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Front cover: Moss sampling in the Limbazu district, Latvia, photo Virgilija Gregorauskiene, Geological Survey of Lithuania.

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The distribution of element concentrations in terrestrial mosses and the organic soil layer was investigated in the eastern Baltic region, an area surrounding the Gulf of Finland. The study was an extension to the project Geochemical mapping of the eastern Barents Region (Barents Ecogeochemistry), the results of which were published in 2004.

New moss and organic soil layer (humus) samples were collected in 2003 from 191 sites in Estonia, Latvia, and Lithuania. Respective data from southern Finland and the Leningrad region in Russia were obtained from the database of the Barents Ecogeochemistry project to cover the study area. Data from a total of 476 sampling sites were included in this study. New samples from the three Baltic countries were collected according to the Field Manual of the Barents Ecogeochemistry project.

Total element concentrations for Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sn, Sr, Th, Tl, U, V, and Zn were measured by ICP-MS or ICP-AES. Hg concentrations of organic layer samples were measured by Perkin Elmer FIMS-400 atomic absorption spectrometer. ^{134}Cs and ^{137}Cs isotopes were measured using γ-spectrometry. The loss on ignition (LOI), the C and N concentrations and humidity content were additionally determined from the organic layuer samples. The results are presented in 85 element distribution maps.

The continuation of anomalies for elements such as Tl and Cs isotopes south of the Barents Ecogeochemistry project area was examined. The airborne transportation of these elements is discussed. Cs isotopes from the deposition following the Chernobyl nuclear power plant accident in 1986 were still clearly detectable in the organic layer. The source of Tl detected in SE Finland and along the northern coast of Estonia is emissions from industry and power plants that use oil shale as fuel. It was estimated that the heavy metals and other elements in inorganic soil are mostly geogenic in origin, but include fingerprints of older industrial emissions. In mosses, their origin is either recent emissions from anthropogenic sources or also in many cases geogenic dust from open areas.

Keywords (GeoRef Thesaurus, AGI): geochemical surveys, Bryophyta, humus, chemical elements, thallium, ^{134}Cs, ^{137}Cs, dispersion patterns, geochemical maps, human activity, Baltic region, Finland, Leningrad Region

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CONTENTS

1 INTRODUCTION

This study is an extension of the Barents Ecogeochemistry project (Salminen *et al.* 2004). Organic soil samples (ORG) and terrestrial moss samples (MOS) were collected from Estonia, Latvia and Lithuania in 2003. Samples from Finland and Russia included in this project were collected in 2000. All the methodology followed the concept applied in the Barents Ecogechemistry project.

Very high concentrations of environmentally important and potentially harmful elements such as Tl and Cs were detected in the Barents Ecogeochemistry project to the north and east of the Gulf of Finland. These elements are often assumed to be distributed via airborne transportation over longer distances. Thus, the most important aim of this study was to assess the continuation of Tl, ^{134}Cs, and ^{137}Cs isotope anomalies south of the Barents Ecogeochemistry project area and estimate whether Tl is being transported to southern Finland from industrial emissions in Estonia or even farther from Central Europe, and whether the fallout following the Chernobyl nuclear power plant accident also reached the Baltic countries (distribution of Cs isotopes). At the same time, it was estimated whether the heavy metals and other elements in the sampled media are geogenic or anthropogenic in origin.

2 GEOLOGY OF THE STUDY AREA

The study area consists of two different geological units:
(i) the Fennoscandian (Baltic) Shield in Finland and Russian Karelia, north and northeast of Lake Ladoga, and
(ii) sedimentary rocks of the Russian Plate, which cover the Baltic countries and the Russian territory south and southeast of Lake Ladoga. The main lithological units of the bedrock are presented in Figure 1.

The Early Proterozoic Svecofennian megablock of the Fennoscandian (Baltic) Shield comprises the southern and western parts of Finland and is dominated by granitoids and supracrustal rocks (mica schists) and by felsic and mafic metavolcanic rocks (Simonen 1980). The southernmost part of this megablock is strongly migmatized and exhibits a high grade of metamorphism. According to Gaal (1986), the Svecofennian megablock southwest of the suture zone (Raahe-Ladoga zone) is now widely accepted as an ancient island arc environment. Late Proterozoic intrusives such as rapakivi granites and anorthosites are common in the south and southeastern coastal area of Finland.

The Russian plate makes up the northern part of the East European platform and extends south and southeast from the Fennoscandian (Baltic) shield. Within the project area, the Russian plate mainly consists of the structural sub-block of the Slope of the Baltic Shield. The Slope of the Baltic shield extends to the White Sea and Barents Sea in the north and covers most of Estonia and the northern part of Latvia in the south, where it consists of sandstones, argillites and clay-limestones of Cambrian, Ordovician, Silurian and Devonian ages. A phosphorite layer, rich in heavy metals, follows the northern coastline of Estonia. Most of the Latvian area consists of Palaeozoic (Devonian) sandstones and in the southernmost part also limestones (Permian and Early Triassic and Jurassic). In Lithuania, younger Late Jurassic and Cretaceous limestones (southern and western Lithuania) and sandstones (northeastern Lithuania) prevail; in the central and northeastern part, Devonian sandstones are the most common.

3 HUMAN ACTIVITIES IN THE STUDY AREA

The map of human activities (Figure 2) is based on the work of the project Northern Europe Geochemistry (Salminen *et al.* 2009) and gives a general overview of the location of different anthropogenic activities in the study area.

3.1 Population density and traffic

The project area is a highly developed industrial region with a great variety of industrial production and agricultural activity. The high population density and ever-increasing traffic, especially in the Leningrad region but also in South Finland and the Baltic countries, are threats to man's balance with nature.

The map of human activities (Figure 2) provides an overview of the various economic and other activities in the region. The highest population density and greatest variety of industries occur in the southwestern part of the region, including the Baltic countries, the southern part of Finland and the Leningrad region in Russia. Oil processing, pulp and paper production and some service industries, such as electric power plants, the food industry, building, agriculture and transport, are also significant.

3.2 Heavy metal industry

Various metallurgical industries exist in Russia. The large Cherepovets metallurgical combine in the Vologda region is one of the most important ferrous metal industrial plants, and processing industries in St. Petersburg produce different types of steel and rolled metal products. Mining products are processed at Harjavalta (Cu and Ni ores) in southwestern Finland. Most of the engineering industry is concentrated around St. Petersburg. The main branches are ship building, machine

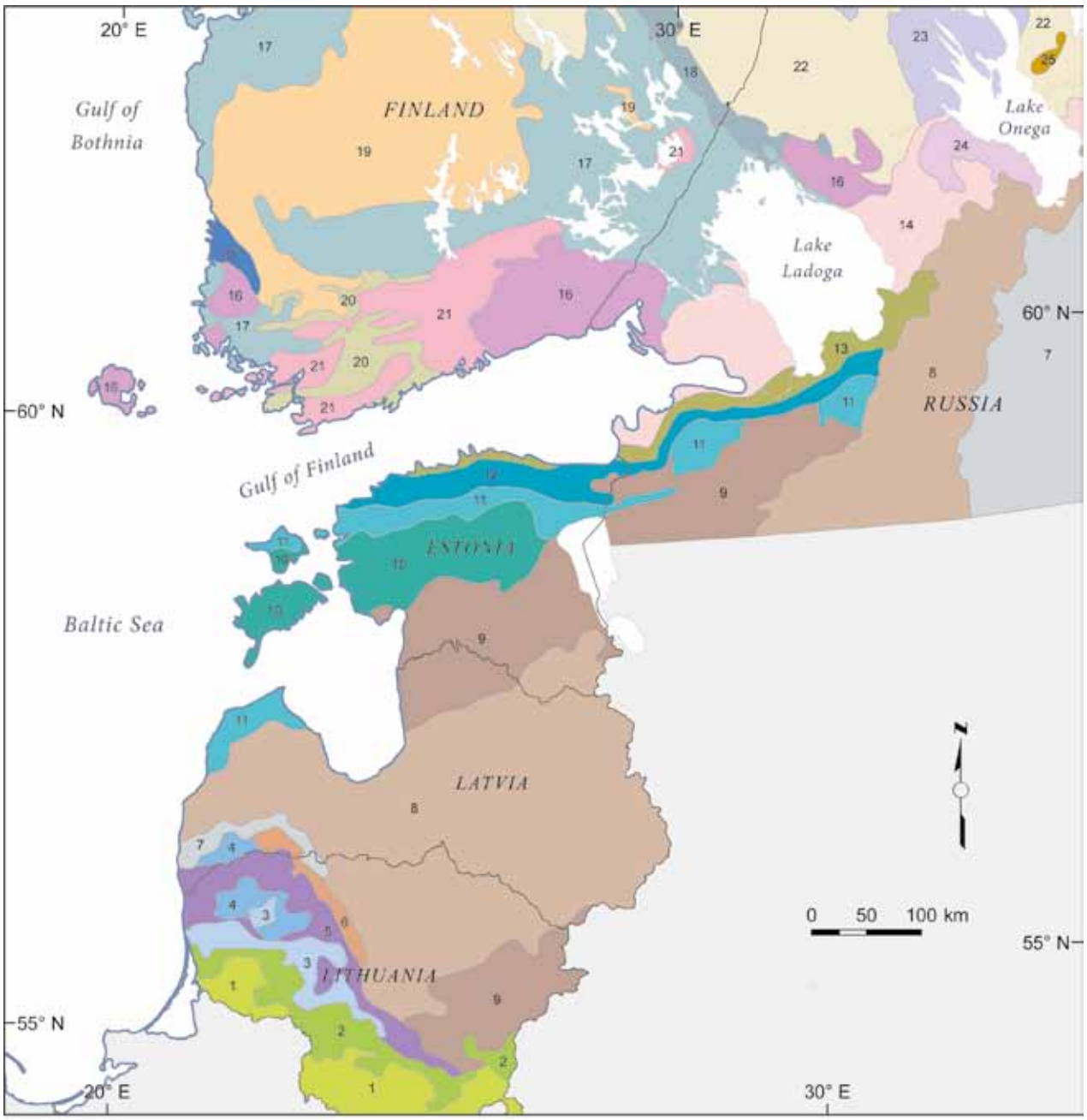


Figure 1. Bedrock of the study area. The map has been compiled from various sources (Simonen 1990, Koistinen *et al.* 2001, Asch 2005).

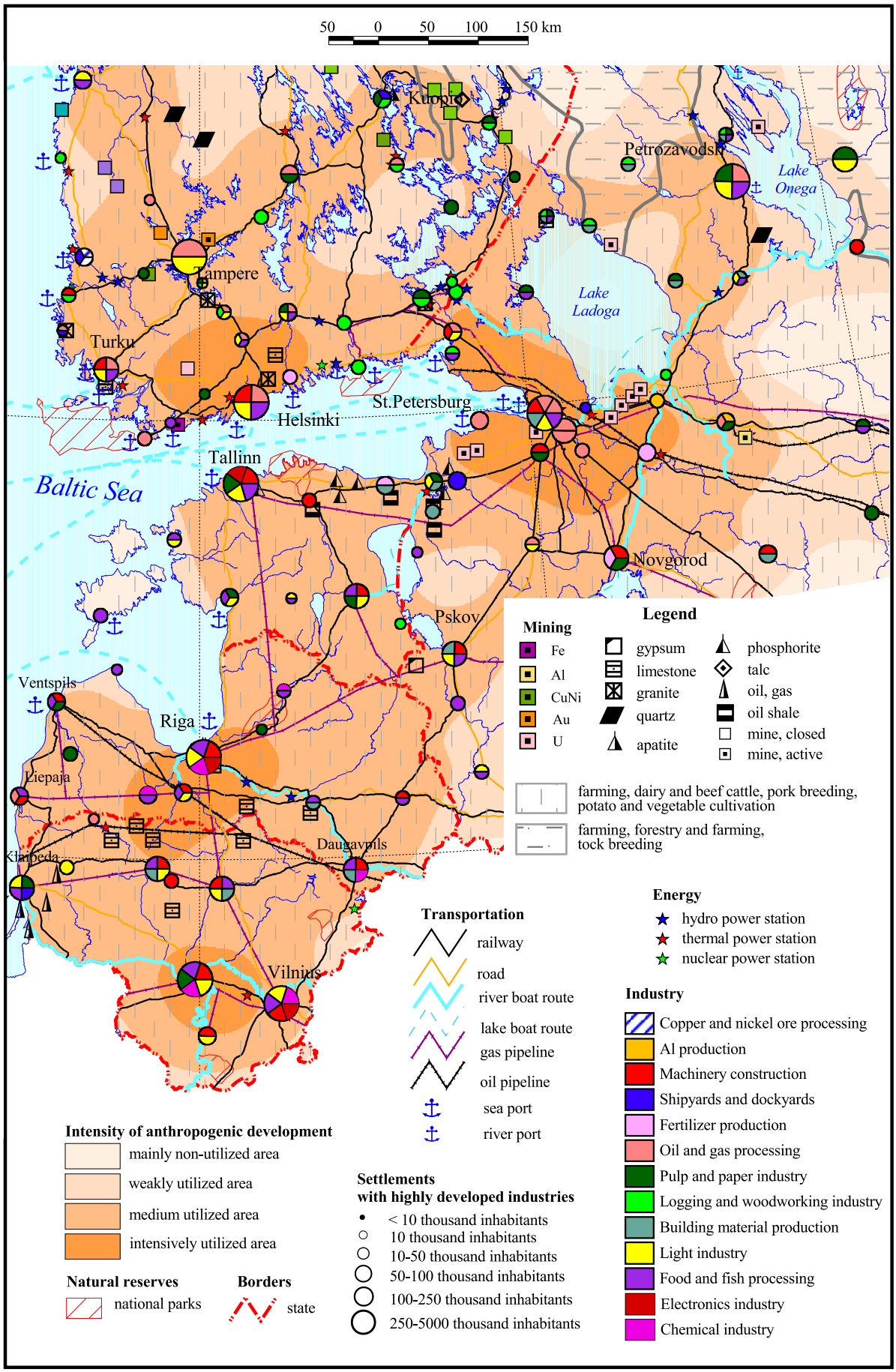


Figure 2. Human activities in the study area. The map is based on data from the Northern Europe Geochemistry (NEG) project (Salminen 2009).

and tool construction, electrotechnical and radio engineering, the production of power-generation equipment, and tractor construction. There are also plants for the construction of equipment for transportation. In Finland, similar industrial activity is concentrated in the coastal area of southern and southwestern Finland. Thus, surrounding the Gulf of Finland is a strong cluster of many types of industries. These areas naturally include a large variety of building industries, including numerous plants for building materials, such as cement factories that use local limestones as a raw material.

3.3 Pulp and paper industry

The forest industry is important for the whole region and includes the timber, pulp and paper industries. In Finland, the pulp and paper industry is mainly located in southeastern Finland. In Russia, it is concentrated in Karelia, northeast of Lake Ladoga, and in the Leningrad region.

3.4 Chemical industry

In Finland, compounds for fertilizers are prepared in Uusikaupunki and Harjavalta. A wide variety of chemical products come from industrial plants in the coastal areas of Helsinki, Porvoo, Turku and Uusikaupunki. In central Lithuania, emissions from the fertilizer plant in Kedainiai have caused some contamination of its surroundings. In the Leningrad region, the chemical industry plants Phosphorit (Kingisepp area) and Slantsy Combine (Slantsy area) use local geological raw materials. The Volkhov aluminium plant also produces superphosphate and is therefore a major source of harmful emissions to the atmosphere. In the northern part of Estonia, the mining of oil shale is a major issue and it is locally used as fuel in power plants. Emissions from the Sillamäe chemical industry plants have been considered a risk to the environment, as they are located next to the Gulf of Finland. Earlier, phosphorite mining and the manufacture of fertilizers was also active in the same area.

3.5 Agriculture

The types of agriculture and the levels of emissions in the region vary considerably. The most heavily cultivated areas are situated in the Leningrad region and in south and southwestern Finland and in all the Baltic countries. In these areas, artificial fertilizers are used in cultivation, and animal husbandry (cattle and poultry) is intensive.

4 METHODS

4.1 Sampling

Data for Finland and Russia were selected from the database of the Barents Ecogeochemistry project (Salminen *et al.* 2004). In the Baltic countries, sampling and field observations were carried out according to the Field Manual of the Barents Ecogeochemistry project (Gregorauskiene *et al.* 2000). All methods were originally tested in different parts of the survey area of the Barents Ecogeochemistry project during a field training course in the summer of 1999 (Salminen 2000). The methods were adapted according to the experience gained during field training.

4.1.1 Selection of sampling sites and sample media

For site selection, all existing information on geology (bedrock and Quaternary deposits), soil types, morphology and vegetation zones was used. The area was divided into drainage basins covering approximately 1000 km^2 each. These drainage basins were subdivided into drainage basins covering approximately 100 km^2 each. Each sample site was located in the 100 km^2 drainage basin that was considered to be the most representative for the whole area. In the selection of the drainage basins, the first priority was given to the most pristine catchments. The dominant landscape conditions in the selected catchments guided the final site selection. The sites needed to be as flat as possible, and steep slopes or river channels as well as ancient lake or sea beaches were therefore avoided. During the final site selection in the catchment, forest clear-cuts and recent sites of forest fires were also avoided. The immediate surroundings of roads, industry and villages were not allowed to sample. The minimum distance to a larger road was defined to be 300 metres, and the minimum distance to minor roads 50 metres.

Two different types of samples were collected from all sites:

(i) the uppermost 3 cm of the organic soil layer (ORG) and

(ii) terrestrial moss (*Hylocomium*) (MOS).

Organic soil mainly consists of decaying plant material. It is sampled to reflect the interplay between the atmosphere, biosphere and lithosphere. It is also used to examine how the long range atmospheric input of elements to the ecosystem accumulates over time. To achieve this aim, samples were preferably collected from forested areas. To reflect the atmospheric input and to obtain a representative sample of decaying plant matter, samples were collected immediately under the green vegetation and including the litter. No admixtures of mineral soil were permitted in this sample.

Terrestrial moss samples are taken to reflect the atmospheric input of elements over a limited time span. Moss has no roots and predominantly relies on element input via precipitation. Due to its large surface area, moss also collects local dust. It has ion exchange properties and can accumulate many elements over time. Moss is collected as a bio-indicator, reflecting variations in the regional composition of the atmosphere rather well for a limited time segment, e.g. 1–3 years.

4.1.2 Quality control samples

For quality control purposes, both materials were collected as duplicate samples from every 15th sampling site. The whole sampling procedure was duplicated. Two different project standard samples of moss and the organic layer were used. One of the samples was collected from southern Finland and the other from the Leningrad region. Both samples were thoroughly homogenised and divided into subsamples, which were then used throughout the laboratory process as project standard samples. In the laboratory, commercial standard sample material was also used.

4.1.3 Materials and equipment for sampling

All necessary equipment and other materials needed for collecting the samples were purchased and delivered by the Geological Survey of Finland to all parties. The coordinates of each sampling site were measured by Garmin12 GPS device. A field sheet was completed for each site. It included data on the local geology, morphology and human activities, among other parameters.

The number of different sample types collected is presented in Table 1. A detailed description of the sampling of different media is provided in the Field Manual of the Barents Ecogeochemistry project (Gregorauskiene *et al.* 2000).

Table 1. The number of different sample types collected during the project.

Sample type	Finland	Russia	Estonia	Latvia	Lithuania	Total
Organic soil layer (ORG)	132	183	55	67	66	474
Terrestrial moss (MOS)	132	183	55	69	67	476

4.2 Analysis

4.2.1 Sample preparation

All sample preparation and analyses, if not otherwise stated, were carried out at the Geolaboratory of the Geological Survey of Finland (GTK) in Espoo, Kuopio, or Rovaniemi.

Field samples from the organic soil layer (ORG) were dried in their original bags at room temperature before sieving. Samples were hand-sieved using 2-mm nylon sieves. Material passing through the 2-mm sieve was used for analysis. To avoid trace element contamination during sieving, all parts of the equipment coming into contact with the samples were made of plastic.

Field samples of moss (MOS) were dried in their original bags at room temperature. The samples were spread on laboratory paper and cleaned of all extraneous material. The cleaned samples were homogenized by milling with a Fritch Pulverisette centrifugal mill, with blades made of titanium, to grain size of <1 mm. To avoid contamination, talcum-free gloves were used during sample preparation.

4.2.2 Analytical methods

Analytical methods (the GTK codes) used for the different sample media are compiled according to the medium in Table 2. A detailed description of each method follows below. The detection limits of each method are presented in Table 3.

4.2.2.1 Method 814G

The residual humidity of air-dried samples was determined by drying approximately 3 g of an air-dried subsample at 105 °C for 2 hours for method 814G. After this, the dried sample was ashed at 550 °C for 2 hours to define the loss on ignition (LOI).

4.2.2 2 Method 206I

A 3-g portion of each organic sample was extracted with 30 ml of de-ionised water at room temperature for two hours. After allowing the solutions to stand overnight, the pH was measured using a Radiometer ION85 analyser.

Table 2. A compilation of analytical methods (GTK codes) used for samples of the organic soil layer (ORG) and terrestrial moss (MOS).

	ORG	MOS
503P/503M	●	●
503H	●	●
201P/M	●	
818G	●	
206I	●	
814G	●	
820L	●	
γ-spectrometry*	●	

*Gamma nuclides (^{137}Cs, ^{134}Cs) were determined at the laboratories of the Finnish Radiation and Nuclear Safety Authority (STUK) in Helsinki and Rovaniemi, Finland, and the Research-Industrial Association V.G. Khlopin Radium Institute in St. Petersburg, Russia.

4.2.2.3 Methods 201P and 201M

Elements in the mobile fraction of the organic layer (ORG) samples were determined by extraction with a buffered 1 M ammonium acetate solution, having a pH of 4.5. A 2-g subsample was weighed into a polyethylene test tube and was extracted with 30 ml ammonium acetate solution at room temperature for two hours. A detailed description of the procedure is presented by Salminen *et al.* (2004). The organic layer samples were analysed by the ICP-AES using a Thermo Jarrell Ash IRIS/Duo ICP-AES instrument for the determination of Al, Ba, Ca, Co, Fe, K, Mg, Mn, Ni, P, S, Sr and Zn.

4.2.2.4 Methods 503P, 503M and 503H

Sample digestion by nitric acid was carried out according to the EPA 3051 standard method (U.S. Environmental Protection Agency 1990) for the organic soil layer, moss and vegetation. A detailed description of the procedure is provided in Salminen *et al.* (2004).

Moss samples were analysed by ICP-AES, ICP-MS and CVAAS: for Al, Ca, Fe, K, Mg, Mn, Na, P and S using a Thermo Jarrell Ash IRIS/dual ICP-AES instrument (503P), and for Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Th, Tl, U, V and Zn using a Perkin Elmer Sciex Elan 6000 (503M). A Perkin Elmer FIMS-400 atomic absorption spectrometer (503H) was used to analyze the samples for Hg.

Organic layer samples were analysed by ICP-AES, ICP-MS and CVAAS: for Al, B, Ca, Fe, K, Li, Mg, Mn, Na, P and S using a Thermo Jarrell Ash IRIS/Duo ICP-AES instrument (503P), for Ag, As, Ba, Be, Bi, Br, Cd, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Th, Tl, U, V and Zn using a Perkin Elmer Sciex Elan 5000 mass spectrometer (503M), and for Hg with a Perkin Elmer FIMS-400 instrument (503H).

4.2.2.5 Method 820L

Carbon and nitrogen in organic soil samples were measured using an Elementar vario MAX CN elemental analyser. A detailed description of the procedure is provided in Salminen *et al.* (2004).

4.2.2.6 Gamma spectrometric measurements

From the organic layer samples (ORG), the gamma nuclides (^{137}Cs, ^{134}Cs) were determined at the laboratories of the Finnish Radiation and Nuclear Safety Authority (STUK) in Helsinki and Rovaniemi, Finland, and the Research-Industrial Association V.G. Khlopin Radium Institute in St. Petersburg, Russia. A detailed description of the procedure is provided in Salminen *et al.* (2004).

5 DATABASE, DATA PROCESSING AND MAP DRAWING

For the Barents Ecogeochemistry project, an integrated database was developed to provide systematic and structured storage and effective use of all the data for complex interpretation and the compilation of geochemical maps. This database, called BarentsBase, is capable of storing all of the heterogeneous field descriptions and analytical data collected during the project. The BarentsBase data include detailed descriptions of the sampled media, sampling procedure, and methods of sample preparation and analysis. Data from Finland and Russia were selected from this database for this project and were combined with data from the Baltic countries in a common Excel file, which was used for map drawing.

The geochemical maps were drawn in the Lithuanian Geological Survey using Golden Software Surfer. The colour surface is based on interpolated data and actual sampling sites are shown as dots; the size of the dots indicates the measured element concentration (classified data) of the sample. The Point Kriging method was applied for data gridding (interpolation) on the contour maps and the linear variogram calculating the 24 nearest neighbours was used.

6 RESULTS

The results of the project are presented here as element distribution maps (Maps 1–85), which show the distribution of elements in the whole study area. Some statistical parameters from the whole data set are provided in Table 4.

Table 3. Detection limits for all elements and methods. For Cs isotopes, the detection limit is sample specific depending on the measurement time.

	Moss (MOS)		Organic layer (ORG)			
			Total		Partial	
Element	DL mg/kg	Method	DL mg/kg	Method	DL mg/kg	Method
Ag	0.01	503M	0.01	503M		
Al	5	503P	15	503P	10	201P
As	0.02	503M	0.02	503M	0.02	201M
B	0.5	503M	5	503P		
Ba	0.05	503M	0.05	503M	0.05	201M
Be			0.02	503M		
Bi			0.2	503M		
Br			20	503M		
C			0.10 %	820L		
Ca	20	503P	50	503P	10	201P
Cd	0.005	503M	0.01	503M		
Co	0.02	503M	0.02	503M	0.05	201M
Cr	0.2	503M	0.2	503M		
Cs						
Cu	0.02	503M	0.02	503M		
Fe	5	503P	5	503P	20(5)	201P
Humidity			0.10 %	820L		
Hg			0.04	503H		
K	50	503P	100	503P	1(10)	201P
Li	0.05	503M	0.2	503P		
LOI			0.05 %	818G/813G		
Mg	5	503P	10	503P	10(1)	201P
Mn	1	503P	1	503P	1	201P
Mo	0.01	503M	0.01	503M		
N			0.05 %	820L		
Na	20	503P	50	503P		
Ni	0.3	503M	2 0.3	503P 503M	0.3	201M
P	30	503P	50	503P	20(30)	201P
Pb	0.02	503M	0.02	503M	0.05	201M
Rb	0.01	503M	0.01	503M		
S	10	503P	50	503P	10	201P
Sb	0.02	503M	0.02	503M		
Sn	0.1	503M	0.1	503M		
Sr	0.01	503M	1 0.01	503P 503M	0.01	201M
Th	0.02	503M	0.02	503M		
Tl	0.005	503M	0.01	503M		
U	0.005	503M	0.01	503M		
V	0.02	503M	0.02	503M		
Zn	0.4	503M	1 0.4	503P 503M	0.4	201M

Table 4. Summary statistics of the analytical results. N = number of samples. ORG = organic soil layer (humus), MOS = terrestrial moss sample, DL = detection limit. For details of the analytical methods, see chapter 5. All concentrations are in mg kg^{-1}, unless otherwise stated.

	Media	Sample processing	N	Minimum	10th percentile	Median	Mean	90th percentile	Maximum	Standard deviation
Ag	MOS	Total	476	<DL	0.02	0.03	0.03	0.04	0.20	0.01
Ag	ORG	Total	473	0.02	0.05	0.12	0.15	0.29	1.19	0.12
Al	MOS	Total	476	46.9	166	316.50	383.30	640.63	4420	303
Al	ORG	Total	473	681	1390	2600	3350	6496	19700	2384
Al	ORG	Amm.acetate	474	<DL	38.5	87.8	134	255	1510	147
As	MOS	Total	476	<DL	0.10	0.18	0.20	0.31	2.68	0.15
As	ORG	Total	473	0.25	0.91	1.56	1.86	2.88	17.80	1.27
B	MOS	Total	476	<DL	1.42	2.98	3.75	7.12	25.60	2.82
B	ORG	Total	473	2.04	5.00	5.00	5.65	7.56	31.50	2.05
Ba	MOS	Total	476	3.35	10.10	18.4	21.7	36.9	261	15.7
Ba	ORG	Total	473	11.6	31.74	65.4	75.2	136.8	241	40.7
Ba	ORG	Amm.acetate	474	4.64	12.20	27.8	30.5	54.2	89.0	16.5
Be	ORG	Total	473	<DL	<DL	0.07	0.11	0.25	0.72	0.11
Bi	ORG	Total	473	<DL	<DL	<DL	0.22	0.27	0.45	0.04
Br	ORG	Total	473	<DL	<DL	28.7	38.7	68.3	272	27.9
C %	ORG	CHN-analyser	473	3.20	23.7	40.8	37.6	47.4	49.8	9.63
Ca	MOS	Total	476	1100	2080	2980	3380	5190	14400	1570
Ca	ORG	Total	473	1330	2104	3570	4920	8550	83600	5060
Ca	ORG	Amm.acetate	474	281	1452	2600	3590	6710	72500	4070
Cd	MOS	Total	476	0.07	0.11	0.18	0.20	0.27	1.67	0.11
Cd	ORG	Total	473	0.08	0.22	0.40	0.42	0.61	3.18	0.21
Co	MOS	Total	476	0.06	0.12	0.20	0.25	0.42	2.02	0.19
Co	ORG	Total	473	0.29	0.56	1.16	1.93	4.10	12.6	1.93
Co	ORG	Amm.acetate	474	<DL	<DL	<DL	0.65	0.94	3.80	0.41
Cr	MOS	Total	476	<DL	0.43	0.68	0.85	1.25	9.07	0.74
Cr	ORG	Total	473	1.35	2.67	4.48	6.46	11.9	152	8.31
^{134}Cs	ORG	γ-spectrometer	474	0.41	1.00	4.00	6.86	15.8	77.3	8.93
^{137}Cs	ORG	γ-spectrometer	474	14.0	69.0	150	592	1660	11460	1188
Cu	MOS	Total	476	1.97	4.05	5.37	5.88	8.15	23.9	2.16
Cu	ORG	Total	473	2.85	5.18	7.60	9.30	13.2	87.3	6.96
Fe	MOS	Total	476	65.50	191	349	442	734	3850	339
Fe	ORG	Total	473	767.00	1540	2890	3820	7290	21400	2930
Fe	ORG	Amm.acetate	474	<DL	<DL	25.4	79.0	157	1500	175
Hg	ORG	Total	473	0.04	0.13	0.20	0.20	0.28	0.42	0.06
Humidity%	ORG	Gravimetric	473	1.00	3.82	6.00	5.85	7.40	10.7	1.38
K	MOS	Total	476	2830	4430	5930	6280	8470	26000	2025.21
K	ORG	Total	473	455	781	1010	1120	1560	4460	438
K	ORG	Amm.acetate	474	93.5	412	695	706	1020	1520	239
Li	MOS	Total	476	<DL	0.10	0.18	0.23	0.40	3.70	0.22
Li	ORG	Total	473	0.20	0.50	1.27	2.34	5.48	31.70	3.20
LOI %	ORG	Gravimetric	473	6.20	42.1	79.3	72.3	91.8	95.9	19.6

	Media	Sample processing	N	Minimum	10th percentile	Median	Mean	90th percentile	Maximum	Standard deviation
Mg	MOS	Total	476	391	815	1100	1190	1650	4979	448
Mg	ORG	Total	473	208	386	624	871	1620	5370	722
Mg	ORG	Amm.acetate	474	69.7	208	386	470	825	2590	318
Mn	MOS	Total	476	33.0	136.0	299	332	533	2040	205
Mn	ORG	Total	473	23.6	67.3	265	430	1007	4880	507
Mn	ORG	Amm.acetate	474	7.50	42.2	168	241	517	1680	240
Mo	MOS	Total	476	0.03	0.08	0.13	0.15	0.21	0.92	0.07
Mo	ORG	Total	473	0.12	0.31	0.47	0.53	0.83	2.09	0.25
N %	ORG	Total	473	0.27	1.00	1.50	1.49	1.97	2.54	0.38
Na	MOS	Total	475	<DL	51.2	71.0	80	117	333	37.2
Na	ORG	Total	473	30.0	36.7	50.0	61	89	424	31.5
Ni	MOS	Total	476	0.45	0.99	1.47	1.77	2.51	16.9	1.44
Ni	ORG	Total	473	1.54	3.23	5.06	6.38	10.6	131.5	6.73
Ni	ORG	Amm.acetate	474	<DL	<DL	0.60	0.74	1.10	8.00	0.56
P	MOS	Total	476	645	1120	1570	1637	2230	3260	435
P	ORG	Total	473	90.2	579	814	8209	1080	2270	223
P	ORG	Amm.acetate	474	20.0	58.2	130	144	242	826	79.0
Pb	MOS	Total	476	1.19	2.87	4.52	4.99	7.59	46.8	2.75
Pb	ORG	Total	473	6.52	15.8	31.1	33.3	49.5	361	21.3
Rb	MOS	Total	476	2.08	10.1	19.9	22.4	37.1	102	12.0
Rb	ORG	Total	473	2.15	4.13	8.15	9.31	15.4	47.7	5.64
S	MOS	Total	476	431	874	1120	1150	1470	2400	248
S	ORG	Total	473	148	889	1540	1540	2150	4310	508
S	ORG	Amm.acetate	474	19.8	74.8	135	138	199	340	50.6
Sb	MOS	Total	476	<DL	0.04	0.08	0.09	0.16	0.36	0.05
Sb	ORG	Total	473	<DL	0.08	0.27	0.34	0.51	27.2	1.25
Sn	MOS	Total	473	<DL	<DL	0.17	0.21	0.36	1.76	0.17
Sn	ORG	Total	473	0.10	0.16	0.51	0.64	1.23	7.34	0.55
Sr	MOS	Total	476	2.07	4.75	8.12	9.46	15.4	44.1	5.01
Sr	ORG	Total	473	6.56	9.80	20.9	23.3	41.2	86.6	12.7
Sr	ORG	Amm.acetate	474	<DL	5.12	10.5	12.4	22.5	43.3	7.16
Th	MOS	Total	476	<DL	0.04	0.07	0.09	0.18	0.96	0.09
Th	ORG	Total	473	0.14	0.33	0.82	1.28	2.63	22.6	1.50
Tl	MOS	Total	476	<DL	0.03	0.08	0.08	0.14	0.32	0.05
Tl	ORG	Total	473	0.05	0.10	0.17	0.18	0.26	0.64	0.07
U	MOS	Total	476	<DL	0.01	0.03	0.04	0.07	0.82	0.05
U	ORG	Total	473	0.05	0.11	0.23	0.37	0.64	17.30	0.84
V	MOS	Total	476	0.46	1.10	1.81	2.25	3.28	53.4	2.97
V	ORG	Total	473	3.61	5.84	9.52	12.1	19.6	303	15.0
Zn	MOS	Total	476	10.9	22.3	30.9	32.6	43.4	151	10.7
Zn	ORG	Total	473	7.7	26.7	44.4	49.0	75.6	207	23.5
Zn	ORG	Amm.acetate	474	<DL	9.71	20.0	22.7	36.8	90.9	13.5

7 DISCUSSION OF ELEMENT DISTRIBUTION PATTERNS AND THE ORIGIN OF ANOMALIES

7.1 Continuation of Tl and Cs anomalies in the Baltic countries

7.1.1 Distribution patterns of thallium

In the geochemical mapping of the eastern Barents Region (Barents Ecogeochemistry project, Salminen *et al.* 2004), the highest Tl concentrations in each studied material (top and bottom soil, stream water, organic soil layer and moss) were detected in southern Finland, southern Russian Karelia and the Leningrad region (Figure 3). The highest values observed from the soil samples were also very close to or even higher than the action limits for contaminated land proposed by the Finnish authorities (see e.g. Assmuth 1997). The distribution pattern of Tl in mosses is especially striking, suggesting airborne transportation of Tl from the south or southwest.

The distribution patterns of Tl in both the moss and the organic soil layer show very similar features (Salminen *et al.* 2004). A striking feature is lateral zonality following the climate and vegetation zones. Thallium concentrations are lower in the tundra/forest tundra vegetation zone than in the northern/middle taiga areas. The lowest values exist in the northeasternmost part of the tundra zone, from where the concentrations increase towards the south and southwest. Local Tl anomalies, however, surround the heavily industrialized areas of Arkhangelsk and Vorkuta in the northern part of Russia.

The distribution patterns of the Tl data markedly differ in the Baltic Sea region from the whole Barents Ecogechemistry project area. This is due to the higher concentration level of Tl in this area (Table 5). As a result of this feature, practically all of the high anomalies of the Barents Ecogeochemistry data are located in this area.

Table 5. Median values of the Tl concentration (mg kg^{-1}) in mosses and the organic soil layer in the whole Barents Ecogeochemistry project and in data from the eastern Baltic Sea region.

	Baltic region	Barents region
Organic soil layer	0.17	0.11
Moss	0.08	0.04

Focusing the survey on the Baltic Sea region only, more details become apparent for the strongest anomaly patterns. The area of very high Tl concentration values in mosses does not continue from southeastern Finland to Estonia on the southern side of the Gulf of Finland, as was supposed. However, in the organic layer samples, very high values are found on the both sides of Estonian-Russian border in the area where oil shale was used for decades as fuel in power plants. In the moss data, the highly anomalous values correspond to densely populated and highly industrialized areas such as St. Petersburg, Helsinki and Turku. However, the largest area of high Tl values is located in southeastern Finland over the rapakivi granite area. In this area, the element association K-Rb-Tl is typical for the young granites, and the Tl concentration is therefore also higher in the local minerogenic dust. On the other hand, according to the prevailing wind directions, emissions from the power plants on the southern coast of Gulf of Finland and from the Kunda cement factory, also located on the northern coast of Estonia, are considered to be the cause of the high Tl values. Cement manufacturing is one important source of Tl. According to McGrath (1998), plants growing around cement factories are most likely to have elevated levels of Tl; *Cruciferae* species accumulated up to approximately 450 mg/kg Tl near a cement plant in Germany. Ashes collected from chimneys of power plants using oil shale as fuel presented values between 7.5–9.0 mg/kg and 27 mg/kg (J. Kivisilla, Eesti Geoloogiakeskus, personal communication). Teinemaa *et al.* (2002) reported that the southern coast of Finland is contaminated by elements such Ca and Tl because of the long-range transport of ash from the Estonian oil shale burning plants.

According to the Geochemical Atlas of Europe (Salminen *et al.* 2005), the Tl concentration of the organic soil layer in the industrialized areas of Central Europe does not differ from the observed values in the Baltic Sea region. Thus, the atlas does not provide any evidence for the long distance airborne transportation of Tl from Central Europe to the area of the Gulf of Finland.

7.1.2 Distribution of caesium

The worst accident in the history of the peaceful use of nuclear energy occurred on 26 April 1986 in Chernobyl, Ukraine. Due to the prevailing meteorological conditions, the radioactive fallout was

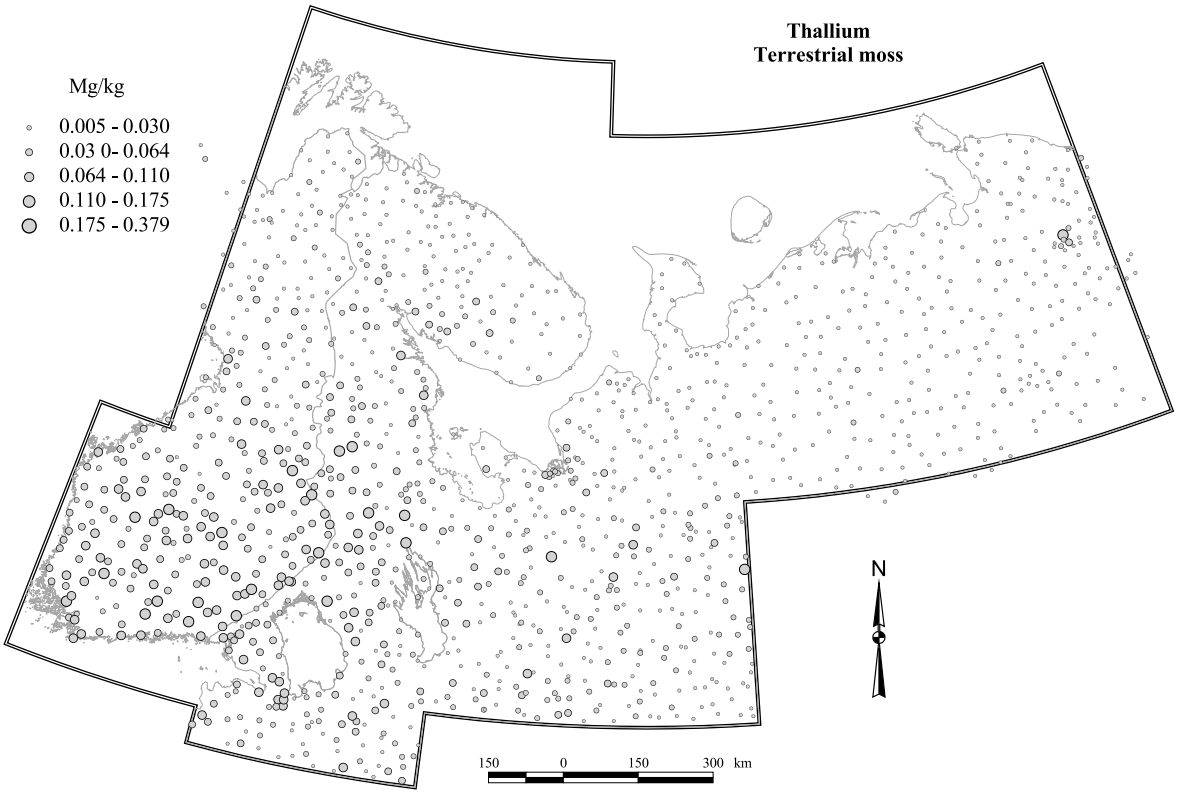


Figure 3. Distribution of Tl in terrestrial mosses (*Hylocomium*) in the area covering Finland and northwestern Russia. The map is reproduced from the data of the Barents Ecogeochemistry project (Salminen *et al.* 2004).

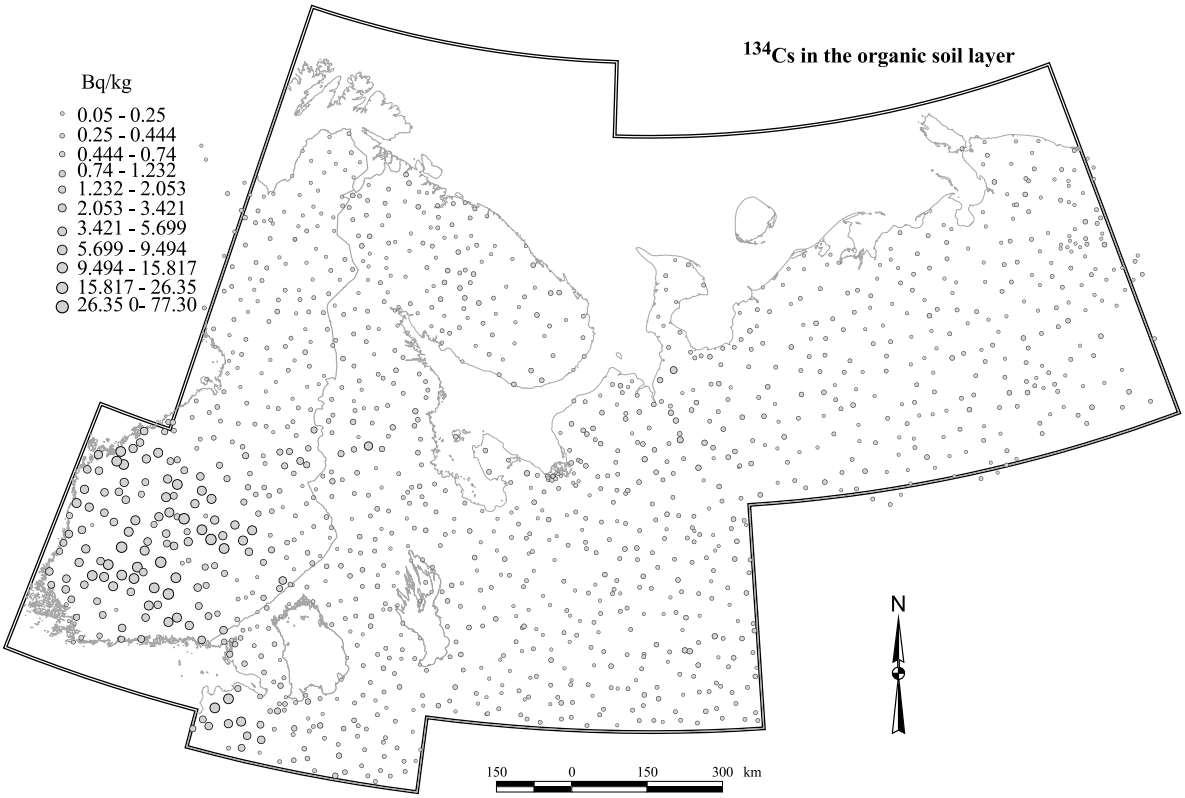


Figure 4. Distribution of ^{134}Cs isotopes in the soil organic layer in the western part of the Barents Ecogeochemistry project. Reproduced from the data published by Salminen *et al.* (2004).

unevenly distributed. Southern Finland and Central Sweden received a relatively high amount of radioactive deposition, but in the Baltic countries the deposition was much less and very unevenly distributed (Realo *et al.* 1995). Leningrad region and the northeastern corner of Estonia belonged to the same higher deposition area as Finland and Sweden. However, western parts of Lithuania and Estonia received a much lower amount of deposition (Rissanen *et al.* 2005)

The Chernobyl-specific radionuclide ^{134}Cs was still detectable from the organic soil layer in 2000-2003 in South Finland and the Leningrad region, despite its relatively short half-life (2 years). Elsewhere in the study area, the original fallout was so much lower that it was no longer detectable. From this sample material, Ylipieti (2008) found some radioactive particles including ^{60}Co, ^{125}Sb isotopes. The ^{137}Cs isotope is more common, and because of its longer half-life, it still describes well the whole area affected by radioactive fallout from Chernobyl.

7.2 Anthropogenic/geogenic origin of the anomalies

Whether the origin of anomalies is geogenic or anthropogenic was roughly estimated by comparing the distribution patterns with information on human activities. Geogenic properties were studied by looking for typical geochemical element associations and landscape properties that indicate a geogenic origin. Observed correlations are described below and Table 6 summarises the proportion of anthropogenic and geogenic components for each studied element.

Although moss samples are generally considered as indicators of anthropogenic airborne pollution, most of the studied elements also showed a clear geogenic component in the element concentration of mosses. In most cases, these components originate via minerogenic dust from open areas such as cultivated fields. This is airborne but not pollution and it belongs to the normal geological variation of elements in nature.

Table 6. Origin of anomalies estimated on the basis of all available information on human activities in and the geological properties of the study area. n.d.= no data.

	MOS		ORG	
Ag		G	a	G
Al	a	G	a	G
As	A	G	A	G
B	a	G		G
Ba		G		G
Be	n.d.			G
Bi	n.d.		A	G
Br	n.d.			G
Ca	a	G	a	G
Cd	A		a	G
Co		G		G
Cr	a	G	a	G
Cu	A		A	G
Fe	a	G	a	G
Hg	n.d.		A	G
K		G		G
Li		G		G
Mg		G		G
Mn		G		G
Mo	A		A	G
Na		G		G
Ni	A		A	G
P		G		G
Pb	A		A	G
Rb		G		G
S	A		A	G
Sb	A		A	G
Sn	A	G	a	g
Sr		G	a	G
Th	A	G		G
Tl	a	G	a	G
U	A	G	a	G
V	A		A	G
Zn	A	G	a	G

A = strong anthropogenic influence,
G = strong geogenic influence
a = weak anthropogenic influence
g = weak geogenic influence

7.2.1 Interpretation of anomalies and estimation of the anthropogenic and geogenic component

Silver (Ag)

	MOS	ORG
Anthropogenic anomalies	The surroundings of St. Petersburg, west of Lake Ladoga, and the northern coastal area of Estonia. The anomaly in W Latvia – NW Lithuania is partly due to the oil industry. In western Lithuania, no respective anomaly was detected in the Geochemical Atlas of Lithuania (Kadūnas *et al.* 1999).	In western Lithuania and Latvia, diffuse contamination by long distance airborne transport. An old anomaly surrounding the Harjavalta smelter in southwestern Finland (no new emissions since 1998 due to the installation of modern cleaning technology).
Geogenic anomalies		In the Shield area, concentrations are higher than in the areas of sedimentary rocks.

Aluminium (Al)

	MOS	ORG
Anthropogenic anomalies	An anomaly at the Russian-Estonian border is due to the exploitation of bauxite deposits and the related industry.	An anomaly at the Russian-Estonian border is due to the exploitation of bauxite deposits and the related industry.
Geogenic anomalies	Most anomalies are geogenic in origin due to minerogenic local dust (respective distribution patterns are also typical for Rb, Tl, Sb and Fe anomalies).	Most anomalies are geogenic in origin (respective distribution patterns are also typical for Rb and Fe). The distribution patterns of the total and ammonium acetate leach are identical.

Arsenic (As)

	MOS	ORG
Anthropogenic anomalies	In NE Estonia, anomalies are related to the local oil shale industry and power plants. In SW Lithuania, cause of the anomalies is Kaliningrad and its industry, together with the local oil industry. In Finland, the Harjavalta smelter and metal industry in Seinäjoki area cause anomalies.	In Finland, the Harjavalta smelter and metal industry in Seinäjoki area also cause anomalies in the organic soil layer. The oil shale industry in the Narva region. In SW Lithuania, possible pollution from the Kaliningrad industrial region.
Geogenic anomalies	In the eastern part of the Russian territory, no potential anthropogenic sources are known. In Lithuania, anomalies also follow the geological structure, which includes the oil deposits, although the oil industry is probably the main reason for high As concentrations. In Saaremaa, high As concentrations appear both in moss and organic layer samples. The sampling site is peatland and no reason for the high As concentrations is known.	See explanation for MOS. In SW Finland, the polymetallic anomaly is due to hydrothermal processes in the upper crust.

Boron (B)
More than half of the ORG results are below the detection limit.

	MOS	ORG
Anthropogenic anomalies	None.	None.
Geogenic anomalies	Most anomalies are closely related to the sedimentary rocks and especially to the carbonate rocks.	All anomalies are related to carbonate-bearing sedimentary rocks.

Barium (Ba)

	MOS	ORG
Anthropogenic anomalies	None.	None.
Geogenic anomalies	Anomalies are very scattered and thus cannot be connected to any particular bedrock unit, except that the anomalies are more numerous in the Shield area than in the area of sedimentary rocks.	The background level is higher in the area of the Fenno-scandian (Baltic) Shield and adjacent areas in the Russian Platform, where the surficial deposits consist of drift from the Shield area. Sedimentary rocks in Russia generally cause different distribution patterns than the sedimentary rocks in the Baltic countries. Distribution patterns from the total and ammonium acetate leach are the same.

Beryllium (Be)

	MOS	ORG
Anthropogenic anomalies	No data.	None.
Geogenic anomalies	No data.	In SW Finland, the polymetallic anomaly is due to hydrothermal processes in the upper crust.

Bismuth (Bi)
Most of the values are below the detection limit. However, high values in southern Finland are interesting.

	MOS	ORG
Anthropogenic anomalies	No data.	A metal smelter in Harjavalta and industry in the Helsinki region and other parts of the southern coast.
Geogenic anomalies	No data.	In SW Finland, the polymetallic anomaly is due to hydrothermal processes in the upper crust

Bromium (Br)
The map shows natural variation in element concentrations in the organic soil layer.

Carbon (C)
Apparently, the ORG sample quality in Latvia differs from that in the other countries. The photographs reveal that the sampling sites are in most cases in very old forests where the humus layer is thick and cannot contain very much minerogenic material. This is a natural and clear difference from other countries. Normalizing the data against the C concentration or LOI was discussed, but would probably cause new problems. Otherwise, the variation is natural.

Calcium (Ca)
All anomalies in both moss and humus reflect the bedrock and its carbonate-bearing sedimentary rocks. No difference between total and ammonium acetate leachable concentrations was detected.

	MOS	ORG
Anthropogenic anomalies	The combustion of oil shale in the Narva area and the cement factory in the Kunda area.	The combustion of oil shale in the Narva area and the cement factory in the Kunda area.
Geogenic anomalies	Typically high values above limestones	

Cadmium (Cd)
Cadmium is a strongly biophilic element and its distribution patterns thus share similar features with, for instance, S anomalies.

	MOS	ORG
Anthropogenic anomalies	The southern coast of Finland, the Leningrad region, SW Latvia (industrial area including the Liepaja oil harbour), the surroundings of the Mazeikiai oil plant in Lithuania, and the Vilnius area.	No clearly anthropogenic anomalies can be seen in Russia, Finland, Lithuania or Estonia. The anomaly in SW and W Latvia coincides with a former military and present day industrial area, including the Liepaja oil harbour.
Geogenic anomalies	Probable anomalies in southern Lithuania.	Variation in the background areas is due to geogenic dust.

Cobalt (Co)
The high value in moss in SW Lithuania cannot be explained. Most of the ammonium acetate leachable concentrations are below the detection limit.

	MOS	ORG
Anthropogenic anomalies	Cities of Turku and Helsinki, dust from the Sastamala mine, the Imatra-Svetogorsk industrial area.	None.
Geogenic anomalies	Most of anomalies are considered as geogenic.	All anomalies are considered as geogenic. The polymetallic anomaly in SW Finland is due to hydrothermal processes in the upper crust.

Chromium (Cr)
The distribution patterns are generally much the same as for Co. Both in humus and moss high values are due to minerogenic impurities, such as clay particles

	MOS	ORG
Anthropogenic anomalies	Metal industry of the Turku and Seinäjoki areas, St. Petersburg area, and Narva in Estonia.	In the immediate vicinity of St. Petersburg, Narva and Kunda.
Geogenic anomalies	None.	Most of the anomalies are considered geogenic. The polymetallic anomaly in SW Finland is due to hydrothermal processes in the upper crust.

Caesium (Cs) isotopes

	MOS	ORG
Anthropogenic anomalies	No data	Anomalies caused by emissions following the Chernobyl nuclear power plant accident.
Geogenic anomalies	No data	None.

Copper (Cu)

There is probably a difference in the analytical level between the Barents and Baltic data.

	MOS	ORG
Anthropogenic anomalies	Large anomalies surround Harjavalta smelter and St. Petersburg.	Large anomalies surround Harjavalta smelter and St. Petersburg.
Geogenic anomalies	None.	Outokumpu region in eastern Finland, anomalies in the eastern part of the Russian territory (the Lake Onega area), and south of St. Petersburg.

Iron (Fe)

The reason for single high values in Russia is not known. The analytical level in Latvia is lower than in the other areas. Ammonium acetate and total extraction show similar Fe distribution patterns.

	MOS	ORG
Anthropogenic anomalies	The anomaly in the Imatra-Svetogorsk area is due the local industry. Human activities correlate strongly with the anomalies. The highest concentrations are in densely populated and agricultural areas.	The anomalies in Turku and the Imatra-Svetogorsk area are due to the local industry. Human activities correlate strongly with the anomalies.
Geogenic anomalies	Al and Li correlate with Fe, showing that the main origin is geogenic dust, particularly in agricultural areas.	Al and Li correlate with Fe, showing that the main origin is geogenic dust, particularly in agricultural areas. The polymetallic anomaly in SW Finland is due to hydrothermal processes in the upper crust.

Mercury (Hg)

Observed values of ORG samples are mainly in the range of natural variation. There is no explanation for the high values in the eastern Russian territory.

	MOS	ORG
Anthropogenic anomalies	No data available.	The anomaly in central Lithuania is due to emissions from a fertilizer factory. In SW Lithuania, emissions from the Kaliningrad industries?
Geogenic anomalies	No data available.	

Potassium (K)
Ammonium acetate leachable and total concentrations mostly show similar distribution patterns.

	MOS	ORG
Anthropogenic anomalies	None	None
Geogenic anomalies	Distribution patterns have a good correlation with Rb and Ba. This is an evidence of geogenic dust as the main source of K. Anomaly patterns mainly show natural variation in concentrations. No particular point source can be shown.	Distribution patterns have a good correlation with Rb and Ba. This is an evidence of geogenic dust as the main source of K. Anomaly patterns mainly show natural variation in concentrations. No particular point source can be shown.

Lithium (Li)
Analytical results for Latvian ORG samples are not correct/due to the high LOI.

	MOS	ORG
Anthropogenic anomalies	None.	None.
Geogenic anomalies	Good correlation with Al, Fe and Th. Typically a geogenic element.	Good correlation with Al, Fe and Th. Typically a geogenic element. The polymetallic anomaly in SW Finland is due to hydrothermal processes in the upper crust.

LOI
Compare with carbon

Magnesium (Mg)
Good correlation with Ca. Both materials show similar distribution patterns in Finland, Estonia and Russia. The strongest anomalies are in the most open cultivated areas, while forested areas show lower concentrations.

	MOS	ORG
Anthropogenic anomalies	No anthropogenic anomalies except those that are due to open cultivated areas (Estonia), where minerogenic dust is the cause of the high Mg concentration.	No anthropogenic anomalies except those that are due to open cultivated areas, where minerogenic dust is the cause of the high Mg concentration.
Geogenic anomalies	All anomalies are geogenic. In Latvia and Lithuania they are due to dolomitic bedrock.	All anomalies are geogenic. In Finland, Ammonium acetate leachable concentrations are low because Mg comes from silicates. The polymetallic anomaly in SW Finland is due to hydrothermal processes in the upper crust.

Manganese (Mn)
An anomaly in SE Lithuania also exists in the soil samples (Kadūnas *et al.* 1999). There is an enrichment of Mn in soils due to weathering and suitable pH-Eh conditions. In Russia, the anomalies are very much related to the landscape: high Fe was also recognized in stream waters in the same areas (Salminen *et al.* 2004). No anthropogenic reason is known in Russia. In the Baltic countries, the data show lower Mn concentrations than in the other areas. The distribution patterns of ORG data after the ammonium acetate leach and total analysis are very much the same.

Molybdenum (Mo)

The reason for the high anomaly in Saaremaa is not known.

	MOS	ORG
Anthropogenic anomalies	In the Latvian-Lithuanian border area, the anomalies are due to the influence of the Mazeiku oil industrial area. In the Leningrad region, the Karelian Isthmus and in southern Finland, the anomalies are typically anthropogenic. In Estonia, emissions from the combustion of oil shale cause high anomalies.	In the Latvian-Lithuanian border area, the anomalies are due to the influence of the Mazeiku oil industrial area. In the Leningrad region, the Karelian Isthmus and in southern Finland, the anomalies are typically anthropogenic. In Estonia, emissions from the combustion of oil shale cause anomalies.
Geogenic anomalies	The source of low anomalies in northern Estonia is, in addition to emissions from industry, the local Dichtyonema shale (oil shale).	None.

Sodium (Na)

Latvian MOS samples are most probably contaminated in some way.

	MOS	ORG
Anthropogenic anomalies	None.	None.
Geogenic anomalies	The effect of sea spray can be seen along most of the coasts.	There are many samples that have analytical data below the detection limit. The concentration levels appear slightly different in the Barents and Baltic data.

Nickel (Ni)

The anomaly in SW Lithuania is due to the low quality of the sample.

	MOS	ORG
Anthropogenic anomalies	All anomalies are interpreted to be of anthropogenic origin. The large anomaly in SW Finland is due to the Harjavalta Ni smelter, while north of it is an anomaly that is due to an iron industrial plant. The city of St. Petersburg and industrial areas east of it cause a wide and strong anomaly. The Mazeiku oil industry is the source of the anomaly in NW Lithuania.	Anomalies are mostly identical with the MOS sample anomalies. However, the anomaly caused by earlier operation of the Elektrenai coal power plant and Harjavalta smelter are clearly seen in ORG sample data, but no longer in MOS sample data. The metal industry east of St. Petersburg, and Svetogorsk-Imatra industrial area.
Geogenic anomalies	Single high values throughout the area are due to normal natural variation.	No geogenic anomalies were observed, except the anomaly in S Finland, which has no known anthropogenic cause. In the ammonium acetate leach, most of the results are below the detection limit. However, the patterns are very similar to total leach anomalies, except for the anomaly in S Finland. This confirms the geogenic origin of the anomaly.

Phosphorus (P)

The analytical level of ORG samples seems to be slightly lower in the Baltic countries data compared with the Barents data. For instance, the anomalies caused by phosphorite are clear in Russia but not seen in Estonia.

	MOS	ORG
Anthropogenic anomalies	None.	No clear anthropogenic anomalies were observed. Variation is very small in Finland and in the Baltic countries.
Geogenic anomalies	The highest anomalies are in Latvia, but neither anthropogenic nor geogenic point sources can be detected.	In Russia, the anomalous values have no correlations with C, so the source was interpreted to be geogenic.

Lead (Pb)

The analytical level of ORG samples in Latvia seems to be slightly higher than in the other countries.

	MOS	ORG
Anthropogenic anomalies	In southern Finland and the St. Petersburg region, clear anthropogenic anomalies are due to traffic and other human activities. In the Lithuanian–Polish border area, the top soil and organic rich soils are recognized to be enriched in lead. No local anthropogenic source is known; thus, the strong anomaly in southwestern Lithuania and Latvia is probably due to airborne transportation from some longer distance (Kaliningrad?).	The patterns partly coincide with the anomalies in MOS. Thus, lead in the organic soil layer is partly derived from anthropogenic, and partly geogenic sources.
Geogenic anomalies	None.	Anomaly patterns in southwestern Lithuania and Latvia and southeastern Finland follow the lithological units (Mesozoic zone in Lithuania and Latvia and rapakivi in Finland).

Rubidium (Rb)

	MOS	ORG
Anthropogenic anomalies	None.	None.
Geogenic anomalies	In the Shield area, concentrations are higher due to dust from minerogenic soil, where feldspars include Rb. In southwestern Finland, the high anomaly coincides with a polymetallic anomaly detected in many materials. Anomalies in both MOS and ORG samples are geogenic. There are no known Rb pollution sources in the study area.	In the Shield area, concentrations are higher due to feldspars including Rb. In southwestern Finland, the high anomaly coincides with a polymetallic anomaly detected in many materials. Anomalies in both MOS and ORG samples are geogenic. There are no known Rb pollution sources in the study area. The polymetallic anomaly in SW Finland is due to hydrothermal processes in the upper crust.

Sulphur (S)

There is no known reason for the anomaly in southern Lithuania.

	MOS	ORG
Anthropogenic anomalies	Anthropogenic anomalies surround St. Petersburg; otherwise, the distribution patterns are very similar to those of the ORG sample anomalies.	In northern Lithuania and southern Latvia, the oil industry is a possible source of higher concentrations.
Geogenic anomalies	None.	In Russia, S concentrations correlate with N and P; thus, the metabolism of plants has a strong role in the anomaly formation. Sulphates in the bedrock (gypsum) are one possible source. Anomalies in Russia are considered as geogenic. Ammonium acetate leachable S is higher in the older Barents project data than in the new data from the Baltic countries, thus showing a probably different analytical level.

Antimony (Sb)

	MOS	ORG
Anthropogenic anomalies	Anthropogenic anomalies surround large cities such as St. Petersburg, Helsinki, Turku, Vilnius and Tallinn. There is no known reason for the high anomaly which covers most of Lithuania.	Anthropogenic anomalies surround large cities, as was also seen in the MOS data. There is no known reason for the other anomalies.
Geogenic anomalies	None.	None.

Tin (Sn)

	MOS	ORG
Anthropogenic anomalies	Anthropogenic anomalies in the large area surrounding St. Petersburg. Anomalies in southern Finland are also anthropogenic. In other regions, normal natural variation.	A possible anthropogenic anomaly in western Lithuania, although no reason is known (emissions from the Kaliningrad?).
Geogenic anomalies	SE Finland due to the tin mineralisations in rapakivi.	Generally normal natural variation.

Strontium (Sr)

	MOS	ORG
Anthropogenic anomalies	None.	The Kunda cement factory causes a small anomaly.
Geogenic anomalies	In the Shield area, concentrations are higher because of minerogenic dust from feldspar-rich minerogenic soil	Strontium is a typical geogenic element for the Fennoscandian Shield, where it is closely associated with Ca. A similar relationship is seen in the area with carbonate rocks. Ammonium acetate leachable and total leach results from ORG samples show very similar features.

Thorium (Th)

	MOS	ORG
Anthropogenic anomalies	Anthropogenic anomalies east of St. Petersburg. In the vicinity of Sillamäe in northwestern Estonia there should be an anomaly, but it is very weak. Much stronger anomalies occur south of Sillamäe, but they cannot be connected to the industry in Sillamäe. The Vyborg-Svetogorsk industrial area.	None.
Geogenic anomalies	The map mostly shows normal natural variation.	In Latvia, different concentration levels due to differences in LOI or analytical error. In southwestern Finland, the anomaly is in the area where a large geogenic polymetallic anomaly is located.

Thallium (Tl)

	MOS	ORG
Anthropogenic anomalies	Elevated concentrations are found in the surroundings of large cities (St. Petersburg, Helsinki, Tallinn, Turku). Narva and Kingisepp power plants, which use oil shale, cause low anomalies. An airborne anomaly caused by this industry forms part of the anomaly in SE Finland, although it is mostly geogenic.	Strong anomalies surround the oil shale power plants and Kunda cement factory, thus showing enrichment of Tl in the organic soil layer due to their emissions. The anomaly in the Lithuanian-Latvian border area is also due to a cement factory.
Geogenic anomalies	Concentrations are higher in the area of the Fennoscandian Shield due to K-rich minerals in the bedrock, till, and clay. The reasons for anomalies in western Lithuania and Latvia are not known.	Tl concentrations are higher in the area of the Fennoscandian Shield due to K-rich minerals in the bedrock, till, and clay. Most of the Tl is geogenic.

Uranium (U)

The analytical level in Latvia appears lower; on the other hand, Latvian samples have high LOI values.

	MOS	ORG
Anthropogenic anomalies	In northern Estonia–southwestern Russia, anomalies are due to power plants combusting oil shale. Emissions from industry east of St. Petersburg and in the Vyborg-Svetogorsk area cause clear anomalies. The city of St. Petersburg causes a rather high anomaly. Slightly lower anomalies surround Helsinki and Turku.	Oil shale power plants in Narva and Kingisepp cause anomalies; however, the origin could also be geogenic dust.
Geogenic anomalies	Anomalous values in southern Finland are due to dust from U mineralisations associated with rapakivi. The sources of high values in Saaremaa, central Estonia and northern Lithuania are not known, but they are considered as geogenic.	In Finland, high U values are due to migmatites and young K-granites. The polymetallic anomaly in SW Finland. In Lithuania, anomalies are also interpreted as geogenic.

Vanadium (V)

	MOS	ORG
Anthropogenic anomalies	All the anomalies are interpreted as anthropogenic due to emissions from oil and coal burning by industry. The highest anomalies are in the vicinity of the Imatra-Svetogorsk industries, Mazeikiai oil production, and metal industry east of St. Petersburg. All the large cities also cause anomalies.	Anomalies are seen in old industrial areas. Emissions from the Elektrenai coal power plant have caused an anomaly in ORG samples, but because the plant has not been used during recent years, the respective anomaly is not seen in MOS samples. Mazeikiai, St. Petersburg, Turku, Helsinki
Geogenic anomalies	None.	In southwestern Finland, the V anomaly coincides with a polymetallic anomaly due to the bedrock (the actual source in the bedrock is not known).

Zinc (Zn)

	MOS	ORG
Anthropogenic anomalies	St. Petersburg and the industrial sites east of it show higher concentrations. Helsinki, Tallinn, Turku and other large cities also cause slightly elevated concentrations. A higher anomaly is present in the Liepaja area, Latvia.	Liepaja, St. Petersburg.
Geogenic anomalies	Most of the anomalies are considered as geogenic.	Anomalies are considered as geogenic with minor input from anthropogenic activities described in connection of MOS data. A polymetallic anomaly in SW Finland. AmAc and total leach maps are identical.

8 REFERENCES

Asch, K. 2005. The 1:5 Million International Geological Map of Europe and Adjacent Areas. Hannover: BGR.

Assmuth, T. 1997. Selvitys ja ehdotuksia ympäristövaaraallisten aineiden pitoisuuksien ohjearvoista maaperässä – tiedolliset perusteet, määrittelyperiaatteet, soveltaminen, kehittäminen. Suomen ympäristökeskuksen moniste 92. Helsinki: Suomen ympäristökeskus. 56 p.

Gaal, G. 1986. 2200 million years of crustal evolution: the Baltic Shield. Bull. Geol. Soc. Finland, 58 (1), 149–168.

Gegorauskiene, V., Salminen, R., Reimann, C. & Chekushin V. 2000. Field Manual for Barents Ecogeochemistry project. Geological Survey of Finland, unpublished report S/44/0000/2/2000. 52 p.

Kadūnas, V., Budavicius, R., Gregorauskiene, V., Katinas, V., Kliaugiene, E., Radzevicius A. & Taraskevicius R. 1999. Lietuvos Geocheminis Atlasas – Geochemical Atlas of Lithuania. Vilnius: Geological Survey of Lithuania & Geological Institute. 91 p. + 162 maps.

Koistinen, T., Stephens, M.B., Bogatchev, V., Nordgulen, Ø., Wennerström, M. & Korhonen, J. 2001. Geological map of the Fennoscandian Shield, scale 1:2 000 000. Geological Surveys of Finland, Norway and Sweden and the North-West Department of Natural Resources of Russia.

McGrath S. P. 1998. Phytoextraction for soil remediation. In: Brooks, R. R. (ed.) Plants that Hyperaccumulate Heavy Metals. Wallingford: CAB Intern., 261–288.

Realo, E., Jõ, J., Koch, R. & Realo, K. 1995. Studies on radiocaesium in Estonian soils. Journal of Environmental Radioactivity 29, 111–119.

Rissanen, K, Ylipieti, J, Salminen R., Täht K., Gilucis A. & Gregorauskiene V. 2005. Cs-137 concentrations in the uppermost humus layer in the Baltic countries in 2003. In: Valentin, J., Cederlund, D., Drake, P., Finne, I. E., Glansholm, A., Jaworska, A., Paile, W. & Rahola, T. (eds.) Radiological Protection in Transition, Proceedings of the XIV Regular Meeting of the Nordic Society for Radiation protection NSFS, 27–31 August 2005, Rättvik, Sweden. Swedish Radiation Protection Authority SSI Report vol 15, 327–330.

Salminen, R. 2000. Barents Ecogeochemistry. Field training course 1999, a technical report. Geological Survey of Finland, unpublished report S/41/0000/1/2000, 16.

Salminen, R. 2009. Geochemical Atlas of Northern Europe. Espoo: Geological Survey of Finland. (Electronic publication). Available at: http://www.gtk.fi/publ/negatlas/

Salminen, R., Chekushin, V., Tenhola, M., Bogatyrev, I., Glavatskikh, S. P., Fedotova, E., Gregorauskiene, V., Kashulina, G., Niskavaara, H., Polischuok, A., Rissanen, K., Selenok, L., Tomilina, O. & Zhdanova, L. 2004. Geochemical atlas of the eastern Barents region. Amsterdam: Elsevier BV. (Reprinted from Journal of Geochemical Exploration, vol. 83), 548 p.

Salminen, R. (chief-editor), Batista, M. J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P. J., Olsson, S. Å., Ottesen, R..-T., Petersell, V., Plant, J. **A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A. & Tarvainen, T. 2005**. Geochemical Atlas of Europe, Part 1, Background Information, Methodology and maps. Espoo: Geological Survey of Finland. 526 p.

Simonen, A. 1980. The Precambrian in Finland. Geological Survey of Finland, Bulletin 304. 58 p.

Teinemaa, E., Kirso, U., Strommen, M. R. & Kamens, R. M. 2002. Deposition flux and atmospheric behaviour of oil shale combustion aerosols. Oil Shale 2003, Tallinn, Estonia, 20n.3S, 429–440.

Ylipieti, J., Rissanen, K., Kostiainen, E., Salminen, R., Tomilina, O., Täht, K., Gilucis, A. & Gregorauskiene, V. 2008. Chernobyl fallout in the uppermost (0–3 cm) humus layer of forest soil in Finland, North East Russia and the Baltic countries in 2000–2003. Science of Total Environment, doi:10.1016/j.scitotenv.2008.08.035.

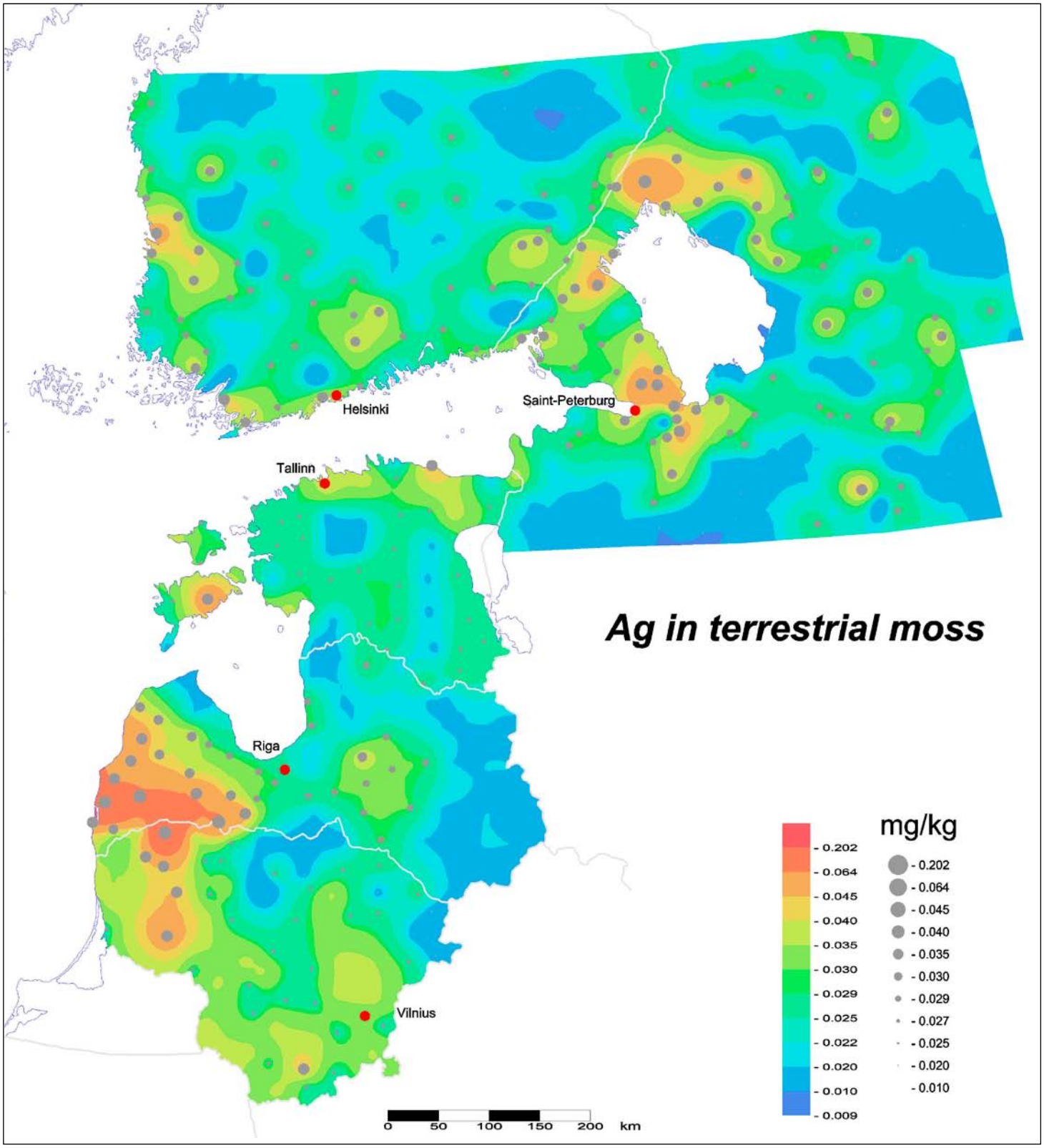
9 THE GEOCHEMICAL MAPS

Maps are organised in alphabetical order according to the chemical symbol of the element in the order: (i) Element concentration in the moss (MOS), (ii) Element concentration in the organic soil layer, total concentration (ORG tot), (iii) Element concentration in the organic soil layer, ammonium acetate extractable concentration (ORG amm. acet.)

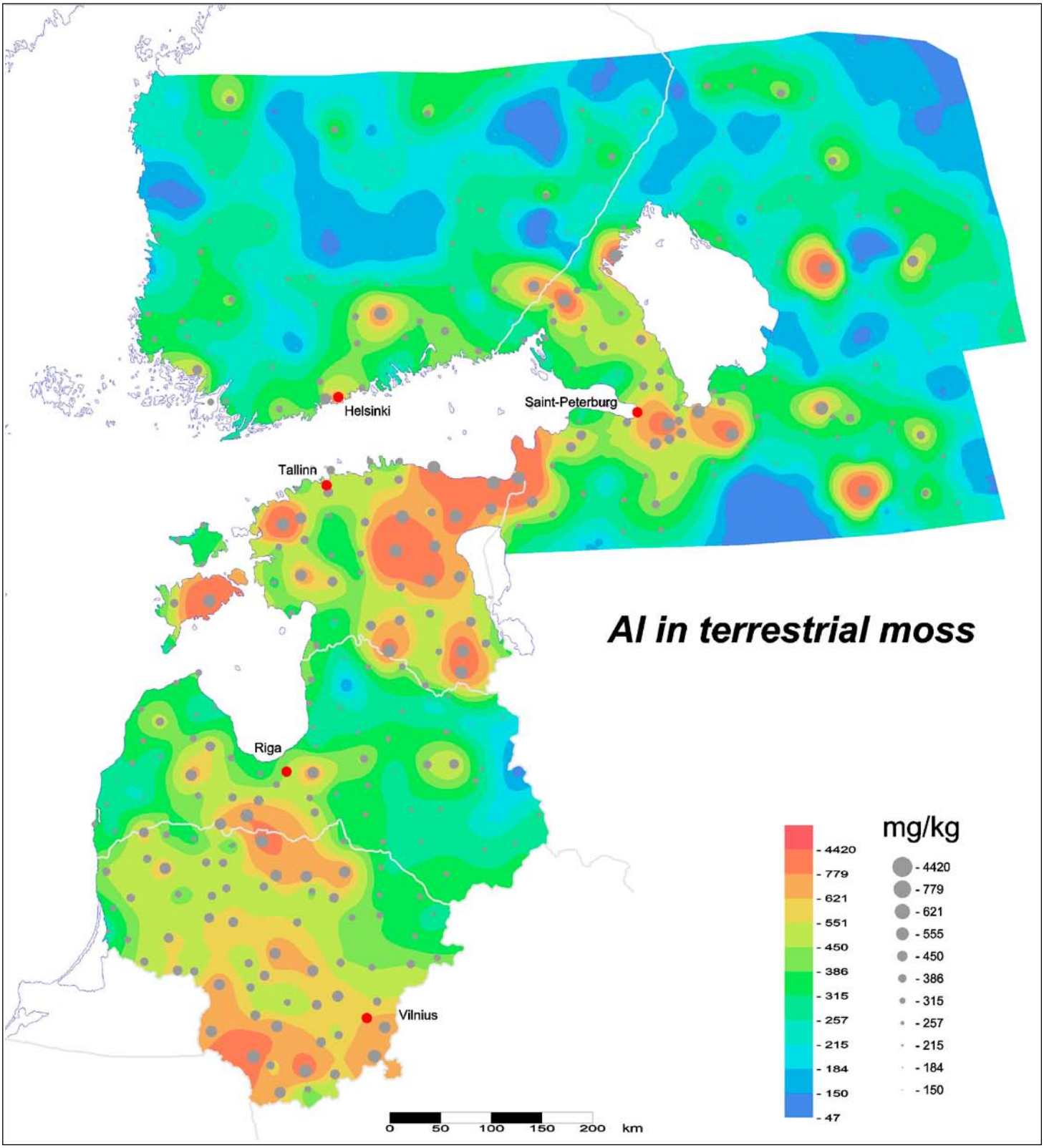
Element maps

Ag – Silver	ORG tot
Al – Aluminium	MOS, ORG tot, ORG amm. acet.
As – Arsenic	MOS, ORG tot,
B – Boron	MOS, ORG tot,
Ba – Barium	MOS, ORG tot, ORG amm. acet.
Be – Beryllium	ORG tot
Bi – Bismuth	ORG tot
Br – Bromium	ORG tot
Ca – Calcium	ORG tot, ORG amm. acet.
Cd – Cadmium	MOS, ORG tot
C – Carbon	ORG tot
Co – Cobalt	MOS, ORG tot, ORG amm. acet.
Cr – Chromium	MOS, ORG tot,
^{134}Cs – Cesium	ORG tot,
^{137}Cs – Cesium	ORG tot,
Cu – Copper	MOS, ORG tot,
Fe – Iron	MOS, ORG tot, ORG amm. acet.
Hg – Mercury	MOS, ORG tot
Humidity	ORG
K – Potassium	MOS, ORG tot, ORG amm. acet.
Li – Lithium	MOS, ORG tot,
LOI – Loss on ignition	ORG
Mg – Magnesium	MOS, ORG tot, ORG amm. acet.
Mn – Manganese	MOS, ORG tot, ORG amm. acet.
Mo – Molybdenum	MOS, ORG tot
N – Nitrogen	ORG tot
Na – Sodium	MOS, ORG tot, ORG amm. acet.
Ni – Nickel	MOS, ORG tot, ORG amm. acet.
P – Phosphorus	MOS, ORG tot, ORG amm. acet.
Pb – Lead	MOS, ORG tot
Rb – Rubidium	MOS, ORG tot
S – Sulphur	MOS, ORG tot, ORG amm. acet.
Sb – Antimony	MOS, ORG tot
Sn – Tin	MOS, ORG tot
Sr – Strontium	MOS, ORG tot
Th – Thorium	MOS, ORG tot
Tl – Thallium	MOS, ORG tot
U – Uranium	MOS, ORG tot
V – Vanadium	MOS, ORG tot
Zn – Zinc	MOS, ORG tot, ORG amm. acet.

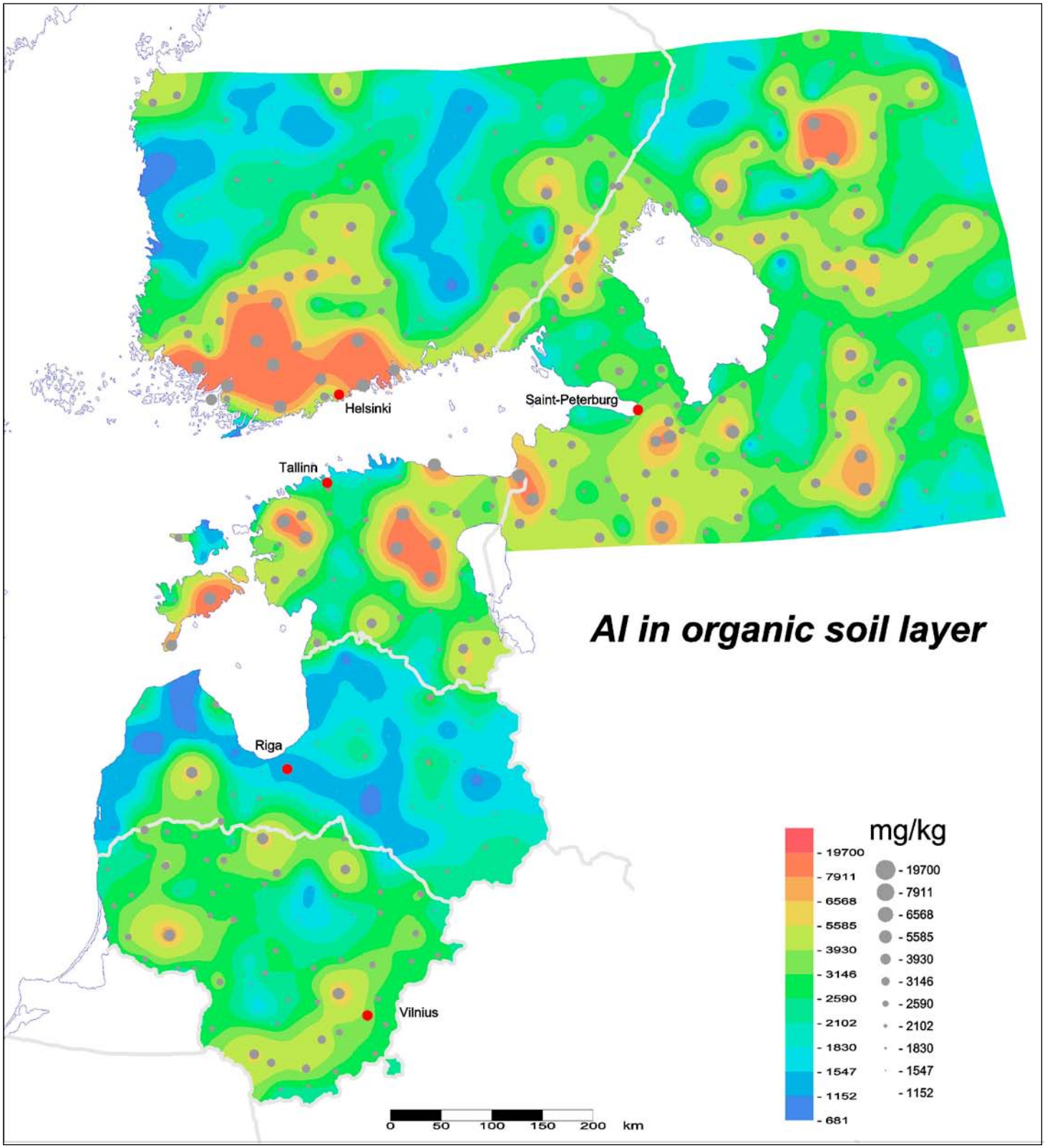
Ag – Silver ORG tot



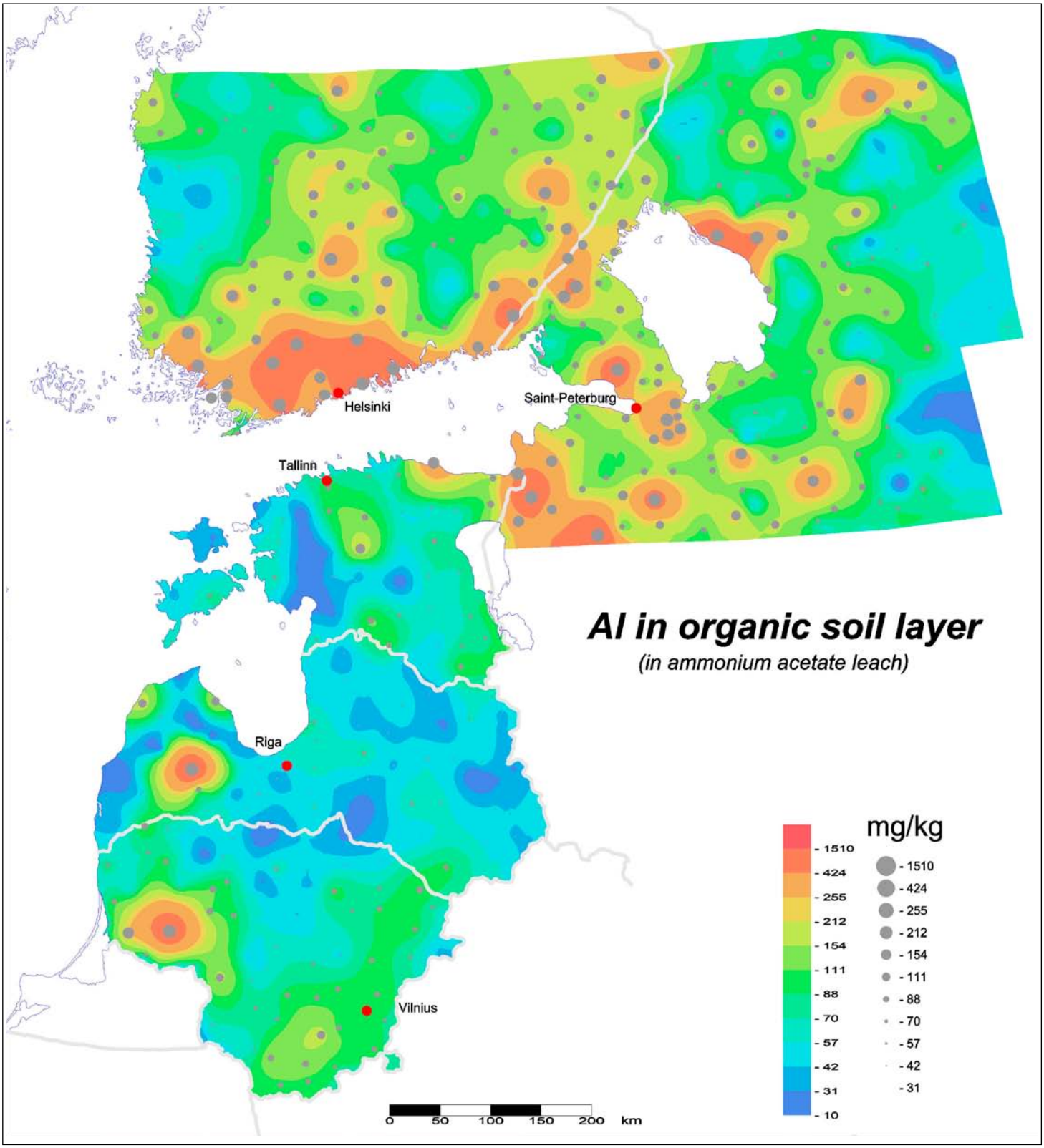
Al – Aluminium MOS



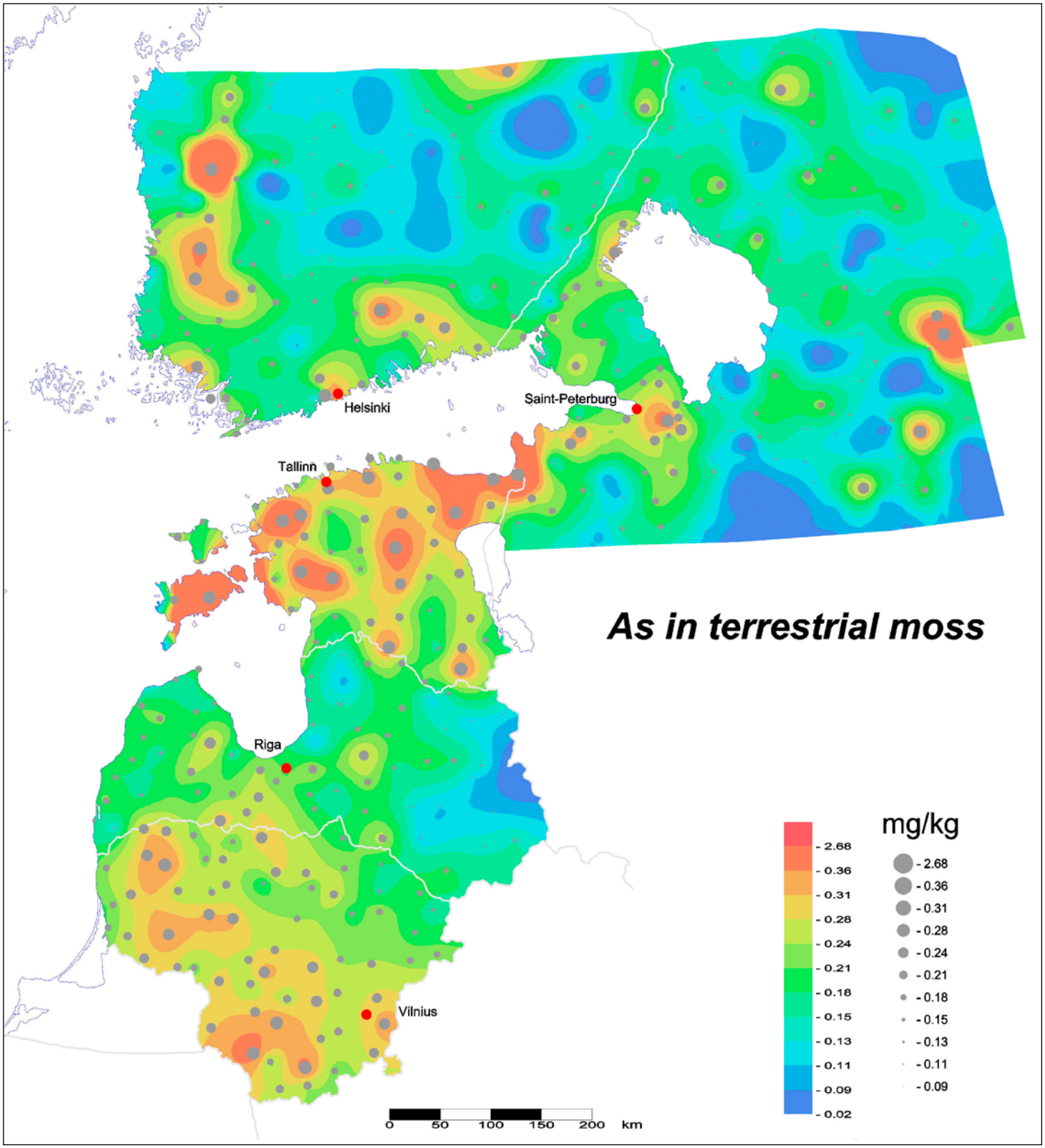
Al – Aluminium ORG tot



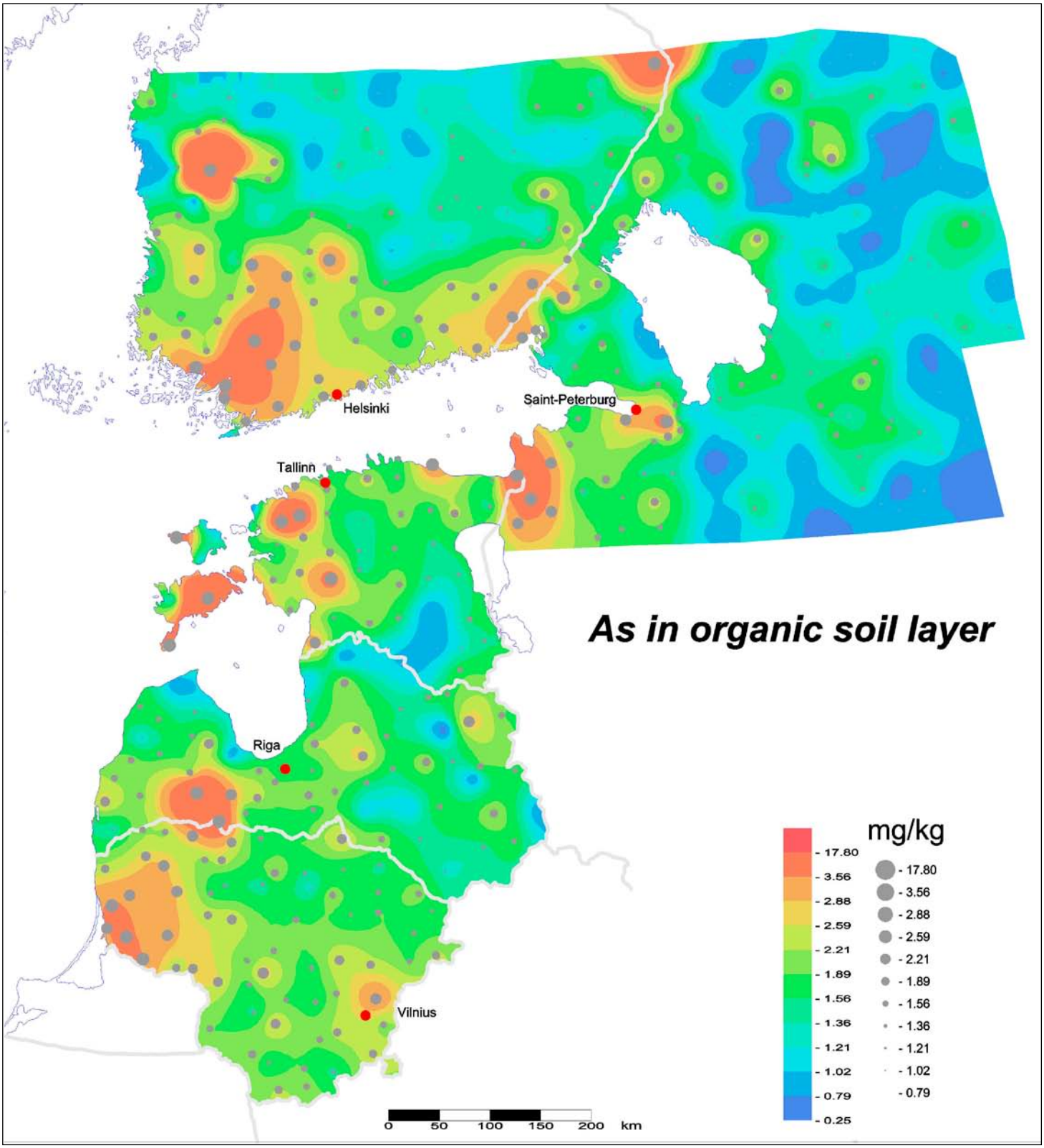
Al – Aluminium ORG amm. acet.



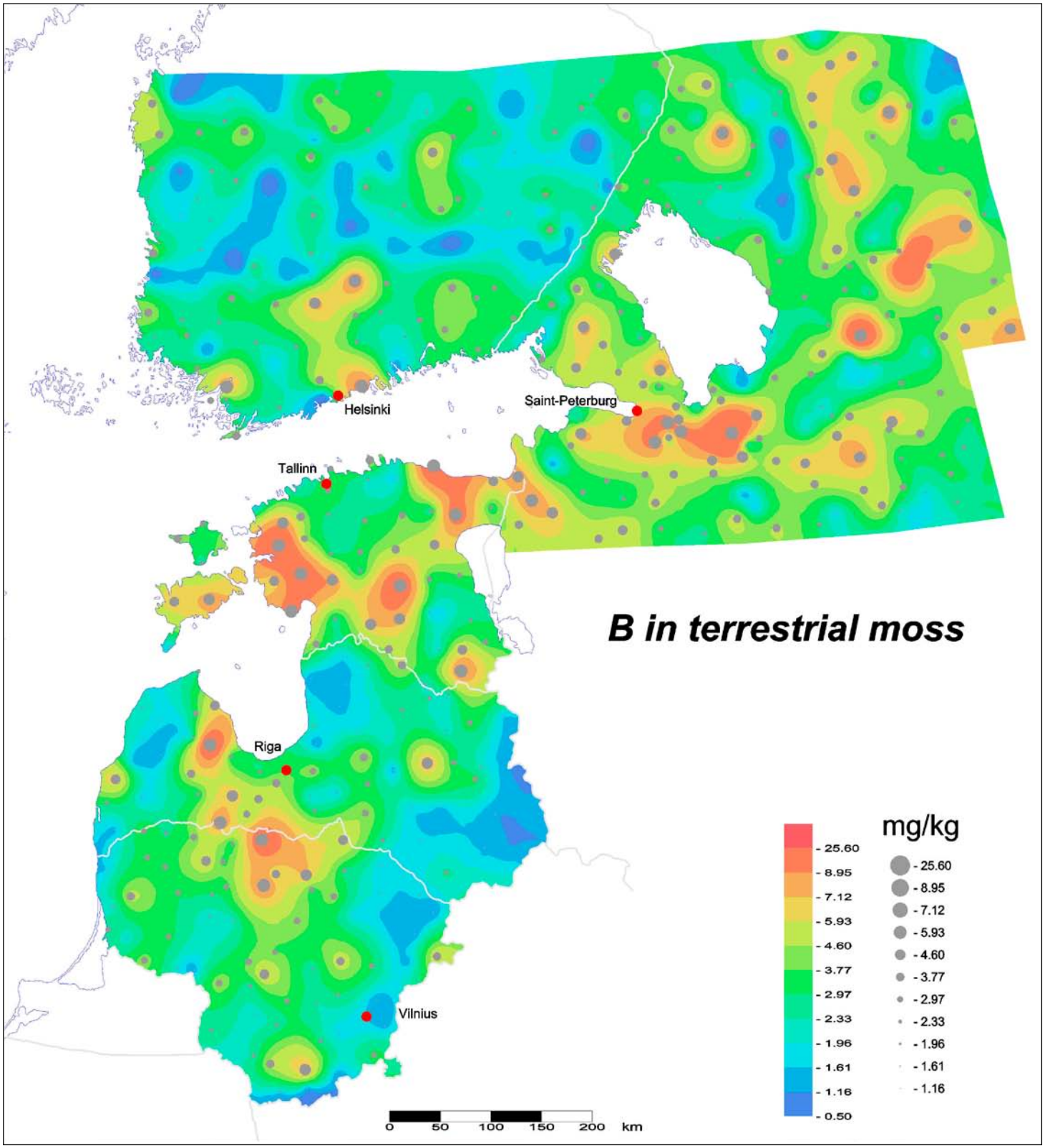
As – Arsenic MOS



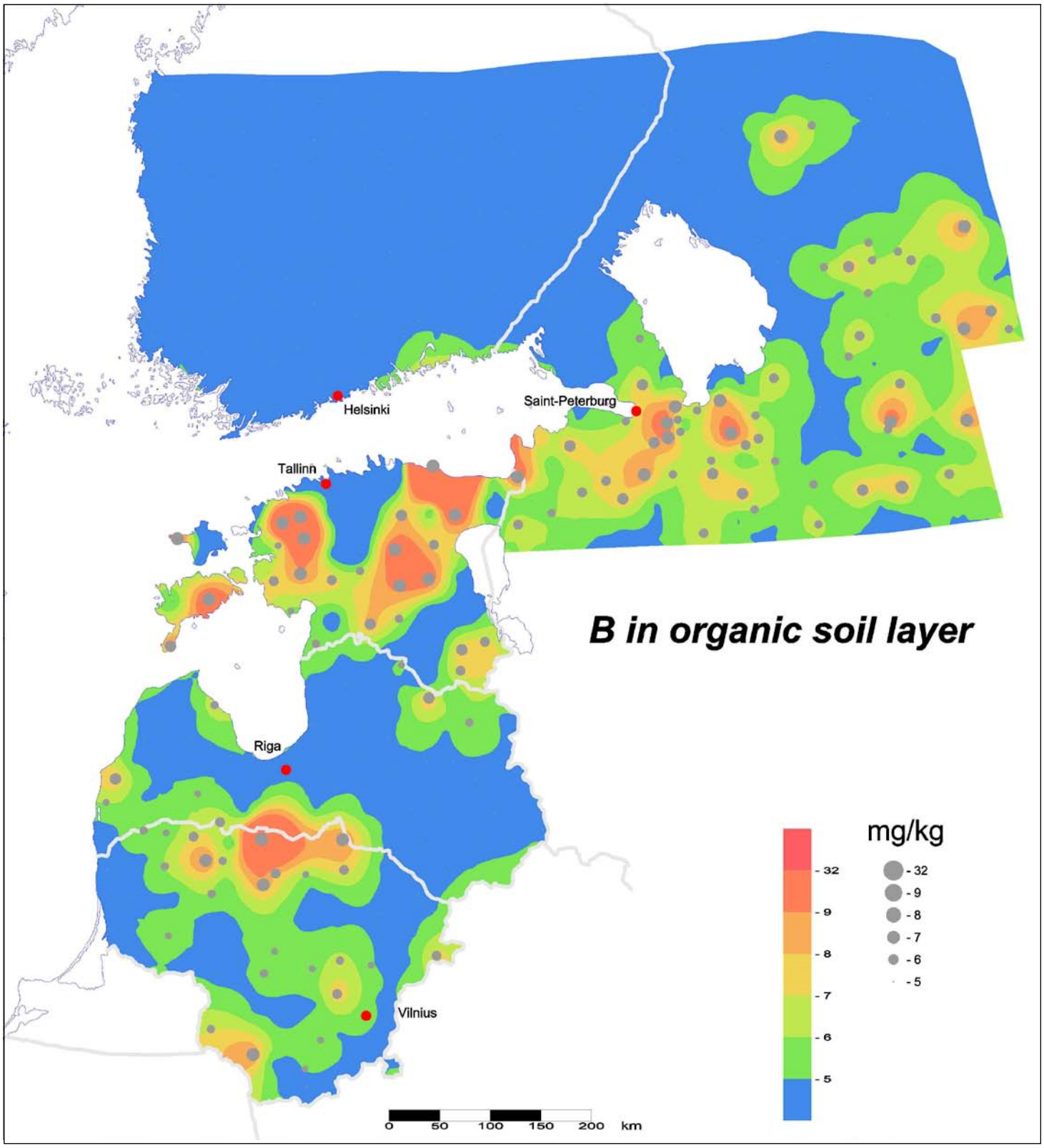
As – Arsenic ORG tot



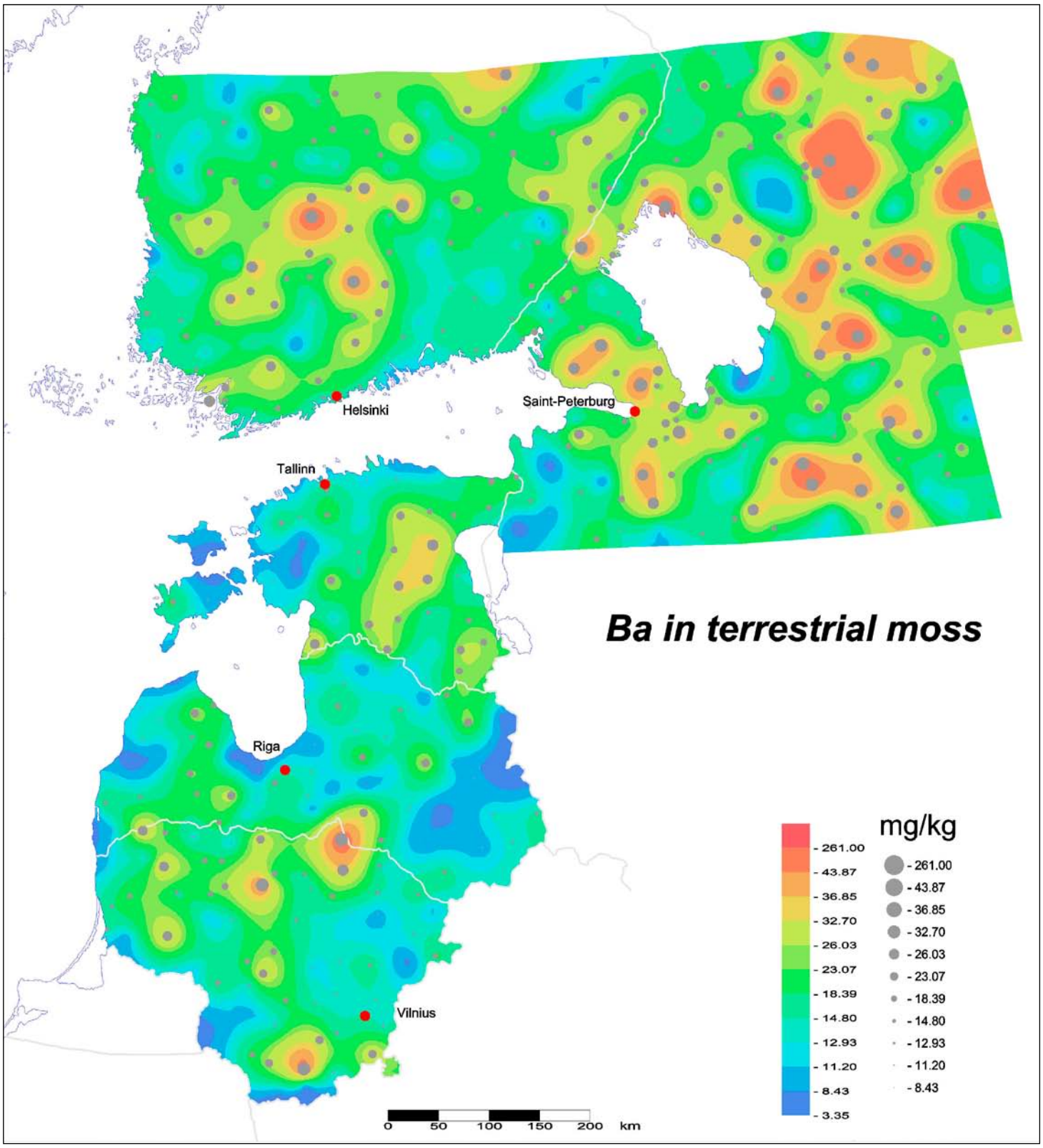
B – Boron MOS


B in terrestrial moss
Helsinki
Saint-Peterburg
Tallinn
Riga
Vilnius
mg/kg
- 25.60
- 8.95
- 7.12
- 5.93
- 4.60
- 3.77
- 2.97
- 2.33
- 1.96
- 1.61
- 1.16
- 0.50
0 50 100 150 200 km

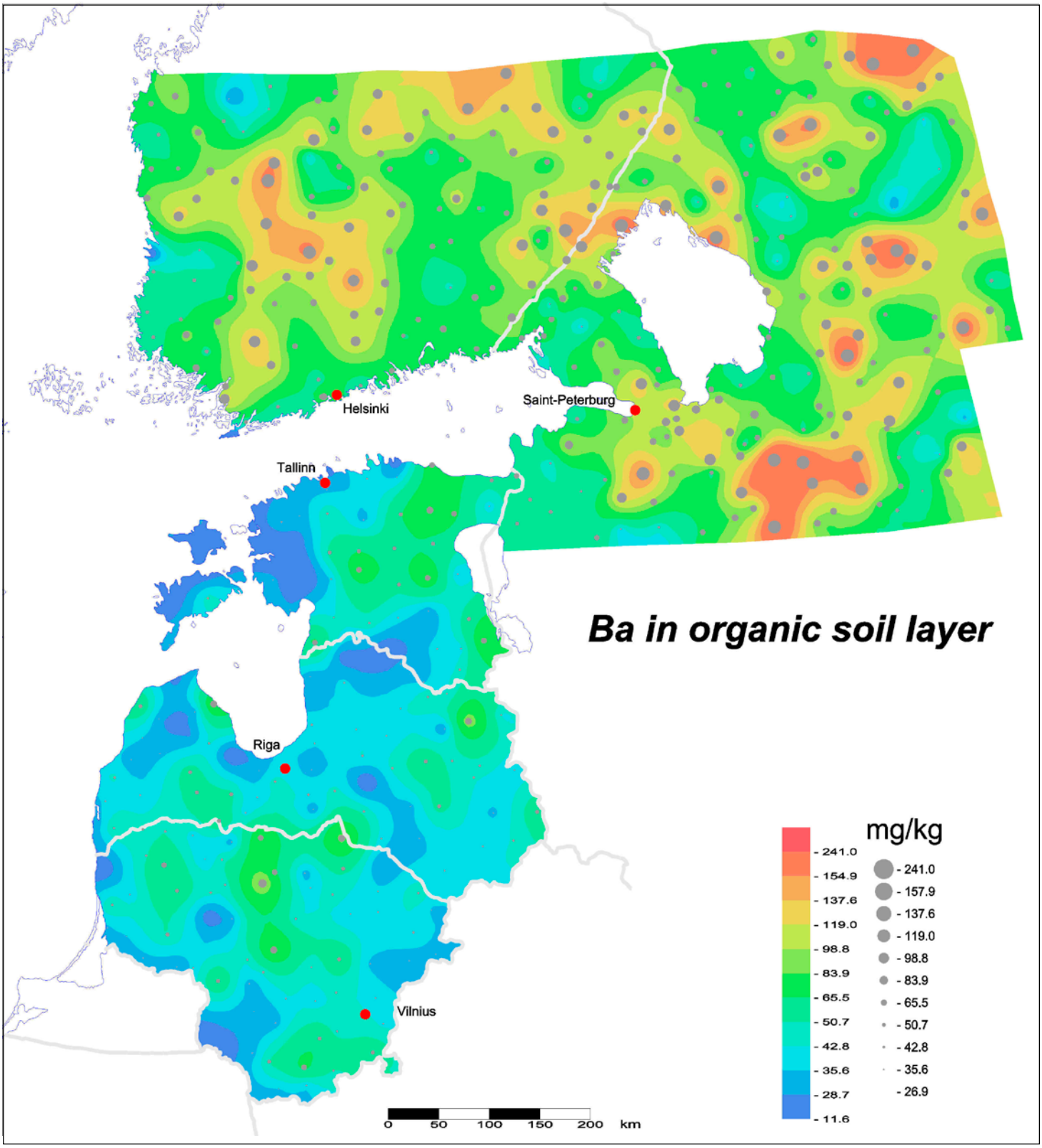
B – Boron ORG tot



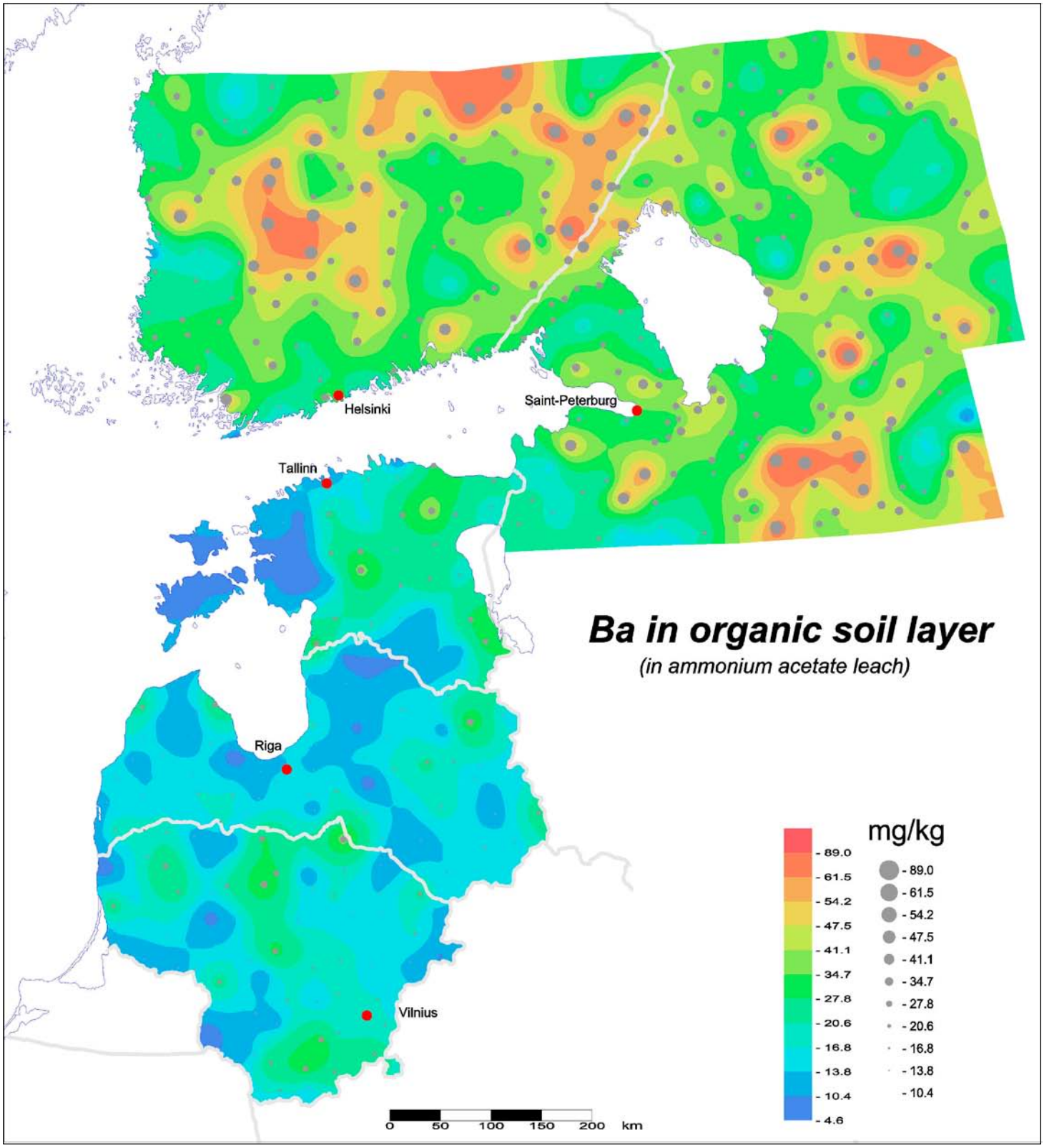
Ba – Barium MOS



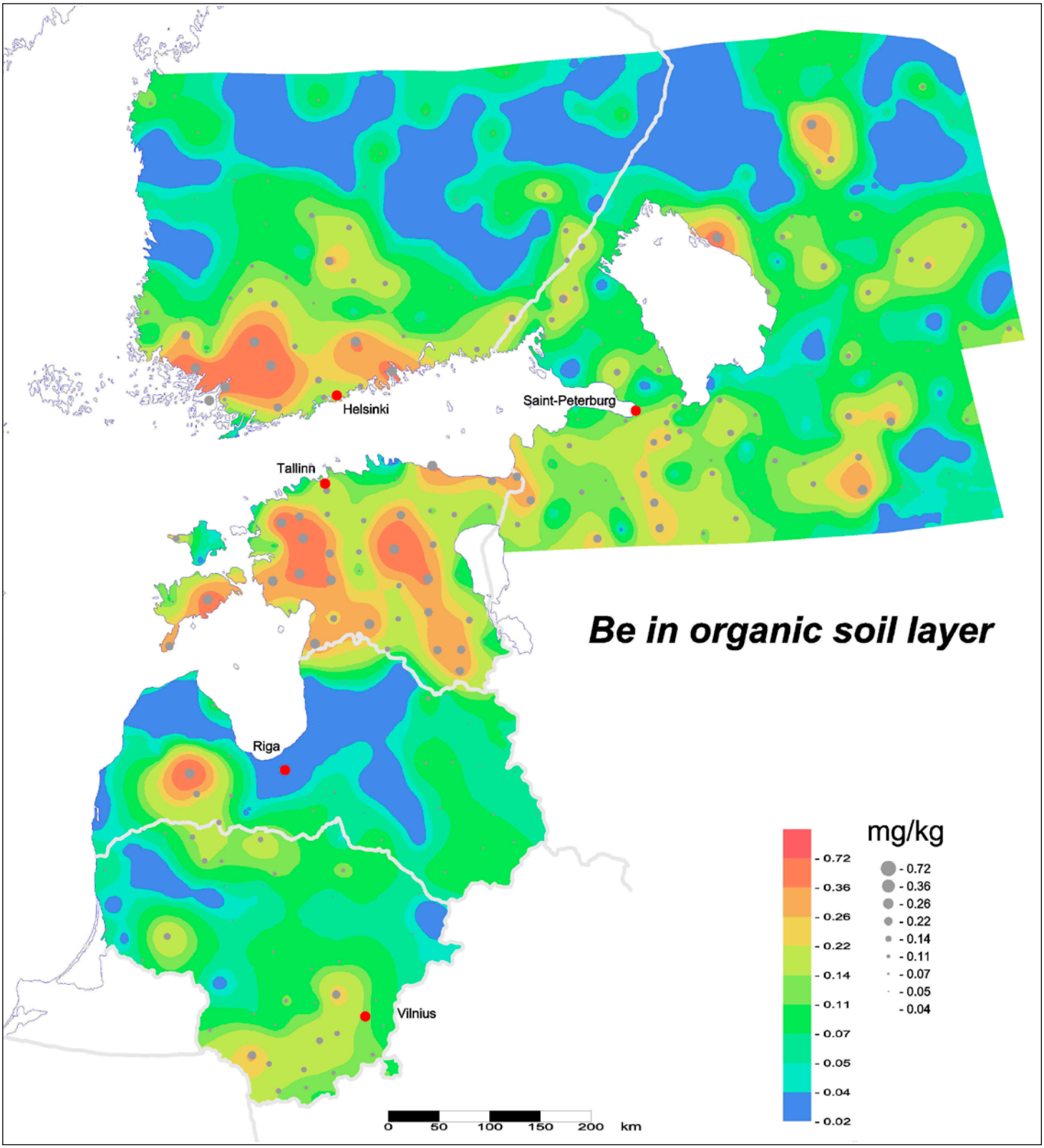
Ba – Barium ORG tot



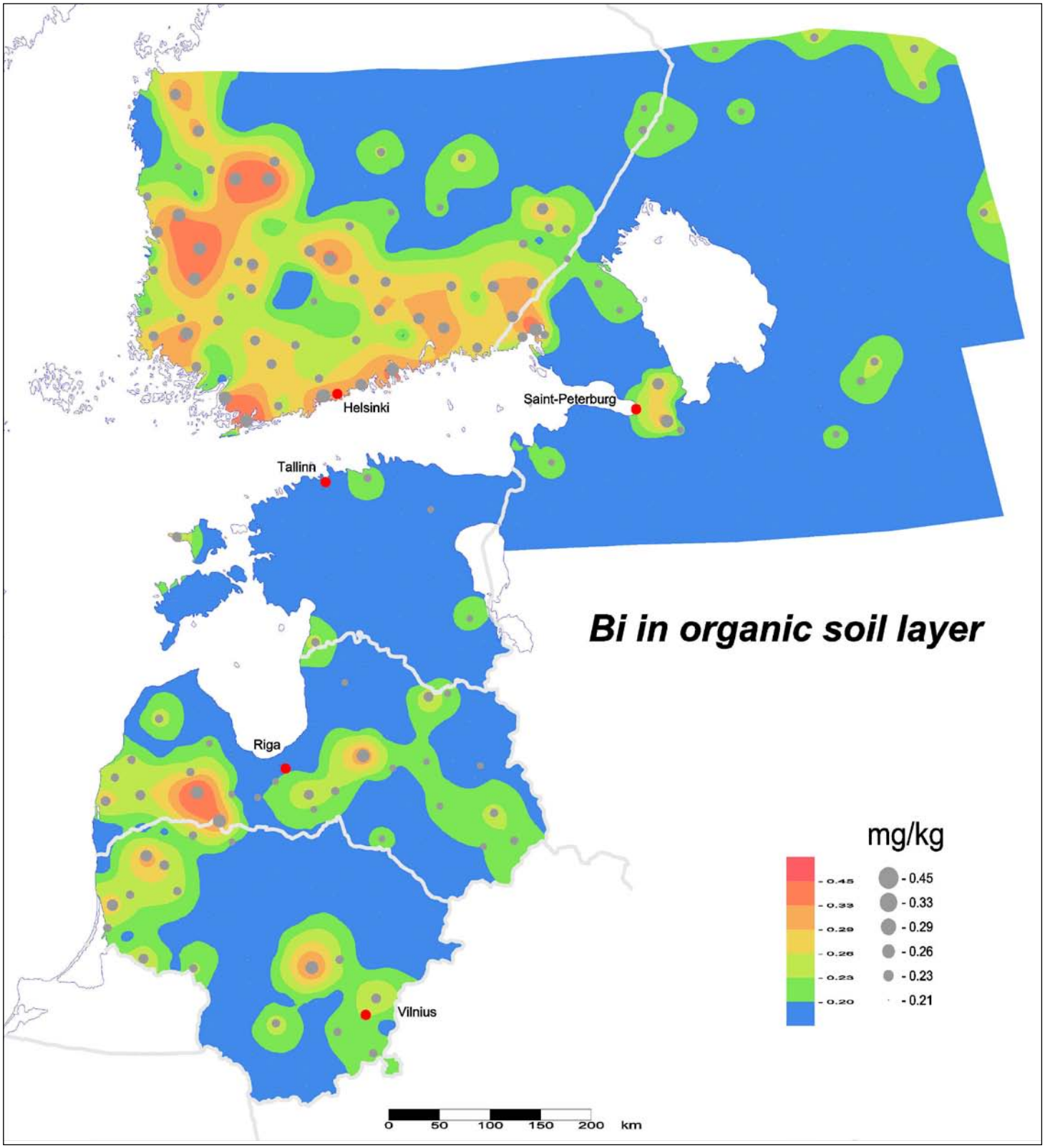
Ba – Barium ORG amm. acet.



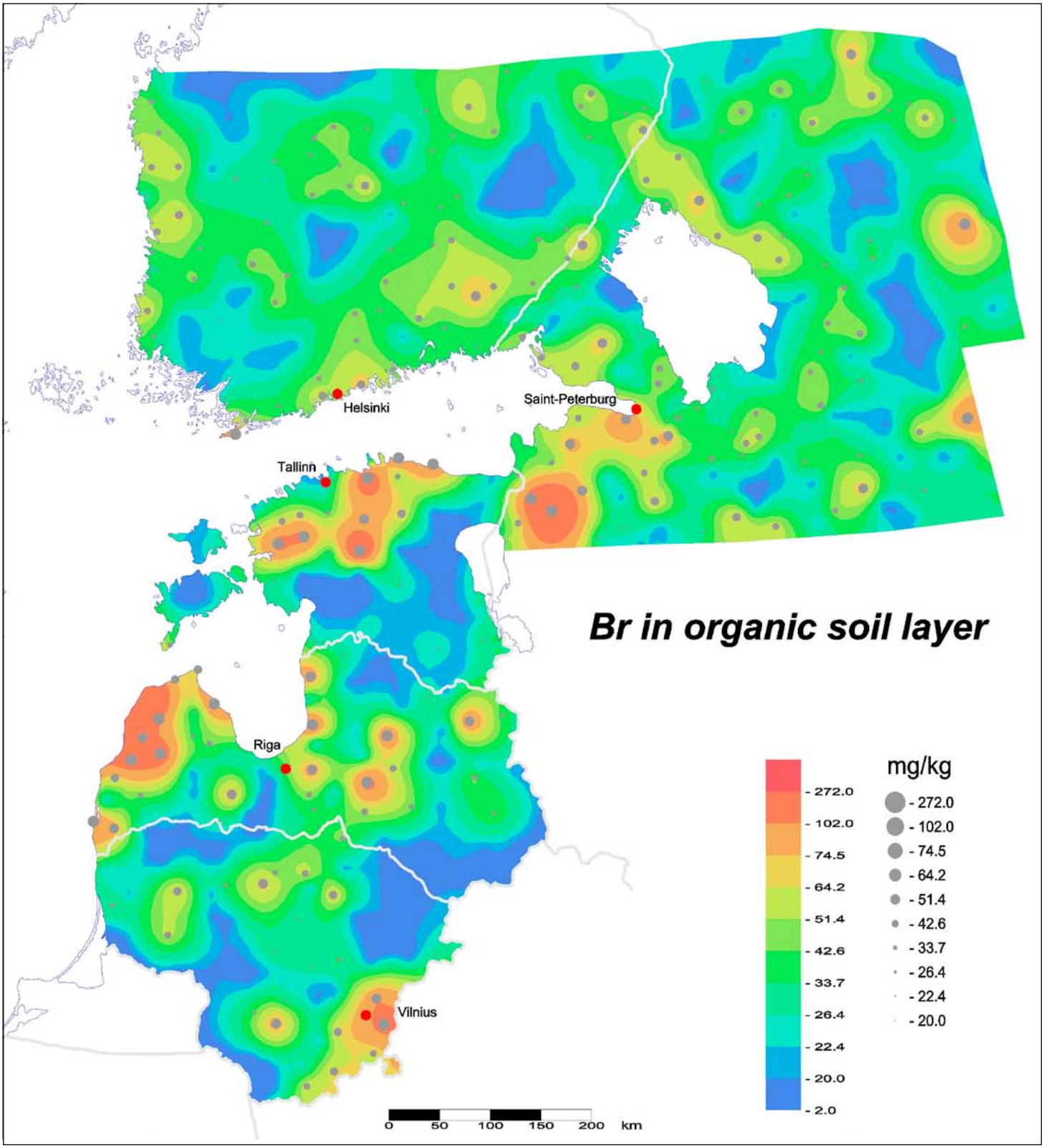
Be – Beryllium ORG tot



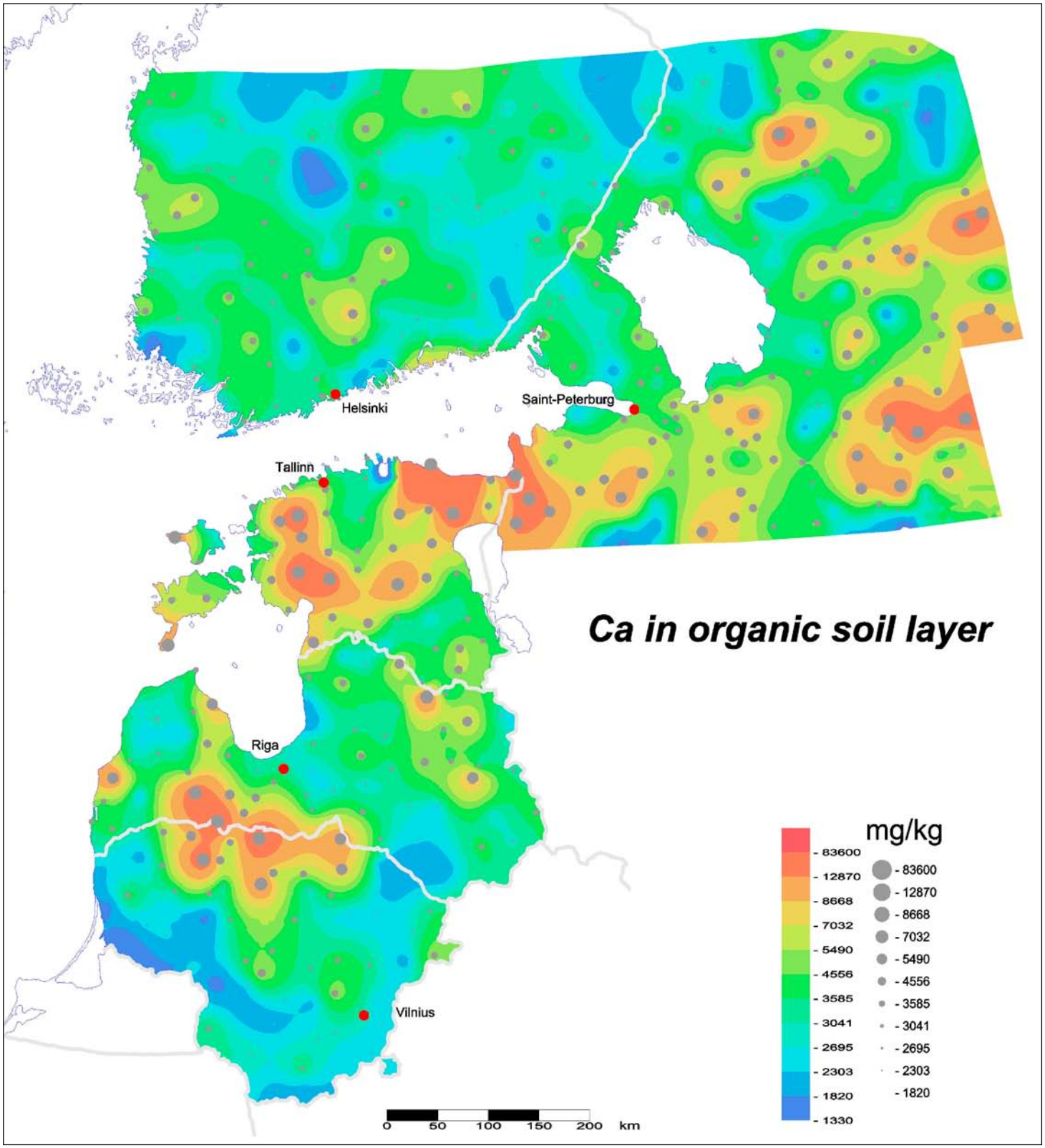
Bi – Bismuth ORG tot



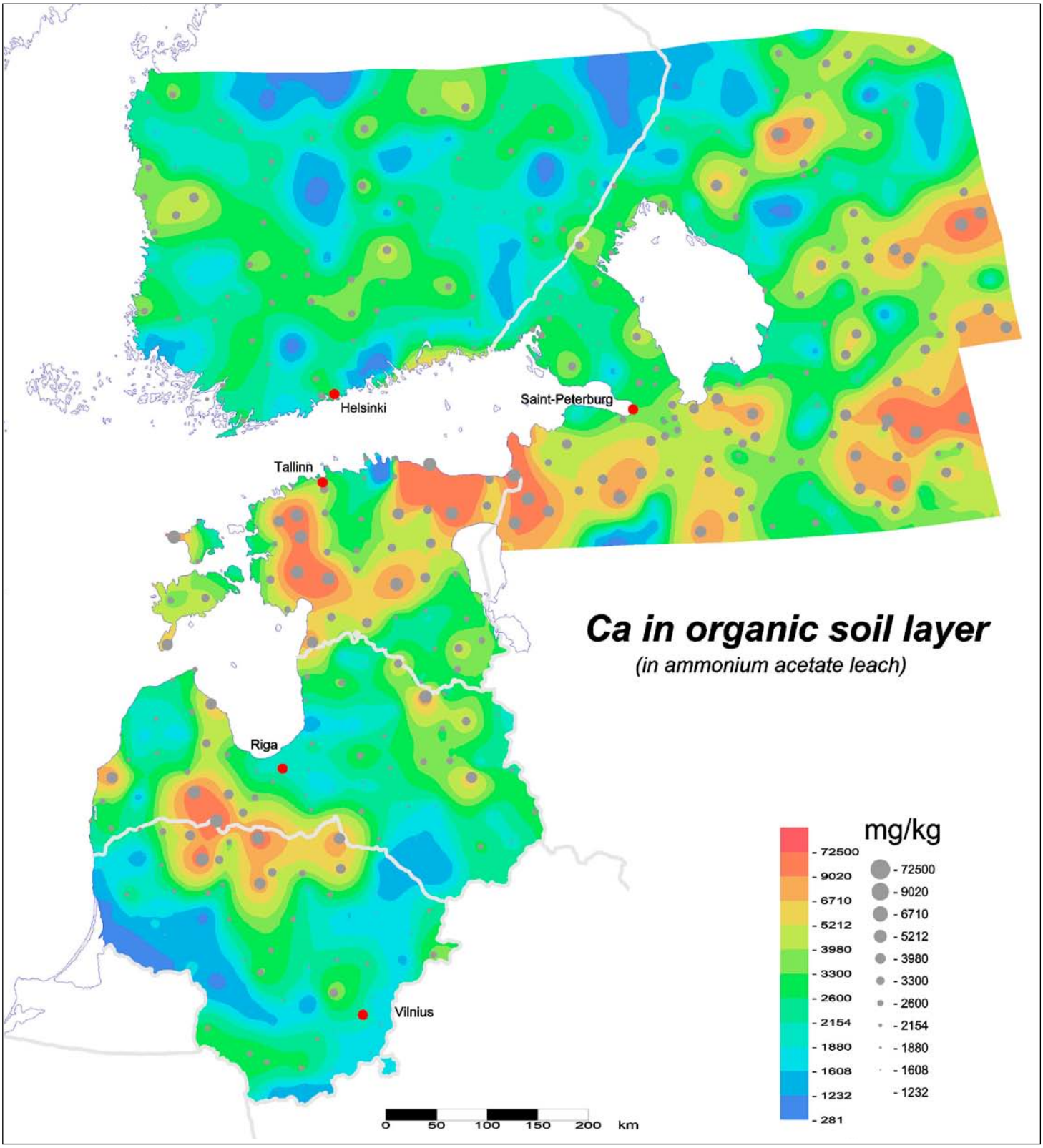
Br – Bromium ORG tot



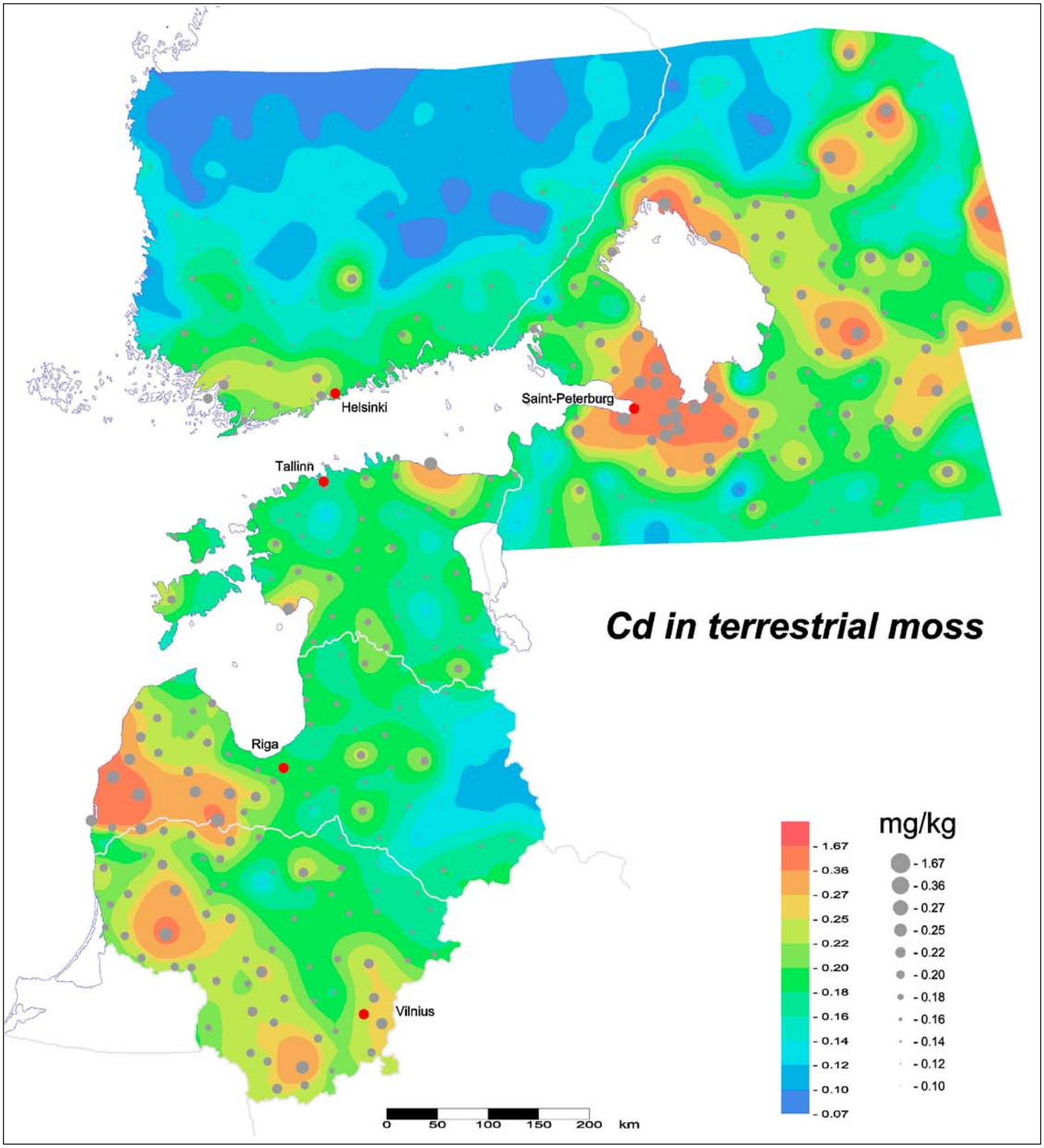
Ca – Calcium ORG tot



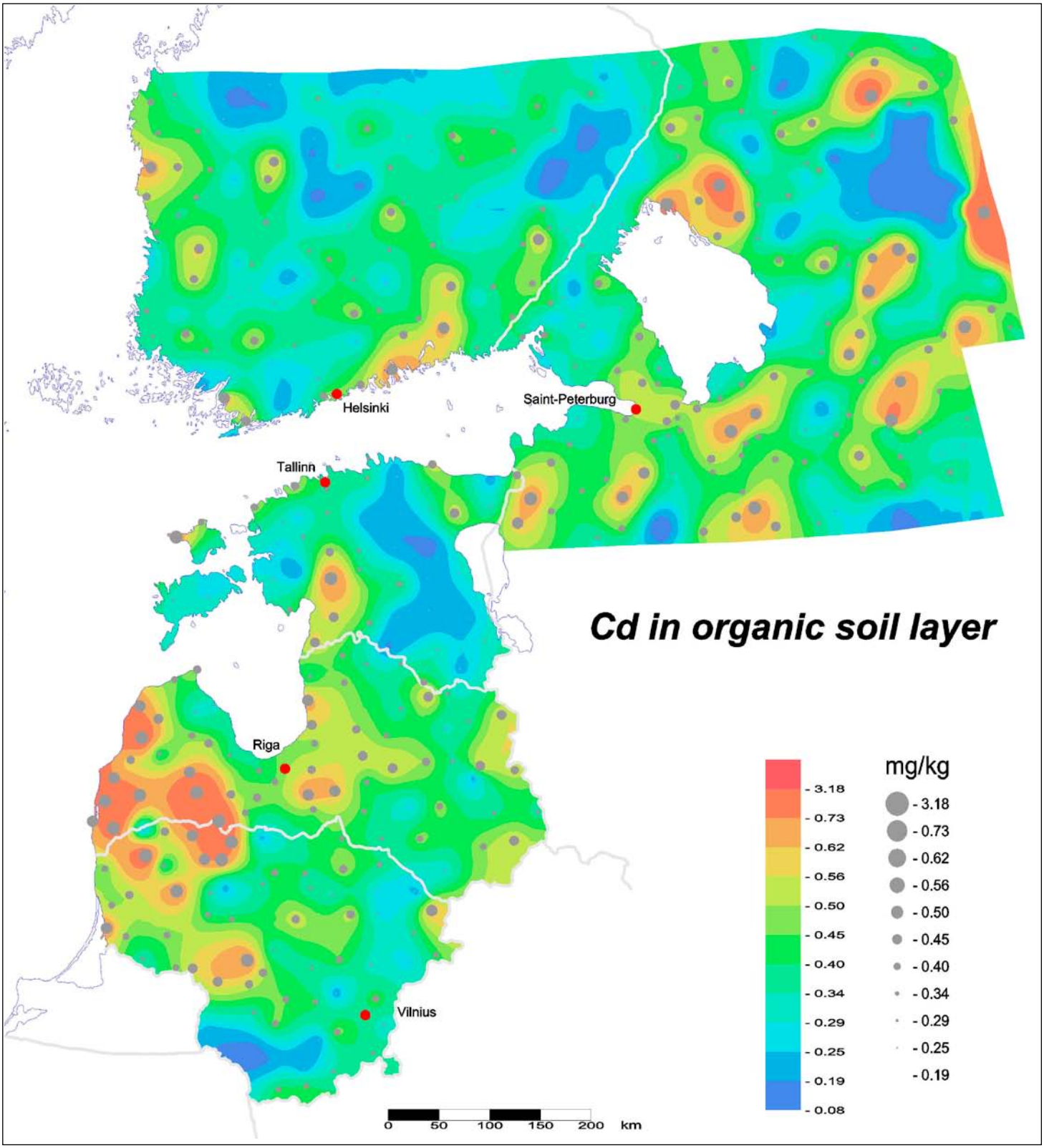
Ca – Calcium ORG amm. acet.



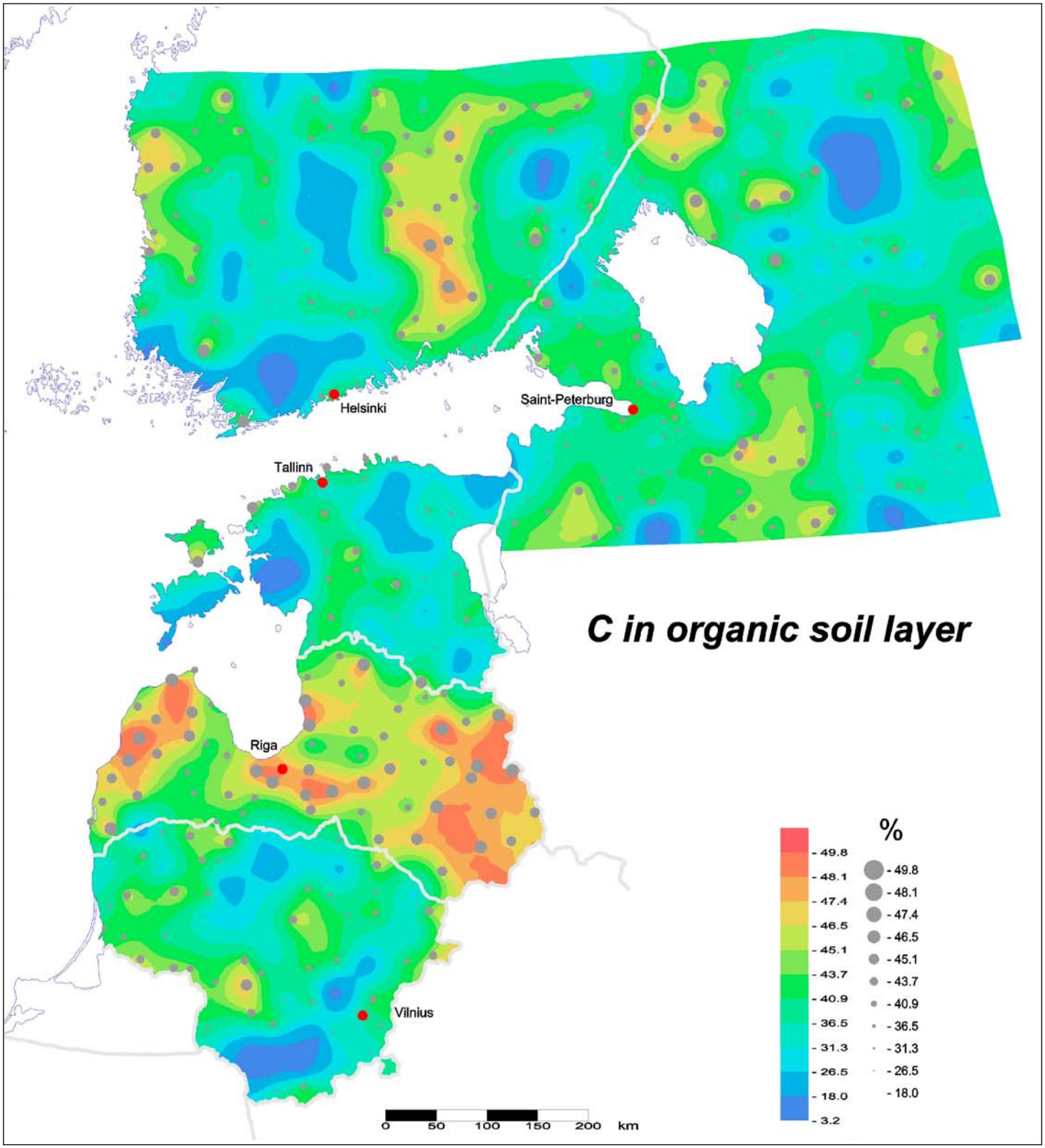
Cd – Cadmium MOS



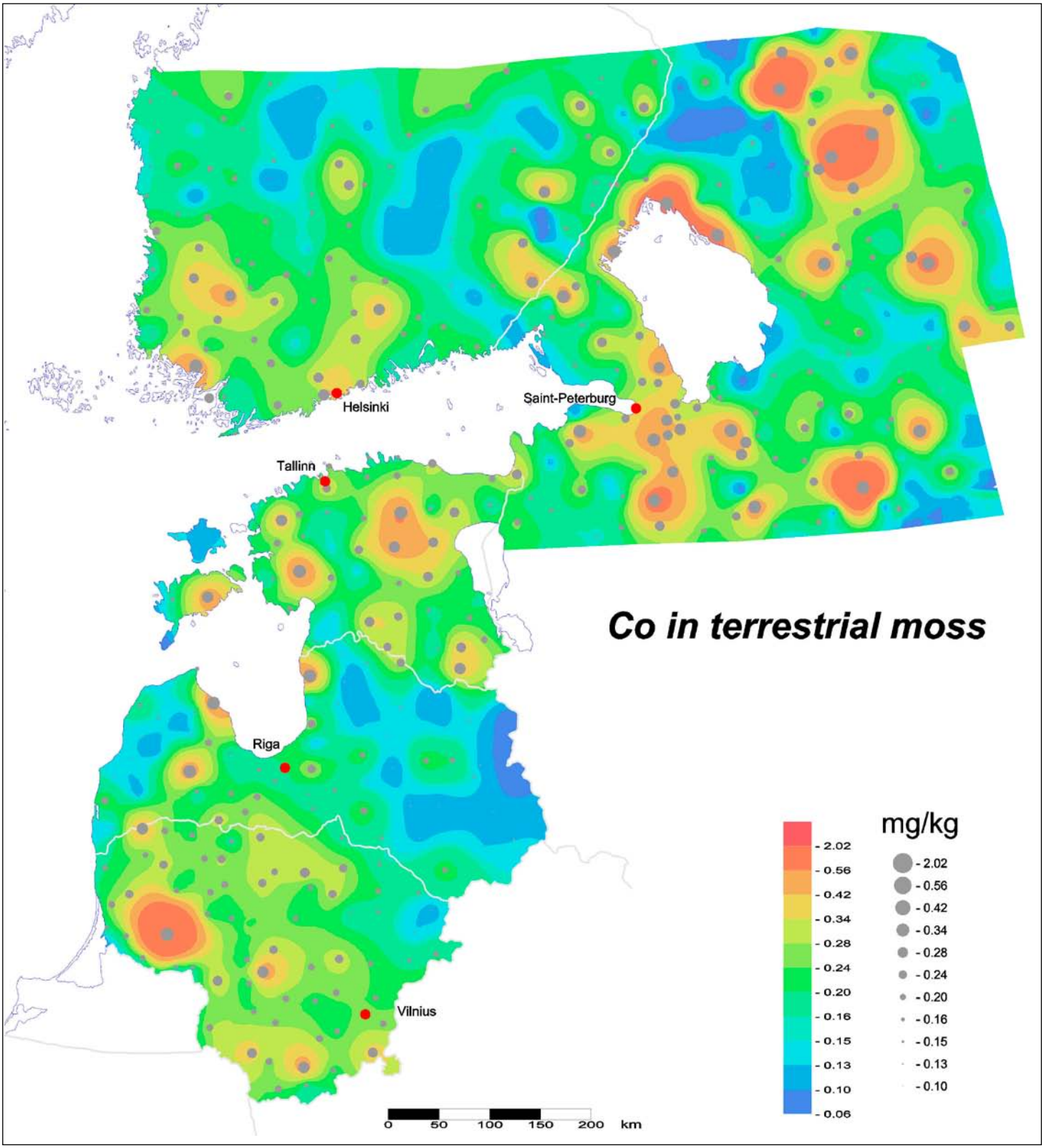
Cd – Cadmium ORG tot



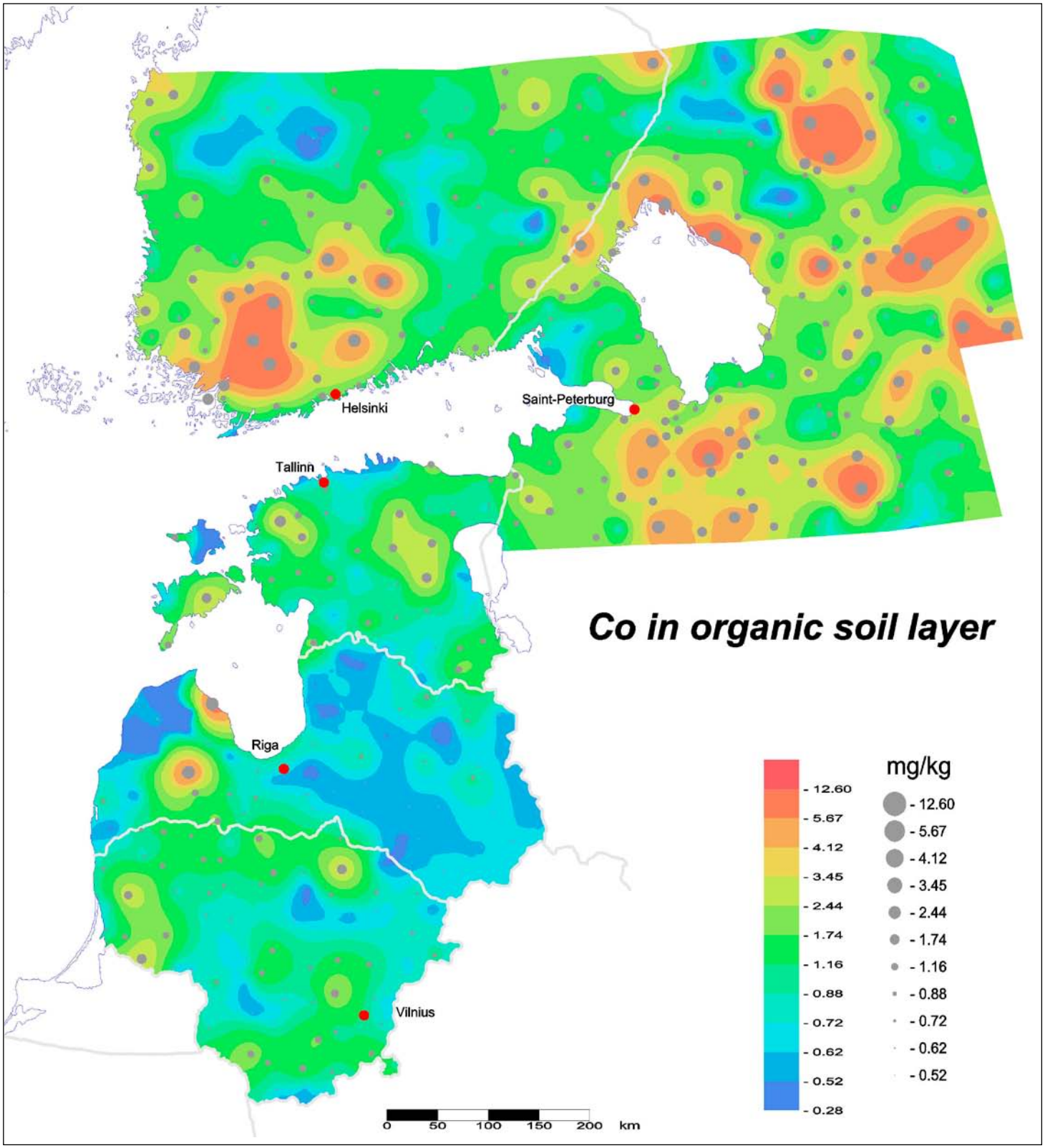
C – Carbon ORG tot



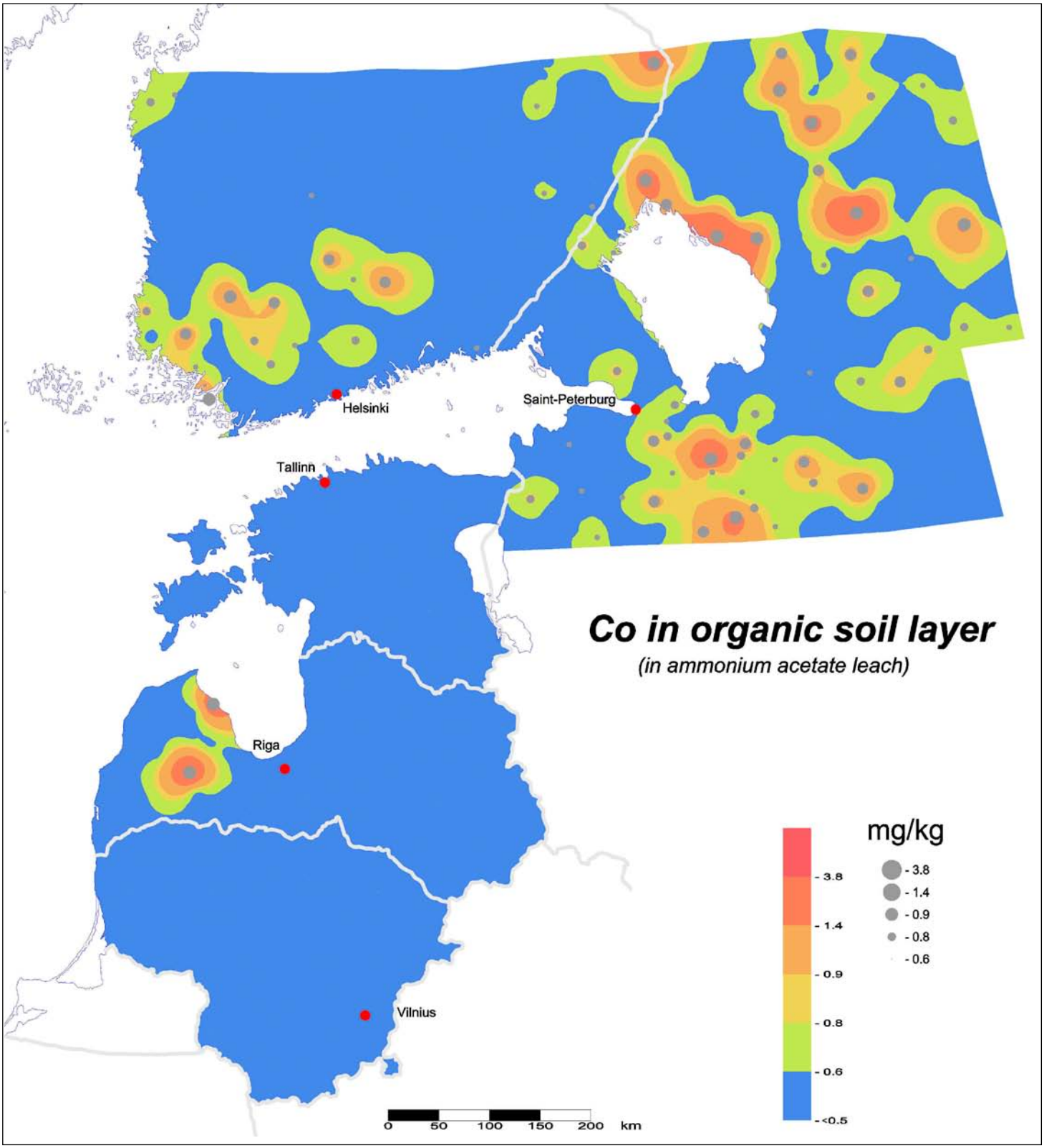
Co – Cobalt MOS



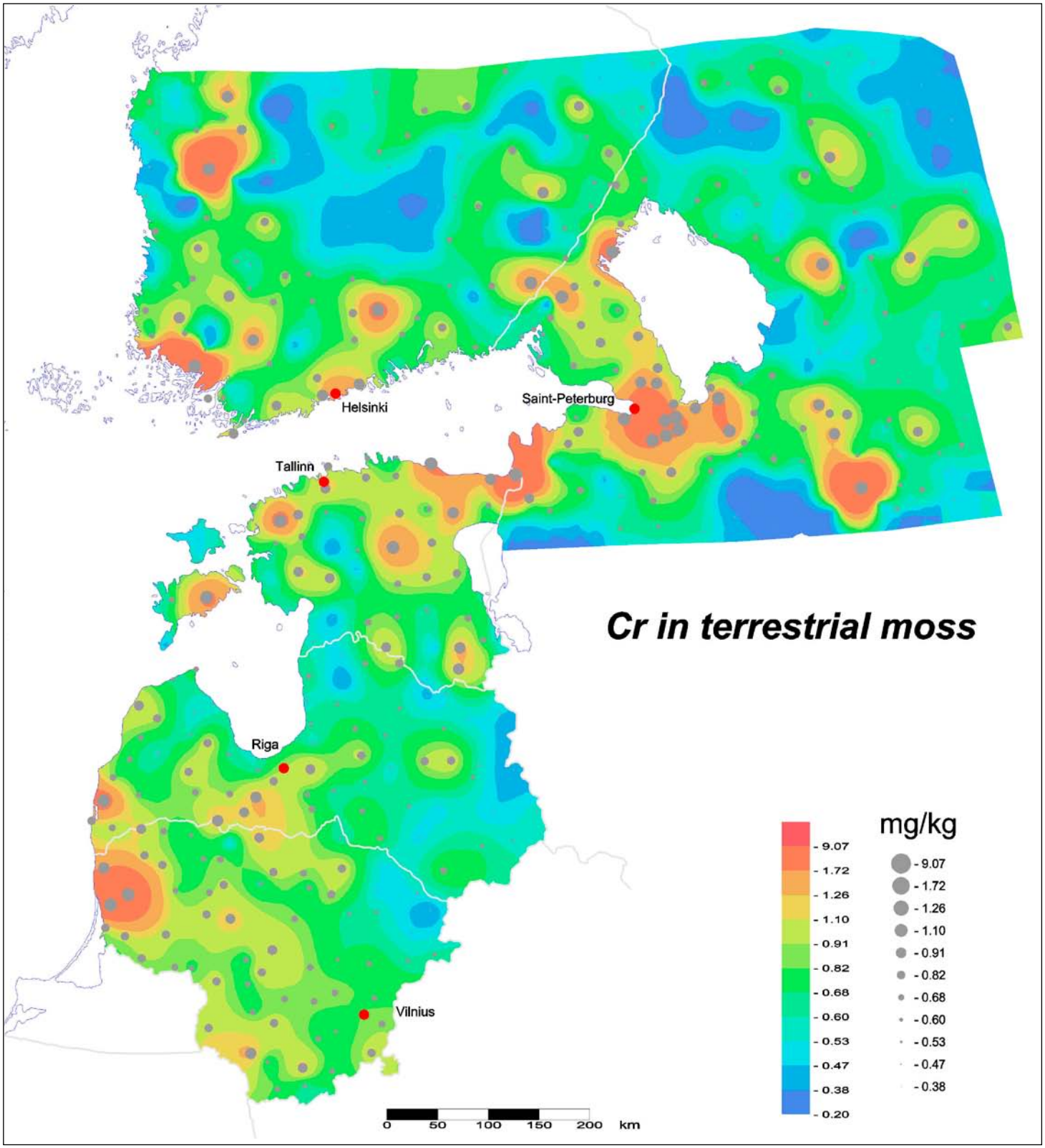
Co – Cobalt ORG tot



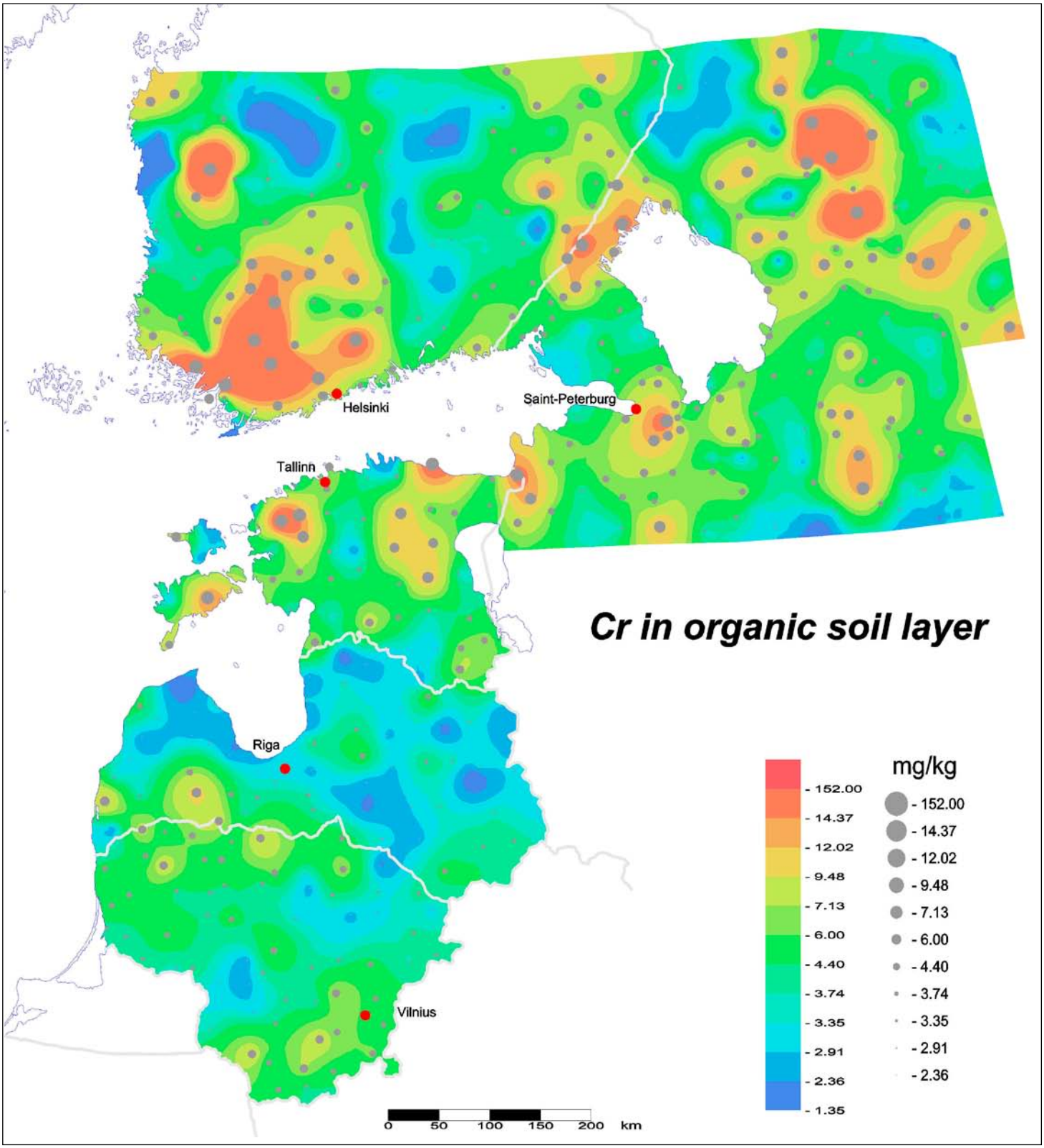
Co – Cobalt ORG amm. acet.



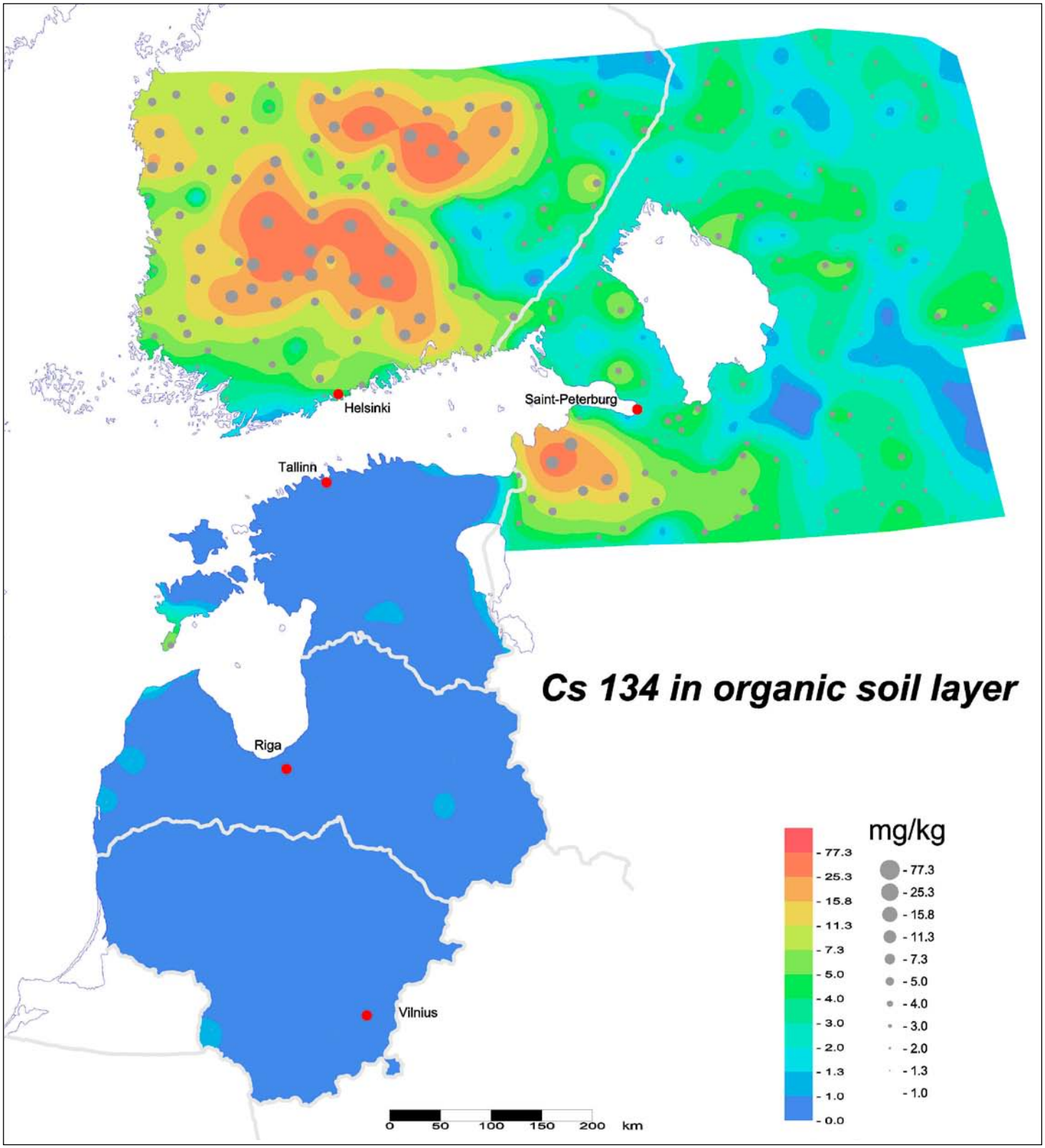
Cr – Chromium MOS



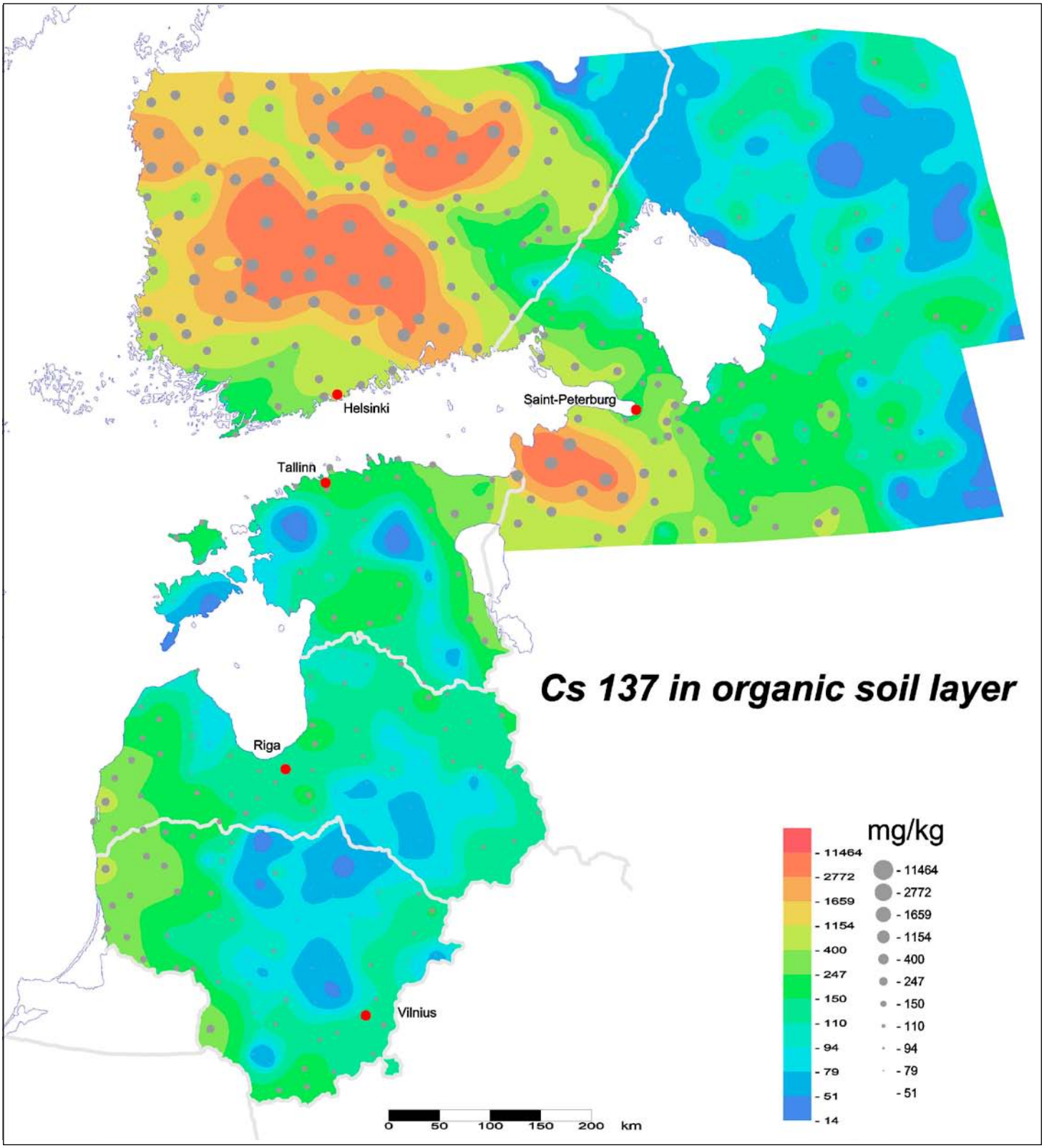
Cr – Chromium ORG tot



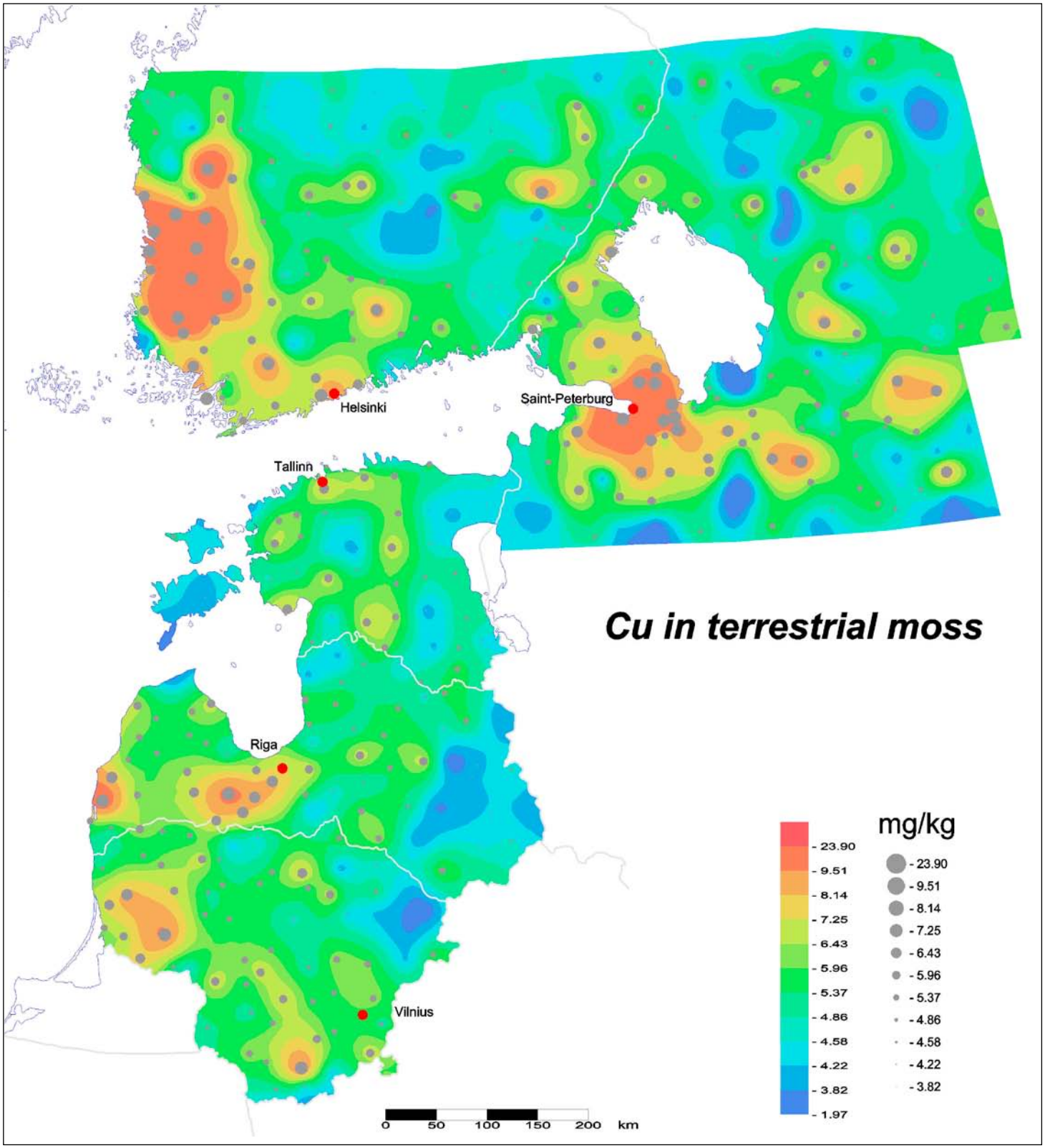
^{134}Cs – Cesium ORG tot



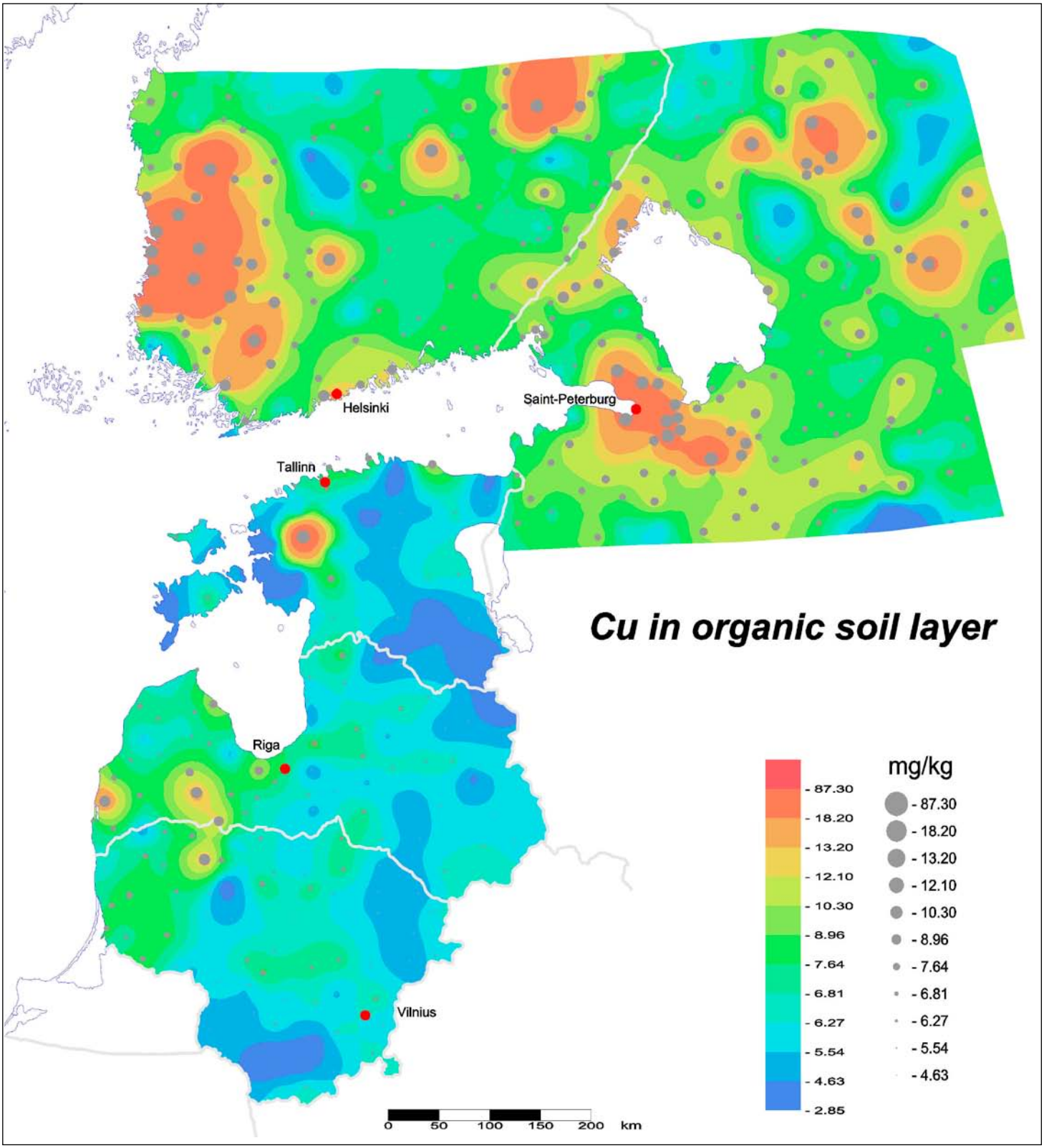
^{137}Cs – Cesium ORG tot



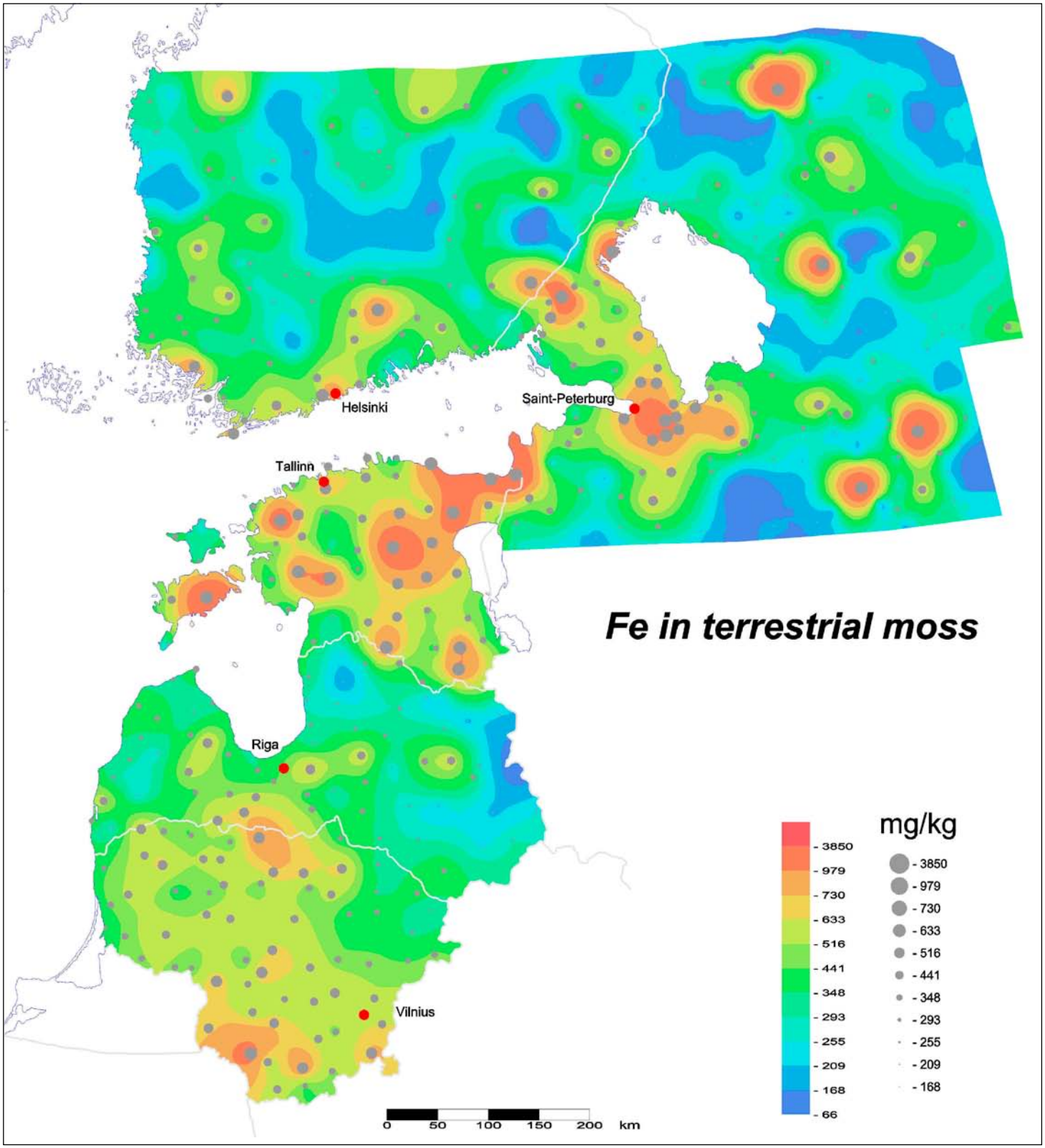
Cu – Copper MOS



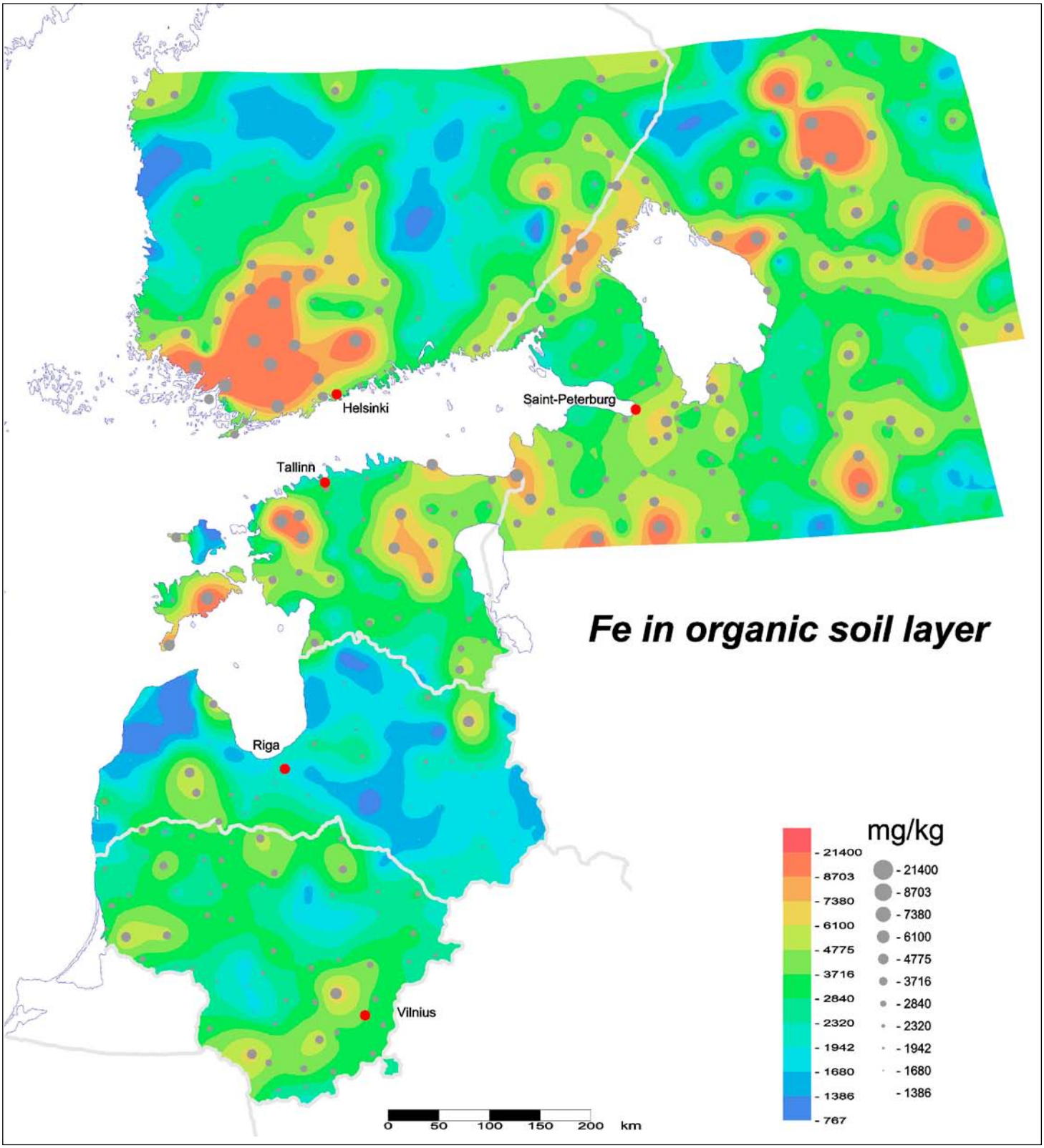
Cu – Copper ORG tot



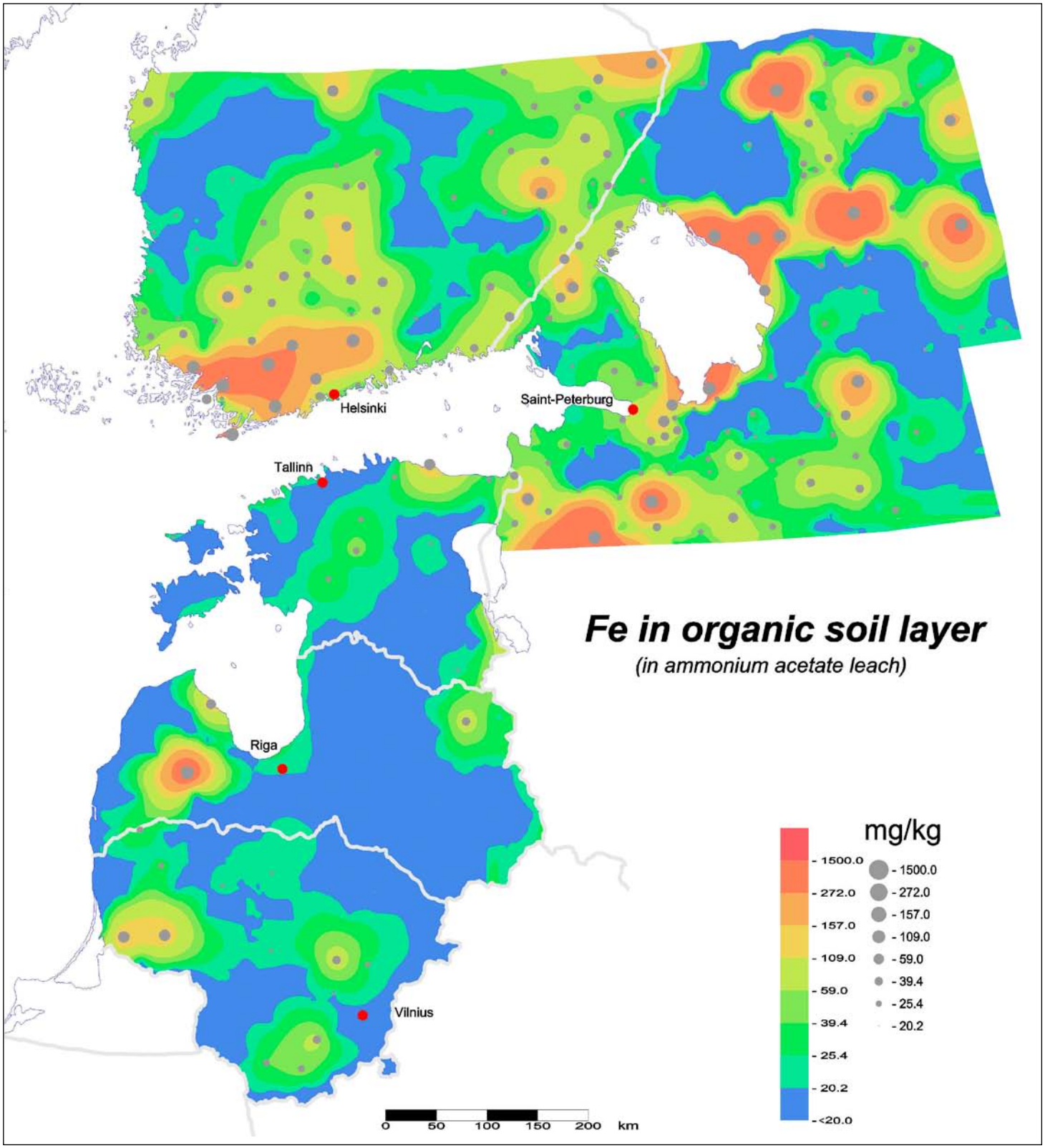
Fe – Iron MOS


Fe in terrestrial moss
Helsinki
Saint-Peterburg
Tallinn
Riga
Vilnius
mg/kg
- 3850
- 979
- 730
- 633
- 516
- 441
- 348
- 293
- 255
- 209
- 168
- 66
0 50 100 150 200 km

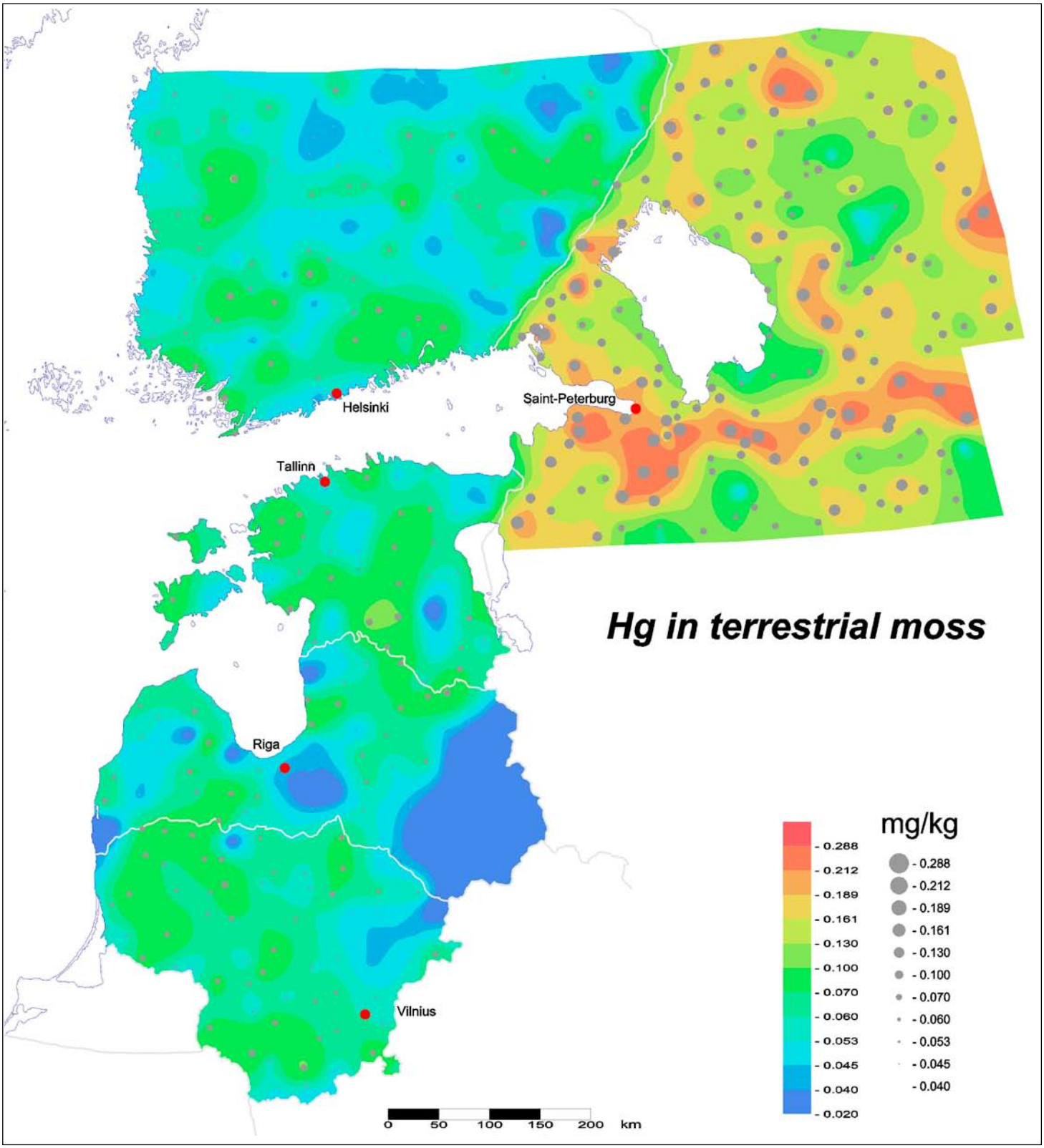
Fe – Iron ORG tot



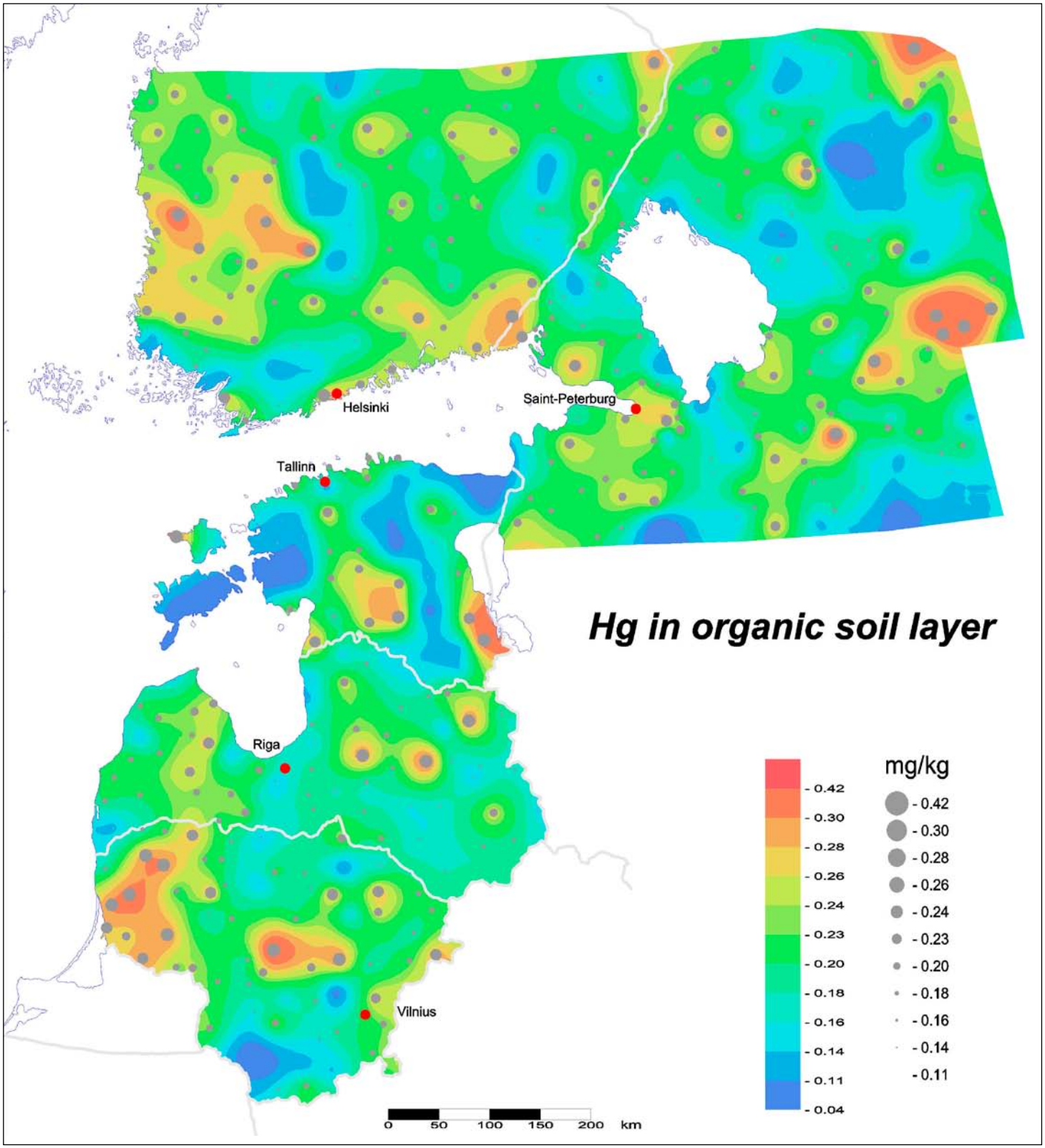
Fe – Iron ORG amm. acet



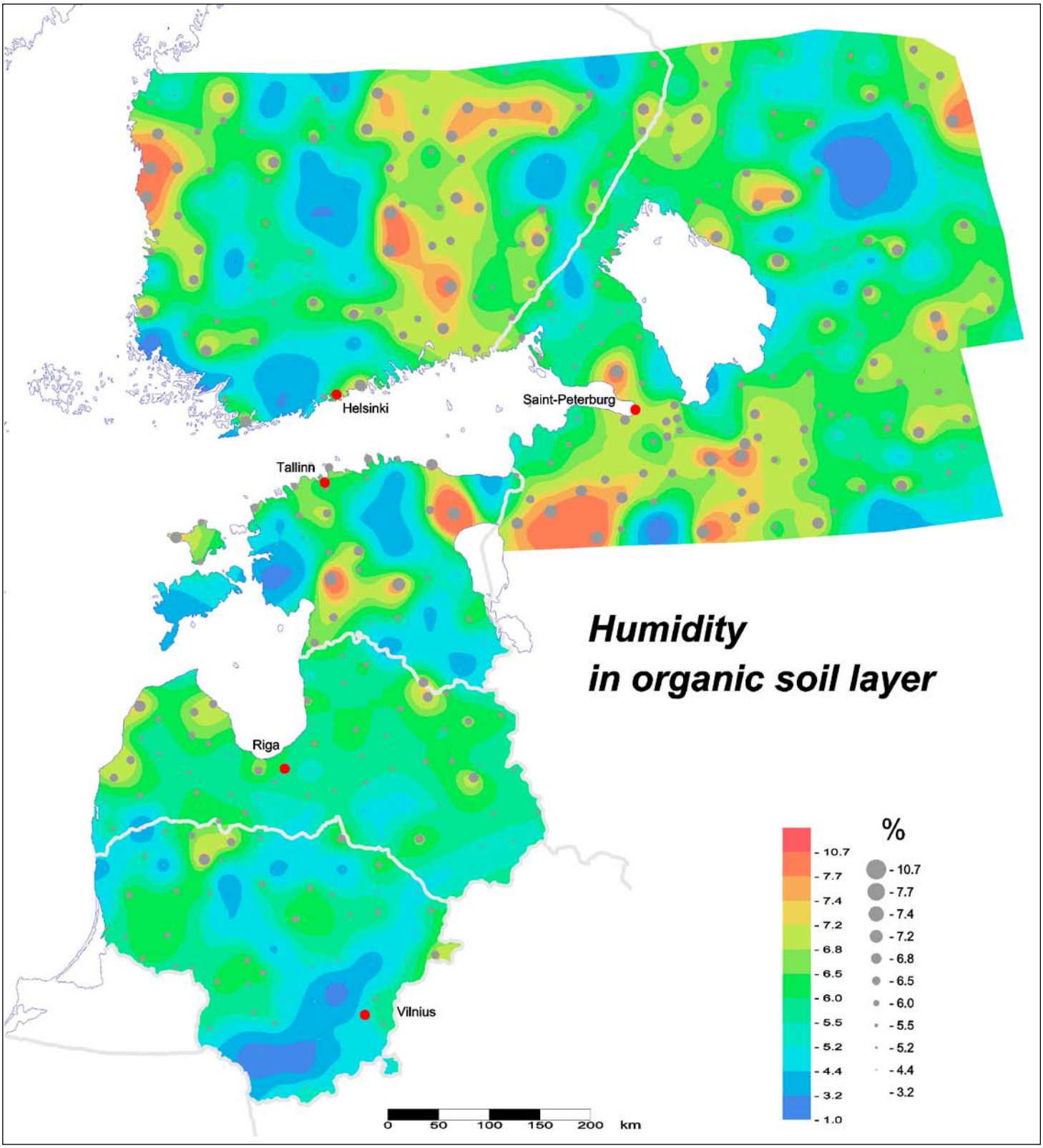
Hg – Mercury MOS



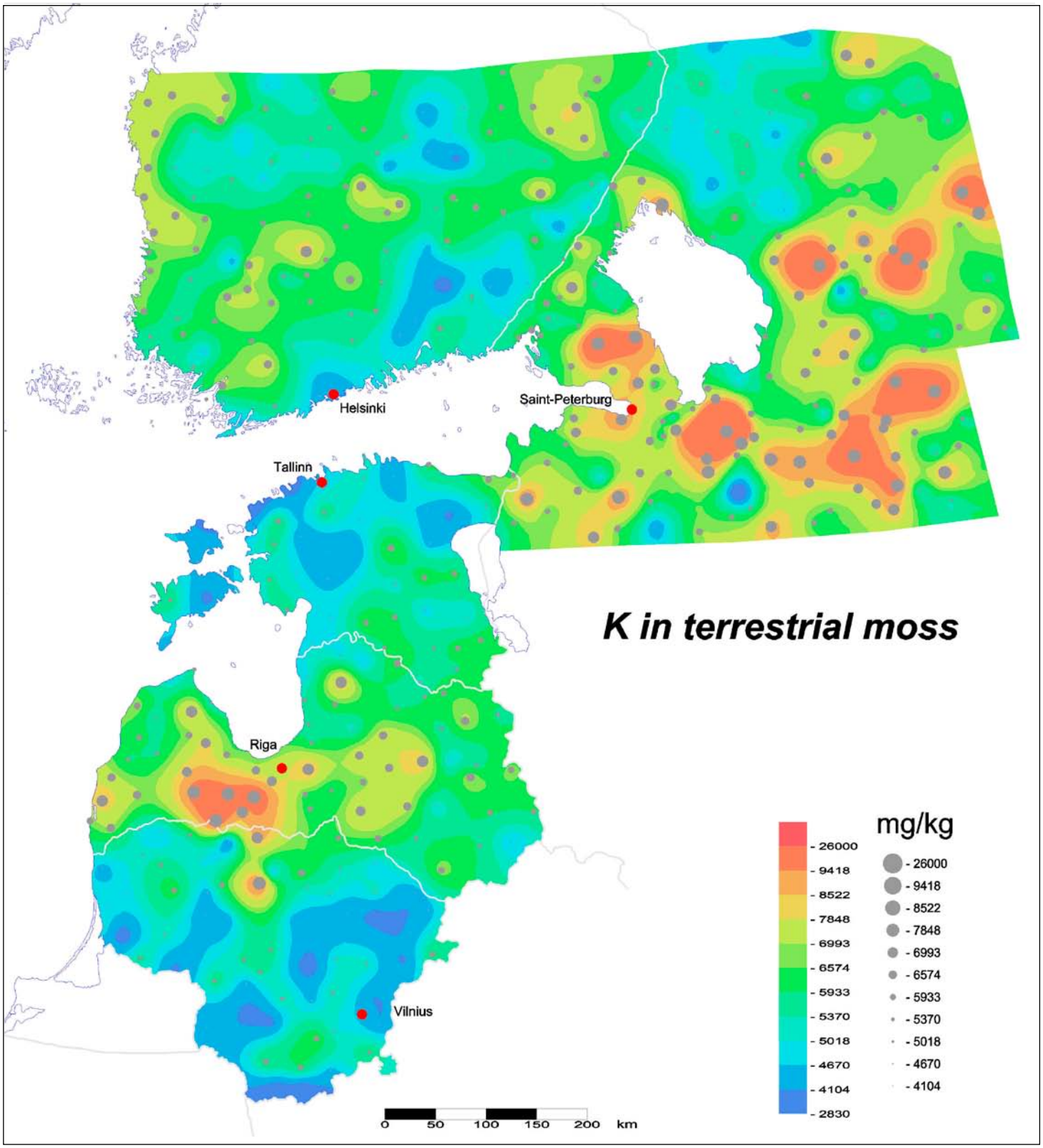
Hg – Mercury ORG tot



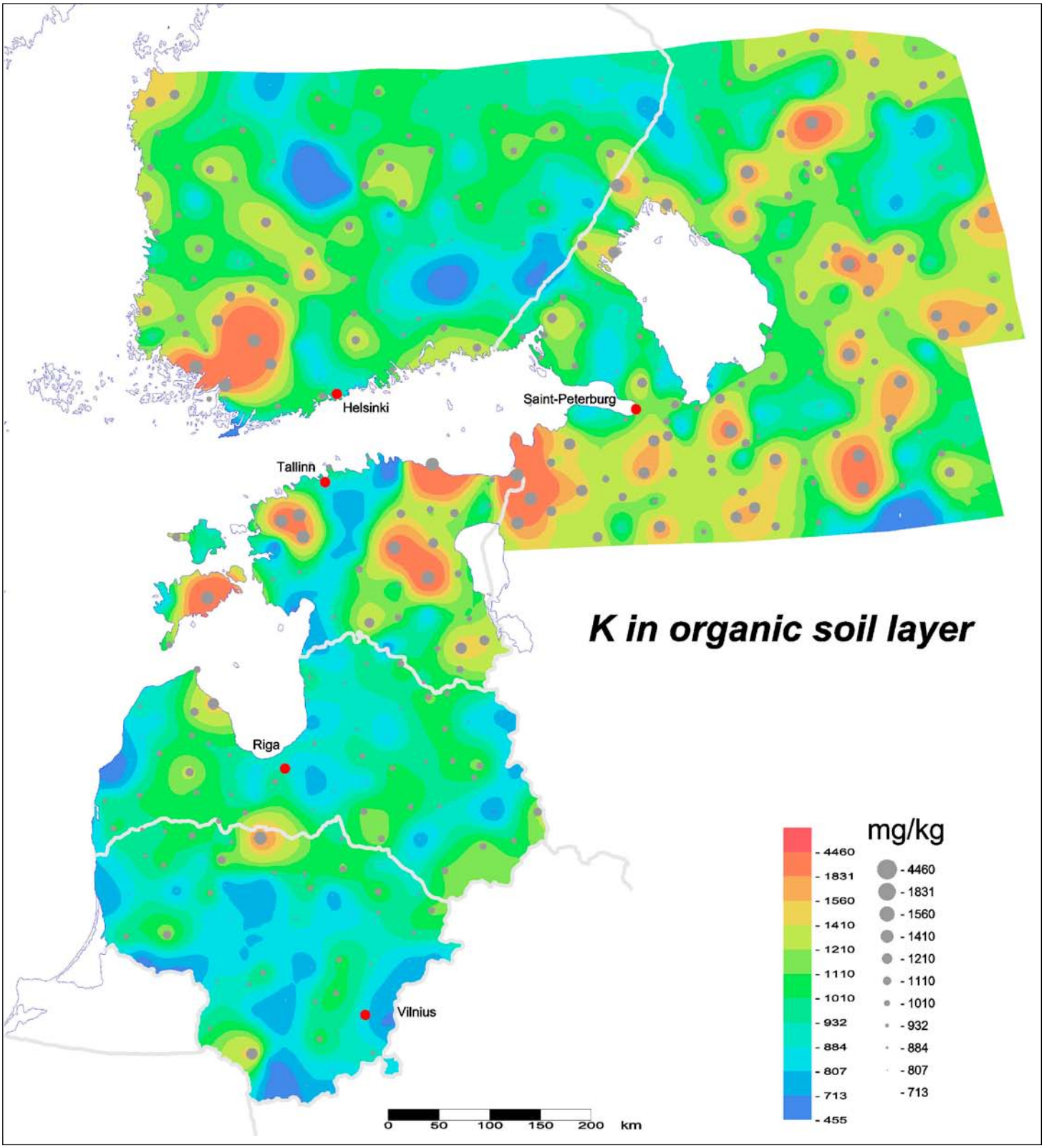
Humidity ORG tot



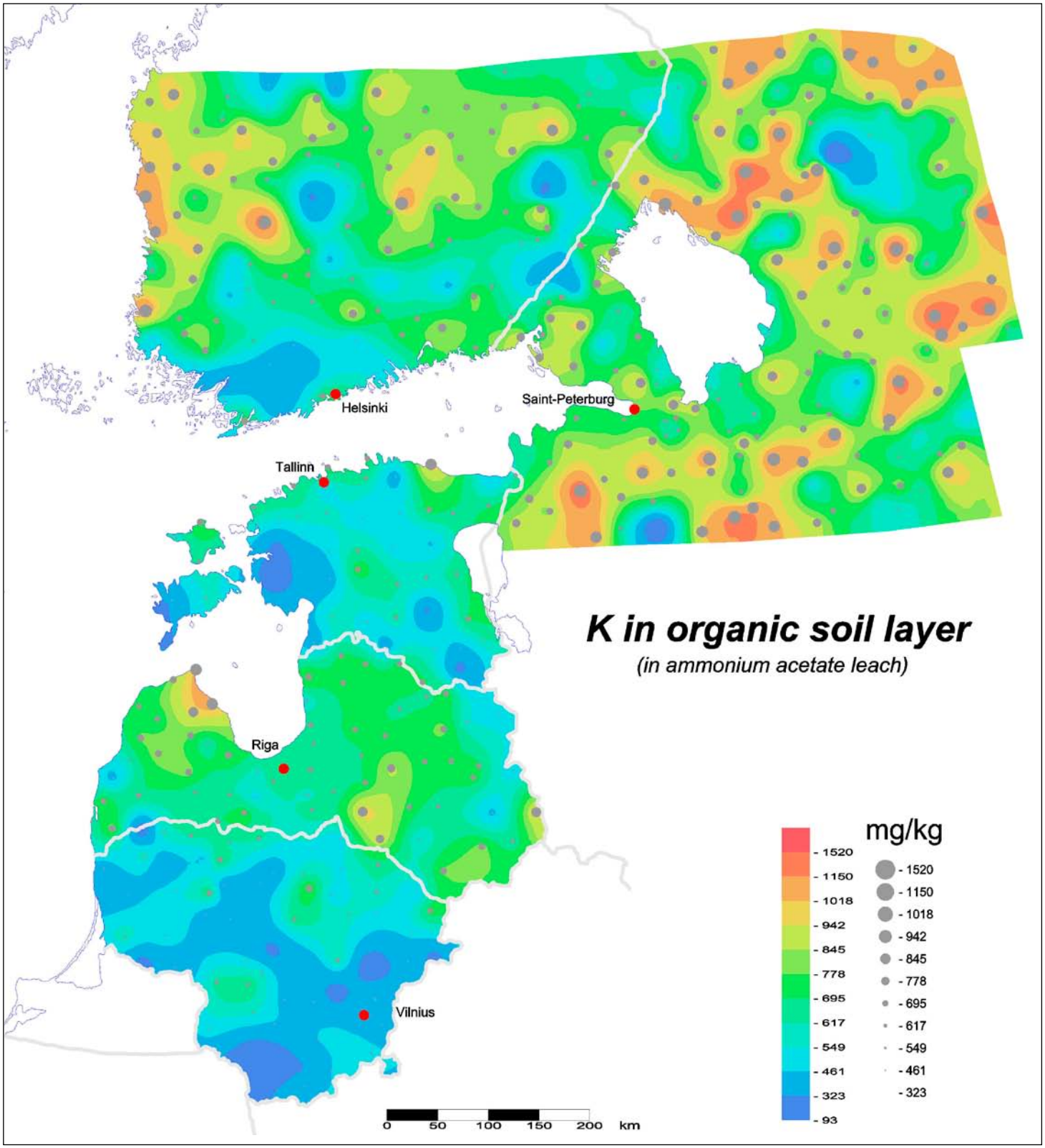
K – Potassium MOS



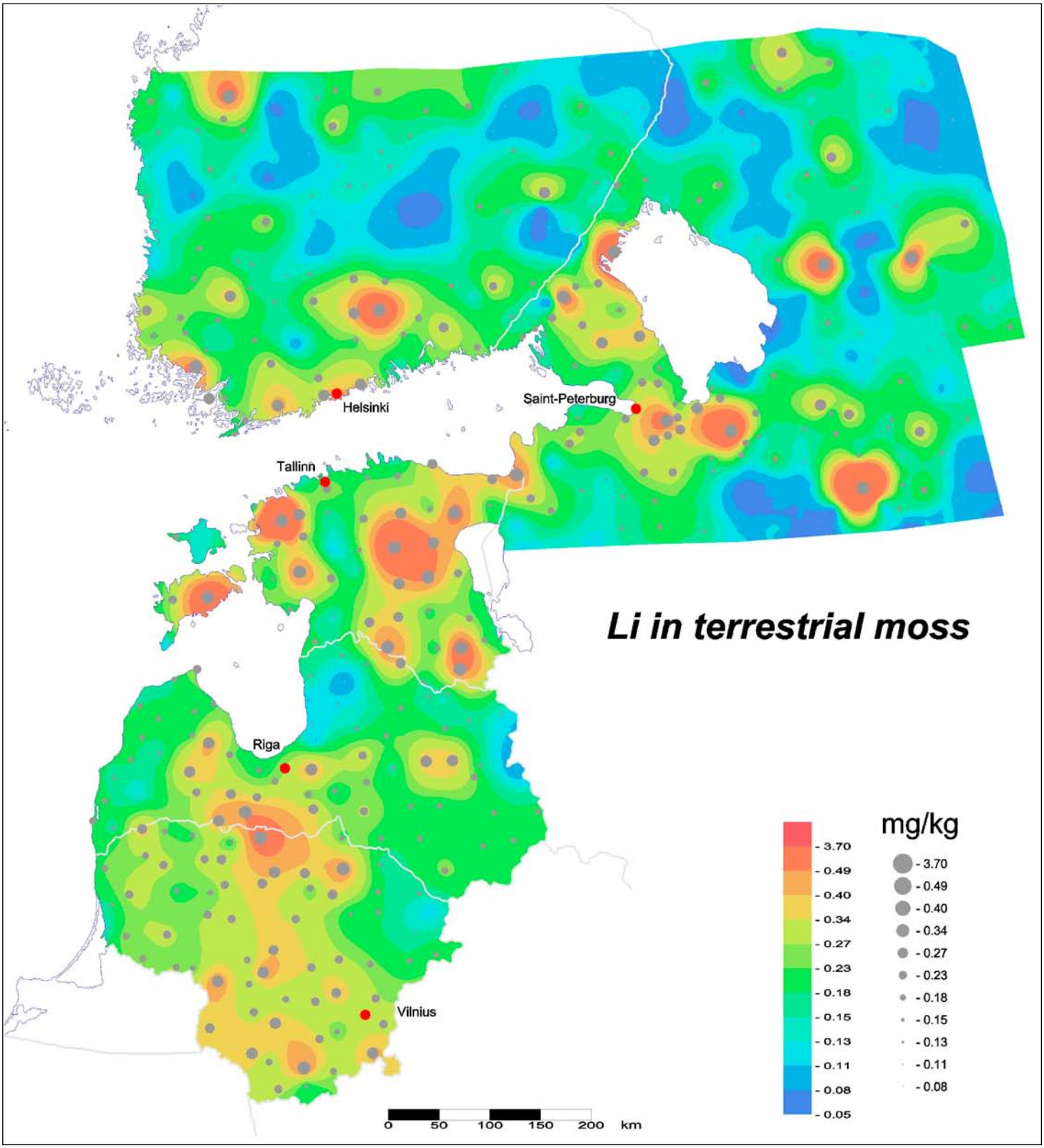
K – Potassium ORG tot



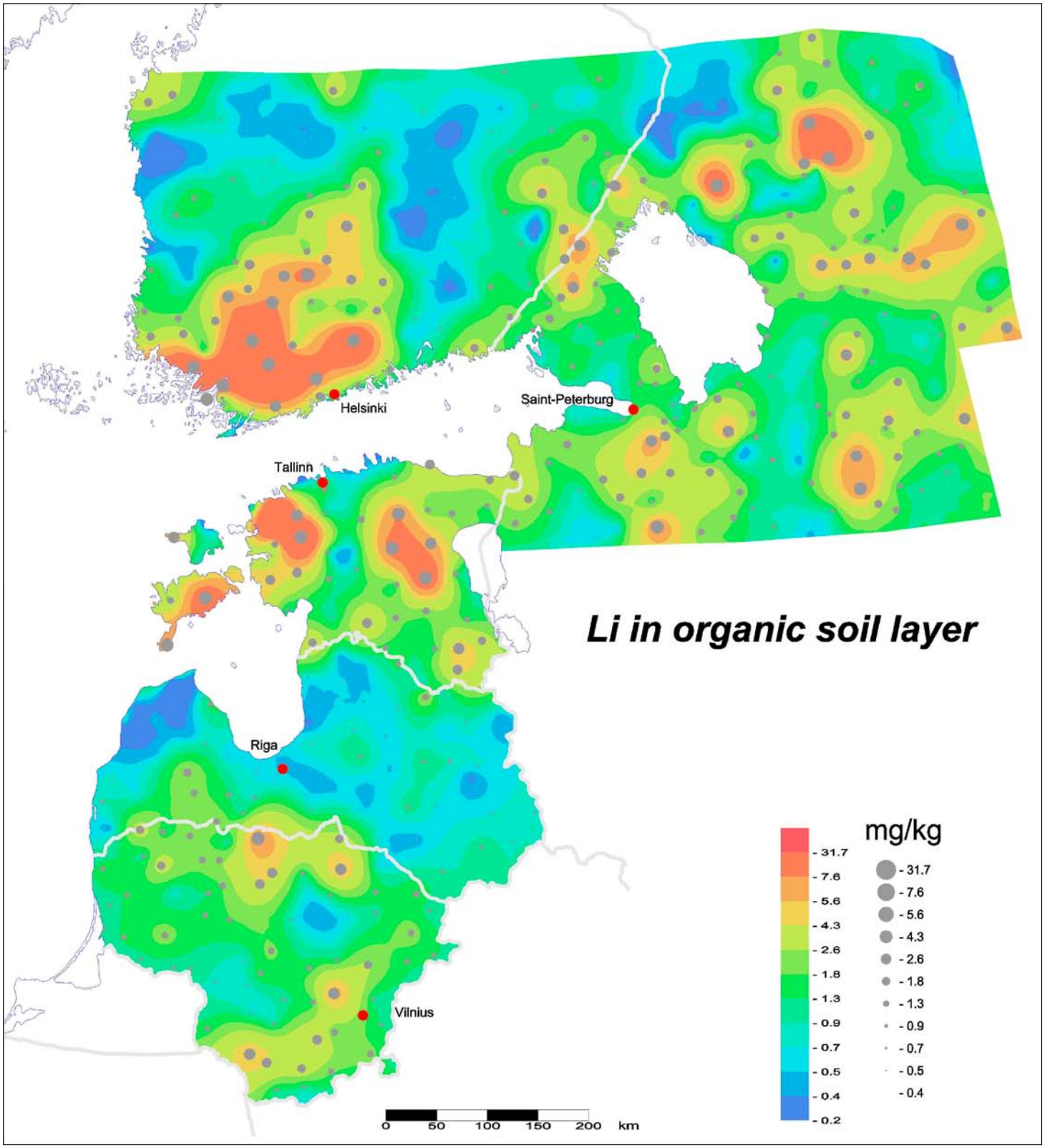
K – Potassium ORG amm. acet.



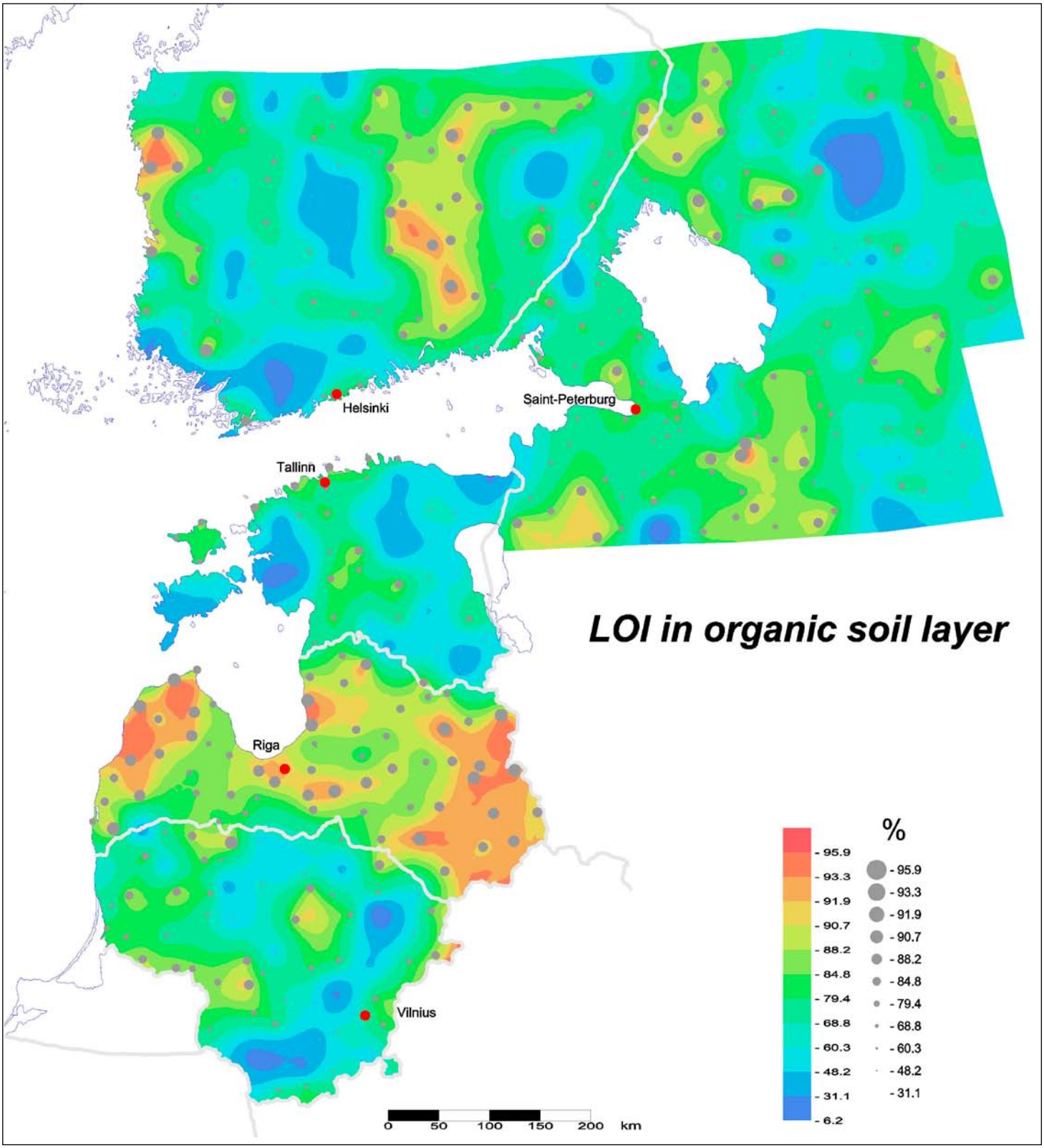
Li – Lithium MOS



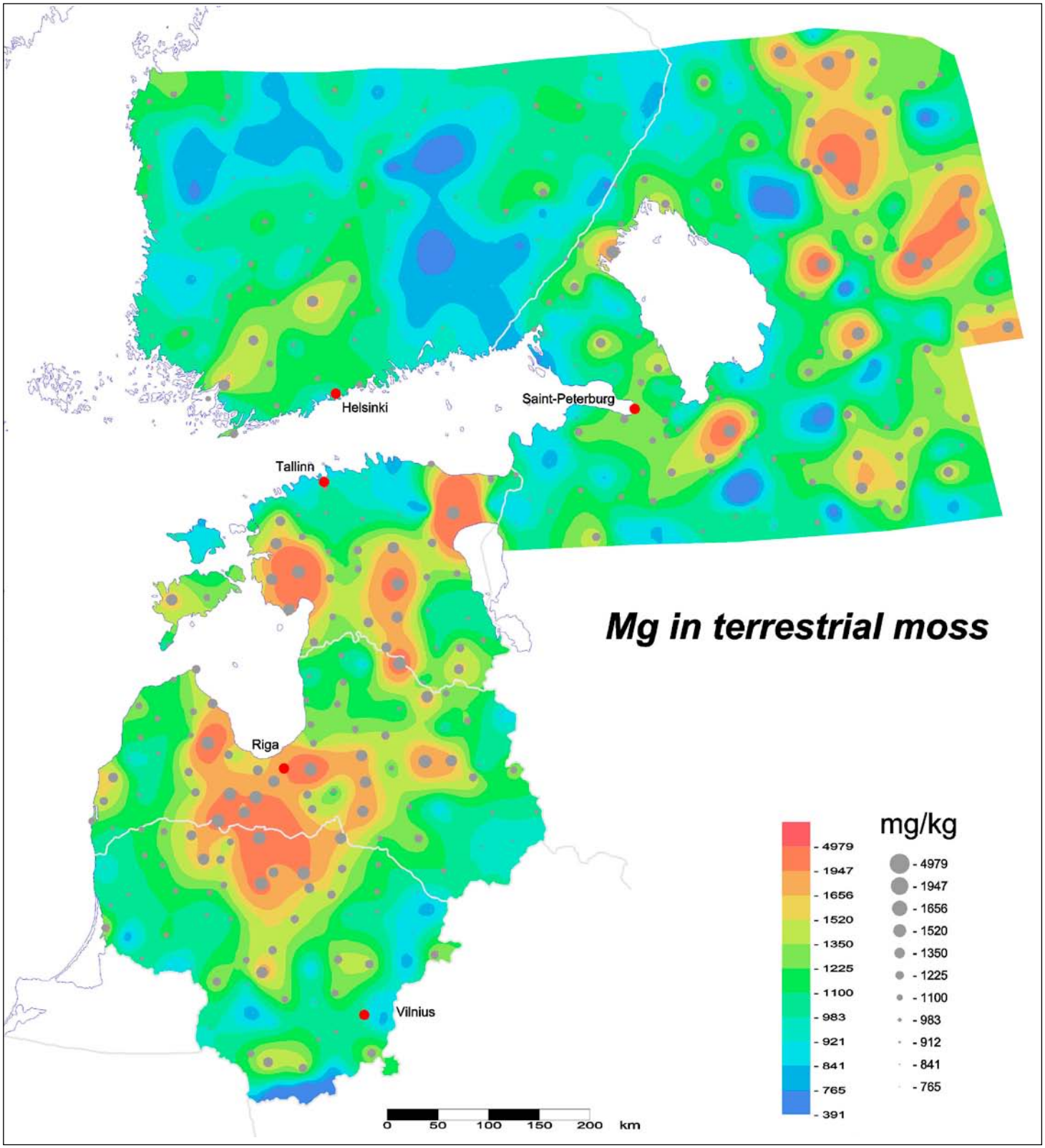
Li – Lithium ORG tot



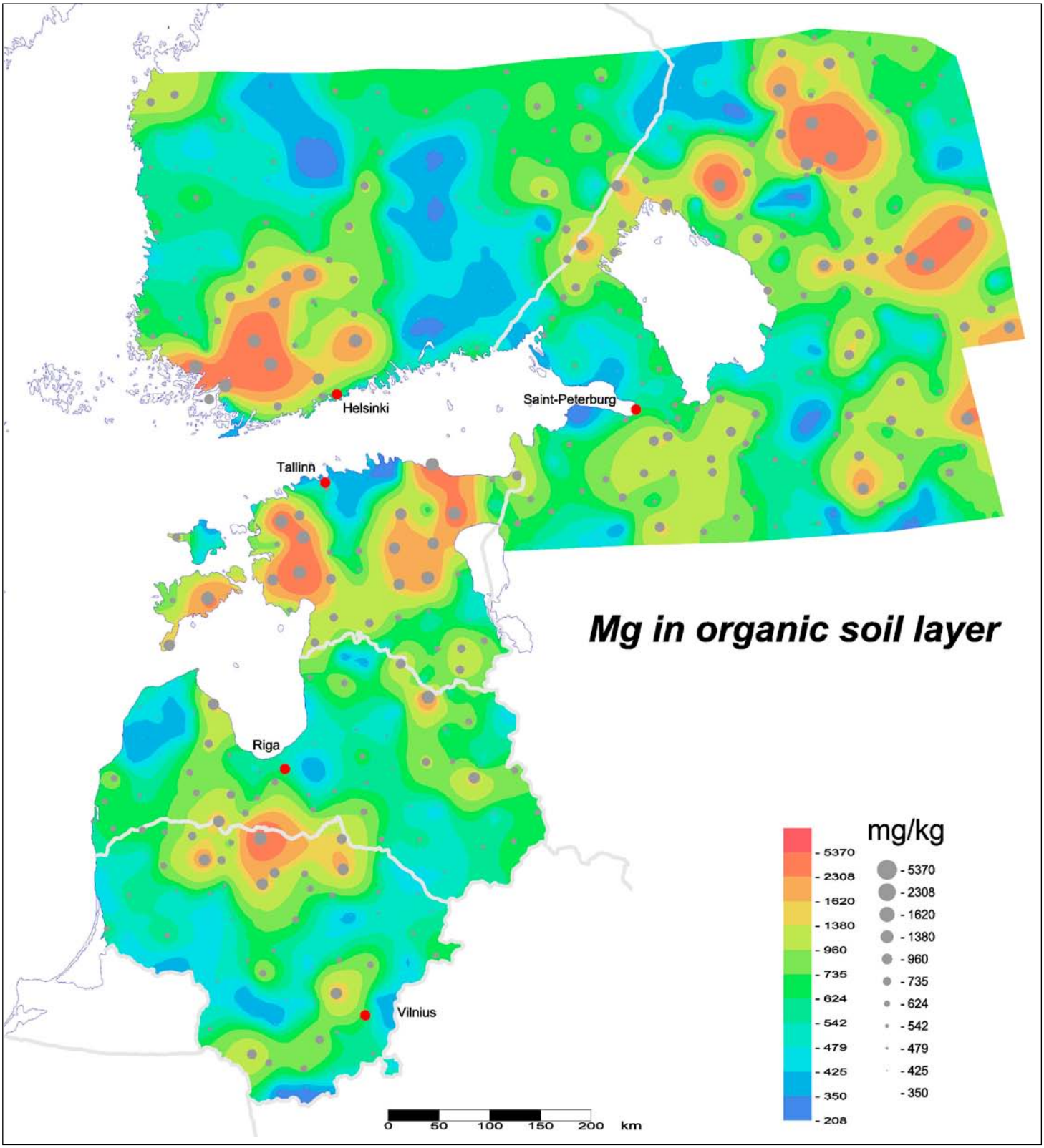
LOI – Loss on ignition ORG tot



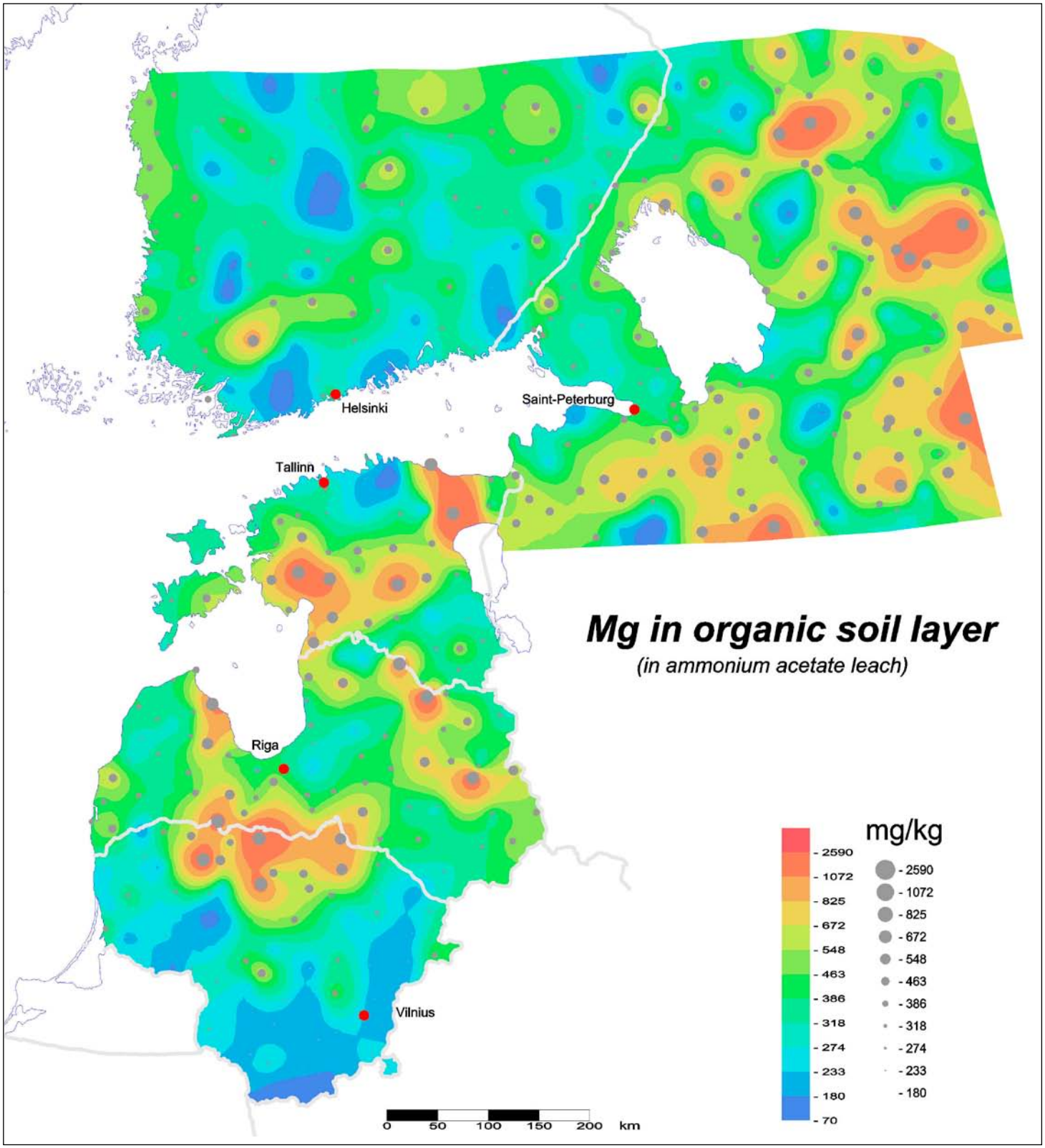
Mg – Magnesium MOS



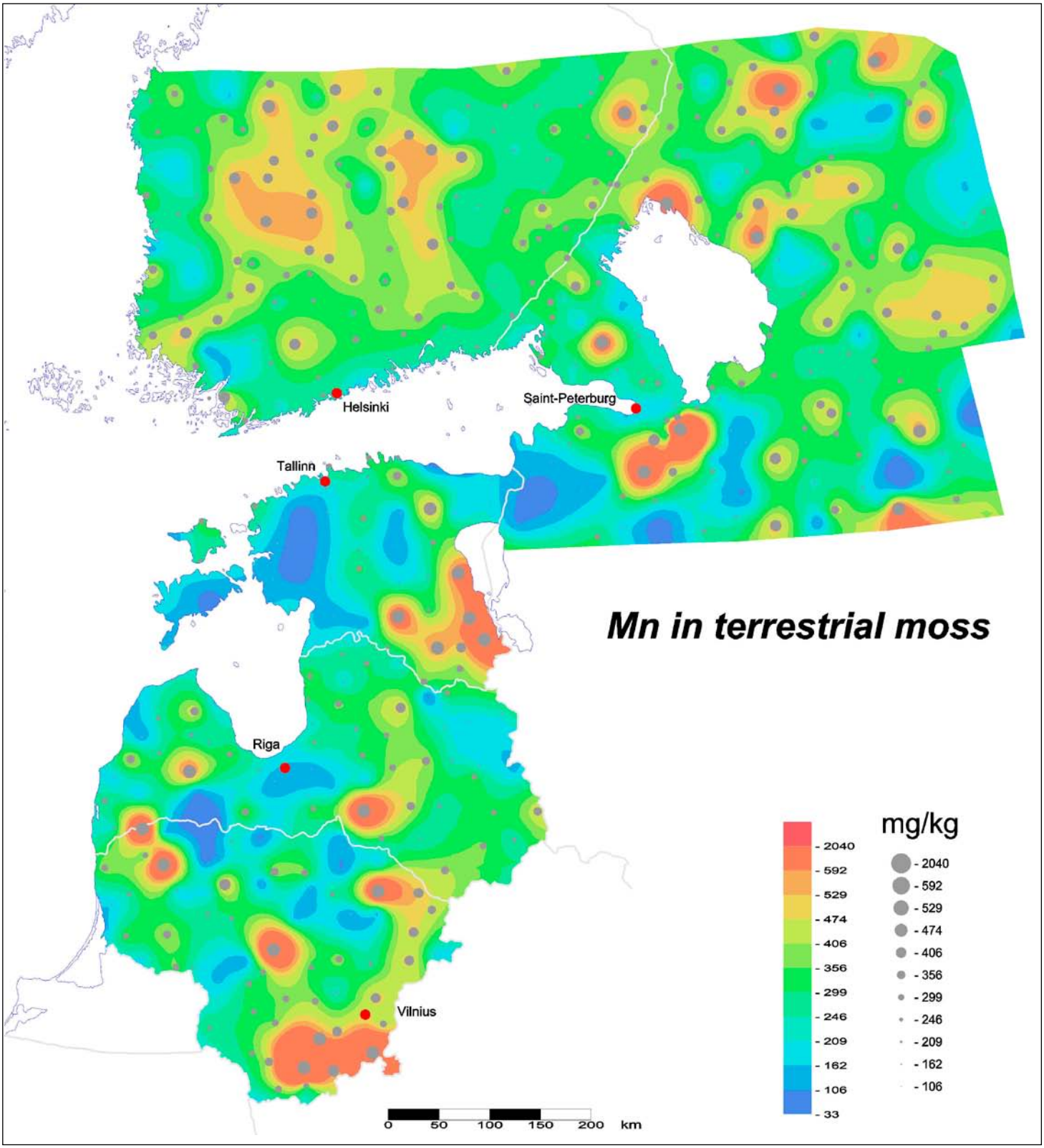
Mg – Magnesium ORG tot



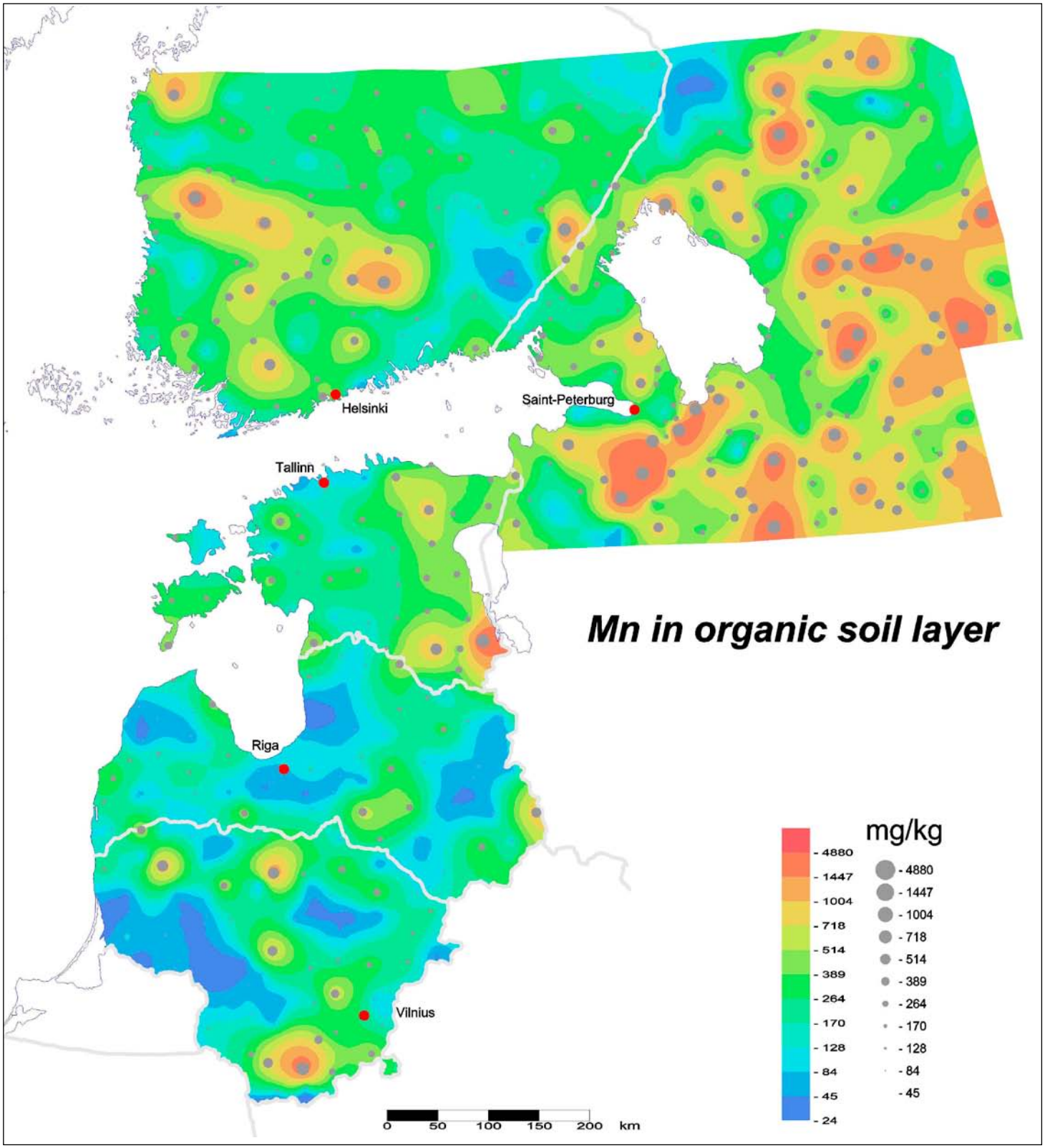
Mg – Magnesium ORG amm. acet.



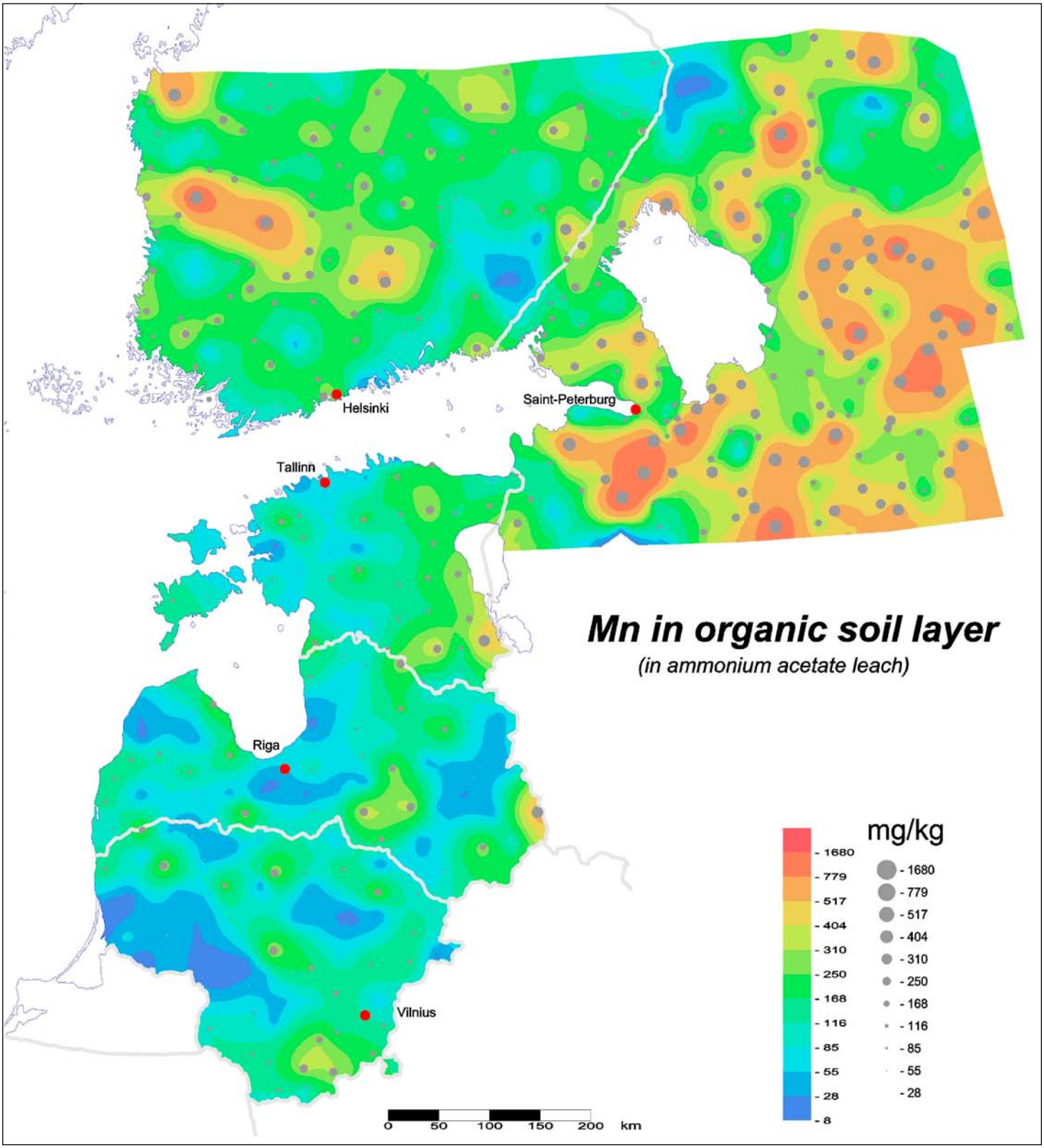
Mn – Manganese MOS



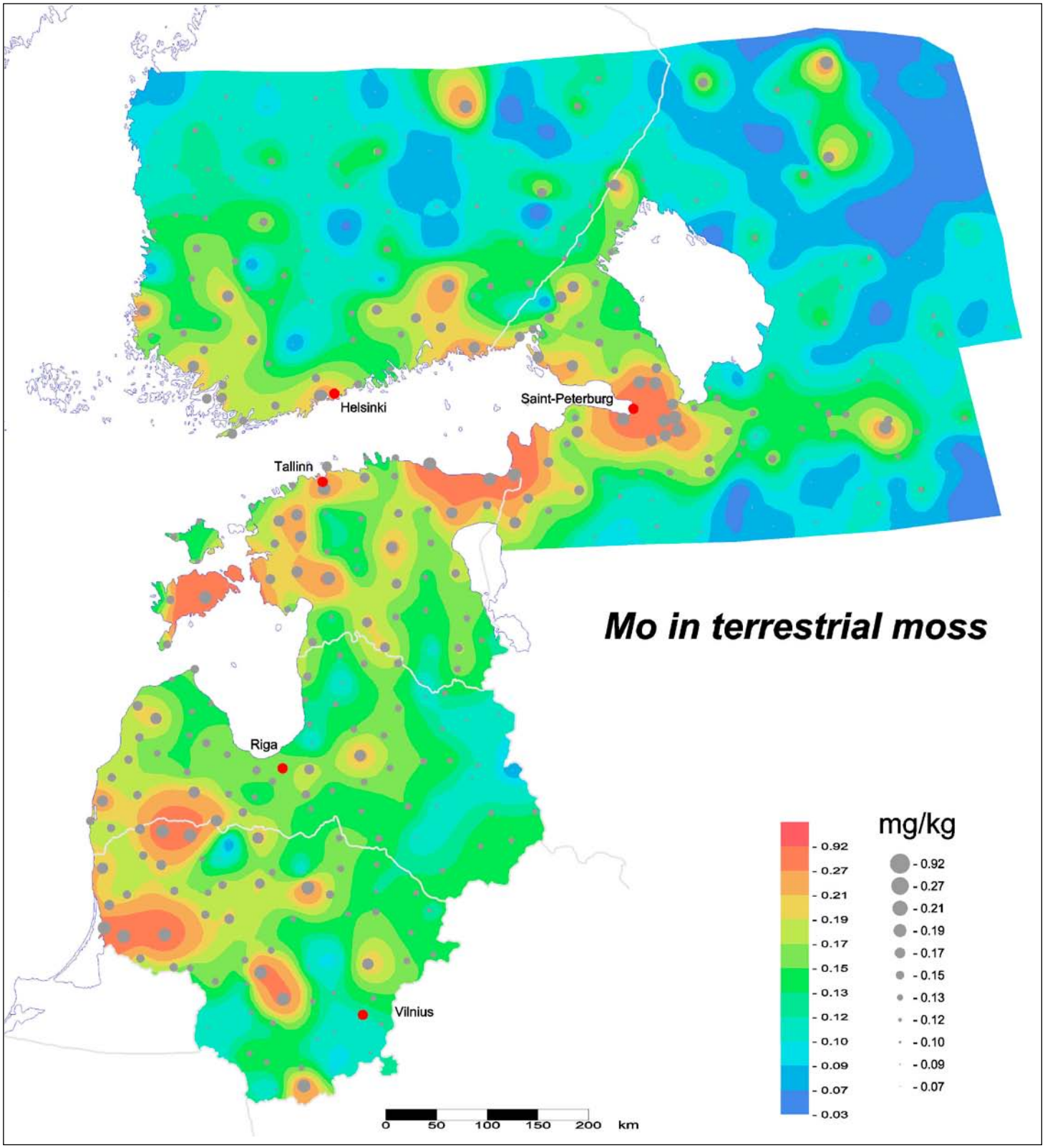
Mn – Manganese ORG tot



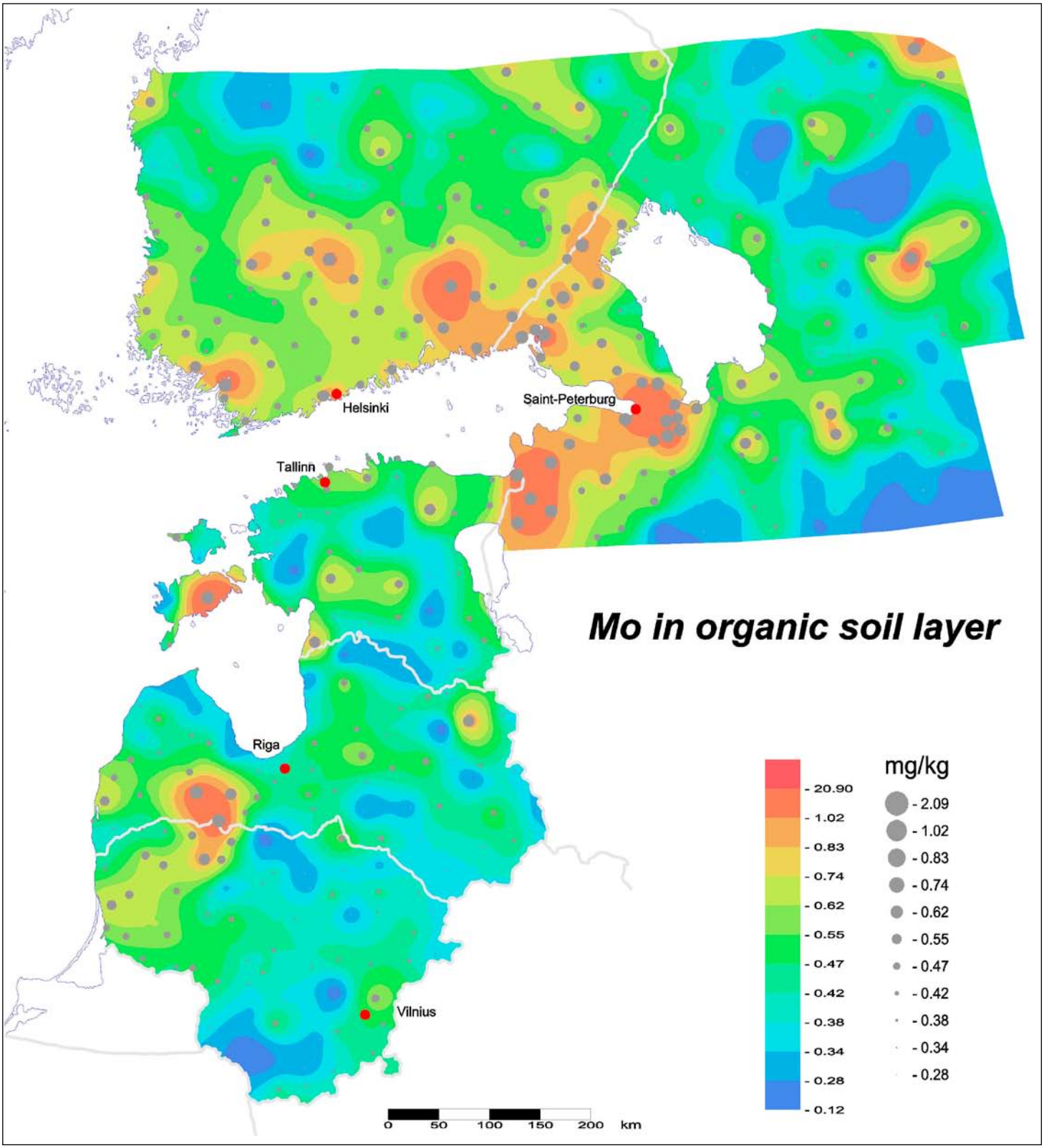
Mn – Manganese ORG amm. acet.



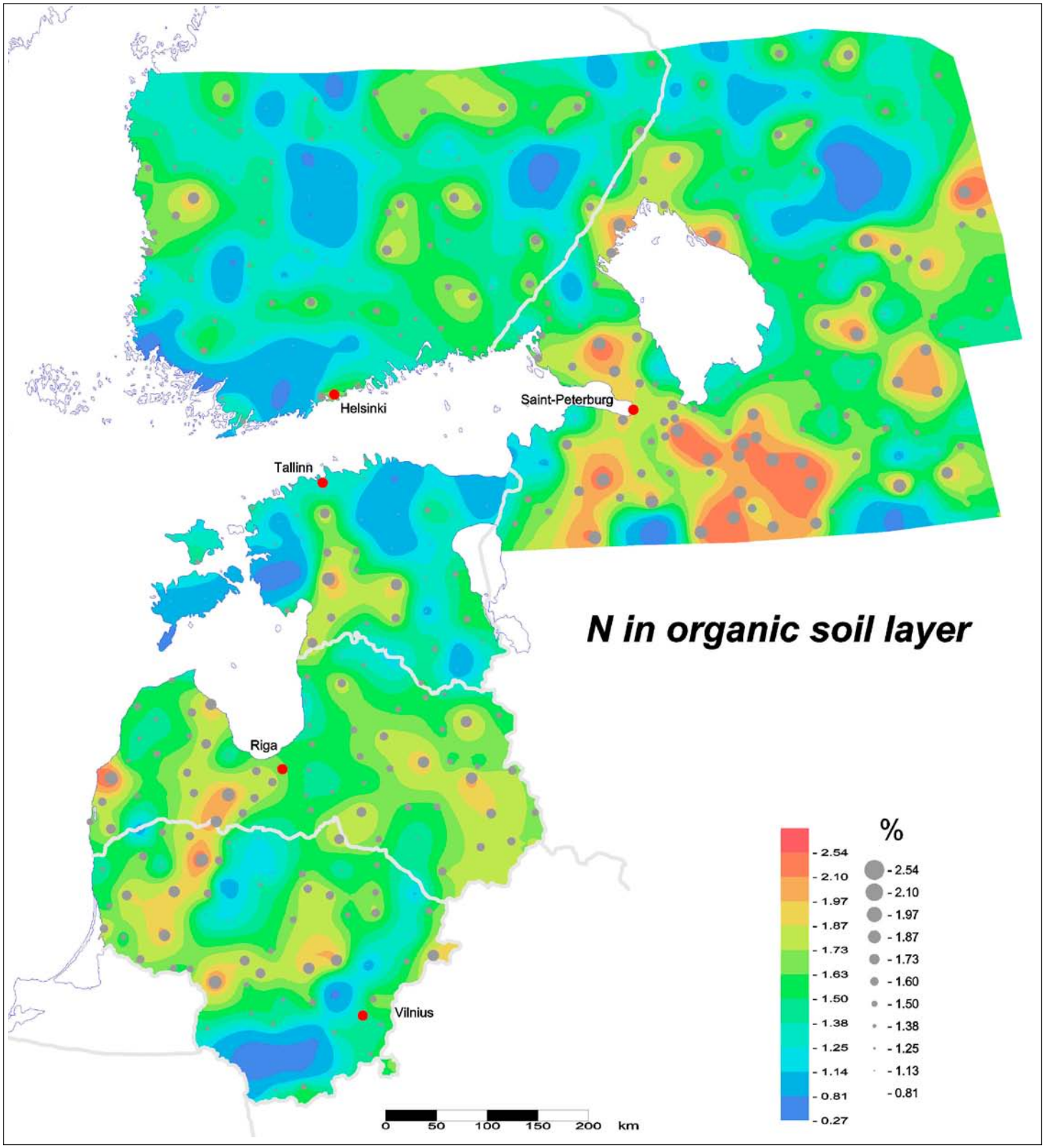
Mo – Molybdenum MOS



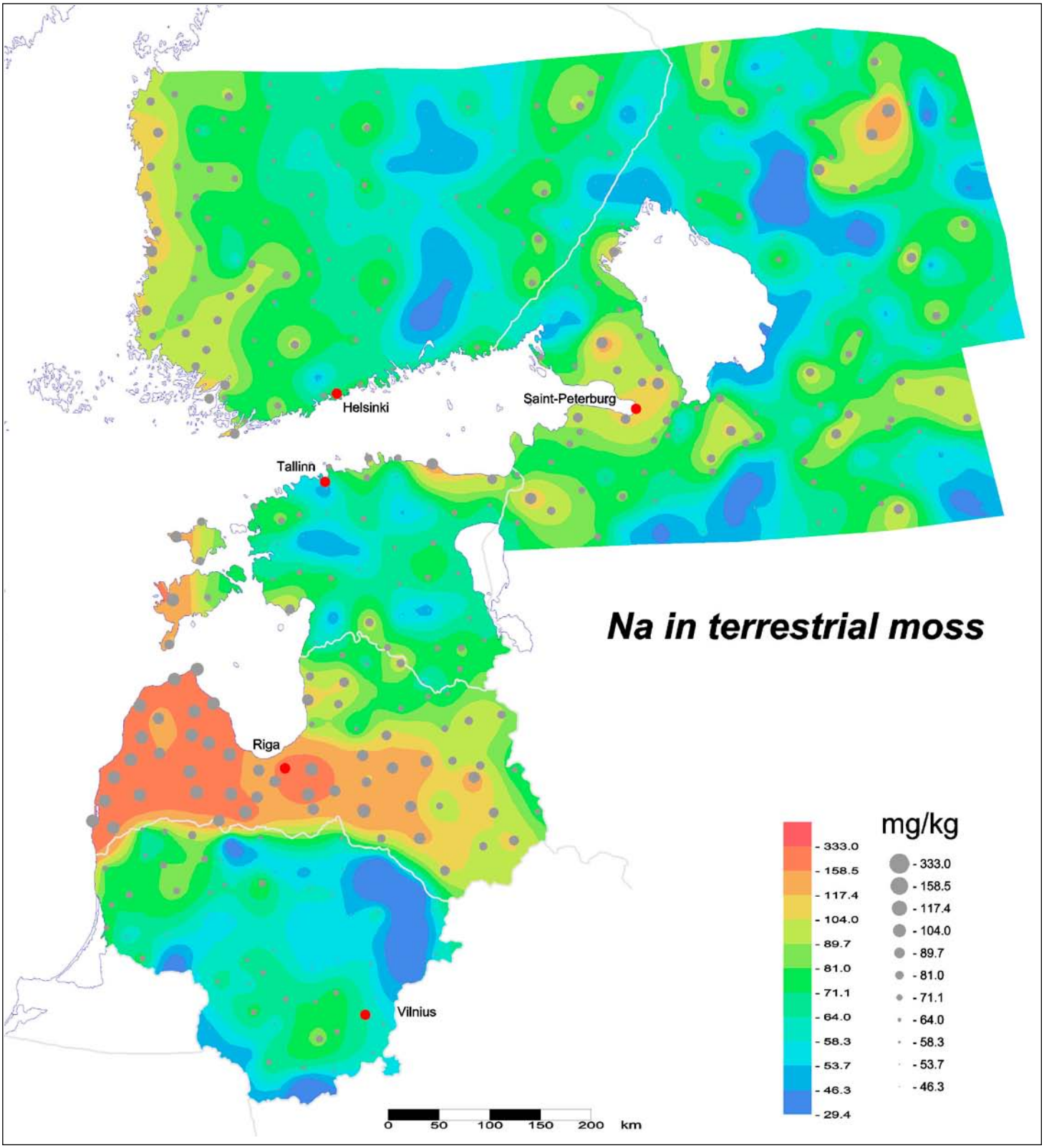
Mo – Molybdenum ORG tot



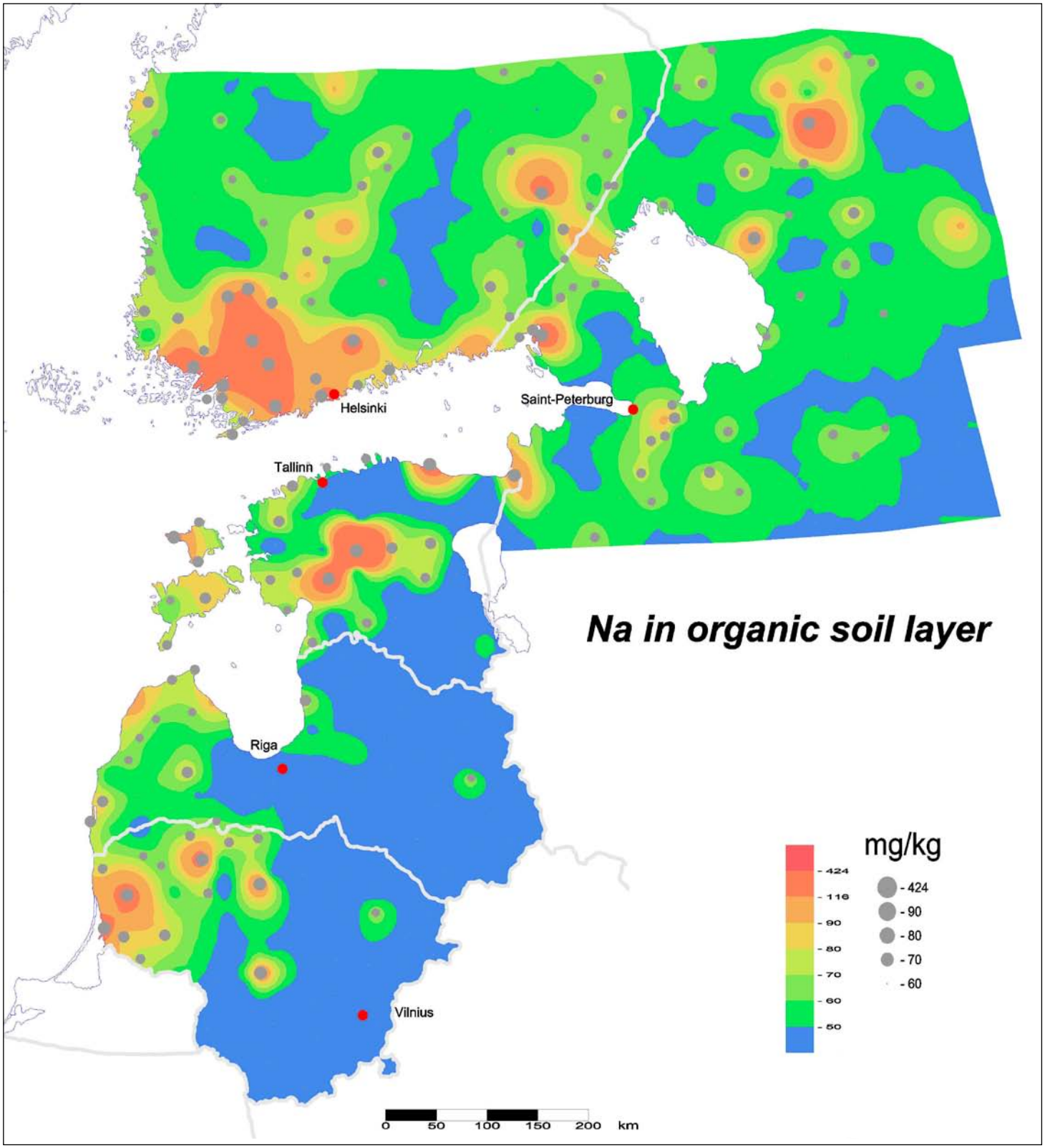
N – Nitrogen ORG tot



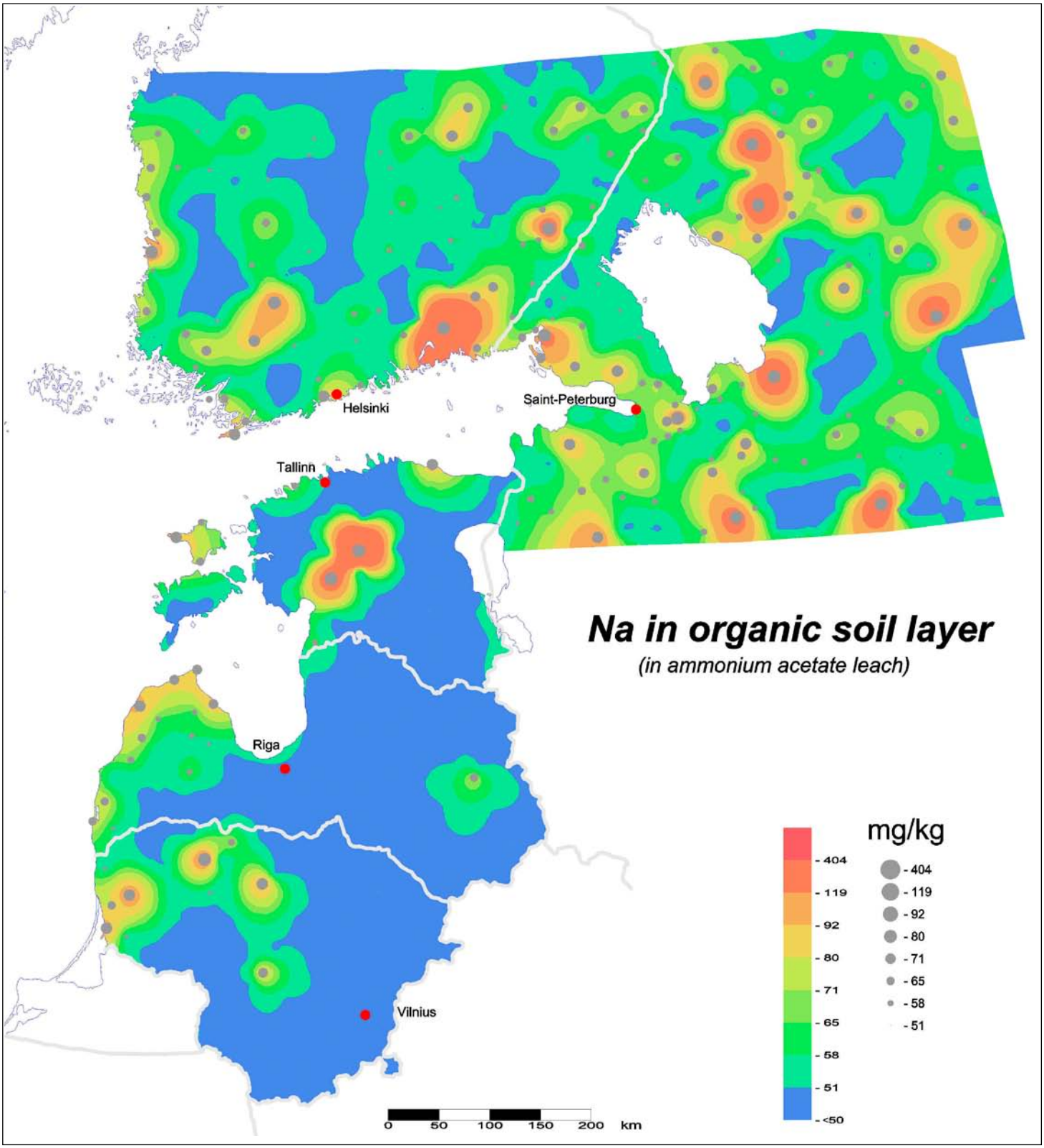
Na – Sodium MOS



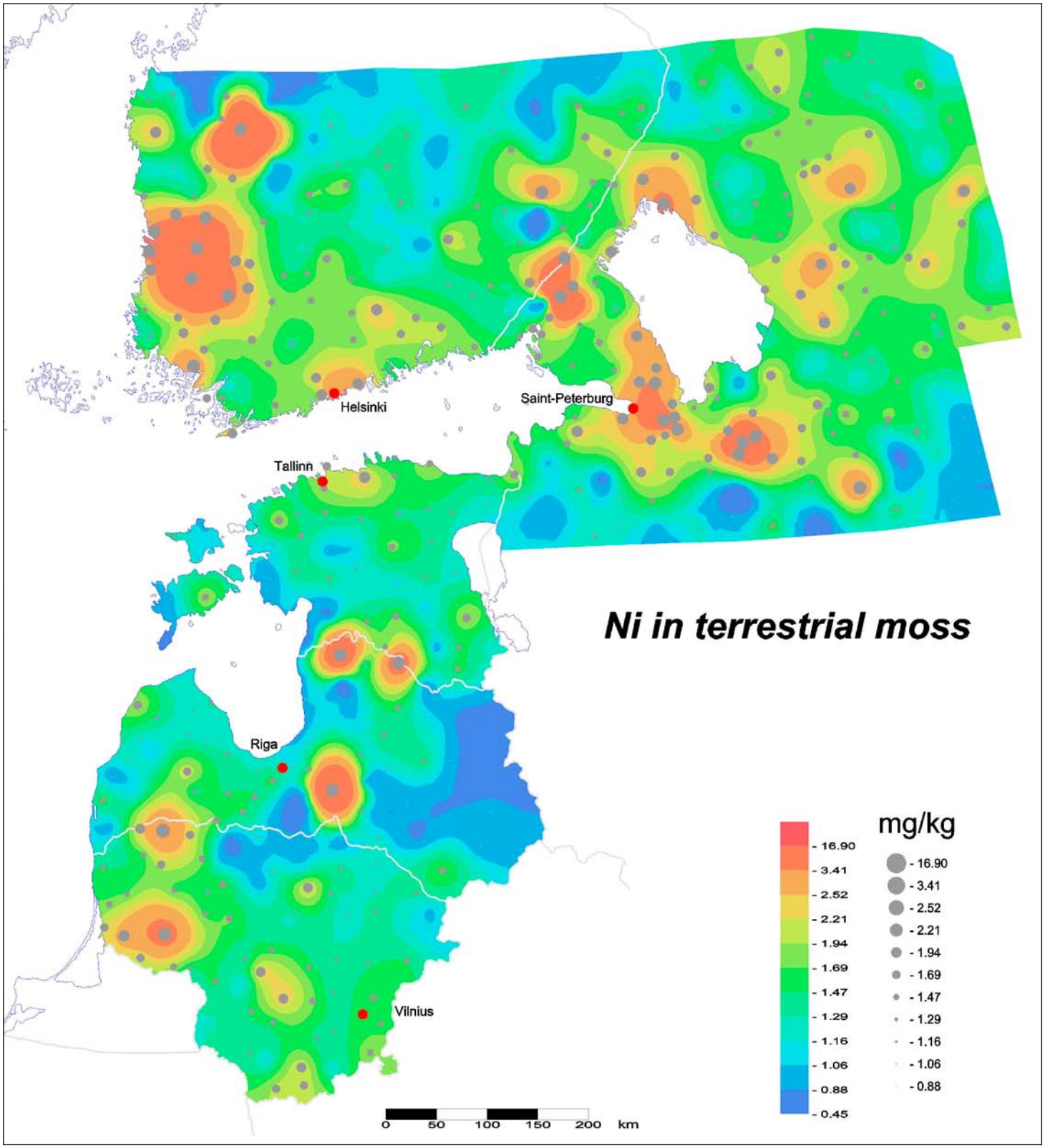
Na – Sodium ORG tot



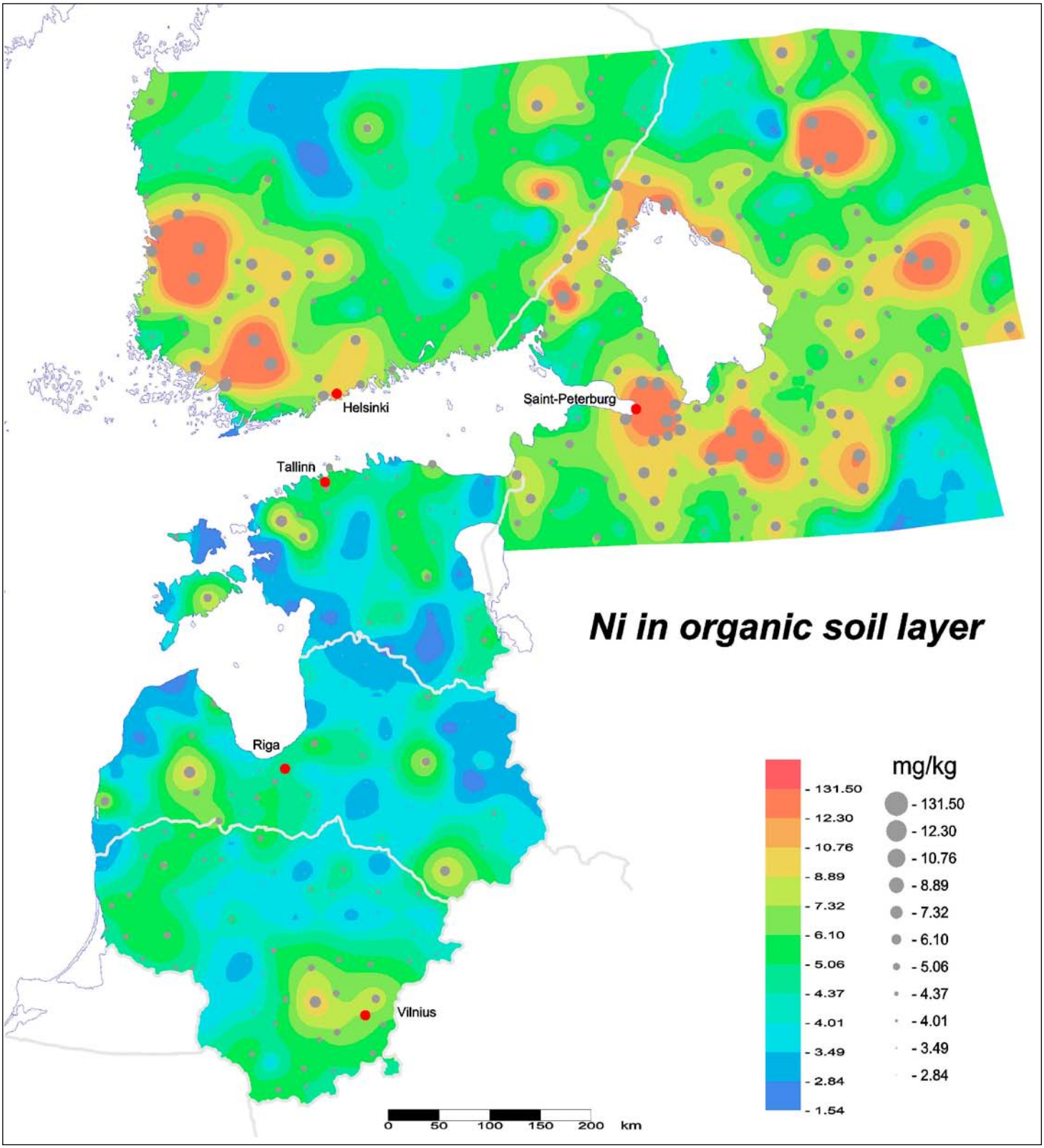
Na – Sodium ORG amm. acet.



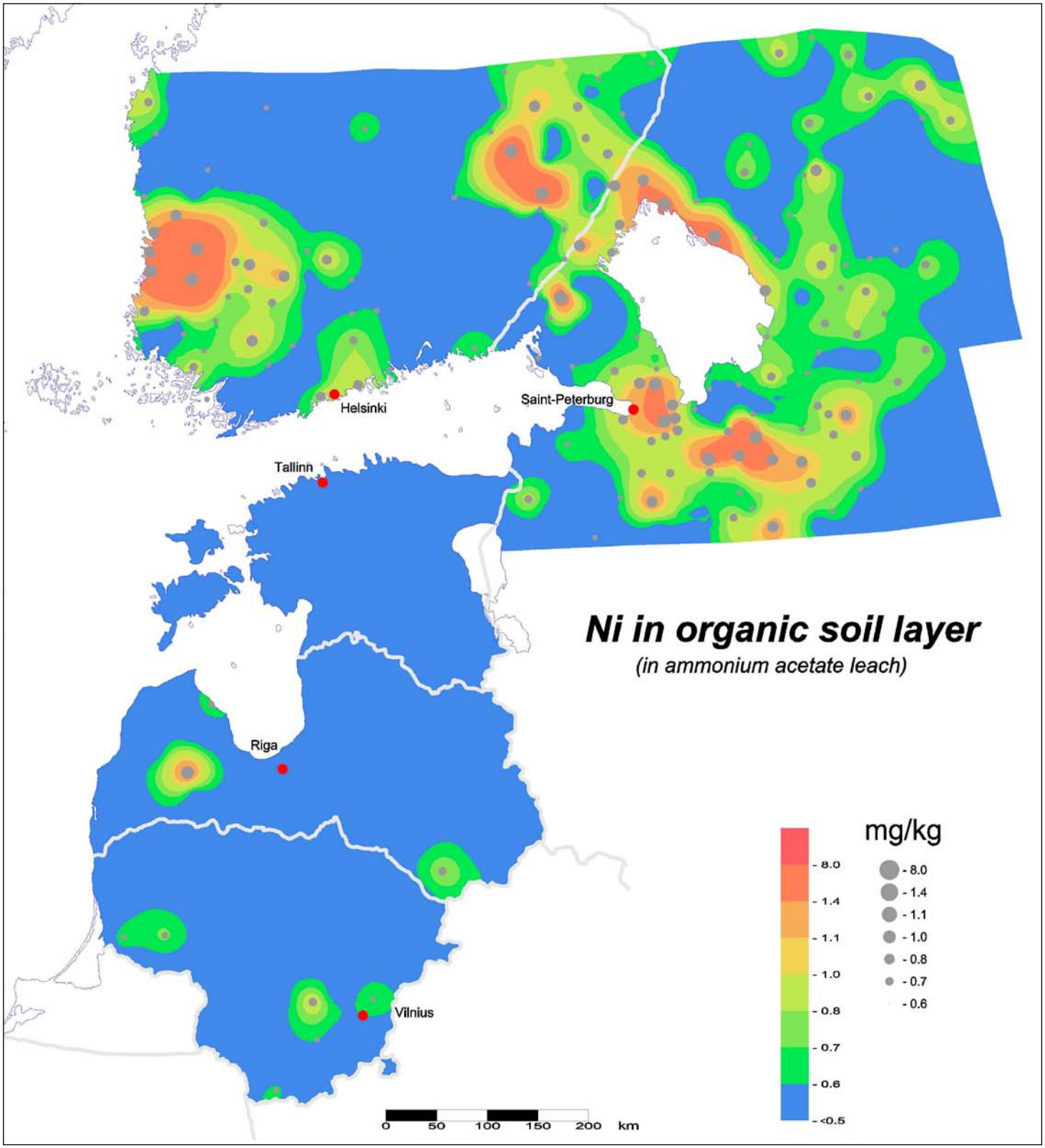
Ni – Nickel MOS



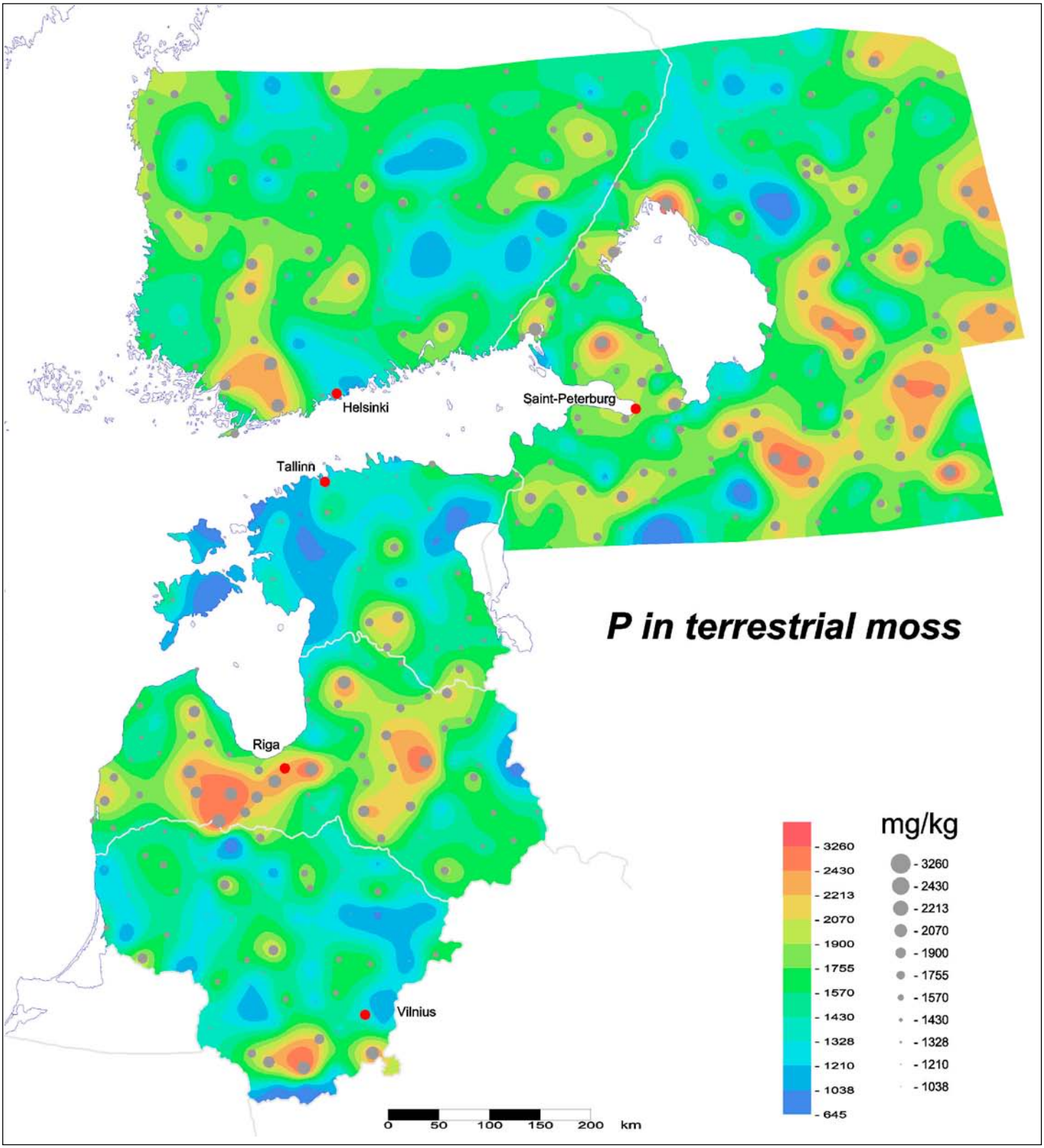
Ni – Nickel ORG tot



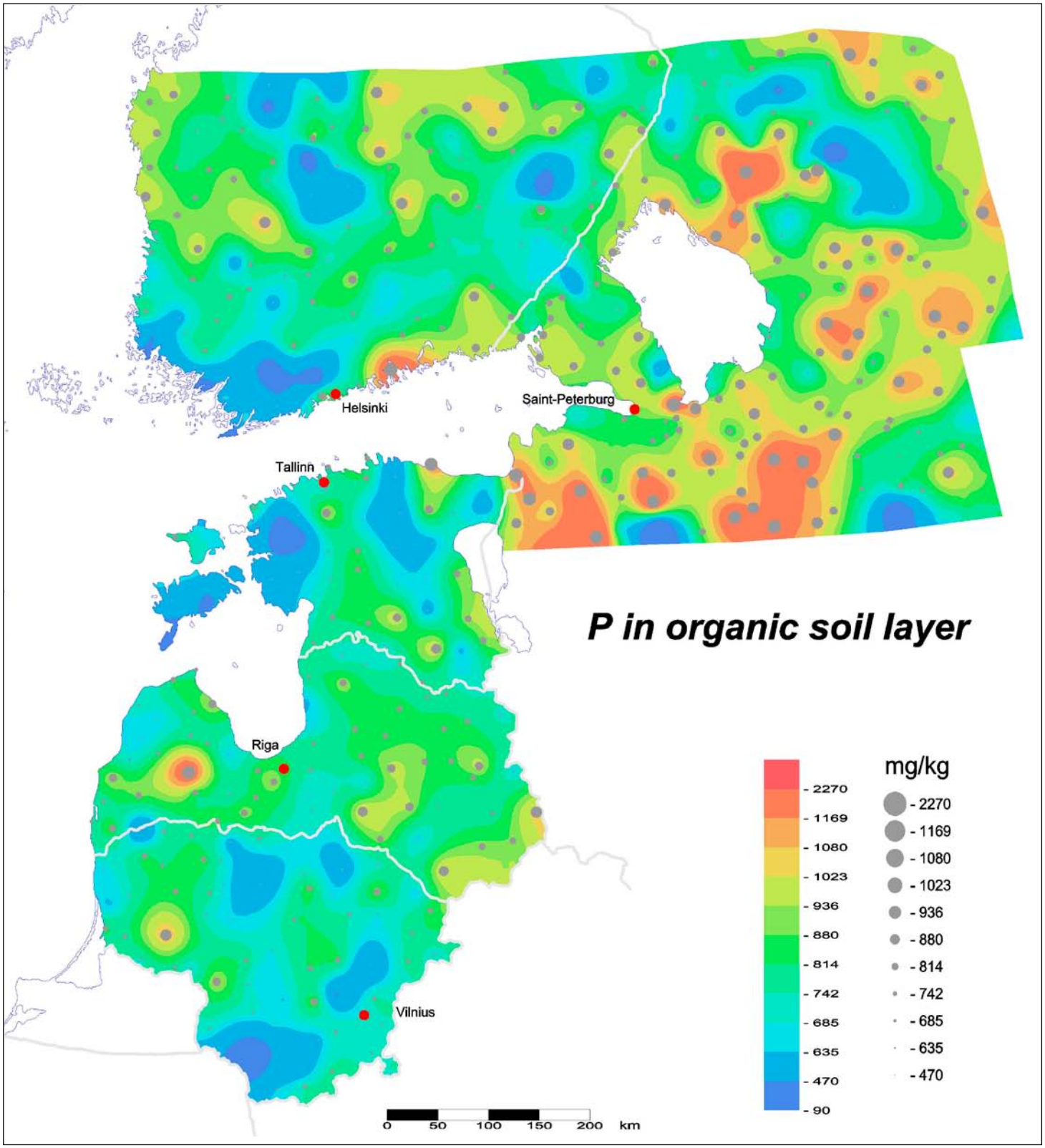
Ni – Nickel ORG amm. acet.



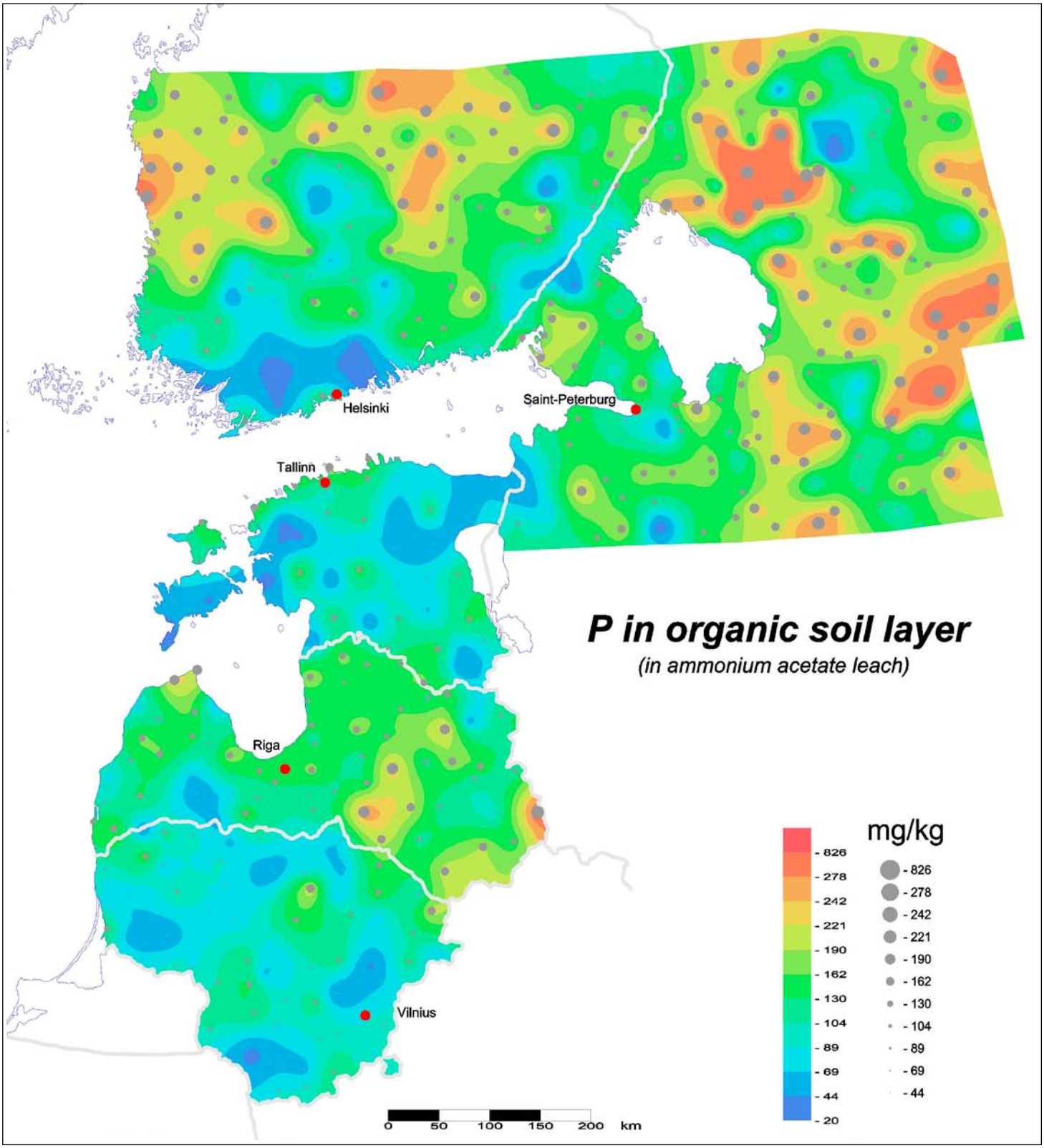
P – Phosphorus MOS



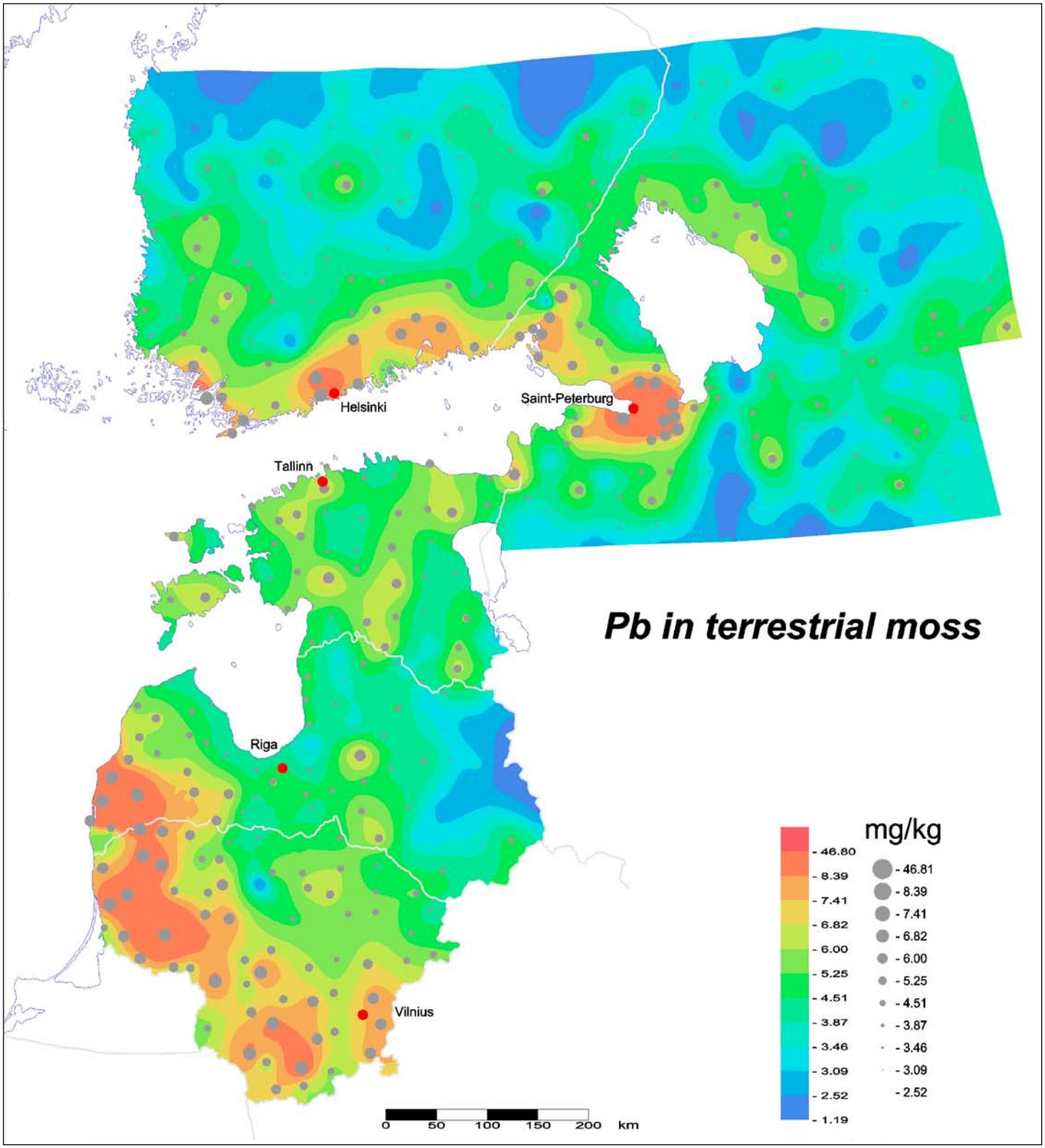
P – Phosphorus ORG tot



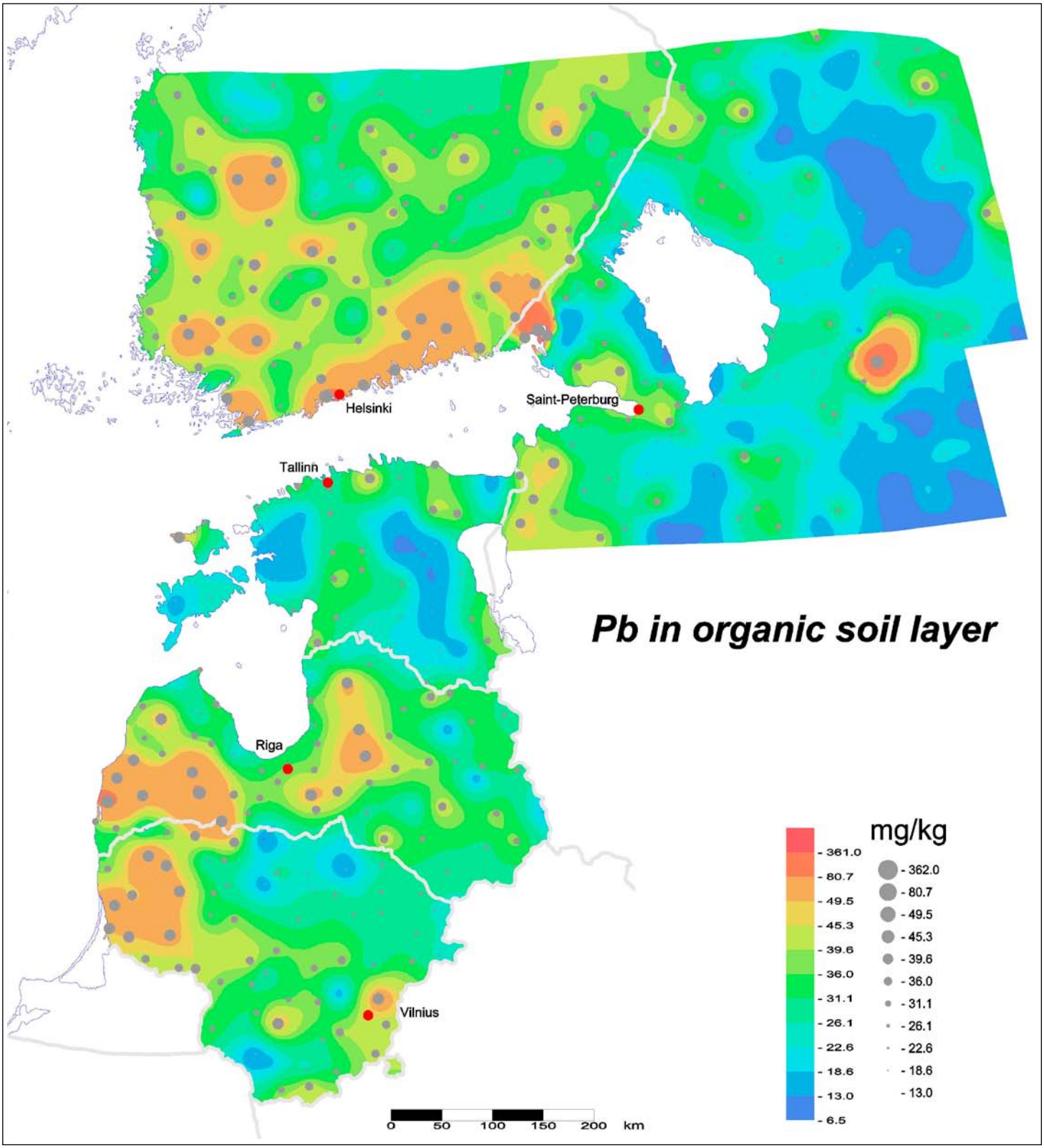
P – Phosphorus ORG amm. acet.



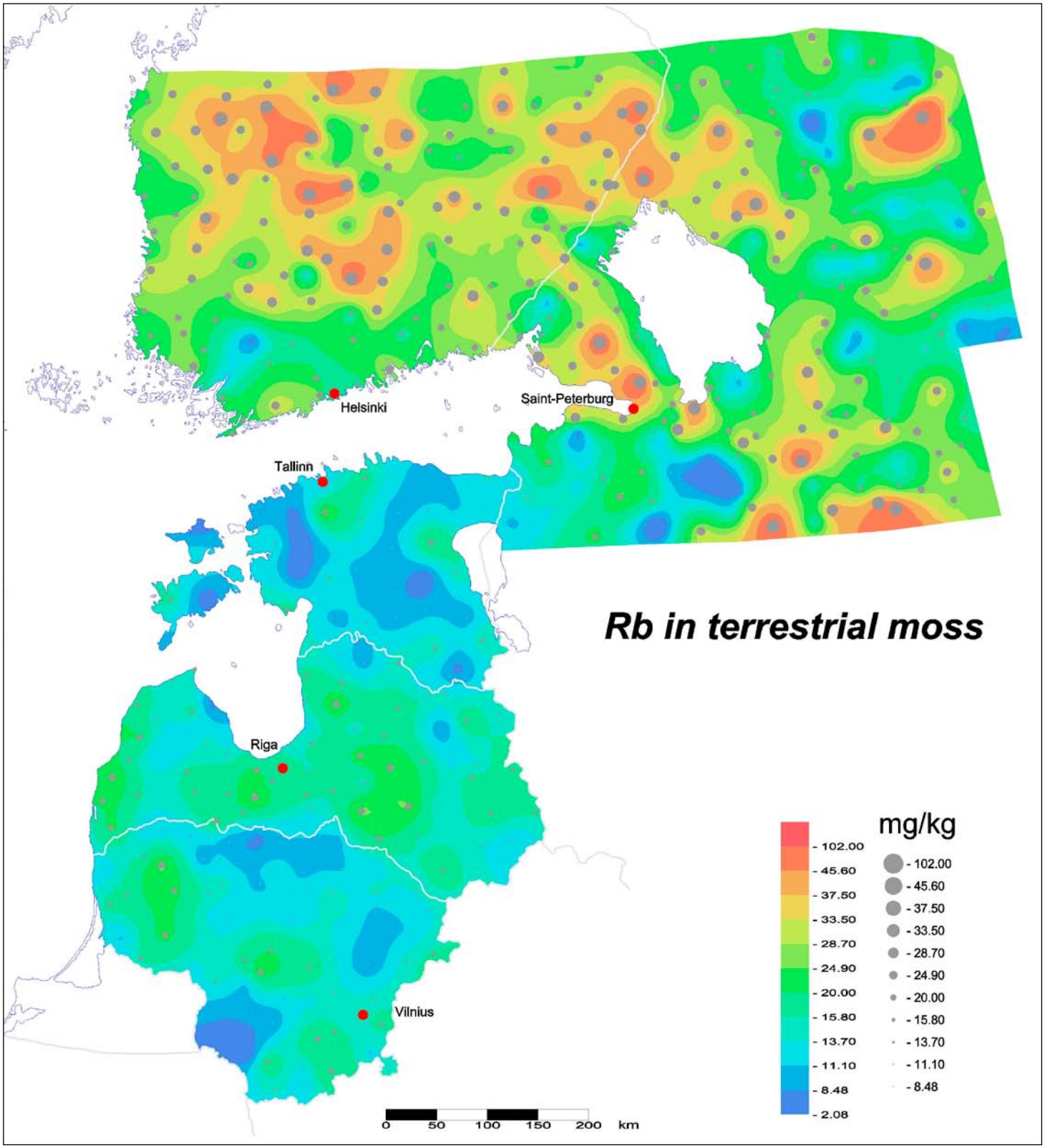
Pb – Lead MOS


Pb in terrestrial moss
Helsinki
Saint-Peterburg
Tallinn
Riga
Vilnius
mg/kg
- 46.80
- 8.39
- 7.41
- 6.82
- 6.00
- 5.25
- 4.51
- 3.87
- 3.46
- 3.09
- 2.52
- 1.19
- 46.81
- 8.39
- 7.41
- 6.82
- 6.00
- 5.25
- 4.51
- 3.87
- 3.46
- 3.09
- 2.52
0 50 100 150 200 km

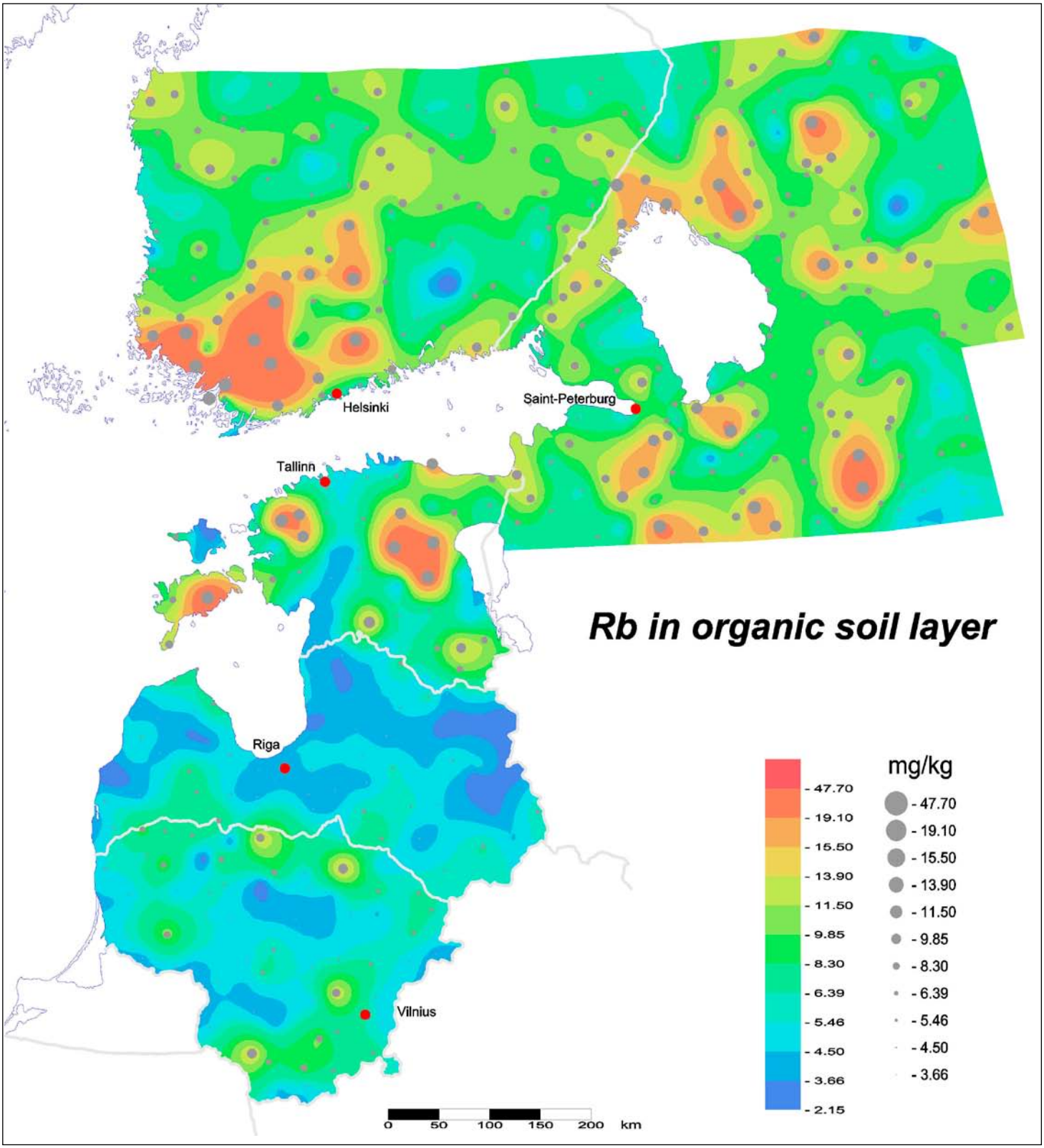
Pb – Lead ORG tot



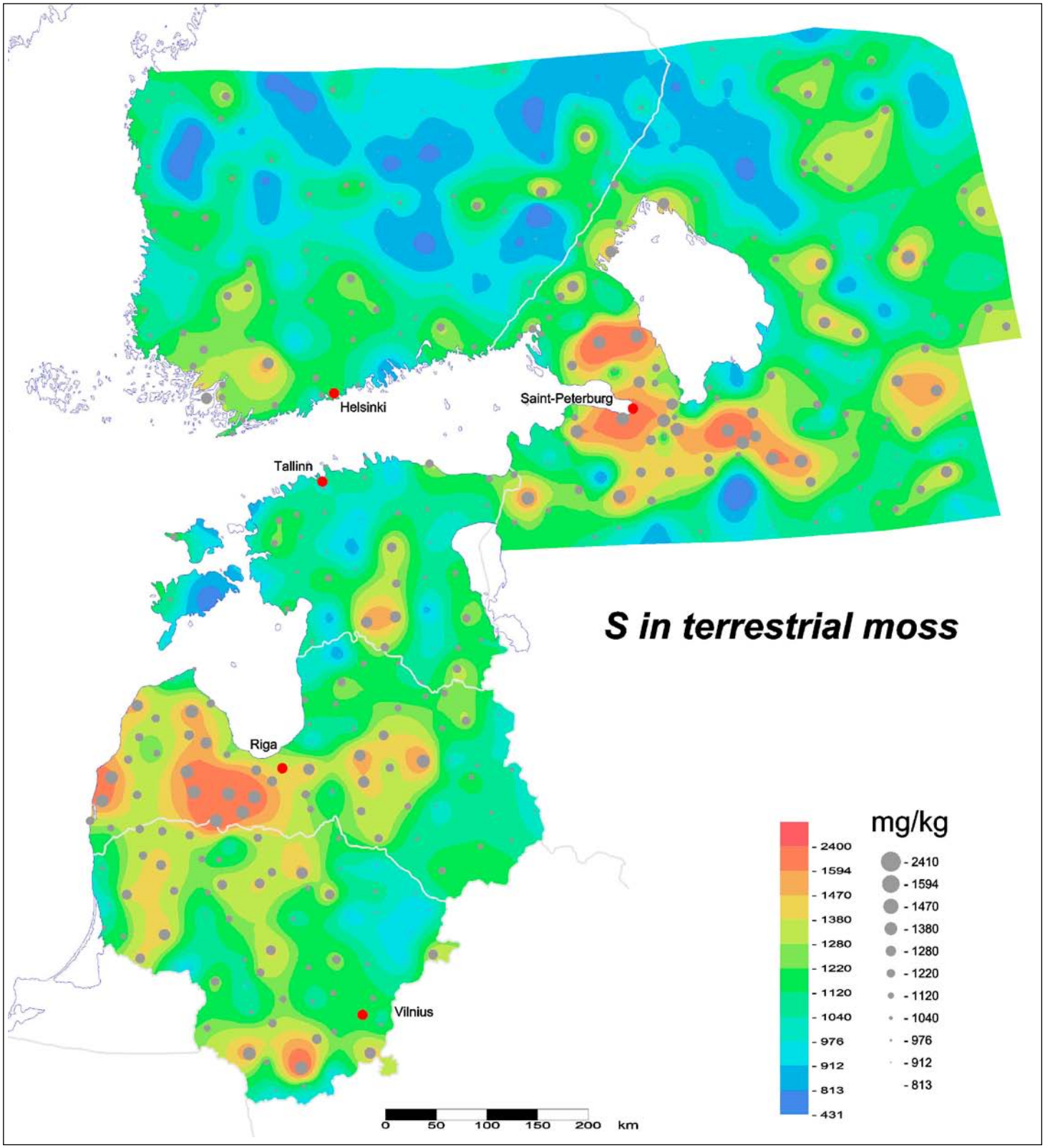
Rb – Rubidium MOS



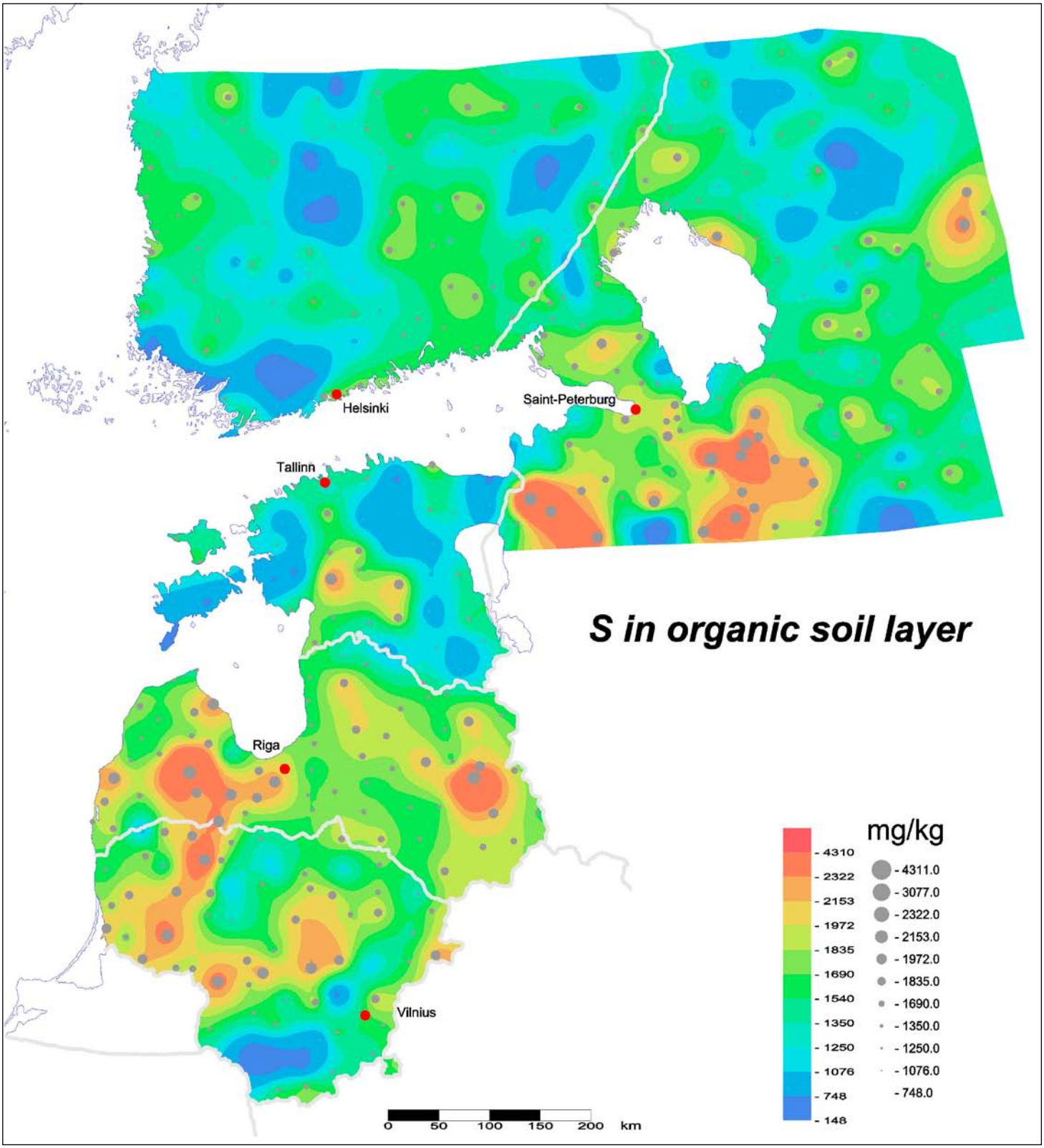
Rb – Rubidium ORG tot



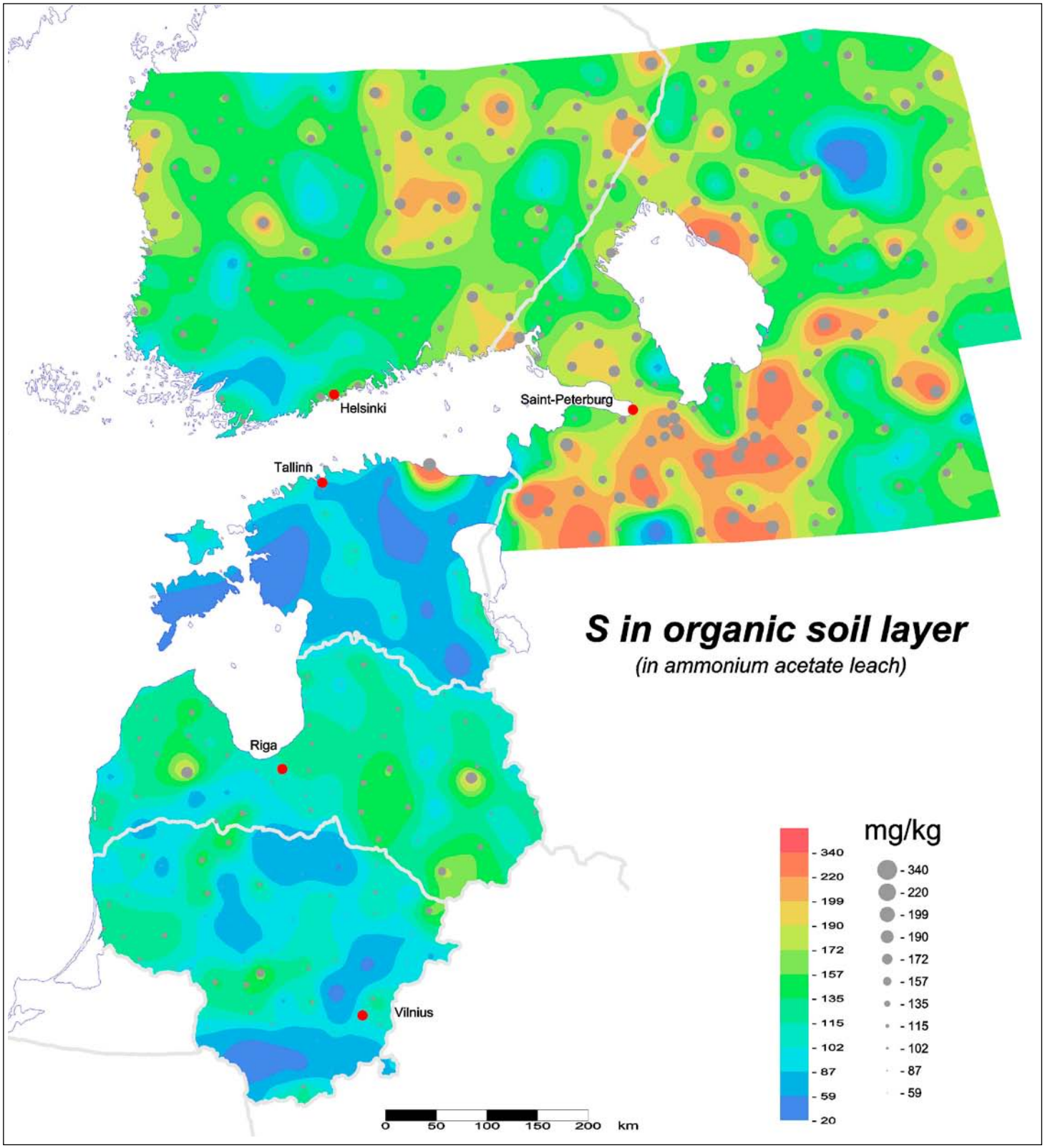
S – Sulphur MOS



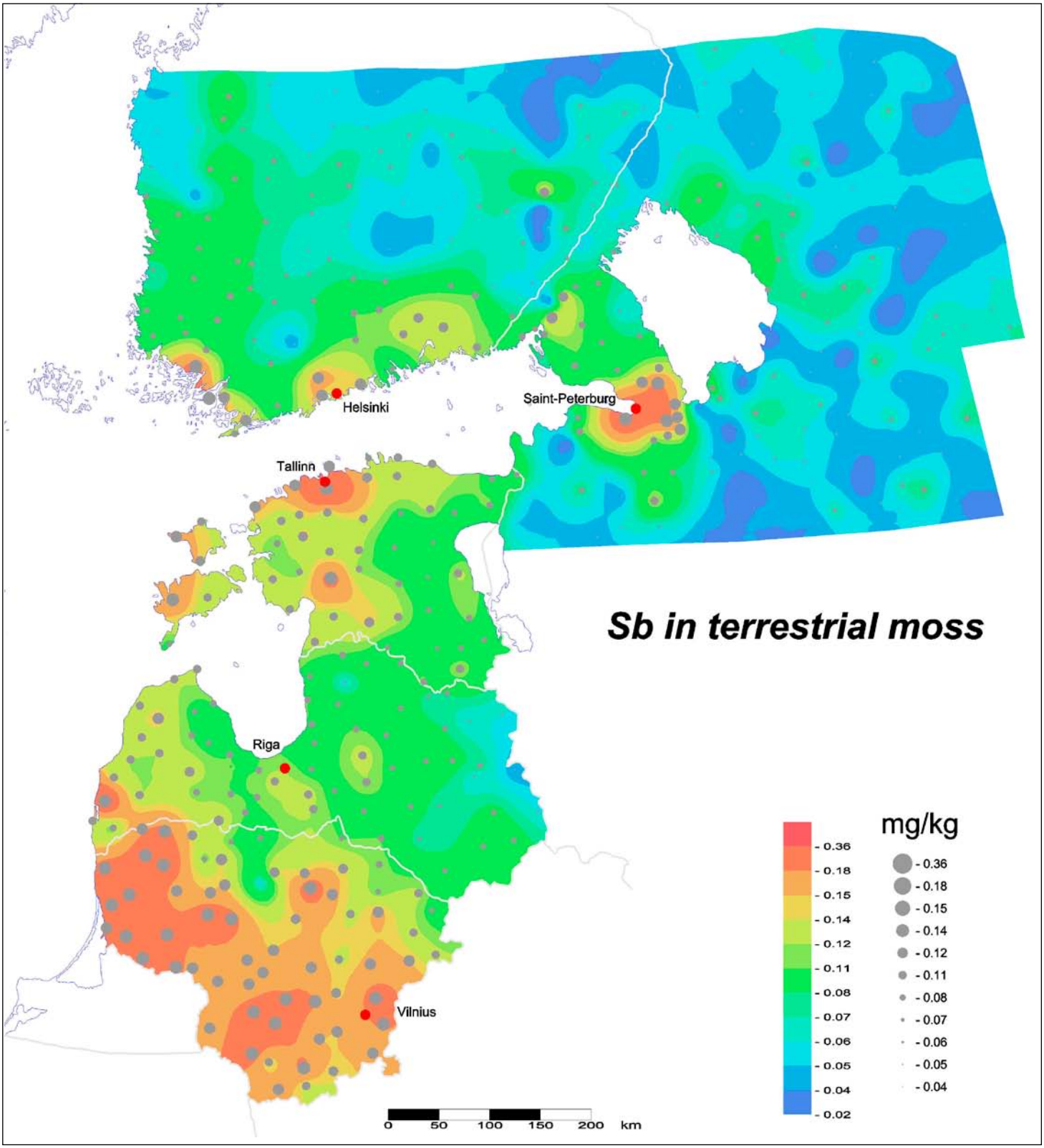
S – Sulphur ORG tot



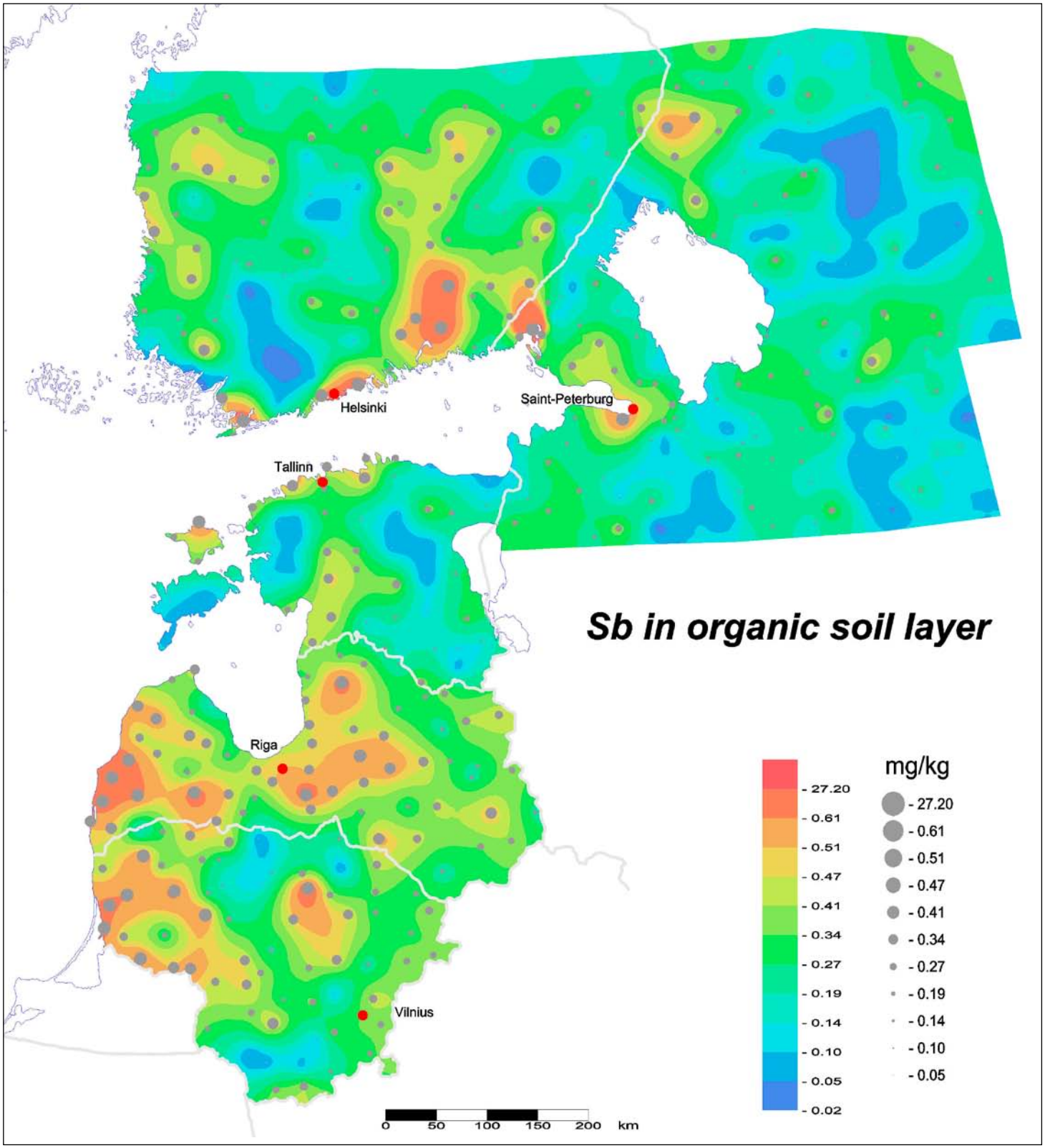
S – Sulphur ORG amm. acet.



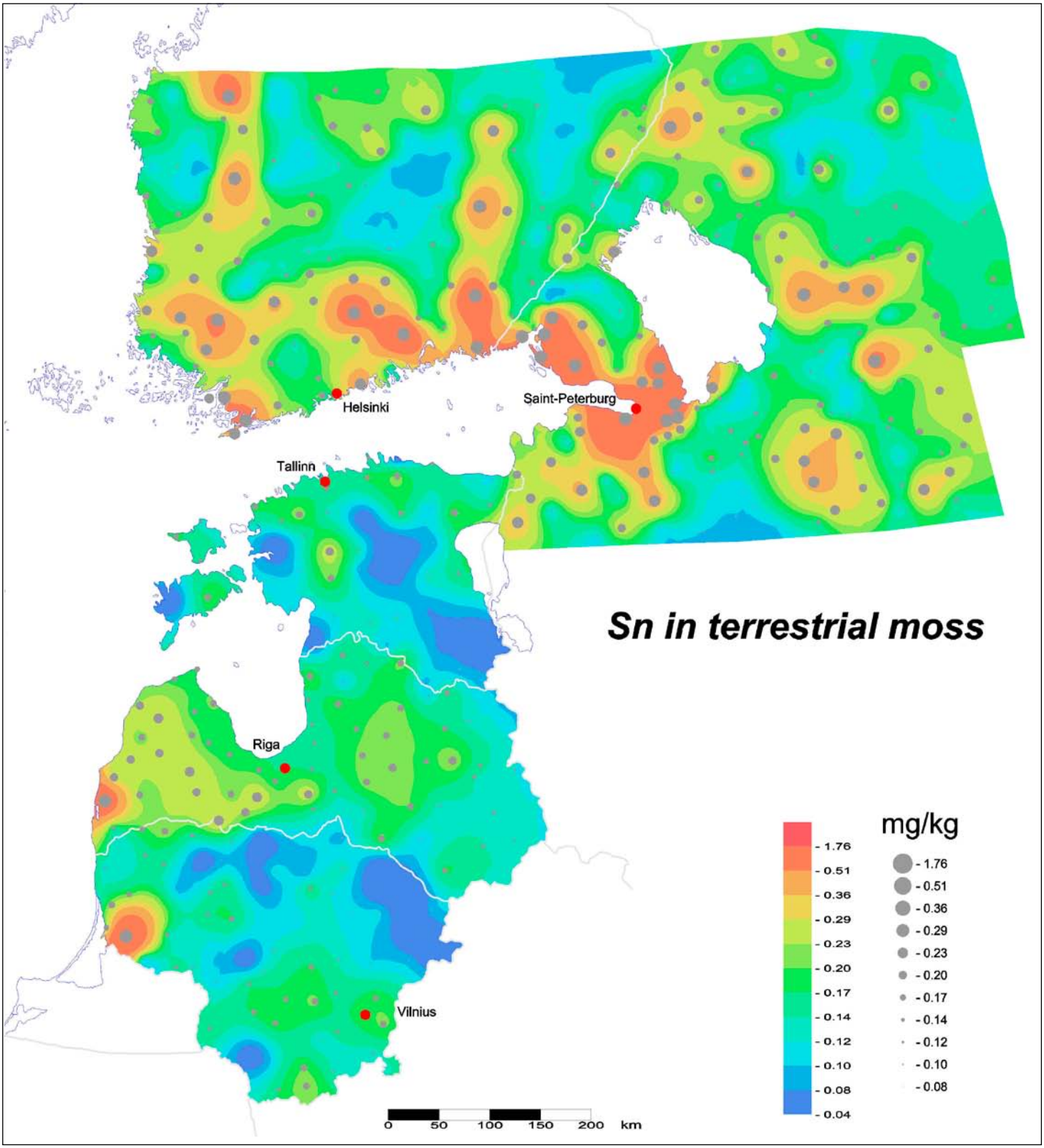
Sb – Antimony MOS



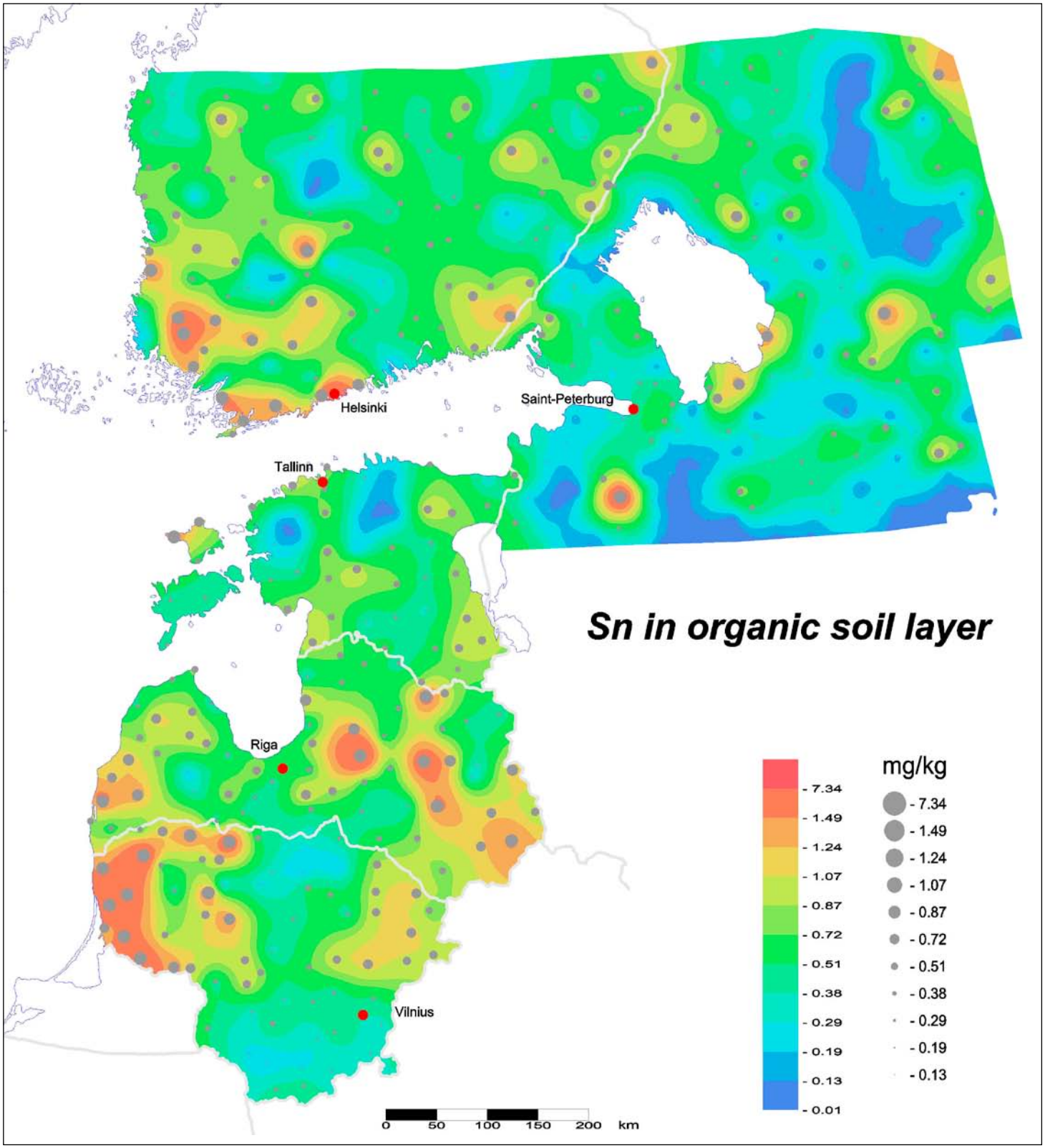
Sb – Antimony ORG tot



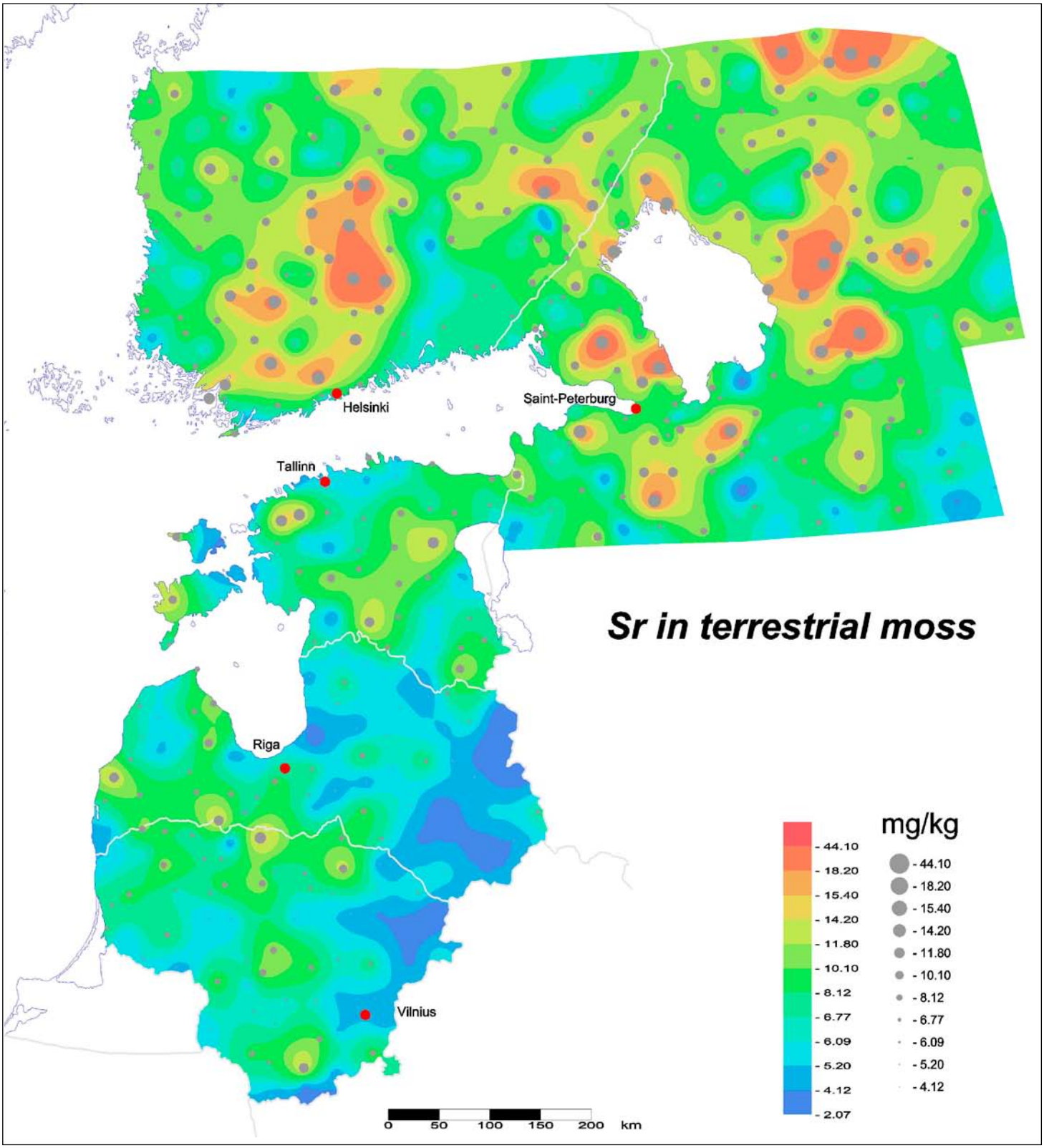
Sn – Tin MOS


Sn in terrestrial moss
Helsinki
Saint-Peterburg
Tallinn
Riga
Vilnius
mg/kg
- 1.76
- 0.51
- 0.36
- 0.29
- 0.23
- 0.20
- 0.17
- 0.14
- 0.12
- 0.10
- 0.08
- 0.04
0 50 100 150 200 km

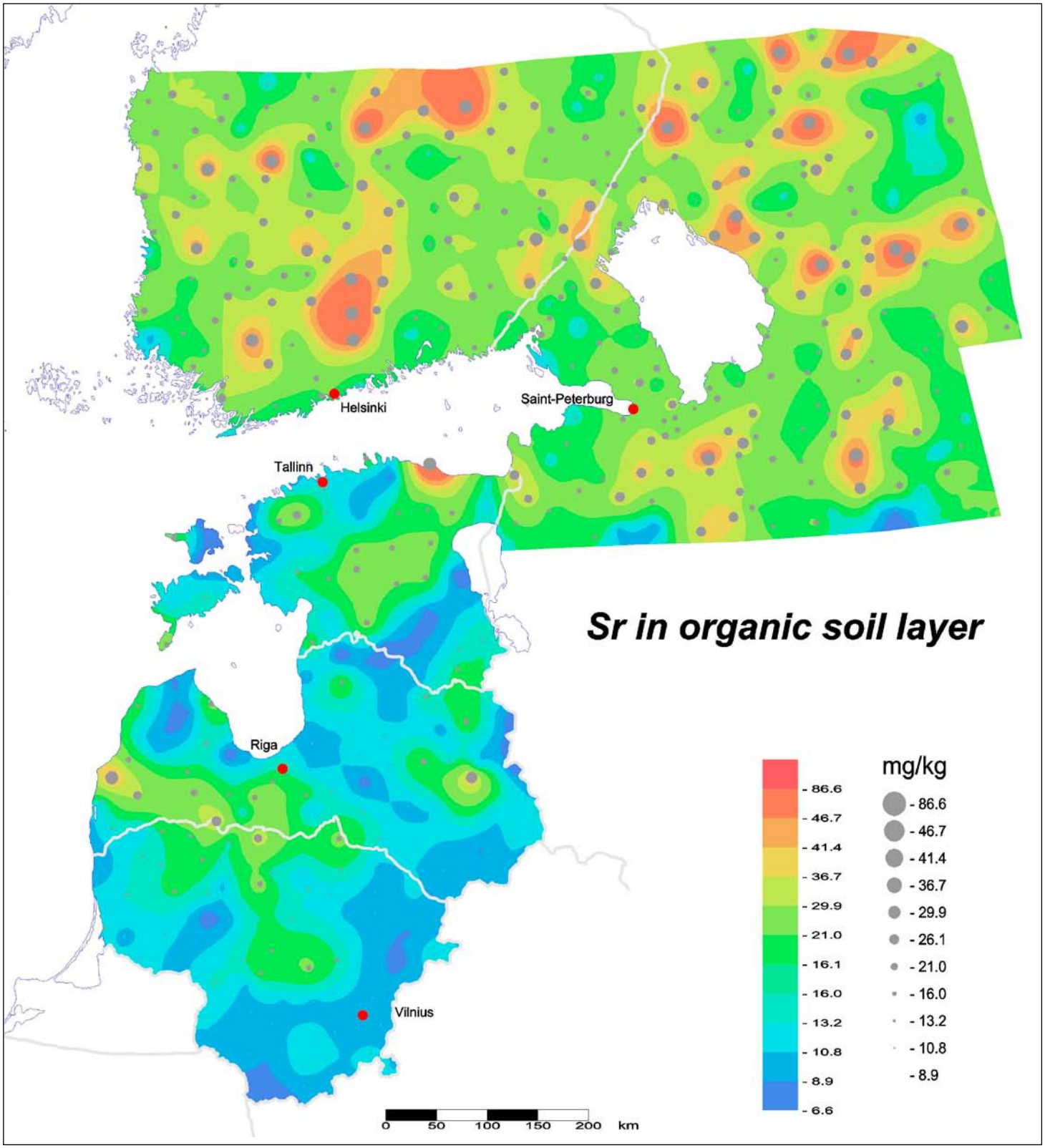
Sn – Tin ORG tot



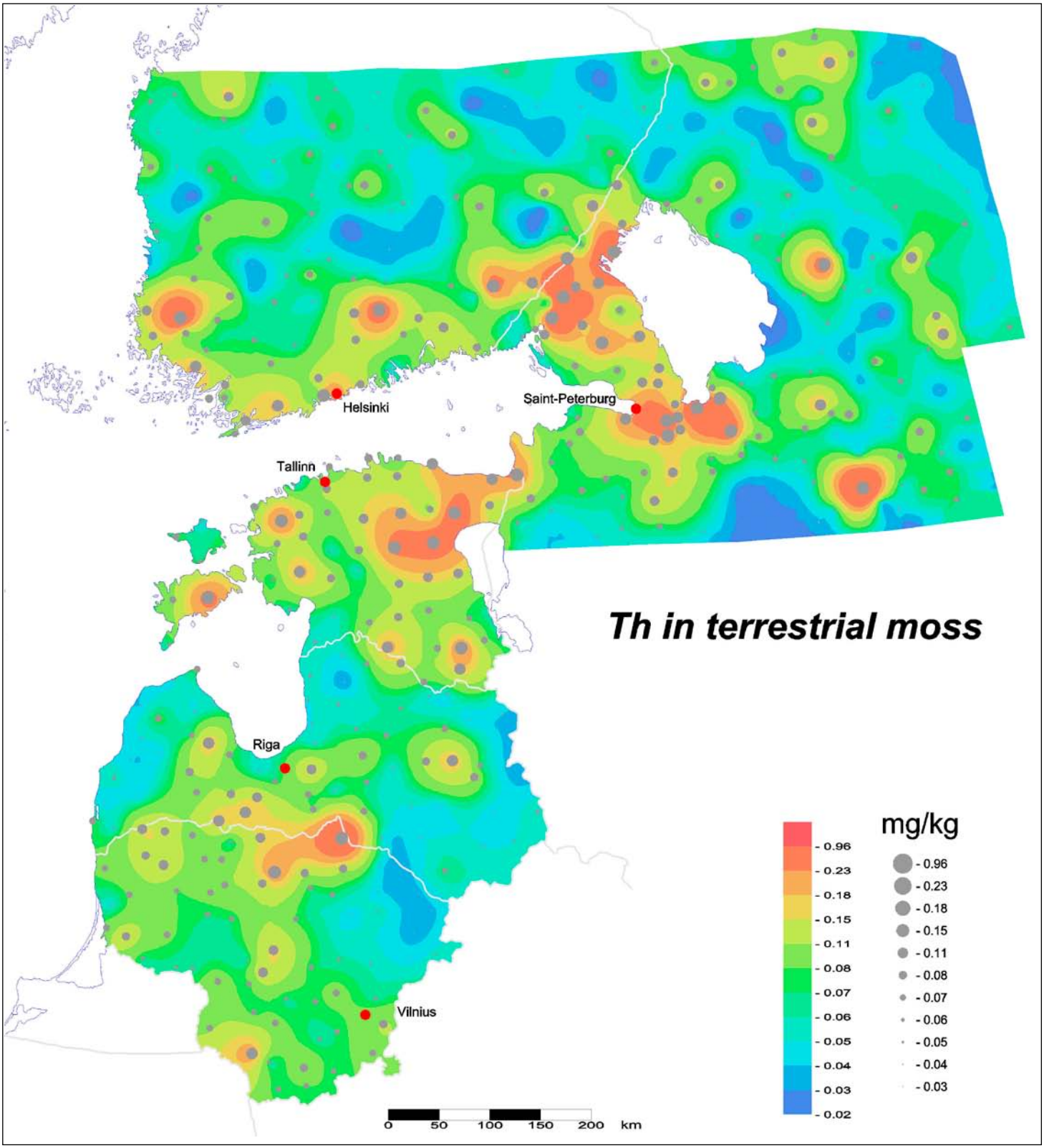
Sr – Strontium MOS



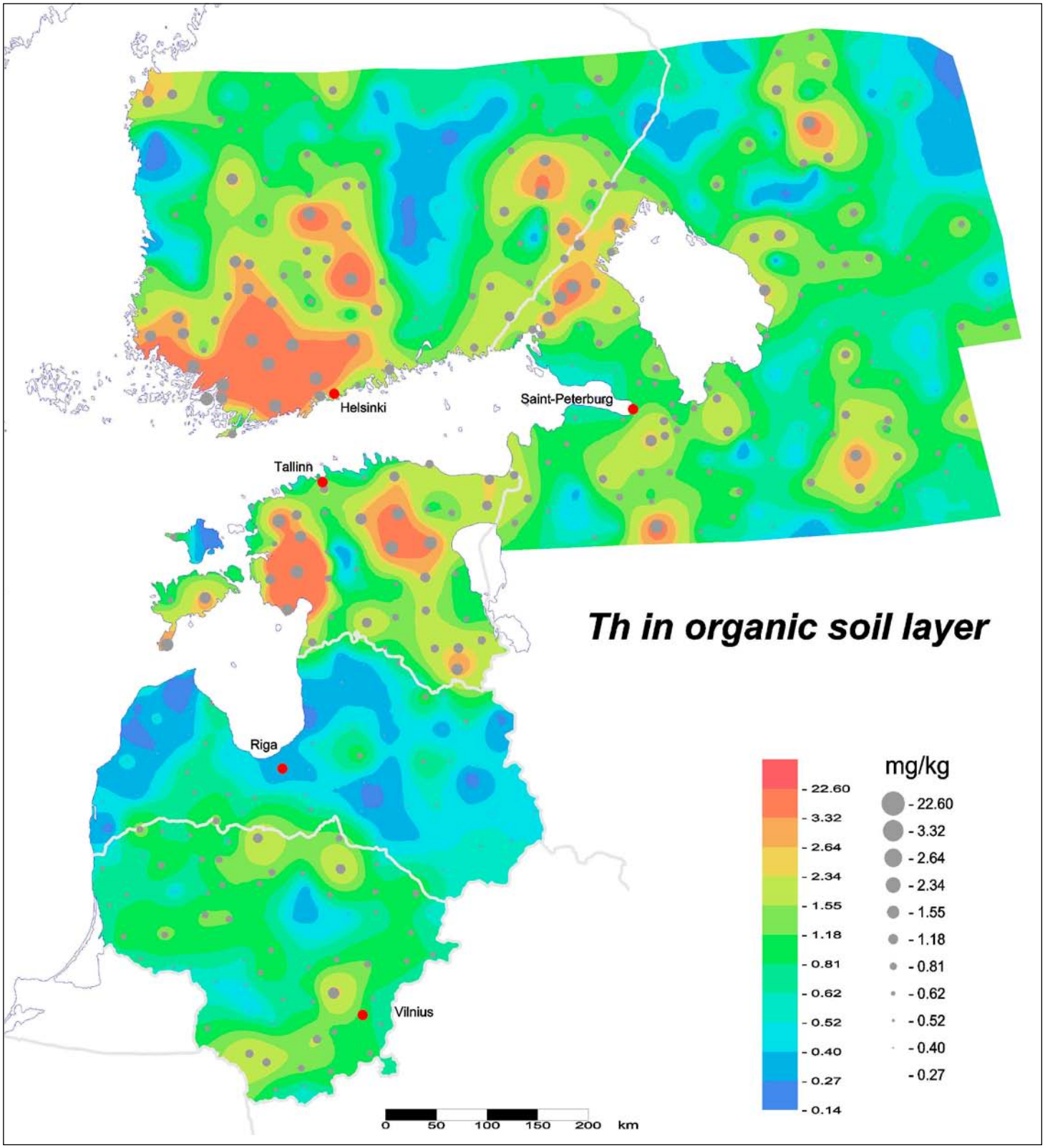
Sr – Strontium ORG tot



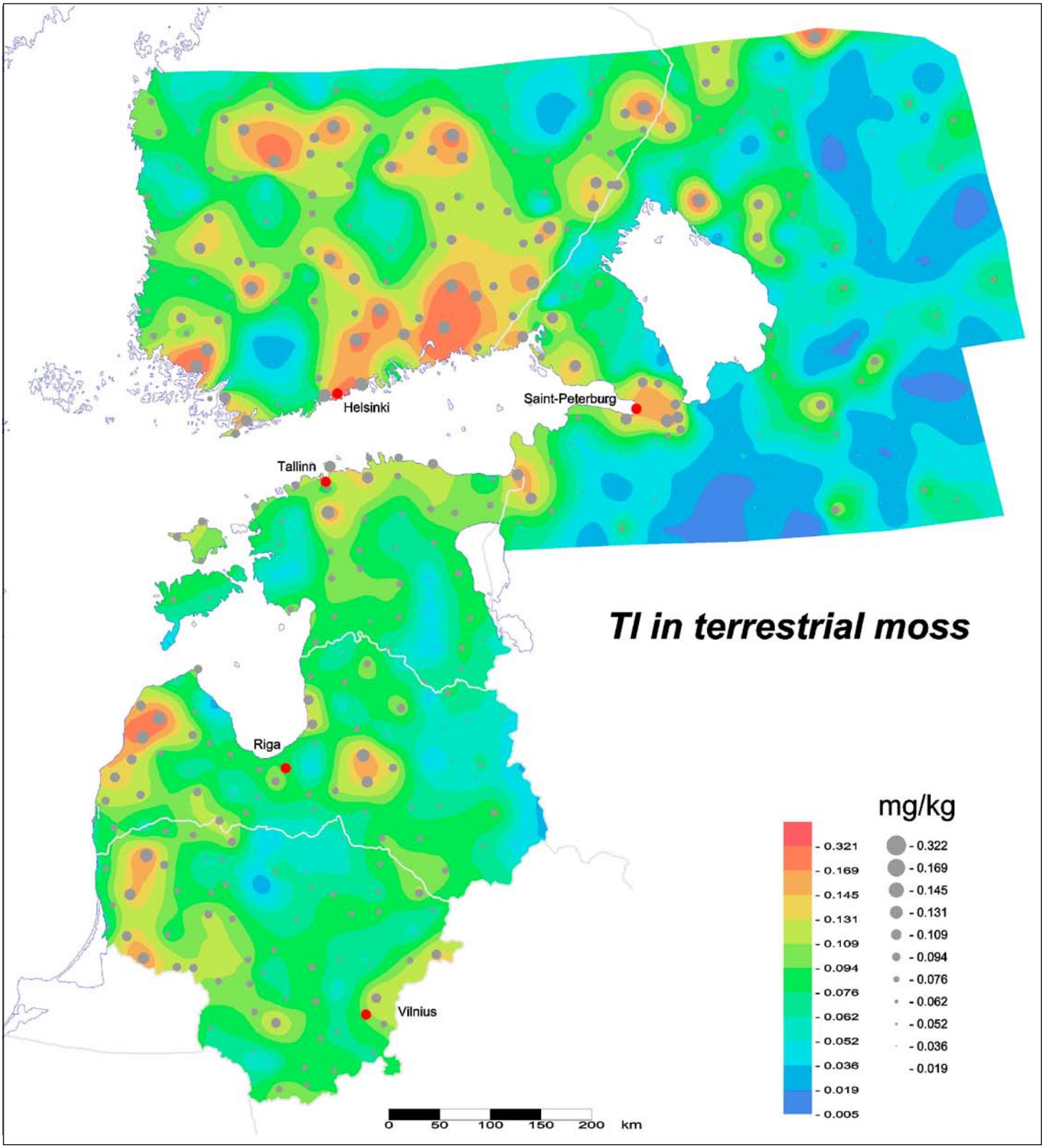
Th – Thorium MOS



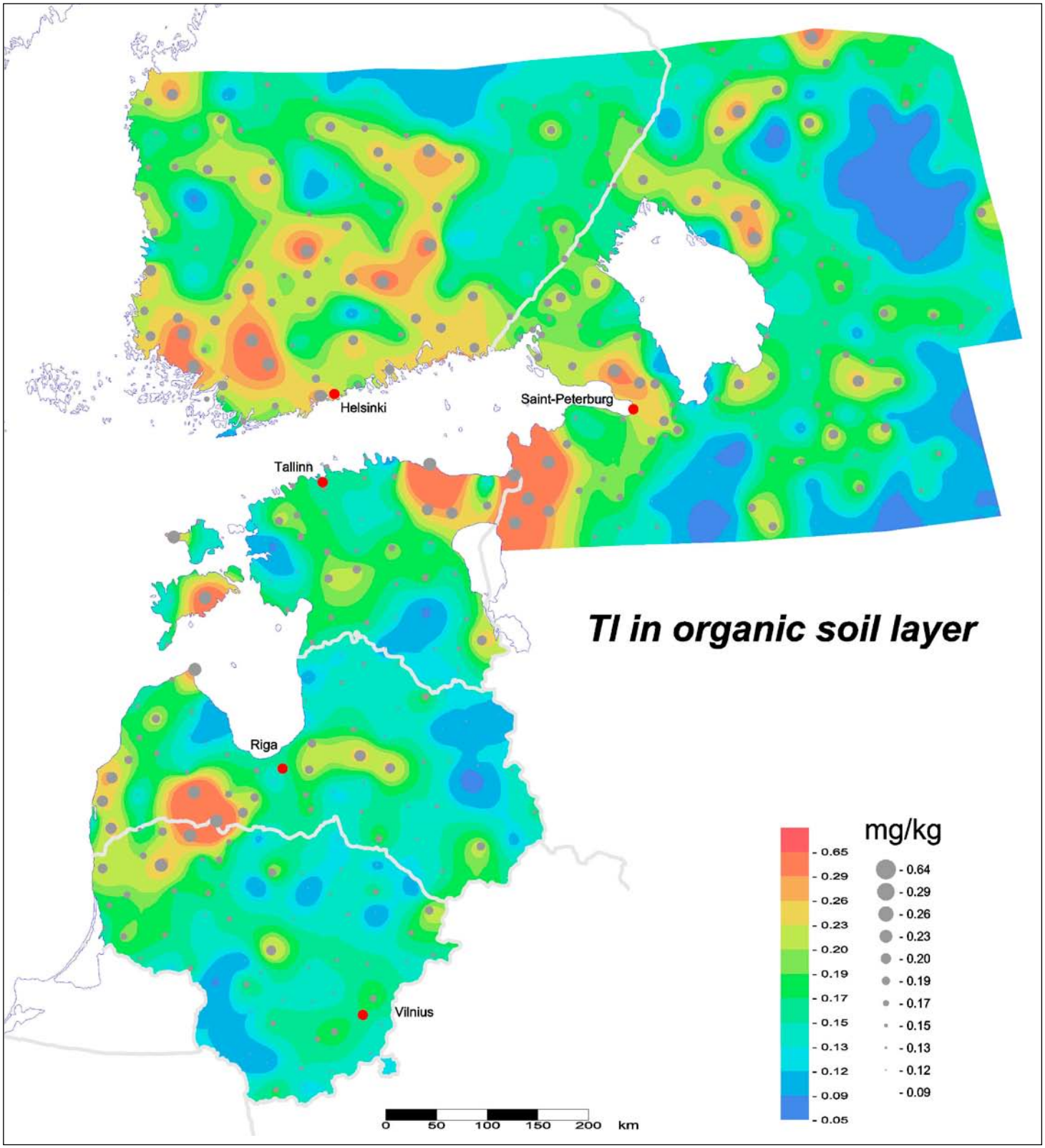
Th – Thorium ORG tot



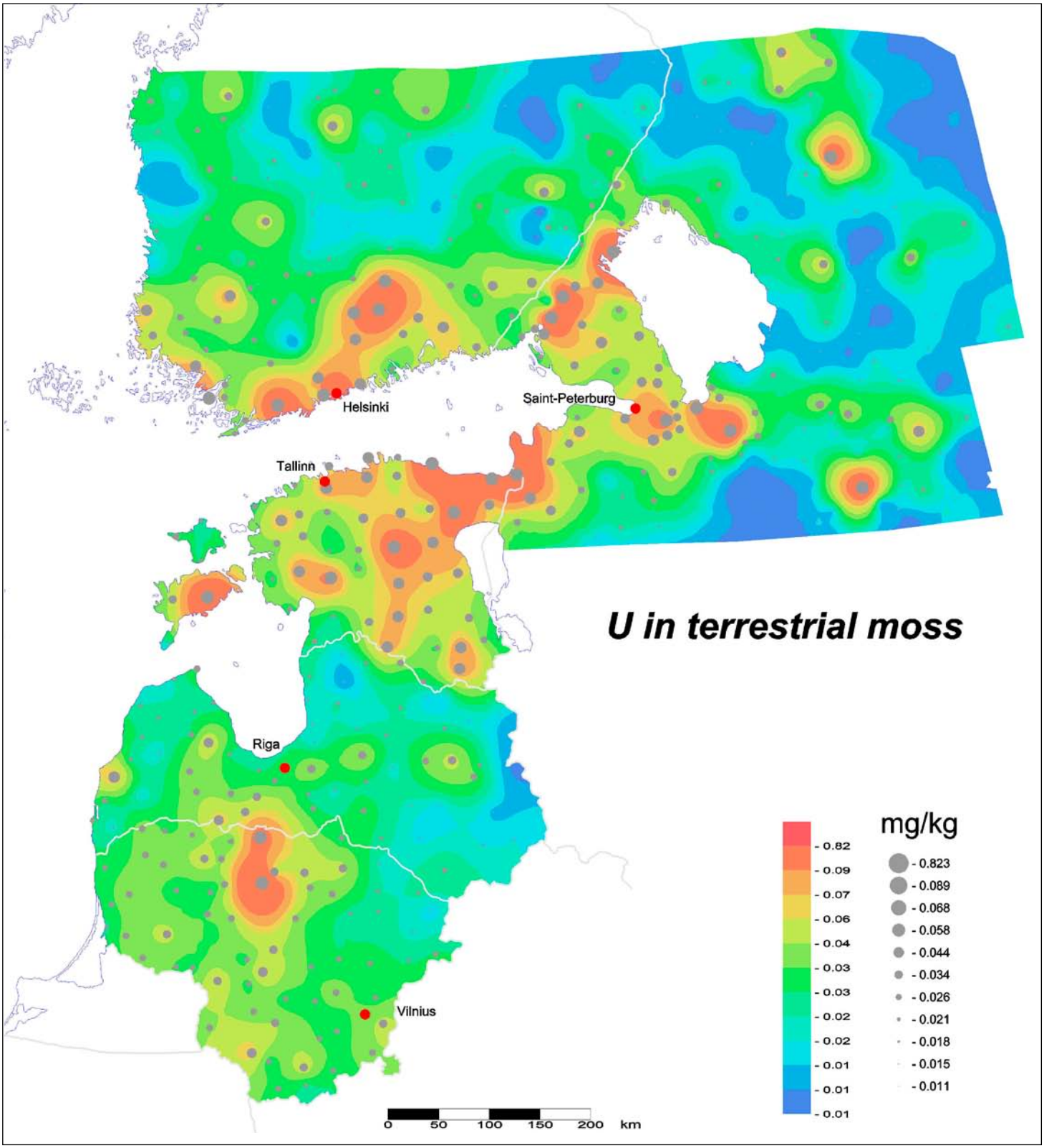
Tl – Thallium MOS



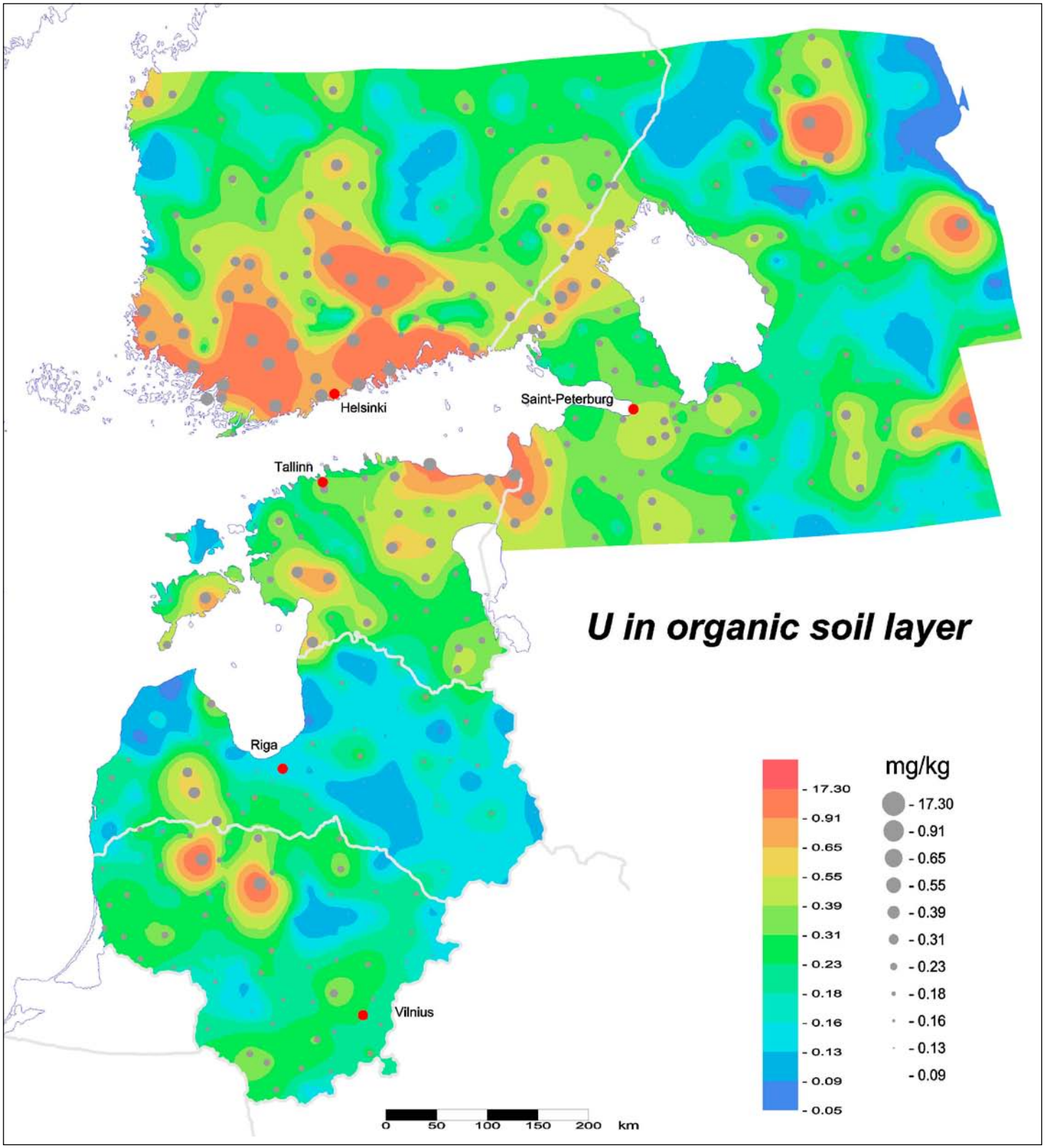
Tl – Thallium ORG tot



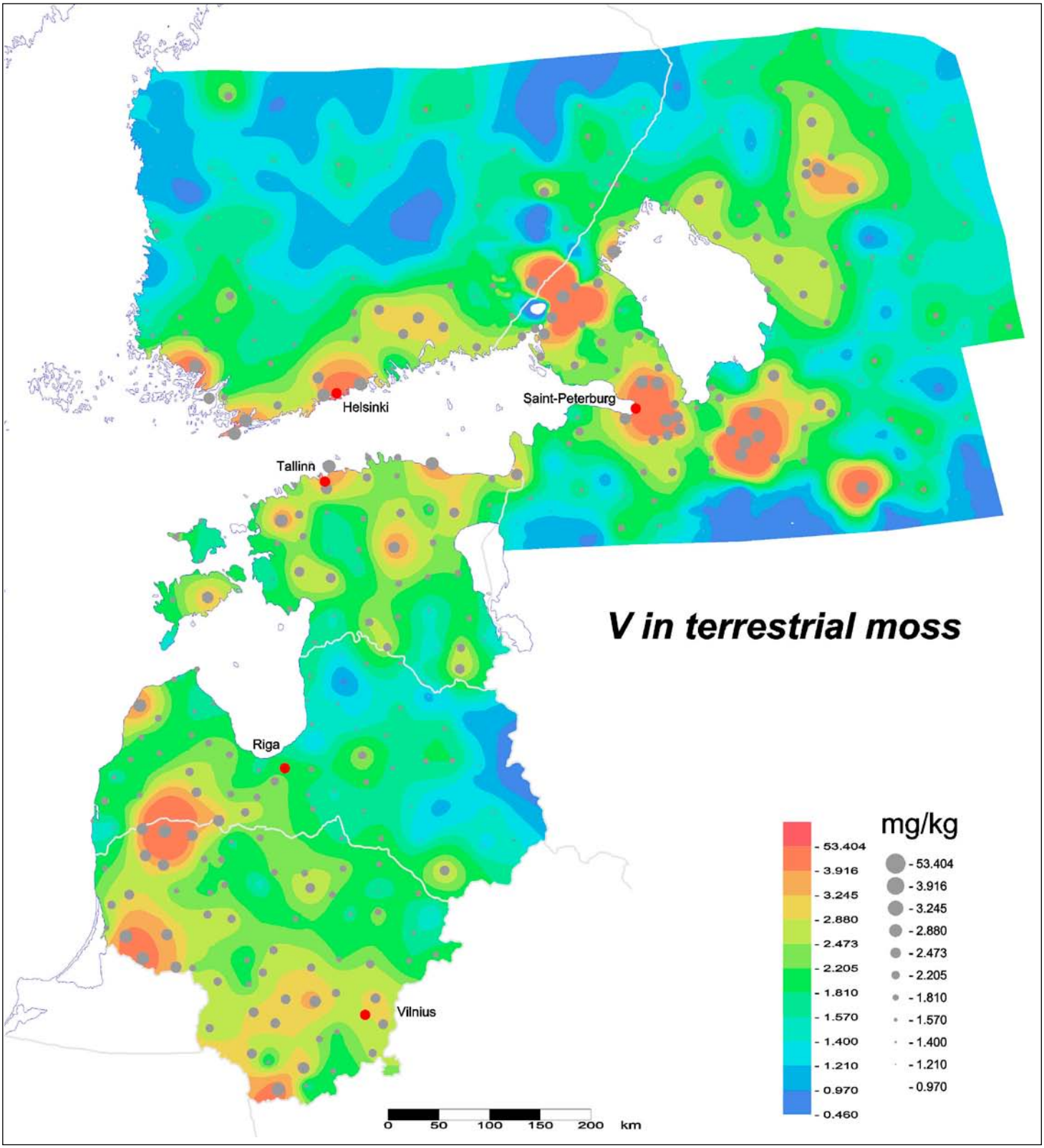
U – Uranium MOS



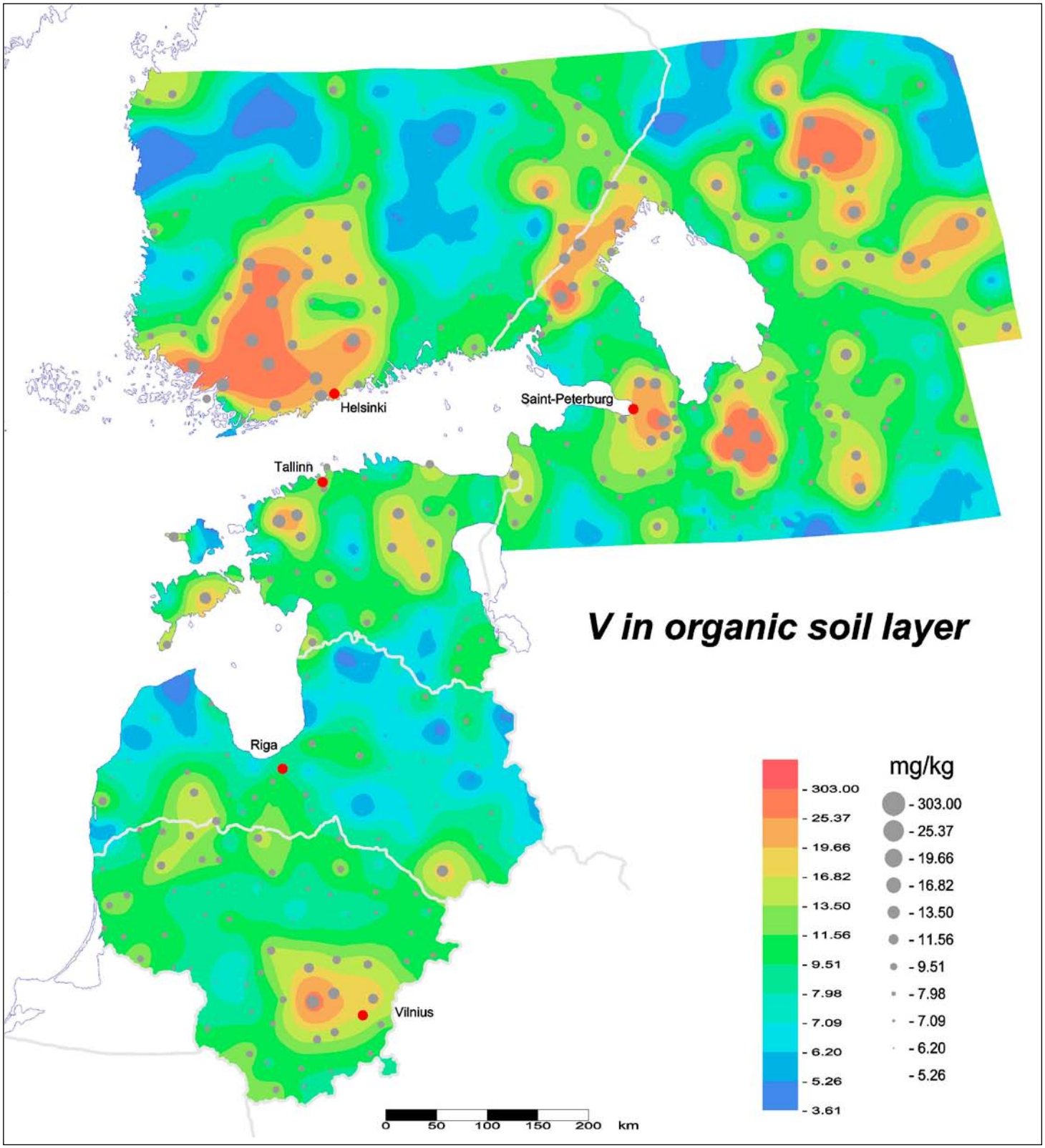
U – Uranium ORG tot



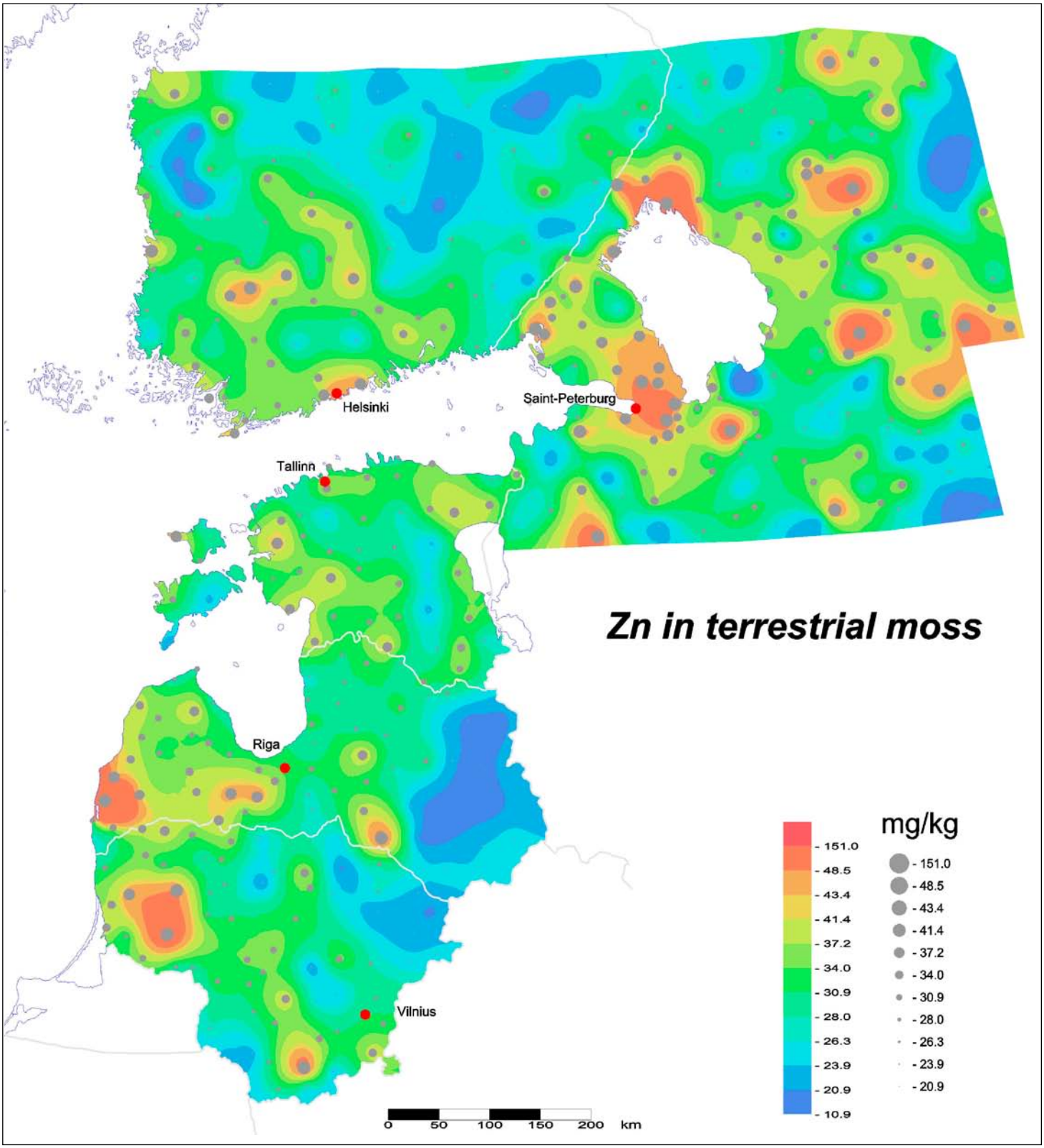
V – Vanadium MOS



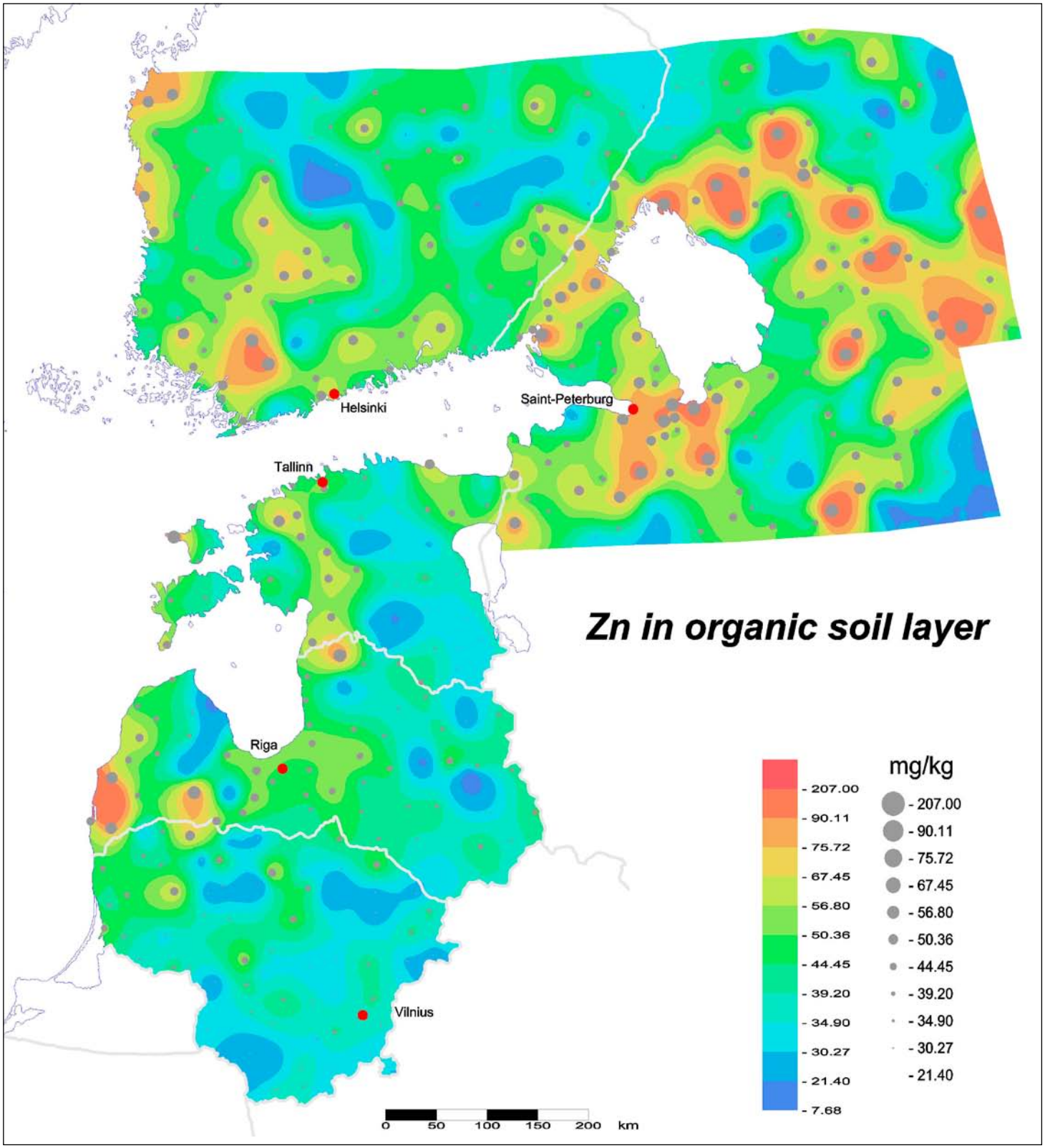
V – Vanadium ORG tot



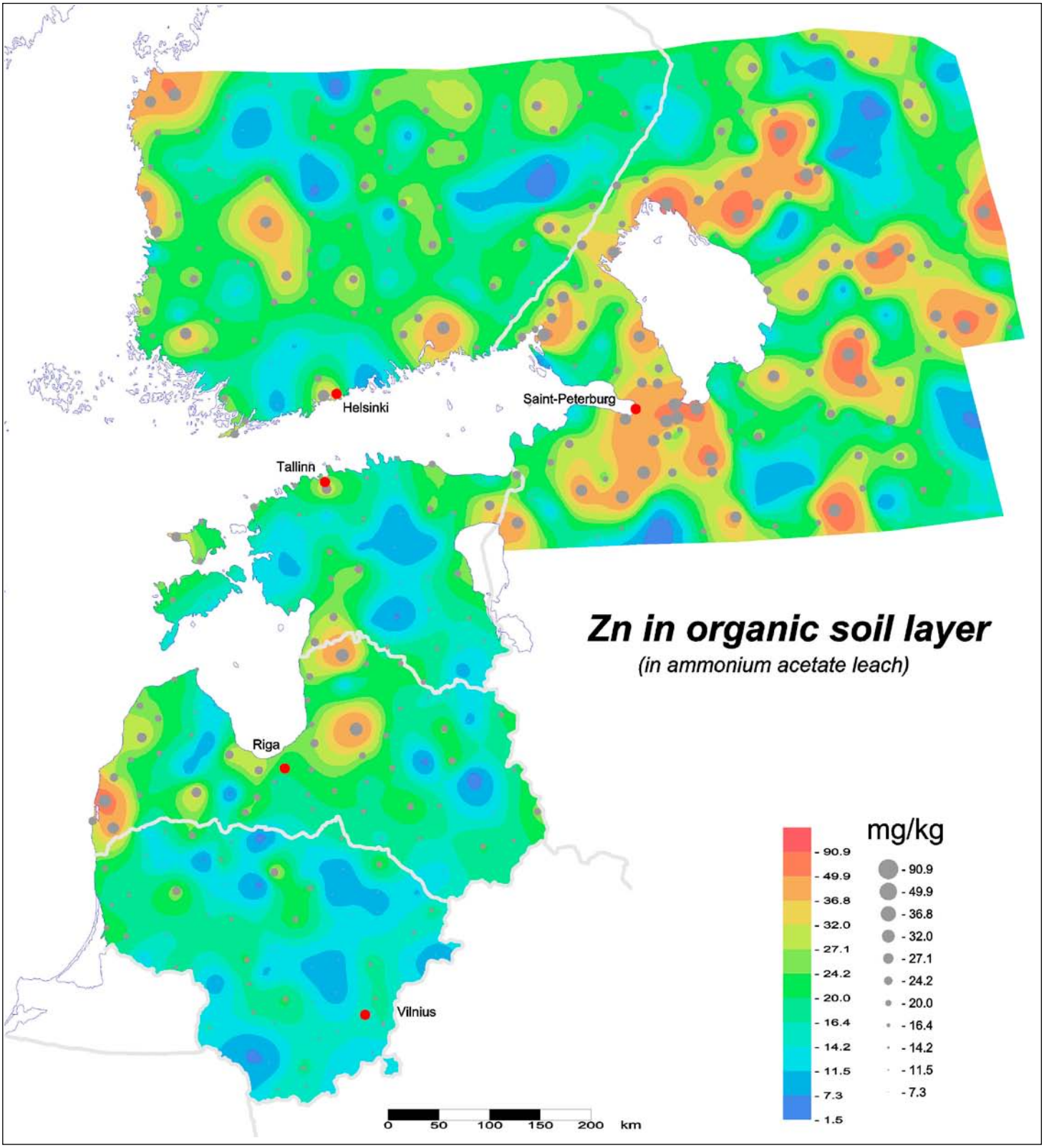
Zn – Zinc MOS


Zn in terrestrial moss
Helsinki
Saint-Peterburg
Tallinn
Riga
Vilnius
mg/kg
- 151.0
- 48.5
- 43.4
- 41.4
- 37.2
- 34.0
- 30.9
- 28.0
- 26.3
- 23.9
- 20.9
- 10.9
0 50 100 150 200 km

Zn – Zinc ORG tot



Zn – Zinc ORG amm. acet.



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In 2000, the Barents Ecogeochemistry project detected very high concentrations of environmentally important and potentially harmful elements such as Tl and Cs in the topmost organic soil layer to the north and east of the Gulf of Finland. In 2003, additional organic soil layer (humus) and terrestrial moss samples were collected from the Baltic countries. These samples, together with selected samples from the Barents Ecogeochemistry project, were used to define the distribution of elements in terrestrial mosses and the organic soil layer in the eastern Baltic region.

Cs isotopes from the fallout following the Chernobyl nuclear power plant accident in 1986 were still clearly detectable in the organic soil layer. The source of Tl detected in SE Finland and along the northern coast of Estonia is mainly emissions from the cement industry and power plants that use oil shale as fuel, but also geogenic dust from feldspar-rich minerogenic soil. Heavy metals and other elements detected in organic soil were estimated to be mostly geogenic in origin, but include fingerprints of older emissions from local industries. In mosses, their origin is either recent anthropogenic emission or, in many cases, local geogenic dust from open areas. Besides Cs isotopes from Chernobyl, no other long range airborne transportation of heavy metals, e.g. from the industrial areas of Central Europe, was detected.

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