there are only minor differences in zinc median values in humus between the three areas. There are major differences in C-horizon median values between the three areas, where the Jarfjord area has the highest zinc concentrations. Reimann et al. (1998) show that emissions from the smelter in Nikel plays a role for deposition of zinc on the humus layer. Karasjok median values in humus are increasing from 1995 to 2005. This suggests that human sources like traffic might contribute to zinc in the humus layer in this area.

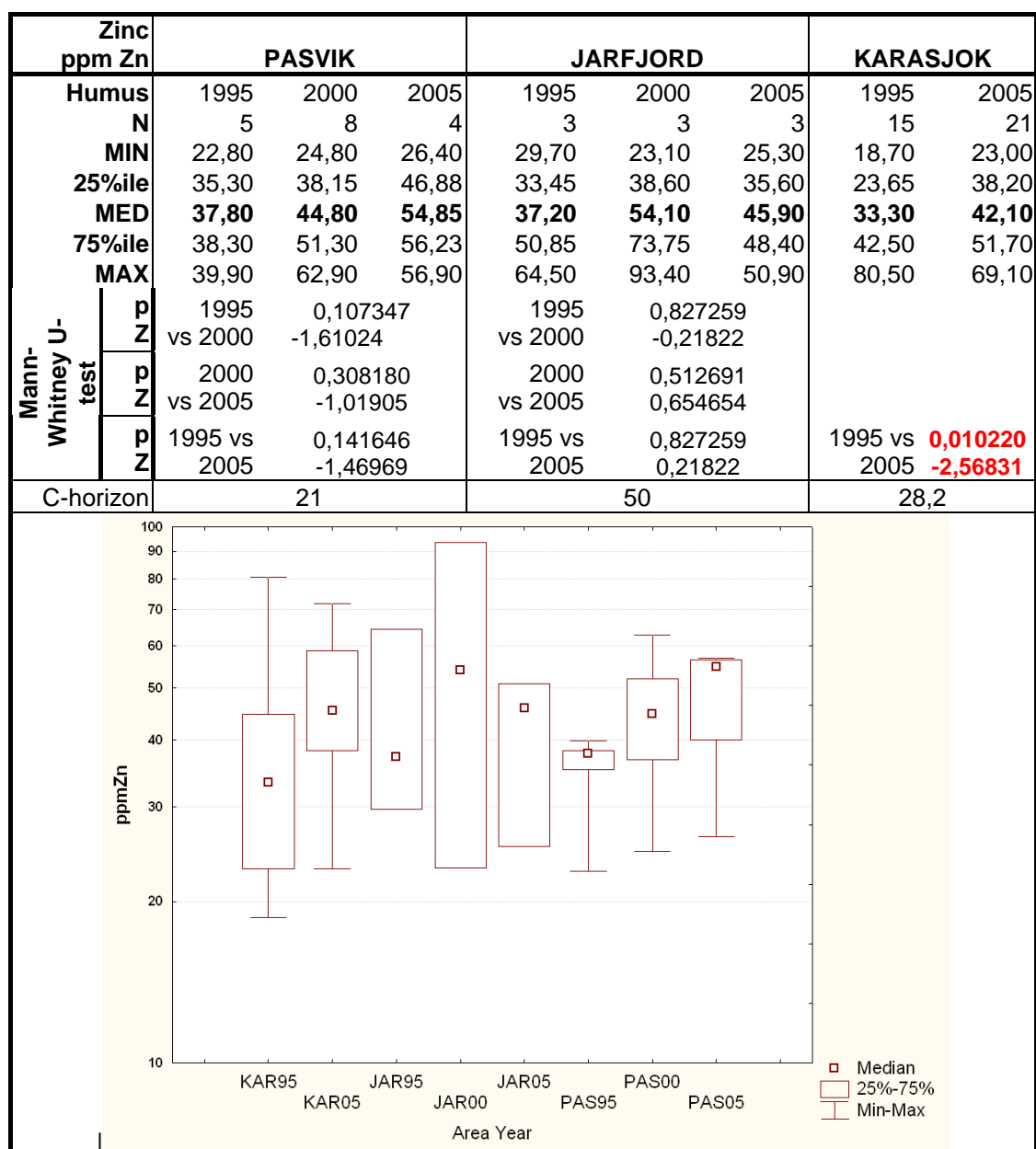


Figure 11. Zinc: Descriptive statistics and results of statistical comparison between time groups.

4.9 Cobalt

Cobalt median values appear to be relatively uniform in Pasvik and Jarfjord, and about twice as high as in the Karasjok area (Figure 12). There is no clear temporal trends for Pasvik, while a significant increase is seen in Jarfjord from 1995 to 2000, followed by an insignificant decrease. There is a small increase in cobalt concentrations in Karasjok from 1995 to 2005, this is not significant, however. Cobalt is the only metal which has higher C-horizon median values than the humus median values in all three areas. The Karasjok median values in humus are 12 – 15 % of the C-horizon value, in Pasvik and Jarfjord the corresponding figures are 60 - 90% and 25 –50% respectively. Reimann et al. (1998) show that the smelter in Nikel clearly affects the levels of cobalt in Pasvik and Jarfjord.

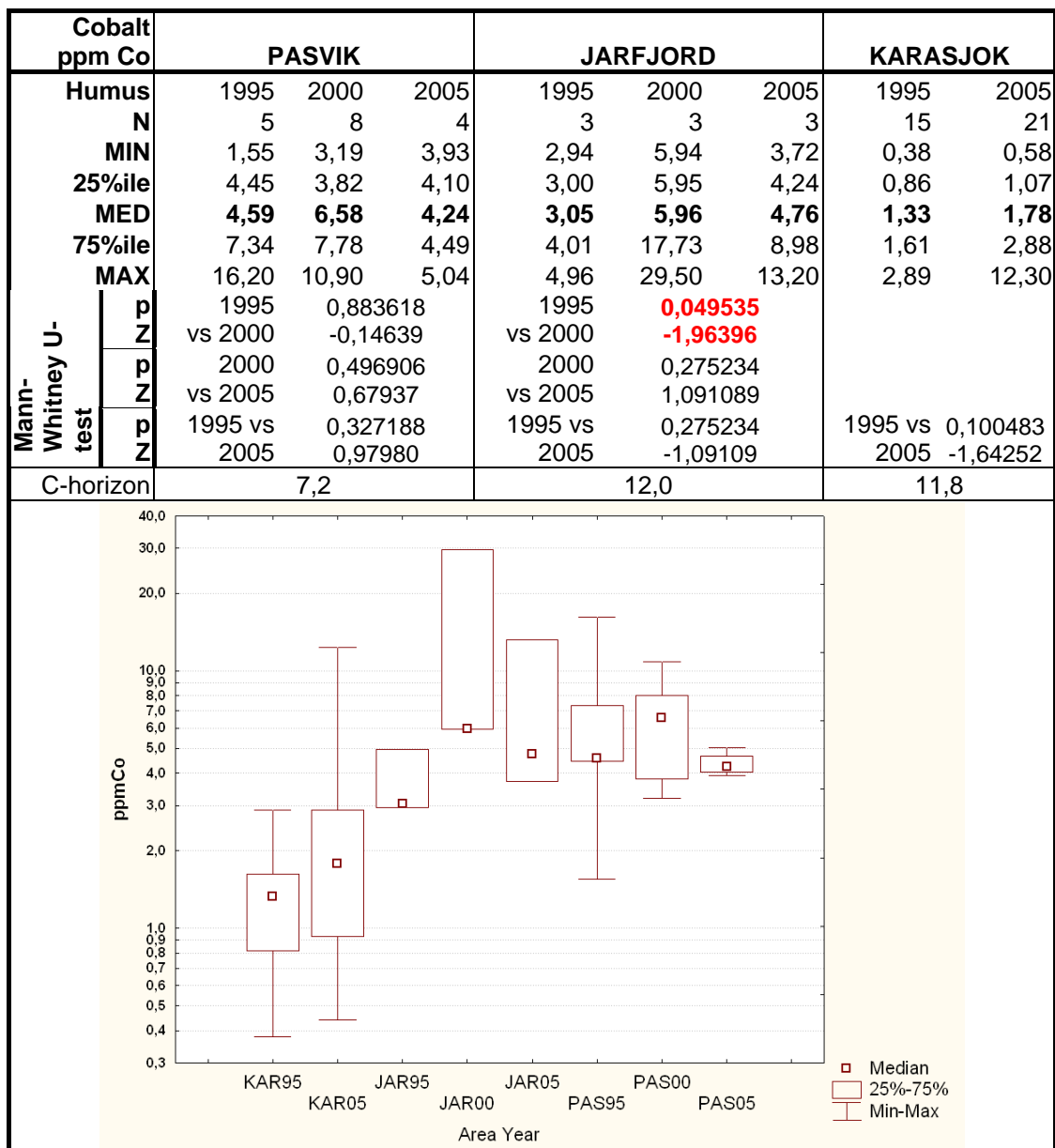


Figure 12. Cobalt: Descriptive statistics and results of statistical comparison between time groups.

4.10 Polycyclic aromatic hydrocarbons

Analysis of polycyclic aromatic hydrocarbons (PAH) in humus was not included to the same extent as metals and arsenic in the 1995 material. The number of samples analysed for PAH is very limited, as shown in Table 1 below. For 2000 and 2005 the number of samples for PAH-analysis is significantly larger. The sumPAH₁₆ concentrations in humus are generally low in all three areas. One sample from Pasvik 1995 has a value of 2,455 mg/kg dry matter. This might be a local fire in the area, which has attributed PAH to the humus. Comparison of median values for 2000 and 2005 in Pasvik show an increase from 0,150 to 0,270 mg/kg dry matter. There is hardly any change in Jarfjord. Since only one sample was analysed from the Karasjok area in 1995 (0,032 ppm) it is not feasible to evaluate whether there is a temporal decrease when comparing with the 2005 median value of 0,300 ppm. The Karasjok area has a higher median value than Pasvik and Jarfjord for 2005. Local sources like forest fires and emissions from traffic are believed to be of major importance in all three areas.

Pasvik			Jarfjord			Karasjok	
1995	2000	2005	1995	2000	2005	1995	2005
N = 1	N = 8	N = 4	N = 2	N = 3	N = 3	N = 1	N = 21
2,455	0,150	0,270	0,017	0,150	0,180	0,032	0,300

Table 1. Sum PAH₁₆ median values ($\mu\text{g}/\text{kg}$ dry matter) for Pasvik, Jarfjord and Karasjok areas. The number of samples (N) are listed for the different sampling campaigns.

5. SUMMARY

Levels of copper and nickel show increasing temporal trends for the Jarfjord area although no statistically significant changes are seen within the 1995 – 2005 decade, whereas copper and nickel concentrations in Pasvik are relatively constant for the 10 years period 1995 to 2005. Zinc and lead, on the other hand shows increasing trends in Pasvik and relatively constant levels in the Jarfjord area. Arsenic levels are relatively uniform in Pasvik, and slightly decreasing in Jarfjord. For other heavy metals like cadmium, mercury and cobalt there are no clear temporal trends in neither Pasvik nor Jarfjord.

Comparison with Karasjok shows, that copper, nickel, arsenic, cadmium, cobalt and most likely zinc are deposited in Pasvik and Jarfjord from emissions from Nikel and Zapoljarnyi. Lead and mercury, which are found in similar concentrations in all 3 areas, seem to originate from long-range transport from outside the region. A study of lead isotope ratios of these samples is already initiated, and will hopefully shed more light on the sources of lead in the humus layers.

The deposition data from Svanvik for copper and nickel show through comparison with the copper and nickel concentrations in humus in the Pasvik area, that the annual deposition contributes less than 1 %.

Occurrence of PAH in the humus layer is more random in all three areas. The most likely sources of PAH are believed to be local fires and possibly exhaustion for combustion engines (traffic, farming, forestry, reindeer herding).

6. RECOMMENDATIONS

- Several heavy metals have varying temporal trends in Pasvik and Jarfjord. Therefore there ought to be a repetition of soil sampling in 2010 in all three areas in order to expand the temporal trend.
- Evaluate further on the fate of the contaminants in the humus layer. Will they stay in the soil or will they be transported into groundwater, streams or lakes, and thereby become more accessible in the terrestrial and aquatic ecosystems? Particularly possible climatic

changes combined with changes in precipitation might alter ability of the humus layer to retain deposited heavy metals.

- Degradation or erosion of the humus layer might cause higher mobility of heavy metals and arsenic and thus cause increased availability of these compounds to the terrestrial and aquatic ecosystems, including the food chains. Therefore processes causing increased erosion should be assessed and avoided in order to avoid increased mobilization of the heavy metals bound to the humus layer.

7. REFERENCES

- AMAP, 1997. Arctic pollution issues: A state of the arctic environment report. Arctic monitoring and assessment programme. 188 pages.
- Hagen L. O., Sivertsen B. Og Arnesen K., 2004. Grenseområdene i Norge og Russland. Luft og nedbørskvalitet, april 2003 – mars 2004. NILU rapport, OR 61/2004. 71 sider.
- Reimann C., Äyräs M., Chekushin V., Bogatyrev I., Boyd R., Caritat P. de, Dutter R., Finne T. E., Halleraker J. H., Jæger Ø., Kashulina G., Lehto O., Niskavaara H., Pavlov V., Räisänen M. L., Strand T. and Volden T. (1998). Environmental geochemical atlas of the Central Barents Region. NGU – GTK – CKE special publication. 745 pages.
- StatSoft, Inc. (2006). Electronic Statistics Textbook. Tulsa, OK: StatSoft. WEB: <http://www.statsoft.com/textbook/stathome.html>.
- Tukey J. W. (1977). Exploratory data analysis. Addison-Wesley, Reading, 506 pp.
- Yoccoz N., Tømmervik H., Bakkestuen V., Nikonov V. V., Lukina N., Jensen H. K. B., Finne T. E. and Henttonen H., 2001. Environmental and pollution impact research and competence build-up in Northern Norway through integrated ecological and geological and remote sensing studies. Interreg IIA status report, 22 pages.