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Geochemistry of atmospheric deposition in the Kymi district (Finland) and in the Karelian Isthmus (Leningrad Region, Russia)

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GEOCHEMISTRY OF ATMOSPHERIC DEPOSITION IN THE KYMI DISTRICT (FINLAND) AND IN THE KARELIAN ISTHMUS (LENINGRAD, RUSSIA)

Espoo 1997

The Geological Survey of Finland, the Northwest Regional Geological Centre, St. Petersburg, and the Russian Academy of Sciences, St. Petersburg, carried out an ecogeochemical investigation in the Kymi district in southeastern Finland and in the Karelian Ithmus in Russia to establish the anthropogenic contribution to the deposition of elements on topsoil. The study was based on snow sampling conducted in March 1993 and 1994, and on analytical data on meltwater, unashed solid residue (organic + mineral dust) and ashed residue (mineral dust) in snow.

Atmospheric deposition of the contaminants studied is heaviest around the St. Petersburg megapolis and in the Imatra-Svetogorsk area, which represents a coherent trans-border zone of environmental contamination. Industrial plants are the main sources of heavy metals. The other anomalous areas detected seem to be of local character only.

Long-distance atmospheric transportation of heavy metals and sulphur across the Gulf of Finland has a minor impact on depositions in the region investigated. Atmospheric depositions in the Karelian Isthmus and in the Kymi district are approximately of the same order of magnitude for both heavy metals and sulphur. Average levels of aerial SO_4^{2-} and Pb depositions are lower than those in Central Europe. There are, however, no marked differences in the depositions of other heavy metals.

Airborne deposition of heavy metals in the anomalous areas contaminates top soil and forest vegetation in particular. This was verified in the Karelian Isthmus, where a marked similarity was found between the areal distribution of metal depositions and contamination of ground ecosystems. The airborne dust is enriched in Pb, Cd, Zn, Cu, Ni and V compared with the background values in soil (ratio >1) but the concentrations of Cr, Mn, Ba, Sr are lower (ratio < 1).

Although winters 1993 and 1994 were very different from each other in respect of the depth and water storage of snow cover, snow proved to be a well-suited medium for attaining the target set for the present study.

Key words (GeoRef Thesaurus, AGI): environmental geology, geochemical surveys, snow, atmospheric fallouts, airborne pollutants, heavy metals, sulfur, pollution, forest soils, vegetation, Kymi Province, Finland, Karelian Isthmus, Russian Federation

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Geologian tutkimuskeskus Espoossa (GTK) ja Venäjän luoteisen alueen geologiakeskus (NWRGC) sekä tiedeakatemia Pietarissa (RAS) ovat selvittäneet ihmistoiminnan vaikutusta maan pinnalle tulevaan alkuaineslaskeumaan. Tämä ympäristögeokemiallinen (ekogeokemiallinen) tutkimus tehtiin Kymen läänin kaakkoisosassa ja Karjalan kannaksella ja se perustui talvikausina 1993 ja 1994 kerättyjen luminäytteiden veden sekä tuhkistamattoman kiintoaineen (orgaanisen ja mineraalisen pölyn) ja tuhkistetun kiintoaineen (mineraalisen pölyn) analyysitietoihin.

Pietarin ympäristön ja Imatran-Svetogorskin suuret teollisuuslaitokset ovat merkittävimmät raskasmetallilähteet. Viimeksi mainittu alue edustaa tutkimusalueen yhtenäisintä, valtakuntien rajan ylittävää, voimakkaan laskeuman vyöhykettä. Raskasmetalli- ja rikkilaskeumat ovat Kymen alueella ja Karjalan kannaksella keskenään samaa suuruusluokkaa. Raskasmetallien ja rikin ilmateitse tapahtuvalla kaukokulkeumalla Suomenlahden yli on pieni merkitys. Raskasmetallien laskeumat eivät merkittävästi poikkea muualla Euroopassa mitatuista arvoista. Sulfaatti- ja lyijylaskeumat ovat jopa alhaisempia kuin Keski-Euroopassa.

Voimakkaan laskeuman alueilla raskasmetallit rikastuvat maan pintaosaan ja kasvillisuuteen. Tämä näkyy selvästi Karjalan kannaksella, jossa suurimmat metallilaskeumat esiintyvät samoilla alueilla missä sammalissa on todettu poikkeuksellisen korkeita raskasmetallipitoisuuksia. Lyijy, kadmium, sinkki, kupari, nikkeli ja vanadiini ovat rikastuneet ilman kuljettamaan pölyyn, jossa niiden pitoisuudet ovat korkeammat kuin vastaavat maaperän tausta-arvot (suhde >1). Sen sijaan kromia, mangaania, bariumia ja strontiumia on pölyssä vähemmän kuin maaperässä (suhde <1).

Vaikka talvet 1993 ja 1994 poikkesivat lumen määrän ja muiden ilmastollisten olosuhteiden suhteen paljon toisistaan, lumi osoittautui sopivaksi näyteaineksi ympäristöön ilmateitse tulevaa laskeumaa tutkittaessa.

Avainsanat (Fingeo-sanasto, GTK): ympäristögeologia, geokemialliset tutkimukset, lumi, laskeumat, ilmalevinteiset epäpuhtaudet, raskasmetallit, rikki, saastuminen, metsämaat, kasvillisuus, Kymen lääni, Suomi, Karjalan kannas, Venäjä

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Геологический научно-исследовательский Центр, Северо-западный Региональный Геологический Центр и Российская Академия Наук провели эколого-геохимические исследования в районе Кюми (юго-восточная Финляндия) и на Карельском перешейке (Россия) для установления антропогенного вклада в выпадениях элементов на поверхность почв. Изучение основывалось на опробовании снега, проведенном в марте 1993 и 1994 годов, и на аналитических данных по талой воде и осадку из снега, неозоленному (органическая и минеральная пыль) и озоленному (минеральная пыль).

Атмосферные выпадения загрязнителей наиболее существенны вокруг С.-Петербурга и в Иматра-Светогорской промышленной зоне. Промышленные предприятия являются основным источником выбросов тяжелых металлов, и Иматра-Светогорский район представляет собой совместную трансграничную зону загрязнения окружающей среды. Остальные выявленные аномальные зоны имеют локальный характер.

Дальний атмосферный перенос тяжелых металлов и серы через Финский залив составляет незначительную долю выпадений в исследованном регионе. Атмосферные выпадения на Карельском перешейке и в районе Кюми приблизительно одинаковы как по тяжелым металлам, так и по сере. Средний уровень аэрогенных SO_4^{2-} и Pb здесь ниже, чем в центральной Европе. По остальным тяжелым металлам существенных различий не отмечено.

Атмосферные выпадения тяжелых металлов загрязняют поверхность почв и растительность в аномальных зонах. Это подтверждается на Карельском перешейке, где обнаружено заметное сходство пространственного распределения атмосферных выпадений тяжелых металлов и загрязнения наземных экосистем. Аэрогенная пыль обогащена Pb, Cd, Zn, Cu, Ni и V по сравнению с фоновыми содержаниями их в почвах (отношение > 1), содержания же Cr, Mn, Ba, Sr ниже фоновых (отношение < 1).

Хотя зимние сезоны 1993 и 1994 годов существенно различались по мощности снега и величине влагозапаса, снег оказался весьма информативным материалом для решения поставленной задачи.

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CONTENTS

1. INTRODUCTION

This study is a joint ecogeochemical project to analyse snow and thus determine the content of airborne pollution in the border zone of the Kymi district, Finland and the Karelian Isthmus, Leningrad Region, Russia. The objective is to establish the anthropogenic contribution to the deposition of elements on topsoil. The project is part of the scientific/technical cooperation between Finland and Russia under the theme 3.1 Ecogeochemical research in border areas (Protocol of the 17th meeting of the working group of the Finnish-Soviet cooperation in geology, 23-27.9.1991).

Part of the field work, chemical analyses and data processing were done by the teams of the Geological Survey of Finland (GSF). The organizations responsible for the same tasks in Russia were the North-West Regional Geological Centre (NWRGC) and the Centre for Ecological Safety of the Russian Academy of Science (CES/RAS). The Experiment Research Expedition (OME), the St.

Petersburg Geological Expedition (PACE) and the Mechanobr Co. also participated in sampling, analytical research and data processing. The State Company Mineral digitized the maps.

Snow in both the Kymi district and the Karelian Isthmus was sampled twice: in March 1993 and in March 1994 with a method jointly agreed upon during field excursions. The methods to be used for sample preparation, chemical analysis, data processing and interpretation, and compiling the report were standardized at several meetings. A preliminary report with monoelement maps, compiled using the ALKEMIA program (cf. Ahlsved et al. 1991) was released in January 1995 (Lahermo et al. 1995). The statistical classification and interpretation of the results were done as proposed by the Russian team. In addition to the denominated authors Victor Popov (PACE), Olga Valter (OME) and Victor Mishin (NWRGC) participated in the project.

2. METHODS

2.1 Field work

The first snow samples were taken in March 1993 in an area extending from Imatra-Lappeenranta-Hamina in Finland to Svetogorsk-Kamennogorsk-Vyborg-Primorsk (formerly Finnish Enso-Antrea-Viipuri-Koivisto) in Russia (Fig. 1). The samples were collected from open places, such as cultivated fields, clear-cut areas and treeless bogs. The snow was taken as a continuous vertical column with a 100 cm long acrylic or polyamide (nylon) tube with an inner diameter of 92 mm (Fig. 2).

The lowermost wet and icy snow, or firn, contaminated by the topsoil was removed. The size of the samples varied from 2 to 4 kg. The number of snow cores (1-9) taken at one sampling point depended on the thickness of the snow. Altogether 29

sites in Finnish and 35 in Russian territory were sampled in the first round. For comparison 10 duplicate samples were collected in both territories.

In the following winter (1994), 29 previous and 10 new sites in the Kymi district and 112 sites in the Karelian Isthmus were sampled. Of the latter, which covered the entire area of the Karelian Isthmus to St. Petersburg in the south and to Lake Ladoga in the east, 35 were old sites and 77 were new ones (Fig. 1). Samples from the Kymi district and those from the western part of the Isthmus were divided into two equal parts to permit parallel treatment and comparison by the participating laboratories in Finland and Russia.

Fig. 1. The study area in the Kymi district (Finland) and in the Leningrad Region (Russia). Snow was sampled west of the dotted line in March 1993 and in the whole study area in March 1994.

Fig. 2. Snow sampling.

2.2 Sample preparation

The melted snow samples were measured for electrical conductivity, pH and $KMnO_4$ consumption, and analysed for the main anions (SO_4^{2-}, Cl^-, NO_3^-) without any pretreatment. The snow used for the analysis of cations was prepared differently by the Finnish and Russian laboratories. At GSF, the snow samples were melted at room temperature and vacuum-filtered through a membrane (< 0.45 µm). At the Mechanobr laboratory the water was filtered through "blue ribbon" cellulose acetate paper at normal air pressure. At both laboratories the filtered water was stabilized by adding concen-

trated suprapure HNO_3 before analysing the samples by ICP-AES, ICP-MS and AAS methods.

The filter with the residual solid material on it was dried and weighed. At GSF it was dissolved in 10 ml of concentrated HNO_3 in a microwave oven and diluted to 50 ml. At the Mechanobr laboratory the filter with the residue was ashed by gradually raising the temperature to 500°C. The ash, comprising the mineral phase of the snow was weighed and dissolved in 20 ml of HNO_3 (1:1) at 120 °C and diluted to 50 ml before analysis.

2.3 Analytical methods

The properties and contents of snow melt were determined at the chemical laboratory of GSF as follows: potentiometric measurement of conductivity (EC) and that of pH were done immediately after melting of the snow samples. The anions (SO_4^{2-}, NO_3^-, Cl^- and F^-) were determined chromatographically, and the main cations and trace elements were analysed by ICP-AES and/or ICP-MS. At the Mechanobr laboratory, pH and F^- were measured potentiometrically, SO_4^{2-}, NO_3^- and Cl^- were determined by titrimetric and photometric methods and cations were analysed by AAS and ICP-AES methods. The duplicate samples (in 1993)

were pretreated and analysed similarly at both laboratories, thus permitting harmonization of the methods and results.

In the following year (1994), the 39 samples collected from the Kymi district and the 45 samples from the western part of the Karelian Isthmus were divided in the field into two equal parts and sent to the Finnish and Russian laboratories for analysis. After preparation as described above the liquid part was analysed at GSF but the solid part at the Mechanobr laboratory. The liquid and solid phases of the other samples collected from the Karelian Isthmus were analysed by Mechanobr only.

2.4 Data processing and compilation of maps

The analytical data served as basis for variables derived for interpretation and map compilation. The following variables were used:

1) Element concentrations in liquid phase, µg/l
2) Element concentrations in unashed solid phase (total residue or dust), µg/g
3) Element concentrations in ashed solid phase, mineral residue or dust, µg/g
4) Element concentrations in solid phase related to the total volume of filtered water C_{sl}, µg/l, according to the formula

$$C_{sl} = (C_s * M)/V$$

where C_s =   element concentration in ashed or unashed solid phase, µg/g
       M =   weight of ashed or unashed solid phase, respectively, g
       V =   volume of filtered water, l

5) Atmospheric deposition of elements P, µg/m² or mg/m², according to the formula

$$P = C * V/A$$

where   C =   sum of element concentrations in liquid and solid phase, µg/l
       V =   volume of filtered water, l
       A =   sum of total area of sampling tubes, m²

The principal variables for the map compilation were the atmospheric depositions P. The element concentrations in liquid phase and in the mineral residue were used as additional values to improve the accuracy of the interpretations. A general model for the sum of the depositions Z_c of anthropogenic metals (Zn, Cu, Ni, V, Cr, Pb, Cd) for each sampling site was compiled according to the formula

$$Z_c = \sum_{i=1}^{n}(P_i/P_b) - (n-1)$$

where P_i = deposition value of the ith element at a sampling site, $\mu g/m^2$
                P_b = background deposition value for the element, $\mu g/m^2$
                n = number of elements

The arithmetic mean of deposition for samples with $P_i < 3*S$ (standard deviation) for each element was used to calculate P_b and Z_c separately for each site. The sample set was trimmed by excluding samples with $Z_c > 5$, and P_b was assigned the arithmetic mean of the deposition of each heavy metal in the trimmed sample set. This background value was then used to calculate Z_c for the original sample set.

The sampling grid was irregular. Distributions of the concentrations were skewed for most elements. Thus the data were divided into 3-6 classes depending on the distribution of the element. Factors affecting the concentrations of the elements such as roads, densely populated settlements and the distribution of closely related elements (e.g. Na^+ and Cl^-) were taken into account. Initially, the contour maps were compiled manually. The final maps were digitized into Arc Info format and plotted by the State company Mineral in St.Petersburg.

3. RESULTS

3.1 Climatic characteristics of snow samples

Climatically winters 1993 and 1994 were very different from each other. Winter 1993 was mild. The permanent snow cover did not come until the second half of the winter, and the Gulf of Finland was frozen only for the last winter months. This resulted in abundant mineral dust and sea salt deposition, because both the ground and the sea were uncovered.

The water storage (water equivalent) of snow in 1993 was only 60-70% of that of the next winter. Loss on ignition (LOI), or the amount of organic material in the dust of snow in the Karelian Isthmus, was almost constant in both years, except in the samples from the Kymi district, where it was substantially higher in 1994 than in 1993 (Table 1).

Table 1. Characteristics of snow samples (average values).

	1993		1994	
	Kymi district	Karelian Isthmus	Kymi district	Karelian Isthmus
Area of sample, m^2	0.038	0.059	0.016	0.016
Thickness of snow, m	n.d.	0.30	0.47	0.39
Volume of water, l	3.0	4.5	2.4	2.0
LOI %	46.5	59.5	74.9	61.1
Total dust, mg/l	18.8	26.3	11.0	3.0
Total dust, mg/m^2	1 630	2 160	1 680	1 640
Mineral dust, mg/l	10.0	10.6	2.8	5.0
Mineral dust, mg/m^2	872	875	422	638
Water storage, l/m^2	86.6	84.3	152	130
Number of samples	29	35	39	112

n.d., not determined
LOI = Loss on ignition

3.1.1 Composition of liquid phase of snow

The concentrations of the anions SO_4^{2-} and NO_3^- in the filtered solution of melted snow were higher in 1994 than in 1993 (Table 2). The mean concentrations in snow from the Leningrad Region in 1993 and 1994 (Yakhnin et al.1997) and in earlier data (Astratov & Rjaboshapka 1989) were between

1 and 3 mg/l for SO_4^{2-} and 0.2 and 2 mg/l for NO_3^-. The global background value of SO_4^{2-} is about 1.5 mg/l (Vasilenko et al. 1985).

Chloride (Cl^-) and sodium (Na) distributions in the coastal area of the Karelian Isthmus are similar. The higher values in 1993 are explained by the marine influence, although the Cl^-/Na ratio in snow (1.0) is not the same as that in sea water (1.8). The

Table 2. Average anion and element concentrations in liquid phase of snow, µg/l.

	1993			1994		
	Kymi district	Karelian Isthmus	Whole study area	Kymi district	Karelian Isthmus	Whole study area
Cl⁻	382	924	638	410	415	414
SO_4^{2-}	1 032	1 488	1 247	1 400	1 657	1 591
NO_3^-	n.d.	892	892	1 306	1 150	1 227
F⁻	n.d.	22	22	n.d.	n.d.	n.d.
Ag	n.d.	n.d.	n.d.	0.003	0.003	0.003
Al	11.0	17.4	14.1	25.7	19.7	21.3
As	0.13	0.19	0.16	0.21	0.21	0.21
Ba	2.09	3.61	2.81	0.79	2.51	2.07
Be	n.d.	n.d.	n.d.	0.03	0.03	0.03
Bi	n.d.	n.d.	n.d.	0.003	0.002	0.002
Ca	367	484	422	284	292	290
Cd	0.07	0.07	0.07	0.02	0.03	0.02
Co	0.04	0.09	0.06	0.01	0.01	0.013
Cr	n.d.	n.d.	n.d.	0.07	0.05	0.06
Cu	2.68	3.59	3.11	0.18	0.23	0.22
Fe	17.7	30.8	22.8	12.9	9.14	10.1
K	159	473	307	112	244	210
Li	n.d.	n.d.	n.d.	0.07	0.05	0.06
Mg	74.1	92.8	82.9	34.6	62.3	55.4
Mn	4.58	5.49	5.01	1.91	4.53	3.85
Mo	0.06	0.06	0.06	0.04	0.04	0.04
Na	395	926	645	233	216	221
Ni	0.73	0.83	0.78	0.39	0.58	0.53
Pb	0.88	1.25	1.05	0.88	0.37	0.51
Rb	n.d.	n.d.	n.d.	0.23	0.37	0.30
Sb	n.d.	n.d.	n.d.	0.02	0.05	0.03
Se	n.d.	n.d.	n.d.	0.13	0.07	0.10
Sr	1.38	1.77	1.57	0.59	0.92	0.84
Th	n.d.	n.d.	n.d.	0.005	0.010	0.008
Tl	n.d.	n.d.	n.d.	0.010	0.009	0.010
U	n.d.	n.d.	n.d.	0.005	0.005	0.005
V	1.03	0.94	0.99	0.85	0.92	0.90
Zn	10.80	15.98	13.20	7.07	6.69	6.79

n.d., not determined

average Na concentration in samples from the Karelian Isthmus was almost four times higher in 1993 than in 1994. In samples from the Kymi district the Na concentrations were only slightly higher in 1993 than in 1994, thus resembling the distributions of most of the other cations. Only the 1994 samples were analysed for rare elements. A marked time-bound variation is, however, seen in the average concentrations of copper (Cu), cobalt (Co) and cadmium (Cd) and in regional differences of barium (Ba) and antimony (Sb) concentrations. All the high mean concentrations were found in samples from the Karelian Isthmus (Table 2).

The large number of relatively low pH values met in snow along the coast suggests that acid deposition increases southwards in the investigated area. $KMnO_4$ consumption, or chemical oxygen demand, varies greatly throughout the study area. The occasionally higher values of this variable may be due to local windblown dust rich in organic material.

3.1.2 Composition of solid phase of snow

The composition of solid phase or dust in all snow samples was relatively constant. In the Karelian Isthmus, however, the concentrations of calcium (Ca), strontium (Sr) and zinc (Zn) deviate substantially from the mean concentrations in the whole study area (Table 3). The distribution of vanadium (V) and nickel (Ni) also deviates from that of the other metals. In 1994 the concentrations were higher due to the high utilization rate of power plants in the cold winter.

The somewhat lower concentrations of almost all heavy metals in the unashed or total dust in the snow samples from the Kymi district in 1994 are explained by the high amounts of organic material in the snow. The concentrations of heavy metals in ashed or mineral dust do not show any such regional variations (Table 4).

The clear differences in the concentrations of some heavy metals between 1993 and 1994 have a

Table 3. Average element concentrations in unashed dust in snow, mg/kg.

	1993			1994		
	Kymi district	Karelian Isthmus	Whole study area	Kymi district	Karelian Isthmus	Whole study area
Al	3 790	4 320	4 040	3 540	6 350	5 620
Ba	100	119	109	71	191	160
Ca	3 640	3 750	3 690	4 950	8 400	7 500
Cd	8.6	4.1	6.5	1.2	2.6	2.2
Cr	28	21	25	21	27	25
Cu	129	104	117	81	115	106
Fe	6 660	6 110	6 400	5 770	6 760	6 500
K	1 840	2 310	2 060	2 550	3 440	3 210
Mg	1 270	1 420	1 340	1 250	2 310	2 040
Mn	175	113	146	106	153	141
Na	733	583	662	1 355	1 276	1 297
Ni	26	21	24	72	88	83
Pb	102	92	97	82	154	135
Sr	23	20	22	18	47	39
Ti	304	271	288	297	404	376
V	25	21	23	42	87	75
Zn	260	166	216	200	393	343

Table 4. Average concentrations of anthropogenic metals in ashed dust in snow, mg/kg.

	1993			1994		
	Kymi district	Karelian Isthmus	Whole study area	Kymi district	Karelian Isthmus	Whole study area
Cd	16	10	13	5	7	6
Cr	53	51	52	83	69	73
Cu	242	257	249	321	296	303
Ni	49	51	50	281	225	240
Pb	190	226	207	326	296	378
V	47	51	49	168	224	209
Zn	486	410	450	795	1 010	954

Table 5. Average element concentrations in dust in snow, µg/l.

	1993			1994		
	Kymi district	Karelian Isthmus	Whole study area	Kymi district	Karelian Isthmus	Whole study area
Al	70.6	111	89.6	39.0	80.1	69.4
Ba	1.8	3.0	2.4	0.7	2.4	1.9
Ca	67.5	97.1	81.5	55.2	107	93.4
Cd	0.16	0.10	0.13	0.01	0.03	0.03
Cr	0.5	0.5	0.5	0.2	0.3	0.3
Cu	2.3	2.5	2.4	0.9	1.4	1.3
Fe	126	160	142	66	91	85
K	36.8	59.5	47.5	28.3	41.6	38.2
Mg	21.7	37.4	29.1	13.7	30.4	26.1
Mn	3.3	3.0	3.2	1.2	2.0	1.8
Na	13.1	14.5	13.8	15.1	15.9	15.7
Ni	0.5	0.5	0.5	0.8	1.0	1.0
Pb	1.9	2.3	2.1	0.9	1.9	1.7
Sr	0.4	0.5	0.5	0.2	0.6	0.5
Ti	5.9	7.2	6.5	3.4	5.2	4.7
V	0.5	0.5	0.5	0.5	1.2	1.0
Zn	5.0	4.3	4.7	2.2	5.0	4.2

Table 6. Average total anion and element concentrations in liquid and dust in snow, µg/l.

	1993			1994		
	Kymi district	Karelian Isthmus	Whole study area	Kymi district	Karelian Isthmus	Whole study area
Cl⁻*	382	924	638	409	415	413
F⁻*	n.d.	22	22	n.d.	n.d.	n.d.
SO₄²⁻*	1 032	1 488	1 247	1 400	1 657	1 592
NO₃⁻*	n.d.	892	892	1 306	1 150	1 227
Ag*	n.d.	n.d.	n.d.	0.003	0.003	0.003
Al	81.7	128.4	103.7	64.7	94.0	86.4
As*	0.13	0.19	0.16	0.20	0.21	0.21
Ba	3.79	6.63	5.14	1.46	4.78	3.91
Be*	n.d.	n.d.	n.d.	0.03	0.03	0.03
Bi*	n.d.	n.d.	n.d.	0.003	0.002	0.029
Ca	433	581	503	340	399	382
Cd	0.23	0.18	0.20	0.03	0.06	0.05
Co*	0.04	0.09	0.06	0.01	0.01	0.01
Cr	0.46**	0.54**	0.50**	0.29	0.33	0.32
Cu	5.0	6.1	5.5	1.1	1.6	1.5
Fe	141	190	164	78	91	87
K	195	532	354	140	283	246
Li*	n.d.	n.d.	n.d.	0.07	0.05	0.06
Mg	95.7	130	112	46.1	90.5	78.9
Mn	8.2	8.5	8.3	3.1	6.3	5.5
Mo*	0.06	0.06	0.06	0.04	0.04	0.04
Na	408	940	659	248	232	236
Ni	1.22	1.36	1.29	1.15	1.55	1.45
Pb	2.74	3.56	3.13	1.77	2.24	2.12
Rb*	n.d.	n.d.	n.d.	0.23	0.36	0.30
Sb*	n.d.	n.d.	n.d.	0.02	0.05	0.04
Se*	n.d.	n.d.	n.d.	0.13	0.07	0.10
Sr	1.80	2.29	2.03	0.77	1.51	1.32
Th*	n.d.	n.d.	n.d.	0.01	0.01	0.01
Ti**	5.88	7.2	6.5	3.4	5.2	4.7
Tl*	n.d.	n.d.	n.d.	0.01	0.01	0.01
U*	n.d.	n.d.	n.d.	0.005	0.005	0.005
V	1.50	1.44	1.47	1.31	2.02	1.84
Zn	15.8	20.3	17.9	9.24	11.6	11.0

* liquid phase; ** dust
n.d., not determined

climatological explanation. Winter 1994 was cold and early snow prevented natural mineral and organic dust from spreading. The intense heating of houses and power plants caused an increase in the relative and absolute amounts of anthropogenic deposition.

The elemental concentrations depend on the amount of dust in snow (Tables 1 and 5). The overall concentrations were therefore higher in 1993 than in 1994 (except for Ni and V). The solubility of the elemental compounds determines whether a metal is concentrated in liquid or in the dust phase. The following order could be calculated from the data (proportion of dissolved element in parentheses):

Na (90%), Ca, K (80%), Mg, Sr (70-80%), Zn (60-75%), Ba, Cd, Mn (50-60%), V (40-70%), Ni (35-60%), Pb (20-40%), Cr, Cu (15-25%) and Al, Fe (10-20%).

Table 6 shows the sum of elemental concentrations in liquid and dust. In 1993 total element concentrations were in many cases higher because

the water equivalent of snow was only half of that in 1994 (Table 7).

3.1.3 Water storage

In 1993 water storage, or the water equivalent of snow, in the Kymi district varied from 75 to 120 l/m² (Fig. 3). The values declined southeastwards from the Salpausselkä zone to the Finnish-Russian border. In the northeastern part of the Karelian Isthmus water storage was generally less than 75 l/m², but in other areas and especially along the coast it exceeded 75 l/m².

In 1994, water storage in the Kymi district was, on average, 150 l/m², while in the Karelian Isthmus it ranged from 75 to 150 l/m² (Fig. 4). The highest value was measured on the coast in the Primorsk (Koivisto) area and in the Zelenogorsk-Iljichevo-Vaskelovo (Terijoki-Jalkala-Lempaalanjärvi) areas. Near St. Petersburg water storage was only 30-60 l/m².

Table 7. Atmospheric deposition in winter periods 1993 and 1994, $\mu g/m^2$

	1993			1994		
	Kymi district	Karelian Isthmus	Whole study area	Kymi district	Karelian Isthmus	Whole study area
Cl⁻*	33 100	85 200	57 700	63 100	53 800	56 200
F⁻*	n.d.	1 929	1 929	n.d.	n.d.	n.d.
SO₄²⁻*	89 200	108 000	98 100	211 700	206 400	207 800
NO₃⁻*	n.d.	72 900	72 900	198 200	158 800	178 200*
Ag*	n.d.	n.d.	n.d.	0.46	0.33	0.39
Al	9 650	15 000	12 200	9 740	12 000	11 400
As*	11.84	17.17	14.40	30.60	30.00	20.20
Ba	325	598	453	221	678	559
Be*	n.d.	n.d.	n.d.	3.89	3.98	3.96
Bi*	n.d.	n.d.	n.d.	0.37	0.21	0.30
Ca	37 200	53 300	44 800	50 100	52 400	51 800
Cd	19.7	14.6	17.3	4.86	7.42	6.68
Co*	3.06	7.87	5.33	2.05	1.85	1.95
Cr	38.7	48.3	43.2	44.4	43.2	43.5
Cu	464	527	494	161	209	196
Fe	12 500	16 700	14 400	12 000	11 500	11 600
K	17 000	35 400	25 700	20 500	36 100	32 000
Li*	n.d.	n.d.	n.d.	11.4	7.29	9.53
Mg	8 350	11 900	10 000	6 830	11 600	10 400
Mn	670	766	715	457	790	703
Mo*	4.96	4.97	4.96	5.61	4.64	5.12
Na	35 000	92 100	62 000	36 300	31 300	32 600
Ni	107.4	116.1	110.1	175.9	205.7	197.9
Pb	239	277	257	270	290	285
Rb*	n.d.	n.d.	n.d.	33.8	50.0	41.9
Sb*	n.d.	n.d.	n.d.	3.45	7.20	5.44
Se*	n.d.	n.d.	n.d.	18.20	9.45	13.90
Sr	153.8	228.0	188.8	114.1	194.9	173.9
Th*	n.d.	n.d.	n.d.	0.80	1.12	0.96
Ti**	514	630	569	523	611	588
Tl*	n.d.	n.d.	n.d.	1.49	1.29	1.39
U*	n.d.	n.d.	n.d.	0.68	0.65	0.66
V	124	114	119	198	256	221
Zn	1 370	1 790	1 570	1 420	1 580	1 540

* liquid phase only; ** dust

3.1.4 Dust

The distribution of total dust (including both organic and mineral material) in 1993 was rather homogeneous throughout the investigated area (Fig. 5), although the amounts of the mineral component of dust varied considerably (Fig. 6). Anomalous mineral dust depositions occurred both in the Kymi district, e.g. in Imatra, where snow samples had been taken on cultivated fields, and near the coast. Nevertheless, the Vyborg (Viipuri) and Svetogorsk-Kamennogorsk (Enso-Antrea) areas were strongly loaded by mineral dust.

In 1994 the distribution of both the depositions of total dust and the ashed mineral component of dust varied greatly (Figs 7 and 8). The Kymi district was characterized by variation in the amounts of organic material (plant detritus) in the samples. On the other hand the amount of minerogenic material is rather even throughout the entire area. In the Karelian Isthmus there were three anomalous areas with high amounts of mineral dust: St. Petersburg and its environs, and the areas of Svetogorsk-Kamennogorsk and Vyborg-Primorsk.

3.2 Atmospheric deposition

3.2.1 Sulphate (SO_4^{2-})

The distribution patterns of atmospheric deposition of sulphate in both 1993 and 1994 are almost identical (Figs 9 and 10). High anomalies were measured during both winters in the Imatra-Svetogorsk area and around Lappeenranta and in Vyborg. In 1994, high concentrations were analysed in places in the Karelian Isthmus where the water storage was high. Scattered anomalies were found close to Primorsk and Zelenogorsk. One high anomaly near Sosnovo (Rautu) was not connected with the high water storage. Obviously, due to scant snow in the vicinity of St. Petersburg, the SO_4^{2-} depositions were low. The high SO_4^{2-} depositions found on the northern shore of the Gulf of Finland in the Kymi district could be due to transport by air from the south.

3.2.2 Chloride (Cl^-)

The distribution patterns of Cl^- were unequivocal (Figs 11 and 12). In 1993 the higher depositions were aligned to the coastline, and in 1994 moderate anomalies were found in densely populated areas such as Toksovo (Kaukolanjärvi), Vaskelovo and Zelenogorsk. In the Kymi district the weak anomalies do not have any visible connection with known emission sources, implying that Cl^- depositions are due to evaporation and transport from the open sea, as suggested by Soveri and Peltonen (1996).

3.2.3 Alkali and alkaline-earth metals (Na, K, Ca, Mg, Sr, Ba)

The distribution of Na is controlled by anthropogenic factors as well as by marine sources. In winter 1993 clear anomalies were found along the coast (Fig. 13). In 1994 the highest depositions of sodium occurred in the industrialized Imatra-Svetogorsk area, due to the soda used in production of pulp (Fig. 14). The other elements of this group occur in heavier depositions in the Karelian Isthmus than in the Kymi district; those of Ba are 2-3, those of K, Mg and Sr 1.5-2 and those of Ca up to two times higher (Figs 15 and 16). Because 70-80% of these metals occur in solution, their depositions especially those of Ca and Mg, to a lesser extent of K correlate with the water storage (see Figs 3 and 4). These elements correlate also with the amount of mineral dust in snow (see Figs 6 and 8). In winter 1993, clear anomalies were found along the coast (Fig. 13).

K, Ca and Mg do not seem to have any anthropogenic source. The behaviour of Ba differs from that of soluble alkalies or alkaline earths (Fig. 16). Very high Ba depositions, 2000-7000 $\mu g/m^2$, were met with close to the St. Petersburg megapolis presumably owing to the large glass industry in the area. In 1993 Ba anomalies were also found close to Vyborg and in the Imatra-Svetogorsk area (2600 $\mu g/m^2$).

3.2.4 Lithophile metals (Al, Fe, Mn, Ti)

Compounds of Al, Fe, Mn and Ti are not easily soluble in water, and hence they occur in snow in mineral dust (Figs 17 - 20). The mean depositions of Al, Fe and Mn in the Karelian Isthmus were 1.5 times and those of Ti 1.25 times higher than those in the Kymi district. The most conspicuous anomalies are in the Svetogorsk-Kamennogorsk area, coinciding there with the anomalous area of mineral dust in snow (Figs 6 and 8). Such correlations were also observed in the Vyborg-Primorsk area and in patches in the Kymi district.

3.2.5 Anthropogenic metals (Zn, Cu, V, Cr, Ni, Pb, Cd)

The bulk of Zn, Cu, V, Cr, Ni, Pb and Cd is emitted by anthropogenic sources. The average abundance of these metals in snow is 10-20% higher in the Karelian Isthmus than in the Kymi district (Figs 21, 22, 24, 26, 27, 29, 30, 31, 32, 34 and 35). Cadmium is an exception, possibly because of analytical discrepancies (Fig. 36). The distribution patterns of metals were rather homogeneous and similar in both winter periods.

All the above metals occur in anomalous quantities in the Imatra-Svetogorsk area. The anomalous haloes of Cu, V and Cr extend to Kamennogorsk (Figs 24, 26, 27, 29 and 30). Maximum metal concentrations both in solution and in dust are found close to Imatra and in the Primorsk area (see e.g. Figs 23, 25, 28 and 33). The coastal area around the Gulf of Finland is also characterized by increased depositions of most heavy metals (Figs 21, 22, 24, 27, 30 and 32). Besides local pollution sources in Primorsk and Vyborg, the sources of high metal depositions along the coast may be on the southeastern shore of the Gulf.

The anomalous patterns of heavy metals in St. Petersburg and its environs are heterogeneous. Driven by southwesterly winds, high V, Ni and Cd values extend north and northeastwards from the centre (Figs 27, 32 and 36). Ni and Cd occur both

in liquid and in dust form, suggesting their technogenic source. There are no distinct sources of the Pb anomalies although some of them coincide with the traffic network (Fig. 35).

Lower anomalies of some heavy metals were found in the vicinity of Hamina and Lappeenranta towns and on the western shore of Lake Ladoga. Near Lappeenranta there was a weak anomalous halo of Cu (Fig. 24) and elevated concentrations of Zn, V and Pb in dust (Figs 23, 28 and 35). Anomalies of Cu, Ni and Pb were recorded north of

Hamina (Figs 24, 32 and 35). Weak anomalies of Zn, Cu, V and Cd were found north of Priozersk (Käkisalmi) on the shore of Lake Ladoga (Figs 22, 24, 27 and 36). Being typical of emissions from the industrial areas, Imatra-Svetogorsk, Vyborg, Primorsk and Zelenogorsk, it is suggested that these metals derive from there. The above main anomalous areas are also visible on the maps of sum deposition calculated from individual distributions of the anthropogenic metals (Figs 37 and 38).

4. DISCUSSION

4.1 Quantitative estimate of atmospheric deposition

Many of the published estimates of annual sulphur and heavy metal deposition levels are based on concentrations in snow melt water and on average annual precipitation (Vasilenko et al. 1985, 1988, Krjuchkov & Makarova 1989). In the investigated region, precipitation (rainfall and snow) is 700 -750 l/m² (Solantie 1987). The ratio of airborne heavy metal deposition in summer to that in winter has not yet been studied in depth and the information available is somewhat contradictory. According to Elpatjevsky (1993), up to 70% of heavy metal fallout comes with rain (wet deposition). Reimann et al. (1995) noted that in background areas of the Kola Peninsula and adjacent territories of Finland and Norway, winter and summer depositions are similar, but near Monchegorsk deposition of the main heavy metals (e.g. Cu, Ni, Co and Cr) released in technological processes is higher in winter. It has also been noticed that SO_4^{2-} and vanadium depositions are heavier in winter than in summer (Vasilenko et al. 1988, Krjuchkov & Makarova 1989, Filov 1993).

The estimation of annual element depositions should therefore be considered as an approximation only. The results vary depending on the climatic history of winter seasons.

Analogous calculations were made in this report to compare our results with published data (Tables 8 and 9). The calculated deposition of Zn in the present study area corresponds to data from the western part of the Leningrad Region and is in good agreement with data from northern Europe. The results for southern Finland and Finnish Lapland

deviate considerably, however, from the general level presented here. The level of Pb depositions in the investigated territory corresponds to the level of background estimates available for Russia and Finland. These values are, however, much lower than those for northern Europe and the USA. Although the data on V, Ni and Cr depositions are inadequate for comparison, there is, nevertheless, some correlation between published data and the results obtained in this study.

The depositions of Cu and Cd in 1993 and 1994 differ considerably from each other. The Cd deposition in 1993 corresponds to the published data. The data on Cu have a dual character, those for 1994 corresponding to earlier data from Finland but those for 1993 correlating better with other estimates.

Airborne Pb depositions are lower in the Karelian Isthmus and southeastern Finland than in Central Europe and the USA (Table 9). For other heavy metals (Zn, Cu, Cr, Ni, V, Cd) the basic difference between the investigated territory and other regions is less pronounced. In the Karelian Isthmus the level of annual SO_4^{2-} deposition is 1-2 g/m², whilst the background value for European Russia is 1.2 g/m² a year (Vasilenko et al. 1988, Belikova et al. 1988). In the Imatra-Lappeenranta area an annual SO_4^{2-} deposition of 3 g/m² has been reported (Sorokin 1993). The results obtained here correspond to these estimates and entitle us to consider that the average level of SO_4^{2-} deposition in the investigated territory is quite normal.

Table 8. Annual atmospheric deposition of heavy metals in the study area, $mg/m^2/yr$.

		Cd	Cu	Cr	Ni	Pb	V	Zn
Background level								
Kymi district	1993	0.13	4.0	0.34	0.95	2.1	1.0	12
	1994	0.024	0.8	0.23	0.9	1.4	1.1	7
Karelian Isthmus	1993	0.12	4.6	0.43	1.05	2.5	1.5	16
	1994	0.043	1.2	0.25	1.0	1.7	1.5	9
Anomalous level*								
Average	1993	0.2-0.3	7.5-11.0	1.2	2.5-4.0	3.0-4.5	4.0-8.0	30-50
	1994	0.15-0.25	2.0-3.0	1.2	2.5-4.0	3.0-4.5	4.0-8.0	15-20
Maximum	1993	0.5-1.5	15-25	2.5-4.0	7-10	10-15	15-25	50-70
	1994	0.5-1.5	15-25	2.5-4.0	7-10	10-15	15-22	25-35

* Computed in anomalous areas

Table 9. Annual atmospheric deposition of heavy metals in various areas, $mg/m^2/yr$.

	Cd	Cu	Cr	Ni	Pb	V	Zn
Southern Finland (1)	0.079	0.71	0.07	-	1.75	-	2.9
Northern Finland (1)	0.031	0.74-3.2	0.03-0.36	-	0.35-1.3	-	0.64-4.5
Leningrad, West * (2)	0.1-0.15	2-4	-	1-1.5	2-4	1	15
Russia, European (3)	0.2-0.5	--	-	1.5-4	-	-	
All Russia (7)	-	--	1.5	-	-	-	
Kola Peninsula (8)	-	6-20	-	5-30	-	-	-
Continental Europe (4,5)	0.2-0.5	1.8-4	0.8-2.2	1-3.4	10-26	1.2	18-55
USA (4, 5, 6)	0.68-2.1	3.7	-	-	17-40	-	47-54
St. Petersburg, Kirovsky industrial area (2)	0.4-0.8	30-40	8-15	10-15	40-120	20-50	100-250

* Southwestern part of the Leningrad Region to the Russian-Estonian border

1. Juntto 1992, 2.Yakhnin et al. (unpublished data, 1992-1994), 3. Rovinsky et al. 1988, 4. Kabata-Pendias & Pendias 1980, 5 Elpatievsky 1993, 6. Smith 1988, 7. Anon 1988, 8. Krjuchkov & Makarova 1989.

4.2 Main anomalous multielement zones

The conditions of snow cover formation vary from winter to winter and in the same region within one winter period. In the vicinity of St. Petersburg the water storage in 1994 was equal to 30 - 60 l/m^2 but in the vicinity of Zelenogorsk it exceeded 200 l/m^2. The value of metal deposition within a season depends on the water storage. Hence, it would be incorrect to compare the different anomalous zones on the basis of the value of a season's metal deposition within the limits of a particular zone. Therefore, here are used the ratios of metal depositions in the anomalous zone to depositions in the background areas with the same value of water storage (Table 10). The following examines the most striking anomalous areas.

4.2.1 Imatra-Svetogorsk-Kamennogorsk area.

The Imatra-Svetogorsk-Kamennogorsk area, which straddles the international border, is characterized by the maximum depositions of Fe, Mn, Zn, V, Cr and Ni (Figs 17 - 32). In both 1993 and 1994 the anomalous deposition levels exceeded the average background level by 3-4 times in this area (Table 10). The annual SO_4^{2-}, Ba, Cu, Pb and Cd depositions were also anomalously high and the average level was 2-3 times the background level (Table 10). The strongest anomalies of SO_4^{2-}, Ba, Fe, V and Cd were found near Svetogorsk and those of Mn and Zn near Imatra. The anomalous area measures ca 50 km from west to east and approxi-

Table 10. Ratios of annual depositions in anomalous zones A-E to annual background values.

	Year	A*	B*	C*	D*	E*
SO_4^{2-}	1993	2.1	1.6	1.3	-	-
	1994	1.8	1.1	1	1.3	0.7
Ba	1993	4	4.5	2.2	-	-
	1994	2.3	2	3.3	1.9	9
Cd	1993	1	1.8	2.3	-	-
	1994	2.5	3	6.5	1.5	1.5
Cr	1993	4.5	3	2.3	-	-
	1994	4	2	4	1.5	3
Cu	1993	1.8	1.9	2.6	-	-
	1994	2	2.5	2	2	2
Fe	1993	3.8	1.9	2.6	-	-
	1994	4.7	4	1.7	1.7	5
Mn	1993	3.5	2	1.4	-	-
	1994	3	1.6	1.8	1.6	3
Ni	1993	3.2	1.7	1.5	-	-
	1994	4	2	3	2	4
Pb	1993	2	1.6	1	-	-
	1994	2	2.4	1	2.8	2
V	1993	3.8	2.8	1.8	-	-
	1994	4.2	3.2	2.5	1.4	7
Zn	1993	3.5	2	3.2	-	-
	1994	2.5	1.5	1.8	2	1.5

*
A - Imatra-Svetogorsk (Enso)-Kamennogorsk (Antrea)
B - Vyborg (Viipuri)
C - Primorsk (Koivisto)
D - Zelenogorsk-Iljichevo (Terijoki- Jalkala)
E - St. Petersburg (Pietari)

mately the same from north to south. The northern end of this area in the Kymi district extends beyond the border of the investigated territory. The haloes of SO_4^{2-} and some heavy metals (Zn, Cu, V, Cd) reach the shore of Lake Ladoga (Figs 10, 22, 24, 27 and 36). The maximum values of annual deposition were 70 mg/m^2 for Zn, 25 mg/m^2 for V, 20 mg/m^2 for Cu, 10-15 mg/m^2 for Pb, and 10 mg/m^2 for Ni.

4.2.2 Vyborg area

The anomaly in the Vyborg area is local in character. The emissions are heaviest along the main roads from Vyborg to St. Petersburg and to Finland (Vaalimaa, Torfjanovka). Most industry and traffic are concentrated in the same zone. Annual depositions of Ba and V were 3-4 times higher and those of heavy metals 1.5-2.5 times higher than the average background levels (Table 10).

4.2.3 Primorsk area

The Primorsk area is characterized by relatively high Ba and heavy metal (Zn, Cu, V, Cr, Ni, Cd) depositions (Figs 16, 21, 22, 24, 27, 30, 32 and 36) and lower Fe and Mn. The maximum Cd depositions were found within the Primorsk area. The annual depositions of heavy metals except Fe and Mn were about twice the background level. The anomalous zone extends for 20-30 km along the coast of the Gulf of Vyborg and for 30-40 km inland on the Karelian Isthmus. The maximum values of annual deposition were up to 70 mg/m^2 for Zn, 25 mg/m^2 for Cu, and 0.44-0.75 mg/m^2 for Cd.

4.2.4 Zelenogorsk-Iljichevo area

The Zelenogorsk-Iljichevo area is characterized by high Zn, Ni and Cd depositions (Figs 22, 32 and

36). The anomalous annual depositions exceed the background level measured in the environment by 1.5-2.0 times (Table 10). Annual SO_4^{2-}, Fe and Mn depositions were lower here than in the other anomalous zones, and depositions were up to 1.7 times the background level. The Zelenogorsk-Iljichevo anomalous area stretches for about 20 km along the coast of the Gulf of Finland and for 25-30 km into the interior of the Karelian Isthmus. The patterns of the highest Pb anomalies coincide main roads in the area (Fig. 35). The maximum level of annual Pb fallout was up to 10 mg/m², that is, 2.5-3 times the average level.

4.2.5 St. Petersburg area

The St. Petersburg area was characterized by high Ba, V, and Ni depositions (Figs 16, 27, and 32). The annual Ba and V depositions were 7-9 times, and those of Ni about 4 times the average background levels (Table 10). The maximum annual deposition calculated for Ba was 35-50 mg/m² and for Ni 10 mg/m².

The Toksovo-Vaskelovo area north of St. Petersburg was characterized by increased depositions of all metals. In addition, the Sosnovo (Rautu)-Michurinskoe (Valkjärvi)-Kirillovskoe (Perkjärvi) zone in the central part of the Karelian Isthmus is worth mentioning, as there the average annual SO_4^{2-} deposition was about 2.4 g/m² and so twice as high as the background level (Fig.10).

4.3 Influence of atmospheric deposition on ground ecosystems

Most atmospheric fallout is retained in humus, and hence forest soils with a podzol profile rich in organic material are more sensitive to heavy metal contamination than are other soil types (Niskavaara et al. 1996, Reimann et al. 1997). On the basis of the average element contents of the Earth and the general information available on different bulk densities (g/cm³) of soils, typical concentrations of metals in the topmost layer (5 cm) of forest soils in the Karelian Isthmus are on average 1400-2000 mg/m² for Zn, 700-1000 mg/m² for V, 500-700 mg/m² for Cu and Cr, 400-600 mg/m² for Ni and Pb, and 10-15 mg/m² for Cd.

Comparison with the data in Table 8 shows that in background areas the influence of airborne metals on their total contents in soil is low. Hundreds of years would be required to double the normal reserve of metals. In the anomalous zones depicted in this study this period might be 3-10 times shorter, which would imply a doubling time of some tens of years. In these cases, the aerial deposition of metals would make an essential contribution to the contamination of forest soils.

The same conclusion holds for forest vegetation. Pine-needles and ground mosses are more sensitive to aerial contamination than is the soil surface. Based on an average dry weight of 0.35-0.4 kg/m² for moss in the Karelian Isthmus (Gol´tsova & Pitulko (1996)), the following estimates are obtained for reserves of metals: 10-20 mg/m² for Zn, 2-3 mg/m² for Cu and Pb and 1.5-2 mg/m² for Ni, Cr and V. According to Rühling et al. (1992), mosses can retain up to 80% of aerial deposition of heavy metals. During an exposure period of 3-5 years the heavy metal contents of mosses would therefore be increased several times over (Gol´tsova & Vasina 1992).

In the Karelian Isthmus a clear correlation was found between the distribution of heavy metals in soils and vegetation (mosses, pine needles) and the aereal pattern of airborne deposition (Yakhnin et al. 1997). This is particularly striking in the zone around St. Petersburg, and in the vicinity of Vyborg and Svetogorsk-Kamennogorsk, where the anomalies in both soils and mosses seem to cross the international border and continue westwards in the direction of Imatra. In the area between St. Petersburg and Vyborg the Pb haloes have similar distribution patterns both in ground ecosystems and in snow. Metal contamination (V, Ni, Zn) of pine needles and mosses, but not of soils, has been reported from the Primorsk area and the coast of Lake Ladoga (Gol´tsova & Vasina, 1992; Yakhnin et al. 1997). It is possible that airborne deposition has not yet lasted sufficiently long nor reached a high enough level to cause any detectable contamination of soils.

The characteristics of airborne mineral and organic dust and its impact on the environment can be evaluated by comparing the element composition of dust with that of soil. The ratios of the element concentrations in snow dust to the average concentrations in underlying soil in the Leningrad Region (Yakhnin et al. 1997) are shown in Table 11.

Dust is enriched in Pb, Cd, Zn, Cu, Ni and V compared with the background values in soil (ratio >1) but depleted in Cr, Mn, Ba, Sr (ratio < 1). Similar results were reported by Saet et al. (1990).

Table 11. Ratios of element concentrations in snow dust to those in underlying soil in Leningrad Region.

Element	Ratio of element concentration in total dust/background concentration in soil	Ratio of element concentration in mineral dust/background concentration in soil
Pb, (Cd)	5-7	10-20
Zn, Cu	3-4	8-12
Ni	1-3.5	2-10
V	0.5-1.3	1-3.8
Cr	0.8	1.6-2
Mn, Ba	0.3-0.5	0.7-1.2
Sr	0.15-0.2	0.25-0.6

5. CONCLUSIONS

The geochemical data of snow derived from the investigated territory revealed consistent areal atmospheric deposition patterns. The main areas of atmospheric pollution, hunreds of square kilometres in extent, lie around the St. Petersburg megapolis and the Imatra-Svetogorsk industrial area, which straddles the Finnish-Russian border. Anomalies of the anthropogenic heavy metals were found up to 30-50 km from the sources, and extended to the shore of Lake Ladoga with diminishing contaminant concentrations. The Vyborg and Primorsk areas were also characterized by large local anomalies.

The long-distance atmospheric transportation of heavy metals across the Gulf of Finland is of minor significance in the depositions of the investigated region. Aerial depositions in the Karelian Isthmus and in the Kymi district are of approximately the same order of magnitude for heavy metals. The same applies to sulphur. In the investigated territory the average levels of aerial SO_4^{2-} and Pb deposition are lower than those in Central Europe. There are, however, no marked differences in the depositions of other heavy metals.

The airborne dust in snow is enriched in Pb, Cd, Zn, Ni and V compared with the background values in soil (ratio >1) but the concentrations of Cr, Mn, Ba, Sr are lower (ratio < 1). The industrial area of Imatra-Svetogorsk area represents a coherent transborder zone of environmental contamination. Industrial plants are the main source of heavy metals into air. The strongest anomalies of SO_4^{2-}, Ba, Fe, V and Cd were found near Svetogorsk and those of Mn and Zn near Imatra.

The airborne deposition of heavy metals in the anomalous areas contaminates soils and, particularly, forest vegetation. This was verified in the Karelian Isthmus, where a marked similarity was found between the areal distribution of metal depositions and contamination of ground ecosystems. More detailed and systematic observations are, however, required before the influence of individual industrial plants and metals on the environment can be assessed.

The problem of the transfer of contaminants across the Finnish-Russian border is a real one in the Imatra-Svetogorsk area. Other anomalous areas investigated are of local character only. Long-distance SO_4^{2-} pollution has also been reported on the north coast of the Gulf of Finland.

A joint project on the complex monitoring of the environment in the Imatra-Svetogorsk area would be the most reasonable way in which to continue this study. The establishing of 10-15 stationary sampling sites on both sides of the international border for monitoring elemental variations in the snow, soil, vegetation, surface water and groundwater could provide a good basis for the project. This should be done by taking into account the existing monitoring installations and research plans in collaboration with the respective organizations working in the area. By carrying out that research in a uniform, methodical way it would be able to investigate cross-border contamination transfer and its influence on the environment and socioeconomic consequences.

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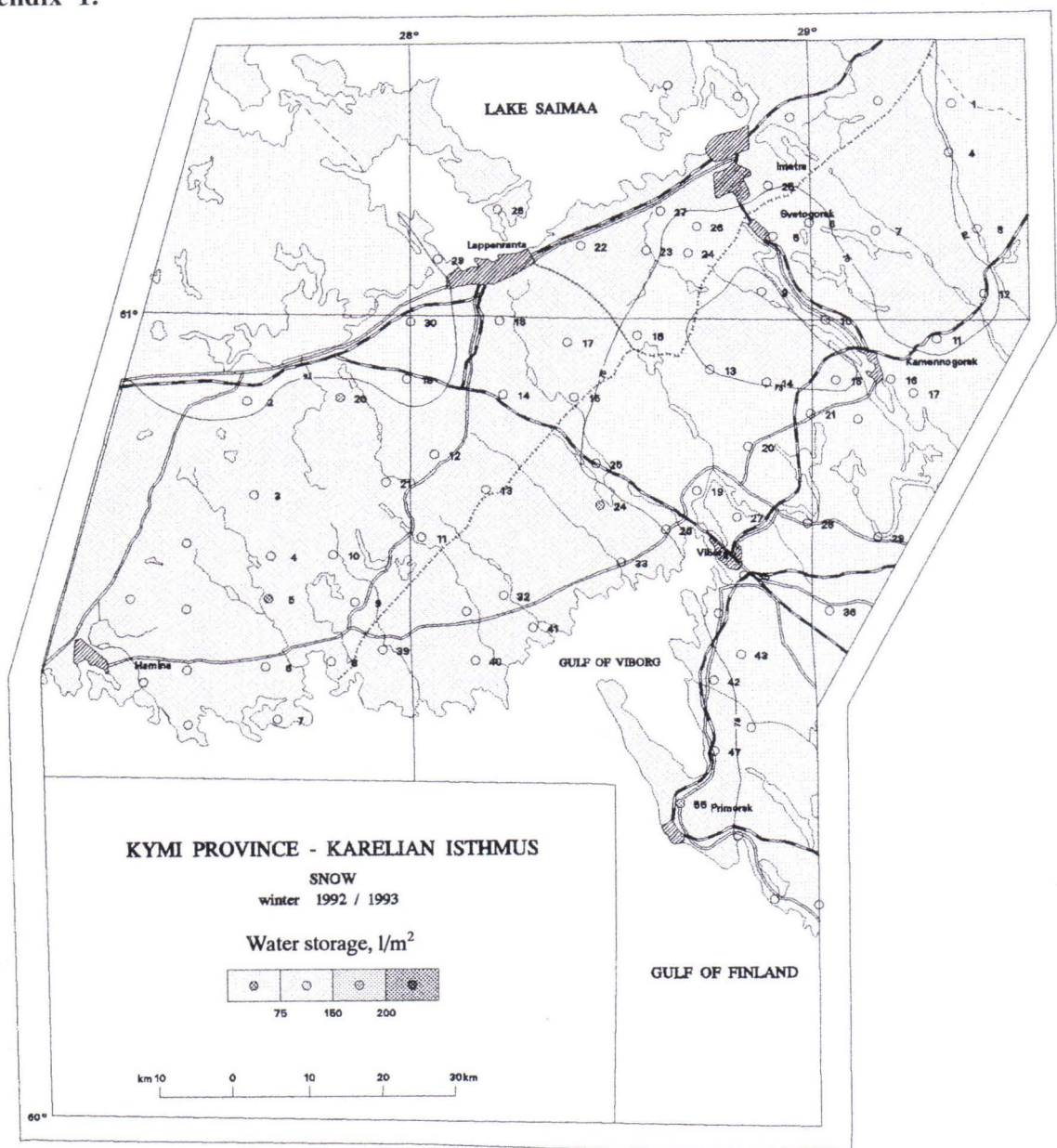
Appendix 1.

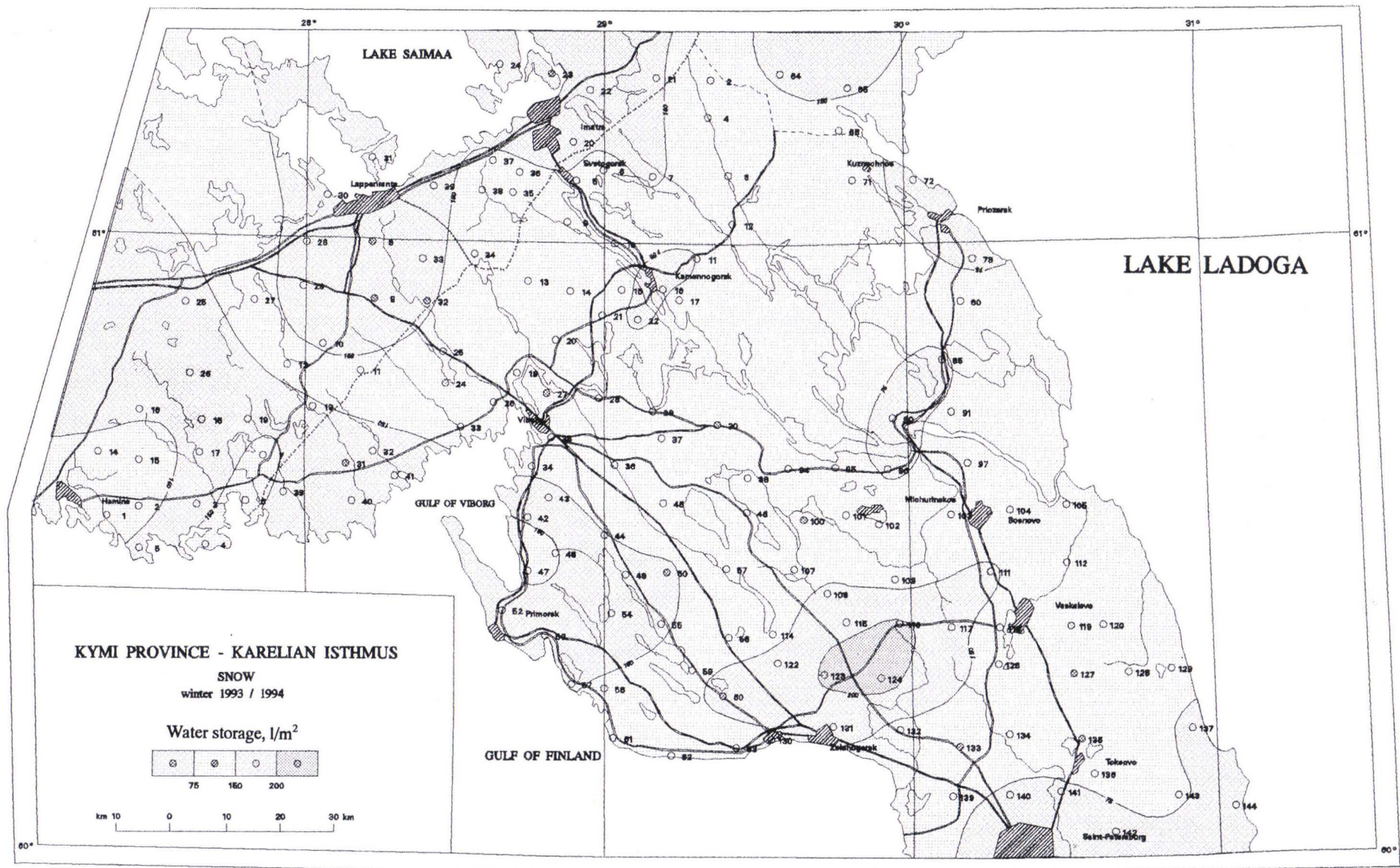Fig. 3. Water storage of snow in winter 1992/1993.

Fig. 4. Water storage of snow in winter 1993/1994.

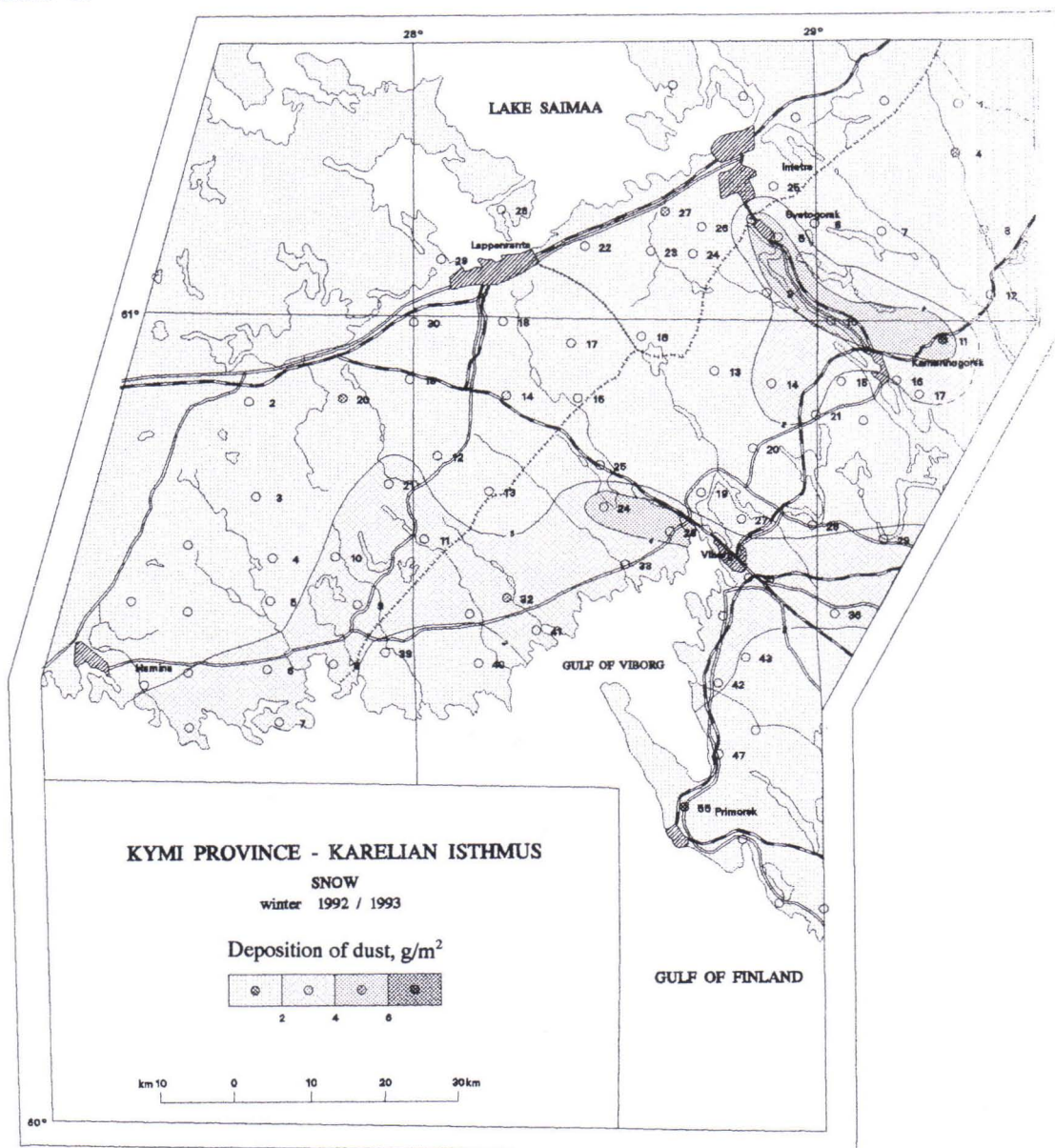Geologian tutkimuskeskus, Tutkimusraportti — *Geological Survey of Finland, Report of Investigation 139, 1997*
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Appendix 1.

Fig. 5. Deposition of total unashed dust (organic and mineral residue) in winter 1992/1993.

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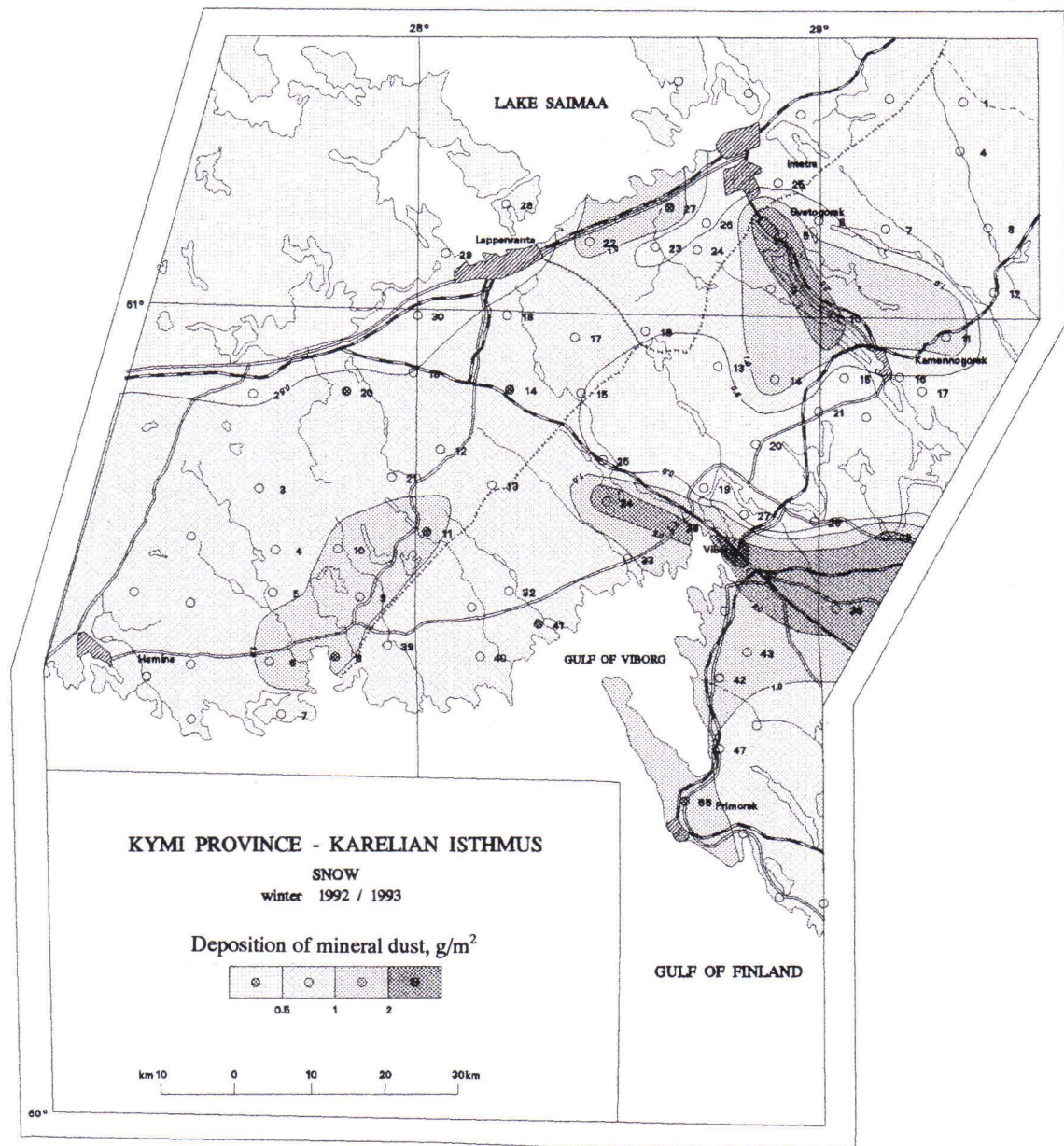
Appendix 1.

Fig. 6. Deposition of mineral dust (ashed residue) in winter 1992/1993.
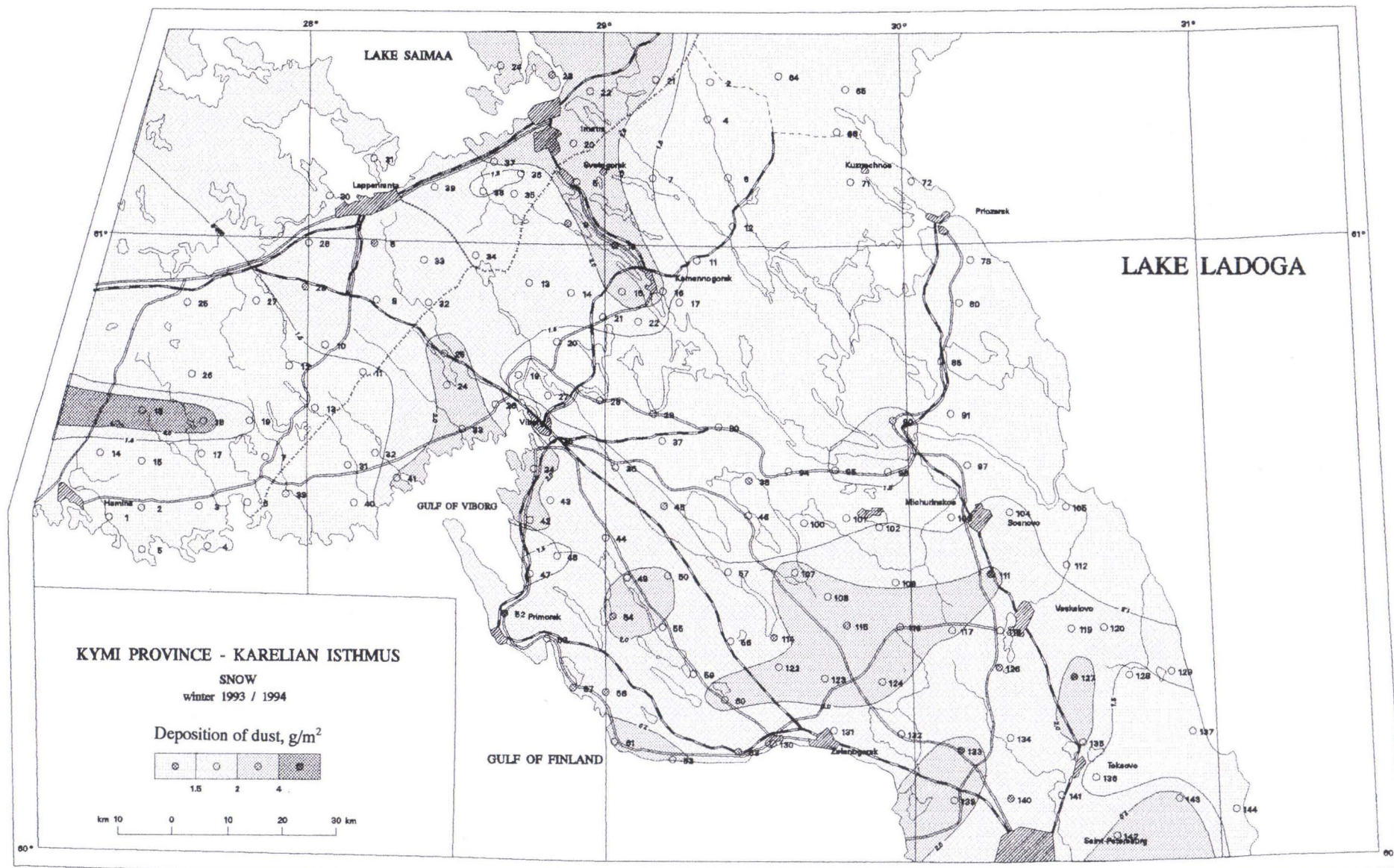
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Fig. 7. Deposition of total unashed dust (organic and mineral residue) in winter 1993/1994.

Fig. 8. Deposition of mineral dust (ashed residue) in winter 1993/1994.

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KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

Winter 1993 / 1994

Deposition of mineral dust, g/m²

0.5   1   2

km 10   0   10   20   30 km

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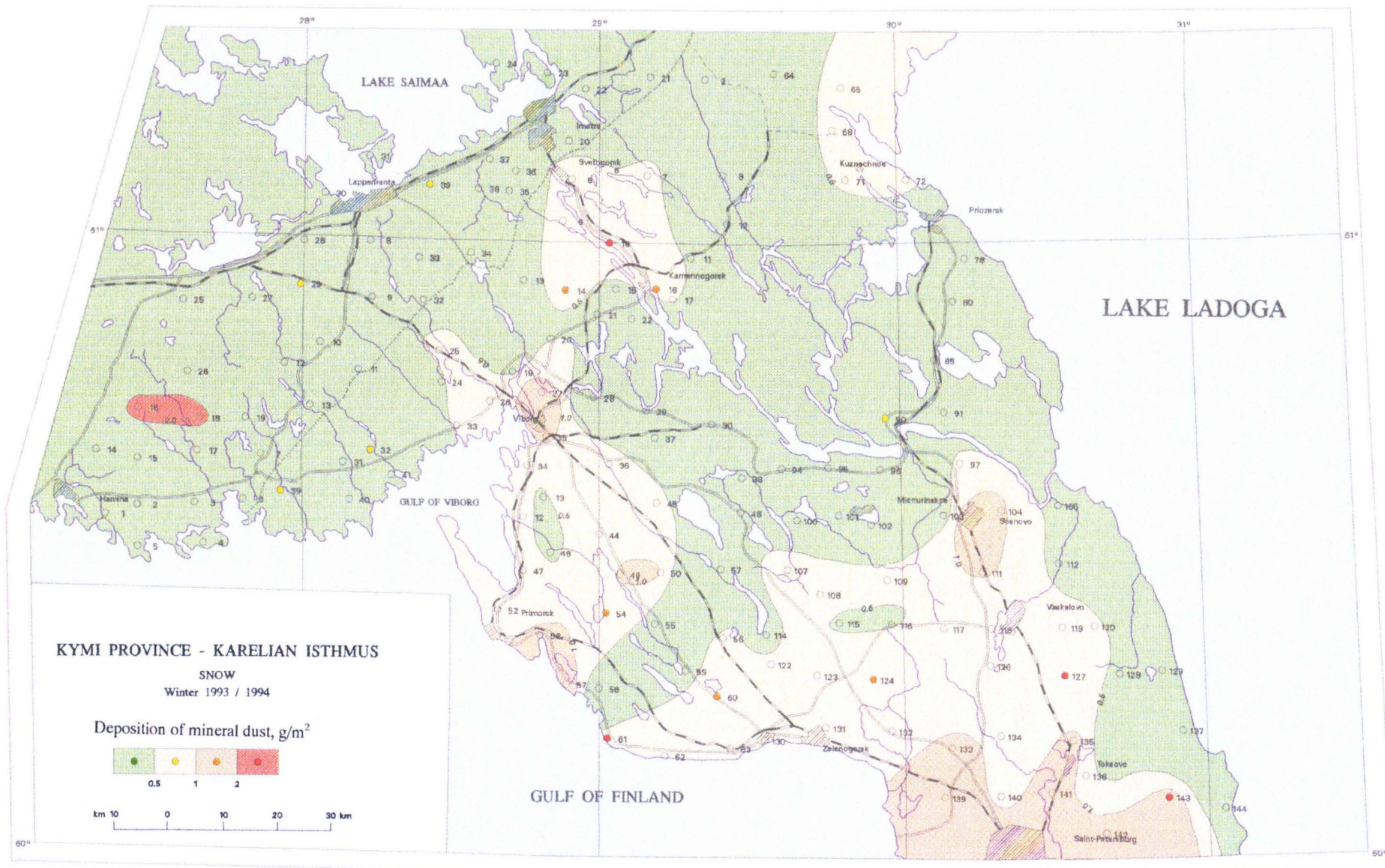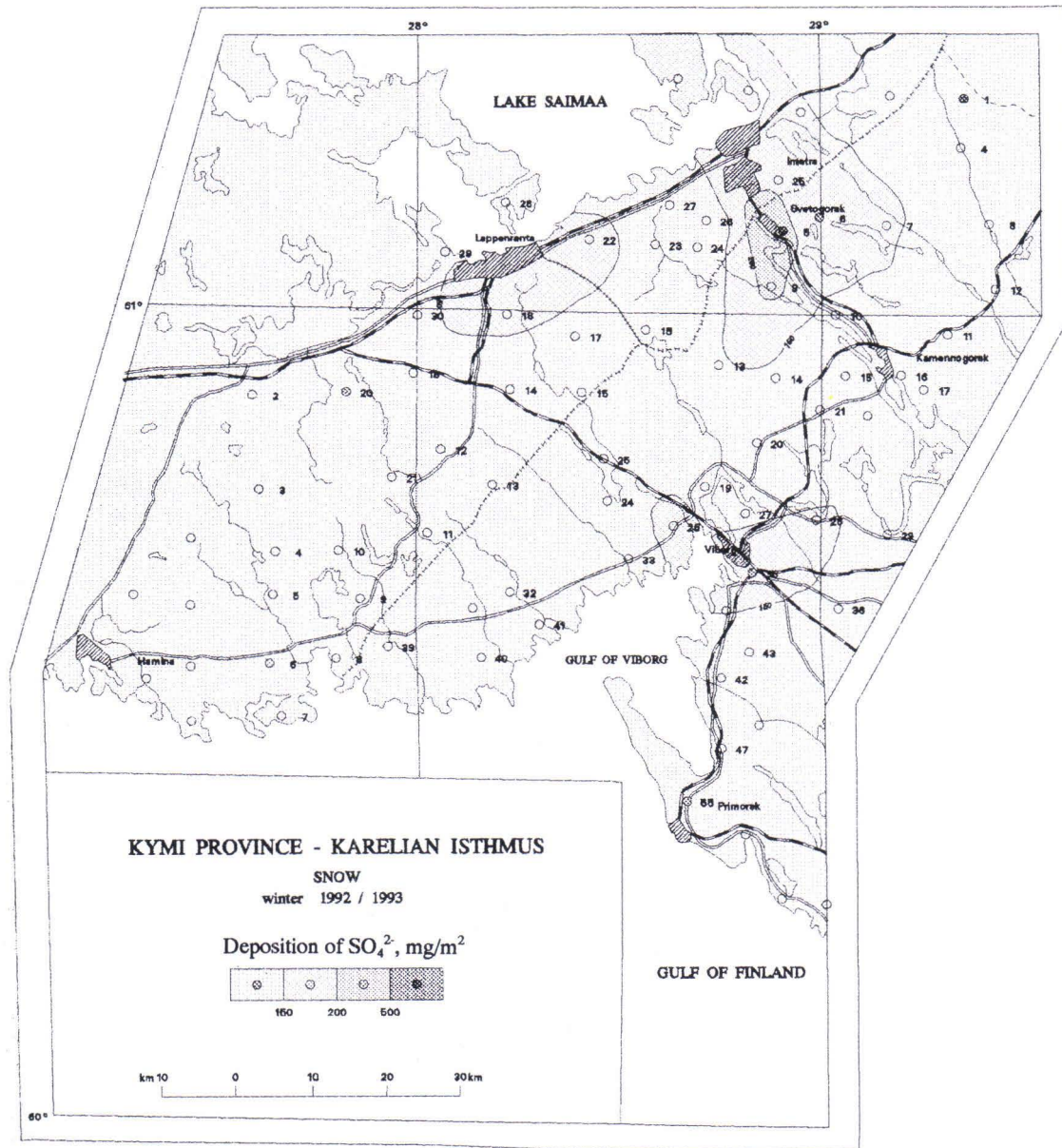
Appendix 1.

Fig. 9. Deposition of sulphate in winter 1992/1993
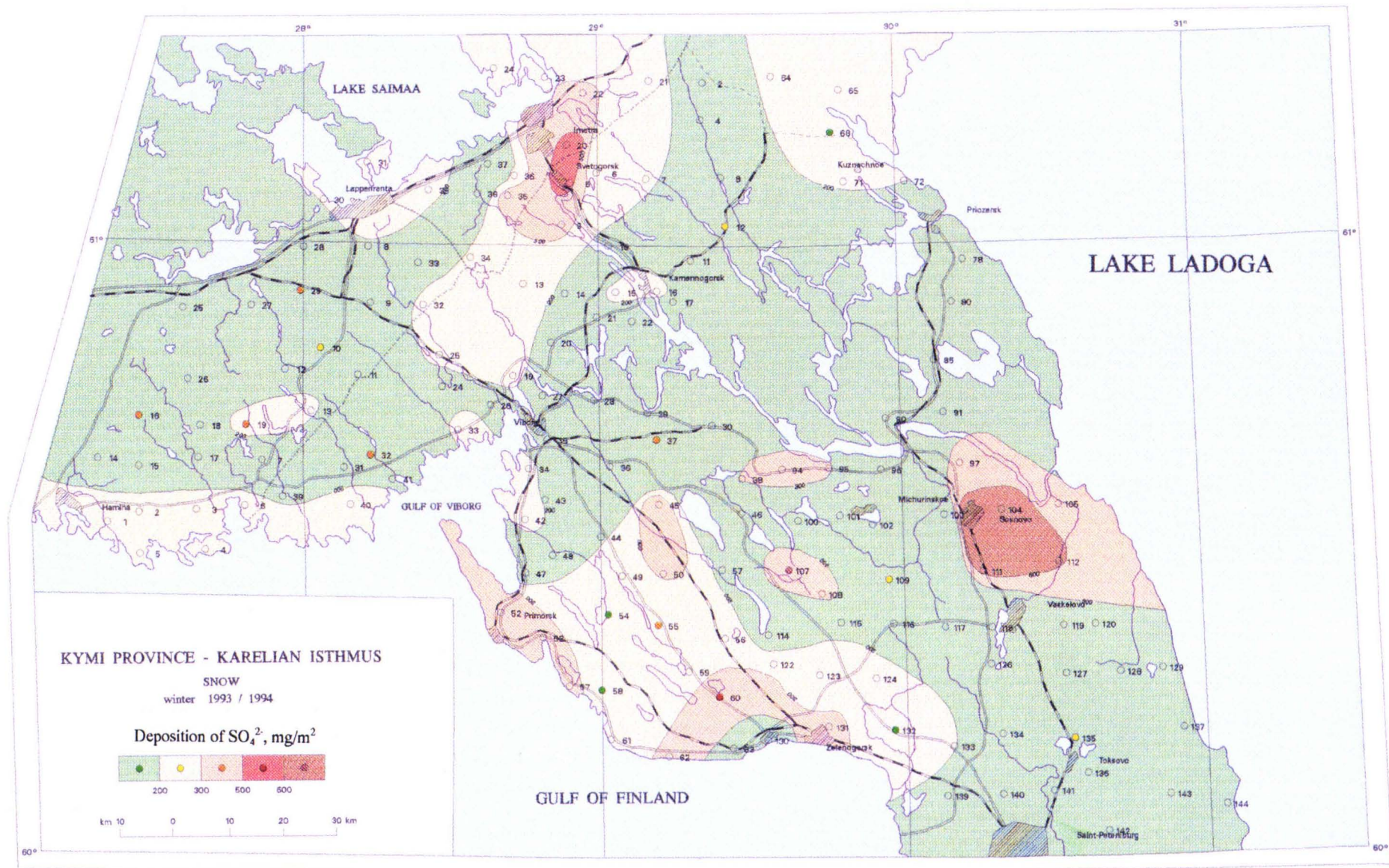
Fig. 10. Deposition of sulphate in winter 1993/1994.

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW
winter 1993 / 1994

Deposition of SO_4^{2-}, mg/m^2

200   300   500   500

km 10   0   10   20   30 km

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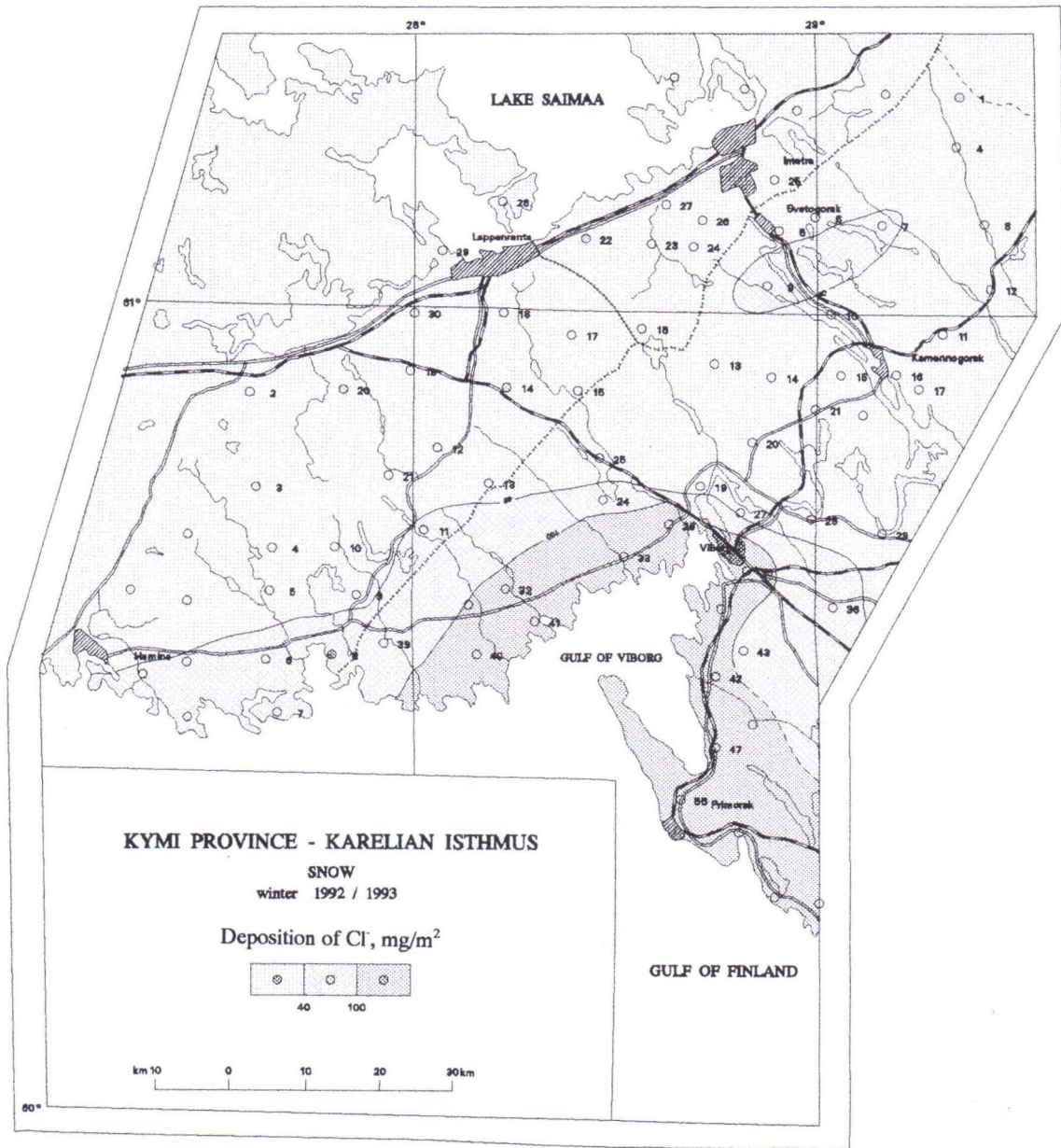
Appendix 1.

Fig. 11. Deposition of chloride in winter 1992/1993.
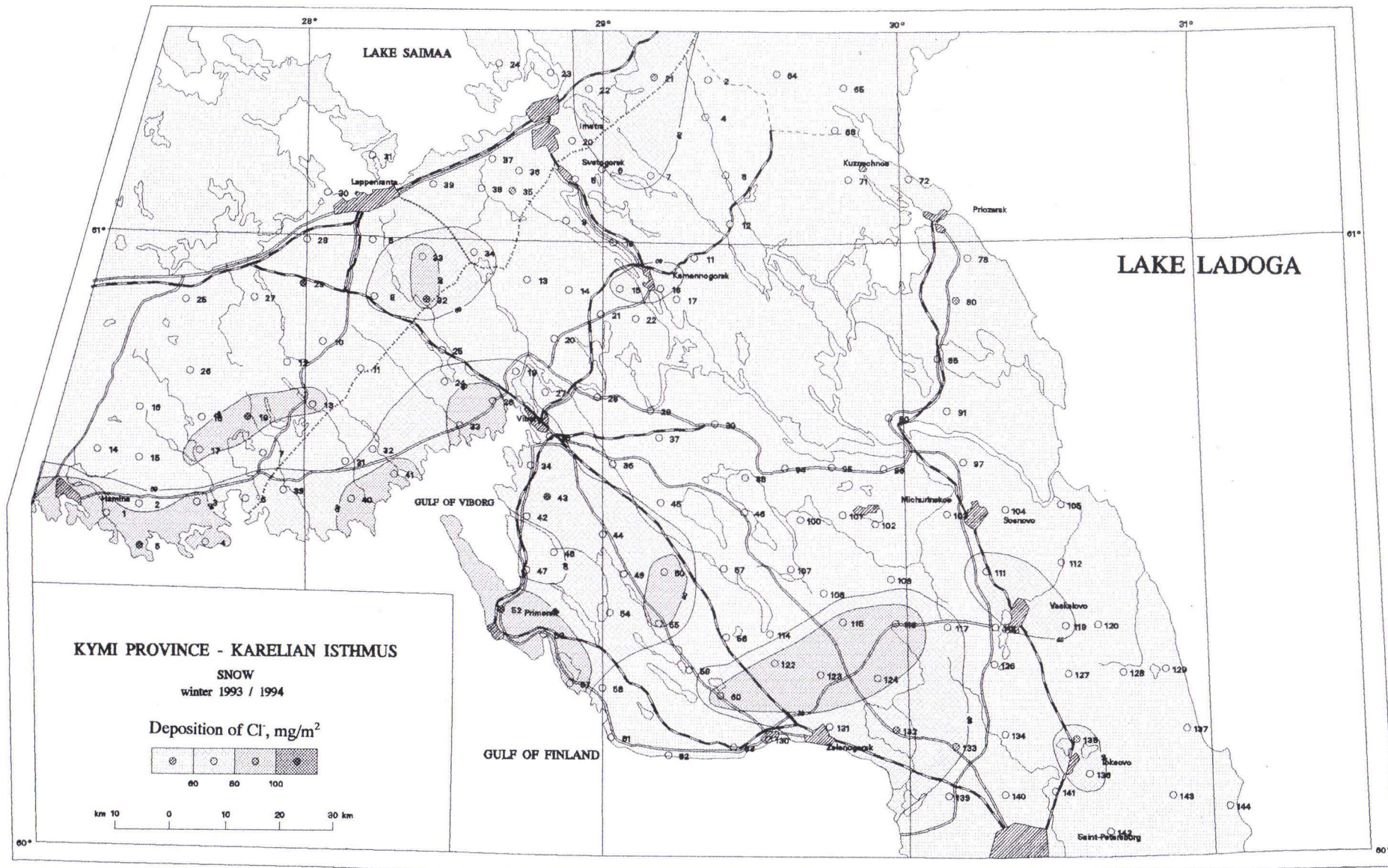
Fig. 12. Deposition of chloride in winter 1993/1994.

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KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Deposition of Cl⁻, mg/m²

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Appendix 1.

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1992 / 1993

Deposition of Na, mg/m^2

50   100   200

km 10   0   10   20   30km

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Fig. 13. Deposition of sodium in winter 1992/1993.

Fig. 14. Deposition of sodium in winter 1993/1994.

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Deposition of Na, mg/m²

30   50   100   200

km 10   0   10   20   30 km
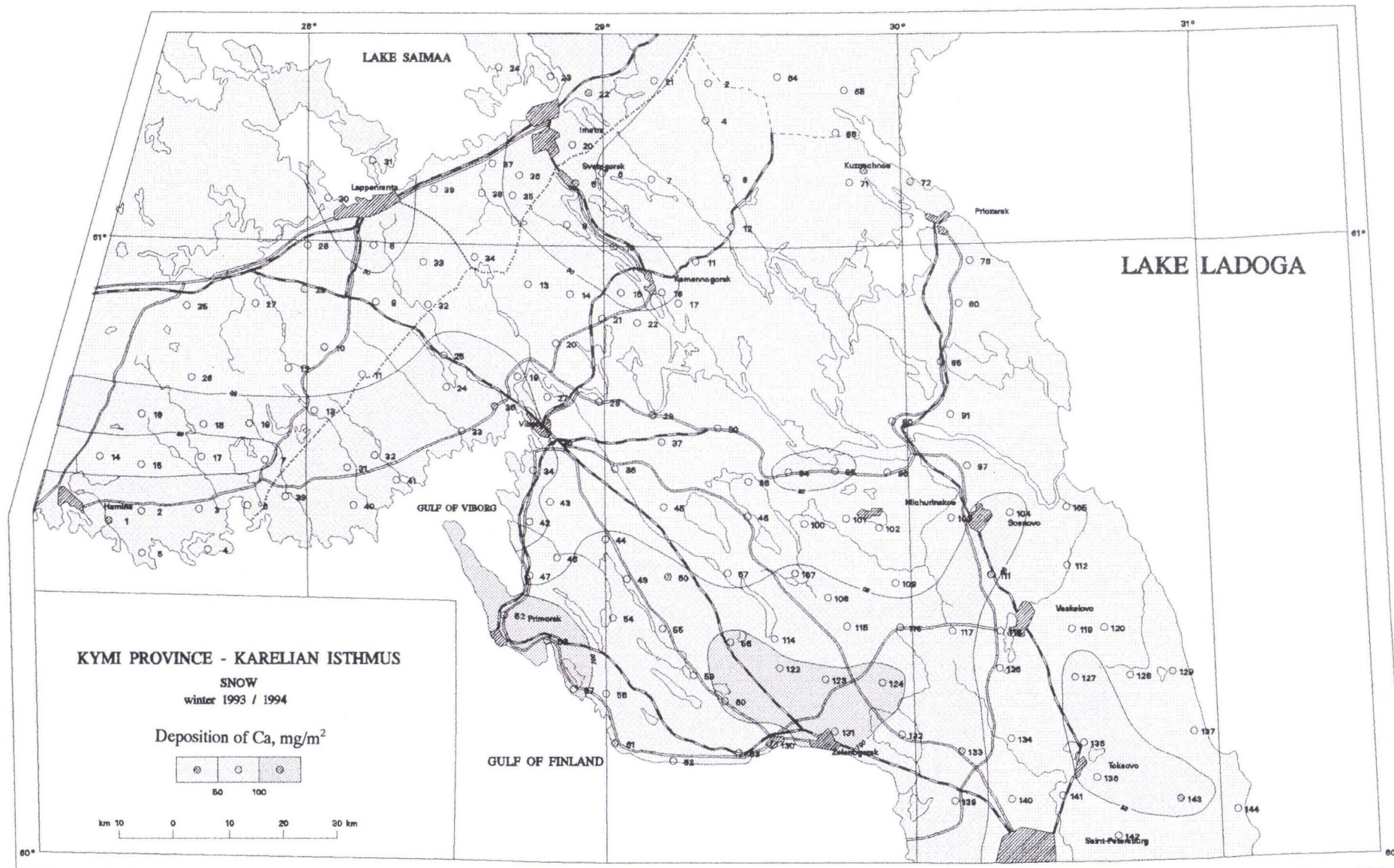
Appendix 1.

Fig. 15. Deposition of calcium in winter 1993/1994.
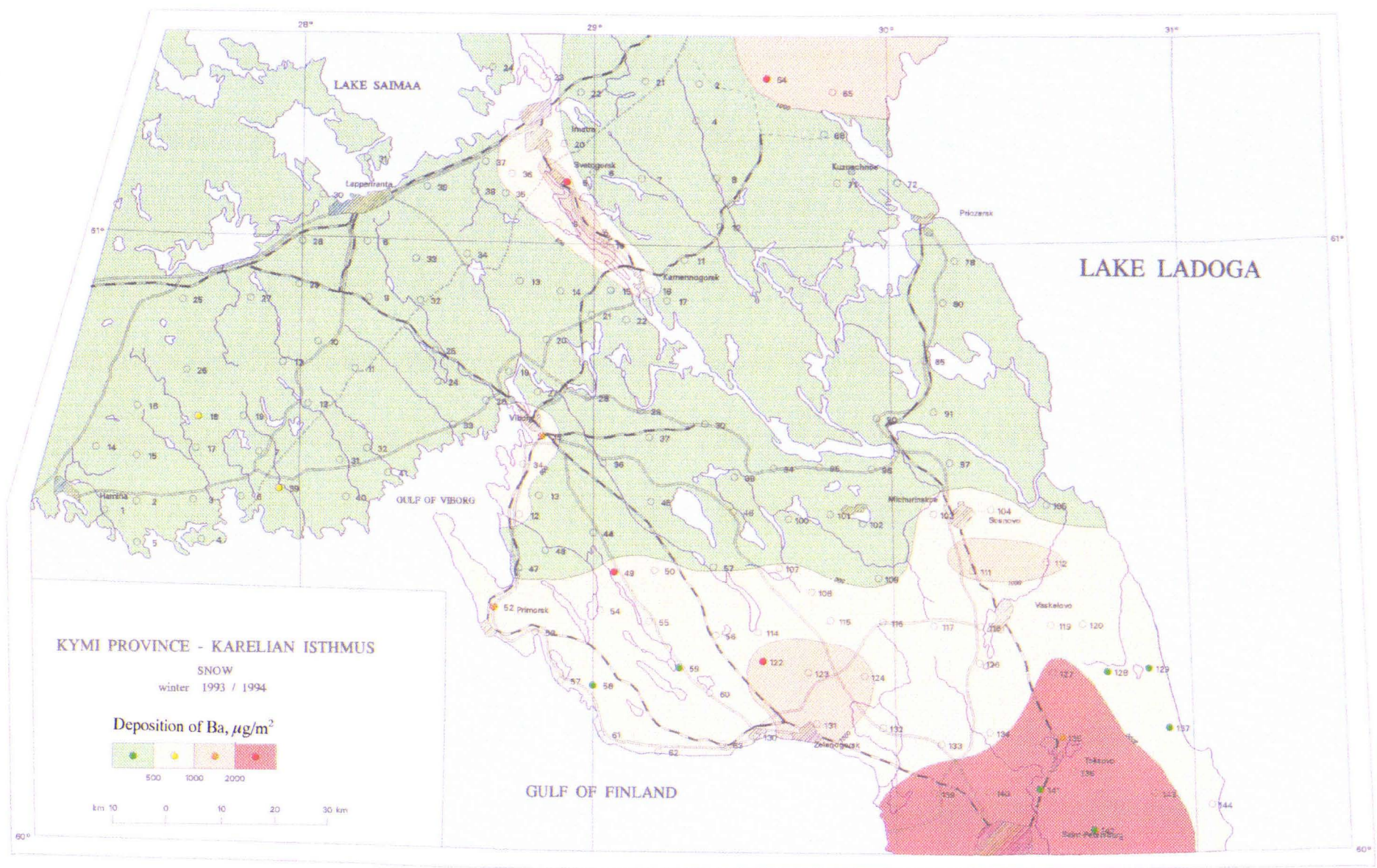
Fig. 16. Deposition of barium in winter 1993/1994.
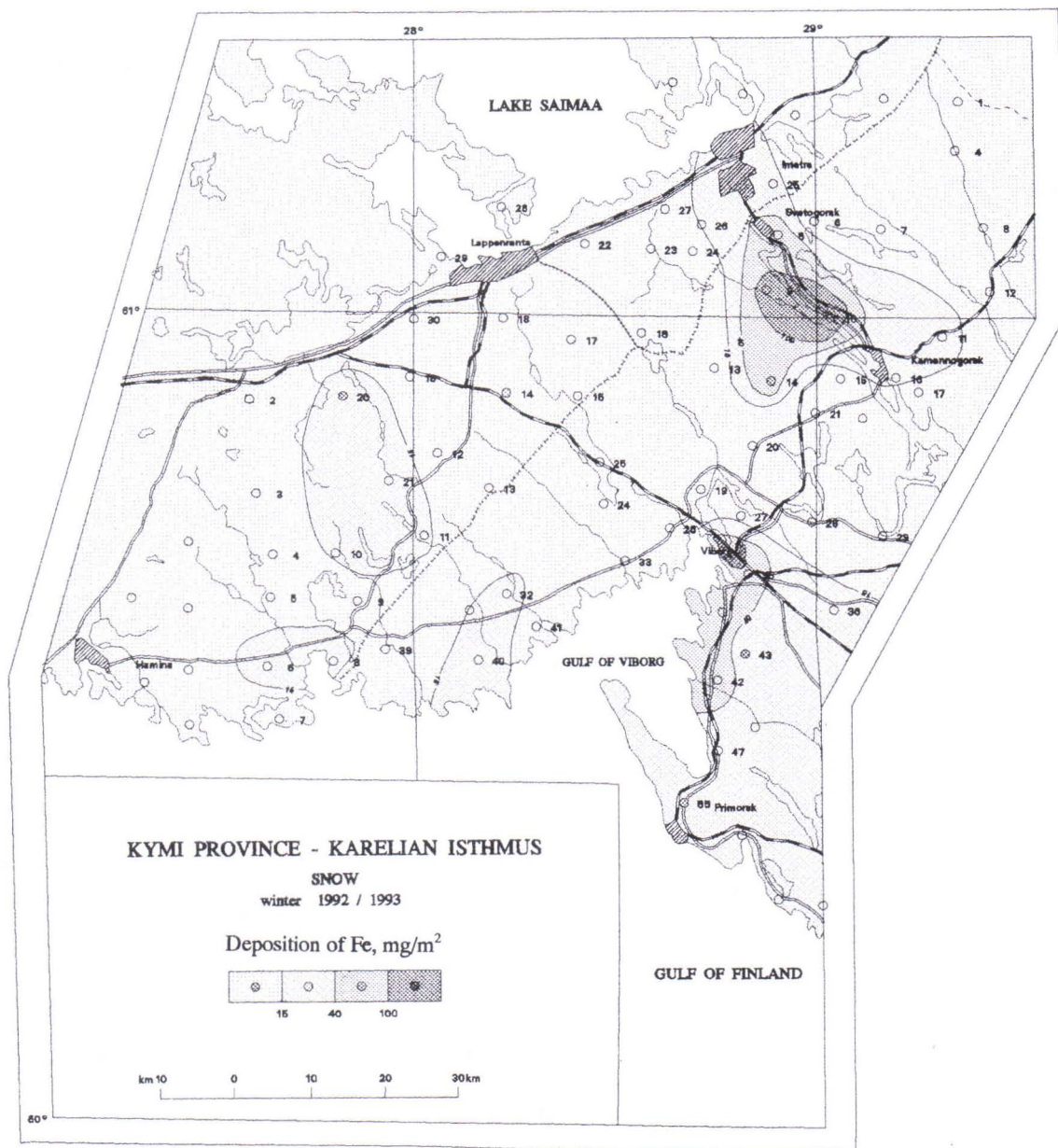
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Fig. 17. Deposition of iron in winter 1992/1993.
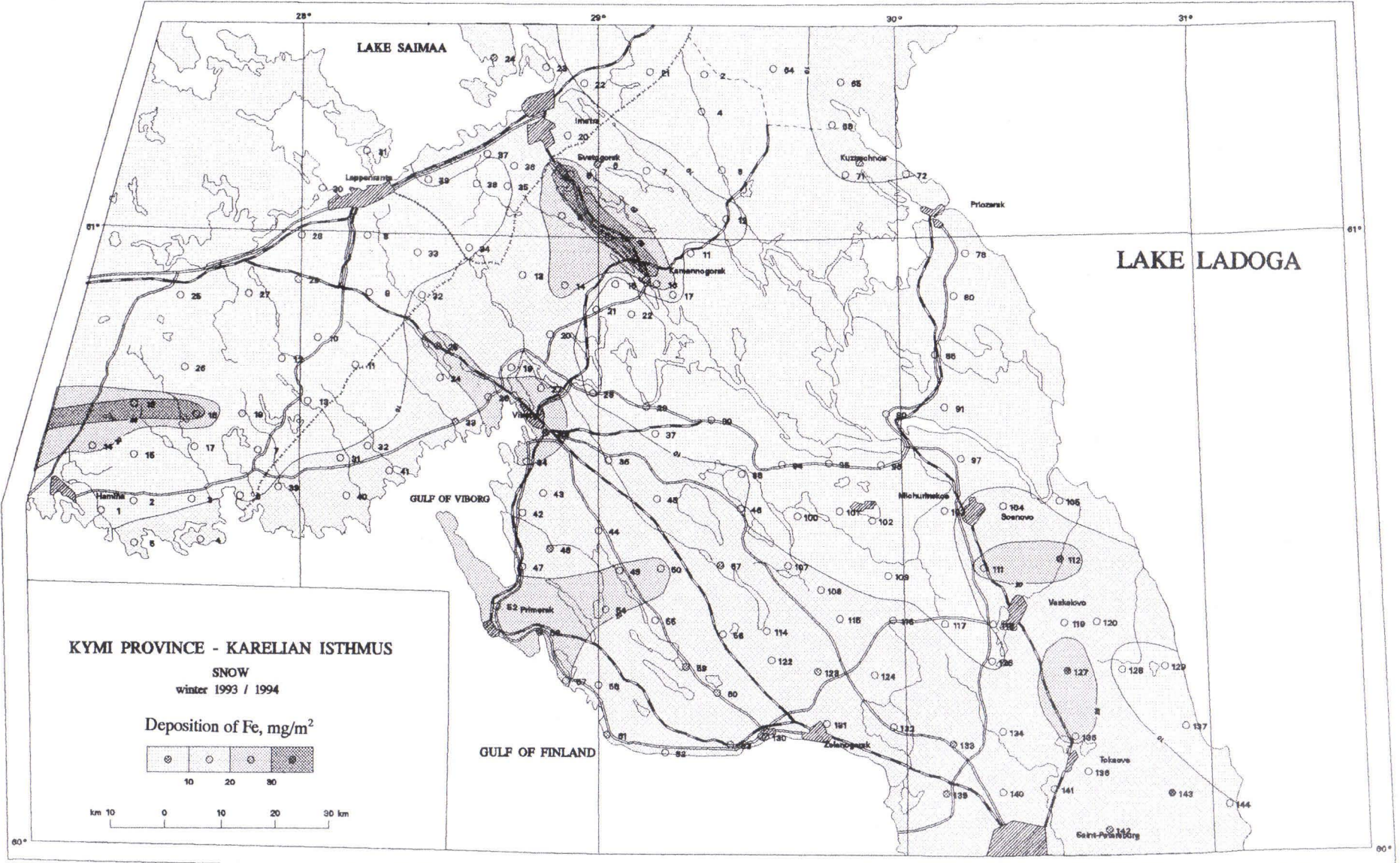
Fig. 18. Deposition of iron in winter 1993/1994.
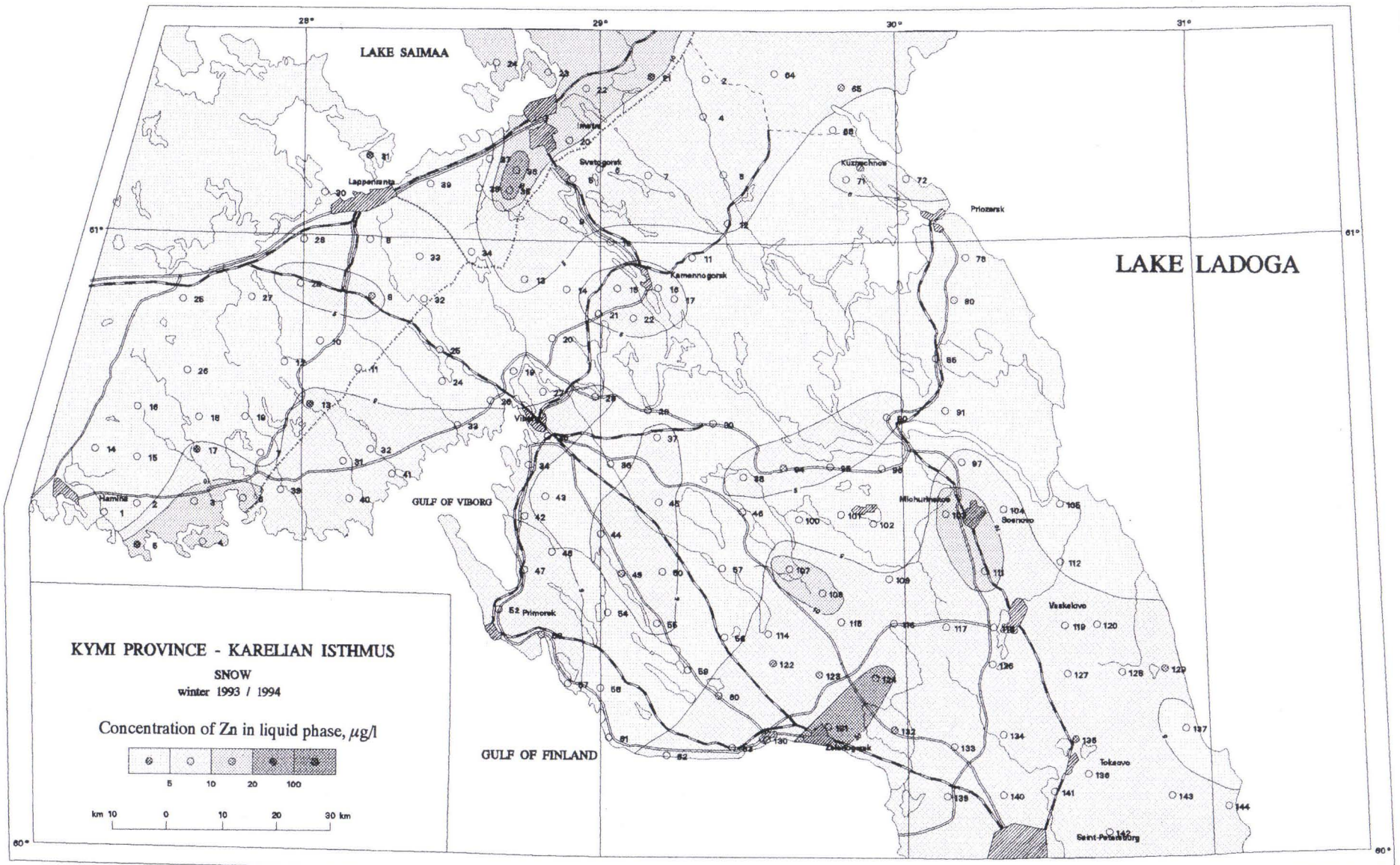
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Appendix 1.

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SNOW

winter 1993 / 1994

Deposition of Mn, $\mu g/m^2$

500   1500   3000

km 10   0   10   20   30 km

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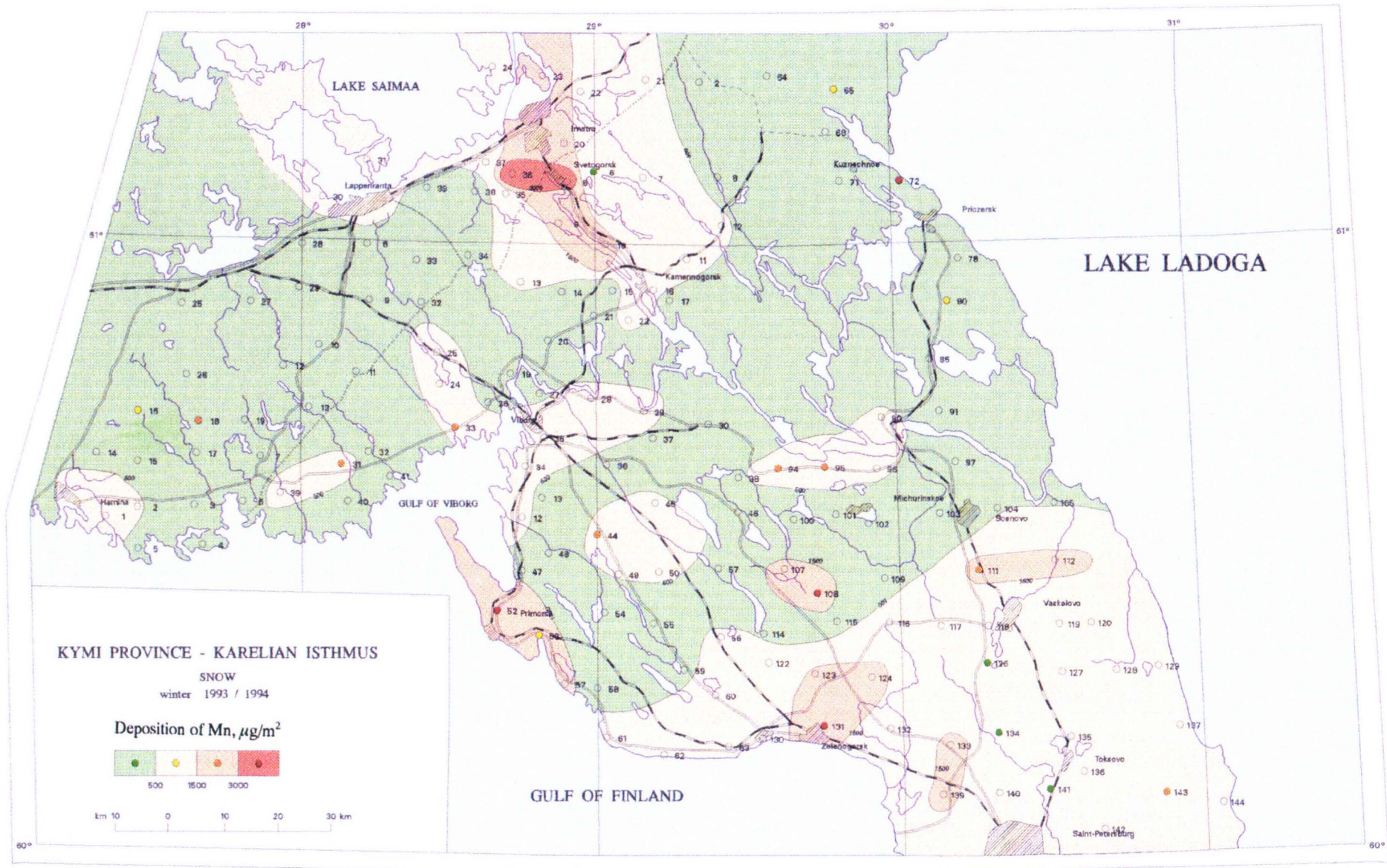
Fig. 19. Deposition of manganese in winter 1993/1994.

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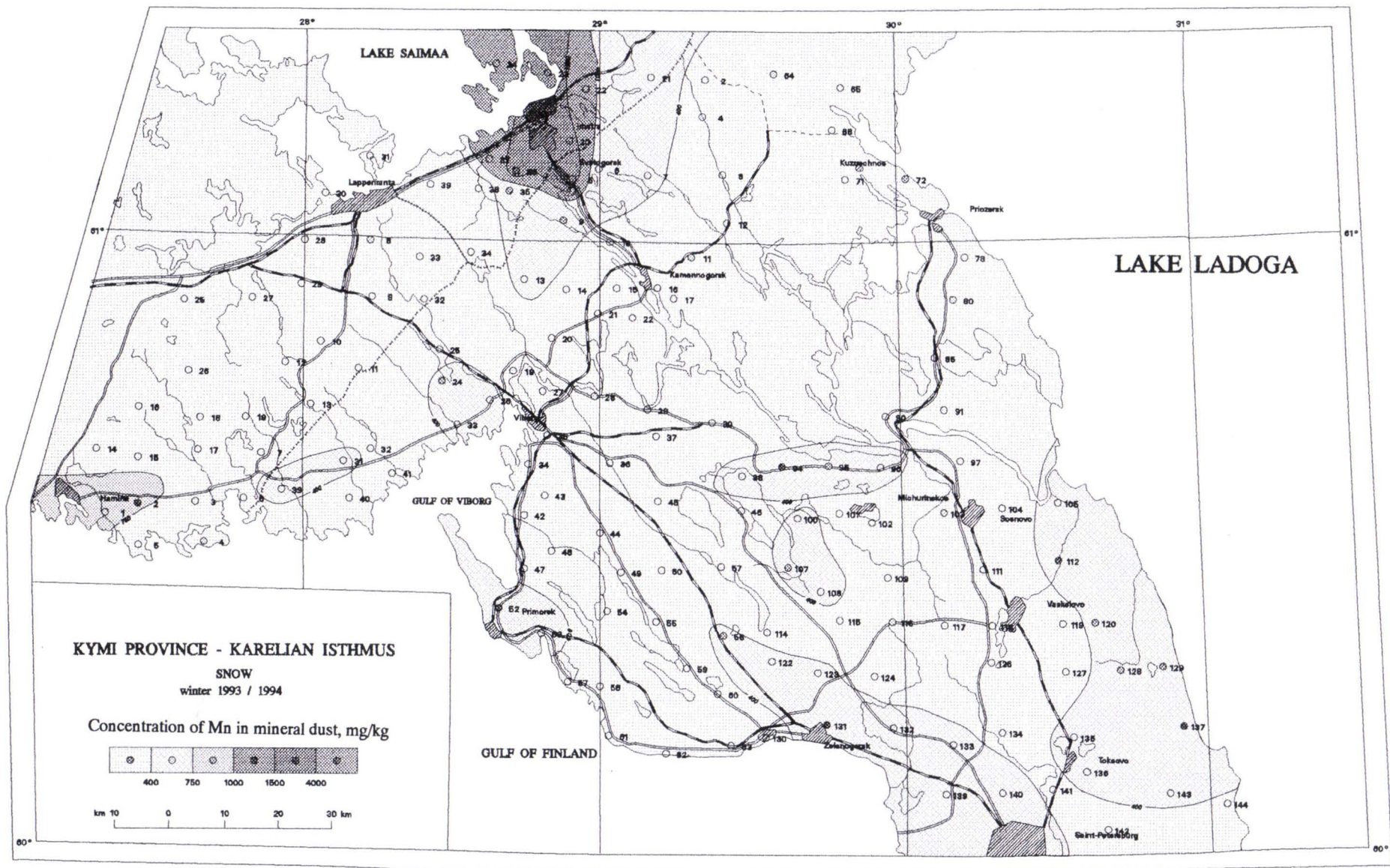
Appendix 1.

Fig. 20. Concentration of manganese in mineral dust (ashed residue) in winter 1993/1994.
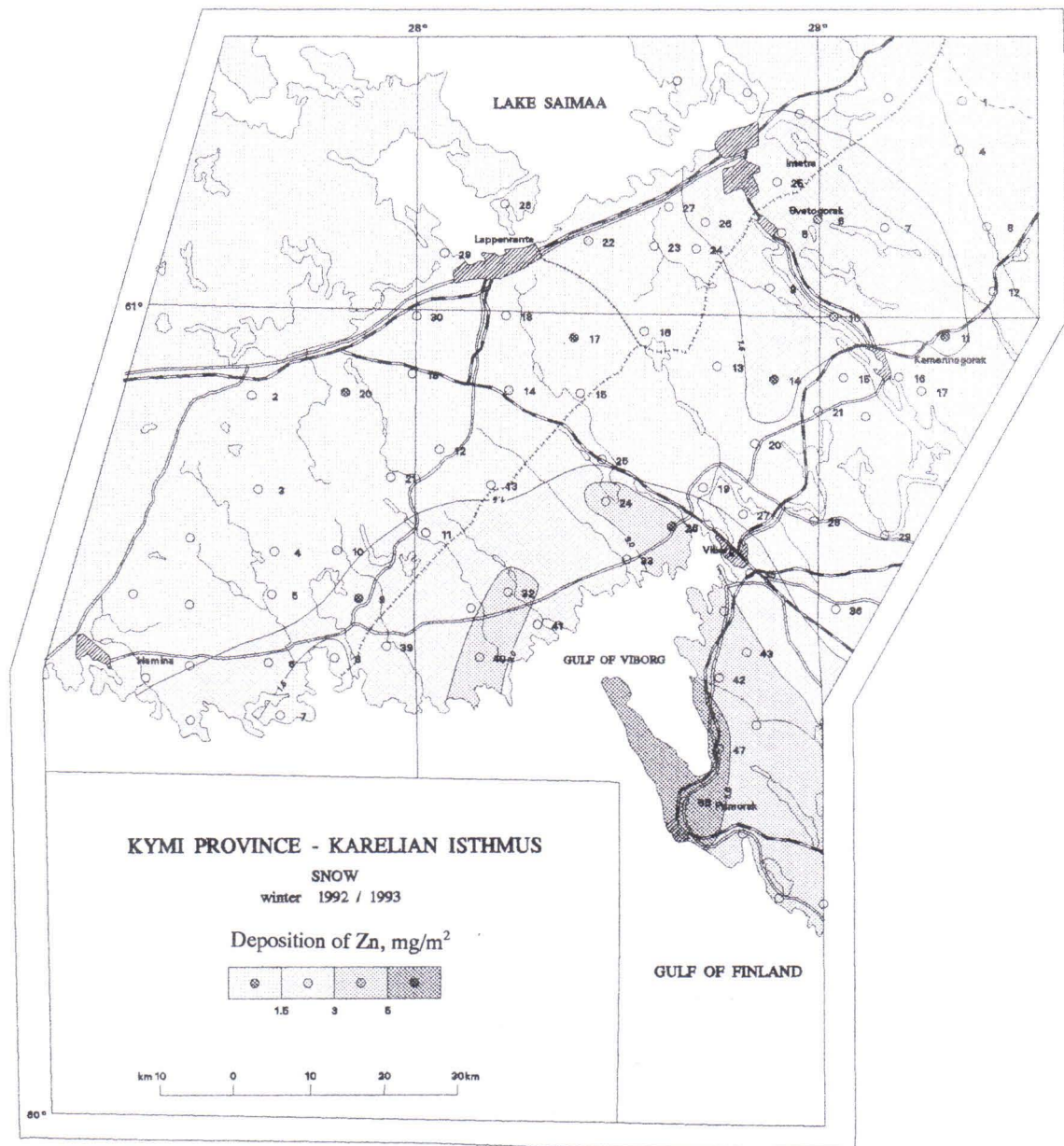
Appendix 1.

Fig. 21. Deposition of zinc in winter 1992/1993.
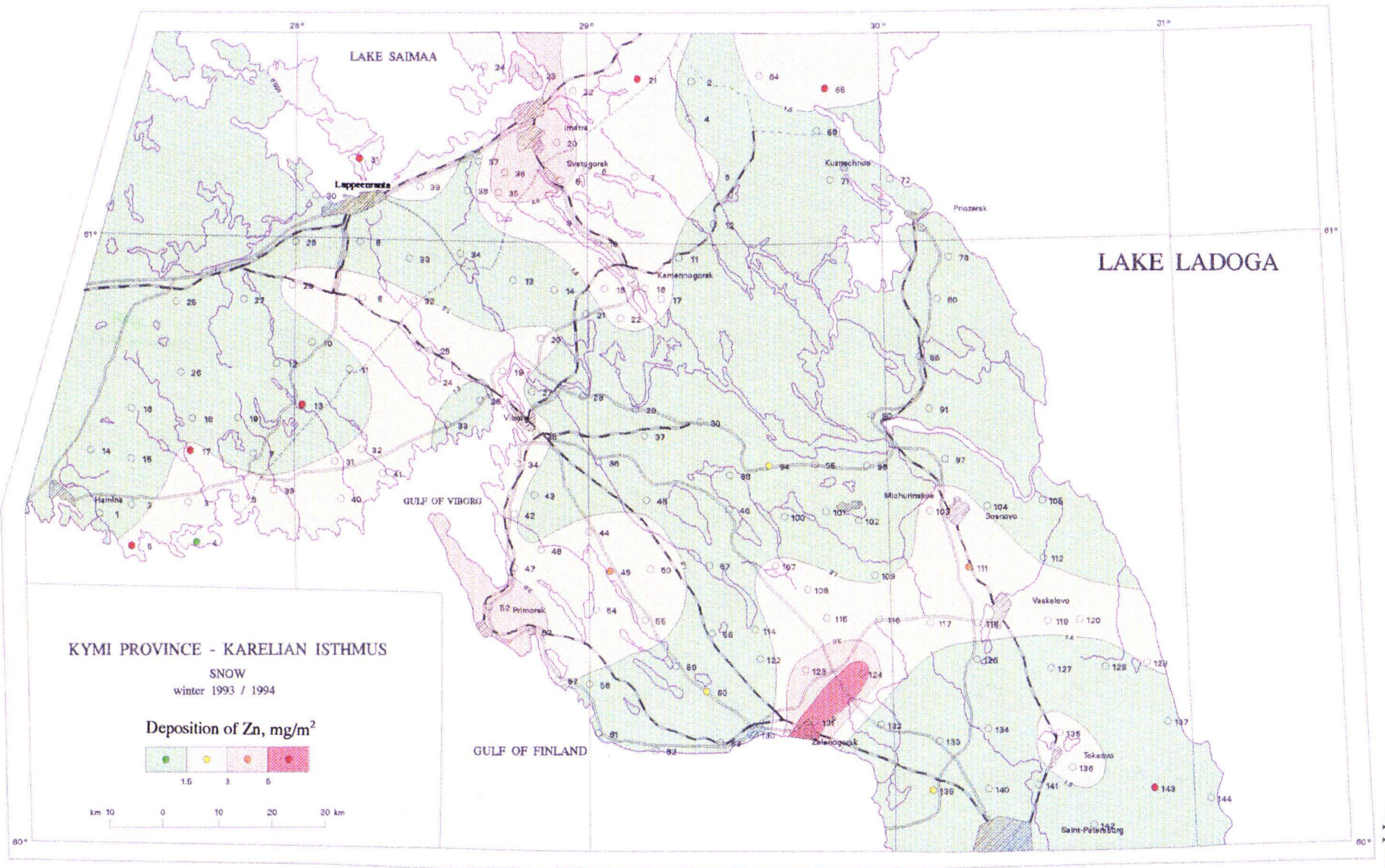
Fig. 22. Deposition of zinc in winter 1993/1994.

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SNOW
winter 1993 / 1994

Deposition of Zn, mg/m²

1.6   3   5

km 10   0   10   20   30 km

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KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Concentration of Zn in liquid phase, μg/l

Fig. 23. Concentration of zinc in liquid phase in winter 1993/1994
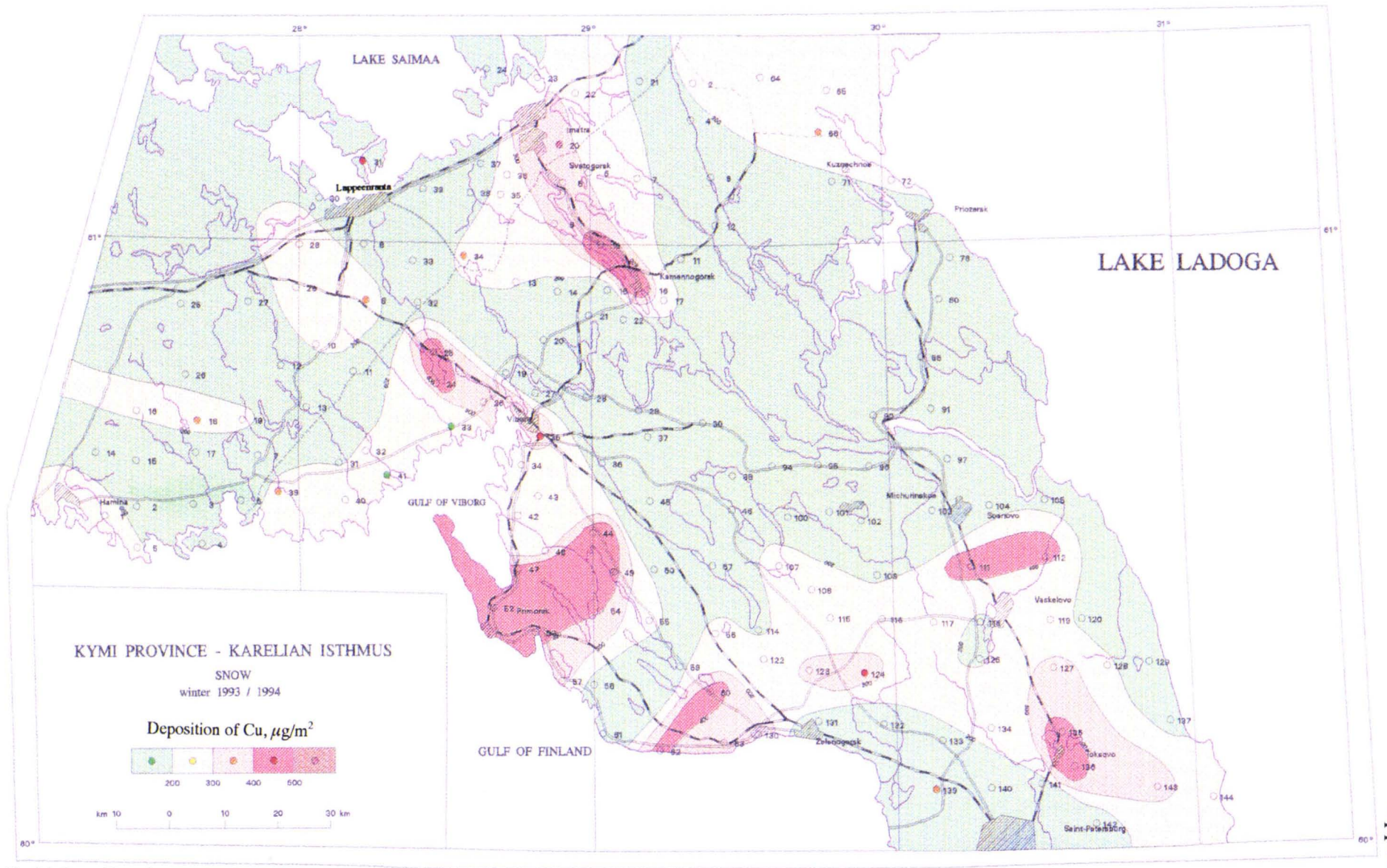
Fig. 24. Deposition of copper in winter 1993/1994.

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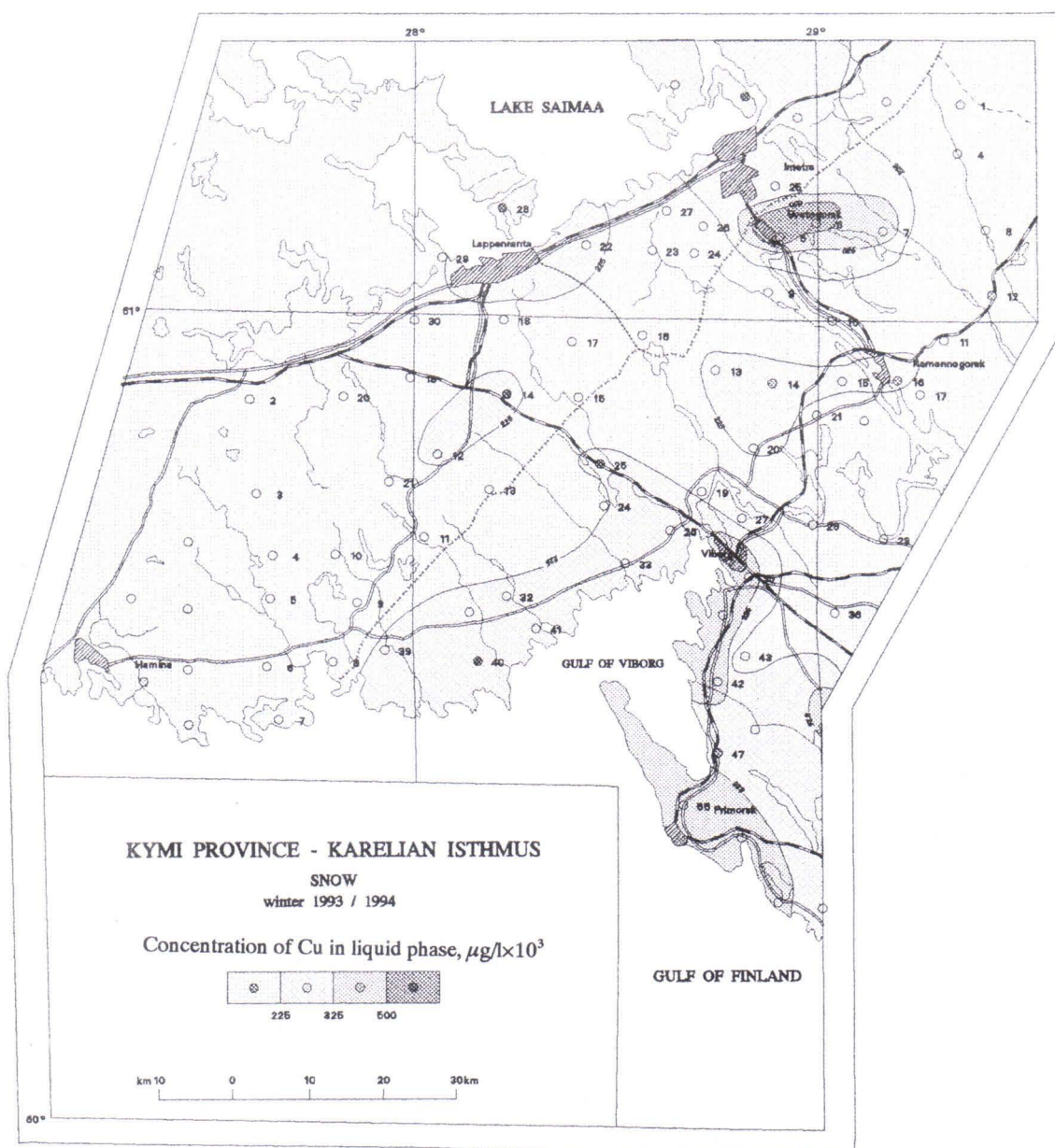
Fig. 25. Concentration of copper in liquid phase in winter 1993/1994.

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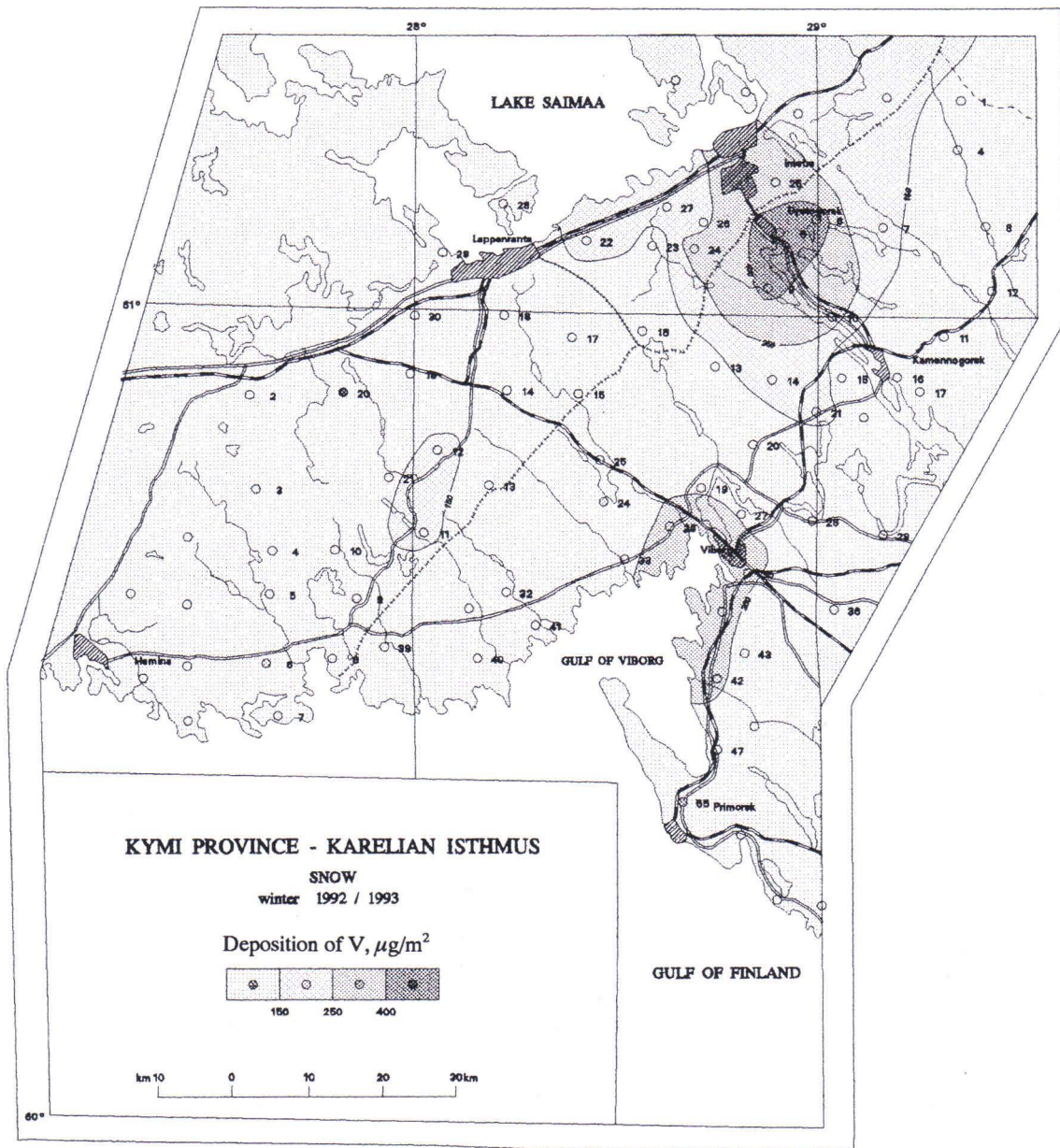
Fig. 26. Deposition of vanadium in winter 1992/1993.
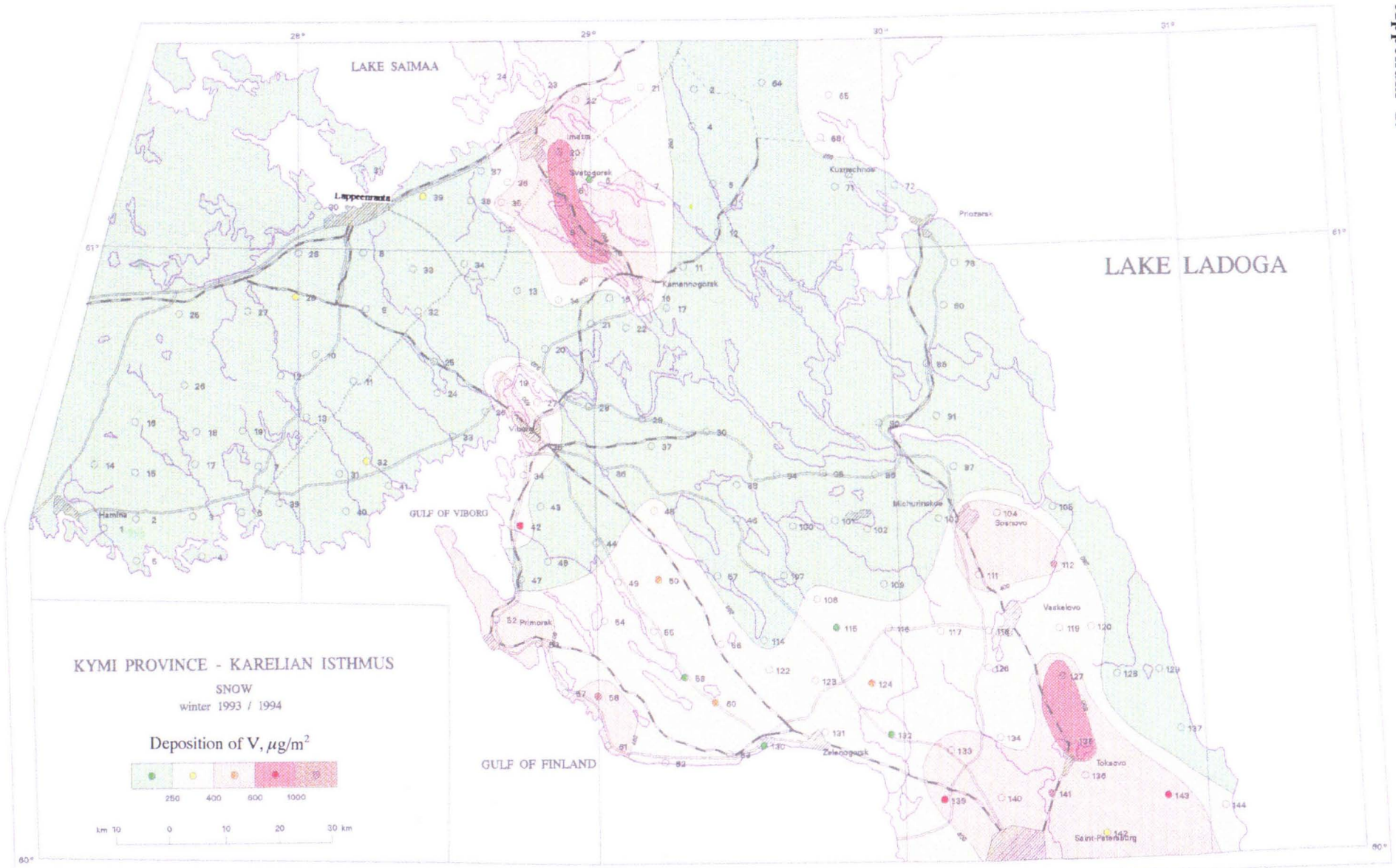
Appendix 1.

Fig. 27. Deposition of vanadium in winter 1993/1994.

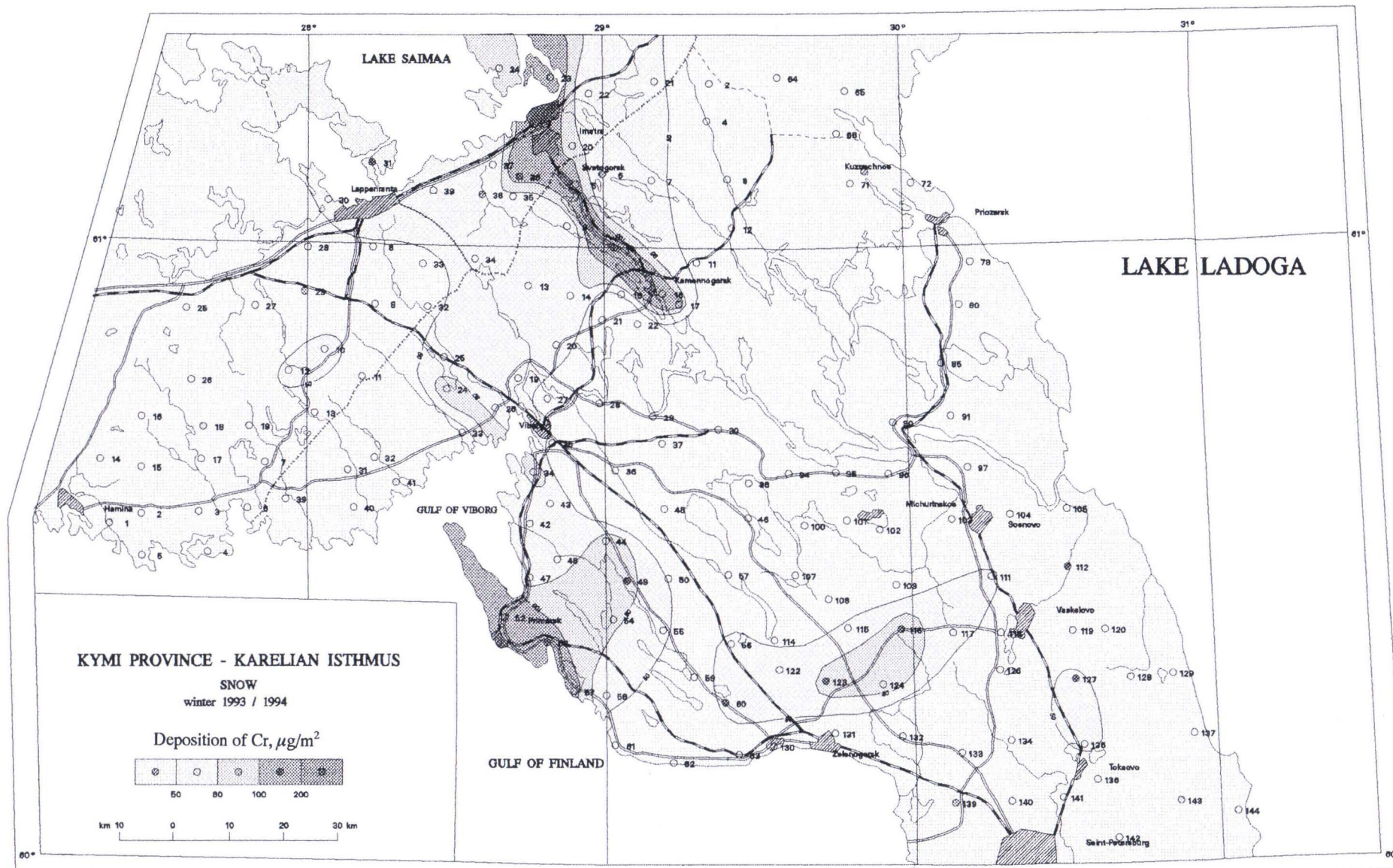Fig. 28. Concentration of vanadium in mineral dust (ashed residue) in winter 1993/1994.

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Concentration of V in mineral dust, mg/kg

200   300   500   700   1000

km 10   0   10   20   30 km

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Imatra

Lappeenranta

Svetogorsk

Kuznechnoe

Priozersk

Kamennogorsk

Viborg

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Hamina

Michurinskoe

Sosnovo

Vaskelovo

Primorsk

Toksovo

Zelenogorsk

GULF OF FINLAND

Saint-Petersburg

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Deposition of Cr, $\mu g/m^2$

50   80   100   200

km 10   0   10   20   30 km

Fig. 29. Deposition of chromium in winter 1992/1993.

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KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1992 / 1993

Deposition of Cr, $\mu g/m^2$

Fig. 30. Deposition of chromium in winter 1993/1994.

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KYMI PROVINCE - KARELIAN ISTHMUS

SNOW
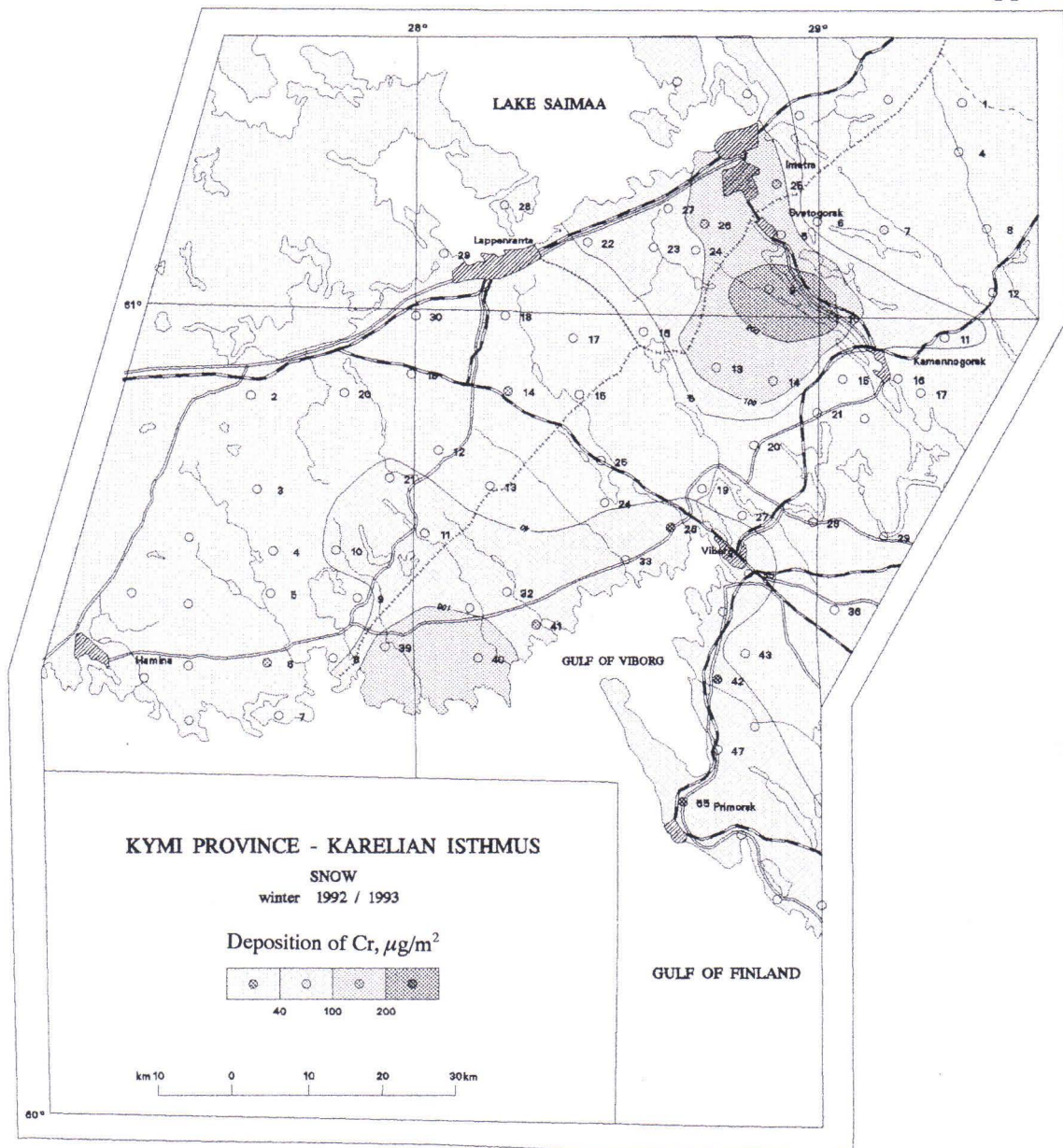
winter 1992 / 1993

Deposition of Ni, $\mu g/m^2$
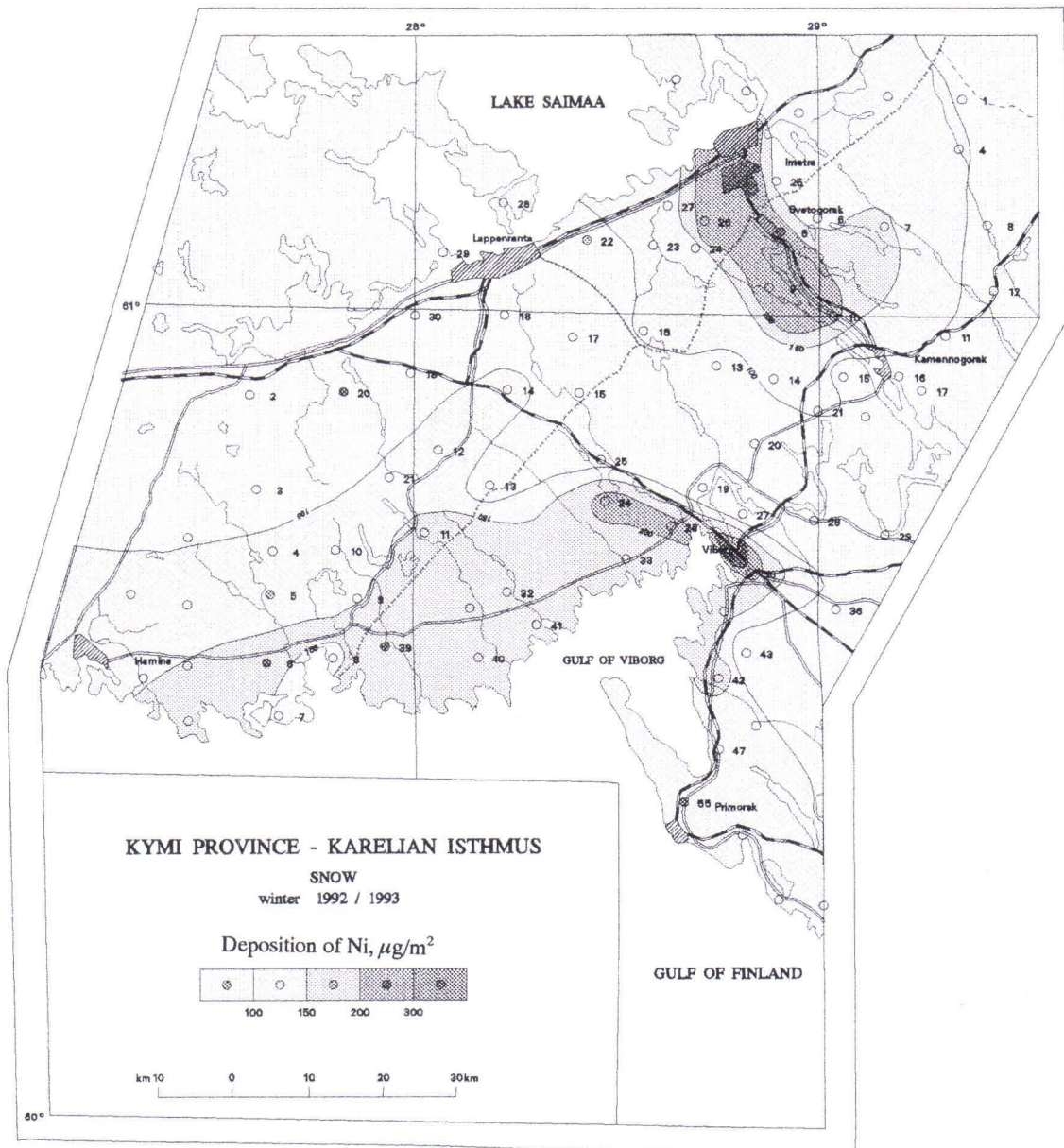
Fig. 31. Deposition of nickel in winter 1992/1993.
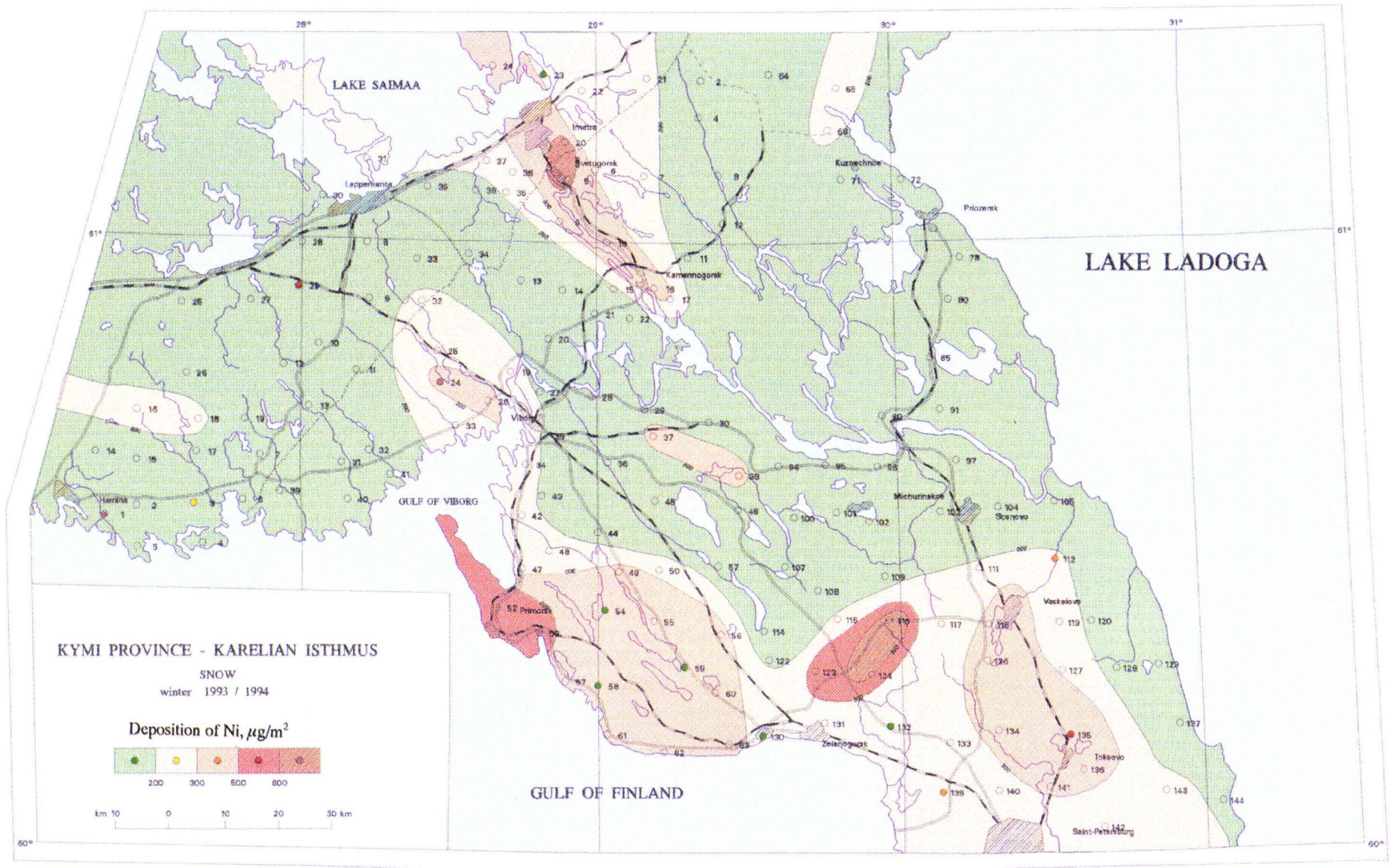
Fig. 32. Deposition of nickel in winter 1993/1994.

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KYMI PROVINCE - KARELIAN ISTHMUS
SNOW
winter 1993 / 1994

Deposition of Ni, $\mu g/m^2$

200   300   500   800

km 10   0   10   20   30 km

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KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Concentration of Ni in liquid phase, μg/l

0.5   0.7   1

km 10   0   10   20   30 km

Fig. 33. Concentration of nickel in liquid phase in winter 1993/1994.

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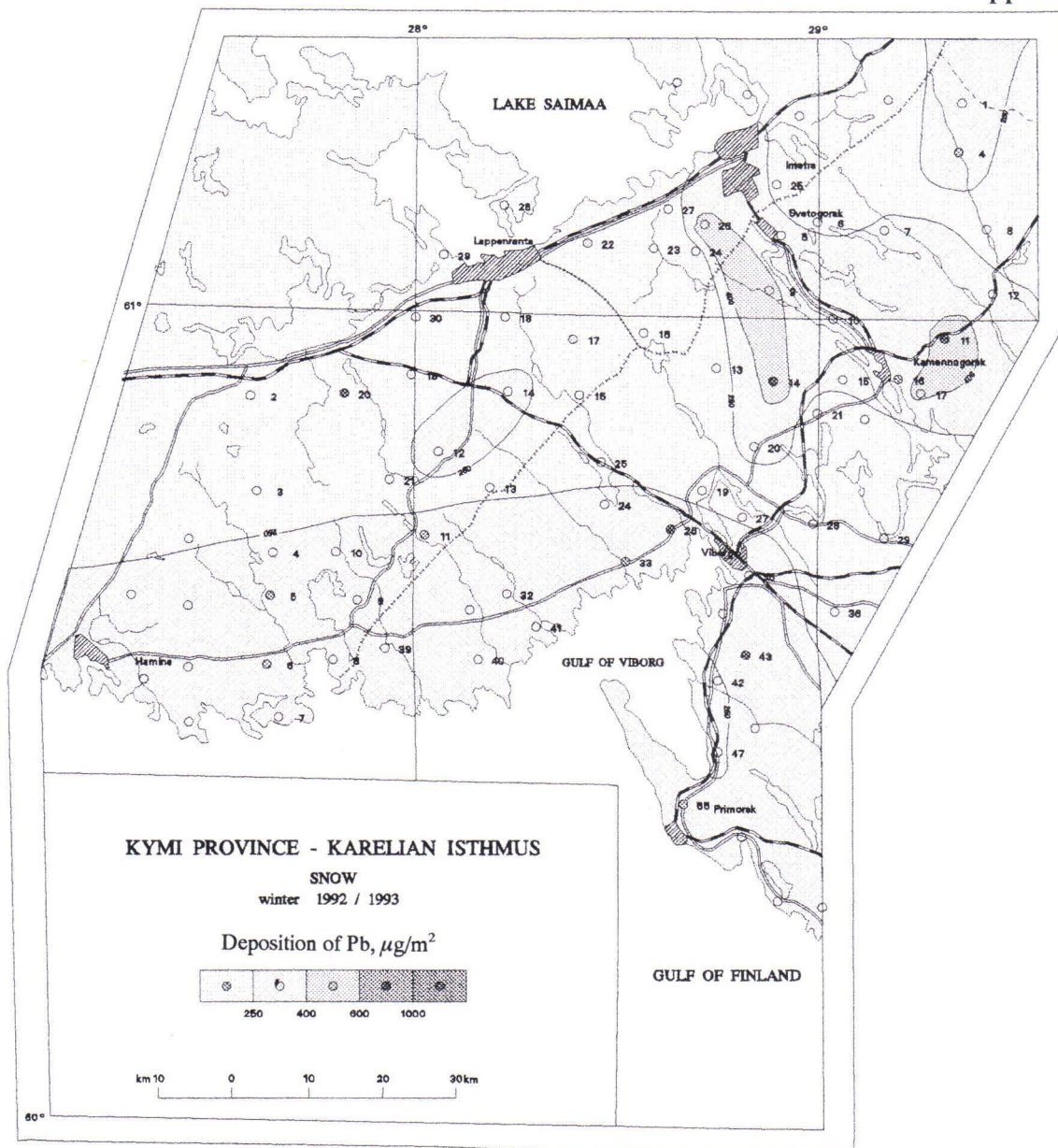
Appendix 1.

Fig. 34. Deposition of lead in winter 1992/1993.
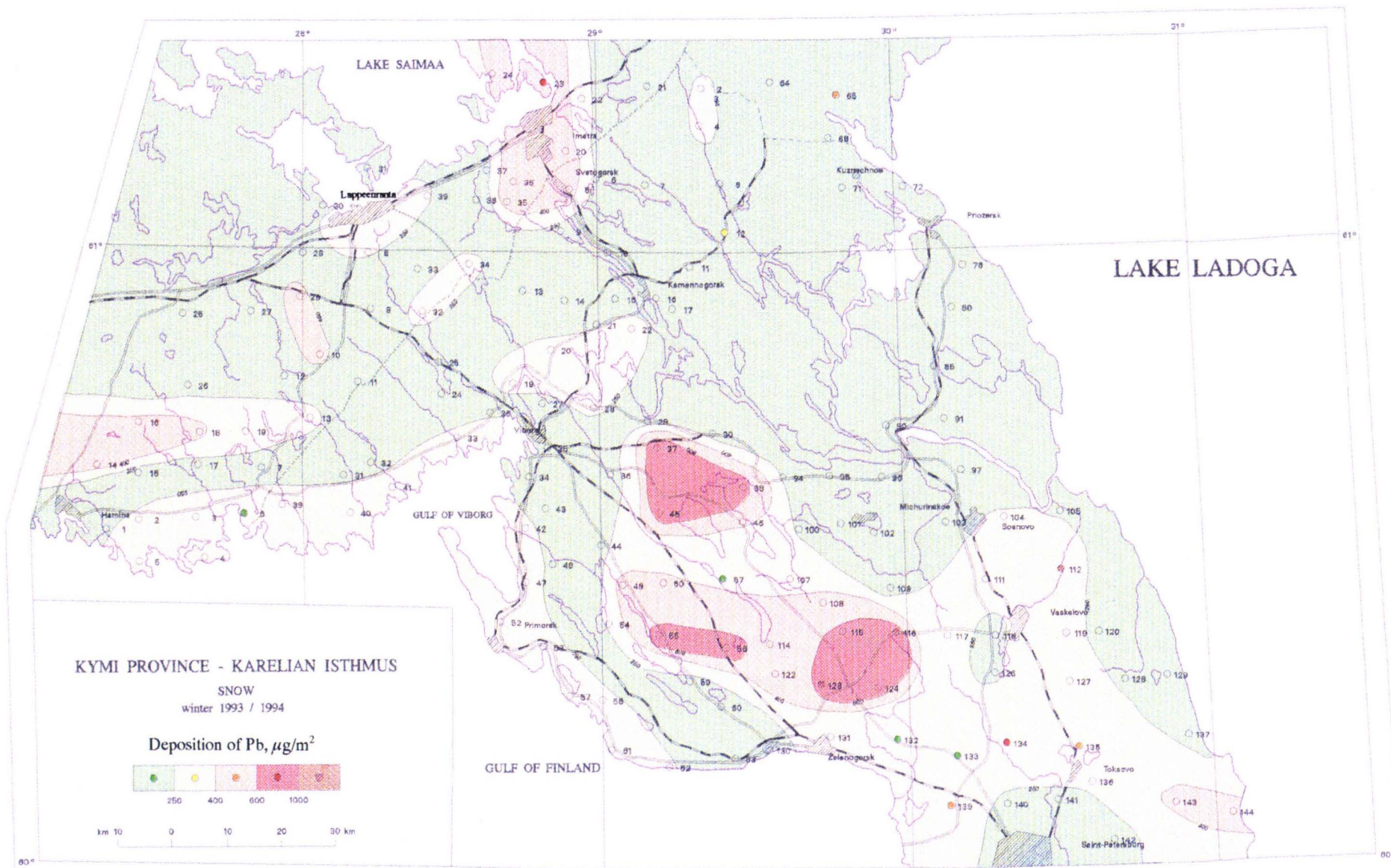
Fig. 35. Deposition of lead in winter 1993/1994.

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Deposition of Pb, $\mu g/m^2$

250   400   600   1000

km 10   0   10   20   30 km

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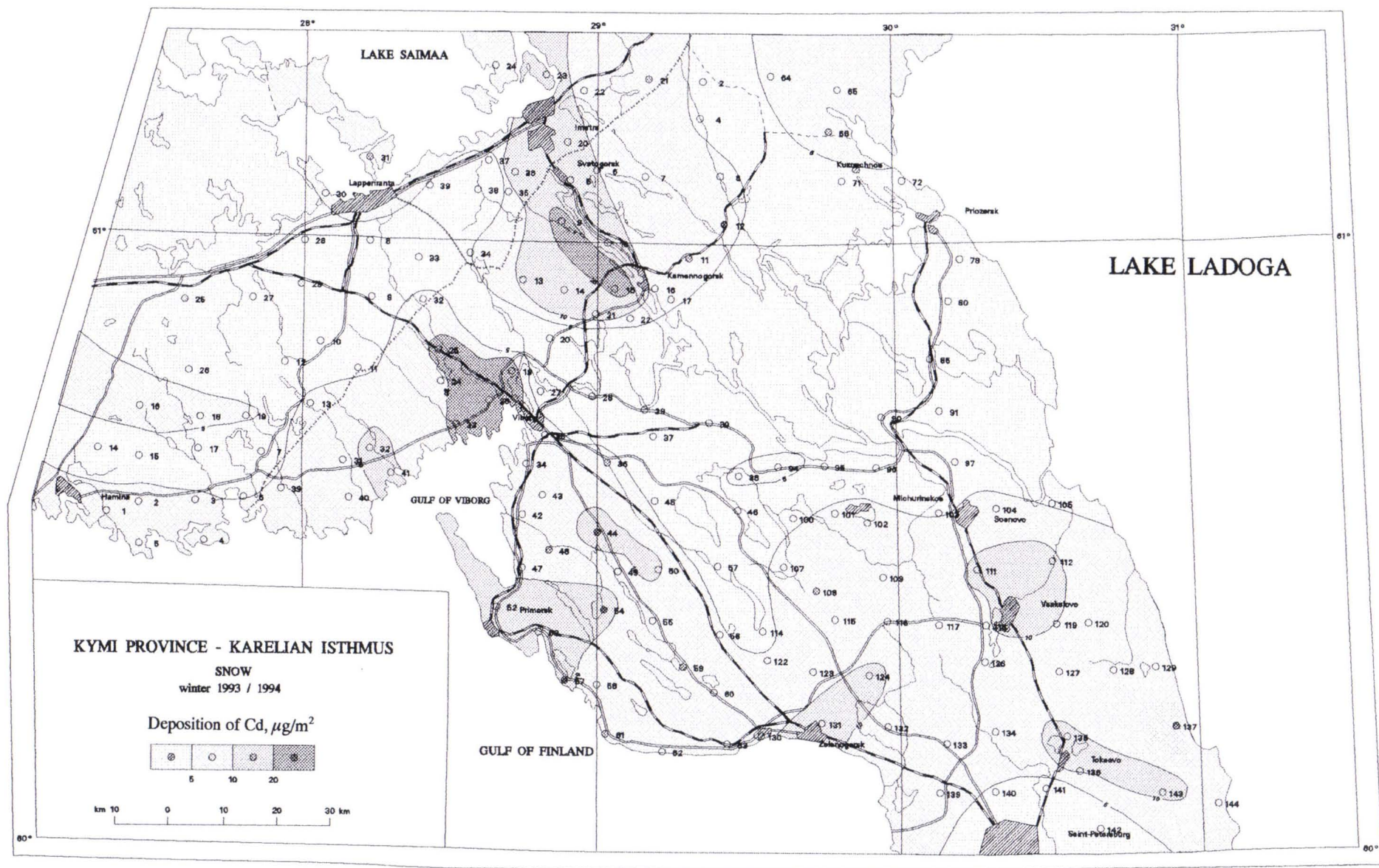
Appendix 1.

Fig. 36. Deposition of cadmium in winter 1993/1994.

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

winter 1993 / 1994

Deposition of Cd, $\mu g/m^2$

Appendix 1.
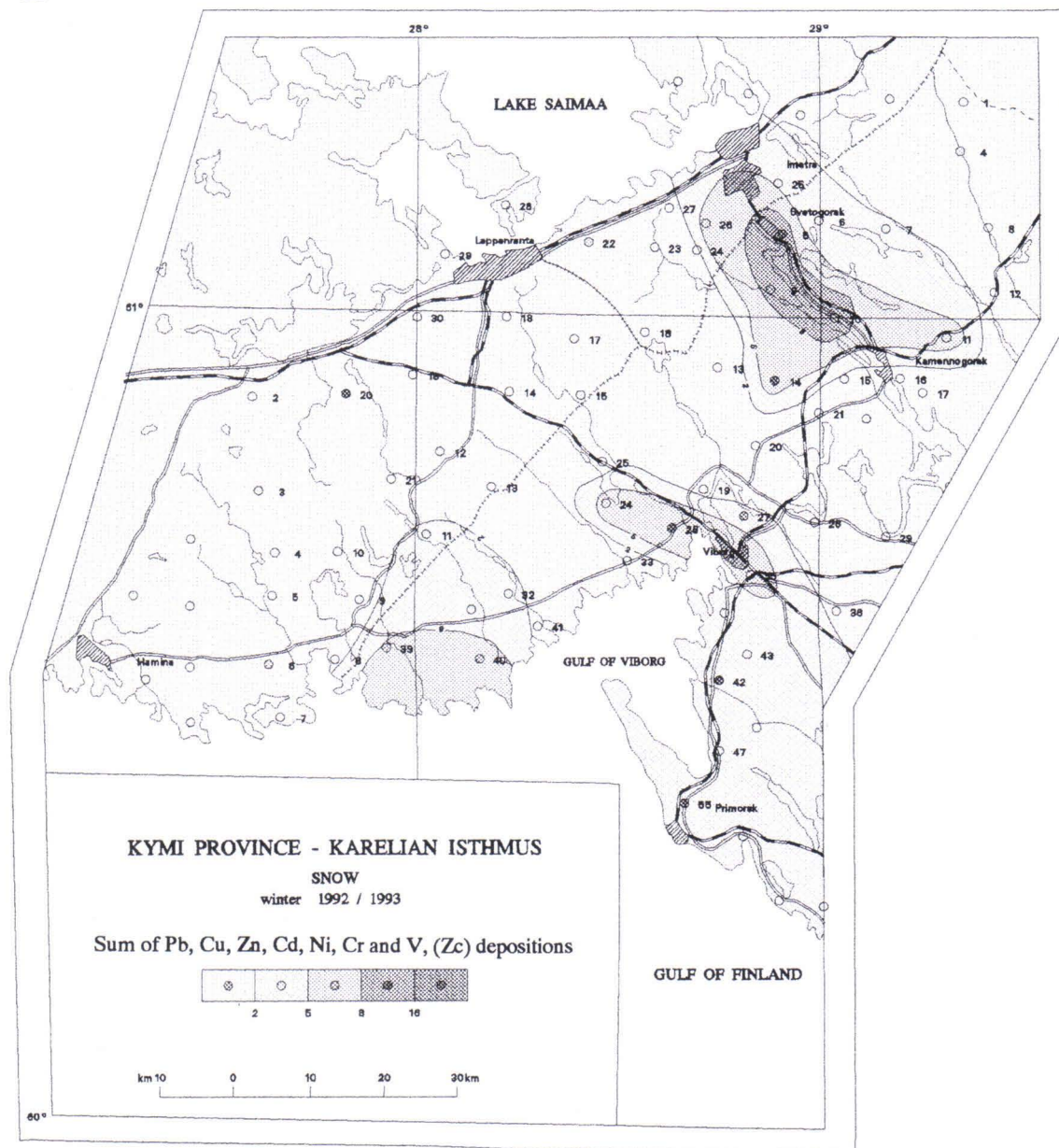
Fig. 37. Sum of depositions (load) of anthropogenic metals in winter 1992/1993.
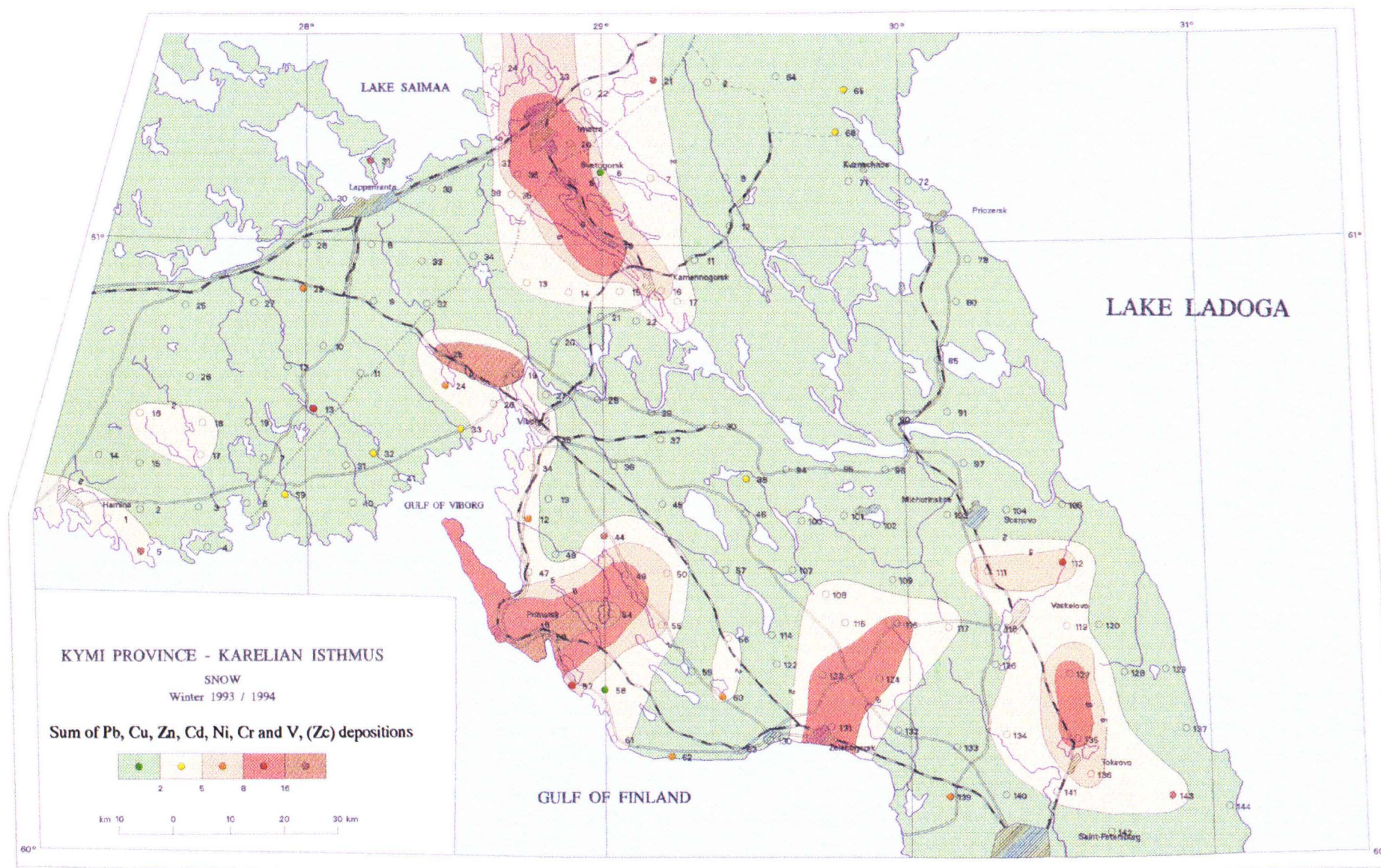
Fig. 38. Sum of depositions (load) of anthropogenic metals in winter 1993/1994.

LAKE SAIMAA

LAKE LADOGA

GULF OF VIBORG

GULF OF FINLAND

KYMI PROVINCE - KARELIAN ISTHMUS

SNOW

Winter 1993 / 1994

Sum of Pb, Cu, Zn, Cd, Ni, Cr and V, (Zc) depositions

2   5   8   16

km 10   0   10   20   30 km

Geologian tutkimuskeskus, Tutkimusraportti — *Geological Survey of Finland, Report of Investigation 139, 1997*
Geochemistry of atmospheric deposition...

Appendix 1.