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Forskningscenter Risø, Roskilde; Palmgren Jensen, F.; Kemp, K.

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Air Pollution in Copenhagen

Part I. Element Analysis and Size Distribution of Aerosols

by Hans Flyger, Finn Palmgren Jensen and Kåre Kemp

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PARTICLES
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[1] ACTIVATION ANALYSIS
ALUMINIUM

[1,2] CHLORINE
VANADIUM

[2] ANTIMONY
BROMINE
CADMIUM
CALCIUM
CASCADE IMPACTOR
CHROMIUM
COPPER
IRON
MANGANESE
MOLYBDENUM
NICKEL
PARTICLE SIZE
POTASSIUM
PROTON BEAMS
SILICON
SULFUR
TIN
TITANIUM
X-RAY EMISSION ANALYSIS
ZINC

[2,3] LEAD

[3] EMISSION SPECTROSCOPY

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Part I

Element Analysis and Size Distribution of Aerosols

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Hans Flyger, Finn Palmgren Jensen and Kåre Kemp

Danish Atomic Energy Commission
Research Establishment Risø
Aerosol Sciences Laboratory
Health Physics Department

Abstract

Aerosols were monitored in Greater Copenhagen in the period June 1973 to July 1974. Size-fractionated cascade impactor samples and unfractionated filter samples were regularly collected and analyzed by neutron activation analysis, spark emission spectroscopy or proton-induced X-ray emission spectroscopy. Concentrations were determined of the following elements: Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Mo, Cd, Sn, Sb, and Pb. All elements showed orders-of-magnitude fluctuations; the mean concentrations were roughly the same as in other large cities. In relation to proposed air quality standards, Pb was the most critical component.

Statistical analysis of variation patterns, size distributions and interelement correlations indicate that automotive exhaust is the source of Br and Pb; fuel-oil combustion is the main source of V and Ni (and partly of S); soil dust raised by wind or by human activity (e. g. traffic) is the main source of Al, Si, Ca, Ti, and Fe.

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CONTENTS

1. INTRODUCTION

Air pollution investigations in Greater Copenhagen were started in 1967 by the Greater Copenhagen Air Pollution Committee. Until 1972 these investigations mainly concerned sulphur dioxide and soot measured by the OECD method[1], and the results were published by the Committee[2]. However, it was evident that determinations of the two pollutants could only lead to a crude picture of the air pollution in the Greater Copenhagen area. Therefore, from December 1972 the programme was extended to include other pollutants, i.e. NO_x, CO, hydrocarbons, total particulate matter (weight), and elemental composition of the particulates (e.g. heavy metals). In addition, meteorological parameters were monitored.

This report presents the results of the element analysis of the particulates including the element analysis of different size fractions of the particulates. The main objectives of this part of the programme, which concentrated on the particulates, were:

1. Evaluation of the pollution load in terms of concentration of pollutants and the dependence on time and location.
2. Characterisation of the particulates in terms of particle size distributions and chemical composition with a view to the health aspects.
3. Estimation of the air pollution contribution from major sources to the ambient air quality.

This report analyzes the results and interprets them in the light of these objectives, but emphasis is also laid on a survey of the results obtained. More complete and detailed treatment of the results is planned for publication in later reports comprising data analyses in combination with other pollution data and meteorological data.

The report first gives an extended summary of the results and the main conclusions. For more detailed information on the measurements, the results and the basis for the conclusions, reference should be made to the following chapters.

The investigations were managed and financed by the Greater Copenhagen Air Pollution Committee. The samples were collected by the Danish Boiler Association and in special cases by the Aerosol Sciences Laboratory of the Danish AEC, who also performed the chemical and physical analysis of the particulate matter and interpreted the data.

2. SUMMARY AND CONCLUSIONS

The evaluation of the mean concentrations and the ranges of variation of the different components of the particulate matter was based on samples partly collected from 24 so-called OECD stations and partly from one mobile station. At the OECD stations, which were uniformly distributed throughout the region, 24-hour samples were collected every day and night (cf. sections 3.1 and 3.2). The mobile station was placed at 12 different locations for periods of 14 days and both 2-hour and 24-hour samples were collected (cf. sections 3.3 and 3.4). The determination of mean concentrations and ranges of variation was performed partly by calculation of means and standard deviations (cf. chapter 6) and partly by plotting cumulative frequency distribution curves (cf. section 8.1).

In order to distinguish between systematic and random variations, an analysis of variance of results from different types of samples was carried out. The differences resulting from geographical phenomena, seasons and day of the week were elucidated by analysis of approximately 600 selected OECD samples (cf. chapter 6). The samples were analyzed for V, Pb, Cl and Al (cf. section 4.1 and 4.2). In addition, investigations were made of the differences resulting from hour of the day, day of the week, distance to busy streets and geographical phenomena on the basis of 2- and 24-hour samples from the mobile station (cf. section 8.2 and 8.3). The analysis comprised all elements with atomic numbers greater than 13, i.e. S and heavier elements (cf. section 4.3).

Cascade impactor samples were collected with a view to investigating the element distribution among the different particle sizes. In order to evaluate the diurnal and seasonal variation of the size distribution, 2-hour and 24-hour impactor samples were collected on selected days and analyzed for all heavy elements. The systematic variations were found by the analysis of variance (cf. section 8.4).

The contribution from major air pollution sources to the air quality was estimated by the trace element content in the particulates. The 24-hour OECD samples were utilized, and the elements V, Pb, Cl, and Al were used as tracers for fuel-oil combustion, automobile exhaust, sea spray and wind-raised soil dust respectively. The contributions were calculated as the ratios between the trace-element concentration in the sample and in particulates from the type of source in question (cf. chapter 6). The composition of the particulates from a specific source type was assumed to be as described in the literature.

Further information about the origin of the air pollutants was obtained by investigation of the correlation between the concentrations of different elements (cf. section 8. 5). Correlated variations of different elements indicate that the origin is similar, but that it can be due to universal factors, e.g. meteorology. Therefore, the analysis of correlation was only used in combination with other characteristics of the air pollutants.

The accountable fraction of the particulates was calculated on the basis of the concentrations measured of the different elements and on the assumptions of the corresponding chemical compounds.

The application of the above methods of data analysis to the particulate matter samples from Greater Copenhagen showed that the pollutants could be divided into groups relative to patterns of variation, distribution among particle sizes, and correlation between elements. The groups proved to be associated with the origin of the pollutants. This classification is maintained in the following description of the results. The main groups are: 1) lead and bromine (Pb and Br), 2) sulphur, vanadium and nickel (S, V and Ni), 3) aluminium, silicon, calcium, titanium, and iron (Al, Si, Ca, Ti, and Fe), 4) other elements, and 5) total weight of particulates. Each group is treated separately in the following summary.

The mean concentration level of Pb measured by the mobile station in the streets was 1500 ng/m^3 compared with proposed standards[3)] of 2500 - 5000 ng/m^3 for long-term exposure. At locations remote from the streets, the level was 4-5 times lower. The highest weekly means were 3000 - 4000 ng/m^3 and were found during winter in the street Smallegade and near cross roads of the two highways in Glostrup. The highest daily mean was 6700 ng/m^3 and the highest 2-hour mean was 17 700 ng/m^3, both measured in Glostrup near the highways. The level of Pb varied with the traffic intensity and was on average a factor of 1.3 and 1.7 higher than the mean in the morning and afternoon rush hours respectively.

The concentration of Br was well correlated with Pb (both originate from automobile exhaust) and at a level approximately a factor of 5 lower. The main amount of Pb and Br was attached to the particles with diameters below 0.5 microns, therefore being respirable. However, in the suburb of Glostrup, Pb was sometimes attached to larger particles and not correlated with Br which indicated an origin other than automobiles.

The results from the network of stationary stations (remote from streets) showed a concentration level of Pb of 200 ng/m^3. The highest concentrations were found in the city (300 - 500 ng/m^3) and the lowest at rural locations (Magleby, Fløng and Søllerød: below 100 ng/m^3). The highest source contribution from automobiles calculated on the basis of Pb concentrations relative to total particulate matter, as measured by the OECD method, was found in Lyngby and was 3.5 per cent. This is less than measured in e.g. Pasadena (8%)5), but slightly more than measured in Chicago (3%)4).

The mean concentrations at the mobile station of S, V and Ni were ≃ 3000, ≃ 25 and ≃ 10 ng/m^3 respectively. The highest measured concentrations were ≃ 10 000 ng/m^3, ≃ 100 ng/m^3 and ≃ 50 ng/m^3 at several locations. The three elements showed nearly identical frequency distributions in 24-hour samples taken in the streets and remote from the streets and in 2-hour samples taken in the streets, with only small systematic variations with time and location. This indicates a uniform and fairly constant emission, which is in agreement with the assumption that the three elements originate from fuel-oil burning by power stations, industry and for central heating. The attachment of these elements to small particles supports the assumption of their origin.

The correlation between the S-concentration of the particulate matter and the V- and Ni-concentrations was not clear, probably because S is emitted as SO_2 and transformed to particles within several hours or a few days.

The relative contribution from fuel-oil combustion to the total particulate pollution was estimated by the relative amount of V in the samples from the network of stationary (OECD) stations. The highest relative contributions were 4% (averaged over one year) and were found at stations in the Amager, Hvidovre and Glostrup districts. This is the same order of magnitude as determined e.g. in Chicago and Pasadena4). The highest absolute concentration of V was 18 ng/m^3 (averaged over one year) and was found at Valby. The level of 8 - 10 ng/m^3, which is the same order of magnitude as in cities such as Los Angeles and San Francisco6), corresponds to 100 - 400 ng/m^3 particulate matter from fuel-oil combustion. This is approximately 10 times less than large cities, such as New York City, where large amounts of residual oil are consumed for heating and electric power generation.

The mean concentration levels of the third group of elements were Al ≃ 800 ng/m^3, Si ≃ 3000 ng/m^3, Ca ≃ 1500 ng/m^3, Ti ≃ 100 ng/m^3, and Fe ≃ 1000 ng/m^3. The health effects of these elements in the above concentrations are believed to be negligible; especially because the major quantity of each element was found on large particles with diameters greater than 5 microns, and as such not respirable. The variation of the concentration levels followed human activities; the concentrations were highest in the middle of the day and the middle of the week, and at localities with high activity e.g. Kompagnistræde, Åboulevarden, Glostrup, and Borgmester Christiansensgade. The elements are supposed attached to particles created by different mechanical processes, i.e. traffic and industry.

The fourth group of elements showed no clear features with respect to variations with time and place and to particle sizes. The mean concentration levels were in all cases relatively low and orders of magnitude lower than the TLV (Threshold Limit Values)$^{7)}$ for working places. However, sporadic occurrences of high concentrations were found at some locations, e.g. Zn, Cd, Sn, and Sb at Glostrup, and Hg at Amagerbrogade.

The mean concentration level of the particulate matter in the city was 40 000 - 80 000 ng/m^3. The variations were relatively small and followed human activity. C, Si and S account for the majority of the particulates, viz. ~40, ~10 and ~11 per cent respectively.

Generally, the grand mean concentrations, i.e. means over time and locations, were, for most of the elements, of the same order of magnitude as in other large cities in Europe and USA. The mean concentration of Pb in the streets was only slightly lower than proposed standards. In addition, Pb was attached to small, respirable particles and thus has high potential effects on health. In spite of the occurrence of relatively low mean concentrations of most of the elements, the investigations showed that concentrations of some elements were sometimes relatively high. Further, the investigations demonstrated a great variety and complexity of aerosols in the urban atmosphere. The information thus obtained gives a useful basis for decisions relating to the abatement of specific pollutants, and for evaluating the general development of air pollution in Greater Copenhagen.

3. SAMPLING

The samples were collected at sampling stations set up by the Greater Copenhagen Air Pollution Committee. The sampling programme included two combined sub-programmes for collecting the following samples: 24-hour OECD samples from an overall network of stationary stations, 2- and 24-hour high-volume samples from a mobile station placed at 12 different locations, and some selected stationary stations, supplemented by 2- and 24-hour cascade impactor samples from the mobile station at two selected locations and the corresponding stationary stations. Further details about the sampling methods are given in the following sections of this report.

The Danish Boiler Association constructed, established and operated the OECD stations and high-volume stations, while the chemical analysis and sampling by cascade impactors[8)] was carried out by the Danish AEC Research Establishment Risø.

3.1. Sampling Locations

Since 1967 a network of 24-hour OECD stations has been in continuous operation. The number of sampling stations has been gradually increased to 28. In the period with which this report is concerned 24 stations were in operation. The network, shown in fig. 1, can be classified into four groups:

1. Group 1100, consisting of the three city centre stations 1100-1102.
2. Group 1200, consisting of the nine city stations 1210-1218.
3. Group 1300, consisting of the seven suburban stations 1330-1336.
4. Group 1400, consisting of five rural stations 1450-1454.

Roughly speaking, the 1200, 1300 and 1400 stations are situated in areas between circles with radii 3-6 km, 7-13 km and 13-25 km, respectively, with their centre in the city centre. The stations were sited between 6 and 12 m above ground level.

In addition, the air was sampled from a mobile sampling station to investigate air pollution in the streets of Copenhagen. Gaseous pollutants (NO_x,CO,HC and SO_2) were measured and samples of particulate matter collected. In addition, the meteorological parameters, wind speed and direction and temperature were measured. The station was placed for 14-day periods at 12 different positions in the area encompassed by the circle of the group 1300 OECD stations. In the period June 1973 - July 1974 the schedule was run through approximately twice. The twelve positions are indicated in fig. 1. Simultaneous with sampling from a mobile station, measurements at the nearest OECD stations were extended. The 24-hour cascade impactor samples were collected at the stationary stations 1101/Frederiksberg and 1331/Glostrup once every four weeks (total 14 times) in the period June 1973 - July 1974. The 24-hour sampling periods were selected randomly, but each day of the week was represented twice.

The 2-hour samples were collected during the 12 consecutive periods of a 24-hour period, on four occasions, within the measuring period June 1973 - July 1974 at stations 1101 and 1331 and the mobile station.

Table 1. A summary of the schedule for aerosol sampling in Greater Copenhagen, June 1973 - July 1974. Further details are described in the text.

Sampling method		Specification	Sampling positions	Selected 24-hours periods	Number of samples	Number of analysis
24-hour OECD	Stationary stations	Sampling	The 24 (●)	Every 24-hour	8000	
		Analysis	21 stations	28 fortnight periods		21x28=588
24-hour high volume	Mobile stations	Sampling	The 12 (●) and (◉)	Fortnight periods	24x13=312	
		Analysis	-	Whole weeks		24x7=168
	Stationary stations	Sampling	The 12 (●) and (◉)	Fortnight periods	24x13=312	
		Analysis	-	Whole weeks		24x7=168
2-hour high volume	Mobile Station	Sampling	The 6 (●)	Whole weeks June 73-July 74	12x7x12=1008	
		Analysis	-	Whole weeks Dec 73-July 74		6x7x12=504
		Sampling	The 2 (1101 and 1331)	Impactor periods June 73-Dec 73	2x12=24	
		Analysis	-	-		2x12=24
	Stationary station	Sampling	The 2 (1101 and 1331)	Impactor periods June 73-Dec 73	2x4x12=96	
		Analysis	-	-		2x4x12=96
24-hour impactor	Stationary station	Sampling	The 2 (1101 and 1331)	14x1 24-hour	2x14x6=168	
		Analysis	-	-		2x14x6=168
2-hour impacter	Mobile station	Sampling	The 2 (1101 and 1331)	Impactor periods	4x12x6=288	
		Analysis	-	-		4x12x6=288
	Stationary station	Sampling	The 2 (1101 and 1331)	Impactor periods	2x4x12x6=576	
		Analysis	-	-		2x4x12x6=576

The four 24-hour periods were selected as the last Tuesdays of the fortnightly periods when the mobile station was in the neighbourhood of stations 1101 and 1301. During these four days it was planned to supplement the sampling of the three stations by 2-hour high-volume sampling, but due to technical difficulties the high-volume samples were only taken on two days.

A summary of the sampling schedule is shown in table 1.

3.2. 24-hour OECD-Samples

The OECD stations were designed in accordance with the OECD standard for measuring soot and sulphur dioxide in urban air[1)]. The samples were automatically taken between 0 and 24 hrs each 24 hours at each station. The particulate matter was collected on Whatman no. 1 filter-paper with an exposure area of 4.9 cm^2 (25 mm diameter), corresponding to a linear velocity of approx. 5 cm/s, and the sulphur dioxide was collected in acidified H_2O_2 solutions.

The main advantages of the OECD network are region-wide and continuous sampling. Thus it was obvious to use these samples for estimation of the pollution contribution from the most widespread types of source. One of the main disadvantages of OECD samples is the small volume of air sucked through the filter, i.e. 2 m^3 in the sampling time of 24 hours. The small amount of particulate matter on the filter-paper required the development of new methods of analysis, as described in sections 4.1 and 4.2.

Among the approximately 8000 samples taken each year, 588 samples were selected for chemical analysis. Samples were selected to give equal representation of the 7 days of the week, 28 fortnightly periods, and 21 sampling localities. Randomly selected permutations of 7 x 7 x 7 latin squares17) were used as base units. The yearly selected samples consist of 3 x 4 of these units.

3.3. 24-hour and 2-hour High-Volume Samples

The particulate matter was taken from the mobile station in the form of 24-hour and 2-hour high-volume air samples at all 12 locations and at the 6 locations marked (◉), respectively. The 24-hour samples were collected by sucking 5-40 m^3 of air through 9 cm^2 or 12 cm^2 of filters, and the 2-hour samples by sucking 5-8 m^3 of air through the same filter areas. Four different types of membrane filter were used: Sartorius cellulose nitrate no. 11302 and cellulose acetate no. 11304, and Millipore cellulose nitrate type AA and cellulose acetate type EA. Only samples from the whole week between the first Thursday and the second Wednesday in the two-week period were selected for chemical analysis. The selected 24-hour samples were taken during the whole measuring period June 1973 - July 1974 both at the mobile station and at the corresponding stationary station, while the selected 2-hour samples were taken in the period December 1973 - July 1974 at the mobile station only.

3.4. 24-hour and 2-hour Cascade Impactor Samples

Cascade impactor samples were obtained by an impactor developed at Risø8). For both 24-hour and 2-hour samples, 2 m^3 of air were sucked through the impactors and the particulates were collected on polystyrene-covered, glass microscope slides on the five impactor stages and by a membrane after the filter(Sartorius 11302 or Millipore type TA). The cut-off aerodynamic diameters (50% efficiency) of the five stages are: 5.6, 2.25, 1.65, 0.66, and 0.35 microns, respectively. For the 24-hour sampling the necessary flow through the impactor jets was obtained by recirculation of the air. In order to obtain well-defined cut-off diameters in the sampling system, and to prevent the large particles from bouncing off and being reentrained in the air flow, the collection plate of the first stage was covered with silicone oil having a viscosity of 200 000 cts.[9]. Thus particles with aerodynamic diameters larger than 5.6 microns were collected at the first stage and only smaller particles were accessible for chemical analyses. The calculated mass median diameters are therefore generally underestimated, and the differences between the results from high-volume samplers and cascade impactors cannot directly be compared.

Table 1 summarizes the sampling scheme as planned for particulate matter and the selection of samples for chemical analysis.

3.5. Particulate Deposition in Sampling Pipes

Since the sampling pipes and flow rates differed for the different types of sample, it was very important to estimate the sampling losses. The calculations of the particle deposition in the sampling pipes were based on the theories described in[10, 11]. We considered three contributions to the deposition originating from sedimentation and molecular diffusion in laminar flow and deposition from turbulent flow. The first and last types of deposition dominate for large particles and the second for small particles. In addition, the cut-off particle diameter of the inlet funnel was calculated as the diameter of particles with the same fall velocity as the inlet air velocity. All calculations were performed assuming 1 g/cm^3 particle density and standard conditions. The characteristics of the sampling inlets and the results of the calculations are shown in table 2. Losses due to non-isokinetic sampling caused by the wind were not taken into account. Therefore, the losses are in some cases underestimated, especially for the 2-hour samples and for the 24-hour samples from the mobile station.

Table 2. The characteristics of the sampling inlet systems and the calculated particle losses

Sampling Method	Flow rate (l/min)	Pipe Diameter (cm)	Pipe Length (cm)	Funnel inlet diameter (cm)	Losses for stated diameters (per cent) 10 micron	5 micron	0.1 micron	Cut off diameter (micron)
OECD	1.4	0.6	200-500	2.5	100	33/66	0.01	39
2-hour HV mobile	40		0	5.0	0	0	0	106
2-hour HV stationary	60		0	5.0	0	0	0	130
24-hour HV mobile	22		0	7.5	0	0	0	52
24-hour HV stationary	5.5	0.95	150	5.0	38	11	0.2	39
2-hour impactor	20	1.5	200	1.5	25	6	0.3	250
24-hour impactor	1.7	0.6	200	5.0	90/100	29/64	0.01	22

4. SAMPLE ANALYSIS

The conventional way of using the OECD samples of particulate matter is to determine the soot concentration by the smoke-shade method1). The results of these measurements and the sulphur dioxide results are to be published by the Greater Copenhagen Air Pollution Committee12). In the investigations described in this report the samples were used for element analysis of the particulates by neutron activation analysis (Al, V and Cl) and by spark emission spectroscopy (Pb).

The high-volume samples were primarily intended for the determination of the concentration of particulate matter by weight. These results will be published together with the above-mentioned soot and sulphur dioxide results. In the present investigation the high-volume samples were used for element analysis by proton-induced X-ray emission spectroscopy of the particulate matter. All elements with atomic numbers larger than 13(Al) were determined.

The element composition of the different particle sizes was determined by proton-induced X-ray emission spectroscopy of impactor samples specially collected for this purpose.

4.1. Neutron Activation Analysis

The elements Al, V and Cl were determined in 24-hour OECD and 2-hour and 24-hour high-volume samples by neutron activation analysis (NAA). The NAA was carried out at the Risø reactor, DR 2. The samples were irradiated for 60 or 120 s, depending on type, at a thermal neutron flux of $7 \cdot 10^{12}$ n/cm^2/s. The gamma spectra were recorded twice, beginning 180 s and 630 s respectively after pile-out at the NaJ (Tl) scintillation detector[13]. The vanadium content was determined by the V^{52} photopeak at 1.44 MeV (half-life = 3.87 min), the aluminium content by the Al^{28} photopeak at 1.78 MeV (half-life = 2.3 min), and the chlorine content by the Cl^{38} photopeak at 2.16 MeV (half-life = 3.73 min). Corrections were performed for the interference between the different photopeaks and the Compton edges. For each batch of samples, blanks and standards were prepared and determined at the same time.

The samples collected on Whatman no. 1 filter paper and cellulose acetate membrane filters were placed in a polyvial, irradiated and counted without any pretreatment. Because the cellulose nitrate filters are highly inflammable, they were dissolved in pyridine in the polyvial prior to irradiation. The detection limits are shown in table 3.

Table 3. Approximate detection limits of neutron activation analysis, ng/m^3

Element	OECD-samples	High volume samples			
		A	B	C	D
V	1	10	1	5	1
Al	150	100	20	500	100
Cl	1000	-	-	-	-

A: 24-hour high volume, mobile station. (Cellulose nitrate filter SM 11302)

B: 24-hour high volume mobile station. (Cellulose acetate filter SM 11304)

C: 24-hour high volume, stationary station and
2-hour high volume. (Cellulose nitrate filter SM 11302)

D: 24-hour high volume, stationary station and
2-hour high volume. (Cellulose acetate filter SM 11304)

4.2. Spark Emission Spectroscopy

Pb was determined by spark emission spectroscopy in the 24-hour OECD samples. The analysis was performed on a spectrograph. The filter paper (Whatman no. 1, 25mm$^{\varnothing}$) was cut into four pieces, and the analyses were carried out on two of these after pressing tablets of the paper (1 x 2 mm$^{\varnothing}$) to fit into a hollow graphite electrode. The detection limit for Pb was 0.1 μg per tablet.

4.3. Proton-induced X-ray Emission Spectroscopy

The elements with atomic numbers greater than 13 were determined in 2-hour and 24-hour high-volume samples and 2-hour and 24-hour cascade impactor samples by proton-induced X-ray emission spectroscopy[14]. The samples were irradiated without any chemical pretreatment with high energy protons generated by the 4 MeV Van de Graaff accelerator at the Niels Bohr Institute[15], Copenhagen. The X-ray spectra were measured by a 30 mm^2 liquid-nitrogen-cooled Si(Li)-detector (Kevex mark AA). The spectra were recorded by a Nuclear Data 2200 pulse height analyser and stored on magnetic tape for later analysis on a Univac 1110 computer.

In order to obtain the best possible sensitivity for the large number of elements, each sample was twice irradiated with protons under different conditions. Elements with atomic numbers $Z \lesssim 20$ were determined by 2 MeV protons. Elements with $20 \lesssim Z \lesssim 30$ were determined by irradiation with 2 MeV protons and with an Al-absorber between samples and detector. The absorber attenuates the X-radiation from the elements Si, S, Cl, and K that are normally present in high concentrations. The dead-time losses are thus reduced and the sensitivity is improved. Finally, the elements with $Z > 30$ were determined by irradiation with 3 MeV protons and an Al-absorber, which drastically reduces the radiation from elements with $Z < 28$. By using higher energy, the yield of the X-ray emission was increased, especially for heavier elements. However, radiation from the filters or polystyrene foil was also increased; therefore the net result is improved sensitivity for heavy elements only. Typical times for the three irradiations were 2, 8 and 8 min respectively and the integrated proton currents were 0.02, 10 and 40 microcoulombs. The proton beam was a 5x5 mm square, and the angle of incidence of the protons was 30°, giving an analyzed area of 5x6 mm^2.

The method of analysis was checked through participation in international intercomparison experiments[16]. Significant discrepancies were

Table 4. Approximate detection limits of proton induced X-ray emission spectroscopy on high volume and impactor samples, ng/m^3

Element	Sample type						
	A	B	C	D	E	F	G
Si	300	300	300	300	75	500	180
S			200	200	4	800	65
Cl	100	100	100	100	5	500	150
K	40	40	40	40	3	30	35
Ca			150	50	8	1000	35
Ti	15	5	20	5	.2	8	8
V	15	5	20	5	.1	8	2
Cr	10	4	10	4	.2	10	50
Mn	10	3	15	3	.1	8	8
Fe					2	75	18
Ni	5	4	8	4	.2	6	2
Cu	5	4	40	4	.7	50	5
Zn			40	3	1.5	70	12
Bp					.1	6	4
Mo	1	1	3	3			
Cd	3	3	10	10	1.2	30	30
Sn	10	5	15	15	1.2	40	40
Sb	5	5	20	20			
Pb					.5	15	7

A: 24-hour high volume, mobile station. (Cellulose nitrate filter SM 11302)
B: 24-hour high volume, mobile station. (Cellulose acetate filter SM 11304)
C: 24-hour high volume, stationary station and
2-hour high volume. (Cellulose nitrate filter 11302)
D: 24-hour high volume, stationary station and
2-hour high volume. (Cellulose acetate filter SM 11304)
E: Impactor stages 1-5. (Polystyrene foils)
F: Impactor after filter (Cellulose nitrate filter SM 11302)
G: Impactor after filter.(Cellulose nitrate filter Millipore TA)

only observed for the lightest elements (S, Cl and K). The cause of these discrepancies was discovered and all the results used in this report are corrected.

The detection limits depend on the type of filter because of the impurities and the amount of filter material, and also to some extent on the composition of the particulates because of spectral interference. Approximate detection limits are listed in table 4.

5. DATA EVALUATION OF THE OECD SAMPLES

The 588 OECD samples selected from approximately 8000 samples (cf. section 3.2) were analyzed by neutron activation analysis and spark emission spectroscopy (cf. sections 4.1 and 4.2). The number of samples was chosen as a compromise between the analysis capacity available and sufficient coverage in time and geographical area.

The results were analyzed by means of an analysis of variance in order to pick out the main variations. In addition, the pollution contribution from different types of source was estimated on the basis of the trace-metal content of the particulates. This chapter gives a short description of the methods of evaluation.

5.1. Analysis of Variance

As described in section 3.2, the samples were selected in accordance with the three-factor experimental method based on latin squares[17]. The three factors were: day of the week, station location and fortnightly period of the year. The analyses of variance were performed assuming the validity of the following hypothesis:

$$x_{ijk} = M + D_i + L_j + P_k + z_{ijkp}$$

where x_{ijk} is the result of the measurement and M is the grand mean. D_i, L_j and P_k are the main effects of the day of the week, locality and period, respectively. z_{ijkr} is the experimental uncertainties. In other words, it was assumed that interaction between the three factors was negligible. If any interactions exist, they contribute to the term indicating experimental error. It is, however, important to emphasize that the present investigations were performed in order to extract the large effects, and the limited selection of samples was the best compromise between the available analysis capacity and the geographical and time coverage.

Since

$$\sum_i D_i = \sum_j L_j = \sum_k P_k = 0,$$

the estimates of the different factors are the following:

$$E(\bar{Y}_i) = M + D_i$$

$$E(\bar{Y}_j) = M + L_j$$

$$E(\bar{Y}_n) = M + P_k$$

$$E(\bar{Y}) = M\,.$$

The main effects were therefore visualised by plotting the different means.

The analysis of variance was performed for the four elements Al, V, Cl, and Pb of absolute concentrations and of amounts relative to the concentration of particulate matter as determined by the smoke-shade method. Investigations showed that in order to fulfil the condition of normal distribution of the data for analysis of variance, the best approximation was achieved when the analysis was performed on the logarithm of the results. This is also in agreement with earlier indications of a log-normal distribution of air pollution data[18)]. It is worthwhile to emphasize that the means are thus geometric means and that the main effects are expressed as factors by which to multiply the grand mean to obtain the different geometrical means.

5.2. Estimation of Contributions from Different Source Types

Because we know the composition of the gases and particulates emanating from the main sources of air pollution [5,19)], the determination of the source contribution leads to determination of the concentration of a great number of pollutants at the same time. The contribution can be evaluated by different methods, but in the present work use was made of the trace metals in the particulate matter.

In a given urban area there are many sources of particulate matter, natural and anthropogenic. The major types of anthropogenic aerosol source in Greater Copenhagen were assumed to be:

1. combustion of fuel-oil
2. combustion of coal
3. combustion of automotive fuel,

while the major natural sources were assumed to be:

1. sea spray
2. soil dust.

These may be either primary or secondary sources depending on whether the particulate material is emitted as such from the source or formed in the atmosphere. If sampling is carried out at a fixed point, the material collected will represent contributions from a variety of sources depending on the nature of the winds. The sampling process leads to an averaging over time of contributions from separate sources.

Assuming the most simple system, where the sampling point is influenced by only one source, j, and the aerosol is not changed during transport from souce to sampling point, the percentage (P_i) of an element, i, in the sampled aerosol is equal to the percentage (P_{ij}) of an element, i, in the particulate matter from the source j[5,19]:

$$P_i = P_{ij}.$$

If more than one source contributes to the aerosol at the sampling point, but only the aerosol from one source contains the element, i, the percentage of the element i given by

$$P_i = P_{ij} C_j ,$$

where C_j is the mass of material from source j per unit mass of aerosol in the volume of air sampled. In this case the source contribution is determined by measuring P_i and P_{ij} as:

$$C_j = \frac{P_i}{P_{ij}}. \qquad (5.2.1)$$

When the element, i, is present in the aerosol from more than one source, the percentage of element, i, at the sampling point is given by

$$P_i = \sum_j P_{ij} C_j . \qquad (5.2.2)$$

If all sources are of the same type (P_{ij} identical), the summation can be omitted and C_j is the sum of contributions from all sources of that type. In this case eqs. (5.2.1) and (5.2.2) are identical. From the definition of C_j, the continuity relation

$$\sum C_j = 1$$

must apply, where C_j is summarized for all sources or types of sources.

Expression (5.2.2) is somewhat simplified in relation to reality because transformation or fractionation of the aerosol may take place in the atmosphere, as a result of diffusion and sedimentation of particles of different sizes having different chemical composition, and also in the source itself. The fractionation can be taken into account by introducing a coefficient of fractionation α_{ij}

$$P_i = \sum_j \alpha_{ij} P_{ij} C_j .$$

Normally the fractionation coefficients are not known and no attempt has been made to take the first type of fractionation into account since the main object was to evaluate the contribution relatively. Below, the calculations are based on eqs. (5.2.1) and (5.2.2).

The first step in the calculation of source coefficients (C_j) must be the selection of tracer elements for each source. A tracer element should make up an essential fraction of the total emission from its source, but should not be present in large amounts in the emissions from other sources.

The composition of emissions, with reference to the tracer elements used for the sources considered in this work, is listed in table 5. The figures are taken from the literature5) since no investigations have been made of the chemical composition of the aerosols emitted from the different sources in Copenhagen. It is obvious from the table that for automibiles, fuel oil, and sea salt, the tracers Pb, V, and Cl, respectively, are very suitable, whereas the Al-concentration is unsuitable for estimation of the relative coal and soil dust contributions.

Table 5. Composition of emission for some pollution sources per cent [5,19]

	Auto	Fuel oil	Coal	Soil dust	Sea Salt
Al	-	0.8-0.5	14.0	5-8.2	-
Cl	6.8	-	-	-	55
V	-	2.5-7	0.08	0.007	-
Pb	40	0.07-0.18	0.12	0.005-0.02	-

6. RESULTS OF THE OECD SAMPLES

The element analysis results of the OECD samples from the stationary stations were evaluated separately for each element, V, Al, Cl, and Pb, specific to fuel-oil combustion, dust blown from soil, sea spray and automotive fuel combustion, respectively (cf. section 5.2).

6.1. Vanadium

The analysis of variance diagram of the natural logarithm for the vanadium concentrations in ng/m^3 and per thousand parts is shown in tables 6 and 7 respectively. Only the variation of relative vanadium content between days of the week was found to be insignificant. The residuals were used for calculation of the standard errors and confidence limits. These results are also shown on figs. 2, 3 and 4. The analysis showed that the concentration of vanadium is slightly enhanced on Thursdays and Fridays, and that the relative amount is almost independent of the day of the week. The variation with location showed high concentrations at the central locations with a maximum at 1213/Valby and a decrease with distance to the centre of the city, whereas the relative amounts were highest in areas with most industries (1218/Amagerværket - 1330/Hvidovre and 1331/Glostrup), while the systematic variations with distance from the

Table 6. Analysis of variance of ln V (ng/m^3) in the aerosol of Greater Copenhagen
June 3 1973 - June 29 1974

Sources of Variation	Sum of Squares	Degrees of freedom	Mean square	Variance ratio	Probability (%)
Between days	12.168	6	2.0280	2.84	> 99
Between locations	120.911	20	6.0456	8.46	> 99.99
Between periods	91.009	27	3.3707	4.72	> 99.99
Residual	368.541	516	0.7142		
Total	592.630	529			

Standard error of:

Geometric mean of one weekday = 1.10
Geometric mean of one location = 1.17
Geometric mean of one period = 1.20
One trial = 2.33

Table 7. Analysis of variance of ln V (o/oo) in the aerosol of Greater Copenhagen June 3 1973 - June 29 1974

Sources of Variation	Sum of squares	Degrees of freedom	Mean square	Variance ratio	Probability (%)
Between days	4.757	6	0.7928	1.58	-
Between locations	45.6834	20	2.2842	4.56	> 99.99
Between periods	40.056	27	1.4836	2.96	> 99.99
Residual	257.717	515	0.5004		
Total	348.213	568			

Standard error of:

Geometric mean of one weekday	= 1.08
Geometric mean of one location	= 1.14
Geometric mean of one period	= 1.17
One trial	= 2.02

centre were slighter. Generally, the concentration of V versus period of the year showed highest concentrations in the winter six months, but the variation within the seasons was rather large probably due to differing meteorological conditions. The relative amounts of V were least in the winter six months, but the variation was also considerable.

Fig. 2 shows the concentration and relative amount of V as a function of the day of the week. Seeing that the variation with the day of the week was small, it represents the mean for the city as a whole. The level 8-10 ng/m^3 corresponds to 100 - 400 ng/m^3 particulate matter from fuel-oil combustion. The relative amount of V indicates that the contribution to the total particulates from residual oil combustion,calculated by equation (4.2.1) and table 5, is 1-3%. The V contribution from soil dust and coal combustion can be estimated by the ratio between V and Al. Since the level of Al concentration was 100 - 200 ng/m^3, the contribution of V from these sources is negligible (cf. table 5).

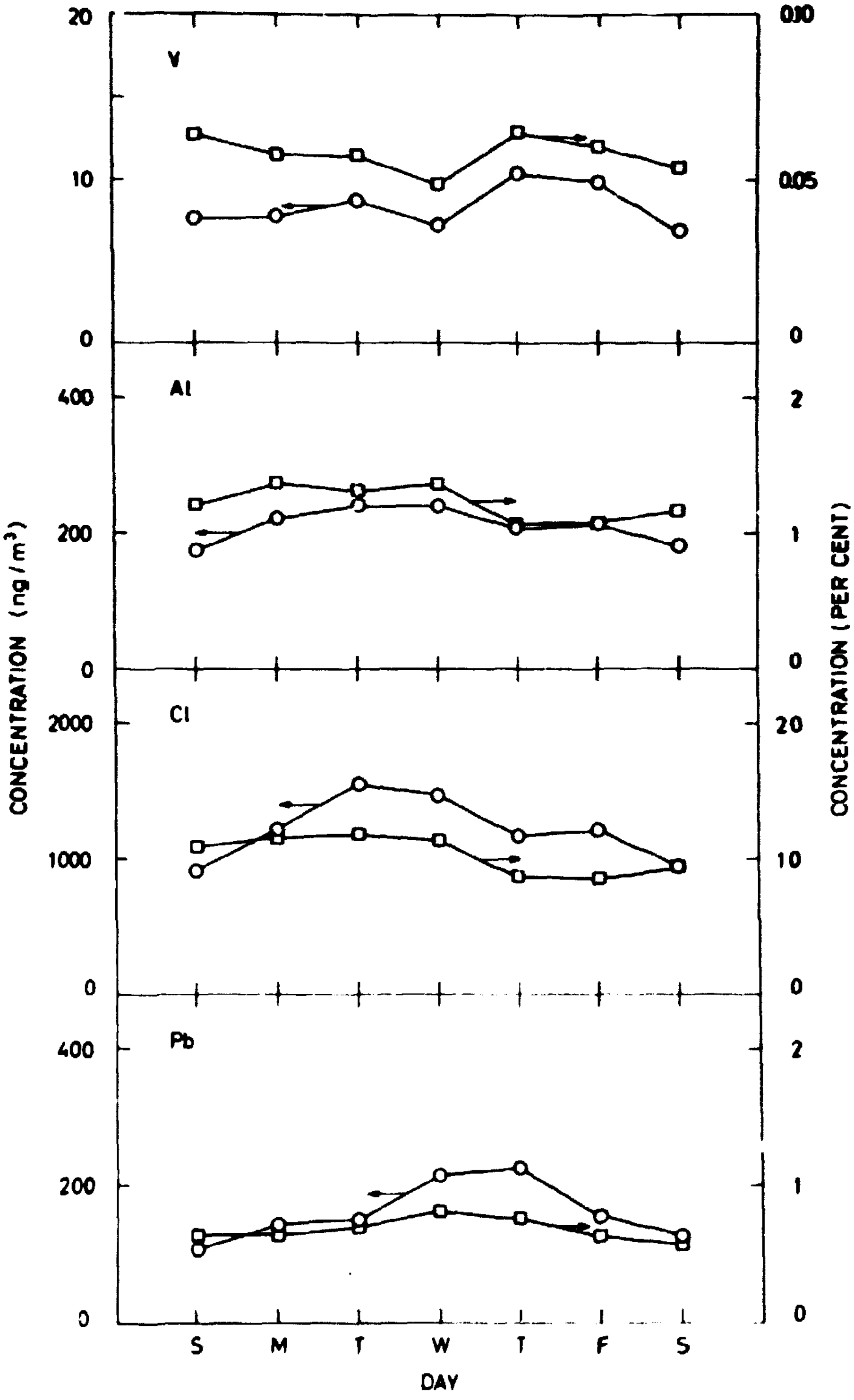


Fig. 2. Geometric mean for each day of the week of the concentration (left-hand axis and points marked ○) and relative amount (right-hand axis and points marked □) of V, Al, Cl and Pb in suspended particulate matter in the period 3 June 1973 to 29 June 1974.

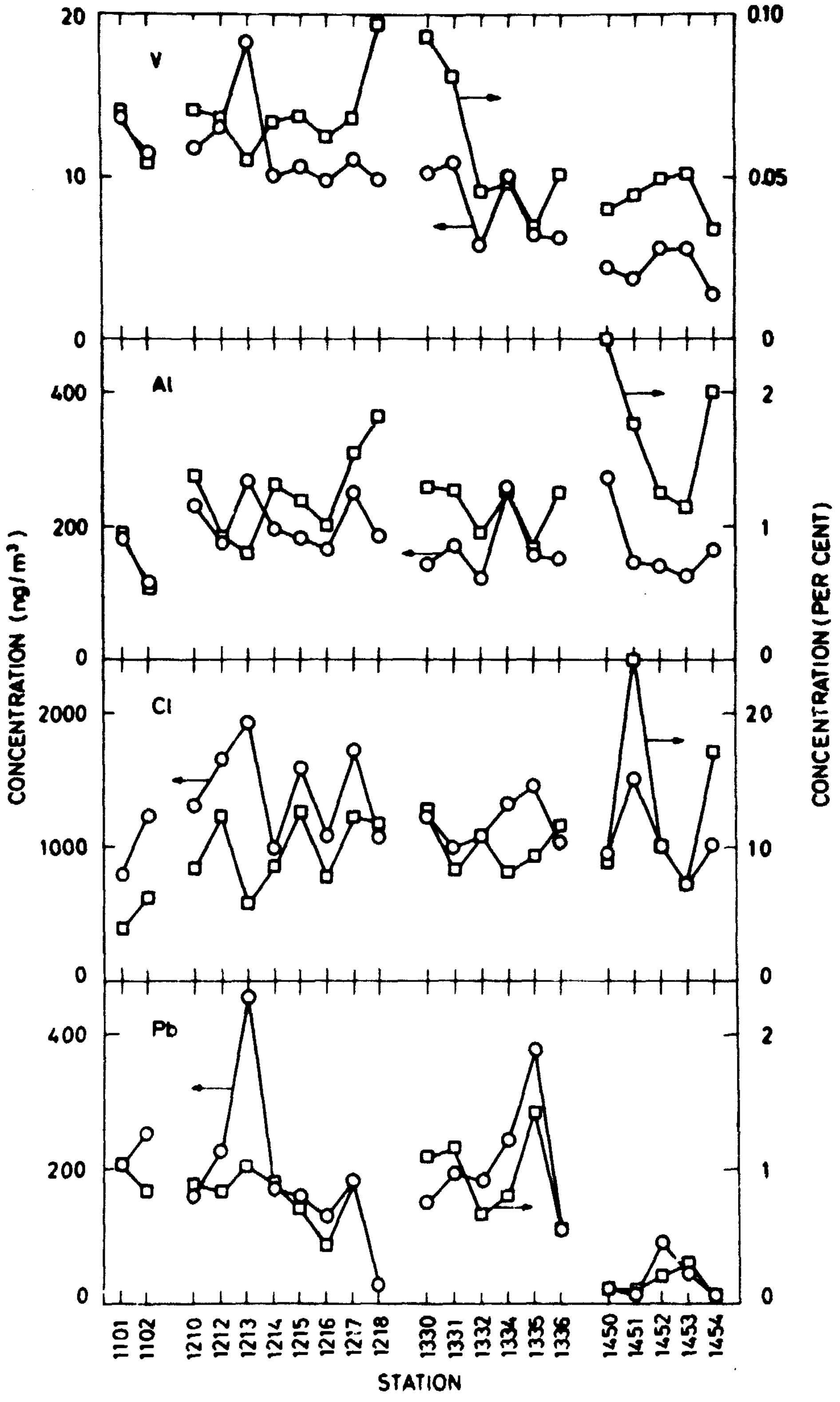


Fig. 3. Geometric mean for each station of the concentration (left-hand axis and points marked ○) and relative amount (right-hand axis and points marked ☐) of V, Al, Cl and Pb in suspended particulate matter in the period 3 June 1973 to 29 June 1974.

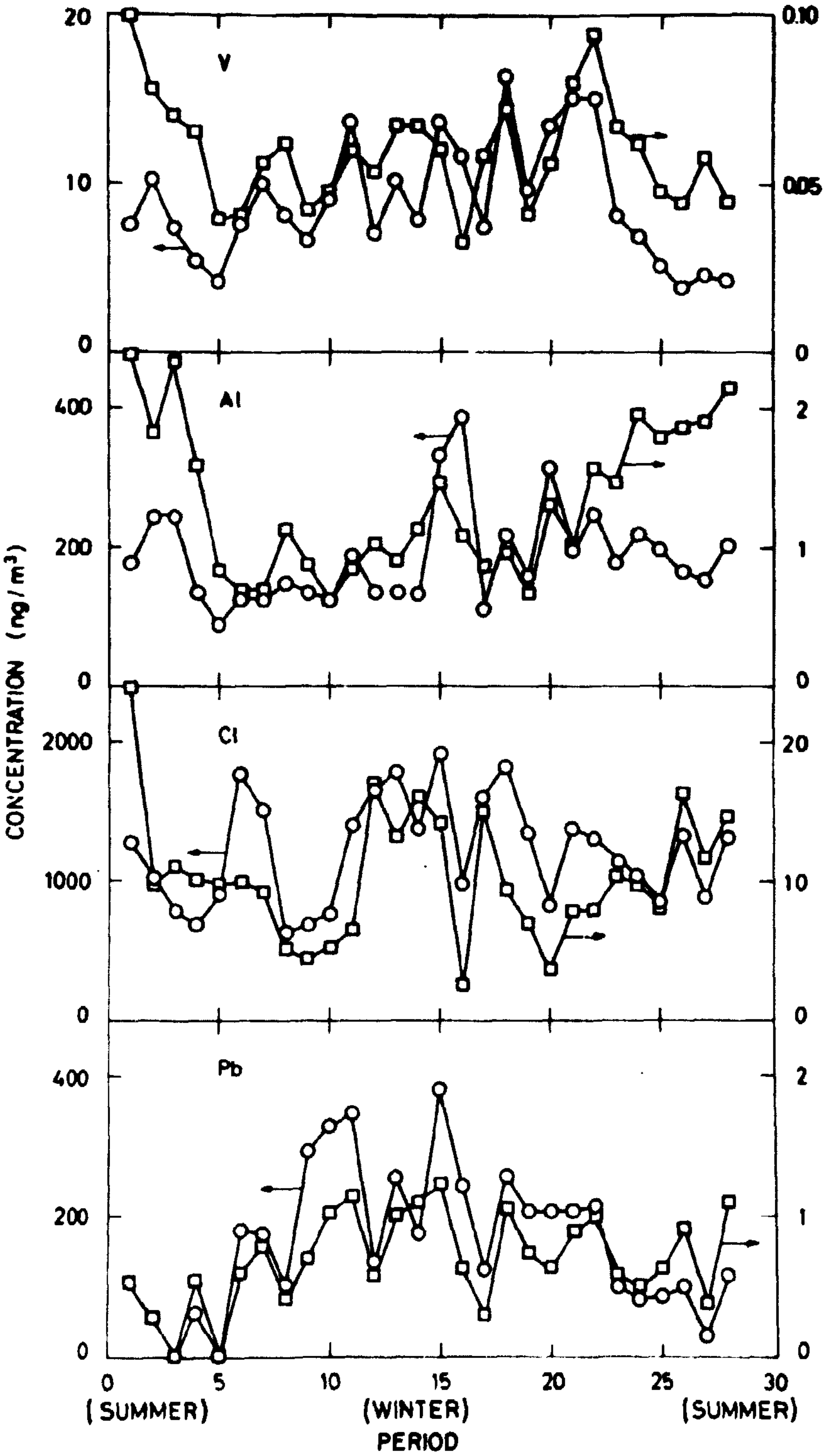


Fig. 4. Geometric mean for each fortnight of the concentration (left-hand axis and points marked ○) and relative amount (right-hand axis and points marked ☐) of V, Al, Cl and Pb in suspended particulate matter in the period 3 June 1973 to 29 June 1974.

From fig. 3 it is evident that the absolute concentration, as well as the relative amount, of V varies with the geographical position. At the rural stations the levels are low, but not so low that they can be explained only by soil dust contribution. These V levels might be due to distant transport[20)], or to local sources in relatively densely populated eastern Denmark. The heavily polluted area around station 1213/Valby showed the highest concentration of V, whereas the highest relative fuel-oil contribution was found at the stations 1218/Amagerværket, 1330/Hvidovre and 1331/Glostrup, which are all situated in the southern part of the city where the largest power stations and industries are located. The largest contribution (geometric mean) from fuel-oil combustion was 1.5-4% with the assumption of fuel-oil combustion as the only emittant and the composition as listed in table 5.

The variation of V-concentration with period of the year (fig. 4) showed the lowest impact of residual-oil combustion in the summer six months and the highest in some periods of the winter six months, probably due to special weather conditions and/or high emission. The relative contributions were highest in the summer of 1973 and in the spring of 1974.

6.2. Aluminium

The analysis of variance diagram showing results for aluminium is given in tables 8 and 9. Similar to V, the variations versus day of the week

Table 8. Analysis of variance of ln Al ng/m^3 in the aerosol of Greater Copenhagen
June 3 1973 - June 29 1974

Source of Variation	Sum of squares	Degrees of freedom	Mean squares	Variance ratio	Probability (%)
Between days	8.032	6	1.3386	2.12	> 95
Between locations	36.029	20	1.8014	2.85	> 99.99
Between periods	64.677	27	2.3954	3.79	> 99.99
Residual	326.501	516	0.6328		
Total	435.238	569			

Standard error of:

Geometric mean of one weekday = 1.09

Geometric mean of one location = 1.16

Geometric mean of one period = 1.19

One trial = 2.22

Table 9. Analysis of variance of ln Al (o/oo) in the aerosol of Greater Copenhagen
June 3 1973 - June 29 1974

Source of variation	Sum of squares	Degrees of freedom	Mean squares	Variance ratio	Probability (%)
Between days	5.048	6	0.8414	1.18	-
Between locations	62.839	20	3.1419	4.42	> 99.99
Between periods	91.877	27	3.4029	4.79	> 99.99
Residual	365.834	515	0.7104		
Total	525.598	569			

Standard error of:

Geometric mean of one weekday = 1.10

Geometric mean of one location = 1.17

Geometric mean of one period = 1.20

One trial = 2.32

for Al-concentration, and particularly of the relative amount, were small, but they showed maxima in the middle of the week. The variation of concentration of Al with location was moderate and not correlated with distance from the centre of the city. The relative amount was highest at the rural stations and at 1217/Østre Elværk and 1218/Amagerværket. The variation versus period was small, except for a short period in the middle of the winter, whereas the relative amount was smallest in the winter half-year. The concentration of Al did not vary systematically with the day of the week, location or period of the year. This indicates that its main source is natural, e.g. soil dust, and not fly ash from the combustion of coal. The relative contribution level, corresponding to 1%, was 10-20%. However, it must be emphasized that the relative amounts were calculated on the basis of the smoke-shade method of determining total particulate matter. This may not take light dust into account, and the relative contribution is probably less than calculated above$^{21)}$. The relative amount of Al varied with location and period of the year in accordance with the assumption of a mainly natural origin for Al. The relative amount was high in summer and, largely speaking, high at the rural stations.

6.3. Chlorine

The analysis of variance of chlorine was uncertain because the content was below the detection limit in many samples; therefore no analysis of variance is shown. The level of Cl-concentrations indicates that 1-3 $\mu g/m^3$ of the particulates originates from the sea. Similar to Al, the relative amount is without much relevance as a result of using the smoke-shade method. The variations with location and periods of the year showed a correlation between absolute and relative amounts, which supports the above indication of an imperfect determination of total particulates.

6.4. Lead

In many samples the lead concentrations were below the detection limit, for which reason an analysis of variance of the logarithm of the lead concentration including these samples was of questionable value. An attempt to include these samples was made by performing the analysis of variance on the lead concentration itself and assuming the undetected concentrations to be equal to zero. Approximately 40% of the samples contained more than 0.4 μg lead, corresponding to 0.2 $\mu g/m^3$. The analysis of variance is shown in tables 10 and 11 for concentration and per thousand, respectively. The variations of concentrations were significant for the three factors, whereas the variation of the relative amount of lead was only significant between locations.

The mean concentration of lead was found to be approximately 160 ng/m^3 which is probably an underestimate considering the above assumption. The concentration was a factor of two higher in the middle of the week than on Sundays. The highest mean concentrations were observed at the locations: 1213/Valby, 1335/Lyngby, 1102/Stormgade, 1334/Gladsaxe, 1212/Ellebjergvej, 1101/Frederiksberg, and 1331/Glostrup, which are all areas with high traffic intensities. Lead concentrations were generally highest in the winter six months.

Table 10. Analysis of variance of Pb (ng/m^3) in the aerosol of Greater Copenhagen June 1973 - June 1974

Sources of Variation	Sum of squares	Degrees of freedom	Mean square	Variance ratio	Probability (%)
Between days	0.9190	6	0.1532	2.275	> 95
Between location	6.4274	20	0.3214	4.773	> 99.99
Between periods	5.3219	27	0.1971	2.927	> 99.99
Residual	33.8727	503	0.0673		
Total	46.5410	556			

Standard error of:

Arithmetric mean of one weekday = 28.3 ng/m^3

Arithmetric mean of one location= 49.0 ng/m^3

Arithmetric mean of one period = 56.6 ng/m^3

One trial =260 ng/m^3

Table 11. Analysis of variance of Pb (o/oo) in the aerosol of Greater Copenhagen June 1973 - June 1974

Source of Variation	Sum of squares	Degrees of freedom	Mean square	Variance ratio	Probability (%)
Between days	326	6	54.4	0.37	-
Between locations	8826	20	441.3	3.02	> 99.99
Between periods	5821	27	215.6	1.48	> 90
Residual	73327	502	146.1		
Total	88300	555			

Standard error of:

Arithmetric mean of one weekday =1.32 o/oo

Arithmetric mean of one location=2.28 o/oo

Arithmetric mean of one period =2.64 o/oo

One trial =12.1 o/oo

As the analysis showed, the variations of the relative amount of lead with day of the week and period of the year were small, whereas the variation with location was greater. The highest relative amount was observed at 1335/Lyngby, 1331/Glostrup and 1101/Frederiksberg, and the lowest at the rural 1400-stations. The highest mean lead concentrations were 400-500 ng/m^3, which is somewhat lower than observed in other large cities; but it must be emphasized that the stations in question are elevated and remote from the streets. As will be shown in a later section, the lead level in the streets is higher (cf. sections 8.1 and 8.3).

The highest mean of the relative amount observed was 1.4% corresponding (cf. table 5) to a contribution of 3.5% to the total particulate matter as measured by the smoke-shade method.

5.5. Summary

To summarize, the concentrations of the trace metals V and Pb in Copenhagen are generally lower than in many other large cities, and thus the impact of the pollution resulting from combustion of fuel-oil and gasoline is less. However, the influence is relatively high locally. The estimates of the relative contributions from automotive, fuel-oil and soil sources are rather similar to those of Chicago, for example[4].

The greatest uncertainties of the estimates are partly due to the short duration of the investigation, which is thus not fully representative of all meteorological conditions, and partly due to the imperfect determination of the total particulates by the smoke-shade method.

7. DATA EVALUATION OF HIGH-VOLUME AND IMPACTOR SAMPLES

The high-volume samples collected from the mobile station and the corresponding stationary stations comprised both 2-hour and 24-hour samples, and also samples collected (not simultaneously) at 12 locations in the region (cf. sections 3.1 and 3.3). The samples were sufficiently large for detailed chemical analysis. Thus, element analysis of them yields information on the concentration levels and also on the diurnal and day-by-day variations of the concentration of different elements. This is important both for comparison with standards and also for the selection of the possible origins of the pollutants.

The impactor samples were also collected with averaging times of 2 and 24 hours. They were sampled at two locations only (cf. section 3.4), and information on size distribution was obtained at the expense of information on concentration variations within the area.

The above information was extracted by evaluation of the cumulative frequency distributions, analysis of variance, correlation between elements and comparison between sample types. These methods are briefly described in the following sections.

7.1. Cumulative Frequency Distribution Curves

A survey of the level and the variation of the concentration of the different elements present in the particulates can be given by the cumulative frequency distribution curves of the measured element concentrations, because they show the means and the standard deviations. The cumulative frequency distributions are plotted separately for the following types of sample: 24-hour and 2-hour high-volume from the mobile station and 24-hour high-volume from the stationary station. All results obtained were included when the graphs were drawn. However, in order to make the graphs clearer, only an extract of the points is given. The three types of sample were plotted separately due to differences in sampling equipment and sampling locations and periods.

Straight-line fits were made in order to determine the geometric mean and standard deviation on the assumption that the results were log-normally distributed[17]:

$$f(c) = a * \exp \left[\left(\log \frac{C}{C_0}\right)^2 / 2 \sigma^2 \right] .$$

In order to prevent extreme concentrations from influencing the fits, the highest and lowest 10 per cent of the results were disregarded. Also measurements with results below detection limits were omitted.

The geometric means (medians) (C_0) and the geometric standard deviations (δ) are extracted from the fits. The uncertainties of the standard deviations are determined from the scatter of the points around the lines. Also the arithmetic means were determined.

7.2. Analysis of Variance

The analysis of variance was performed on element analysis results of samples taken by 2-hour and 24-hour high-volume sampling and 2-hour and 24-hour impactor sampling. The analysis of variance was only performed for elements present in concentrations above detection limits in more than 50% of each type of sample.

The program used was VAR3[22)] which is included in the group of programs STATDATA[23)]. VAR3 executes a three-way analysis of variance according to a factorial division of the data material into groups, possibly containing unequal numbers of observations. The computation can be carried out according to different hypotheses concerning the elimination of parameters in the mathematical model. The present computations were performed only for the hypotheses including all main effects and interactions

$$x_{ijk} = M + A_i + B_j + C_k + AB_{ij} + AC_{ik} + BC_{jk} + ABC_{ijk}$$

where A, B and C are the variations due to the three factors, and i, j and k are indices of the levels of the factors, and M is the grand mean. Due to the absence of replicates, and through this an independent estimate of error, the three-factor term was used as an estimate of the error. All main effects and two-factor interactions were tested relative to this criterion. The three-factor term includes the three-factor interaction and the error; thus, the above approximation is best when the three-factor interaction is small. The significance of the variations was tested by the ratios between the mean square (the sum of squares about the mean divided by the degrees of freedom) of the factor, or the interaction in question, and the mean square of the error. Ratios near one mean that the variations can be ascribed to experimental error, whereas larger ratios appear when the variation is due to the factor, or interactions between factors.

As mentioned in section 6.1, the results were approximately log-normally distributed. The analyses of variance were therefore performed on the logarithm of the results. Although the distributions were not strictly log-normal, they were assumed to be sufficiently so, since the analysis of variance is not very sensitive to the distribution. Results below detection limits were omitted in the analysis of variance.

7.3. Correlations Between Elements

Covariances between the concentrations of the elements were examined in order to obtain additional information on the types of source giving the main contribution of the individual elements.

An approach to the problem is the determination of the linear correlation coefficients. The data were well suited for such calculations since the distributions were, with a reasonable approximation, Gaussian, and the width of the distributions was several times that of the experimental uncertainties. Furthermore, in most cases the correlations were expected to be linear, since the emission from one type of source can on average be regarded as having a fixed composition (cf. section 5.2).

The correlation coefficient between the concentration of two elements in n samples can be calculated as:

$$r = \frac{\sum u_i v_i}{s_u s_v n} \qquad (7.3.1)$$

where

$$s_u = \sqrt{\frac{\sum u_i^2}{n}} , \qquad s_v = \sqrt{\frac{\sum v_i^2}{n}}$$

and

$$u_i = x_i - \frac{\sum x_i}{n} , \qquad v_i = y_i - \frac{\sum y_i}{n} .$$

x_i and y_i are the concentrations of the two elements in samples number i. The summations are performed over all i.

Due to the different accuracy of analysis results from different samples, it is generally necessary to weight the results in relation to the uncertainties. In our investigations the reciprocal sums of the uncertainties of x_i and y_i were chosen as the weights, w_i. After introduction of the weight in equation (7.3.1), the correlation coefficients were calculated as:

$$r' = \frac{\sum w_i u'_i v'_i}{s'_u s'_v w_i} , \qquad (7.3.2)$$

where

$$s'_u = \sqrt{\frac{\sum w_i u'^2_i}{w_i}}, \qquad s'_v = \sqrt{\frac{\sum w_i v'^2_i}{w_i}}$$

and

$$u'_i = x_i - \frac{\sum w_i x_i}{w_i}, \qquad v'_i = y_i - \frac{\sum w_i y_i}{w_i} .$$

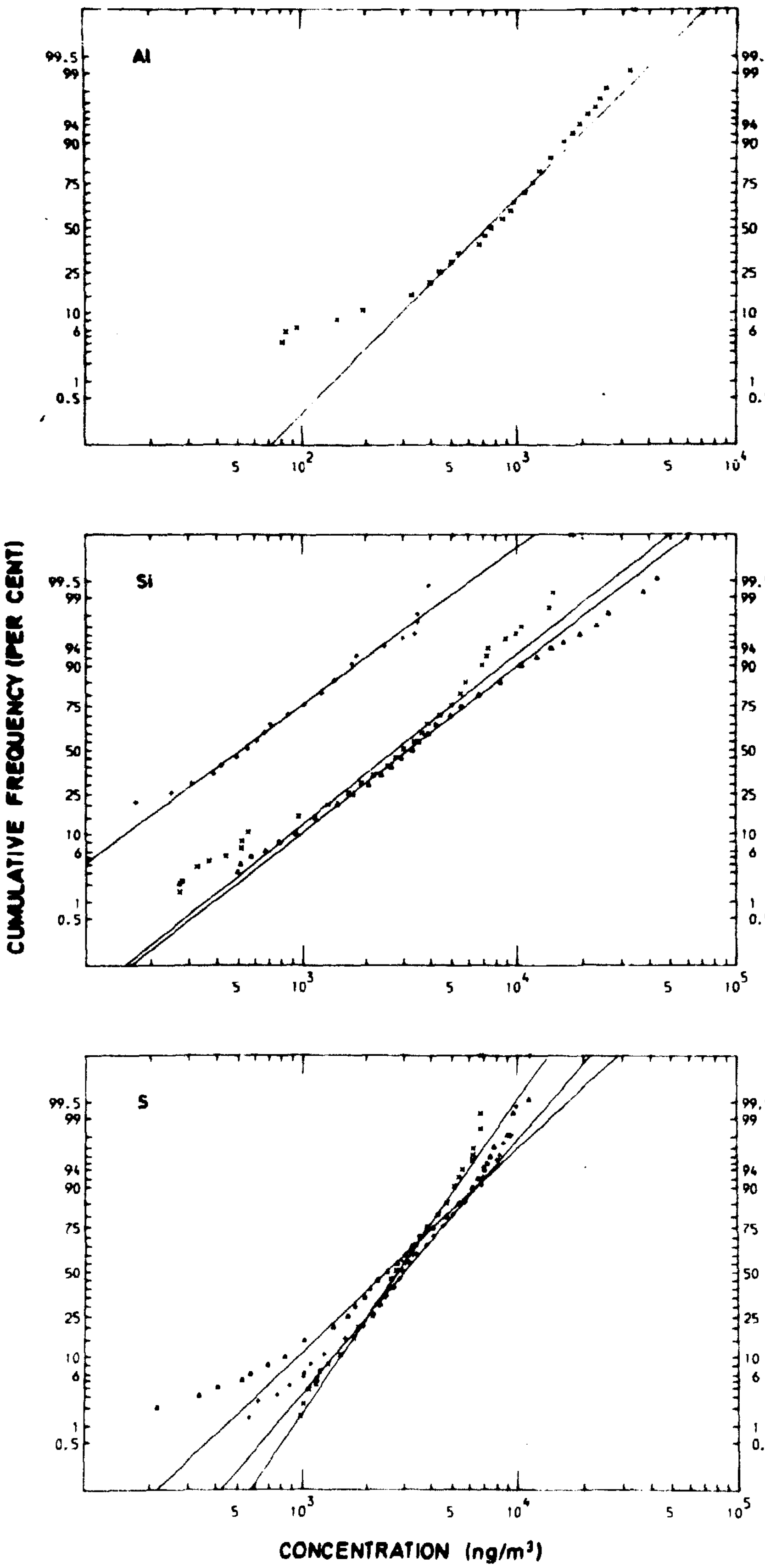
The coefficients were calculated for the 24-hour high-volume results from the mobile and stationary stations separately, for each of the six series of 2-hour high-volume samples, and for each stage of the impactor measurements. Some results from the 24-hour samples,which were obviously abnormal, i.e. heavily inflected by local pollution, were excluded.

8. RESULTS OF THE HIGH-VOLUME AND IMPACTOR SAMPLES

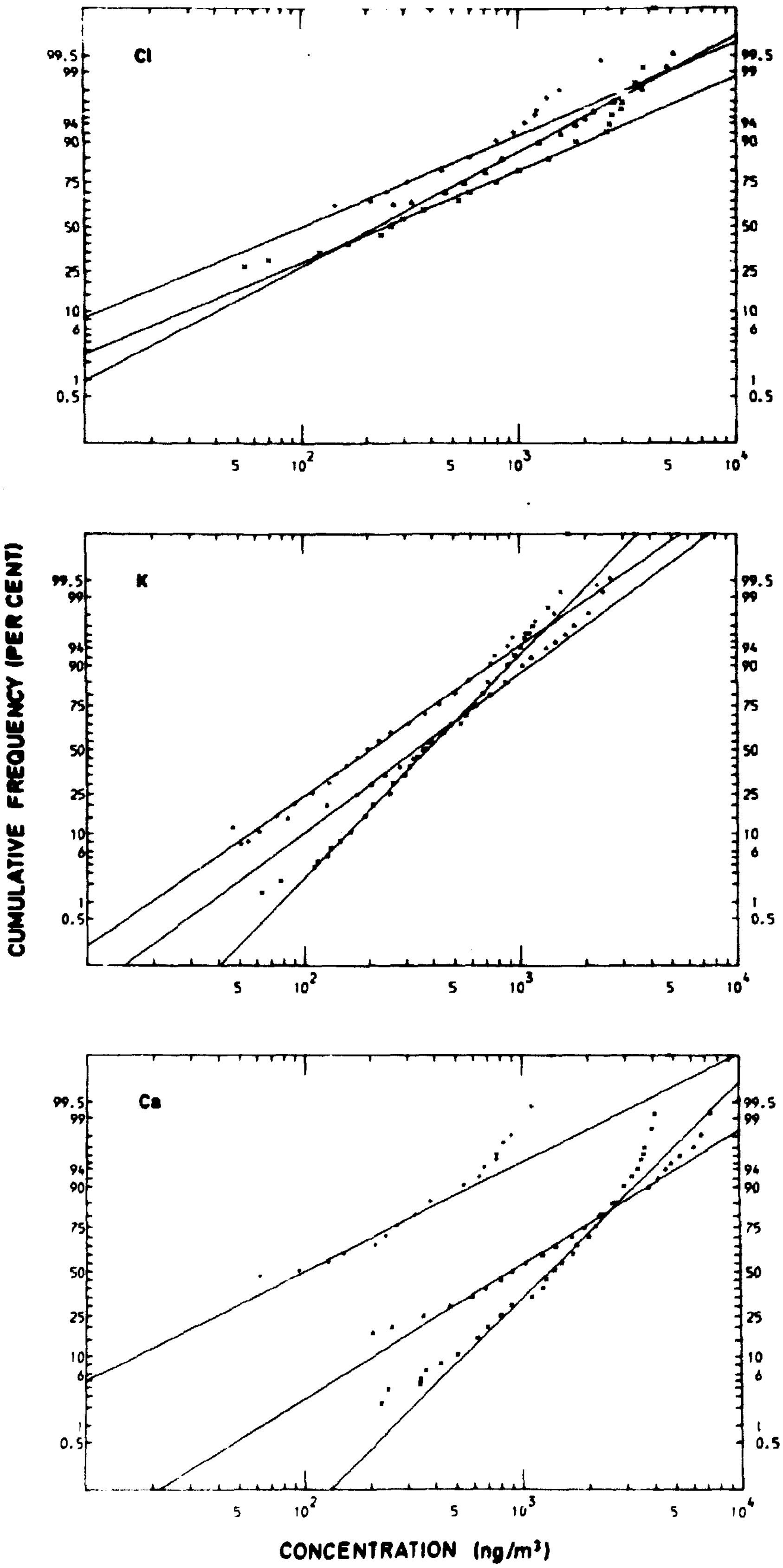
The analysis results from particulate matter samples from the mobile station and the corresponding stationary stations were evaluated in several different ways as described in chapter 7. The present chapter is divided into sections according to the method of evaluation. A survey of the results is given by the cumulative frequency distributions of the different elements. The variations of the element concentrations are given in connection with the analysis of variance of 2-hour and 24-hour high-volume results and 2-hour cascade impactor results. The connections between elements are elucidated by investigations of correlation coefficients. An attempt is made to make an element balance account, and finally comparisons between the different sample types are discussed.

8.1. Cumulative Frequency Distribution of Element Concentrations

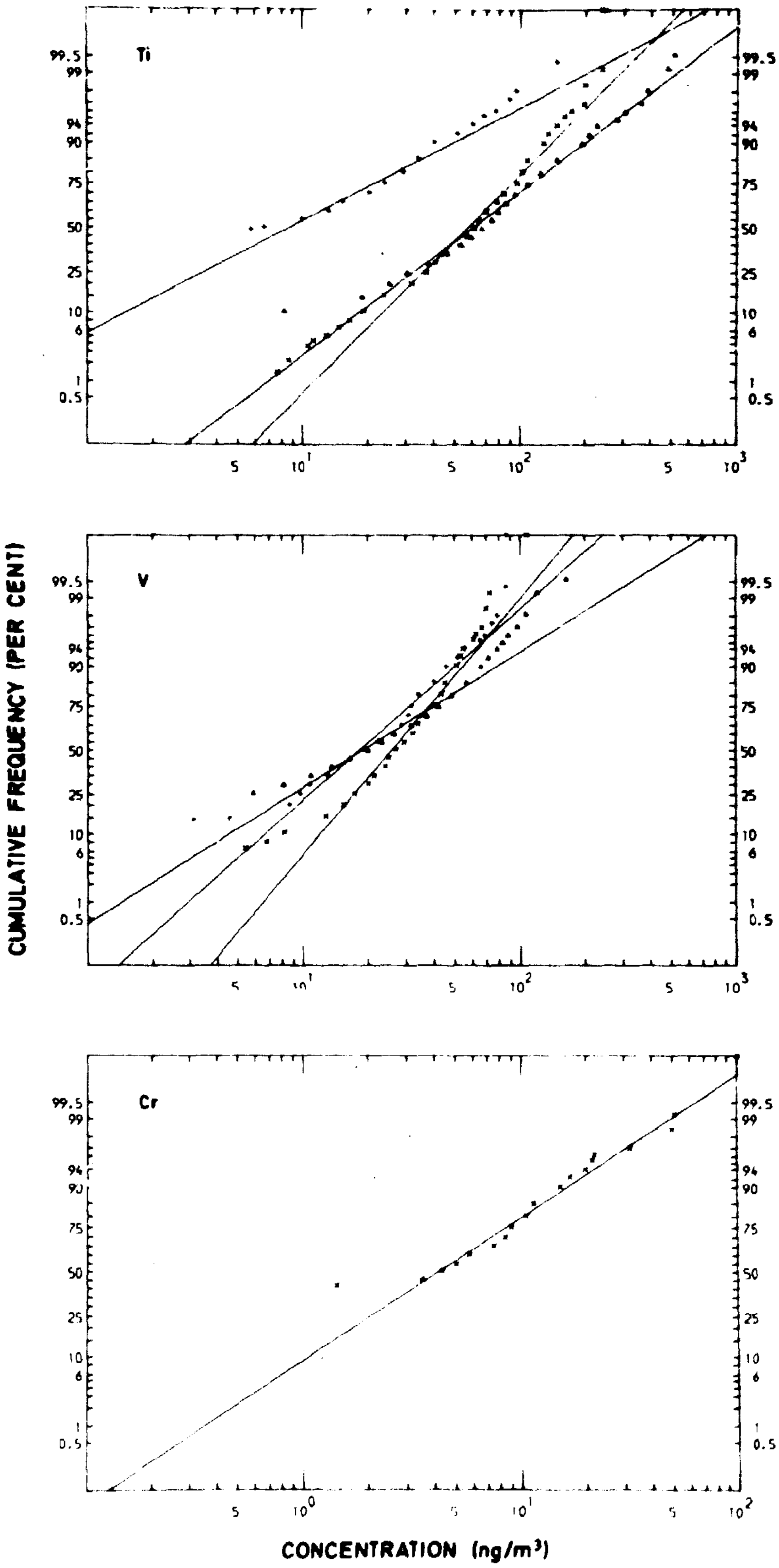
The cumulative frequency distribution of 2-hour and 24-hour high-volume results from the mobile station and 24-hour high-volume results from the stationary stations are shown in figs. 5-25, and the results of straight-line fits to the curves, together with the arithmetic means, are listed in table 12. Concentrations below the detection limits are considered zero in the calculations of the arithmetic means. In cases where more than half of the concentrations were below the detection limits, the values are omitted.



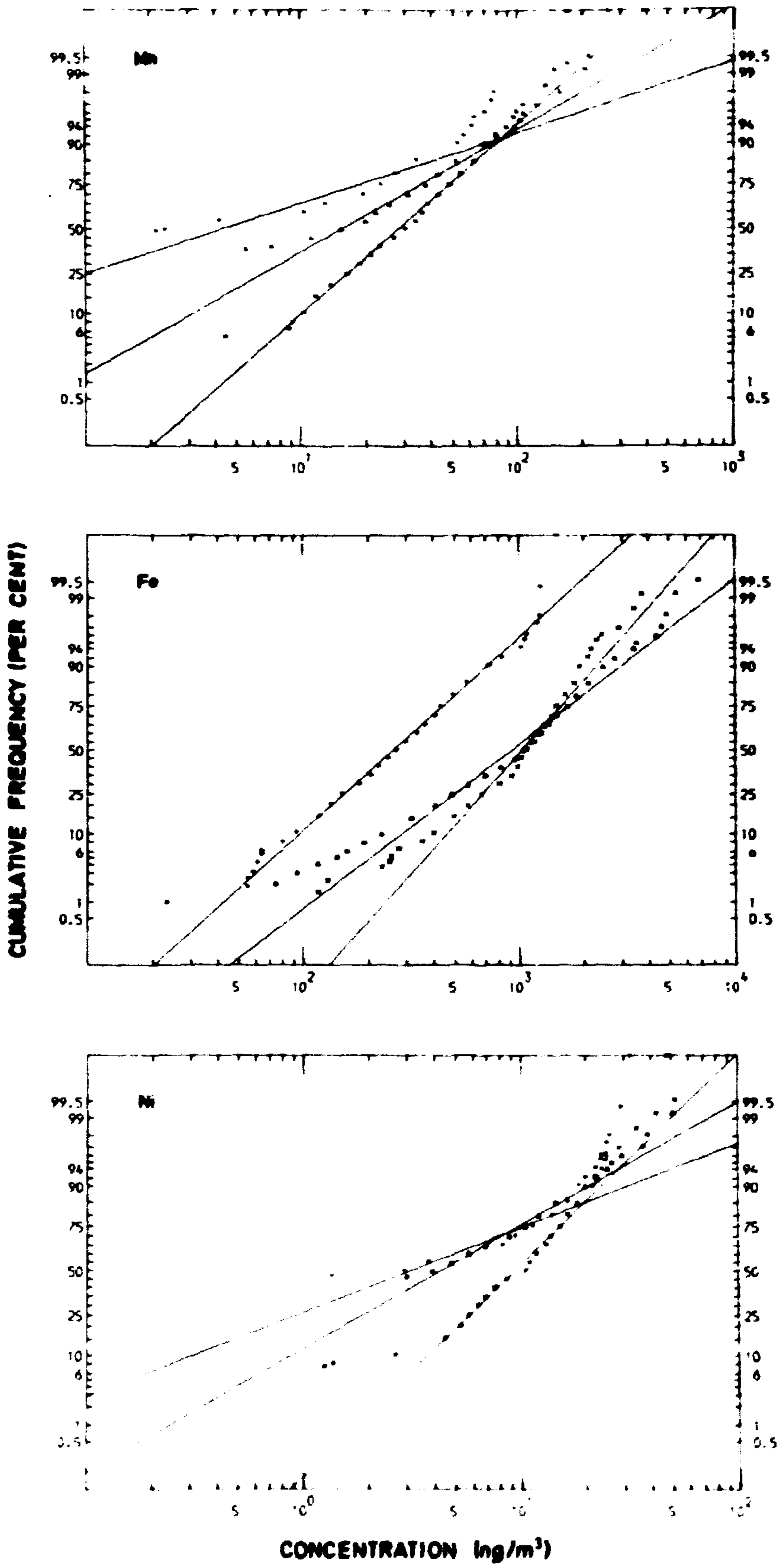
Figs. 5, 6 and 7. Cumulative frequency distribution plots of the concentrations of Al, Si and S in suspended particulate matter sampled by 24-hour (X) and 2-hour (▲) high-volume samplers at the mobile station and 24-hour (+) high-volume sampler at the corresponding stationary station. Sampling period 1973/74.



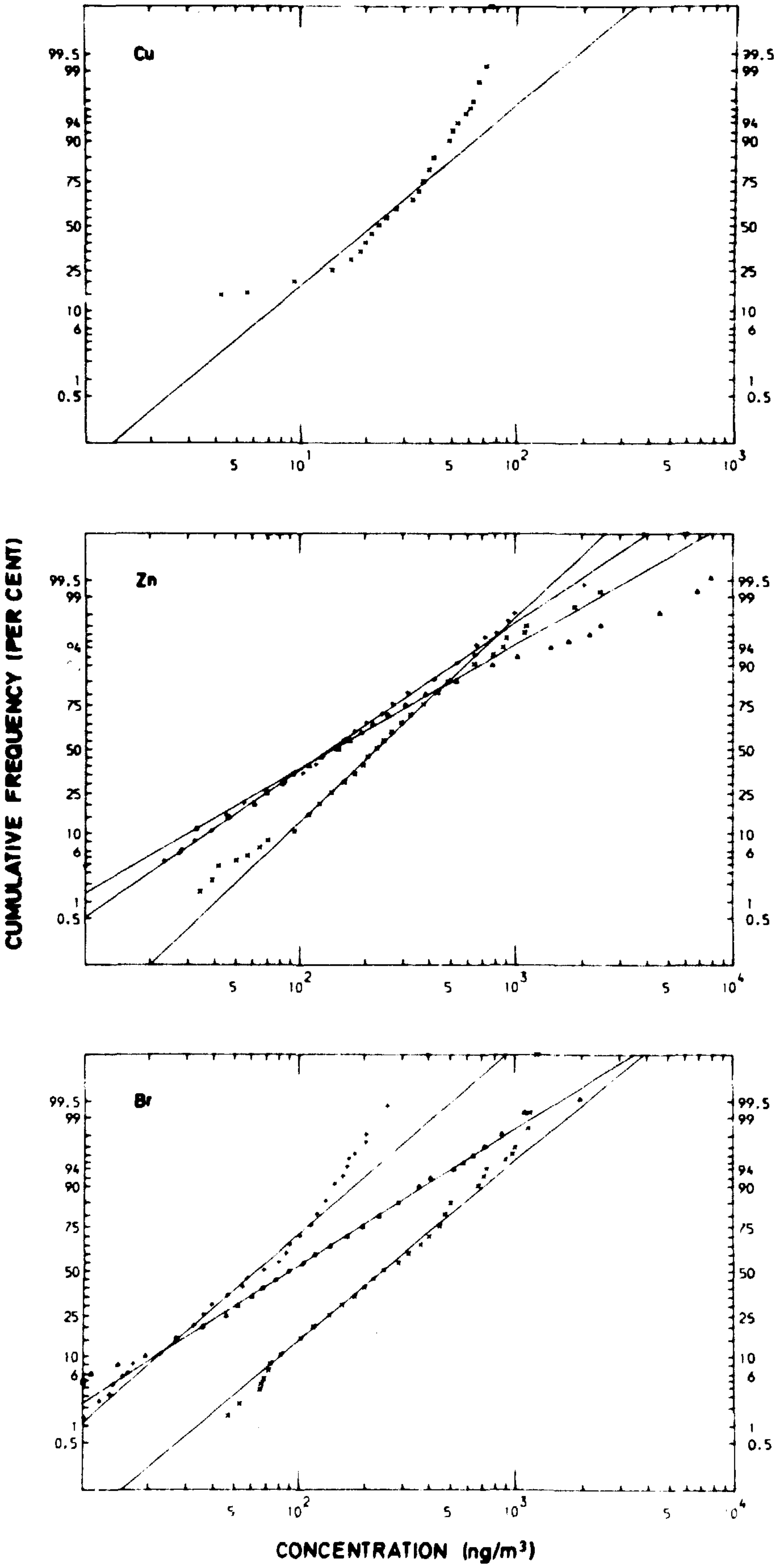
Figs. 8, 9 and 10. Cumulative frequency distribution plots of the concentrations of Cl, K and Ca in suspended particulate matter sampled by 24-hour (X) and 2-hour (Δ) high-volume samplers at the mobile station and 24-hour (+) high-volume sampler at the corresponding stationary station. Sampling period 1973/74.



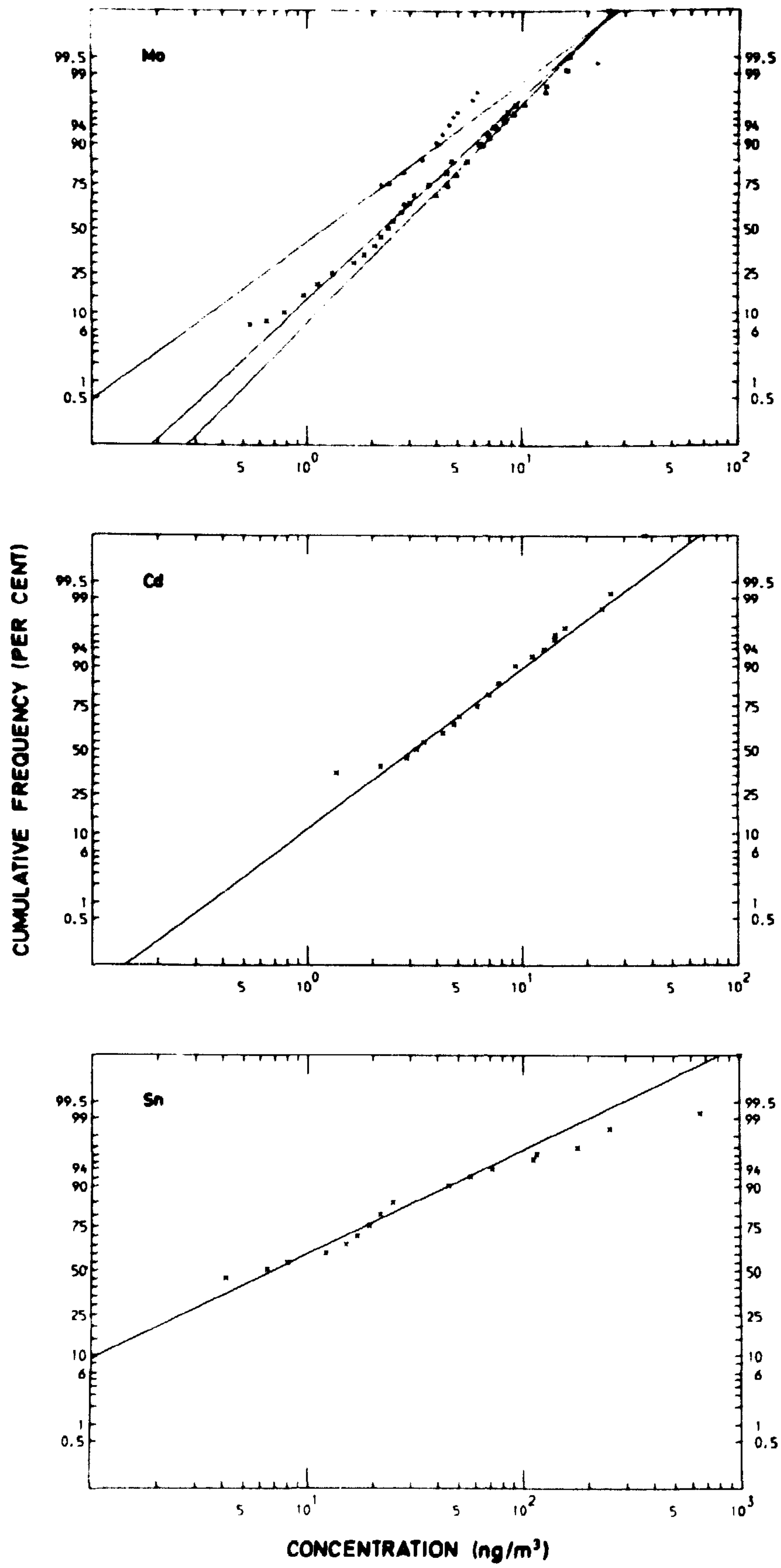
Figs. 11, 12 and 13. Cumulative frequency distribution plots of the concentrations of Ti, V and Cr in suspended particulate matter sampled by 24-hour (X) and 2-hour (Δ) high-volume samplers at the mobile station and 24-hour (+) high-volume sampler at the corresponding stationary station. Sampling period 1973/74.



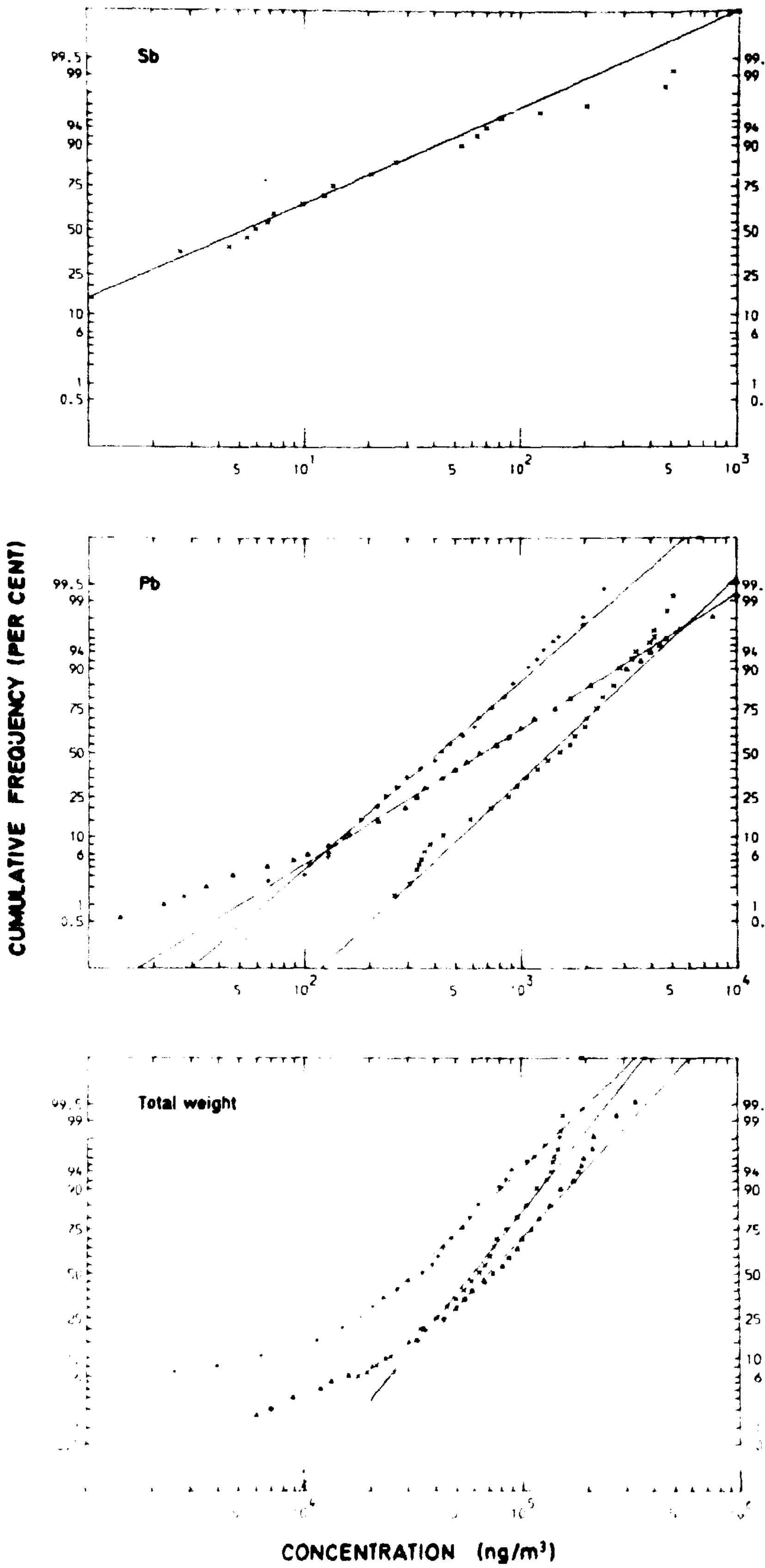
Figs. 14, 15 and 16. Cumulative frequency distribution plots of the concentrations of Mn, Fe and Ni in suspended particulate matter sampled by 24-hour (X) and 2-hour (Δ) high-volume samplers at the mobile station and 24-hour (+) high-volume sampler at the corresponding stationary station. Sampling period 1973/74.



Figs. 17, 18 and 19. Cumulative frequency distribution plots of the concentrations of Cu, Zn and Br in suspended particulate matter sampled by 24-hour (X) and 2-hour (Δ) high-volume samplers at the mobile station and 24-hour (+) high-volume sampler at the corresponding stationary station. Sampling period 1973/74.



Figs. 20, 21 and 22. Cumulative frequency distribution plots of the concentrations of Mo, Cd and Sn in suspended particulate matter sampled by 24-hour (X) and 2-hour (Δ) high-volume samplers at the mobile station and 24-hour (+) high-volume sampler at the corresponding stationary station. Sampling period 1973/74.



Figs. 23, 24 and 25. Cumulative frequency distribution plots of the concentrations of Sb, Pb and total weight of suspended particulate matter sampled by 24-hour (X) and 2-hour (Δ) high-volume samplers at the mobile stations and 24-hour (+) high-volume sampler at the corresponding stationary station. Sampling period 1973/74.

The fits are seen to be in reasonable agreement with the experiments. In many cases, nonetheless, there are too many small and too few high values. This indicates that the real distributions are to be found between the normal and the logarithmic normal distributions, but far closer to the latter.

Generally, the 24-hour results showed parallel distributions whereas the 2-hour results showed larger standard deviations. Only S, V and Ni showed nearly identical distributions. Comparing the three curves, it deserves notice that the 24-hour samples were taken at 12 different positions of the mobile station and at the stationary stations simultaneously. The 2-hour samples were taken at 6 different positions (included in the above 12 positions) at the mobile station only. The agreement between 2-hour and 24-hour high-volume results from the mobile station is, however, generally fair. The displacements of the distributions of the 24-hour results from the stationary station and the mobile station are most evident for some elements, i.e. Al, Si, Ca, T, and Fe. These are mainly attached to large particles (cf. section 8.4) and the displacements are probably due to the different types of sampling equipment used (cf. section 3.5). For Br and Pb, which

Table 12. Arithmetic mean (M_a), geometric mean (M_g) and geometric standard deviation (S_g) of high-volume sampling results in 1973/74

Element	24-hour mobile station			24-hour stationary station			2-hour mobile station		
	M_a	M_g	S_g	M_a	M_g	S_g	M_a	M_g	S_g
Al	872	721	2.0	-	-	-	-	-	-
Si	3650	2750	2.4	773	520	2.6	5070	3170	2.5
S	3090	2820	1.6	3520	3020	1.8	3050	2490	2.1
Cl	620	240	5.2	-	-	-	-	-	-
K	460	376	2.0	325	203	2.7	477	333	2.6
Ca	1580	1330	2.0	-	-	-	1460	880	3.1
Ti	70	57	2.0	17	8.6	3.9	88	60	2.5
V	29	26	1.8	23	18	2.2	28	19	3.0
Cr	7.6	4.2	2.9	-	-	-	-	-	-
Mn	37	28	2.2	16	4.3	8.7	27	15	3.5
Fe	1180	1020	1.9	350	260	2.2	1280	917	2.5
Ni	11.2	9.3	2.1	-	-	-	7.0	4.2	3.4
Cu	25	21	2.3	-	-	-	-	-	-
Zn	362	227	2.1	243	138	2.8	446	144	3.4
Br	324	242	2.3	79	63	2.3	170	91	3.0
Mo	3.1	2.2	2.1	-	-	-	-	-	-
Cd	4.2	3.1	2.6	-	-	-	-	-	-
Sn	32	6.9	4.3	-	-	-	-	-	-
Sb	38	5.2	4.9	-	-	-	-	-	-
Pb	1680	1370	2.4	560	415	2.2	1280	665	3.1
TP	66300	59500	1.8	41100	31800	2.1	83200	70200	1.9

are connected to small particles (cf. section 8.4), it might be concluded that the concentration level of these elements is 3 to 4 times higher in busy streets than in the area as a whole. However, large particles containing Pb and Br, e.g. raised by wind or some other activity, might to some extent influence this ratio. The third group of elements, i.e. S, V and Ni, showed only small differences between the two types of 24-hour results and to some extent between the 2-hour and the 24-hour results. This is in accordance with their attachment to small particles, and the widely distributed and elevated sources of fuel-oil combustion.

The geometric standard deviations were in most cases 2 or more, which means that 2/3 of the values are spread over a factor of 4 or more. S, V and Ni were found to have the narrowest distributions. The variations of the results are described in more detail in sections 8.2 and 8.3, where the effects of sampling hour, day and season and also location are examined.

8.2. Analysis of Variance of 2-hour High-Volume Samples

The analysis of variance of 2-hour high-volume samples was performed with respect to the three factors: time of day (T), day of week (D) and location/period of the first six months of 1974 (L). It is not possible to separate the effect of location and of period of the year, because sampling was performed from the mobile station located at six different positions during the first six months of 1974. The results of the analysis of variance are summarized in table 13, which shows the mean squares of time (T),

Table 13. Mean squares and standard errors (trial) calculated on the basis of a three-way analysis of variance of natural logarithm of 2-hour high-volume sampling results from the mobile station in 1974

Element	Mean squares							Standard error of trial
	L	T	D	LT	TD	LD	LTD	
Si	24.3	5.3	1.8	0.73	0.43	3.50*	0.63	2.21
S	16.4	0.3	0.9	0.52	0.35	2.53*	0.51	2.04
K	19.1*	1.0	1.2	0.62	0.43	2.41*	0.58	2.14
Ca	10.6*	4.0*	3.8*	1.00	0.44	2.52*	0.68	2.28
Ti	18.9*	2.6*	0.9	0.58	0.44	2.57*	0.59	2.16
V	13.0*	0.3	0.3	0.45	0.55	1.84*	0.47	1.98
Mn	9.4*	2.0	1.7	1.08	0.49	2.81*	0.90	2.58
Fe	32.9*	4.1*	1.3	0.68	0.44	3.36*	0.59	2.16
Ni	9.1*	0.3	0.4	0.37	0.61	1.41*	0.42	1.91
Zn	32.0	1.4	3.2*	0.97	0.76	3.64*	0.99	2.70
Br	21.3*	6.5*	2.5*	0.90	0.85	3.88*	0.68	2.28
Pb	31.5*	7.3*	3.5*	1.31	0.86	3.65*	0.97	2.68
TP	3.2*	1.3*	2.3*	0.40	0.34	1.37*	0.42	1.91

L: Location/period. T : Hour of the day. D: Day of the week.
Significance at 5% level is marked with *

day (D) and location (L), and the interactions, LxT, TxD, LxD, and LxTxD of each of twelve elements and the weight of particulates.

The main effect of location, L, was highly significant (higher than 95% is indicated by x) for all elements, but not for weight of particulates), whereas none of the results showed any significant variation due to the factor day of the week, D. Based on the factor T, hour of the day, as source of variation, the results can be divided into two groups: 1) S, V, Ni, and Zn, and 2) all other elements and weights of particulates. The variation with hour of the day, T, was statistically significant for the second group only. The interactions LT and TD were not significant, whereas LD generally were. Although the two-factor interactions LD were statistically significant, they were quite small compared with the main effect of location, L, and the means for the levels of the factors L and T, as shown in figs. 26 and 27, give an adequate summary of the variation of

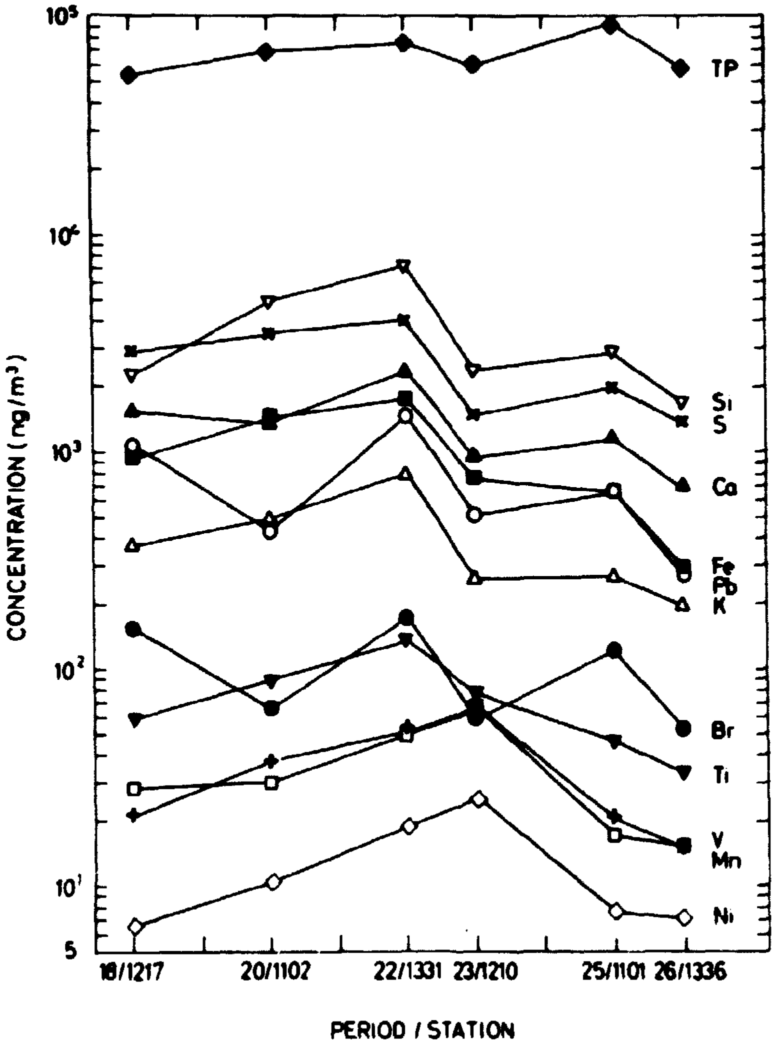


Fig. 26. Geometric mean, for every period-station combination during the first six months of 1974, of the concentration of elements and total particulate matter (TP), sampled by 2-hour high-volume sampler at the mobile station.

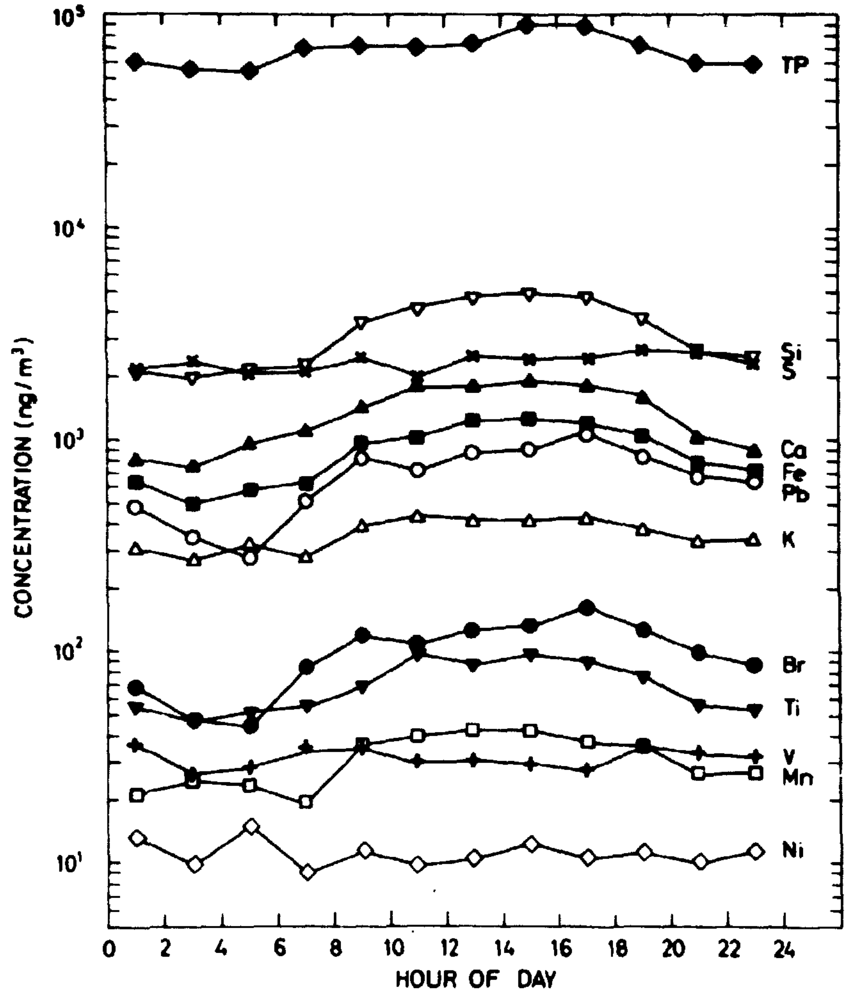


Fig. 27. Geometric mean, for every 2-hour of the day during the first six months of 1974, of the concentration of elements and total particulate matter (TP), sampled by 2-hour high-volume sampler at the mobile station.

the experimental results as a function of the two factors, location/period and hour of the day. The group 1 elements mentioned above showed only small diurnal variations. Especially the variation of the concentrations of S, V and Ni, which all originate from oil combustion, was very small. This indicates that the mean influence of oil combustion is independent of the time of day. On the basis of the diurnal variations, the second group of elements could be divided into two. Br and Pb showed two maxima, one between 8 and 10 a.m. and another between 4 and 6 p.m., corresponding to the rush hours. This is in agreement with the expectation that automotive exhaust is the main source of these elements. The other elements showed a broad maximum between 8 a.m. and 8 p.m. This indicates that these elements and total particulates originate to some extent from a variety of anthropogenic sources.

In spite of the mixing of the geographic and seasonal variation, Br and Pb showed marked maxima at the locations with heavy traffic, 1217/Østre Elværk, 1331/Glostrup and 1101/Frederiksberg, which indicates that location is an important source of variation for these elements. Most of the other elements showed a maximum at 1331/Glostrup. It is not quite clear if this is due to geographic or seasonal factors, but there is heavy industrial activity at this location. The highest concentrations of V and Ni (and Mn) were found at 1210/Sundby that is located in the region with the largest power stations burning fuel-oil. It is not clear why the concentration of S was not highest at this location.

Fig. 28 shows the variations with day of the week. As mentioned earlier, the variations were insignificant, in contrast to the two-factor (LD) variations. Since only relatively few samples form the basis of the points

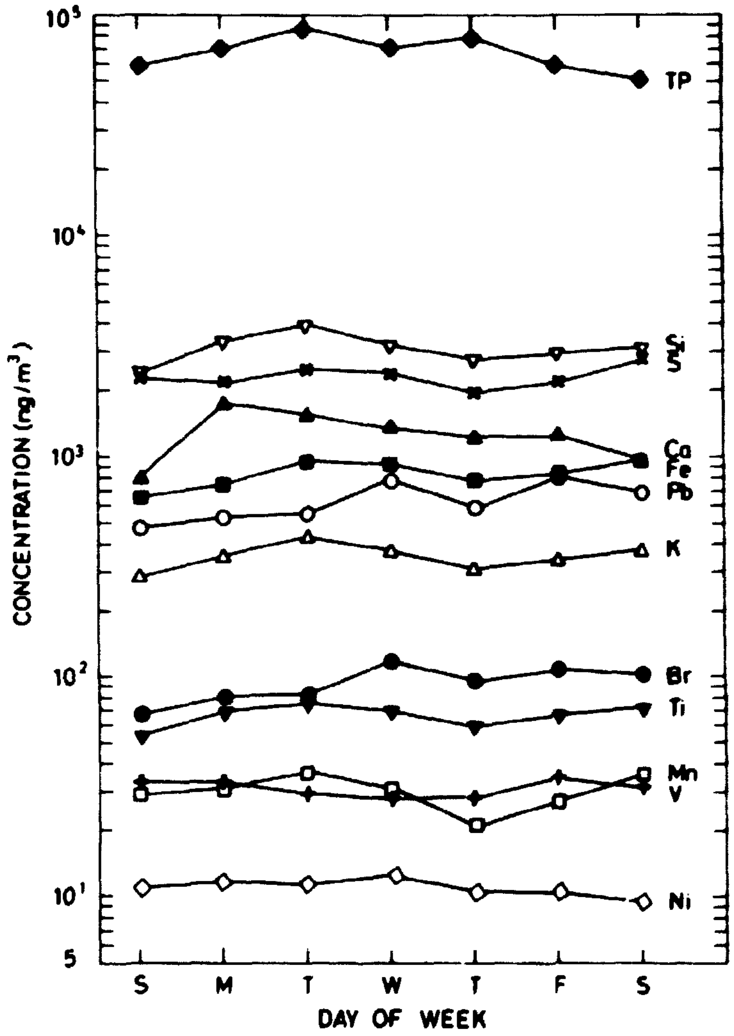


Fig. 28. Geometric mean, for every day of the week during the first six months of 1974, of the concentration of elements and total particulate matter (TP), sampled by 2-hour high-volume sampler at the mobile station.

of the curves, for which reason single results may have large effects on the two-factor variations, the factor D, day of the week, is described more accurately by the 24-hour high-volume sample results described in section 8.3.

Tables 14, 15 and 16 show the main effects relative to the grand means.

Table 14. Normalized geometric means of the element concentrations of each location/period for the 2-hour high-volume sampling results from 1974. The geometric means are normalized by division with the geometric mean of all results of the element concerned.

Element	Location/period					
	1217/18	1102/20	1331/22	1210/23	1101/25	1336/26
Si	0.72	1.58	2.30	0.77	0.91	0.54
S	1.25	1.48	1.73	0.64	0.84	0.57
K	1.05	1.40	2.26	0.74	0.75	0.54
Ca	1.23	1.10	1.91	0.77	0.92	0.55
Ti	0.90	1.34	2.04	1.17	0.69	0.51
V	0.90	1.22	1.65	2.20	0.65	0.49
Mn	0.94	1.00	1.68	2.16	0.58	0.51
Fe	1.13	1.73	2.07	0.90	0.78	0.35
Ni	0.60	0.94	1.71	2.36	0.68	0.64
Zn	1.02	0.71	3.63	0.82	0.59	0.78
Br	1.67	0.70	1.84	0.63	1.30	0.56
Pb	1.71	0.69	2.31	0.82	1.03	0.43
TP	0.81	1.03	1.13	0.84	1.38	0.87

Table 15. Normalized geometric means of the element concentrations of each location/period for the 2-hour high-volume sampling results from 1974. The geometric means are normalized by division with the geometric mean of all results of the element concerned.

Element	Hour of the day											
	0–2	2–4	4–6	6–8	8–10	10–12	12–14	14–16	16–18	18–20	20–22	22–24
Si	0.67	0.63	0.68	0.72	1.16	1.37	1.54	1.57	1.55	1.22	0.84	0.80
S	0.92	1.00	0.90	0.90	1.05	0.86	1.08	1.03	1.06	1.14	1.11	0.99
K	0.87	0.76	0.90	0.79	1.09	1.23	1.18	1.17	1.21	1.07	1.94	0.95
Ca	0.65	0.59	0.76	0.89	1.14	1.41	1.43	1.51	1.45	1.30	0.82	0.73
Ti	0.82	0.70	0.78	0.82	1.02	1.43	1.28	1.44	1.35	1.13	0.83	0.80
V	1.18	0.84	0.90	1.07	1.12	0.94	0.97	0.95	0.89	1.13	1.05	1.00
Mn	0.72	0.79	0.76	0.64	1.21	1.29	1.41	1.41	1.24	1.17	0.89	0.91
Fe	0.76	0.60	0.69	0.75	1.14	1.21	1.45	1.50	1.43	1.25	0.92	0.86
Ni	1.20	0.89	1.37	0.82	1.02	0.88	0.94	1.11	0.95	1.02	0.90	1.04
Zn	0.76	0.86	1.00	0.95	1.43	1.34	1.20	1.03	0.95	0.86	0.79	1.01
Br	0.72	0.51	0.48	0.89	1.29	1.17	1.34	1.41	1.73	1.36	1.05	0.92
Pb	0.76	0.55	0.44	0.81	1.31	1.12	1.37	1.40	1.73	1.31	1.06	1.01
TP	0.84	0.81	0.80	1.02	1.06	1.05	1.07	1.35	1.32	1.10	0.86	0.89

Table 16. Normalized geometric means of the element concentrations of each location/period for the 2-hour high-volume sampling results from 1974. The geometric means are normalized by division with the geometric mean of all results of the element concerned.

Element	Day of the week						
	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Si	0.78	1.09	1.29	1.04	0.90	0.96	1.02
S	1.00	0.93	1.07	1.04	0.84	0.95	1.20
K	0.81	1.01	1.29	1.07	0.88	0.97	1.07
Ca	0.65	1.42	1.26	1.11	0.99	1.00	0.78
Ti	0.81	1.05	1.13	1.05	0.89	1.02	1.09
V	1.09	1.07	0.94	0.90	0.92	1.10	1.00
Mn	0.99	1.04	1.24	1.04	0.71	0.90	1.19
Fe	0.80	0.90	1.15	1.10	0.94	1.02	1.15
Ni	1.01	1.08	1.03	1.14	0.96	0.95	0.87
Zn	0.60	0.82	1.14	1.25	1.02	1.29	1.09
Br	0.73	0.88	0.90	1.27	1.03	1.18	1.11
Pb	0.76	0.85	0.89	1.27	0.94	1.32	1.11
TP	0.87	1.06	1.27	1.07	1.19	0.88	0.76

8.3. Analysis of Variance of the 24-hour High-Volume Samples

The analysis of variance for the 24-hour high-volume samples was performed with respect to the three factors: period of the year/location (P), mobile or stationary station (M), and day of the week (D). Similar to the 2-hour results, the geographic and seasonal effects could not be isolated due to the different sampling locations. However, in this case each sampling location was represented twice within the measuring period of one year thus giving some possibilities of distinction.

The results of the analysis of variance are summarized in tables 17, 18, 19, and 20. The main effect of seasonal variation P (table 17) was highly significant in all cases. The highest mean squares were found for the elements Si, Cl, K, and Ca that are supposed mainly to originate from natural sources, and therefore depend heavily on meteorological conditions. The smallest mean squares were observed for S, V and Ni, indicating a relatively small seasonal (and geographic) variation of fuel-oil combustion. The main effect M (stationary contra mobile station) (table 19) was highly significant for some elements: Si, Ca, Ti, Mn, Fe, Br, and Pb. The variation with M of Br and Pb is probably due to a real difference between

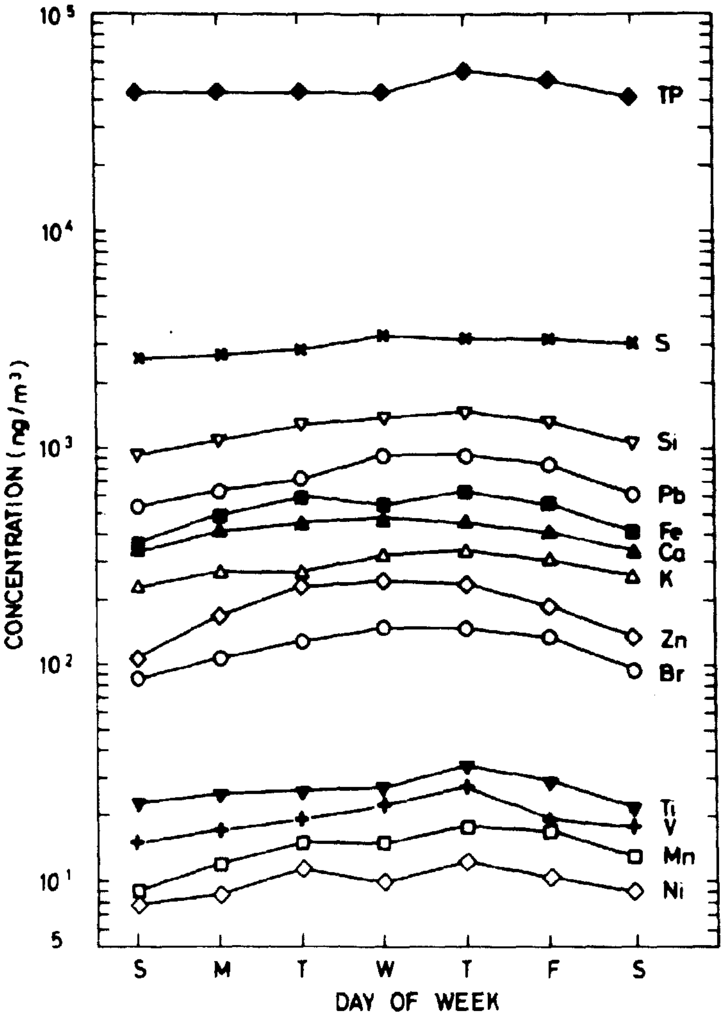


Fig. 29. Geometric mean, for every day of the week during the period June 1973 to June 1974, of the concentration of elements and total particulate matter (TP), sampled by the 24-hour high-volume sampler at the mobile and the stationary stations.

Table 17. **Mean squares and standard errors (trial) calculated on the basis of a three-way analysis of variance of natural logarithm for the 24-hour high-volume results from 1973/74**

Elements	Mean squares							Standard error of trial
	P	M	D	PM	PD	MD	PMD	
Si	5.6■	209■	1.33■	0.46■	0.52■	0.13	0.26	1.67
S	1.5■	0.4	0.47	0.24	0.32■	0.26■	0.11	1.39
Cl	5.6■	44	1.89	2.05■	1.64■	1.89■	0.73	2.35
K	4.9■	34	1.00	0.69■	0.51■	0.33	0.25	1.65
Ca	5.0■	460■	0.85	1.54■	0.35	0.33	0.29	1.71
Ti	3.8■	197■	1.38	0.76■	0.53	0.55	0.44	1.94
V	3.0■	13	1.77■	0.49	0.67■	0.63	0.36	1.82
Mn	3.4■	141■	2.65	1.33■	1.06	0.65	0.80	2.45
Fe	4.2■	152■	1.88■	0.42■	0.46■	0.34	0.23	1.62
Ni	2.5■	0.2	0.81■	0.61■	0.22■	0.11	0.13	1.43
Zn	4.5■	15	4.56■	0.41	0.64■	0.49	0.29	1.71
Br	3.2■	149■	2.20■	0.84■	0.30■	0.70■	0.20	1.56
Mo	2.9■	77	1.04	1.08■	0.58	0.20	0.56	2.11
Pb	3.0■	113■	2.27■	0.57■	0.37■	0.72■	0.21	1.58
TP	1.3■	30	0.51	0.59■	0.37	0.37	0.30	1.73

P: Period/location. M: Mobile or stationary station. D: Day of the week.
Significance at 5% level is marked with ■.

the concentration levels in the streets and at the stationary stations located some distance from the streets. As the other elements in this group are mainly connected to large particles (cf. section 8.4), the large variation is probably due to losses in sampling pipes at the stationary station. However, further experiments are needed to clarify this phenomenon.

For many elements the main effects of day of the week D (table 20) were not or were only weakly significant and the mean squares were generally small. The highest mean squares were observed for Mn, Fe, Zn, Br, and Pb. The variation with day of the week is shown in fig. 29 and table 20. The interactions were significant in many cases; however, the mean squares were generally small compared with the mean squares of the main effect and the results are adequately described by the mean of each factor. The highest mean squares of the interactions were observed for Cl. One explanation is that the concentrations of Cl were sporadically extremely high due to sea spray and thus they contributed to the mean squares of the interactions.

Table 18. Normalized geometric means of the element concentrations of each location/period for the 2-hour high-volume sampling results from 1974. The geometric means are normalized by division with the geometric mean of all results of the element concerned.

Element	Location/Period												
	1102/1	1100/2	1215/3	1217/4	1335/5	1102/6	1213/7	1331/8	1210/9	1212/10	1101/11	1336/12	1202/14
Si	1.03	1.89	1.01	0.40	0.72	1.03	0.72	1.21	0.78	0.91	0.84	0.26	0.30
S	1.25	1.36	1.27	0.93	1.11	0.99	1.15	1.16	1.09	0.91	1.16	0.56	0.54
K	0.96	1.42	0.73	0.60	1.24	4.41	1.72	1.23	0.77	0.90	1.23	0.28	0.54
Ca	1.17	1.82	0.58	0.56	0.62	1.78	0.88	0.79	0.78	0.60	0.64	0.27	0.50
Ti	1.02	1.49	0.82	1.01	1.34	1.52	0.93	0.75	0.93	0.76	1.00	0.34	0.46
V	1.28	1.53	0.68	0.83	0.44	0.72	0.45	0.93	1.51	1.64	1.83	0.54	1.45
Mn	1.12	1.10	0.86	0.54	0.58	1.08	0.57	1.14	1.81	1.13	1.67	0.48	0.99
Fe	1.07	1.65	0.91	0.76	0.88	1.13	1.06	1.10	1.18	1.09	1.07	0.29	0.73
Ni	1.24	1.79	0.90	1.02	0.78	1.13	0.94	1.33	1.46	1.37	1.67	0.69	1.44
Zn	1.09	1.22	0.70	0.78	0.75	1.67	0.93	0.87	1.25	1.38	1.96	0.31	0.79
Br	1.17	0.97	0.75	1.18	0.76	1.57	1.27	1.48	1.88	1.35	2.15	0.58	1.33
Pb	1.20	1.03	0.83	1.17	0.95	1.43	1.40	1.18	1.52	1.10	2.07	0.45	1.23
TP	1.03	1.56	1.06	0.90	0.66	0.95	1.22	1.01	0.80	0.64	1.11	0.68	0.56

Element	Location/Period												
	1100/16	1215/17	1217/18	1335/19	1102/20	1213/21	1331/22	1210/23	1212/24	1101/25	1336/26	1102/27	1100/28
Si	2.03	0.45	1.58	1.50	3.43	1.32	3.00	1.04	2.60	1.30	0.82	0.65	0.75
S	1.46	0.89	1.73	1.15	1.22	1.23	1.29	0.45	1.31	0.90	0.47	0.63	0.78
K	2.14	0.63	1.88	0.96	2.17	1.20	1.93	0.39	1.20	0.86	0.45	0.54	0.94
Ca	2.07	0.74	2.81	0.97	3.00	1.65	2.50	0.59	1.93	1.43	0.68	1.01	0.82
Ti	2.45	0.44	1.54	1.28	3.39	0.91	2.31	0.76	1.27	0.99	0.61	0.78	0.70
V	0.86	0.78	1.38	0.52	2.02	1.72	1.95	1.11	1.59	1.02	0.42	0.80	0.97
Mn	1.23	1.08	3.92	0.87	1.41	1.02	1.24	0.45	2.50	0.87	0.49	0.93	0.72
Fe	1.81	0.26	1.72	1.51	2.36	1.35	1.99	0.90	2.22	0.81	0.46	0.81	0.53
Ni	1.44	0.92	2.50	0.50	1.63	1.16	1.47	0.74	0.98	0.62	0.27	0.48	0.50
Zn	0.77	0.94	1.51	1.11	0.71	1.52	5.34	0.61	1.05	0.57	0.60	0.93	1.19
Br	1.09	0.81	1.49	1.58	0.60	1.81	1.26	0.55	0.44	0.61	0.34	1.19	0.62
Pb	0.77	0.73	1.51	1.54	0.63	1.52	2.56	0.58	0.46	0.66	0.39	1.10	0.79
TP	0.85	0.99	1.05	1.46	1.06	1.48	1.98	0.71	1.60	0.84	0.81	1.41	0.90

Table 19. Normalized geometric means of the element concentrations of each location/period for the 2-hour high-volume sampling results from 1974. The geometric means are normalized by division with the geometric mean of all results of the element concerned.

Element	Station	
	Mobile	Stationary
Si	2.19	0.46
S	0.97	1.04
K	1.37	0.73
Ca	3.21	0.31
Ti	2.12	0.47
V	1.23	0.82
Mn	1.93	0.52
Fe	1.98	0.50
Ni	1.03	0.97
Zn	1.25	0.80
Br	1.97	0.51
Pb	1.80	0.55
TP	1.36	0.74

Table 20. Normalized geometric means of the element concentrations of each location/period for the 2-hour high-volume sampling results from 1974. The geometric means are normalized by division with the geometric mean of all results of the element concerned

Element	Day of the week						
	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Si	0.78	0.89	1.06	1.14	1.24	1.09	0.89
S	0.86	0.91	0.96	1.10	1.08	1.08	1.03
K	0.80	0.94	0.95	1.15	1.20	1.09	0.92
Ca	0.84	1.02	1.05	1.19	1.12	1.00	0.84
Ti	0.88	0.94	0.99	1.02	1.28	1.11	0.83
V	[illegible]	0.87	1.00	1.14	1.40	0.99	0.96
Mn	0.66	0.85	1.10	1.08	1.36	1.21	0.94
Fe	0.72	0.95	1.18	1.10	1.25	1.09	0.82
Ni	0.80	0.88	1.16	1.01	1.24	1.06	0.92
Zn	0.59	0.94	1.28	1.36	1.33	1.03	0.75
Br	0.73	0.91	1.08	1.25	1.25	1.12	0.80
Pb	0.74	0.87	0.97	1.27	1.30	1.15	0.84
TP	0.94	0.96	0.95	0.95	1.22	1.09	0.91

8.4. Analysis of Variance of the Cascade Impactor Samples

The analysis of variance of the 2-hour cascade impactor samples was performed with respect to the three factors: stage of the impactor, S, hour of the day, T, and location, L. The analysis of variance was limited to include only one of the sampling days. Later on an examination was made to see if there was any inconsistency between the result of the analysis and the results of the other three sampling days. The main object of this analysis of variance was to deduce the size distribution and to find out if there is any interactions between the size distribution and hour (S x T) and location (S x L), e. g. in the form of different size distributions at different locations or hours of the day and night.

The analysis of variance results are summarized in table 21. The main effect of the stage of impactor, S, was highly significant. This result should be evaluated in relation to our efforts to construct the cascade impactor to collect an equal mass of urban, suspended particulate matter$^{9)}$ at each impactor stage. It means that the elements determined were not distributed in the same way as the total particulates. However, the weight of the particulates cannot be determined by the samples collected with the impactor, and so the actual size distribution of total particulates cannot be directly measured and compared with the assumed. The main effect of the diurnal variation, T, was generally consistent with the results found for the

Table 21. Mean squares and standard error (trial) calculated on the basis of a three-way analysis of variance of natural logarithm for 2-hour impactor results from 2 April 1974.

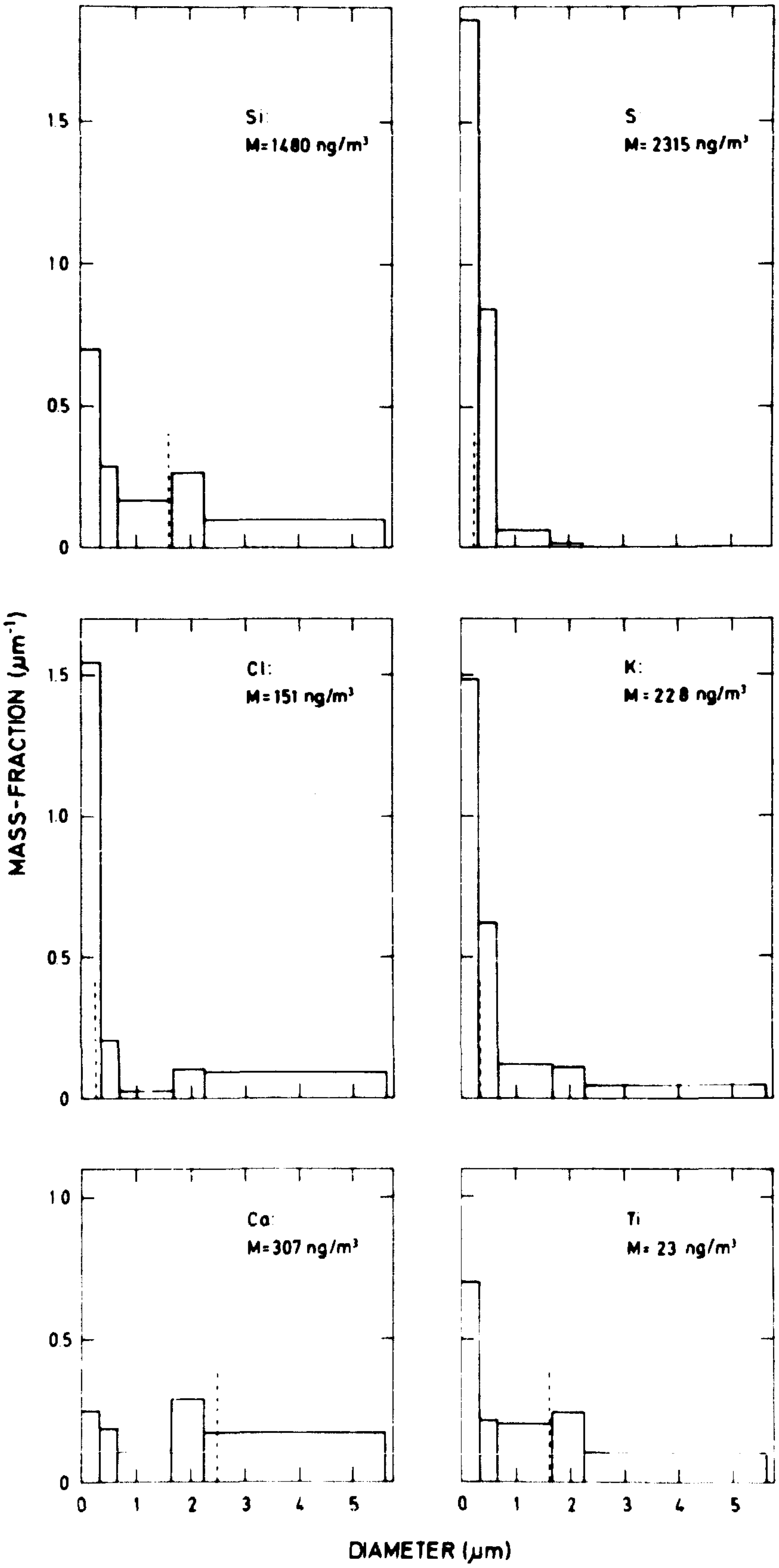
Element	Mean squares							Standard error of trial
	S	T	L	ST	TL	SL	STL	
Si	8*	1.5*	0.2	0.3*	0.1	0.4*	0.08	1.33
S	121*	0.7	2.4	0.5	0.5	0.8*	0.30	1.73
Cl	54*	1.5*	2.2	0.6*	0.5*	2.2*	0.30	1.73
K	23*	0.6*	1.5	0.3*	0.1	0.5*	0.14	1.45
Ca	27*	1.6*	0.5	0.3	0.4*	0.5*	0.17	1.51
Ti	1[illegible]*	1.6*	0.5	0.2*	0.2	0.3*	0.10	1.37
V	97*	5.9*	3.2	0.6	2.3*	2.4*	0.30	1.73
Mn	14*	1.9*	0.5	0.3*	0.3*	0.7*	0.10	1.37
Fe	24*	4.3*	0.5	3.4*	2.7*	6.5*	0.12	1.41
Ni	36*	1.9*	0.8	0.2*	1.1*	0.6*	0.10	1.37
Cu	26*	1.7*	11.3*	0.3	1.6*	0.2	0.30	1.73
Zn	27*	5.0*	50.6*	0.3	4.5*	0.5*	0.20	1.56
Br	34*	4.6*	0.3	0.5*	0.6*	0.4*	0.20	1.56
Pb	69*	5.2*	4.0*	0.3*	3.3*	0.5*	0.19	1.55

S: Stages of the impactor. T: Hour of the day. L:Location.
Significance at 5% level is marked with *

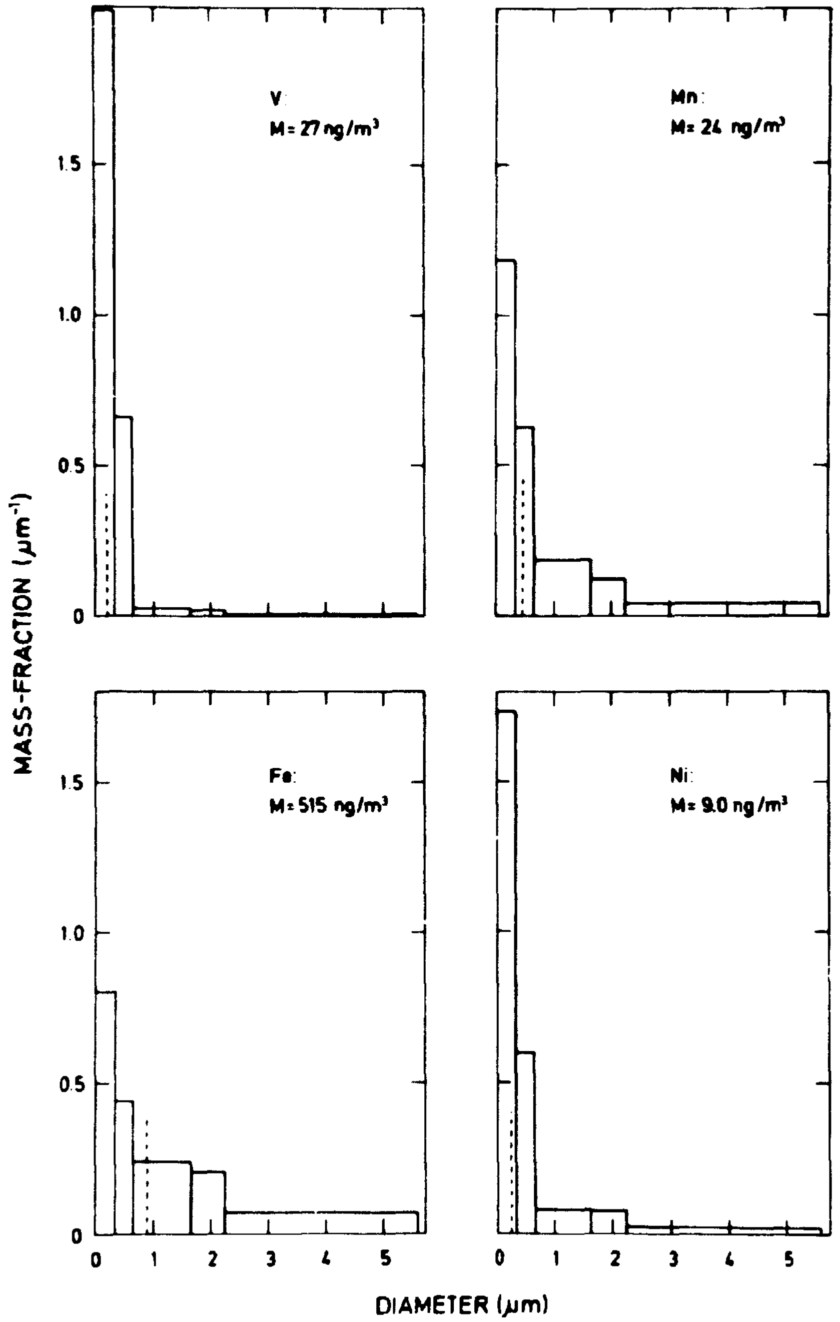
2-hour high-volume samples. Only the mean squares (variation with respect to hour of the day) of V were surprising high. A more detailed examination showed that on the day in question the diurnal variation of V really was considerable and differed at the two sampling locations (relatively high T x L - interaction). The main effects of the location L were small except in the case of Cu and Zn, which fact is due to extremely high concentrations of these metals (a factor of 5-10 higher than the means) for part of the day at the 1331/Glostrup mobile station. In some cases the interactions ST and SL were significant, but the mean squares were relatively small for all elements except Fe. A more detailed examination showed that the size distribution of the Fe-concentration differed at different hours and locations; but in all measurements the concentrations of Fe at the different stages did not deviate more than a factor of 2. This means that the size distribution of Fe is relatively broad. For all other elements analyzed, the interactions were small, and thus no evident variations were observed of the size distribution with hour and location. Figs. 30 - 43 show the size distributions due to the main effect S calculated as the geometric means of each stage. The distributions were normalized with the total weight of the elements and divided by the diameter interval of each stage. Thus the concentration of an element in a given size interval is the area below the curve multiplied by the mean.

The mass median diameters (MMD) of each element were determined by the intersection with 50 percentile in a plot of the cumulative frequency distribution in a logarithmic probability coordinate system and linear interpolation (log-normal distribution) between the points. The MMD's are indicated by dotted lines in the graphs.

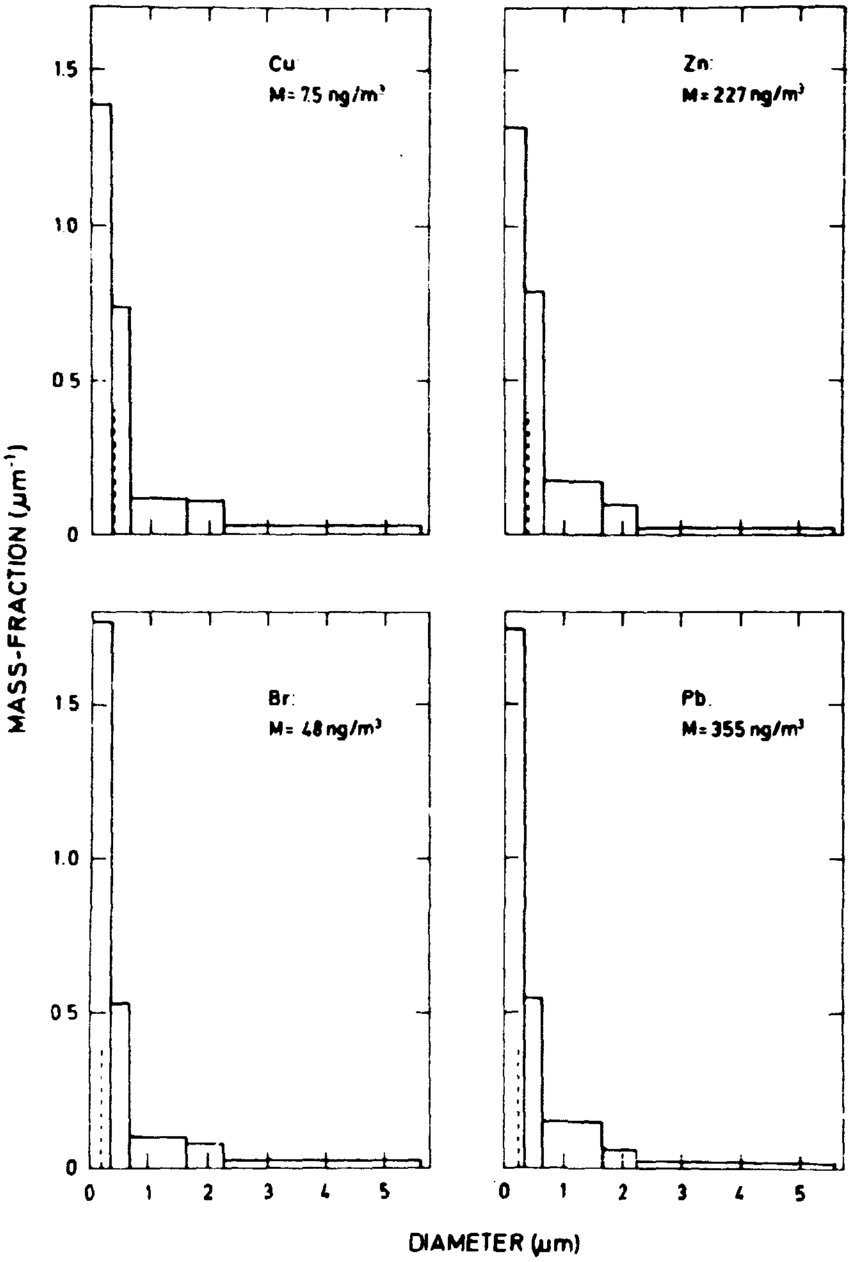
The main results of the determination of size distributions were that all elements presumably originating from combustion, i. e. S, V and Ni from fuel oil and Br and Pb from automobile exhaust, were principally attached to small particles. On the other hand, elements believed to be produced by wind-blown dust or mechanically-produced aerosols, i. e. Si, Ca, Ti, and Fe, were distributed nearly uniformly in the size interval 0-5.6 microns. As mentioned later (cf. section 8.7), large amounts of these elements were attached to even larger particles. The other elements showed size distributions lying between the above extremes. The other 2-hour and the 24-hour impactor results roughly confirm the results of the analysis of variance. No systematic seasonal variation was observed



Figs. 30 - 35. Geometric mean for every stage of the impactor on 2 April 1974 of the concentrations of Si, S, Cl, K, Ca and Ti determined by 2-hour sampling with the cascade impactor. The means are normalized with the total concentration (M) of the elements and the size interval of the stages. The mass median diameters (MMD) of the collected particulates are marked with dotted lines.



Figs. 36-39. Geometric mean for every stage of the impactor on 2 April 1974 of the concentrations of V, Mn, Fe and Ni determined by 2-hour sampling with the cascade impactor. The means are normalized with the total concentration (M) of the elements and the size interval of the stages. The mass median diameters (MMD) of the collected particulates are marked with dotted lines.



Figs. 40-43. Geometric mean for every stage of the impactor on 2 April 1974 of the concentrations of Cu, Zn, Br and Pb determined by 2-hour sampling with the cascade impactor. The means are normalized with the total concentration (M) of the elements and the size interval of the stages. The mass median diameters (MMD) of the collected particulates are marked with dotted lines.

for any elements in the 24-hour results. The most evident discrepancy was observed at station 1331/Glostrup, where very large concentrations of the metals Cr, Zn, Cd, Sn, and Pb were found sporadically in particles with diameters between 1 and 3 microns. They probably originated from a factory in the neighbourhood. Another characteristic type of episode was observed when the north wind was blowing. In such cases the concentration of Cl on particles with diameters between 2 and 3 microns was extremely high (4-5 $\mu g/m^3$) at all stations simultaneously, probably due to sea spray from the Kattegat.

In conclusion, the main features of the size distributions of the different elements on particles below 5.6 microns in aerodynamic diameter are, apart from the special phenomena mentioned, described by figs. 30-43.

8.5. Correlation Between Elements

The calculated correlation coefficients between the elements found in the 24-hour H.V. samples from the mobile station are listed in table 22. The total number of samples included was 128. Only values calculated on the basis of more than 64 of the samples are listed. As a consequence of the great number of degrees of freedom, the 99% probability level corresponds to $r_{ij} \simeq 0.2$, while $r_{ij} \simeq 0.5$ corresponds to a probability for positive correlation of 99.999%. The uncertainties on r_{ij}, calculated on the basis of the scatter of the points, were approx. $\pm$ 0.15 for values below 0.5 and smaller for larger values. With a few exceptions the tabulated values were representative for all the results.

Table 22. Correlation coefficients (x 100) between elements of 24-hour high volume sampling results from the mobile station 1973/74

	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Mo	Cd	Sn	Sb	Pb	TP
Al	■	73	26	6	35	47	77	17	6	23	58	13	0	12	14	38	1	-	3	15	42
Si		■	47	30	58	77	92	19	23	54	88	21	15	28	8	56	19	1	8	8	63
S			■	24	47	51	56	35	33	45	59	46	33	33	22	32	28	12	12	42	64
Cl				■	2	17	25	4	14	18	35	2	5	4	13	13	-	-	-	14	26
K					■	64	61	21	34	41	60	35	28	40	10	34	17	35	8	16	46
Ca						■	85	29	61	59	83	33	45	42	38	65	30	25	9	37	59
Ti							■	27	38	52	89	27	31	32	18	64	20	8	8	22	70
V								■	-	39	41	85	40	48	26	27	35	33	19	31	23
Cr									■	67	45	-	-	47	53	-	-	-	-	48	-
Mn										■	67	34	21	39	10	47	19	6	2	10	43
Fe											■	39	40	47	30	69	40	11	6	33	74
Ni												■	42	44	29	30	39	-	15	34	25
Cu													■	53	70	55	55	-	26	76	40
Zn														■	41	42	57	66	48	45	38
Br															■	41	66	48	30	93	32
Mo																■	37	-	10	43	58
Cd																	■	-	43	75	40
Sn																		■	-	54	-
Sb																			■	32	20
Pb																				■	42
TP																					■

Regression plots were drawn in several cases; examples of these are shown on fig. 44, with regression lines plotted. Apart from simple linear correlation, no covariance was observed on the plots except in the case of Br and Pb in the 2-hour high-volume measurements at station 1331/Glostrup (fig. 44). This was probably due to a combination of local industrial and motor car pollution (see below).

Positive correlations were found for the majority of element combinations. This is probably due to the general influence of the meteorological conditions. Some elements were, however, extremely closely correlated, $r_{ij} \simeq 0.8$. The greatest correlation coefficients was found within the three groups: a) Si, Ti and Fe, b) V, Ni, and c) Br and Pb. The elements in a) are traditionally identified as soil elements, while two of the main sources of anthropogenic pollution, oil combustion and motor car exhaust, contribute compounds containing elements in groups b) and c) respectively.

In order to determine whether some elements originate from one of the three sources mentioned, the average was calculated of the correlation coefficients between the elements in the three groups and the other element (table 23.).

Ti did not correlate particularly well with Si and Fe in the samples from the 24-hour measurements at the stationary station. Ti was therefore in this case substituted by Ca in group a). The Br-Pb correlation was not evident in the measurements at station 1331/Glostrup; the reason may be local pollution from an industrial area in the vicinity. Another group can here be formed of Sn, Sb and Pb.

Elements that in general correlated much closer to one group than to the two other were selected. The following elements may be placed in the soil group: Al, Si, K, Ca, Ti, Cr, Mn, and Mo. Moreover, close correlation was found to the total amount of dust, which might indicate that a major part of this dust is soil products. No elements other than V and Ni could be placed in the oil combustion group. S was not found in this group. This is probably because the sulphur is emitted as gaseous SO_2, while the particulate sulphur is formed from the gas within some hours or a few days. Cd and Cu were apparently connected with the motor car group together with Br and Pb, but the data permitted no definite conclusions. The special 1331/Glostrup group, Sn, Sb and Pb, was complete ' by Zn and Cl.

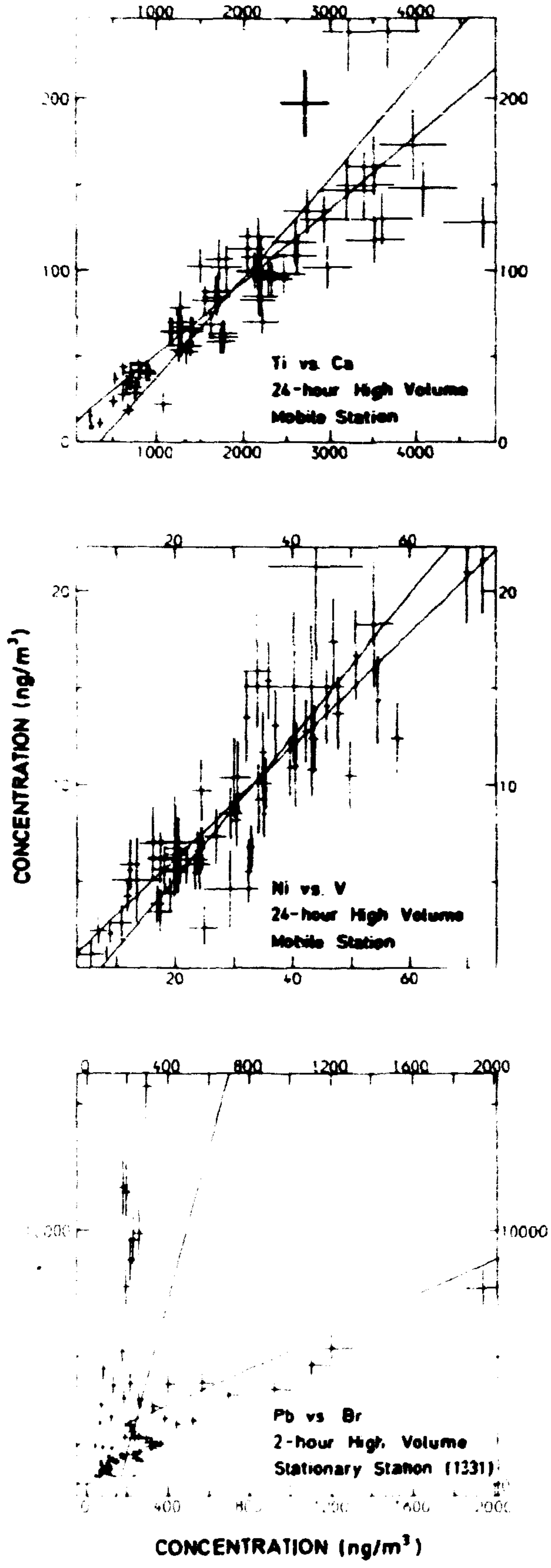


Fig. 44. Regression plots of Ti-Ca (24-hour high-volume samples, mobile station), Ni-V (24-hour high-volume samples, mobile station) and Pb-Br (2-hour high-volume samples, station 1331/Glostrup). Two regression lines, determined on the basis of the two-element concentration as independantly variable, are drawn in each plot.

Table 23. The average of the correlation coefficients between the concentration of the elements in the three groups, a) (Si, Ti and Fe), b) (V and Ni) and c) (Br and Pb) and the concentration of the other results. The calculations were performed for 24-hour and 2-hour high volume sampling results.

Element Group		24-hour high-volume		2-hour mobile station					
			Mobile Station	1217	1102B	1331	1211	1101	1336
Al	a	0.69	-	-	-	-	-	0.83	0.46
	b	0.15						0.09	(0.25)
	c	0.15						0.69	0.16
Si	a	0.90	0.80	0.88	0.97	0.94	0.88	0.93	0.75
	b	0.20	0.58	0.16	0.08	0.61	(0.55)	0.20	(0.28)
	c	0.15	0.02	0.54	0.59	0.17	0.01	0.68	0.12
S	a	0.54	0.52	0.54	0.34	0.76	0.69	0.02	0.40
	b	0.40	0.55	0.36	0.09	0.82	(0.37)	0.43	(0.35)
	c	0.15	0.40	0.27	0.33	0.23	0.07	0.12	0.55
Cl	a	0.30	0.11	0.08	(0.42)	0.31	0.10	-	0.24
	b	0.03	0.22	0.10	(0.39)	-	(0.56)	-	-
	c	0.15	0.02	0.03	(0.52)	0.78	0.07		0.56
K	a	0.59	0.62	0.89	0.94	0.94	0.85	0.79	0.05
	b	0.28	0.49	0.26	0.11	0.71	(0.35)	0.19	(0.11)
	c	0.13	0.41	0.51	0.55	0.17	0.08	0.62	0.32
Ca	a	0.82	0.79	0.92	0.74	0.84	0.63	0.89	0.11
	b	0.31	0.72	0.18	0.06	0.62	(0.40)	0.24	(0.03)
	c	0.37	0.43	0.60	0.74	0.20	0.04	0.60	0.35
Ti	a	0.90	0.61	0.93	0.97	0.94	0.85	0.91	0.75
	b	0.27	0.35	0.27	0.21	0.65	(0.26)	0.22	(0.46)
	c	0.20	0.03	0.56	0.61	0.18	0.20	0.35	0.04
V	a	0.29	0.64	0.31	0.21	0.57	0.43	0.28	0.28
	b	0.85	0.79	0.78	0.86	0.92	-	0.82	-
	c	0.28	0.34	0.31	0.06	0.18	0.20	0.35	0.04
Cr	a			-	-	-	-	-	-
	b								
	c								
Mn	a	0.58	0.62	0.77	0.85	0.74	-	0.49	0.35
	b	0.36	0.59	0.26	0.10	0.48		0.49	(0.23)
	c	0.10	0.05	0.42	0.51	0.16		0.44	0.08
Fe	a	0.88	0.82	0.91	0.97	0.91	0.85	0.93	0.69
	b	0.40	0.66	0.31	0.12	0.70	(0.48)	0.43	(0.42)
	c	0.31	0.24	0.60	0.62	0.20	0.17	0.79	0.45
Ni	a	0.29	0.66	0.18	0.07	0.74	-	0.28	-
	b	0.85	0.79	0.78	0.86	0.92	-	0.82	
	c	0.31	0.34	0.24	0.07	0.16		0.40	
Cu	a	0.28	-	-	-	-	-	-	-
	b	0.41							
	c	0.73							
Zn	a	0.36	0.19	0.24	0.06	0.08	0.22	0.67	0.16
	b	0.46	0.33	0.20	0.08	0.05	(0.15)	0.28	(0.25)
	c	0.43	0.49	0.19	0.11	0.68	0.09	0.64	0.03
Br	a	0.19	0.21	0.60	0.61	0.55	0.10	0.71	0.28
	b	0.27	0.31	0.28	0.06	0.28	(0.14)	0.41	(0.03)
	c	0.93	0.83	0.92	0.96	0.26	0.88	0.76	0.74
Mo	a	0.63	0.50	0.58	0.26	0.57	-	0.23	-
	b	0.28	0.69	0.27	0.15	0.25		0.02	
	c	0.72	0.20	0.37	0.33	0.35		0.37	
Cd	a	0.23	-	-	-	0.39	-	-	-
	b	0.38				0.12			
	c	0.70				0.30			
Sn	a	0.07	0.14	[illegible]	-	0.23	-	0.78	-
	b	0.33	0.12	0.12		0.13		0.23	
	c	0.51	0.19	0.34		0.78		0.71	

8.6. Element Balance Account

The elements mentioned in the previous sections make up only a fraction of the total weight of particulates. However, it is interesting to examine how large this fraction is, or better how large is the share of particulates which can be accounted for by the elements and their compounds. Hereby an upper limit for the remaining share of the particulates can be estimated. Most of the elements determined are metals and other electro-negative elements; they are probably mostly bound as salts or oxides. The exceptions are S, Cl and Br. As a first approximation it was assumed that the composition of the chemical compounds was as shown in table 24. The electro-negative elements were assumed to be bound as oxides and S as SO_3. S is probably present as sulphates, but for calculation purposes, these can be regarded as a combination of oxides and SO_3. Therefore, it

Table 24. Assumed compounds and percentages of total weight of particulate matter of 24-hour high volume samples from the mobile station 1973/74

Compound	Percentage of total weight
Al_2O_3	2.4
SiO_2	10.3
SO_3	11.8
NaCl	3.2
K_2O	0.82
CaO	3.1
Ti_2O_3	0.14
VO_2	0.083
MnO_2	0.085
Fe_2O_3	2.4
NiO	0.024
CuO	0.054
ZnO	0.61
MoO_2	0.006
CdO	0.010
SnO_2	0.082
SbO_2	0.080
PbO, PbClBr, $PbBr_2$	3.9
Sum	37.7

is unnecessary to distinguish between different sulphates. Cl was assumed to be bound as sea salt and in lead compounds from automobile exhaust. Also Br was assumed to be found in the lead compounds. Other salts, e.g. nitrates and carbonates, were not taken into account in the calculations.

The results of the calculations on 24-hour high-volume data from the mobile stations are shown in table 24. The presented results are averages of the whole measuring period and of all measuring localities. Arranged in order of size, the most important contributions are: S, Si, Pb, Cl, Ca, Fe, and Al.

It is worthwhile noticing that the contribution from lead compounds, which constitute approximately half of the particulates from automobiles, was higher than found in section 6.4. This is probably due to the different sampling positions; the mobile station was normally located near the pavement, while the OECD stations were located some hundred meters from the streets.

Besides the above elements, C constitutes an important share of the particulates. Another investigation has shown that C constitutes approximately 40%. Hence most of the particulates can be totally accounted for.

The table also shows the standard deviation of the per cent contribution sum. This standard deviation was approximately 1/4 of the sum though the standard deviations of the individual elements were 1/2 or more of the concentrations of the elements.

Table 25 presents results of the calculations of the data from the mobile and the stationary stations for the two six-month periods separately. Also shown are the analytical mean errors calculated on the basis of the standard error of the element and weight determinations and the standard deviations of the sums. It is important to notice the very high standard deviations of the sums from the stationary stations. A more detailed examination of the individual calculations of these data shows several sums above 100% and below 10%. It is not definitely possible to explain these results on the basis of the measurements, but some possible explanations are: 1) sampling faults, 2) analytical errors, or 3) weight errors. An indication of the most probable explanation could be given by comparison between the data from the mobile and the stationary stations where sampling was performed simultaneously. The days with especially high (>100%) or low (<10%) sums were picked out and also the ratios between the concentrations of weight of particulates, S, Si and Pb, respectively, at the mobile and at the stationary stations. These ratios were compared with the mean ratios (cf. section 8.1). In all cases the ratios of the weight of particulates were found to be

Table 25. **Calculated sum of averages of different groups of samples**

Sample type	Sum of averages (per cent)	Average analytical S.D. (per cent)	S.D. of the results (per cent)
Mobile station 1973	37.9	4.0	10.5
Mobile station 1974	37.5	3.6	9.1
Stationary station 1973	67.6	11.5	72.3
Stationary station 1974	36.1	6.1	23.1

a factor of 2-4 smaller than the mean for sums below 10% and a factor of 2-15 higher than the mean for sums above 100%. For the elements the deviations from the means were smaller and did not systematically agree with the high and low sums. This might indicate that the weighing is more uncertain than stated for the stationary stations where the total amount of particulates was smaller (a factor of 8) than at the mobile station.

8.7. Comparison Between the Different Types of Sample

Disagreements between results of analyses of particle samples collected simultaneously at the same location by different types of sampling equipment may arise for a variety of reasons, e.g. sampling faults, different particle size fractionation in the sampling equipment, inexpedient sample handling, systematic errors of the analysis or uncertainty of the analysis. Therefore, a more detailed investigation of the disagreements leads not only to an evaluation of the consistency of the results, but possibly also to additional information on the particulates and to the selection of the most important reasons for the disagreements.

In the present sampling programme direct comparisons can be made between the 24-hour and the corresponding twelve 2-hour high-volume samples from the mobile station and also the 2-hour high-volume and 2-hour impactor samples from the mobile station. The comparisons were made by the linear correlation coefficient and by the mean and standard deviation of the ratio between the results of the two types of sample in question.

The 24-hour and 2-hour high-volume samples were collected simultaneously at the mobile station in six different positions (● in fig. 1) during the first six months of 1974. The sampling characteristics of the two equipments were very alike, only the inlet velocities differed, which resulted in different cut-off diameters. However, for both sampling equipments cut-off diameters are very high (>100 microns, cf. table 2) and essentially no mass is normally found in that high range of particle size; therefore both sample types are believed to include all the particulate matter. The average concentrations of twelve 2-hour sampling periods were compared with the concentration determined by the corresponding 24-hour samples. Analytical results below detection limits were omitted. Only days with less than two missing 2-hour results were included in the investigation. For each element and the weight of particulates, table 26 shows the correlation coefficients, the average ratio between 2-hour and 24-hour results and the standard deviation of the ratio, as well as the standard deviation of the 24-hour averages of the 2-hour results. The interpretation of the correlation coefficient is uncertain if the population is not normally distributed and/or the standard deviation (variation) of the true results is small compared with the uncertainty of the analyses. This is the reason why the standard deviation of the results and an estimated average of the analytical uncertainty are included in the table. As a supplement to the correlation coefficient, the ratio and standard deviation of the ratio are also given.

In all cases the average ratios were near one. For all elements the ratios were either not or only slightly significantly less than one and for the weight of particulates the ratios were slightly higher than one. This indicates small systematic errors in sampling, filter handling or the analysis. For most of the elements the standard deviations of the ratios were larger than expected from the analytical uncertainty. Only for V and Ni, the standard deviations of the ratios are determined by the analytical uncertainty. For most of the elements the correlation coefficients were 0.7 - 0.9. For V and Ni they were very small (0.1 and - 0.1) and also for Ca and the weight of particulates they were relatively small (~0.55), which might be due to the relatively large analytical uncertainty compared to variations of the results.

Table 26. Comparison between 2-hour and 24-hour high-volume samples from the mobile station in 1974.

Element	Ratio 2-hour/24-hour	S.D. of ratio (per cent)	S.D. of results (per cent)	Average analytical uncertainty (per cent)	Correlation coefficient	Number of samples
Si	0.85	28	87	11	0.88	29
S	0.97	26	56	11	0.78	30
K	0.89	35	71	11	0.80	24
Ca	0.77	40	67	12	0.55	22
Ti	0.92	40	66	20	0.82	24
V	1.12	55	61	35	0.10	15
Mn	0.84	39	75	20	0.68	14
Fe	0.86	28	69	11	0.88	30
Ni	0.86	48	71	40	-0.13	10
Cu	0.98	42	152	15	0.76	26
Br	0.80	55	96	12	0.84	28
Pb	0.92	42	87	12	0.68	30
TP	1.27	44	34		0.57	27

In conclusion, the consistency between the 24-hour and 2-hour high-volume results was, for most of the elements, influenced by factors other than the analytical uncertainty (e.g. sampling and handling). Therefore the standard deviations of the ratios between the two types of results were relatively large, whereas the average ratios were near one.

The 2-hour high-volume and 2-hour impactor samples were collected simultaneously by the mobile station at 1101/Frederiksberg and 1331/Glostrup. Only particles with aerodynamic diameters below 5.6 microns were collected by the impactor, unlike the high-volume sampler where all particles smaller than ~100 microns (cf. table 2) were collected. In table 27 the same figures as in table 26 are shown for the two impactor sampling days of 1974. The ratios between the high-volume and the impactor results were larger than one. They were smallest for elements attached to small particles, i.e. S, V, Br and Pb (cf. section 8.4), and largest for elements attached to larger particles, i.e. Si, Ca and Ti. The ratios of Ni and Cu were not in accordance with this, which disagreement is possibly due to the few results above the detection limits and the high analytical uncertainty.

Apparently, large amounts of particulate matter are attached to large particles (>5.6 microns), especially in the case of some elements. For each element the percentage of mass attached to particles smaller than 5.6

Table 27. Comparison between 2-hour high volume and 2-hour impactor results from the mobile station.

Element	Ratio HV/Imp	S.D. of ratio (per cent)	S.D. of results (per cent)	Correlation coefficient	Number of samples	Mass below 5.6 microns (per cent)
Si	15.0	70	12	0.54	22	6.7
S	1.54	35	12	0.89	24	64.9
K	6.4	62	12	0.76	23	15.7
Ca	11.4	89	15	0.64	23	8.8
Ti	14.7	69	30	0.86	24	6.8
V	1.96	38	40	0.96	14	5.1
Mn	5.5	79	25	0.70	18	18.2
Fe	6.8	53	12	0.75	24	14.7
Ni	5.3	94	45	0.76	11	19.0
Cu	18.0	74	45	0.73	11	5.6
Zn	3.5	67	20	0.97	22	28.9
Br	1.71	51	15	0.79	24	58.5
Pb	1.55	47	15	0.72	24	64.5

microns was calculated. This is also shown in table 27. On the whole these results are consistent with ref. 24), which states that approximately 60% of the volume (mass) of urban aerosols is attached to particles larger than 5.6 microns.

The correlation coefficients and the standard deviations of the ratio should be evaluated in connection with the above considerations. The correlation coefficients concern the whole amount of particulate matter from the high-volume samples, but only the smaller particles of the impactor samples. Therefore, the correlation coefficients were smaller for some of the elements attached to large particles. Correspondingly, the standard deviations of the results were largest for these elements (apart from Ni and Cu) because the impactor samples only include a part of the particulate matter.

In conclusion, the comparison between 2-hour high-volume samples and 2-hour impactor samples yielded additional information on the content of different elements in large particles. To a lesser extent it also yielded information on the experimental uncertainty.

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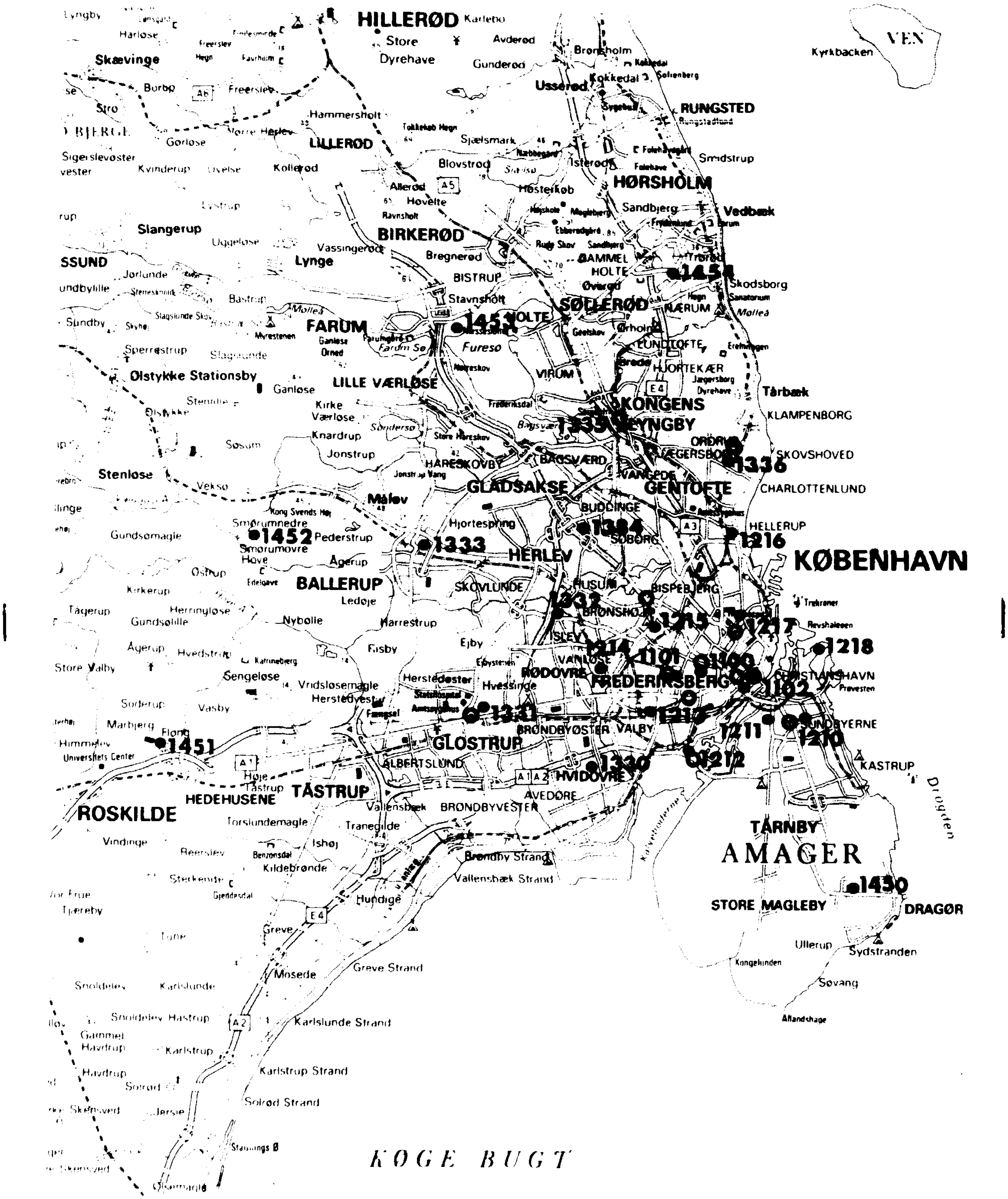

Fig. 1. The sampling network of Greater Copenhagen. The OECD stations are indicated by ●. The sampling positions of the mobile station are marked by **O** (24-hour sampling only) and ● (2-hour and 24-hour sampling). The corresponding stationary stations are connected to these with solid lines.

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