

NILU TR: 21/94

NILU : TR 21/94
REFERENCE : Q-303
DATE : MARCH 1995
ISBN : 82-425-0646-9

Trace elements in the summer street-dust of Oslo

Eduardo de Miguel



NILU

Norsk institutt for luftforskning
Norwegian Institute for Air Research
Postboks 100 - N-2007 Kjeller - Norway

Preface

The study herein described is the result of a four-month scholarship awarded to the author by the Secretariat for Cultural Exchange Programs (The Research Council of Norway) and the Spanish Ministry of Foreign Affairs.

I would like to express my gratitude to the Norsk Institutt for Luftforskning (NILU) for providing invaluable technical and personal assistance. Special thanks are due to Mr. Steinar Larssen for advising the research project and for his contributions to this report, and to Mr. Oddvar Røyset for overseeing the analytical part of the study and for guidance in the interpretation of the results.

Thanks are also extended to Ms. Torunn Berg and Mr. Jozef Pacyna for providing most helpful suggestions and information, and for reviewing the draft version of this report.

I am particularly indebted to Ms. Ann-Marie Berge for her invaluable assistance in the sample collection and in the preparation of the manuscript, to Ms. Marit Vadset for her kind and patient collaboration in the physical and chemical preparation of the samples and for carrying out the ICP-MS analyses, and to Mr. Derk Stijfhoorn from the Institutt for Energiteknikk (IFE) for providing the facilities and equipment for drying and sieving the samples.

Lastly, Ms. Astrid Røstad, Mr. Finn Bjørklid, Mr. James Rydock, Mr. Tor-Øivind Gunstrøm and many others have assisted in different ways and to all of them I would like to extend my gratitude.

Contents

	Page
Preface	1
Summary	5
1. Introduction	7
2. Map of trace elements and sampling strategies	8
3. Sampling campaign	10
3.1 Methods and materials.....	11
4. Sample preparation and analysis	11
5. Results and interpretation	13
5.1 Validation of the sampling strategy. Stability of maps.....	20
5.2 Mean elemental concentrations in the street dust of Oslo. A comparison with Madrid.	21
5.3 Statistical Analysis of the data: Multivariate Techniques.....	22
5.3.1 “Natural” Elements.....	25
5.3.2 “Urban” Elements.....	26
5.3.3 Elements with a mixed origin or geochemically altered.....	28
5.4 Distribution patterns of elements	28
6. Discussion and conclusions	29
7. References	31
Appendix A Description of the sampling campaign	33
Appendix B Maps of concentration of chemical elements in the street-dust of Oslo	39

Summary

The elemental composition, possible sources and patterns of distribution of the street dust of Oslo were investigated during the summer of 1994. A total of 224 samples of street dust were collected from an area of 14 km² covering most of downtown Oslo and some residential areas to the north of the city.

According to Visman's sampling methodology, the area under study was divided in 14 mapping units (with an area of 1 x 1 km²) and 16 sampling increments of approximately 150 g were collected in each one of them. A composite sample was prepared for each mapping unit and the 16 sampling increments from mapping unit 16 plus 8 other sampling increments of special relevance were also analysed separately. The samples were collected from streets and roads with a small plastic brush and stored in air-tight plastic bags for transportation to the laboratory, where all-plastic sieves were used to separate the fraction below 100 µm. The samples were acid digested and analysed by Inductively Coupled Plasma - Mass Spectrometry at the Laboratory of Inorganic Chemistry of the Norwegian Institute for Air Research (NILU).

Maps of elemental concentrations were prepared for the different heavy metals and their resolution and stability was determined by ANOVA statistical techniques. Multivariate statistical methods, i.e., Principal Component, Factor and Cluster Analyses, were employed in the interpretation of the results. There seems to be two distinct groups of elements:

- 1) "Natural" elements (characterised by the presence of Ga, La, Mn, Sr, Th and Y), whose origin seems to lie in the soil particles that through the process of soil resuspension are incorporated to the street dust of Oslo, and
- 2) "Urban" elements (Ba, Cd, [Co], [Cu], Mg, Pb, Sb, Ti and Zn), which have a mostly anthropogenic origin, and for which the main sources appear to be traffic, and building construction/renovation and weathering and corrosion of building materials.

A third group of elements ([Ca], Cs, [Fe], [Mo], Ni, Rb, [Sr], and U) seem to have a mixed origin or may have undergone geochemical changes from their original sources. The element Be has an anomalous behaviour most likely due to the presence, in a few samples, of unaltered grains of beryl.

For some "urban" elements, i.e. Cu, Pb and Zn, the steep concentration gradient from the suburban and residential north towards downtown Oslo, to the south, follows the increasing urban character of the mapping units in that direction. The highest concentrations of these elements are found in mapping units 17 and 18, which cover the administrative and commercial centre of Oslo.

A comparison with a similar study carried out in Madrid, Spain, shows that the mean Pb concentration in the street dust of the Spanish capital is ten times higher than in Oslo. The discrepancy between the figures for lead in both cities reflects with extraordinary accuracy the difference between the average lead content of the petrol burnt in Oslo and Madrid at the time of both studies.

Trace elements in the summer street-dust of Oslo

1. Introduction

According to the World Commission on Environment and Development, one person in ten lived in a city of one million or more inhabitants in 1980. By the turn of the century, the Commission predicts that almost half of humanity will live in cities (WCED, 1987). Understanding and monitoring urban environments is therefore of growing interest for the scientific community.

One of the numerous geochemical features of urban environments is that they can be regarded as spatial domains where a steady flow of incoming trace elements is submitted to changes in their physico-chemical states before being disposed of and accumulated within their limits. Among other possibilities, trace elements concentrate on urban surfaces as dust particles of a wide range of sizes (often referred to as "street dust"). These particles may have been generated in the city (traffic, heating systems, building construction and renovation, etc...) or may have been brought into it airborne, and they may have an anthropic origin or come from natural sources (i.e. soil resuspension).

The health implications of the inhalation and/or ingestion of dust particles with high concentrations of trace elements is the subject of intense debate and the research carried out so far offers contradictory results (Harvey et al., 1985 a; McBride et al., 1985). It seems clear, nevertheless, that children are the sector of the population at highest risk. It has been suggested that the habit of "pica" (i.e. the ingestion of non-food material, essentially dust and dirt on toys and children's hands) can contribute significantly to the body burden of trace elements. In the case of lead, high blood-levels of that element could potentially be a cause of behavioural or cognitive impairment (Rundle et al., 1985; Thomas et al., 1985; Harvey et al., 1985 b; Biggins and Harrison, 1980).

Because of the health implications discussed above, there is a credible need for assessing the concentration levels of trace elements in street dust. Maps can be used, and have often been used in other fields of Environmental Geochemistry, as a convenient tool to present the information gained from the analysis of individual samples and facilitate the interpretation of the results. The choice of the size of the mapping unit and the number and mass of the sampling increments taken in each one (sampling strategy) determines the accuracy and precision of the final graphic display and the validity of the conclusions drawn from the information conveyed therein.

2. Map of trace elements and sampling strategies

The most common approach to the production of geochemical maps uses a regular grid to divide the area under investigation in a number of mapping units, all equal in shape and size.

Each mapping unit is represented by just one concentration value. This value results either from the analysis of one composite sample made up of a number of sampling increments taken within the mapping unit or from computing a mean value out of the analytical results of each of the sampling increments. The former alternative is usually preferred since it allows for reduced laboratory expenses, although valuable information regarding internal heterogeneity of the mapping unit is lost.

The precision with which the mean concentration of an element is estimated for each mapping unit will be determined by the mapping unit's internal heterogeneity as well as by the sampling strategy and the laboratory procedures employed. Precision can be improved at the expense of higher costs (higher density of sampling locations, more analytical determinations, etc...). It is therefore desirable to explore the relationship between precision and the different parameters that can affect it before the sampling campaign is designed.

Visman's sampling methodology (Llamas et al., 1990; Merks, 1985; Visman, 1947) considers the total variance associated with each mean concentration value as the sum of four different terms:

- 1) distribution variance
- 2) composition variance
- 3) preparation variance and
- 4) analysis variance.

The last two terms account for the variance arising from all the processes that take place in the laboratory ("laboratory variance"), from the moment the raw samples arrive in it until the final analytical results are produced.

$$\text{var}_{\text{TOT}}(X_i) = \frac{\text{var}_{\text{COMP}}(X_i)}{m \times n} + \frac{\text{var}_{\text{DIST}}(X_i)}{n} + \text{var}_{\text{PREP}}(X_i) + \text{var}_{\text{ANAL}}(X_i)$$

where: X_i : Mean concentration of element i in the mapping unit.
 m : Mass of sampling increment.
 n : number of sampling increments in the mapping unit.

The sum of the first two terms is normally referred to as "sampling variance". The "distribution variance" accounts for the heterogeneity in the spatial distribution of an element's concentration (mass/mass) over the mapping unit; it is mass-independent and can only be reduced by increasing the number of sampling increments within each mapping unit. The "composition variance" quantifies the heterogeneity in the composition of individual particles or particle clusters, and is

inversely related to the mass of the total sample collected from each mapping unit.

The laboratory variance can be estimated by duplicating samples and the distribution and composition variances can be determined from a pilot-study. In it, a mapping unit representative of the whole area under investigation is sampled, and two samples, one approximately ten times bigger (mass) than the other, are collected in each sampling location. From these two sets of samples (big and small), the distribution and composition variances can be determined as follows:

$$\text{var}_{\text{COMP}}(X_i) = \frac{\bar{m}_{\text{SMALL}} \times \bar{m}_{\text{BIG}} \times [\text{var}_{\text{SMALL}}(X_i) - \text{var}_{\text{BIG}}(X_i)]}{\bar{m}_{\text{BIG}} - \bar{m}_{\text{SMALL}}}$$

$$\text{var}_{\text{DIST}}(X_i) = \text{var}_{\text{BIG}}(X_i) - \frac{\bar{m}_{\text{SMALL}} \times [\text{var}_{\text{SMALL}}(X_i) - \text{var}_{\text{BIG}}(X_i)]}{\bar{m}_{\text{BIG}} - \bar{m}_{\text{SMALL}}}$$

Visman's methodology is, in essence, a two-level (distribution and composition variances) nested ANOVA design (formulas 2 and 3 can be derived from the mathematical expression of such a design) with two additional levels to account for the preparation and analysis variance.

A pilot-study was carried out in Madrid (Llamas et al., 1990 and 1991), yielding information about the size and number of sampling increments that should be collected from each mapping unit in order to achieve a certain precision in the estimate of the mean concentration for that mapping unit (Figure 1). These parameters are different for the different elements.

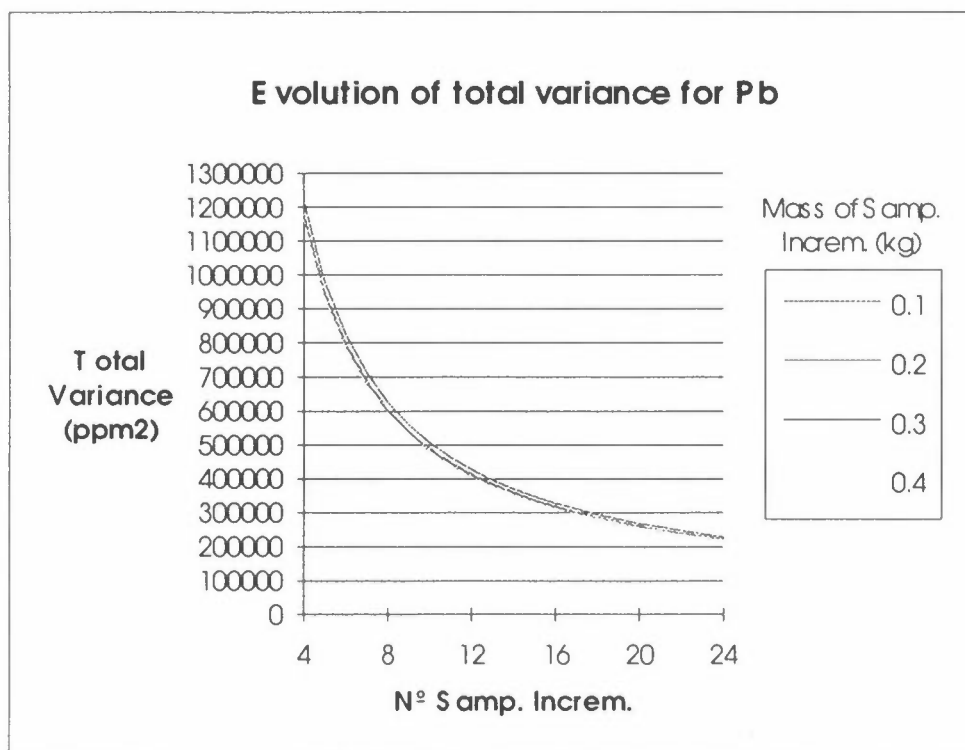


Figure 1: Evolution of the total variance associated with the estimate of the mean concentration of lead in a mapping unit in Madrid.

In accordance with the results of Madrid, and for the size ($1 \times 1 \text{ km}^2$) of the Oslo mapping unit, it was decided that 16 increments of a minimum of 50 g should be collected from each unit.

3. Sampling campaign

The capital city of Oslo is located at the innermost end of the Oslo fjord, in southeastern Norway, and has a population of 475000. Some features of Oslo are relevant in explaining the concentration levels and patterns of distribution of trace elements in street dust particles in the city.

Oslo is surrounded by forests, and features numerous large green areas within the city limits. Both circumstances suggest that soil particles should be a major source of street dust.

The main wind direction in summer day-time is SW.

In Oslo and elsewhere in Norway, streets and roads are subject to intense weathering during the winter months due to harsh climatic conditions and to the use of studded tyres (tyres with metal spikes), which in Norway may be used throughout most of the cold season. These circumstances lead to degradation of the paved surface and, consequently, enhanced dust generation (by at least one order of magnitude, compared to summer conditions).

Electricity generated from hydropower is widely used for space heating in Oslo, as in most of Norway. Therefore, fossil fuel burning for space heating should not be a significant source of airborne trace elements in Oslo, especially during the summer season when the sampling campaign took place.

In 1993, 76 % of all the petrol used by automobiles in the Oslo district was unleaded petrol. The remaining 24 % petrol had lead contents of less than 0.15 g/l. This circumstance has resulted in significantly lower values of lead concentration in the street dust of Oslo than in some other European cities (see below). It has also proved Pb less useful as a traffic indicator, contrary to what has been common in past research.

3.1 Methods and materials.

The sampling campaign took place from Aug. 2nd. till Aug. 23rd. and it extended over an area of 14 km², covering most of downtown Oslo and some suburban districts to the north of the city. Sample collection was discontinued during rain episodes and resumed 24 h after the precipitation had ceased.

Fourteen mapping units of 1 x 1 km² have been sampled. In each one of them, 16 sampling increments of approx. 150 g were collected by brushing with a small paintbrush the urban surface (sidewalk, road, gutter...) where the dust had accumulated. The sampling increments thus collected were stored, with the help of a small plastic spade, in double air-tight plastic bags for transportation to the laboratory.

The sampling campaign is described in detail in Appendix A.

4. Sample preparation and analysis

Each sampling increment was weighed upon arrival at the laboratory, then oven-dried for 72 h at a temperature of 45 °C and weighed again. Once dried, approx. 50 g of each of the 16 sampling increments from a given mapping unit were mixed and sieved through a 250 µm and a 100 µm mesh, and the rest was stored as backup samples.

The sieving set was designed and constructed at NILU. It consists of two sieving stages, which can accommodate clothes of varying mesh size, plus a top cover and a bottom plate. The sieving set was all-plastic to avoid metal contamination.

The decision to analyse the fraction below 100 µm is supported by the fact that particles with aerodynamic diameters under 100 µm can be transported by "suspension" (as opposed to "saltation" for particles between 100 and 500 µm or "creep" for particles between 500 and 1000 µm) and the finest among them (< 10 µm) may remain airborne for a long time (Nicholson, 1988; Sehmel, 1980).

The fraction under 100 µm collected from the bottom plate of the sieving set and stored in an air-tight polypropylene container was a composite sample

representing a whole mapping unit. From this sample, 0.25 g were weighed and transferred to a teflon bomb.

The polypropylene containers and the teflon bombs used for the digestion of the samples had been previously pre-cleaned for 24 h in a bath of 3% nitric acid and rinsed with MilliQ water. The teflon bombs were further cleaned by filling half of each bomb with 20% nitric acid and heating them in a stove at 150 °C for 48 h.

Each sample was digested with a mixture of 2.5 ml of HNO₃, 2.5 ml of HClO₄ and 5 ml of HF in a stove at 120 °C for 8 hours. The solution thus obtained was heated on an open hot plate until the solvent evaporated and only a dry residue was left. This residue was redissolved with 1 % HNO₃ and the solution transferred to polypropylene graduated containers which were subsequently filled up to 50 ml with 10 % HNO₃. These solutions were further diluted 1:100 with 1 % HNO₃ solution containing 50 ppb of Sc, In and Re as internal standards. Six blanks were prepared and analysed. All the acids used were Merck Suprapure. The use of HClO₄ and HF should ensure, respectively, that the trace elements bound to organic matter and contained in silicate matrixes are incorporated to the solution.

The sixteen sampling increments collected from mapping unit 16 (1601 - 1616) plus a number of sampling increments which bear a special interest (because they are representative of different dust sources, i.e. traffic under different driving conditions, house building or renovation, car parks, etc. or to allow for comparisons between sampling increments within one same mapping unit) were in addition prepared and analysed individually. In these cases, 0.125 g were weighed and transferred to the teflon bombs where the sample was digested with 1.25 ml of HNO₃, 1.25 ml of HClO₄, and 2.5 ml of HF. The preparation and analytical procedures were identical to those above mentioned.

Four duplicate samples were prepared, two from individual sampling increments and two from composite samples. The results of these analysis are shown in Table 3.

All samples were analysed by Inductively Coupled Plasma - Mass Spectrometry with a *VG Elemental* PQ1 instrument at the Laboratory of Inorganic Chemistry of the Norwegian Institute for Air Research (NILU). The ICP-MS instrument was run under standard conditions. The whole mass spectrum from 7 to 240 amu was recorded in scan mode (with scan jump over the areas 14-22, 29-30, 32-33, 36-42 and 79-81).

The calibration was performed using aqueous standards preserved with 2 % HNO₃, added appropriate internal standards (Sc, In, Re) at concentrations of 10 and 50 ppb. For some major elements (Na, Mg, Fe, Ca, S, P) calibration was also performed at 1, 10 and 100 ppm, depending on the sensitivity of the element. For these elements, the extended dynamic range mode (analog mode) of the detector was used.

The samples were introduced by an ordinary concentric Meinhard nebulizer, fed by a Gilson peristaltic pump. The plasma and ion optics were optimised on ^{115}In to maximum signal.

5. Results and interpretation

The results of the analysis for the fourteen composite samples (samples 100 to 1900) and for the 24 individual sampling increments (1601-1616, 106, 602, 1210, 1701, 1704, 1802, 1913 and 1914) are shown in Tables 1 and 2. They have been calculated from the readings of the ICP-MS instrument, which are given in $\mu\text{g/l}$, according to the following expression:

$$X_{ij} = \frac{[(R_{ij} \times \text{DF}) - \text{Blank Mean Value}_i] \times V}{m_j}$$

where: X_{ij} ($\mu\text{g/g}$): Concentration of element i in sample j
 R_{ij} ($\mu\text{g/l}$): Reading of the instrument for element i in sample j .
 Blank Mean Value $_i$ ($\mu\text{g/l}$): Mean concentration of element i in the series of blanks.
 DF: Dilution factor.
 V (l): Volume of digested samples
 m_j (g): weight of sample j .

The concentration of As, B, Bi, Cl, Cr, Hg, Li, S, Te, Tl and V are not included and are not used in the statistical interpretation either because most of the analytical results fall below the detection limit (defined as the mean plus three times the standard deviation of the set of concentration values for the blank solutions) or because of interference problems.

The use of HClO_4 in the digestion of the samples gives rise to serious interference problems due to high Cl residual concentrations. The compounds $^{35}\text{Cl}^{16}\text{O}$, $^{37}\text{Cl}^{16}\text{O}$ and $^{40}\text{Ar}^{35}\text{Cl}$, have the same molecular weights as the isotopes ^{51}V , ^{53}Cr and ^{75}As , respectively, which are used to measure the concentration of vanadium, chromium and arsenic. Minor interferences might be expected for ^{56}Fe (iron concentration is actually measured for ^{57}Fe) and ^{58}Ni and ^{60}Ni due to calcium oxide ions $^{40}\text{Ca}^{16}\text{O}$, $^{42}\text{Ca}^{16}\text{O}$ and $^{44}\text{Ca}^{16}\text{O}$. Although the intensity of these interferences is low (relative abundance of ^{42}Ca and ^{44}Ca are approx. 1 %), the high concentrations of Ca in the samples analysed suggest that one should be careful when interpreting results for Fe and especially for Ni.

Table 1: Concentration of major elements (ppm, dry matter).

SAMPLE ID	Al	Ca	Fe	Mg	Na	Ti
100	65372.2	35461.0	47729.7	11931.0	20535.0	6835.6
300	59241.0	35382.0	46027.1	13145.0	18170.0	6552.2
500	60060.3	45684.0	50709.9	14514.0	18384.0	7787.8
600	63733.0	50941.0	50182.1	13299.0	19543.0	7226.8
700	54843.0	37252.0	53134.7	12610.0	17991.0	7273.9
800	50345.0	40491.0	54142.4	12580.0	18423.0	7953.3
1100	52690.7	39321.0	50022.7	12854.0	18377.0	7389.8
1200	55516.7	43295.0	49397.4	13078.0	18175.0	8238.5
1300	56505.7	38521.0	50696.1	12104.0	18082.0	7180.0
1400	56690.7	41921.0	55138.5	12734.0	20634.0	7837.2
1600	66497.6	49938.0	55191.2	13044.0	20834.0	7418.1
1700	68551.4	50565.0	54592.1	14773.0	21566.0	7935.8
1800	62182.7	45759.0	51066.0	13904.0	20050.0	7260.9
1900	61151.9	43137.0	52293.2	14056.0	19361.0	7438.2
1601	45433.6	31552.0	41318.1	10035.0	14636.0	6182.0
1602	55211.2	40915.0	52340.6	15135.0	15869.0	7582.2
1603	62648.6	45288.0	58464.9	16299.0	18699.0	7679.9
1604	61302.3	30793.0	52224.6	13869.0	15704.0	5754.4
1605	56040.2	45158.0	50034.3	13335.0	16061.0	6980.4
1606	59527.7	44023.0	51625.3	12793.0	17752.0	7439.4
1607	62632.0	43321.0	64588.0	12615.0	20836.0	8072.6
1608	63854.9	38913.0	55196.8	12088.0	19069.0	6658.3
1609	62731.4	42029.0	62988.0	14185.0	18624.0	8260.5
1610	59958.2	49601.0	66260.9	13733.0	18194.0	8840.0
1611	63126.2	46438.0	64450.8	13100.0	18524.0	9249.3
1612	63335.1	103840.0	49669.2	14857.0	18190.0	7278.7
1613	60477.8	39644.0	45907.9	11860.0	18919.0	6119.1
1614	67501.5	47285.0	53316.2	11774.0	21125.0	6281.9
1615	69994.7	46478.0	59400.1	12637.0	23441.0	8315.5
1616	76318.2	43715.0	44874.5	9645.7	25956.0	6124.6
106	60020.9	10619.0	27100.5	7505.5	19312.0	4056.1
602	60580.5	53190.0	59285.3	17979.0	18775.0	10705.1
1210	31477.1	90338.0	33019.3	26288.0	7544.9	24838.9
1701	56174.1	26747.0	39130.6	11685.0	13978.0	5160.7
1704	66831.6	49057.0	53100.9	13081.0	20937.0	7525.8
1802	65431.1	43558.0	51344.3	15442.0	21092.0	7286.4
1913	62757.0	41560.0	61274.7	12575.0	20102.0	7694.3
1914	65427.7	41470.0	62720.7	13549.0	21222.0	8150.3

Table 2: Concentration of trace elements (ppm, dry matter) [1/2]

SAMPLE ID	Ba	Be	Cd	Co	Cs	Cu	Ga	La	Mn	Mo	Ni
100	562.130	2.748	0.259	18.140	2.112	81.360	19.150	61.398	915.100	3.195	33.260
300	516.140	1.692	1.344	18.800	1.336	75.260	14.800	46.425	749.100	2.053	40.060
500	485.990	1.635	1.905	18.060	1.719	99.890	16.120	42.946	804.600	5.064	39.380
600	455.570	1.401	1.308	17.300	1.006	90.560	17.200	43.095	803.800	4.634	45.070
700	517.290	35.491	2.121	19.910	1.110	103.690	17.910	47.506	805.200	4.634	42.630
800	507.320	1.618	1.371	19.400	1.017	129.110	16.960	45.034	816.300	3.759	39.830
1100	458.520	1.463	1.579	16.960	1.454	96.220	15.590	43.803	763.100	2.600	44.190
1200	634.320	2.081	1.283	20.850	1.540	108.460	15.230	45.748	769.900	2.867	42.790
1300	571.480	1.471	0.697	15.790	1.521	112.000	13.700	54.309	782.800	3.769	40.130
1400	537.320	1.783	1.777	20.930	0.725	127.500	16.540	44.034	867.300	6.000	40.570
1600	505.190	23.681	2.381	17.780	1.321	121.350	17.570	50.072	894.000	3.204	40.600
1700	599.490	2.745	0.591	21.280	1.333	250.690	18.000	54.036	940.100	5.700	49.530
1800	545.220	2.173	1.315	20.450	1.105	203.510	17.790	46.792	851.600	5.791	39.580
1900	470.210	1.972	0.374	16.730	1.095	128.820	17.060	45.202	897.400	2.741	41.430
1601	484.690	1.148	2.748	13.240	1.309	161.600	12.690	42.069	667.800	3.618	28.330
1602	454.660	1.726	2.406	20.890	1.444	124.840	15.530	41.554	872.500	4.788	42.770
1603	567.650	2.233	0.836	21.450	1.854	166.470	18.510	45.322	968.000	7.628	57.580
1604	557.180	2.049	-0.037	18.070	2.564	93.680	16.900	44.087	792.100	3.824	54.390
1605	448.500	1.251	-0.038	17.900	1.747	93.820	17.640	41.516	765.100	3.096	49.430
1606	454.040	1.799	1.049	16.100	1.433	57.140	16.060	47.220	837.400	2.737	26.100
1607	529.360	2.386	2.295	19.820	1.021	227.290	17.240	44.776	994.900	7.205	38.910
1608	553.080	2.576	1.006	18.240	1.994	134.950	17.510	52.212	1020.200	4.841	45.120
1609	441.660	2.072	0.659	19.750	1.357	103.550	16.480	48.965	969.100	4.579	42.710
1610	525.790	2.455	3.320	18.770	1.674	399.270	19.270	58.318	1007.900	8.150	69.380
1611	449.080	1.577	0.347	18.460	0.728	84.860	17.210	60.270	1022.200	2.866	27.890
1612	519.800	2.109	2.461	20.320	1.897	106.690	16.740	46.979	925.500	6.863	46.650
1613	454.470	2.443	-0.037	14.490	0.815	128.730	16.090	54.057	705.400	4.464	32.190
1614	527.700	1.188	-0.037	18.090	1.313	97.630	17.760	44.373	929.800	5.945	36.520
1615	470.360	1.782	1.959	22.180	0.947	92.460	18.860	57.725	963.500	3.080	26.640
1616	621.450	3.626	-0.038	20.030	1.209	59.140	22.150	87.070	846.700	3.775	26.790
106	585.820	1.641	-0.037	10.930	2.076	24.920	17.060	52.295	934.200	2.580	33.380
602	516.700	2.000	6.254	18.490	1.043	133.880	16.510	45.159	850.000	6.826	38.120
1210	1657.600	1.322	11.697	35.470	1.816	135.700	11.340	23.949	497.700	5.446	38.510
1701	598.210	88.257	-0.039	16.390	2.287	44.390	13.610	51.978	825.400	3.255	44.320
1704	520.370	2.385	1.571	23.480	1.086	179.350	14.360	42.303	880.800	5.815	37.460
1802	458.190	3.407	0.183	20.470	0.879	95.090	16.750	42.240	925.100	3.060	35.990
1913	565.070	1.830	1.979	16.690	1.521	190.850	19.240	50.109	923.700	6.447	44.910
1914	563.440	2.400	1.359	20.910	0.617	133.560	19.590	53.320	907.300	4.980	31.670

Table 2 cont.: Concentration of trace elements (ppm, dry matter) [2/2]

SAMPLE ID	P	Pb	Rb	Sb	Sr	Th	Ti	U	Y	Zn
100	955.400	92.600	85.220	1.913	347.390	9.657	6835.600	2.495	25.852	185.070
300	1276.200	83.170	63.550	2.527	317.330	6.388	6552.170	1.496	23.569	213.370
500	1195.200	133.130	65.750	7.250	365.520	6.759	7787.770	2.459	24.740	328.050
600	1062.700	166.550	62.420	5.905	341.130	7.291	7226.770	2.086	22.562	310.420
700	905.700	196.200	60.700	5.703	327.620	7.624	7273.910	2.402	24.554	293.810
800	1176.100	270.680	50.240	9.107	307.450	5.756	7953.290	2.142	20.526	304.880
1100	1018.100	183.930	61.440	6.497	337.230	7.048	7389.790	2.618	21.850	339.710
1200	1033.600	254.160	66.570	8.033	339.540	7.699	8238.540	2.575	23.157	1111.800
1300	833.800	201.090	66.810	6.750	341.340	7.396	7180.020	2.199	24.150	415.740
1400	774.700	203.090	56.960	5.824	322.330	6.333	7837.240	2.532	23.261	346.970
1600	1433.000	166.760	70.660	6.545	404.740	9.518	7418.070	2.417	26.746	425.400
1700	1358.700	227.000	79.920	8.161	386.950	9.139	7935.780	3.300	27.001	576.270
1800	1056.300	176.970	66.980	7.599	364.870	7.869	7260.850	2.484	26.321	529.300
1900	1127.800	170.990	60.410	6.609	319.700	7.896	7438.170	2.583	24.318	387.450
1601	1025.000	175.330	59.100	6.545	304.180	5.872	6182.040	1.906	21.671	433.460
1602	-756.800	185.180	65.910	6.582	364.090	6.863	7582.200	1.634	22.655	457.870
1603	856.300	413.210	73.750	10.878	418.250	6.794	7679.900	2.604	25.110	321.700
1604	1149.800	143.660	99.530	4.369	314.860	7.576	5754.380	2.754	23.231	298.680
1605	1165.100	180.600	66.190	2.602	368.300	7.233	6980.370	1.602	24.888	178.370
1606	1057.400	112.860	58.820	3.297	361.430	7.097	7439.380	2.367	25.933	171.840
1607	1202.800	263.720	74.720	16.904	393.230	7.770	8072.550	2.502	25.610	371.570
1608	-854.700	152.050	83.980	5.571	348.940	12.000	6658.270	3.014	27.812	513.010
1609	1350.100	100.370	71.060	3.597	402.500	7.508	8260.530	2.287	27.246	243.440
1610	1364.100	243.730	66.120	7.903	402.430	10.805	8840.030	8.161	32.879	636.670
1611	-835.100	129.000	60.600	2.625	402.630	8.282	9249.310	2.569	32.140	189.590
1612	1300.700	202.770	79.920	4.286	436.190	8.468	7278.650	3.103	24.953	884.640
1613	1655.900	102.760	66.110	6.866	384.610	8.977	6119.090	2.746	23.185	268.750
1614	-825.600	98.850	67.990	5.038	354.140	8.847	6281.850	2.119	25.364	877.170
1615	-854.700	211.040	69.950	4.680	445.860	9.753	8315.500	2.349	29.518	296.010
1616	1912.300	76.690	99.760	2.988	535.770	11.655	6124.550	3.537	31.244	248.480
106	-828.700	55.450	97.050	-0.279	176.700	8.152	4056.140	2.857	22.034	117.100
602	1190.200	569.400	61.100	11.362	383.000	9.366	10705.140	2.789	24.727	412.170
1210	-816.300	913.390	55.930	21.650	336.710	4.854	24838.930	1.682	11.772	12267.340
1701	2201.000	84.910	93.020	1.295	281.760	9.169	5160.670	4.416	27.343	207.820
1704	1270.200	319.070	68.690	9.607	389.360	7.265	7525.840	2.321	23.853	875.830
1802	-864.900	125.460	60.510	5.907	343.070	7.256	7286.420	1.919	25.696	272.740
1913	-851.400	218.340	65.120	9.264	378.800	8.459	7694.280	2.387	27.342	627.430
1914	1651.600	197.430	71.960	6.928	390.070	7.957	8150.330	2.433	29.993	369.490

Duplicate samples were prepared for two composite samples (samples 1100 and 1900) and two sampling increments (sampling increments 106 and 1614). The results for the duplicate samples are shown as charts in Figures 2 and 3. With the exception of Be, the elemental concentrations seem to agree acceptably well in each pair of duplicate samples.

A likely explanation for the anomalous behaviour of Be could be the fact that the soils in and around Oslo have evolved from a parent material in which Be minerals, i.e., beryl ($3\text{BeO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$) occurred. Unaltered Be-bearing grains of this mineral should still be found in the soil and could be resuspended and incorporated to the street dust of Oslo. The presence of one or more of these grains in a sample of street dust can explain the high Be concentrations in a limited number of analysis, as opposed to the rest of the samples where these particles are absent and which reflect the background Be concentration in the street dust of Oslo (1.9 ppm).

In order to minimize the effect of this anomalous behaviour on the estimate of Be mean values and to ensure the stability of Be concentration maps (see chapter 5.1), the mass of the sampling increment collected in each sampling location should be increased.

Table 3: Elemental concentrations (ppm, dry matter) of pairs of duplicate samples.

SAMPLE ID	106	2020	1100	3030	1614	4040	1900	5050
Al	60020.9	53219.1	52690.7	60641.8	67501.5	63314.2	61151.9	57886.5
Ba	585.820	546.470	458.520	519.250	527.700	568.790	470.210	546.470
Be	1.641	53.609	1.463	1.846	1.188	2.188	1.972	2.160
Ca	10619.0	10136.0	39321.0	44877.0	47285.0	48786.0	43137.0	42678.0
Co	10.930	10.930	16.960	20.050	18.090	18.690	16.730	19.980
Cs	2.076	1.603	1.454	1.829	1.313	1.901	1.095	1.256
Cu	24.920	26.070	96.220	103.370	97.630	124.360	128.820	139.230
Fe	27100.5	24974.0	50022.7	54760.4	53316.2	55935.4	52293.2	56240.1
Ga	17.060	15.560	15.590	17.310	17.760	16.680	17.060	16.430
La	52.295	47.592	43.803	49.349	44.373	55.972	45.202	47.269
Mg	7505.5	7088.4	12854.0	14018.0	11774.0	11983.0	14056.0	14657.0
Mn	934.200	849.100	763.100	826.100	929.800	873.600	897.400	917.200
Mo	2.580	2.466	2.600	4.042	5.945	8.645	2.741	5.675
Na	19312.0	19019.0	18377.0	20756.0	21125.0	19497.0	19361.0	19003.0
Ni	33.380	38.130	44.190	34.340	36.520	36.300	41.430	46.200
Pb	55.450	54.060	183.930	210.250	98.850	130.040	170.990	194.420
Rb	97.050	88.130	61.440	66.570	67.990	67.460	60.410	57.940
Sr	176.700	145.470	337.230	356.910	354.140	346.860	319.700	347.110
Th	8.152	8.169	7.048	6.745	8.847	10.250	7.896	7.721
Ti	4056.1	4117.3	7389.8	7852.9	6281.9	6530.7	7438.2	7949.4
U	2.857	2.551	2.618	2.045	2.119	2.704	2.583	2.715
Y	22.034	20.554	21.850	24.002	25.364	26.331	24.318	23.251
Zn	117.100	107.770	339.710	340.040	877.170	881.730	387.450	423.090

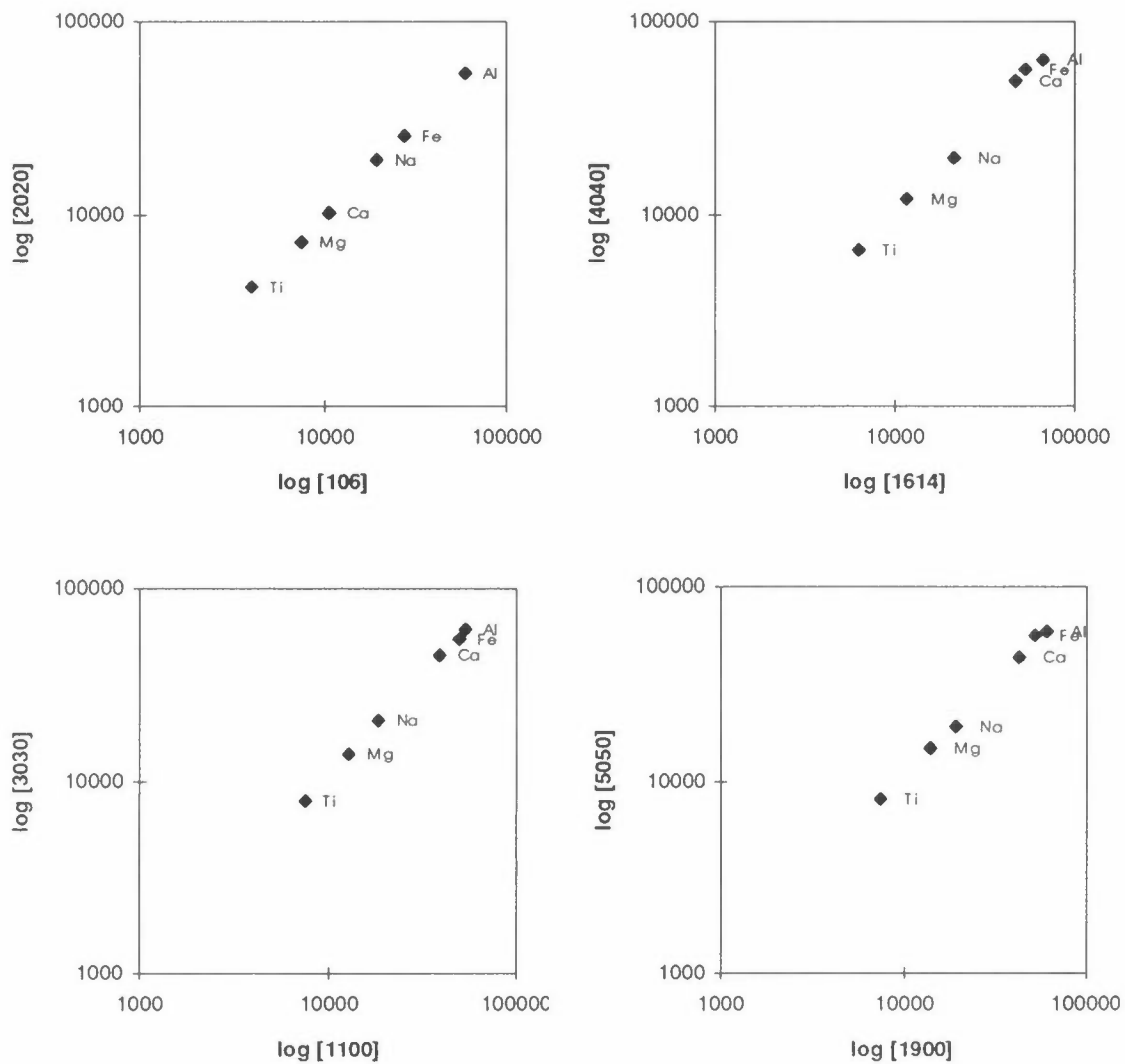


Figure 2: Plot of concentration of major elements (ppm, dry matter) in pairs of duplicate samples.

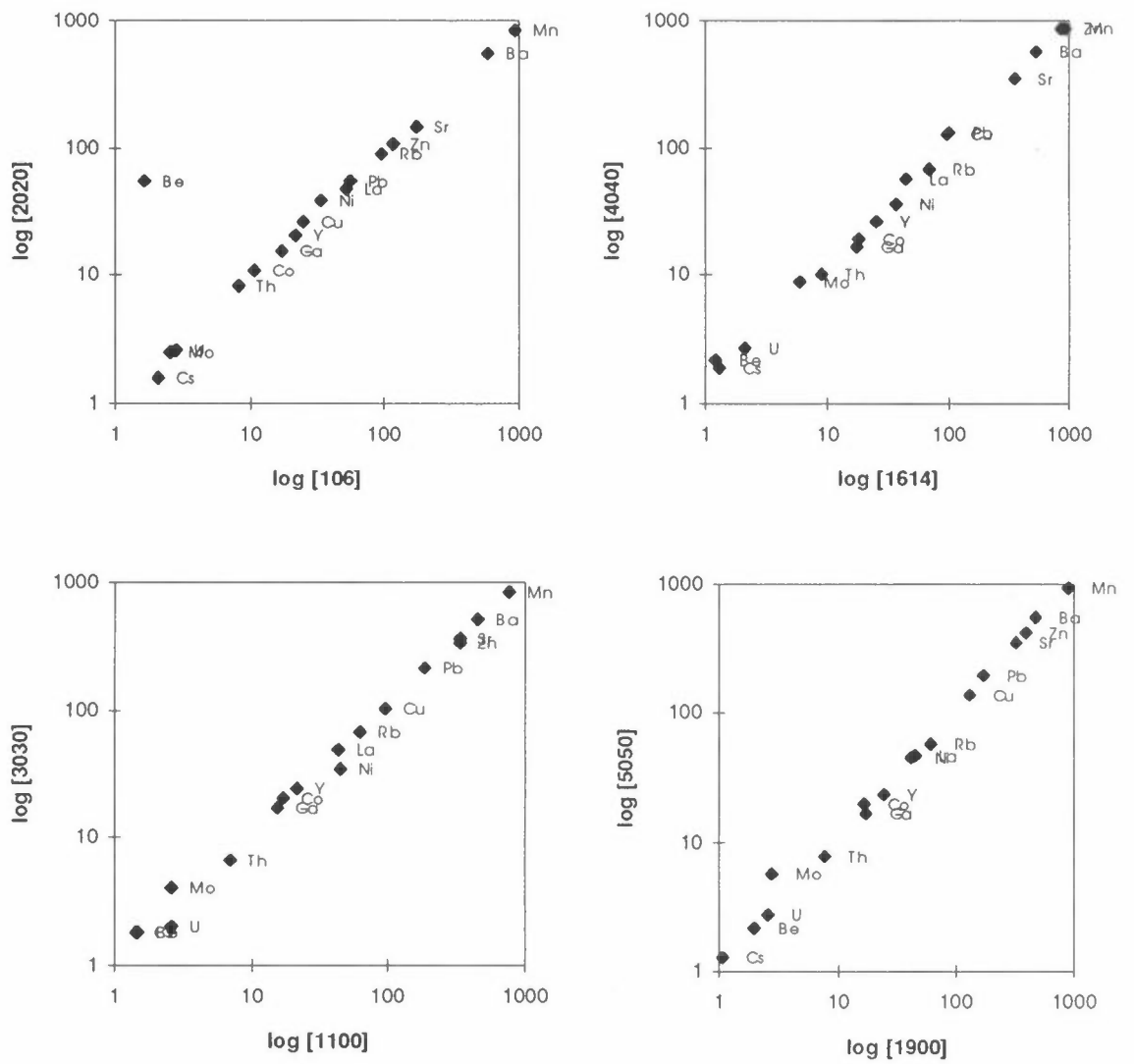


Figure 3: Plot of concentration of trace elements (ppm, dry matter) in pairs of duplicate samples.

5.1 Validation of the sampling strategy. Stability of maps.

A map can be considered “stable” or “robust” when the internal variability of the mapping units is small compared to the variability between mapping units (Miesch, 1976). Since the contribution of the distribution variance to the total internal variance is by far the largest (Llamas et al., 1990), the latter, s_{ω}^2 , can be estimated by the variance of the set of sampling increments collected from mapping unit 16. The assumption is made that the total internal variance thus determined for mapping unit 16 is similar to that of the rest of the mapping units (variability “within” mapping units).

The variability “between” mapping units, s_a^2 , can be estimated from the variance of the set of 14 mean elemental concentrations, $s^2(\bar{X}_i)$, as follows:

$$s_a^2 = s^2(\bar{X}_i) - \frac{s_{\omega}^2}{n_{\omega}}$$

where n_{ω} is the number of sampling increments collected in each mapping unit.

Table 4 shows the variability “between” and “within” mapping units for every elemental concentration, and also the ratio of one to the other and the stability of each map.

Table 4: Stability of the maps of elemental concentrations in Oslo.

Element	Variability between mapping units (1)	Variability within mapping units (2)	Variance ratio (1/2)	Stability (%)
Al	26274653.8	45063312.1	0.5831	0.5
Ba	2600.80272	2925.44538	0.8890	0.1
Be	106.612563	0.39192207	272.0249	-
Ca	12079129.8	263314340	0.0459	25
Cd	0.34877464	0.97740449	0.3568	2.5
Co	2.72646014	5.80503333	0.4697	1
Cs	0.10681929	0.23366025	0.4572	1
Cu	1871.31606	6858.58391	0.2728	5
Fe	4181890.72	56957502.6	0.0734	25
Ga	1.8961407	4.01434667	0.4723	1
La	20.2235082	130.184857	0.1553	10
Mg	529556.835	3047225.33	0.1738	10
Mn	2943.51117	12890.558	0.2283	5
Mo	1.47586289	3.1976839	0.4615	1
Na	978529.34	8487783.13	0.1153	25
Ni	2.99843711	163.260567	0.0184	50
P	30754.3511	88358.1636	0.3481	2.5
Pb	2395.39474	7018.54933	0.3413	2.5
Rb	68.0586566	157.887033	0.4311	1
Sb	3.12725732	13.4092133	0.2332	5
Sr	570.689995	3050.10446	0.1871	10
Th	1.19056761	3.1939298	0.3728	2.5
Ti	141216.371	1128775.49	0.1251	10
U	0.00930363	2.28704278	0.0041	50
Y	2.81173241	11.6986721	0.2403	5
Zn	48657.8366	51598.583	0.9430	0.1
Mean Ratio	excluding Be		0.3200	2.5

For the mean variance ratio, the average stability of the maps of elemental concentrations (excluding Be) is 2.5 %. For 21 of the 26 elements considered, the stability of their maps is less than 10 %, i.e. for the average variability among mapping units, any two of them will be displayed as significantly different with a significance level of 10 %. These results can be considered as highly satisfactory.

The evaluation of the resolution of the maps is more subjective, and it will depend on the maps' original purpose. In the case of lead, for example, two mapping units with the same real mean concentration would be displayed as significantly different with a significance level of 5 % when the difference between the estimated mean Pb concentrations in both mapping units were higher than 60 ppm. This difference of 60 ppm in measured values represents the limit value for the critical region in a test with null hypothesis: "there is no difference between mapping units" and alternative hypothesis: "the difference between mapping units is equal or greater than 99 ppm", with $\alpha=0.05$ and $\beta=0.10$. The resolution accomplished for the different maps can be improved by collecting a larger number of sampling increments from each mapping unit.

5.2 Mean elemental concentrations in the street dust of Oslo. A comparison with Madrid.

From the data set of the composite samples, the mean value in Oslo and the standard error have been calculated for each elemental concentration (Tables 5 and 6). Each one of the 14 composite samples is made up of 16 sampling increments collected at different locations within a particular mapping unit. Therefore, the figures shown in the first column of Tables 5 and 6 can be regarded as the mean value of 224 field samples. Although fewer locations and a smaller area were sampled in Madrid (Llamas et al., 1990 and 1991), some preliminary comparisons can be attempted (Tables 5 and 6).

The concentration of Al, Fe and Ti (only major elements available for comparison) are respectively 1.5, 2.5 and 7 times higher in Oslo than in Madrid. This finding reflects the different composition of the bedrock from which the soils in Oslo and Madrid have evolved.

Table 5: Mean and standard error values for the concentration of the major elements in the street dust of Oslo and Madrid (ppm, dry matter).

Elements	Mean (Oslo)	Std.err. (σ/v)	Mean (Madrid)	Std.err. (σ/v)
Al	59527	5394	44000	2000
Ca	42691	5342		
Fe	51452	2782	22000	4000
Mg	13188	849		
Na	19295	1228		
Ti	7452	460	1100	200

Table 6: Mean and standard error values for the concentration of the trace elements in the street dust of Oslo and Madrid (ppm, dry matter).

Elements	Mean (Oslo)	Std.err. (σ/v)	Mean (Madrid)	Std.err. (σ/v)
Ba	526.156	52.760		
Be	5.854	10.327		
Cd	1.308	0.640		
Co	18.741	1.758	3.0	1.0
Cr			61.0	13.0
Cs	1.314	0.348		
Cu	123.459	47.958	188.0	43.0
Ga	16.687	1.465		
La	47.886	5.325		
Mn	832.879	61.230	362.0	23.0
Mo	3.982	1.294		
Ni	41.361	3.633	44.0	9.0
P	1086.236	190.465		
Pb	180.451	53.236	1927.0	912.0
Rb	65.545	8.828		
Sb	6.316	1.991		
Sr	344.510	27.592		
Th	7.598	1.179		
U	2.413	0.390		
V			17.0	4.0
Y	24.186	1.882		
Zn	412.017	227.778	476.0	53.0

Regarding trace elements, the concentrations of Ni and Zn are very similar in both cities, while those of Mn and Co are, respectively, twice and six times higher in Oslo. The last two trace elements available for comparison, Cu and Pb, exhibit concentration values which are 1.5 and 10 times higher in Madrid.

The discrepancy between the figures for lead in both cities reflects with extraordinary accuracy the difference between the average lead content of the petrol burnt in Oslo and Madrid at the time of both studies. The percentage of leaded petrol used in Madrid in 1990 and in Oslo in 1993 was, respectively, 100% and 25%, with lead contents of 0.40 g/l and 0.15 g/l. These figures yield an average lead-in-petrol concentration of 0.4 g/l for Madrid and 0.0375 g/l for Oslo, again ten times higher in the Spanish capital, as is the case for the average lead-in-street dust concentration. This finding proves that the gradual shift from leaded to unleaded petrol has resulted in a proportional reduction in the concentration of lead in dust particles under 100 μm in urban environments.

5.3 Statistical Analysis of the data: Multivariate Techniques.

In order to better describe and interpret the results, a number of multivariate analysis techniques have been employed, i.e. Principal Component Analysis, Factor Analysis and Cluster Analysis. The elemental concentrations of Be, Cd, P and Sb have not been included in some of the statistical analyses, either because of their anomalous behaviour (as in the case of Be - see discussion above) or because of the presence of a number of observations below the detection limit (Cd, P and Sb).

Principal Component and Factor Analyses have been run with the whole set of data and also with the subset which includes only the elemental concentrations of the sampling increments (38 and 24 observations, respectively). Although small differences occur, there is a good agreement between the results in both cases (Table 7). Three factors explain most of the variability (70%) of the data. The first two factors seem to reflect the “urban” and “natural” sources of the street dust of Oslo; a third, one which comprises (Ca), Cs, (Cu), (Mo), Ni, P, Rb and U, appears to group those elements with a mixed origin or elements which have undergone geochemical changes from their original sources (elements in brackets show significant loadings also in one of the first two factors).

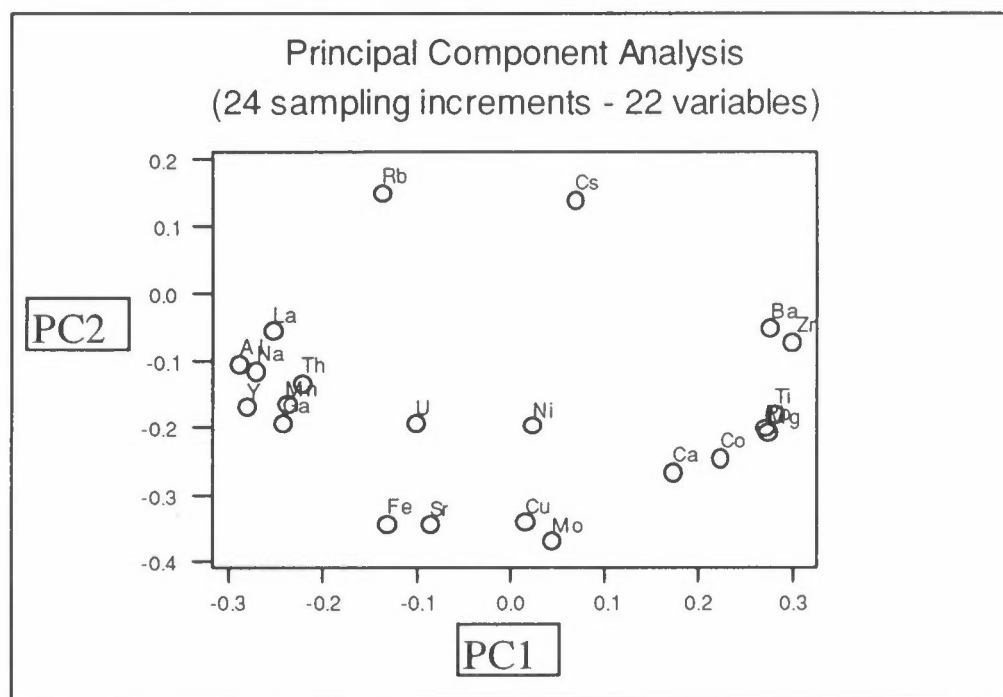


Figure 4: *Principal Component Analysis. Plot of Principal Components 1 and 2.*

Table 7: Factor Analysis (38 Observations - 22 Variables). Sorted Rotated Factor Loadings and Communalities

Variable	Factor1	Factor2	Factor3	Community
Mg	0.890	0.000	0.000	0.852
Ti	0.880	0.000	0.000	0.878
Pb	0.876	0.000	0.000	0.838
Co	0.852	0.000	0.000	0.739
Ca	0.766	0.000	0.000	0.595
Zn	0.763	-0.500	0.000	0.833
Ba	0.686	-0.495	0.000	0.739
Mo	0.592	0.000	0.000	0.609
Cu	0.494	0.000	0.000	0.519
Y	0.000	0.834	0.000	0.831
Al	0.000	0.798	0.000	0.795
Na	0.000	0.796	0.000	0.808
Ga	0.000	0.782	0.000	0.677
Fe	0.000	0.781	0.000	0.668
Mn	0.000	0.757	0.000	0.666
Sr	0.000	0.735	0.000	0.659
Th	0.000	0.612	0.485	0.663
La	0.000	0.600	0.000	0.599
Cs	0.000	0.000	0.767	0.792
U	0.000	0.000	0.735	0.678
Ni	0.000	0.000	0.660	0.519
Rb	0.000	0.000	0.659	0.600
Variance	6.4278	6.4118	2.7147	15.5544
% Var	29.2	29.1	12.3	70.7

A very similar pattern results from a Cluster Analysis of the variables (i.e. elemental concentrations). Three distinct groups can be observed in Figure 5. The first one, which includes Cd and Sb, seems to correspond to the “urban factor”; the second one is almost identical, with the exception of Sr, to the abovementioned “natural factor”, and the third one reflects again a mixed origin, incorporating some of the variables which had been previously assigned to the “urban factor” (Ca, Cu, Mo).

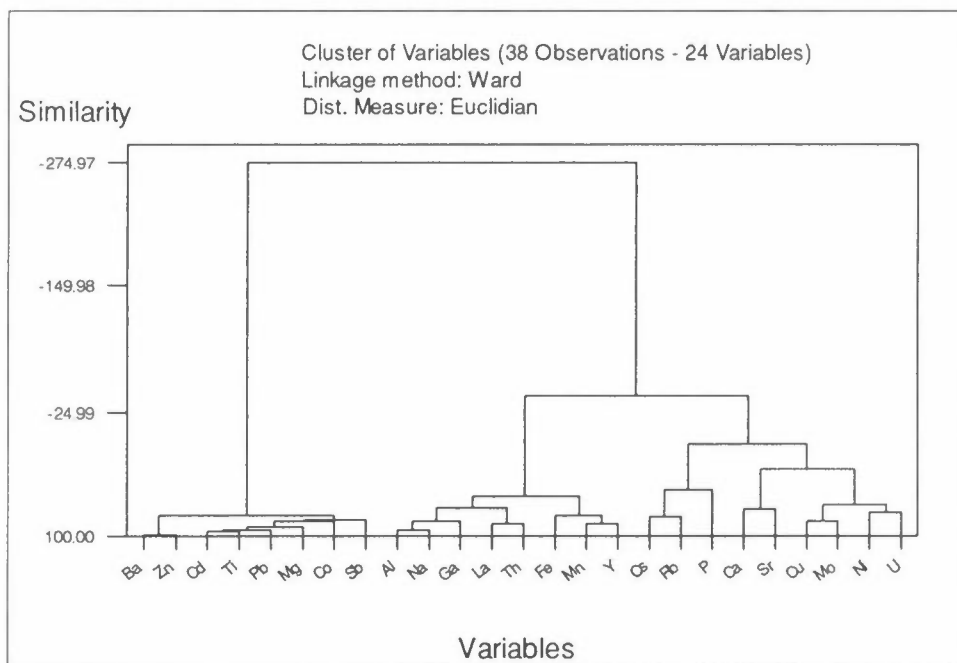


Figure 5: Cluster of Variables

This classification in three groups is supported by the results of Principal Component Analysis, Factor Analysis and Cluster of Variables for the subset of variables including only trace elements (Table 8 and Figure 6).

Table 8: *Factor Analysis for trace elements (38 Observations - 17 Variables). Sorted Rotated Factor Loadings and Communalities*

Variable	Factor1	Factor2	Factor3	Community
Y	0.921	0.000	0.000	0.873
Ga	0.811	0.000	0.000	0.659
Mn	0.787	0.000	0.000	0.630
La	0.738	0.000	0.000	0.646
Th	0.737	0.000	0.000	0.684
Zn	-0.630	0.615	0.000	0.779
Sr	0.614	0.000	0.000	0.582
Ba	-0.587	0.579	0.000	0.717
Sb	0.000	0.851	0.000	0.848
Pb	0.000	0.805	0.000	0.850
Mo	0.000	0.762	0.000	0.690
Co	0.000	0.745	0.000	0.650
Cu	0.000	0.710	0.000	0.653
Cs	0.000	0.000	-0.886	0.870
Rb	0.000	0.000	-0.704	0.645
Ni	0.000	0.000	-0.595	0.525
U	0.524	0.000	-0.575	0.676
Variance	5.3562	4.3112	2.3095	11.9769
% Var	31.5	25.4	13.6	70.5

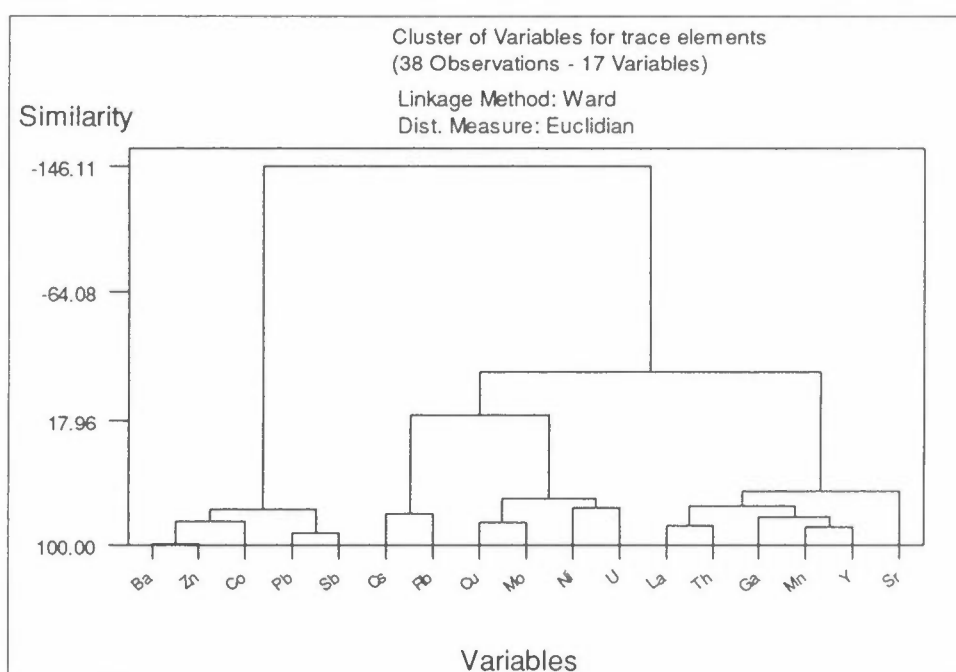


Figure 6: *Cluster of Variables for trace elements*

5.3.1 "Natural" Elements.

Together with most of the major elements (the exception being Ca and Mg), this group of elements is characterised by the presence of Ga, La, Mn, Sr, Th and Y. Their origin lies in the soil particles that through the process of soil resuspension

are incorporated to the street dust of Oslo. For the particle size fraction studied (below 100 μm), soil resuspension should account for a large proportion of the total mass of street dust in Oslo.

Although the problem of the nature and origin of an urban soil is not fully understood, the association of elements which makes up this group of “natural” variables is coherent with the alkaline composition of some of the most abundant rock formations around Oslo (e.g., the syenites that lie to the north of the city) which, during the last glacial episode, could have been weathered and given rise to part of the top soil in and around the norwegian capital (Oftedahl, 1960).

The absence of Ca and Mg from this group of elements reflects the fact that although both elements are present in the bulk of soil particles which become resuspended, other urban sources of Ca and Mg (most notably, cement dust) explain most of their spatial variability, thus forcing Ca and Mg to join the groups of elements with an “urban” or “mixed” origin.

5.3.2 “Urban” Elements.

The group of “urban” elements includes Ba, Cd, (Co), (Cu), Mg, Pb, Sb, Ti and Zn (elements in brackets show significant affinity for the group of elements with a mixed origin). Within this group of “urban” elements, two sources, at least, can be identified:

- a) traffic, and
- b) building construction/renovation and weathering and corrosion of building materials.

The influence of traffic is characterized by Zn and Ba, and to a lesser extent by Pb and Cu. Zinc and barium are highly correlated in the street dust of Oslo (their Pearson Correlation Coefficient is 0.973) and both can be traced to automobiles (Kowalczyk et al., 1982). Ba dispersions are widely used as detergents/dispersants and oxidation and corrosion inhibitors in lubricating oils for diesel and other combustion engines, and as smoke suppressant additives in diesel fuels. The highly basic Ba dispersions which have been used as smoke suppressant additives contain large amounts (e.g., about 20%) of dispersed barium compounds. Similarly, zinc compounds have been employed extensively as antioxidants (e.g., zinc carboxylate complexes and zinc sulfonates) and as detergent/dispersant improvers for lubricating oils (Drew, 1975). Tyre wear has also been reported to contribute significantly to the Zn load in street dust, especially in the form of coarse dust particles (Stigliani and Anderberg, 1991; Friedlander, 1973).

Historically, lead has been the most reliable tracer of traffic and much work has been done on the generation, distribution and size and chemical composition of lead-bearing exhaust particles, as well as on their health implications. However, nowadays in Oslo, as in most European cities, the gradual shift from leaded to unleaded petrol as fuel for automobiles has reduced traffic emissions of this element to an extent that it is highly debatable whether exhaust particles are still the major source of Pb in the street dust of some areas of the city.

The average lead-in-street dust concentration in Oslo (Table 6) is fairly close, for the same particle size ($< 100 \mu\text{m}$), to the mean Pb content of urban soils in Madrid, of 130 ppm (De Miguel et al., 1991) or that of soils of parks in Glasgow, of 131 ppm (Farmer and Lyon, 1977). If the average Pb concentration in the urban soil of Oslo were of the same magnitude, soil particles would account for a large proportion of Pb in street dust and the influence of vehicle emissions would only be significantly noticed at locations with high-density traffic. Elsewhere, lead sources of a different kind (e.g., building renovation) could be of similar or higher importance. Although the results of this study seem to support these tentative assumptions, they will only be confirmed through a study of urban soils in Oslo.

Oxidation of lubricating oils upon exposure to air at high temperatures results in the formation of organic acids, alcohols, ketones, aldehydes and other organic compounds which are corrosive to metal. This corrosive action causes wear of the metal parts which come into contact with the oil and which in many cases consist of zinc, copper and cadmium-bearing alloys (Drew, 1975) or, as in the case of sinterized materials used in the automobiles' oil pump, of Ni (2 - 4 %), Cu (1.5 - 2 %) and Mo (0.5 - 1.5 %). This process results ultimately in the release of those metals to the urban environment and their accumulation in the street dust. Although Cu seems to originate from more than one source, the high copper concentrations in samples collected close to busy roads suggests that the mechanism just described has a special significance for this element.

Two sampling increments (1612 and 1210) were collected in the proximity of buildings which were being renovated. The high concentrations of Ca in both locations (more than twice the average in Oslo) and the ratio Mg/Ca of 0.14 in sampling increment 1612 (Kowalczyk et al., 1982) suggests that cement dust is a major component of these two samples.

Sampling increment 1210 shows the highest concentrations for most of the trace elements analysed. Paint flakes from the facade are very likely responsible for the unusually high lead content, while corrosion of metal structures can explain the anomaly for some of the other trace elements. It is worth noting that Zn reaches a surprising concentration of 1.2 % in this sample. Again, corrosion of galvanized-metal parts must have contributed significantly to the Zn load in this location. The same explanation can be offered for the unexpected concentrations of Cd in sample 1210 (and to a lesser extent, in sample 1612), since this element, as an impurity in Zn, is found in significant amounts in galvanized metals. Cadmium is also used in pigments and could therefore be present in paint flakes, contributing to the total Cd load of the street dust in the proximity of old buildings or buildings undergoing renovation.

The weather conditions in Oslo and the proximity to the fjord should account for the enhanced importance of metal corrosion as a source of trace elements in street dust.

The large number of building construction and building renovation works that take place during the summer in Oslo indicates that their role as a source of trace elements in street dust is not limited to the sampling increments mentioned above,

but that it has a far reaching influence throughout the city (as exemplified in the average sample 1200).

The origin of Co and Sb is less clear. Both elements are enriched in the fly-ash from coal combustion, but this is an unlikely source of dust particles in the summer time, when the sampling campaign took place. It is also doubtful that refuse incineration, another source of Sb in urban environments, would have a significant influence in the Norwegian capital. Antimony is associated with non-ferrous ores, especially Cu ores, and Co is found in Ni, Pb, Cu and Fe ores (Adriano, 1986). During the smelting of these ores, Co and Sb are released to the atmosphere as stack dust particles which can travel long distances from the emission point. Although the concentrations of Sb found in southern Norway have been related to long-range aerial transport (Berg et al., 1994), it is debatable that this should also be the source of Sb and Co in the street dust of Oslo.

5.3.3 Elements with a mixed origin or geochemically altered.

This group of elements includes Cs, Ni, Rb and U, with Ca, Cu, Fe, Mo and Sr showing some affinity for it. All these elements lie somewhere in between the two groups which have been previously described. Some of them seem to participate from both characters, "urban" and "natural", and their origin is to be found not only in the process of soil resuspension but also in typically urban sources, i.e. cement dust, for Ca and accompanying Sr; traffic, for Cu and, probably, Mo; and metal corrosion, for Fe.

The separation of Cs, Rb, Sr and U from the group of "natural" elements is very likely due to a process of geochemical differentiation from the original source of these elements. This process is best illustrated by the behaviour of U and Th. Both elements have similar electron configurations, occur in nature in the tetravalent oxidation state, their ions have similar radii and can substitute extensively for each other. Uranium and thorium are incorporated to the street dust of Oslo through the process of soil resuspension and, consequently, both would be expected to be included in the group of "natural" elements.

Under oxidizing conditions, however, uranium forms the uranyl ion (UO_2^{2+} , oxidation state +6) whose compounds are soluble in water. Therefore, under the conditions that prevail in urban soils and street dust, uranium behaves as a mobile element and can be separated from thorium, which exists only in the tetravalent oxidation state and whose compounds are generally insoluble. This fact could explain the separation of uranium from the group of "natural" elements.

5.4 Distribution patterns of elements

The maps displaying the concentration of a number of elements in the street dust of Oslo are shown in Appendix B. These graphical presentations reveal distinct patterns of distribution for some elements.

The spatial distribution of "urban" elements like Cu, Pb and Zn is characterised by a steady increase in concentration in the direction north-south, which is more clearly revealed once the influence of the anomalous sample 1210 has been removed from the mean concentration value assigned to mapping unit 12.

Minimum values are found in the northernmost mapping units while the highest concentrations are located in mapping units 17 and 18, which cover the central district of Oslo (see Appendix A). Concentrations of these elements also increase, although less dramatically, from east and west towards the centre of the area under investigation.

The steep concentration gradient from the suburban and residential north towards downtown Oslo, to the south, reflects with surprising accuracy the increasing “urban” character of the mapping units in that direction. This “urban” character peaks in mapping units 17 and 18, which constitute the commercial and administrative centre of the city and where features such as the Norwegian Parliament, Oslo’s Town Hall, the Royal Castle, main street Karl Johans gate, Oslo’s Central Railway Station, the old town, ring road “Ring 1”, the National Theatre, the Aker Brygge commercial area, etc... can be found.

The map of lead concentration shows that, although this element follows the general trend for “urban” elements, the highest value is reached in mapping unit 08. A possible explanation for this fact is the presence of a nearby smelter and some associated industries, which were closed down a few years ago. If this tentative assumption proves to be correct, it would support the hypothesis that soil particles are one of the major sources of lead in the street dust of Oslo: since direct emissions from the smelter and/or the nearby factories have ceased for some years now, the origin of the lead in the street dust of mapping unit 08 should be found in the lead that accumulated over the years in the soil around the above mentioned industrial facilities.

As opposed to the general trend in the spatial distribution of the “urban” elements, most of the “natural” elements reach their highest concentration in northernmost mapping unit 01, reflecting the lack of urban features in that area and its mostly residential nature.

Due to their nature and their multiple sources, those elements with a mixed origin or which have undergone geochemical changes do not display a common pattern of distribution and their spatial interpretation is not straightforward.

6. Discussion and conclusions

The research project that has been described in this Technical Report does not attempt to answer all the questions that such a complex problem as the street dust in urban environments pose. However, the main goals of this study have been achieved (i.e. the statistical preparation and interpretation of robust and precise concentration maps and the characterisation of the elemental composition of the summer street-dust of Oslo), and a number of conclusions can be drawn from this work.

In the first place, a combination of statistical techniques (Visman’s methodology and Analysis of Variance) has proven to be a reliable tool in the design of a sampling campaign for particulate materials, when the final aim is to produce maps with a pre-determined degree of precision, resolution and stability. These

maps of elemental concentrations in street dust reveal the changing nature (i.e., residential, typically urban) of the different districts within the city under investigation and help locate areas worth of further, more detailed study.

Multivariate analysis techniques (Principal Component Analysis, Factor Analysis and Cluster Analysis) have been used to unveil the relationships among different elements. Three factors explain 70 % of the total observed variance of the data set. This fact seems to suggest that the elements in the street dust of Oslo can be classified in three groups: "urban" elements, "natural" elements and elements with a mixed origin or which have undergone geochemical changes from their original sources. Soil resuspension/mobilisation is the most likely source of "natural" elements, while "urban" elements seem to originate mostly from traffic and from building construction/renovation and weathering and corrosion of building materials.

The ratio of the mean lead concentration in the street dust of Oslo to that of Madrid (1:10) is almost identical to the ratio of the average lead content of the petrol burnt in the norwegian capital to that of the petrol burnt in the spanish one at the time of both studies. This finding proves that the gradual shift from leaded to unleaded petrol has resulted in a proportional reduction in the concentration of lead in dust particles under 100 μm in urban environments.

Lastly, the most important conclusion to be drawn from this work is the need for further research to attain a clear understanding of the geochemistry of urban environments in general, and the relationship between street dust and soil in particular.

Among relevant topics for further research, the following can be mentioned:

- 1) The study of the elemental composition of different size fractions of street dust: Assuming that dust particles from urban sources constitute the finest size fraction of street dust, it would facilitate the discrimination between urban and natural dust particles and could yield relevant information regarding individual urban sources and their intensities.
- 2) The speciation of the chemical elements in the street dust: In order to investigate the potential health risks derived from the ingestion and/or inhalation of street dust particles, it is essential to determine under which chemical form the different elements are present in the street dust.
- 3) The study of the elemental composition of the soils in and around Oslo: It would allow to further investigate the relationship between street dust and soil in Oslo. Comparison of results with similar projects carried out in Madrid and elsewhere could yield valuable information regarding the importance of the processes of soil resuspension and dust deposition in urban environments.

7. References

- Adriano, D.C. (1986) Trace Elements in the Terrestrial Environment. Springer-Verlag.
- Berg, T., Røyset, O. and Steinnes, E. (1994) Trace Elements in Atmospheric Precipitation at Norwegian Background Stations (1989-1990) Measured by ICP-MS. *Atmos. Environ.*, 28, 3519-3536.
- Biggins, D.E. and Harrison, R.M. (1980) Chemical Speciation of Lead Compounds in Street Dusts. *Environ. Sci. Technol.*, 14, 336-339.
- De Miguel, E., Llamas, J.F., Cjacon, E., Perez, M. and Gomez, F. (1991) Investigación geoquímica ambiental en suelos y plantas. 1ª Fase. Madrid (Technical Report, Instituto Tecnológico y GeoMinero de España (Geological Survey of Spain)).
- Drew, H.M. (1975) Metal-Based Lubricant Compositions. Noyes Data Corporation.
- Farmer, J.G. and Lyon, T.D.B. (1977) Lead in Glasgow Street Dirt and Soil. *Sci. Total Environ.*, 8, 89-93.
- Friedlander, S.K. (1973) Chemical Element Balances and Identification of Air Pollution Sources. *Environ. Sci. Technol.*, 7, 235-240.
- Harvey, P.G., Hamlin, M.W., Kumar, R., Morgan, J., Spurgeon, A. and Delves, T. (1985 a) Blood Lead, Behaviour and Intelligence Test Performance in Young Children. In T.D. *Internat. Conf. on Heavy metals in the environment*. Athens 1985. Ed. T.D. Lekkas. Edinburgh, CEP Consultants. Vol. 1, pp. 48-50.
- Harvey, P.G., Spurgeon, A, Morgan, J, Chance J. and Moss., E. (1985 b), A Method for Assessing Hand-To-Mouth Activity in Children as a Possible Transport Route for Toxic Substances. In: *Internat. Conf. on Heavy metals in the environment*. Athens 1985. Ed. T.D. Lekkas. Edinburgh, CEP Consultants. Vol. 1, pp. 436-437.
- Kowalczyk, G.S. Gordon, G.E. and Rheingrover, S.W. (1982) Identification of Atmospheric Particulate Sources in Washington, D.C., Using Chemical Element Balances. *Environ. Sci. Technol.*, 16, 79-90.
- Llamas, J.F. Del Barrio, S. and De Miguel, E, (1990) Toma de muestras en el estudio geoquímico de un área urbana. Aplicación al caso de metales pesados aerotransportados. *Boletín Geológico y Minero de España*, 101-6, 919-931.
- Llamas, J.F. Chacon, E. and De Miguel, E, (1991) Metales pesados en la atmósfera de Madrid. *Boletín Geológico y Minero de España*, 102-1, 135-147.

- McBride, W.G., Carter, C.J., Bratel, J.R., Cooney, G. and Bell, A. (1985) Study of Health Effects of Lead in Urban Children. In: *Internat. Conf. on Heavy metals in the environment*. Athens 1985. Ed. T.D. Lekkas. Edinburgh, CEP Consultants. Vol. 1. pp. 330-332.
- Merks, J.W. (1985) Sampling and Weighing of Bulk Solids. Trans Tech Publications.
- Miesch, A.T. (1976) Geochemical Survey of Missouri - Methods of Sampling, Laboratory Analysis and Statistical Reduction of Data. Washington DC (U.S. Geol. Survey. Prof. Paper 954-A).
- Nicholson, K.W. (1988) A Review of Particle Resuspension. *Atmos. Environ.*, 22, 2639-2651.
- Oftedahl, C. (1960) Permian Rocks and Structures of the Oslo region. In: *Geology of Norway*. Olaf Holtedahl, ed., (Norges Geologiske Undersøkelse Nr. 208).
- Rundle, S.A., Inskip, M.J., Duggan, M.J. and Moorcroft, J.S. (1985) Lead-In-Dust on Children's Hands. In: *Internat. Conf. on Heavy metals in the environment*. Athens 1985. Ed. T.D. Lekkas. Edinburgh, CEP Consultants. Vol. 1, pp. 457-459.
- Sehmel, G.A. (1980) Particle Resuspension: A Review. *Environ. Intl.*, 4, 107-127.
- Stigliani, W.M. and Anderberg, S. (1991) Industrial Metabolism and the Rhine Basin. *Options*, Sept. 1991.
- Thomas, J.F.A., Culbard, E., Delves, T., Harvey, P.G., Sherlock, J., Davies, A., Quinn, M.J., Morgan, J., Smart, G., Spurgeon, A., Thornton, I. and Watt, J. (1985) Lead Intake of Young Children from Dust and Other Sources. In: *Internat. Conf. on Heavy metals in the environment*. Athens 1985. Ed. T.D. Lekkas. Edinburgh, CEP Consultants. Vol. 1, pp. 317-319.
- Visman, J. (1947) De Monsterneming van Heterogene Binomiale Korrelmengsels Drukkery de Waal. Groningen.
- World Commission on Environment and Development (1987) Our Common Future. Oxford University Press.

Appendix A

Description of the sampling campaign.

The sampling campaign started on Aug. 2nd, 1994. It drizzled during the night of Aug. 1st to Aug. 2nd and the early morning of Aug. 2nd, a fact that did not affect the sample collection on Aug. 2nd. On this day, mapping unit no. 16 was sampled. The nature of mapping unit no. 16, where residential, commercial, building and road construction activity and heavy traffic areas are represented, led to the decision of analysing each of the 16 sampling increments separately in order to characterise the above mentioned potential sources of trace elements in street dust.

Heavy rain on the evening of Aug. 2nd forced the sampling campaign to stop for 24 hours. It was resumed on Aug. 4th, when mapping unit no. 11 was sampled. The nature of this sampling unit is not homogeneous since together with a majority of sampling increments from residential areas, some busy streets and a park are also present.

It rained on Aug. 5th and again 24 h were allowed before collecting samples. Mapping unit 01 was sampled on Aug. 7th. A large construction site for a new hospital, which was not shown on the map, covered a fairly wide area within the central part of the mapping unit. Since access to the construction site was forbidden and some small roads had been removed or altered, the sampling increments in this mapping unit were not collected in a strictly regular pattern, as is the case in the rest of the sampling units. The nature of this sampling unit is almost purely suburban-residential, with some of the sampling increments collected from pathways in forests. The southern most part of the mapping unit is affected by a traffic corridor (Ring 3) with heavy traffic under cruise driving conditions.

On Aug. 8th, mapping unit 03 was sampled. It encompasses the Blindern campus of Oslo University and it has a strictly residential-suburban nature. Only one sample increment collected from a terrace might have abnormal concentrations of some elements since the sides of the terrace were coated with metal panels.

Mapping unit 17, sampled on Aug. 9th, covers part of downtown Oslo and can be described as having a predominantly commercial nature. Some medium and heavy traffic areas are also present, as well as the park and gardens of the Royal Castle to the northwest, from which two sample increments were collected. The southernmost part of the mapping unit covers the Aker Brygge commercial area (a pedestrian zone) and one of the piers on the Oslo fjord. Dust does not accumulate easily in this southern sector due to street washing and moderate sea breeze.

On Aug. 10th, the 16 sampling increments from mapping unit 05 were collected. The northernmost part of this unit has a marked suburban-residential character, while the southern half, which covers the Majorstuen district, is mostly commercial in nature. Heavy traffic is also present as the ring road "Ring 2" and road 168, coming from the north-west, cut across this mapping unit.

Mapping unit 12 was sampled during the afternoon of Aug. 10th and the morning of Aug. 11th. Its nature is both commercial and residential. A strong influence of resuspended soil particles should be expected since extensive green areas are

present in this unit. On the afternoon of the same day mapping unit 06 was sampled. Although of a predominantly residential nature, the northern part of this unit is influenced by the traffic corridor "Ring 2" and some sampling stations were located in commercial zones. Again, resuspended soil should contribute predominantly to the accumulated street dust for the same reasons as just stated for mapping unit 12.

Mapping unit 07 was sampled on Aug. 15th after it had heavily rained on Aug. 13th and there had been moderate precipitation on the morning of Aug. 14th. In some sampling stations remaining moisture had compacted dust into a cake, which was nevertheless sampled. Although these are not ideal sampling conditions, a positive side-effect might be expected: the finer fraction of street dust had been most likely integrated into the cake and could therefore be present in the global sample, whereas in most other mapping units these smaller particles are lost through resuspension as the sample is collected. One possible consequence of this fact is the finding of higher concentrations of those trace elements which tend to be enriched in the finest fraction.

Mapping unit 07 has a mixed nature, encompassing residential areas, traffic corridors - especially Oslo's Ring 2 - and some old industrial quarters, whose influence is difficult to estimate since activity there seems to have ceased to a large extent.

Mapping unit 18, sampled on Aug. 16th, lies to the east of unit 17 and together with the latter covers most of downtown Oslo. Its nature would be strictly commercial, were it not for the influence of the traffic corridor "Ring 1" which cuts across the mapping unit and is represented in approximately a fourth of all the sampling increments collected from this unit.

Collection of dust was difficult at some stations located on streets which had been washed the night before. An interesting feature of this unit is its purely urban character with an almost complete absence of bare soil. Soil particles, therefore, should not contribute as much to the total load of street dust as in other mapping units. This fact may lead to higher trace element contents in unit 18 due to the absence of "dilution" with resuspended soil (concentration of trace elements is higher in "urban" sources, i.e. traffic, construction activities, burning of fossil fuels..., than in soil).

Stop-and-go traffic, which is characteristic of commercial areas, is well represented with half of the sampling increments collected in or near car parks or taxi or bus stops. Stop-and-go traffic and traffic from "Ring 1" can be expected to be the main sources of trace elements in this mapping unit.

Mapping unit 13 was sampled on Aug. 17th. It has a mixed nature where commercial, residential and green areas are present. No heavy traffic was apparent at the time of the sampling.

It rained with variable intensity from Aug. 17th till Aug. 20th which caused the sample collection to be halted for four days and it was resumed on Aug. 22nd. On that day mapping unit 08 was sampled. Although mostly residential in nature, it

has some commercial areas and is crossed by “Ring 2”, from which three sample increments were collected.

Mapping unit 14, located south of unit 08, has a more commercial nature than the latter and it is also crossed by “Ring 2” as well as by at least two streets with medium-to-high traffic intensity. It was sampled between Aug. 22nd and Aug. 23rd.

In the afternoon of Aug 23rd the last mapping unit included in this study, unit 19, was sampled. It encompasses the commercial districts of Grønland and Tøyen, and is crossed by the innermost urban ring road in Oslo, “Ring 1”, as well as by some heavy traffic streets. There are some green areas in the north- and southeast of this unit.

Appendix B

Maps of concentration of chemical elements in the street-dust of Oslo

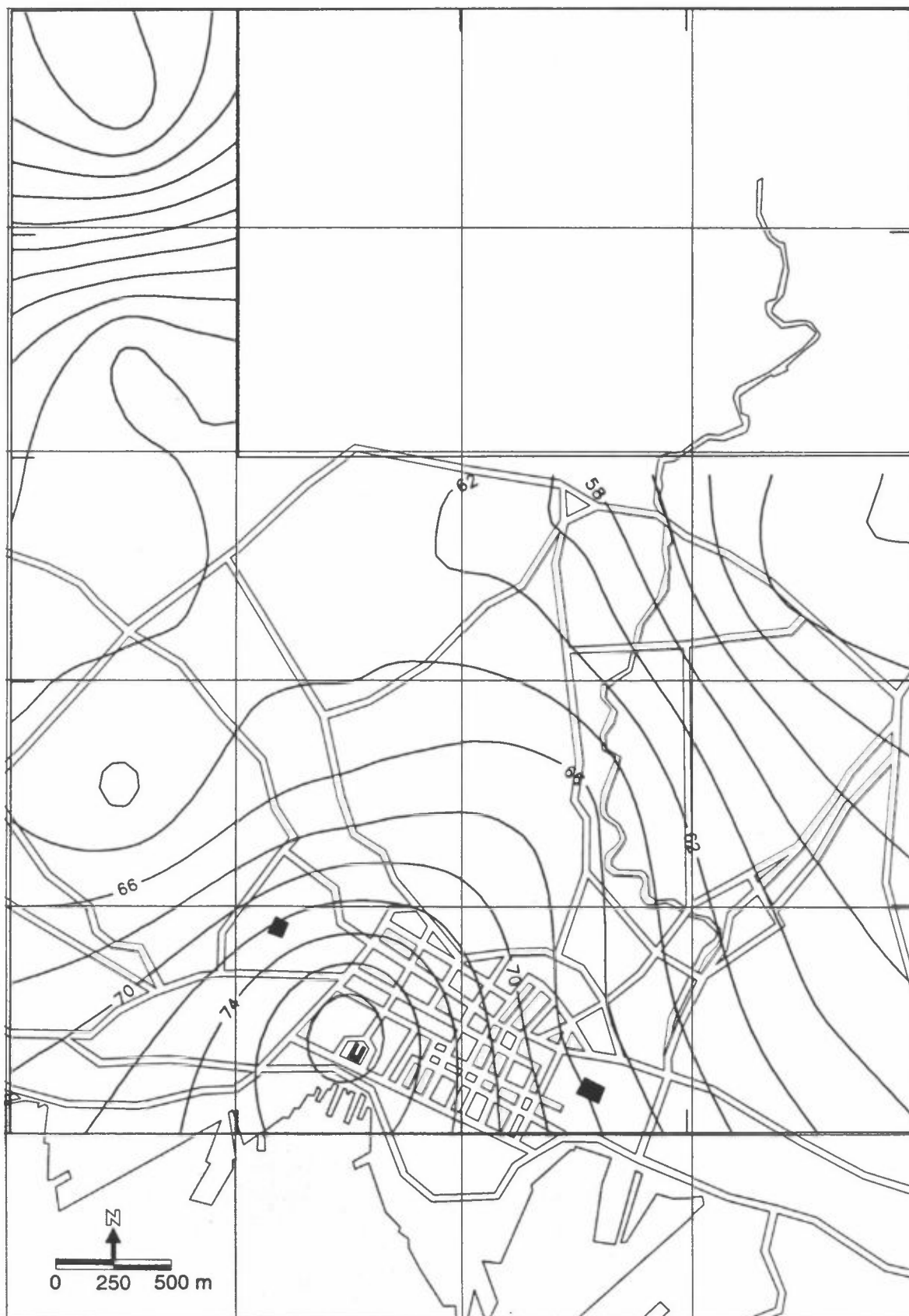


Figure B1: Concentration of Rb in the street dust of Oslo (ppm, dry matter).

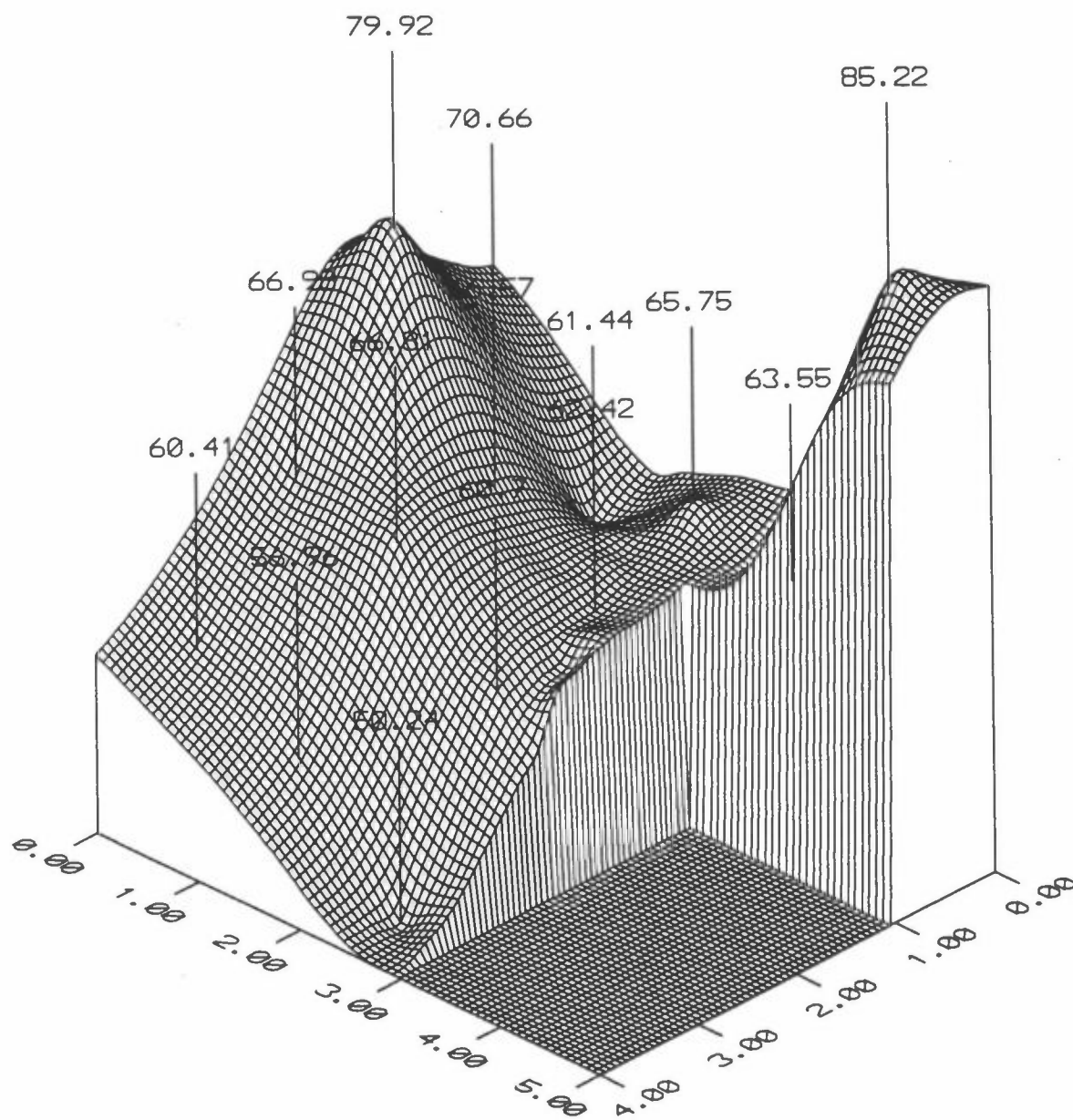


Figure B1: Cont.

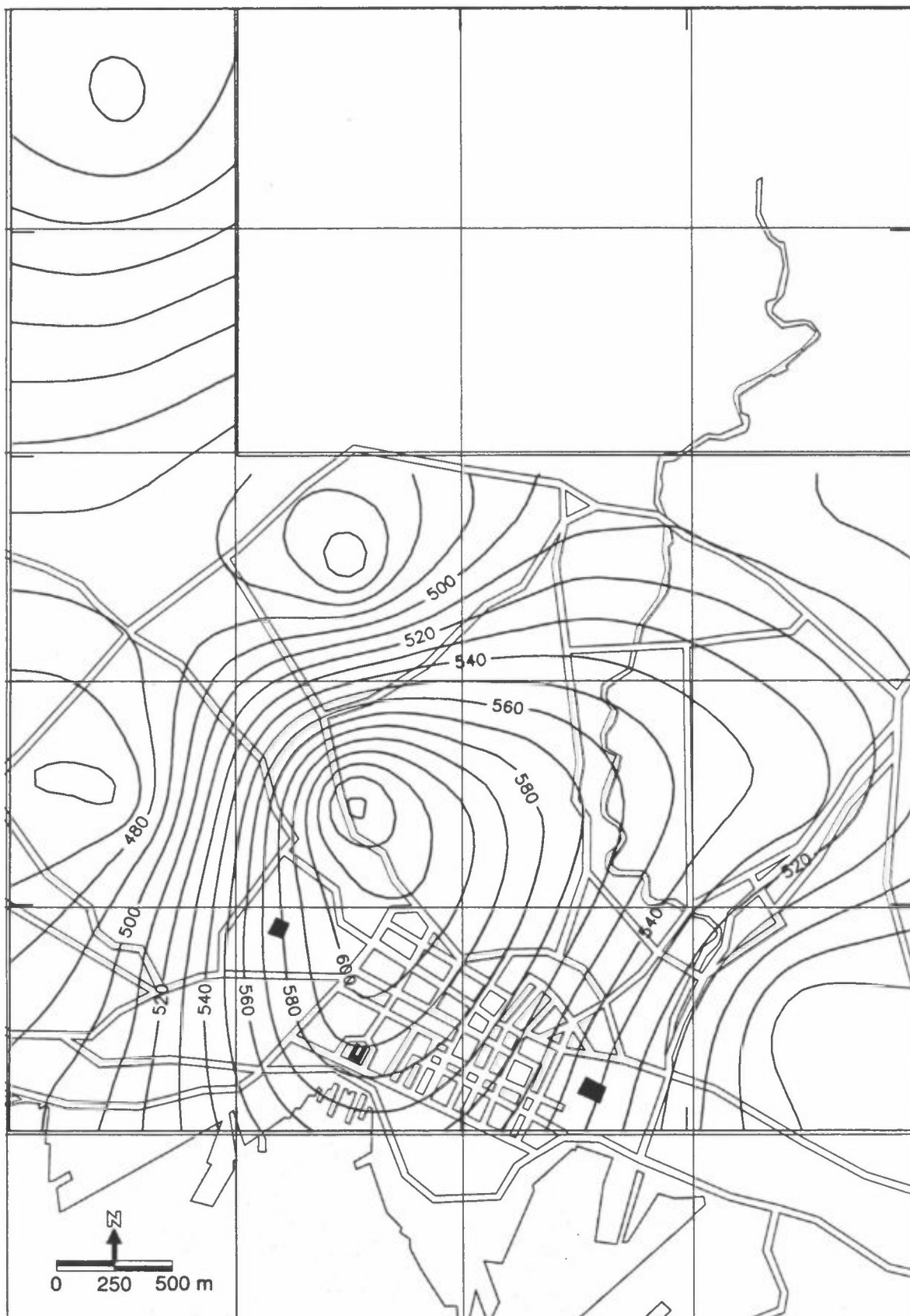


Figure B2: Concentration of Ba in the street dust of Oslo (ppm, dry matter).

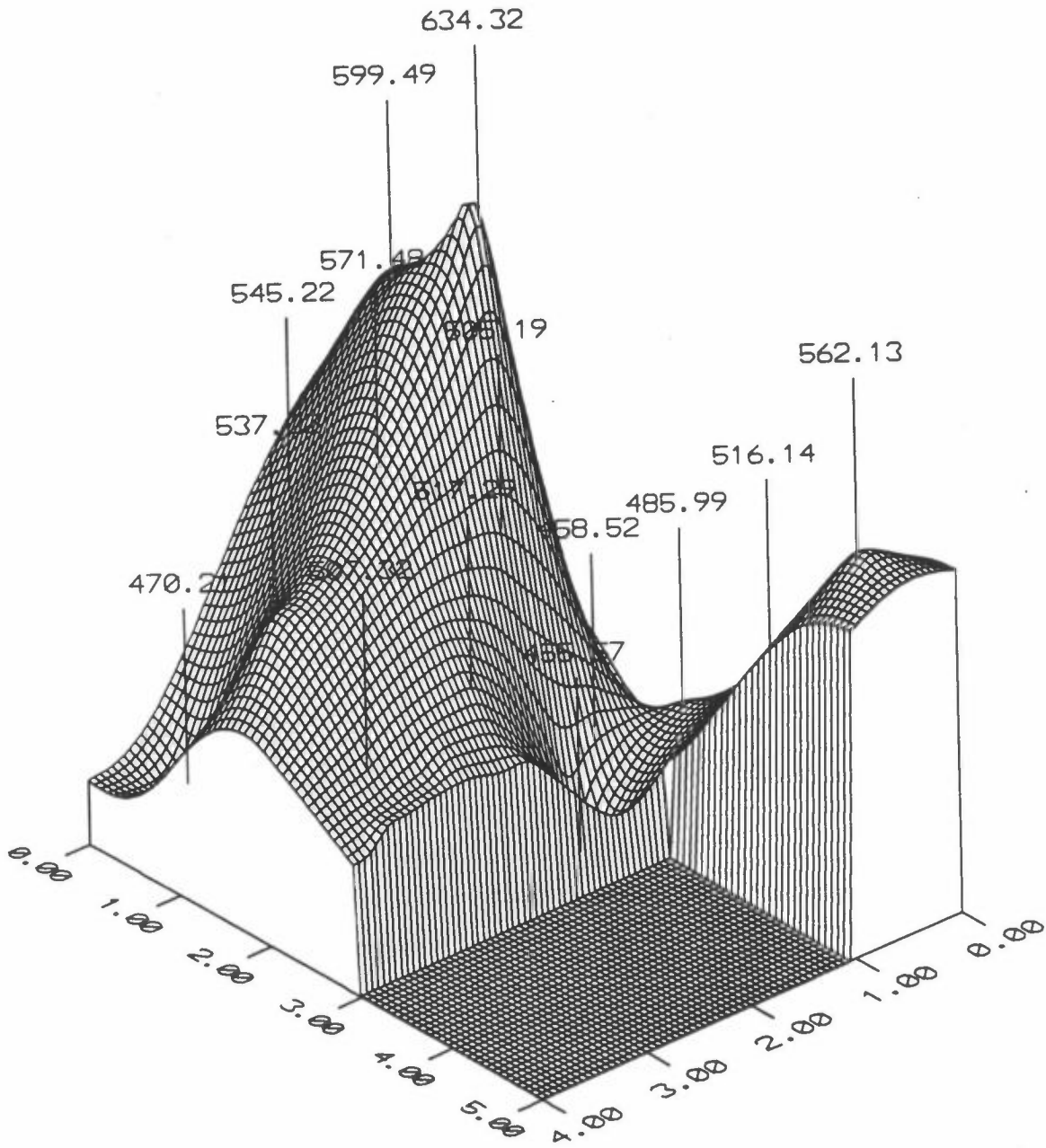


Figure B2: Cont.

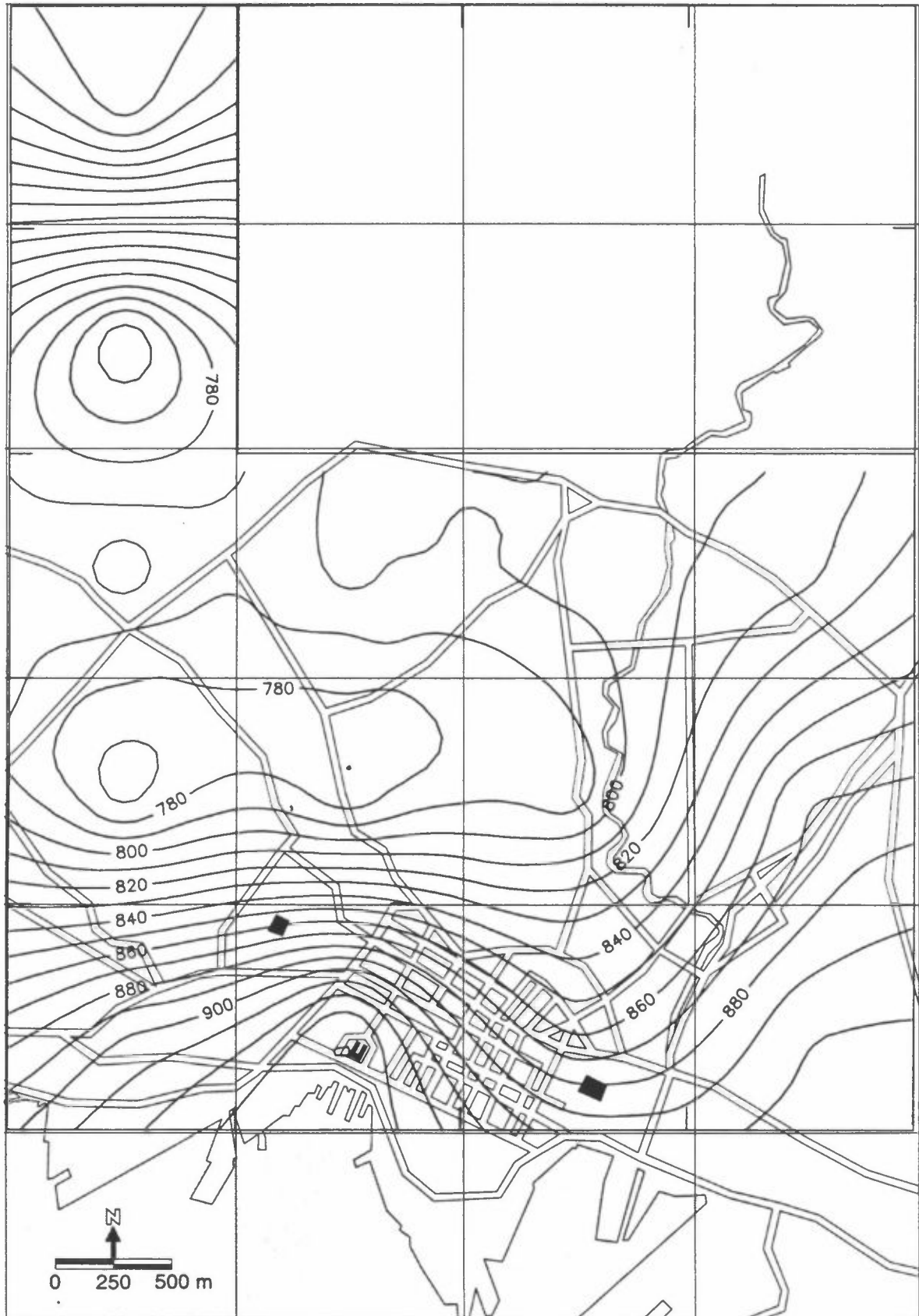


Figure B3: Concentration of Mn in the street dust of Oslo (ppm, dry matter).

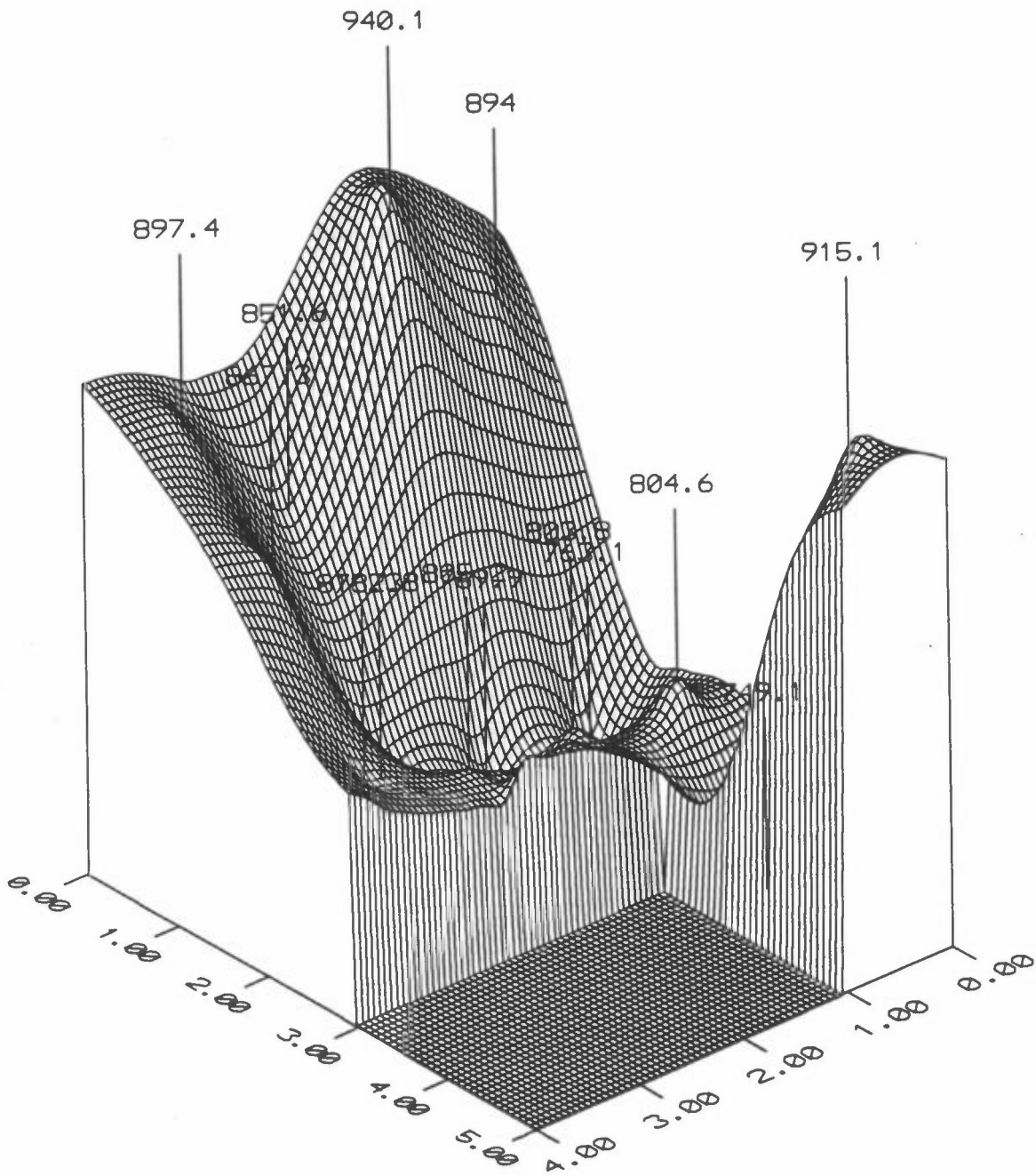


Figure B3: Cont.

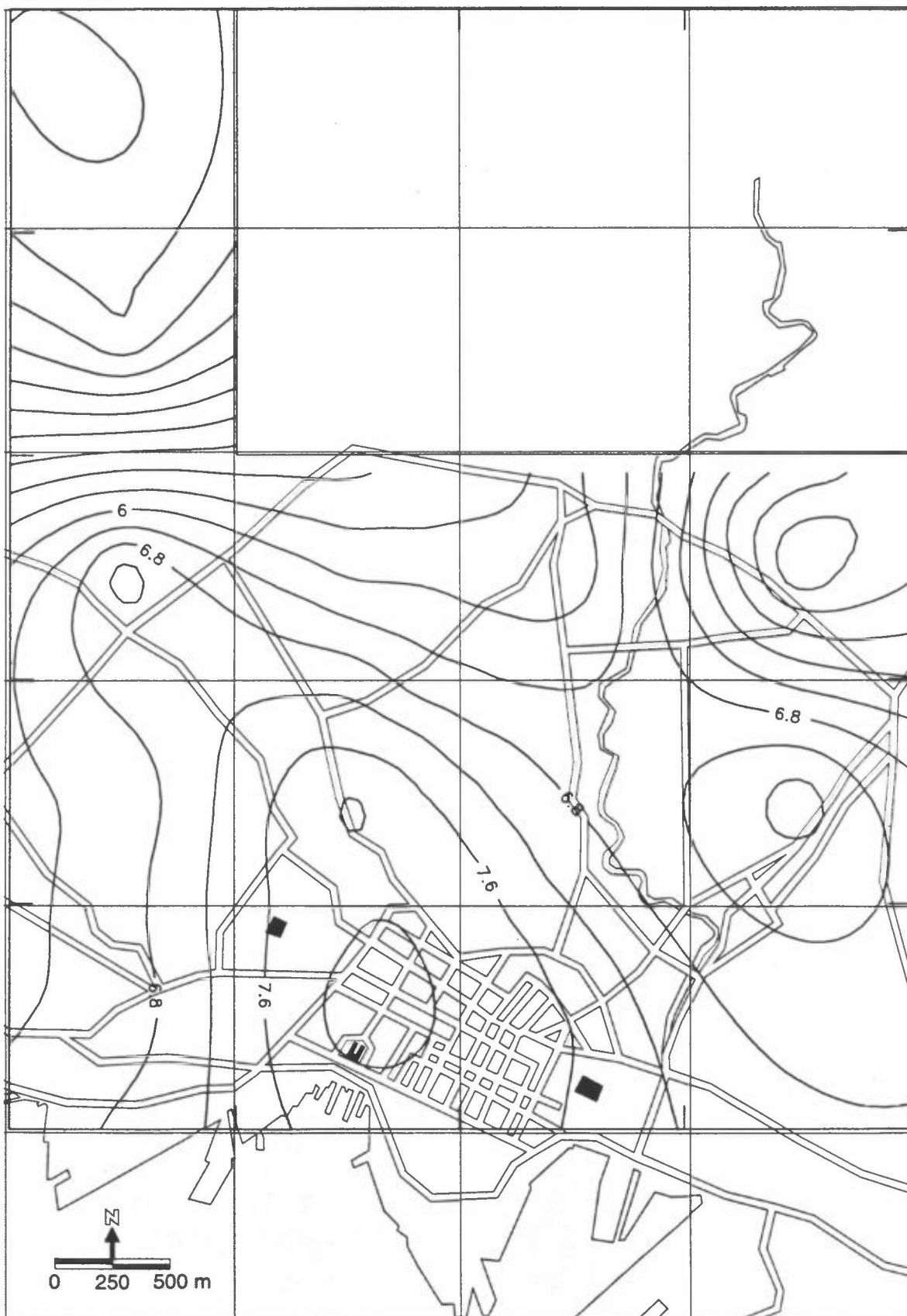


Figure B4: Concentration of Sb in the street dust of Oslo (ppm, dry matter).

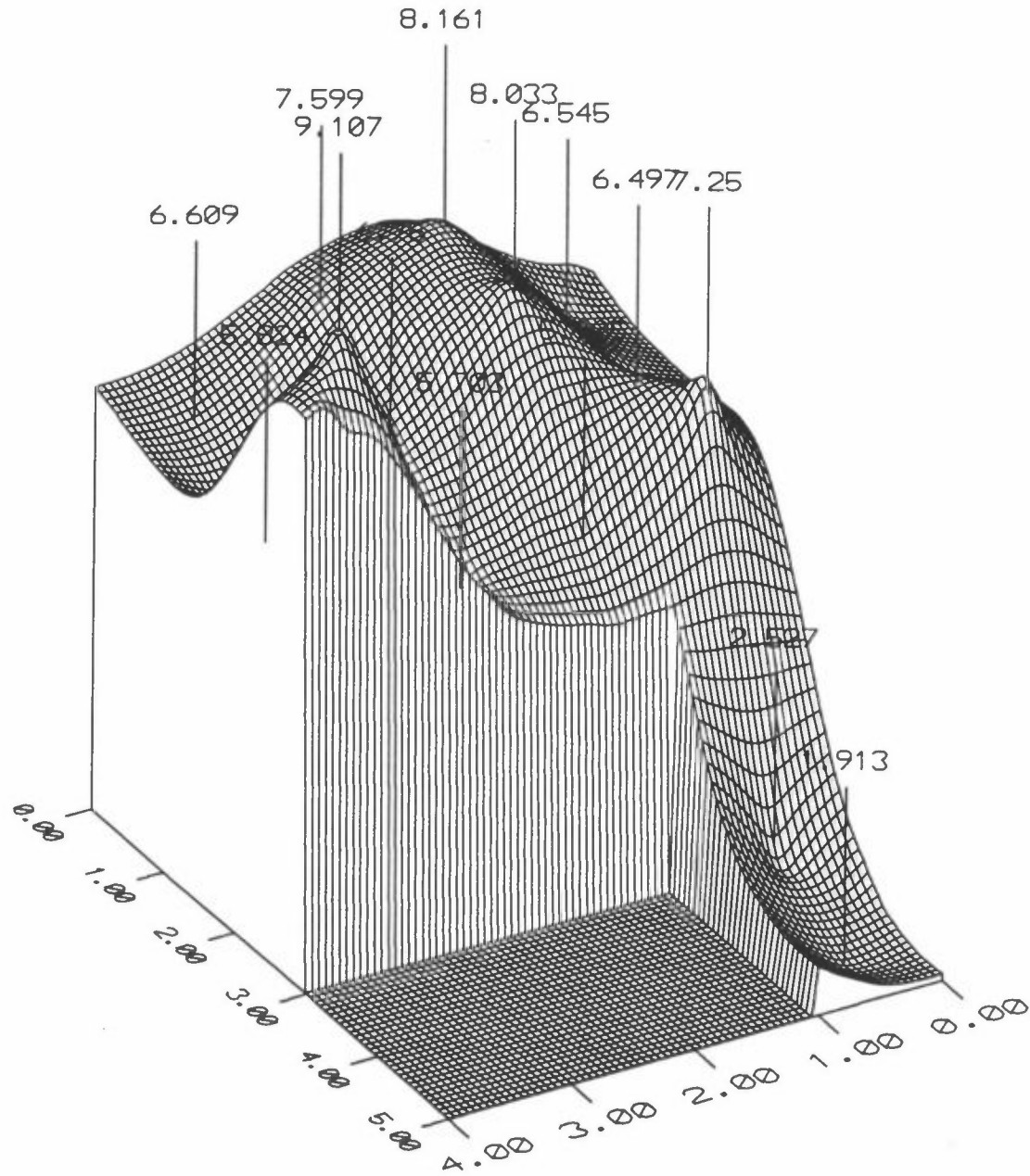


Figure B4: Cont.

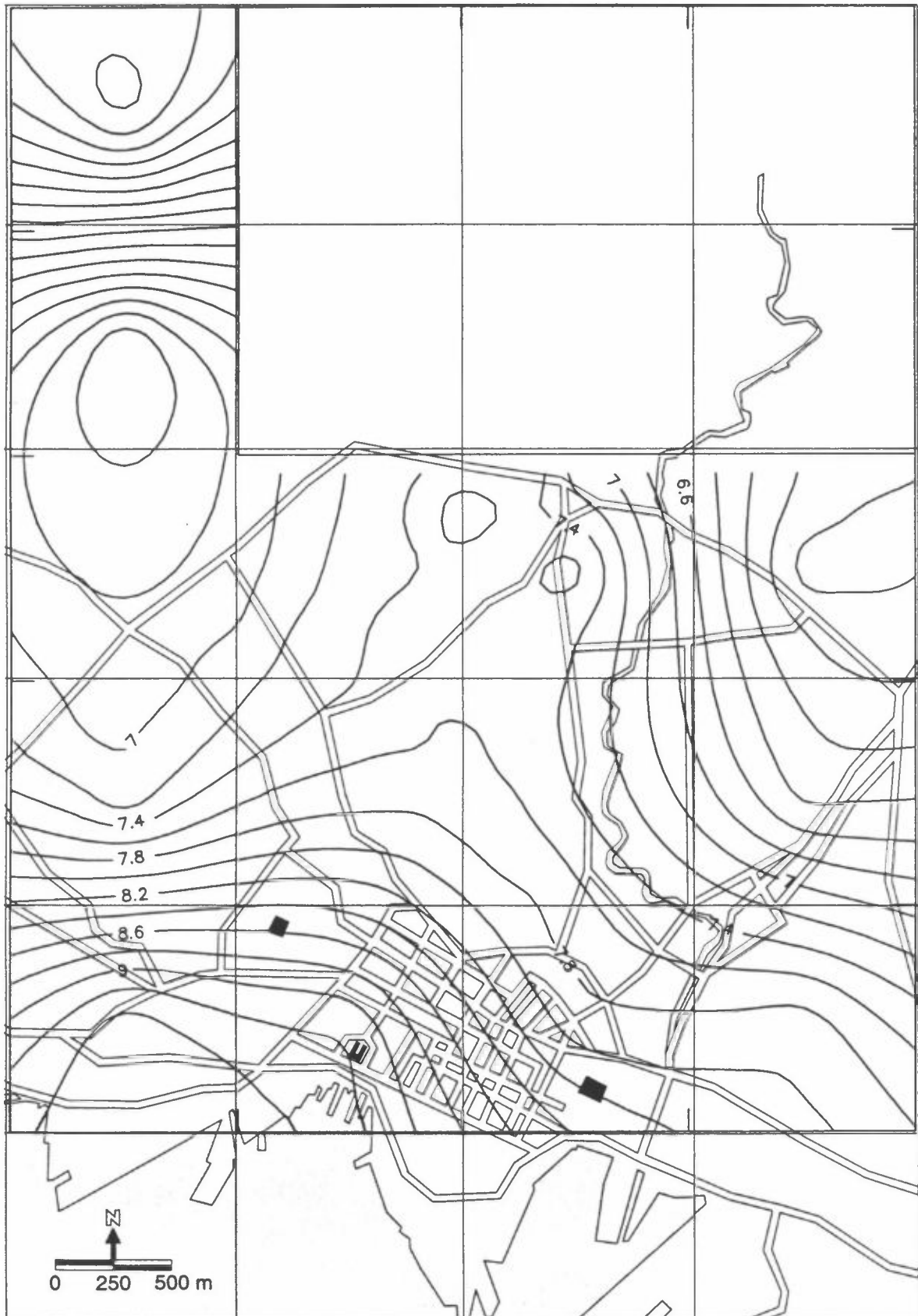


Figure B5: Concentration of Th in the street dust of Oslo (ppm, dry matter).

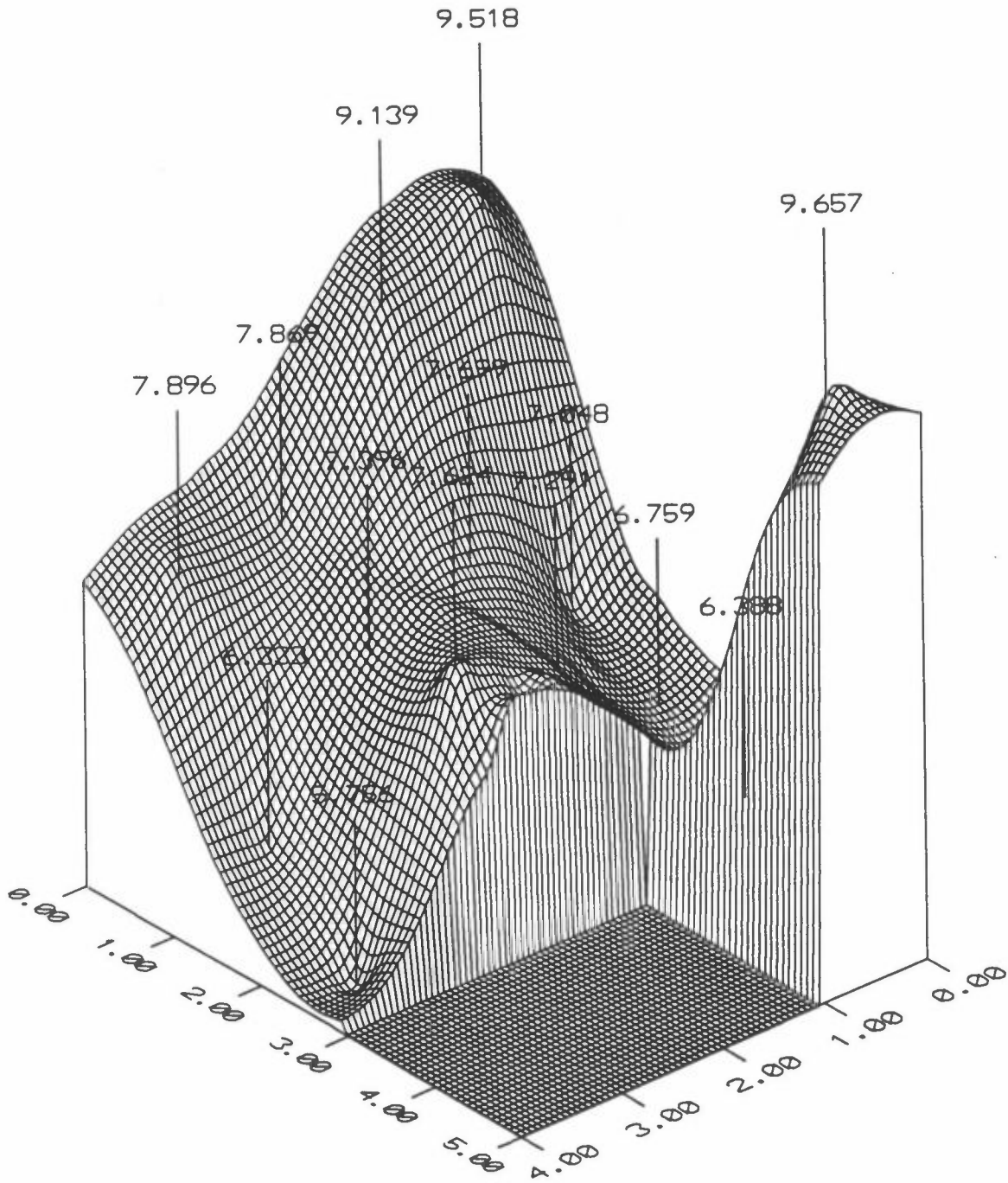


Figure B5: Cont.

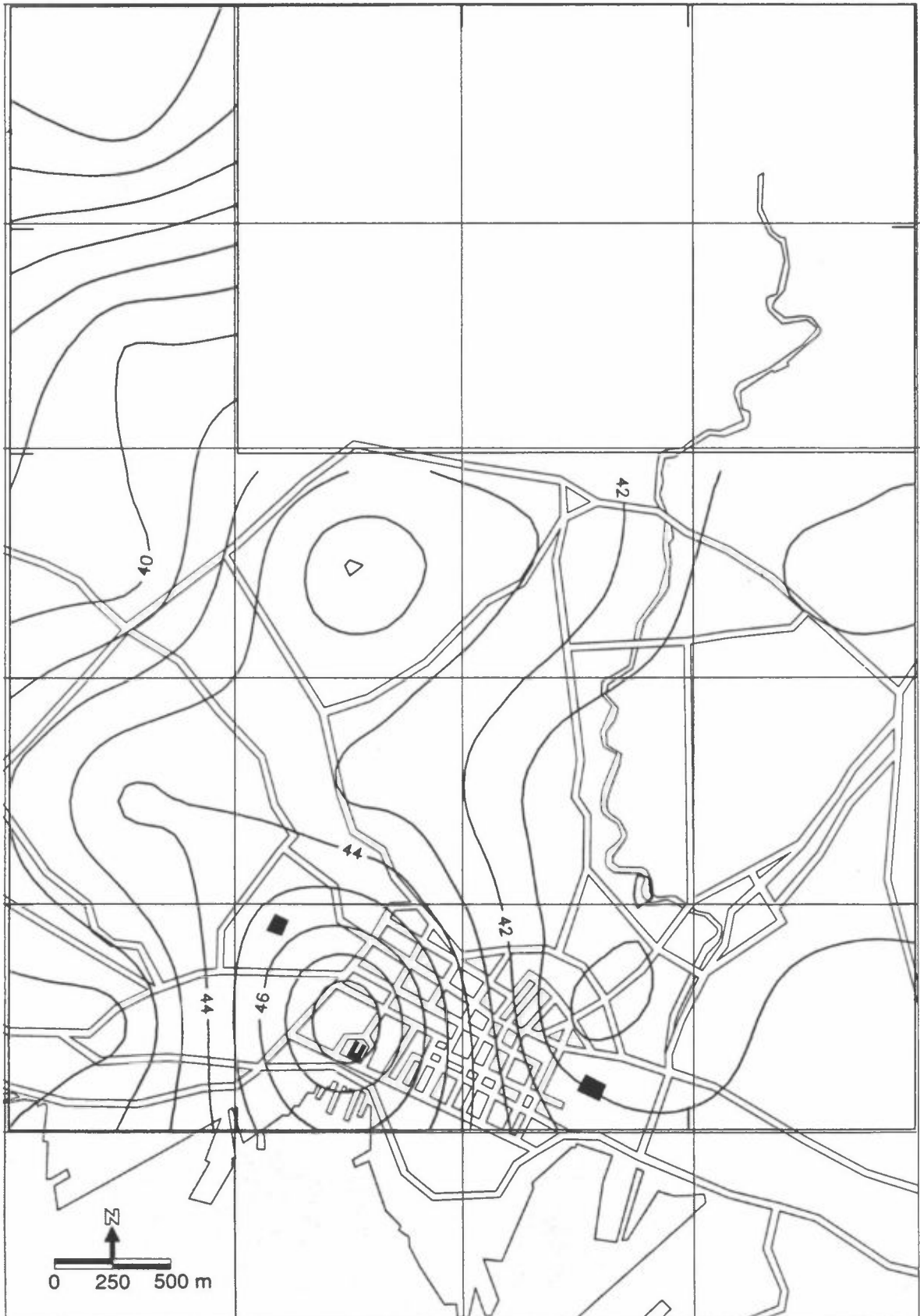


Figure B6: Concentration of Ni in the street dust of Oslo (ppm, dry matter).

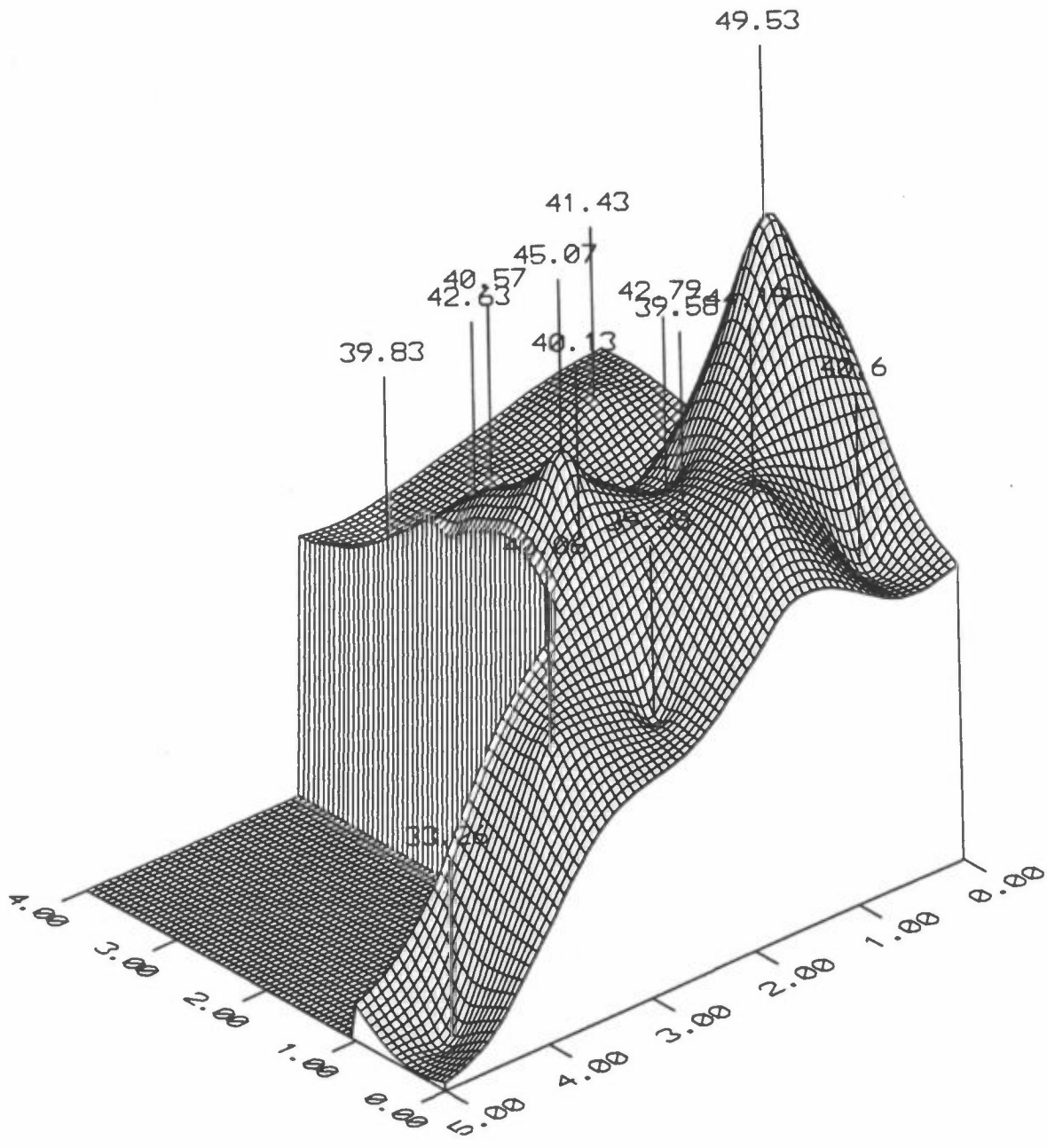


Figure B6: Cont.

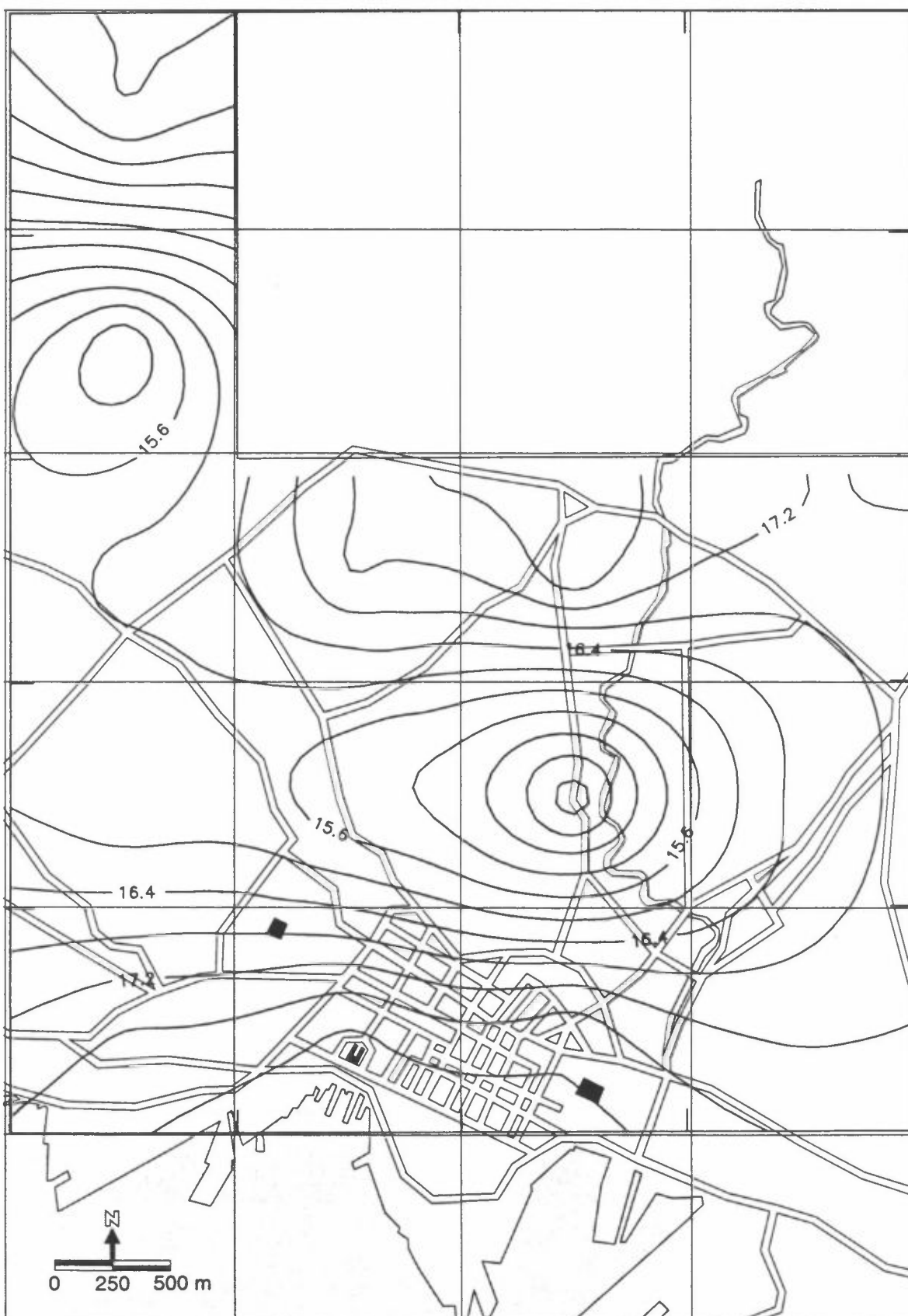


Figure B7: Concentration of Ga in the street dust of Oslo (ppm, dry matter).

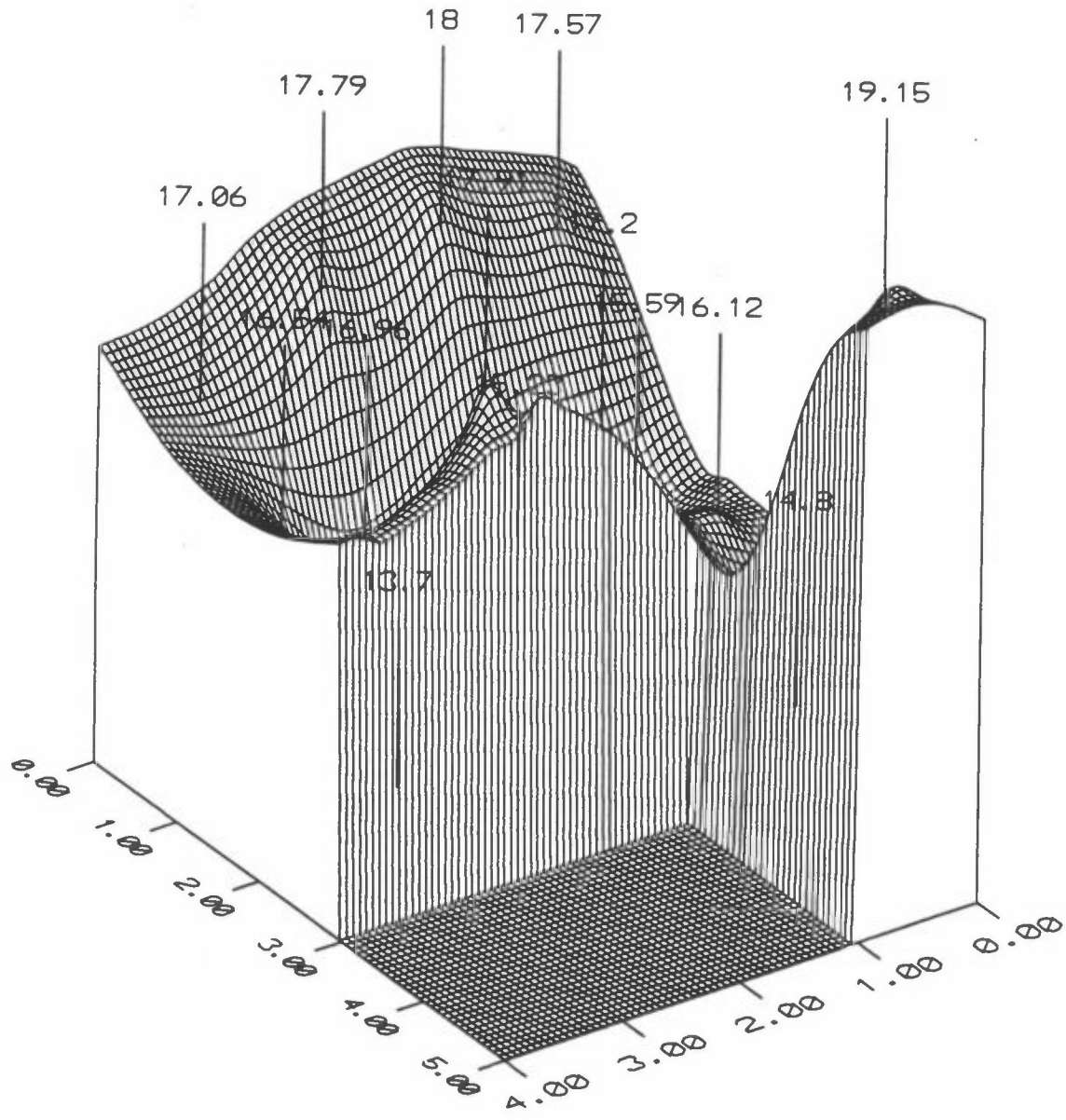


Figure B7: Cont.

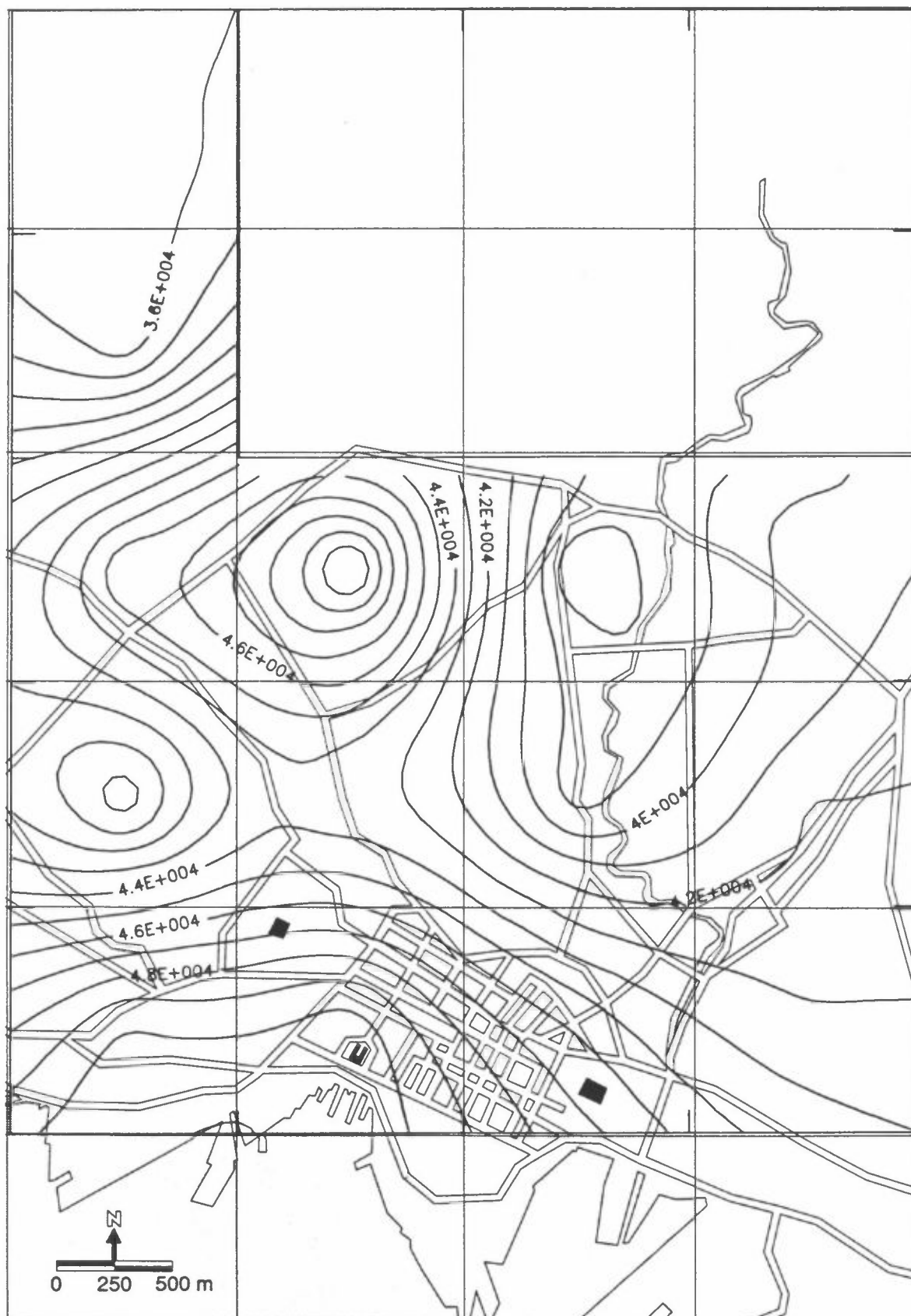


Figure B8: Concentration of Ca in the street dust of Oslo (ppm, dry matter).

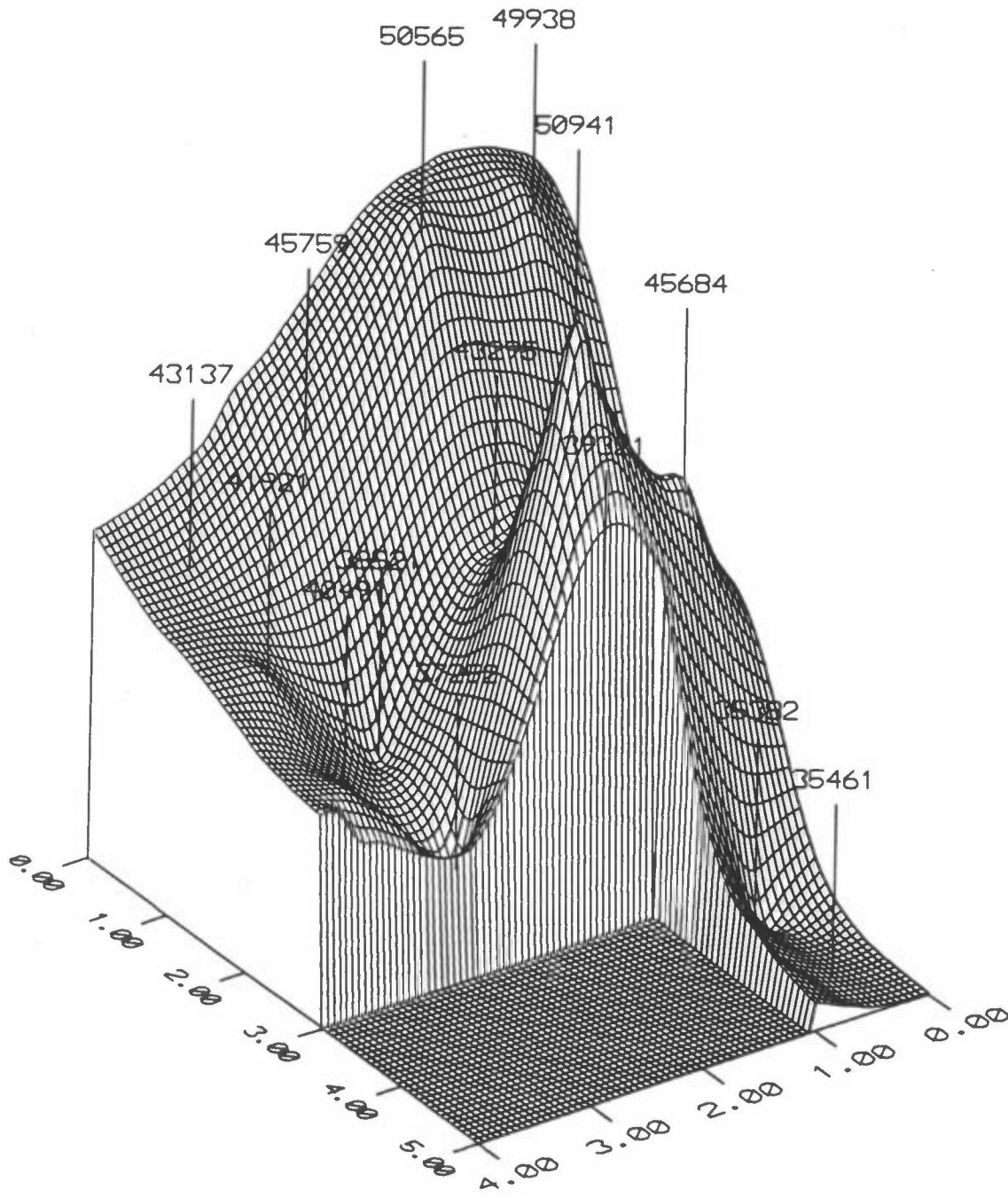


Figure B8: Cont.

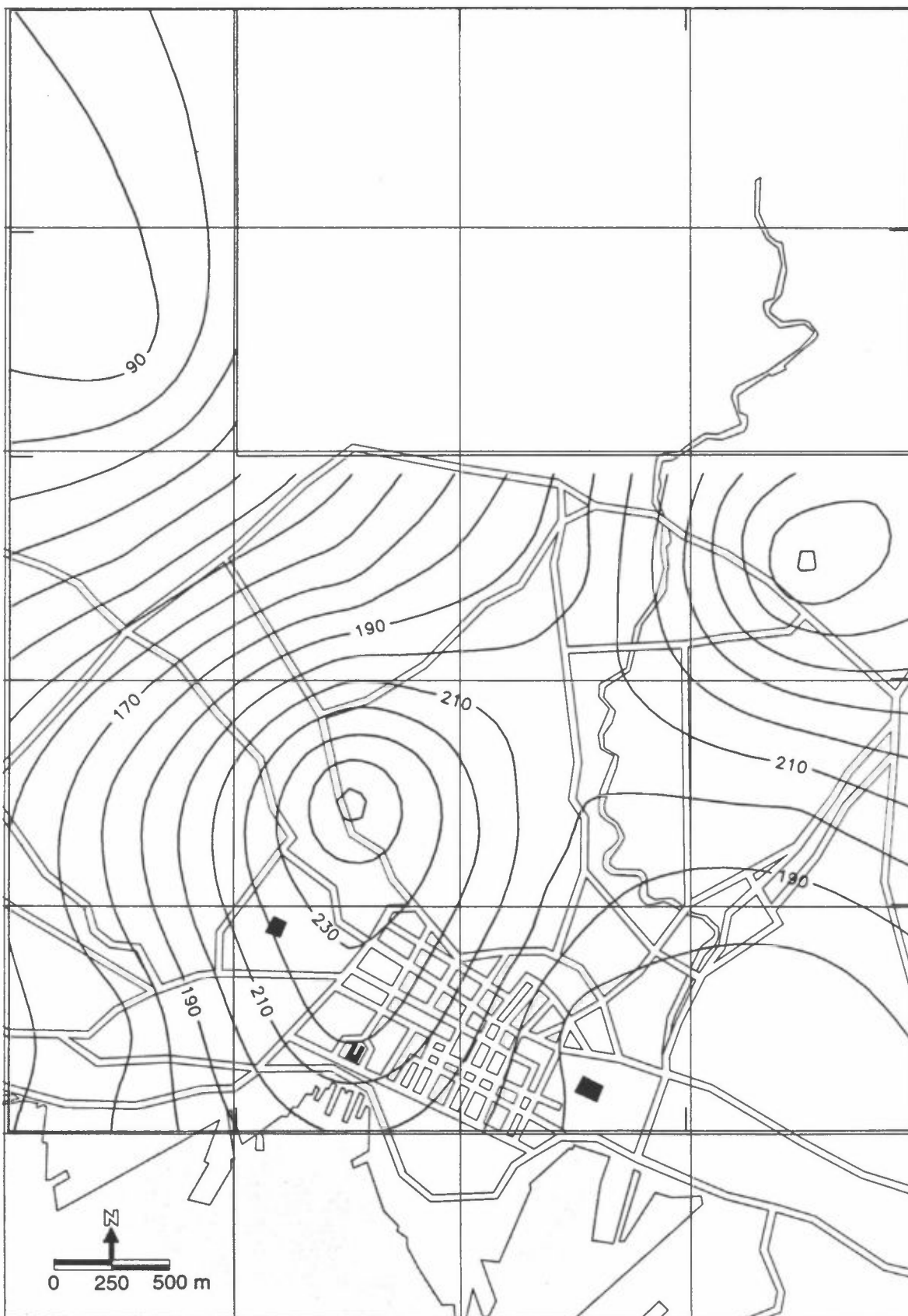


Figure B9a: Concentration of Pb in the street dust of Oslo (ppm, dry matter).

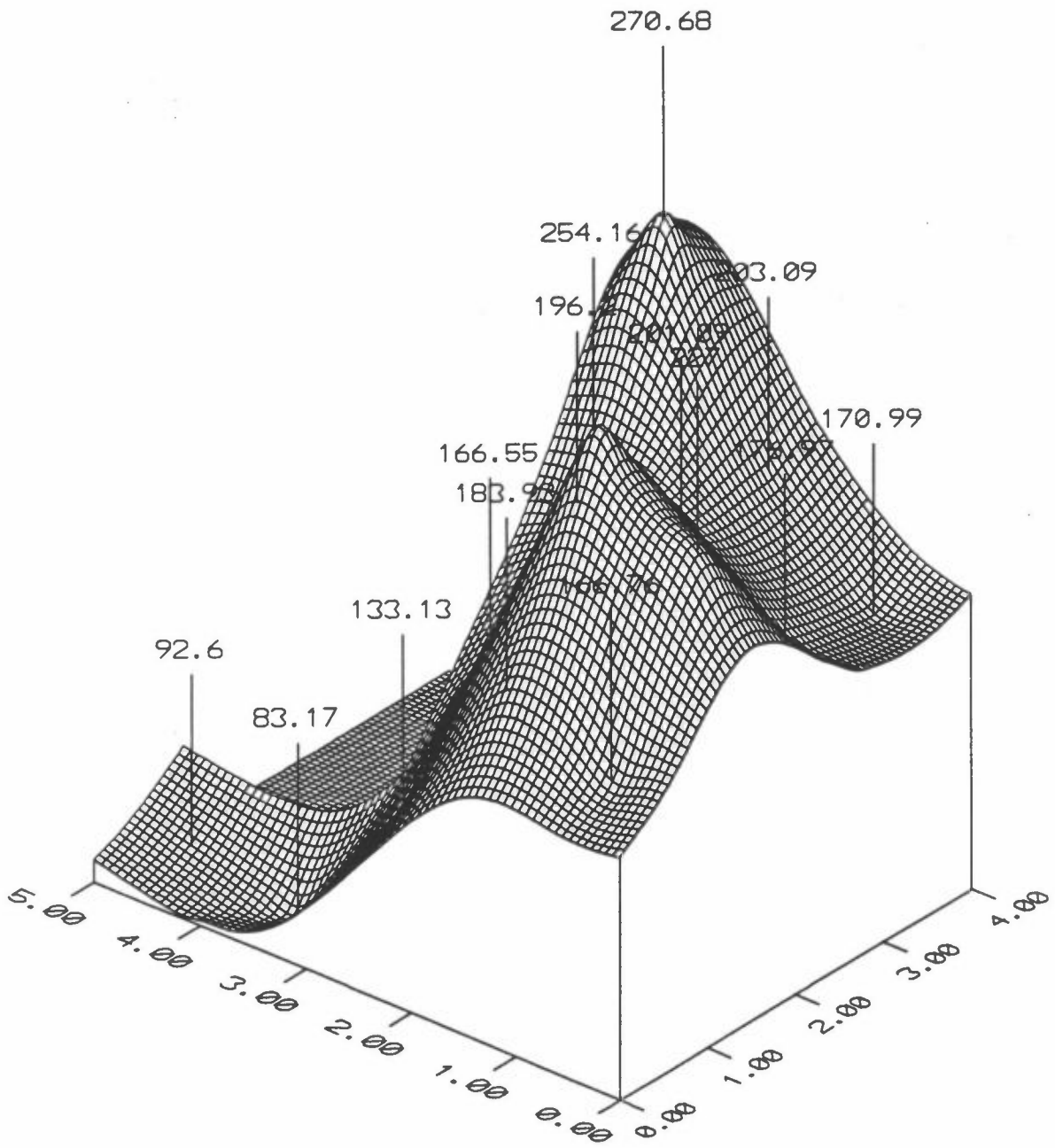


Figure B9a: Cont.

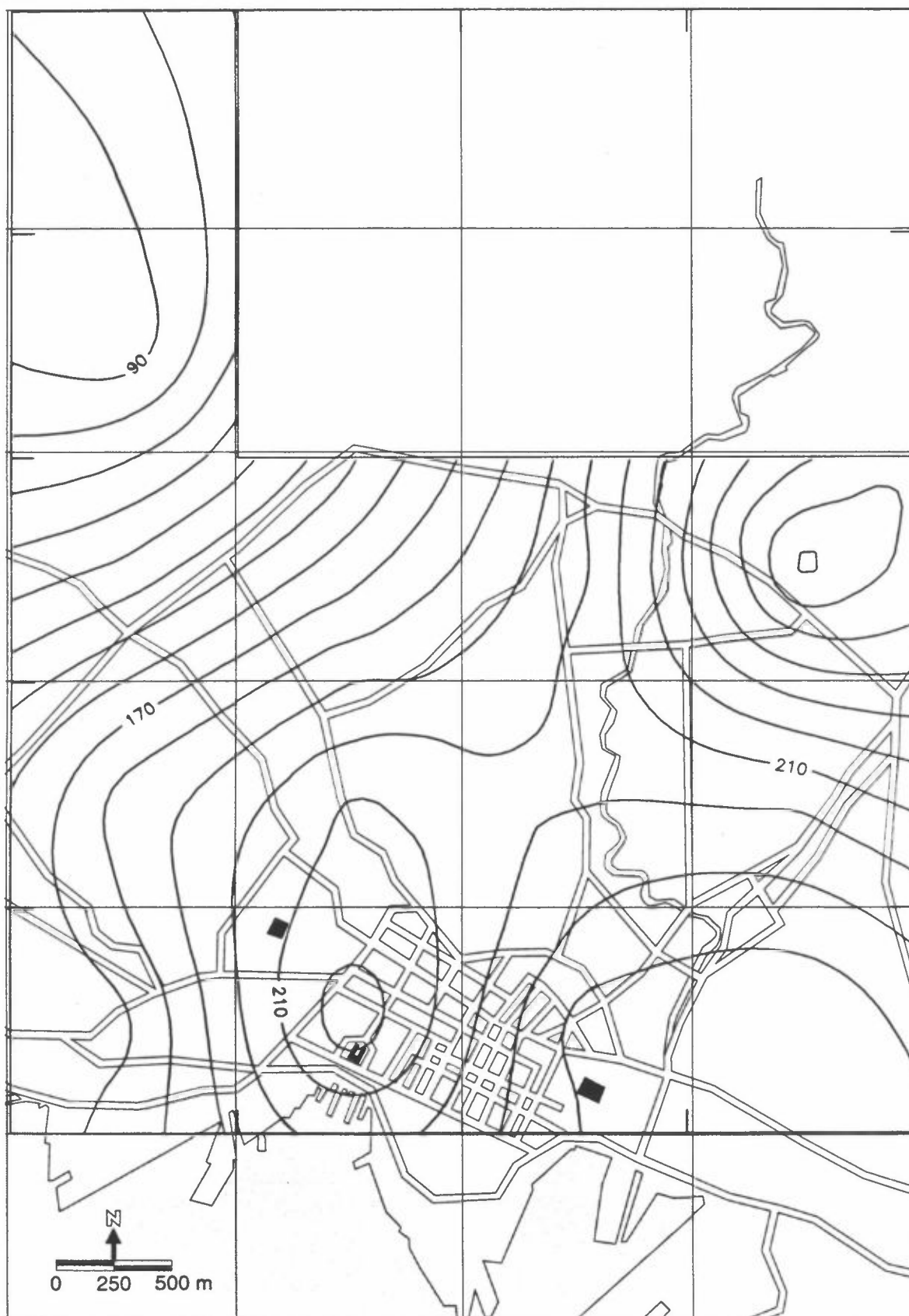


Figure B9b: Concentration of Pb in the street dust of Oslo (ppm, dry matter) without the influence from sample 1210.

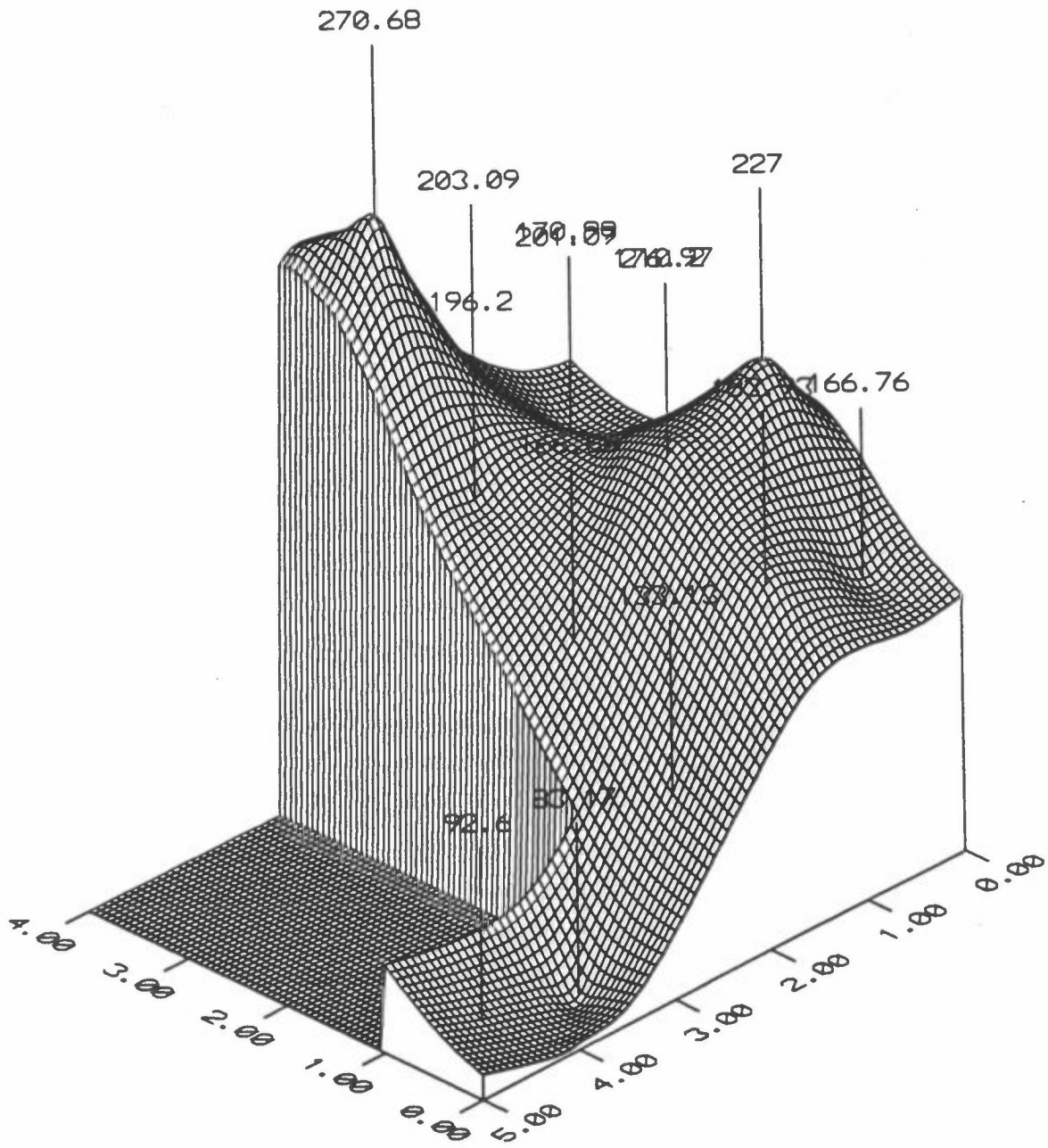


Figure B9b: Cont.

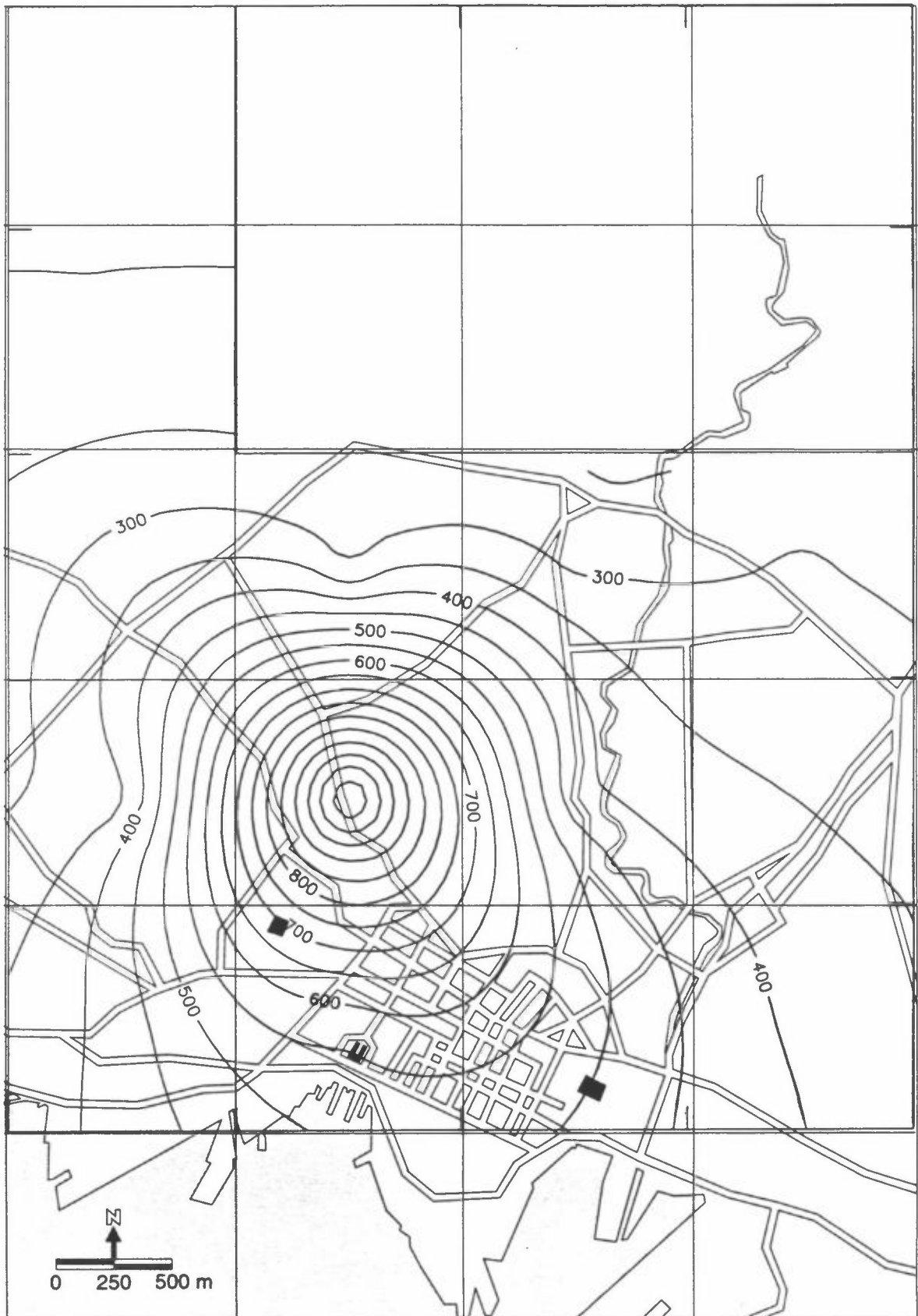


Figure B10a: Concentration of Zn in the street dust of Oslo (ppm, dry matter).

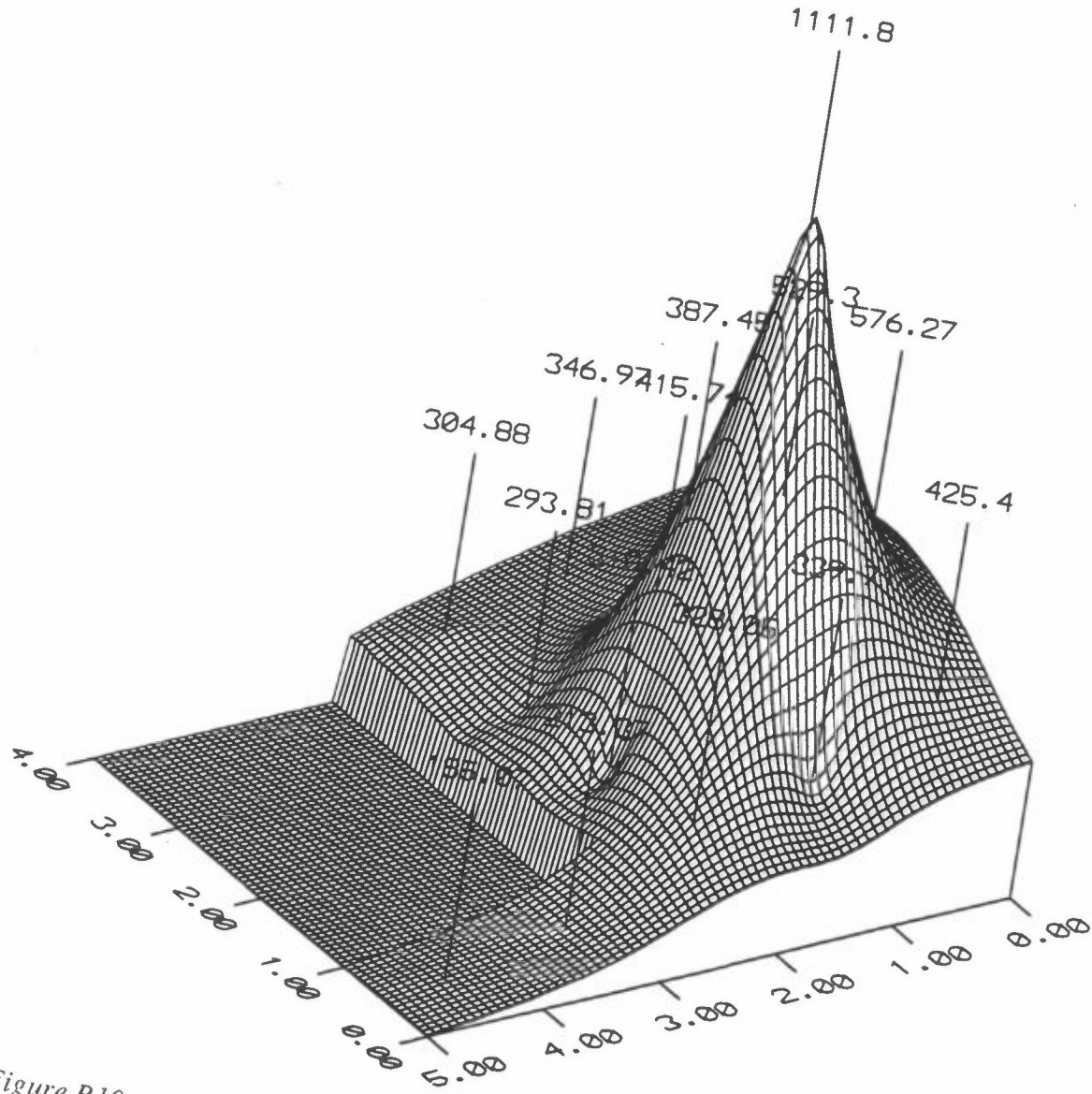


Figure B10a: Cont.

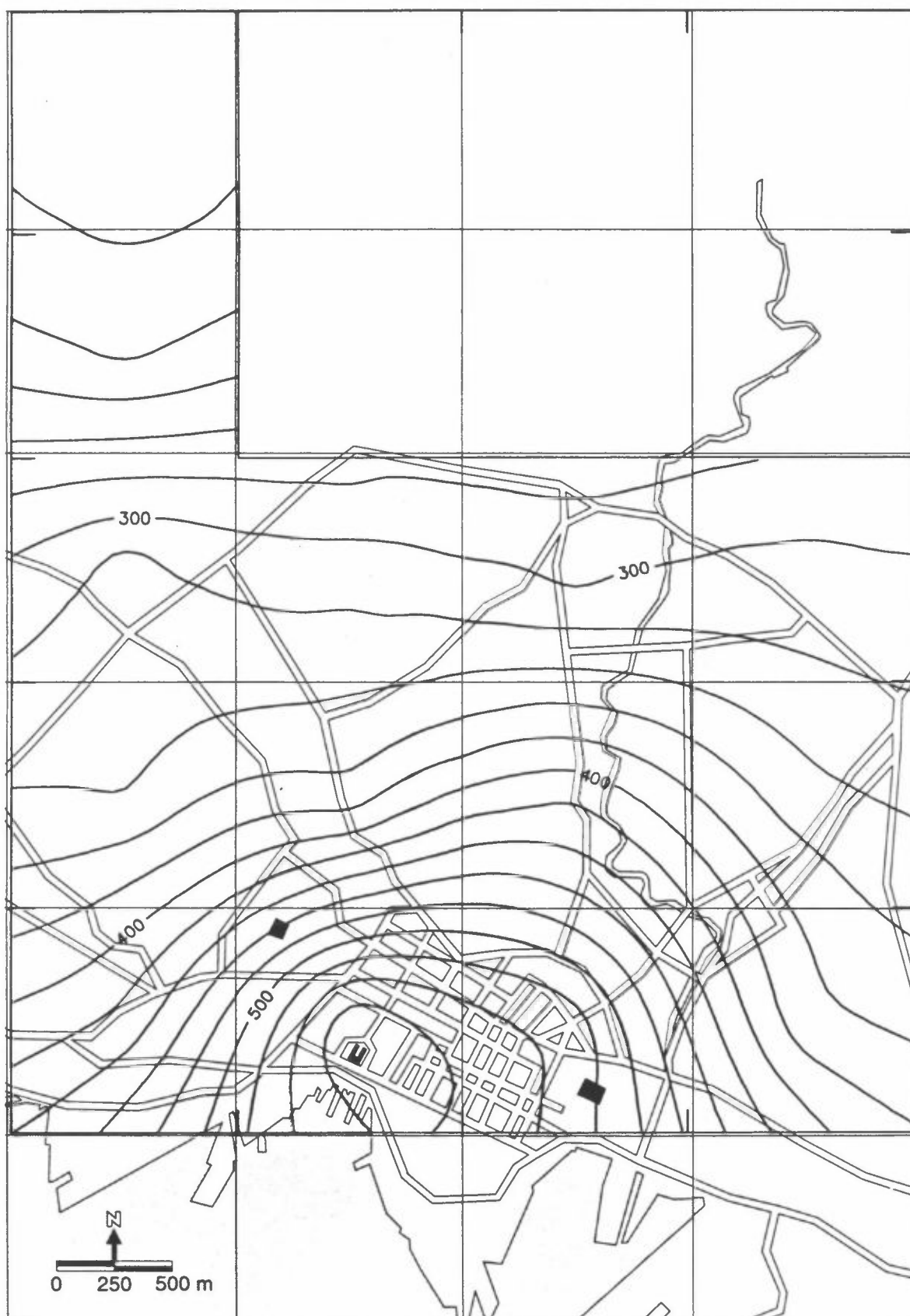


Figure B10b: Concentration of Zn in the street dust of Oslo (ppm, dry matter) without the influence from sample 1210.

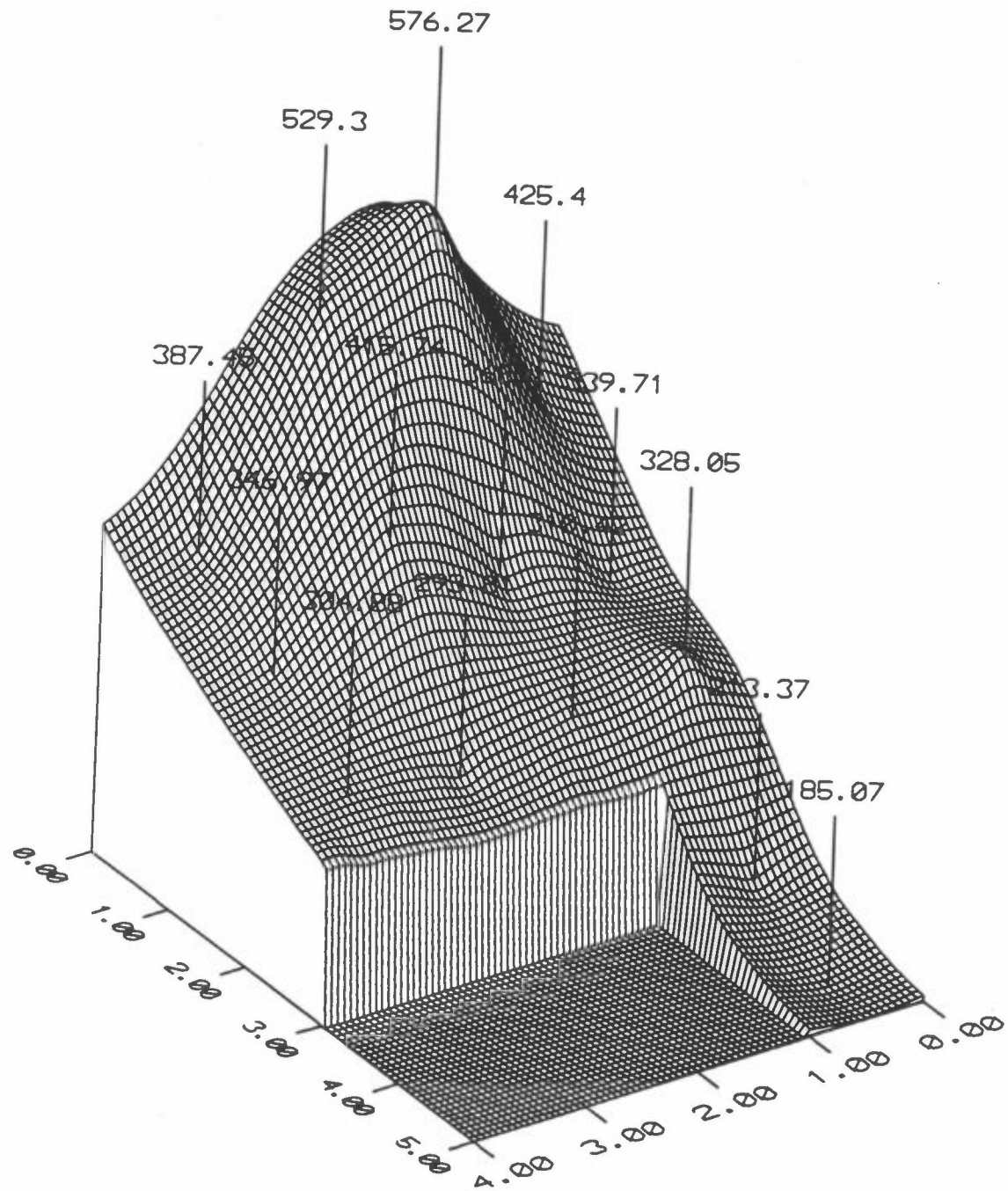


Figure B10b: Cont.

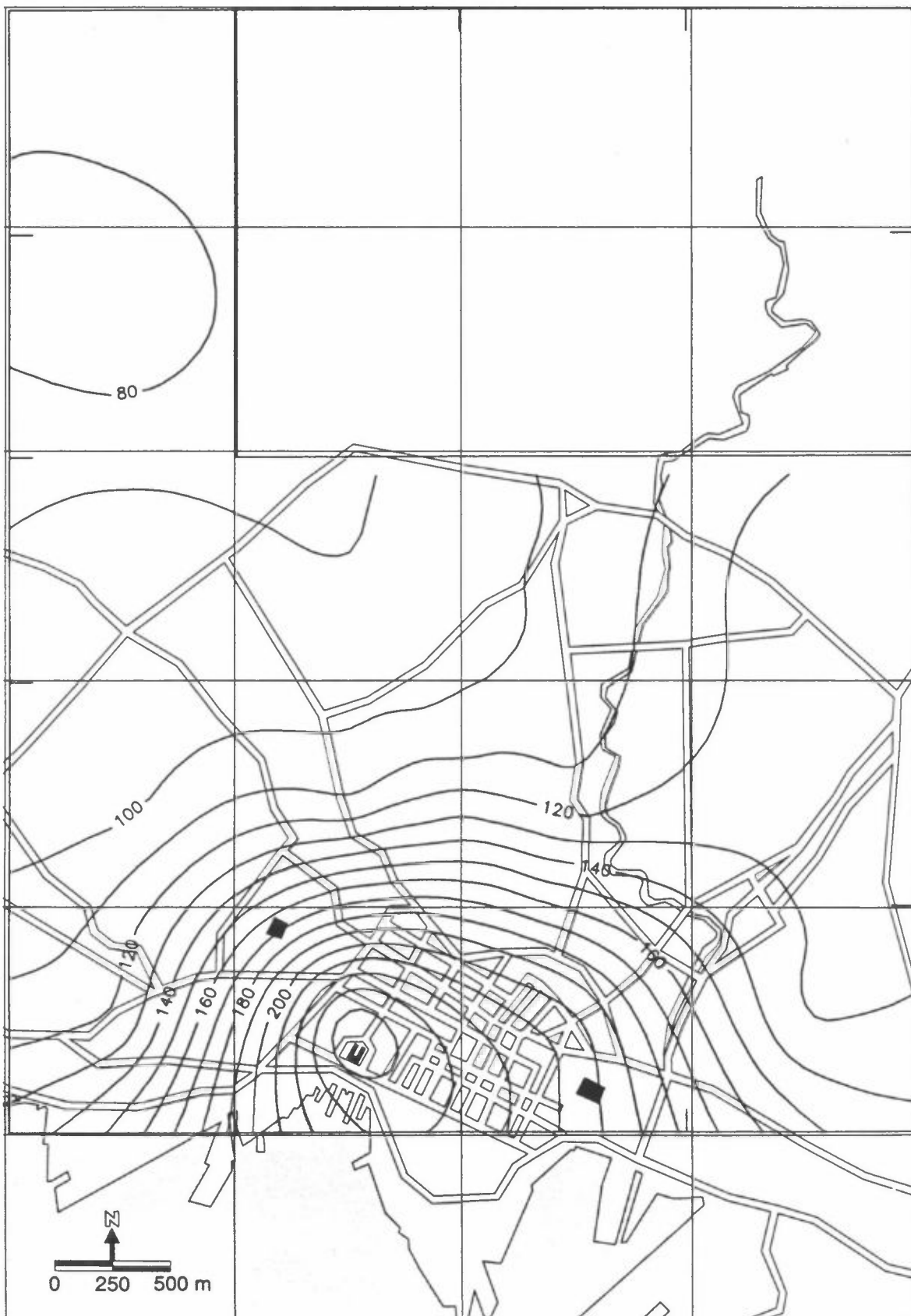


Figure B11: Concentration of Cu in the street dust of Oslo (ppm, dry matter).

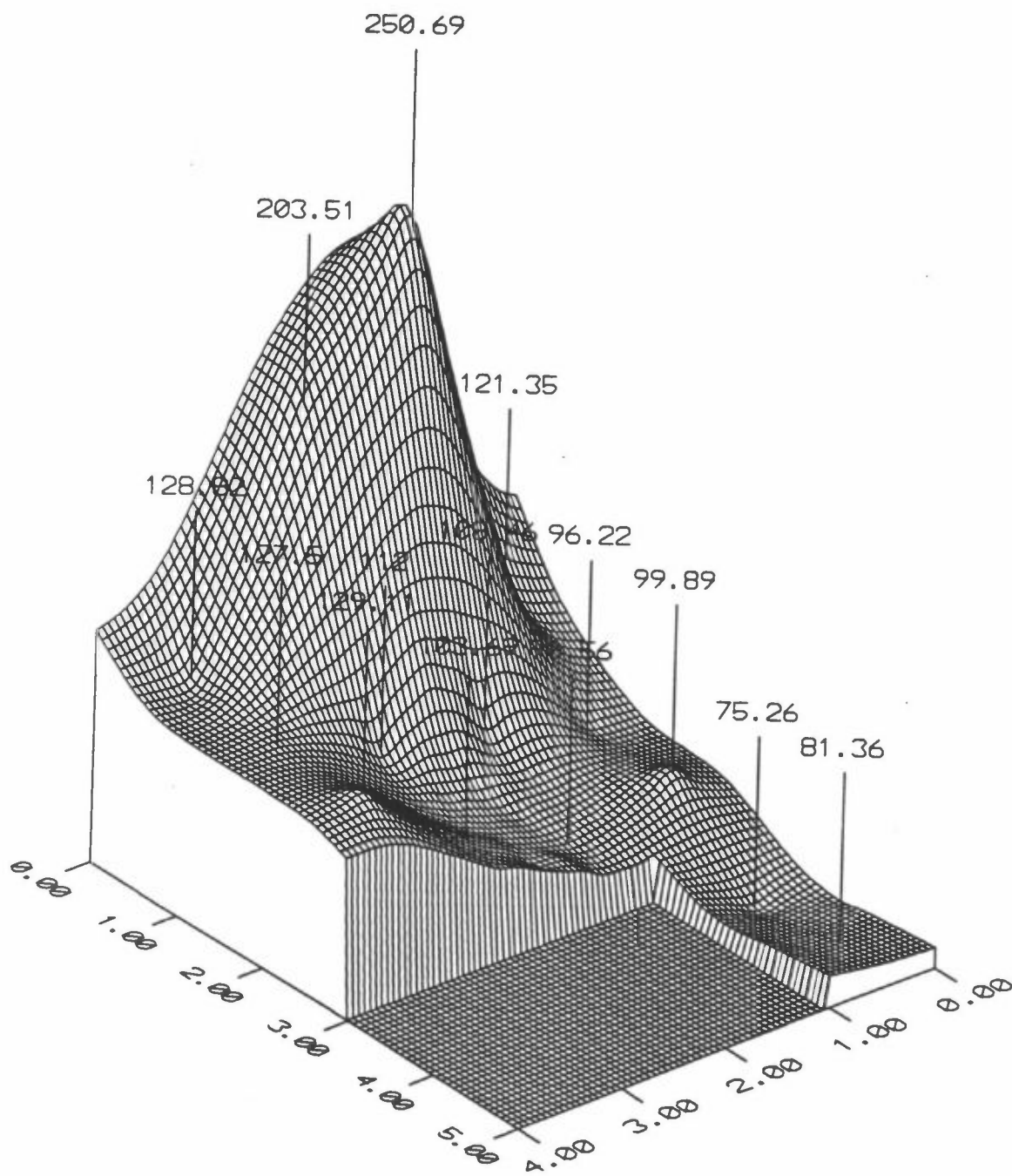
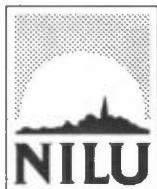


Figure B11: Cont.



Norsk institutt for luftforskning (NILU)

P.O. Box 100, N-2007 Kjeller - Norway

REPORT SERIES TEKNISK RAPPORT	REPORT NO. TR 21/94	ISBN-82-425-0646-9	
DATE 20.4. 1995	SIGN. <i>Eduardo Miguel</i>	NO. OF PAGES 66	PRICE NOK 105.-
TITLE Trace elements in the summer street-dust of Oslo		PROJECT LEADER Steinar Larssen	
		NILU PROJECT NO. Q-303	
AUTHOR(S) Eduardo de Miguel		CLASSIFICATION * A	
		CONTRACT REF.	
REPORT PREPARED FOR: NILU			
<p>ABSTRACT</p> <p>This technical report describes a study on the elemental composition of the street-dust of Oslo, carried out during the summer of 1994. The statistical preparation of the sampling campaign, the analysis of the samples by ICP-MS and the interpretation of the results with the help of multivariate statistical techniques are presented in detail. Maps of concentration in street-dust have been prepared for a number of elements and relevant conclusions have been drawn.</p>			
NORWEGIAN TITLE			
KEYWORDS street dust	urban geochemistry	geochemical maps	
ABSTRACT (in Norwegian)			

- * Classification
- A Unclassified (can be ordered from NILU)
 - B Restricted distribution
 - C Classified (not to be distributed)