NILU TR : 18/85
REFERENCE: E-8557
DATE : NOVEMBER 1985

THE CHEMICAL COMPOSITION OF AEROSOLS IN ZABADANI VALLEY, SYRIA

Jozef M. Pacyna

NORWEGIAN INSTITUTE FOR AIR RESEARCH
P.O. BOX 130, N-2001 LILLESTRØM
NORWAY

ISBN 82-7247-647-9

ABSTRACT

The chemical composition of aerosols measured during a short period in 1985-08 in Zabadani Valley, near Damascus, Syria, is presented. Very high concentrations of several anthropogenic elements in some samples indicate transport of air pollutants likely from industrial sources in the Damascus area, particularly from cement and sugar production, glass, ceramic and textile manufacturing, and motor vehicle traffic. Natural elements due to windblown dust are present in all samples. More measurements and emission estimates are required in order to study source-receptor relationships for air pollutants in the Damascus region.

LIST OF CONTENTS

THE CHEMICAL COMPOSITION OF AEROSOLS IN ZABADANI VALLEY, SYRIA

1 INTRODUCTION

One of the main tasks of air pollution studies today is to assess the contributions of source emissions to the deposition of pollutants at receptors in urban and remote areas. Trace elements seem to be a very useful tool for assigning source regions (or source groups) to the materials sampled at the receptors. During the past few years there has been a growing interest in using the multi-elemental composition of the areosol as its own tracer, i.e., to indicate its area of origin even after long-range transport (see, for example, Husain et al., 1983; Rahn and Lowenthal, 1984; Pacyna, 1985a; Olmez and Gordon, 1985).

Size-differentiated aerosol sampling may add greatly to the understanding of the role of long-range transport in source apportionment. Today, it is generally agreed that the mass-size distributions of the aerosols in urban and highly industrialized areas normally show two modes (Whitby, 1978). Fuel combustion and many industrial processes initially produce a large number of particles in the <0.05 μm diameter size range, as does the conversion of gaseous components to particulate phase. Shortly after emission, these very small particles tend to agglomerate and end up in the ca. 0.1 to 2.5 μm diameter size fraction, the so-called accumulation mode. Because of reduced mobility further agglomeration and growth becomes a very slow process. Particles >2.5 μm are generally produced by various mechanical dis integration processes, for which deposition by gravity cannot be neglected. In remote areas most of these particles are likely to be due to natural processes active in the vicinity of the measuring station (e.g., windblown dust, sea salt particles).

This report presents first results from aerosol physical property and chemical composition measurements, carried out in Zabadani Valley, near Damascus, Syria, during August 1985. The aim of the measurements was to examine whether (1) Zabani is a mixing zone for particulate air pollutants

from anthropogenic sources in Damascus and nearby urban areas and natural emissions of drylands and desert, and whether (2) Syria is a mixing zone of long-range transported anthropogenic pollutants from other countries in the Middle East and Europe and natural emissions from the deserts of Arabia and Africa.

2 EXPERIMENTAL

Samples were collected on the roof of the Al Faissal Hotel in the Zabadani Valley, about 40 km west of Damascus, Syria. A two filter (stacked) sampler was used to collect coarse and fine particle fractions in August 1985, during a session of the Arab School of Science and Technology. The 50% cut-points of the two filter sampler, operated at 8 l min^{-1} was 2 μm aerodynamic diameter. The coarse particle separator was a 47 mm diameter, 5.0 μm pore size Nuclepore filter followed by a 0.4 μm pore size Nuclepore back-up filter, both clamped in a 47 mm dia. plastic dual filter holder.

Sampling began on 1985-08-04 and continued until 1985-08-10. The chemical composition of aerosols collected on 26 coarse/fine particle filter sets was determined by atomic absorpton spectrophotometry (AAS), instrumental neutron activation analysis (INAA), and particles induced X-ray emission (PIXE). In addition, SO_4^{2-} NO_3^-, Cl^- and Mg^{2+} concentrations were measured by ion chromatography (IC). The Norwegian Institute for Air Research (NILU) provided financial support for the analyses of the 26 filter sets by AAS, the results of which are reported here. The relevant information is given in Table 1.

Aerosol number size distributions were measured by an OPC in 5 size ranges >0.5 μm dia. on 1985-08-07. Lumped number concentrations for all particles >0.5 μm diameter were obtained in the period 1985-08-06 to 1985-08-08.

3 RESULTS AND DISCUSSION

The concentrations of Mn, Zn, Pb, Cd and Ni in fine (<2.0 μm diameter) and coarse (>2.0 μm diameter) fractions of particles are shown in Figure 1, and

concentrations of SO_4^{2-}, NO_3^-, Cl^- and Mg^{2+} in Figure 2. Very clear concentration peaks of all trace elements in fine fraction were observed on 1985-08-07 between 16:16 and 22:22 h local time. The element peaks were duplicated by enhanced concentrations of SO_4^{2-} in the fine fraction of particles. Very high concentrations of anthropogenic Cd, Pb, Ni, Zn and Mn suggest that the pollutants measured at Zabadani on 1985-08-07 had originated in industrial regions. Since no data exists so far on wind speed and direction during sampling, it is difficult to judge what emission sources may have contributed to this pollution load. The extremely high Cd concentrations may implicate sources in Damascus and its surroundings. No quantitative emission estimates from the various sources in the area exists. Based on visual observations, the following sources can be suspected as the main contributors of trace elements: (1) cement plants in Damascus and Adra, (2) glass and ceramic factory, (3) textile production, and (4) sugar producing plant. The latter is important due to the energy-intensive technology of sugar production. Air pollutants from the cement plant consist mainly of non-toxic dust, emitted as very fine particles. However, there are certain processes in the cement plants emitting dust containing several trace elements: the feed, the fuel-fired kiln, and the clinker-cooling and handling systems. In some of these, a mixture of shale and limestone is exposed to high temperatures, resulting in emission of volatile elements, particularly Cd and Pb. The emission rates of these elements during cement production are affected by: (1) the type of production process (wet or dry), (2) the type of fuel used in the grinding mill, (3) the type of fuel used for kiln firing, and (4) the type of emission control equipment. The author has reviewed recent anthropogenic source emission literature and calculated emission factors (Pacyna, 1985b), some shown in Table 2. Volatile elements, such as Cd and Pb, evaporate during the cement production process and condense as fine <0.1 µm diameter particles, subject to atmospheric transport.

There were rather low particle number concentrations measured in the >0.5 µm dia. fraction on 1985-08-07 (see Table 3). However, this data does not provide information about particle concentrations in the <0.5 µm dia. fraction, and neither does the particle size distribution shown in Figure 3. The bimodal curve in Figure 3 with two modes in the 0.5-1.0 and 2.0-5.0 µm dia. ranges is very similar to this suggested by Whitby (1978) for aerosols in urban and industrialized regions. Thus, it can be speculated that, on 1985-

08-07 Cd and Pb and several other elements were emitted from industrial sources in the Damascus area and transported as fine particles. This hypothesis should be regarded tentative, because no meteorological data are available for this region.

Sources other than cement plants may also contribute to the pollution load measured at Zabadani on 1985-08-07. The most significant source of particulate lead emissions in glass production is the regenerative furnace during the melting process, for which the uncontrolled Pb emission factor is 2.5 kg t^{-1} glass produced (U.S. EPA, (1979)).

Enhanced concentrations of Pb in both particle size fractions were observed on 1985-08-09 and 1985-08-10. Since none of the other elements showed similar behaviour, gasoline combustion must be considered as a major contributing source. Increased concentrations of NO_3^- in coarse particles can support this suggestion, since the internal combustion engine is the main source of the NO_X emissions (see, e.g., Pacyna, 1985c).

The natural constituents measured in this study included Mn, Zn, SO_4^{2-}, NO_3^-, Mg^{+2} and Cl^-, and were collected mostly in the coarse particle fraction. Windblown dust can be attributed as the major source of these constituents, but Cl^- is probably of sea-salt origin.

It is difficult to explain the presence of Cd in coarse particles. Enhanced Cd concentrations observed from time to time are likely due to anthropogenic sources. Combustion of residual oil in the hotel and then emissions of Cd through a small stack cannot be excluded. If so, low concentrations of Ni are surprising, since the residual oil combustion is usually a major source of Ni emissions.

A comparison of concentrations measured on 1985-08-07 with the concentrations observed in some urban and industrial locations in the world is presented in Table 4. Although concentrations measured during a few hours at Zabadani and mean yearly values in the United Kingdom or Brussel are not strictly comparable it may be interesting to note that the values observed at Zabadani on this one occasion are within the annual concentration range measured in urban and industrial areas.

4 CONCLUDING REMARKS

The very limited results presented here do not satisfy all the objectives, specified in the introduction of this report. They show merely a way of data interpretation with respect to source-receptor relationships for air pollutants on regional and local scales. Future work should include: (1) emission survey of SO_2, NO_x and selected trace element sources on local and regional scale, and (2) measurements of aerosol parameters over longer periods at several locations in the Damascus area and near the remote deserts.

A comprehensive, reliable emission inventory requires a substantial amount of accurate, up-to-date technical data. In many countries these data are available on source categories, pollutant features and locations of industrial sources and areas. These pertain to both nation-wide emission surveys (regional scale) and single source area surveys (local scale), e.g., Damascus. The assessment of the atmospheric emissions can be based on information from obtained questionnaires and direct measurements. Then emission factors and permissible emission rates can be calculated for main source categories and certain individual processes, and direct measurements can verify the estimates. Such data could be used to predict changes in emission patterns in Syria, due to future addition of new air pollution sources, expansion of existing ones, or improved control strategies. Useful indications may also be gained for the design and management of air quality monitoring networks in Syria.

Measurements during extended periods should be carried out at few locations within and outside Damascus to provide a broader information on the chemical composition of aerosols. Concentrations of a number of additional elements (other than those reported here) are now being determined by the INAA and PIXE analytical methods, at the University of Gent, Belgium. However, more information will be required (in regard to the number of samples and a number of stations) in order to assess source-receptor relationships for air pollutants in the Damascus region. Then the emission data can be related to measured air concentrations with the help of simple model calculations and wind sector statistics (e.g., Pacyna et al., 1984; Pacyna, 1985a). This would allow to select a group of elements for further appliction in source

apportionment. Meteorological parameters, such as wind speed and direction, air temperature, and relative humidity should be made available as well.

The model estimates would help to better understand air pollutant deposition processes under the dry conditions characteristic of Syria.

5 ACKNOWLEDGEMENTS

The author thanks Professor John W. Winchester, Florida State University, FL, U.S.A., for his encouragement to participate in the Damascus Air Pollution Experiment (DAPEX); the Arab School of Science and Technology and particularly Drs. Nabil Harfouch, Ayman Habal, Fawza Monem and Fouad Abo Samra, for providing the opportunity to carry out the measurements; the Norwegian Institute for Air Research (NILU) for financing the AAS analyses, and Dr. Val Vitols, NILU, for helpful discussions.

6 REFERENCES

Husain, L., Webber, J. and Canelli, E. (1983) Erasure of midwestern Mn/V signature in an area of high vanadium concentration. J. Air Poll. Contr. Assoc., 33, 1185.

Kowalczyk, G.S., Choquette, C.E. and Gordon, G.E. (1978) Chemical element balances and identification of air pollution sources in Washington, D.C., Atmos. Environ., 12, 1143-53.

Kretzschmar, J.G., Delespaul, I. and De Rijck, Th. (1980) Heavy metal levels in Belgium: a five year survey. Sci. Total Environ., 14, 85-97.

McInnes, G. (1979) Multi-element survey: analysis of the first two years' results. Rept. LR 305 (AP) Warren Spring Laboratory, Stevenage, Herts, U.K.

Olmez, I. and Gordon, G.E. (1985) Rare earths: atmospheric signatures for oil-fired power plants and refineries, Science, 229, 966-968.

Pacyna, J.M., Semb, A. and Hanssen, J.E. (1984) Emission and long-range transport of trace elements in Europe, Tellus, 36B, 163-178.

Pacyna, J.M. (1985a) Source-receptor relationships for trace elements in Northern Europe and the Norwegian Arctic. J. Water, Air and Soil Poll., (in press).

Pacyna, J.M. (1985b) Emission factors of atmospheric elements. In: Toxic metals in the atmosphere. J.O. Nriagu and C.I. Davidson, eds., John Wiley & Sons, Inc. (in press).

Pacyna, J.M. (1985c) "Sources of air pollution". In: Proc. Arab School of Science & Technology, Zabadani Valley, Syria, August 3-16.

Rahn, K.A. and Lowenthal, D.J. (1984) Elemental tracers of distant aerosols, Science, 223, 132.

Tomza, U., Maenhaut, W. and Cafmeyer, J. (1982) Trace elements in atmospheric aerosols at Katowice, Poland. In: Trace Substances in Environmental Health - XVI, D.D. Hemphill, ed., University of Missouri, U.S.A.

US EPA (1979) Compilation of air pollutant emission factors, Third ed., AP-42, Suppl. No. 9, U.S. Environmental Protection Agency, Research Triangle Park, NC, U.S.A.

Whitby, K.T. (1978) Physical characteristics of sulfur aerosols, Atmos. Envviron., 12, 135-159.

Table 1: Sampling time and air sample volumes.

Filter No.		Sampling time			Sample volume, m^3
Coarse	Fine	Date	Start*	End*	
3	4	1985-08-04/05	22:25h	08:25h	5.10
7	8	1985-08-05	15:03h	23:43	4.46
11	12	1985-08-06	00:30h	07:38	3.64
15	16	1985-08-06	11:57h	19:30	3.85
19	20	1985-08-06/07	20:14h	07:14	5.61
23	24	1985-08-07	08:49h	15:38	3.48
27	28	1985-08-07	16:16h	22:22	3.11
31	32	1985-08-07/08	23:08h	07:01	4.02
35	36	1985-08-08	07:20h	21:09	7.05
39	40	1985-08-08/09	22:25h	06:35	4.17
43	44	1985-08-09	06:56h	21:01	7.18
47	48	1985-08-09/10	21:35h	07:13	4.91
51	52	1985-08-10	07:40h	21:00	6.80

* Local time (GMT + 2h)

Table 2: Emission factors of lead and cadmium from cement manufacturing, in g t^{-1}.

Process	Lead emission factor			Cadmium emission factor		
	Type of emission control			Type of emission control		
	Multi-cyclone	ESP	Baghouse	Multi-cyclone	ESP	Baghouse
Dry process (total)	16.0	4.0	0.16			
- kiln/cooler	12.0	3.0	0.12	0.60	0.15	0.01
- dryer/grinder	4.0	1.0	0.04			
Wet process (total)	12.0	3.0	0.12	0.05	0.02	0.02
- kiln/cooler	10.00	2.5	0.10	0.04	0.01	0.01
- dryer/grinder	2.0	0.5	0.02	0.01	0.01	0.01

Table 3: Number concentrations of particles (m^{-3}) in the >0.5 μm diameter fraction during 1985-08-06 to 1985-08-08.

Sample No.	Sampling time			Sampling rate, $m^3 \cdot min^{-1}$	Particle number concentration, particles/m^3	Standard deviation particles/m^3	Standard error particles/m^3	Temperature/Rel. humidity
	Date	Start*	End*					
1	85-08-06	18:58h	22:38h	$5.66\ 10^{-4}$	$172\ 10^4$	$25.2\ 10^4$	$6.3\ 10^4$	27.8^0C/-
2	85-08-06	22:42h	7:14h	$5.66\ 10^{-4}$	$204\ 10^4$	$42.6\ 10^4$	$12.1\ 10^4$	
3	85-08-07	14:10h	15:38h	$5.66\ 10^{-4}$	$158\ 10^4$	$21.4\ 10^4$	$5.1\ 10^4$	27.1^0C/32%
4	85-08-08	20:20h	20:30h	$5.66\ 10^{-4}$	$321\ 10^4$	$38.6\ 10^4$	$10.9\ 10^4$	32.8^0C/44%

* Local time (GMT + 2h)

Table 4: Trace element concentrations, in ng m^{-3}, of air particulates at Zabadani on 1985-08-07 and other urban and industrial locations.

Trace element	Zabadani, Syria 1985-08-07	Mean yearly in urban United Kingdom, (McInnes, 1979)	Mean yearly in Brussels, 1972-1977 (Kretzschmar et al., 1980)	Mean daily in Katowice, Poland (Tomza et al., 1982)	Mean daily in Washington, DC, U.S.A. (Kowalczyk et al., 1978)
Mn	29.6	31.0	99- 132	700	27
Zn	444	260	325- 707	1760	150
Pb	122	340	1162-3336		1400
Cd	13.2	2.8	8- 15	37	
Ni	167	13.0	37- 44	46	27

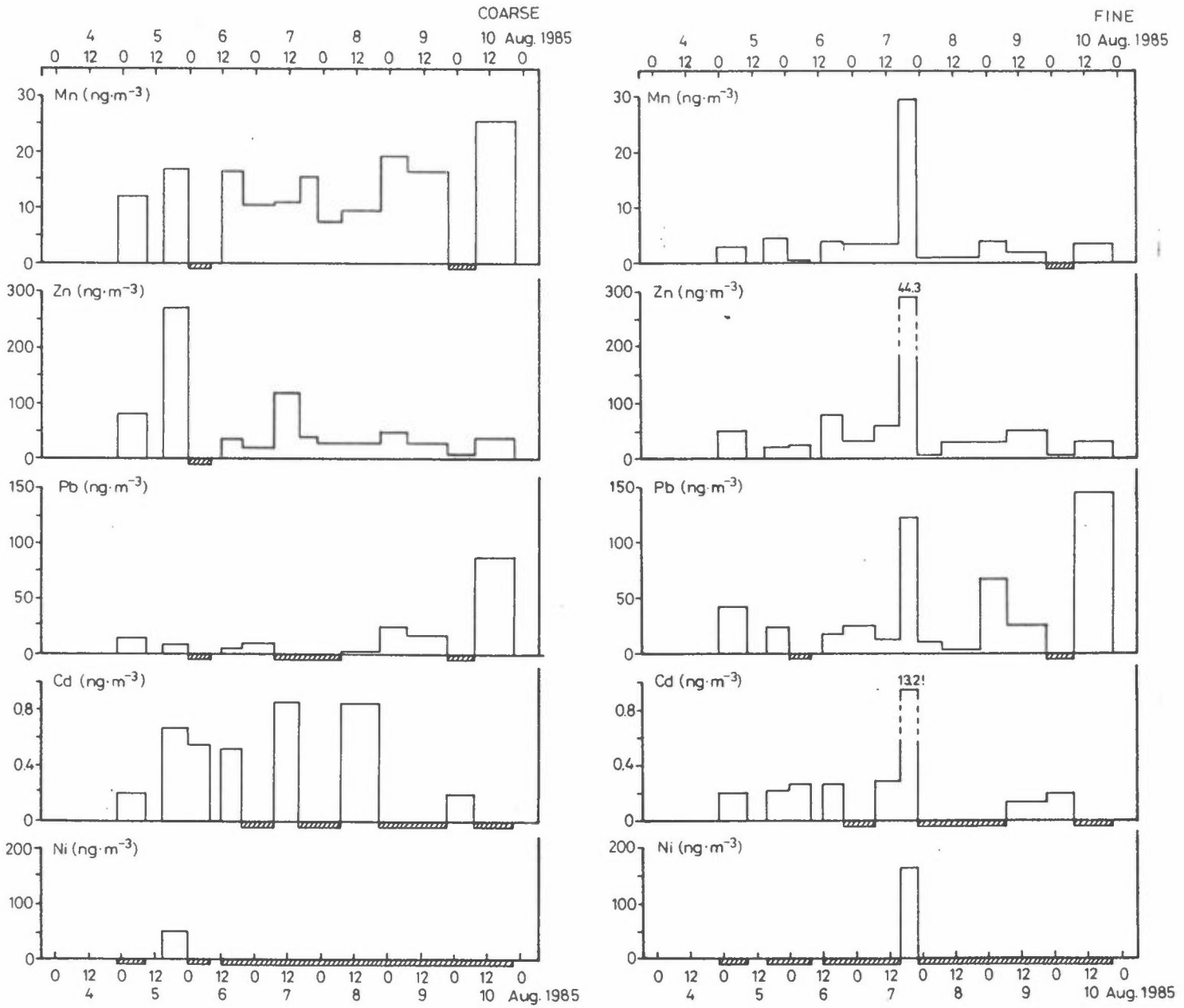

Figure 1: Concentrations of Mn, Zn, Pb, Cd and Ni in fine and coarse fractions of particles.

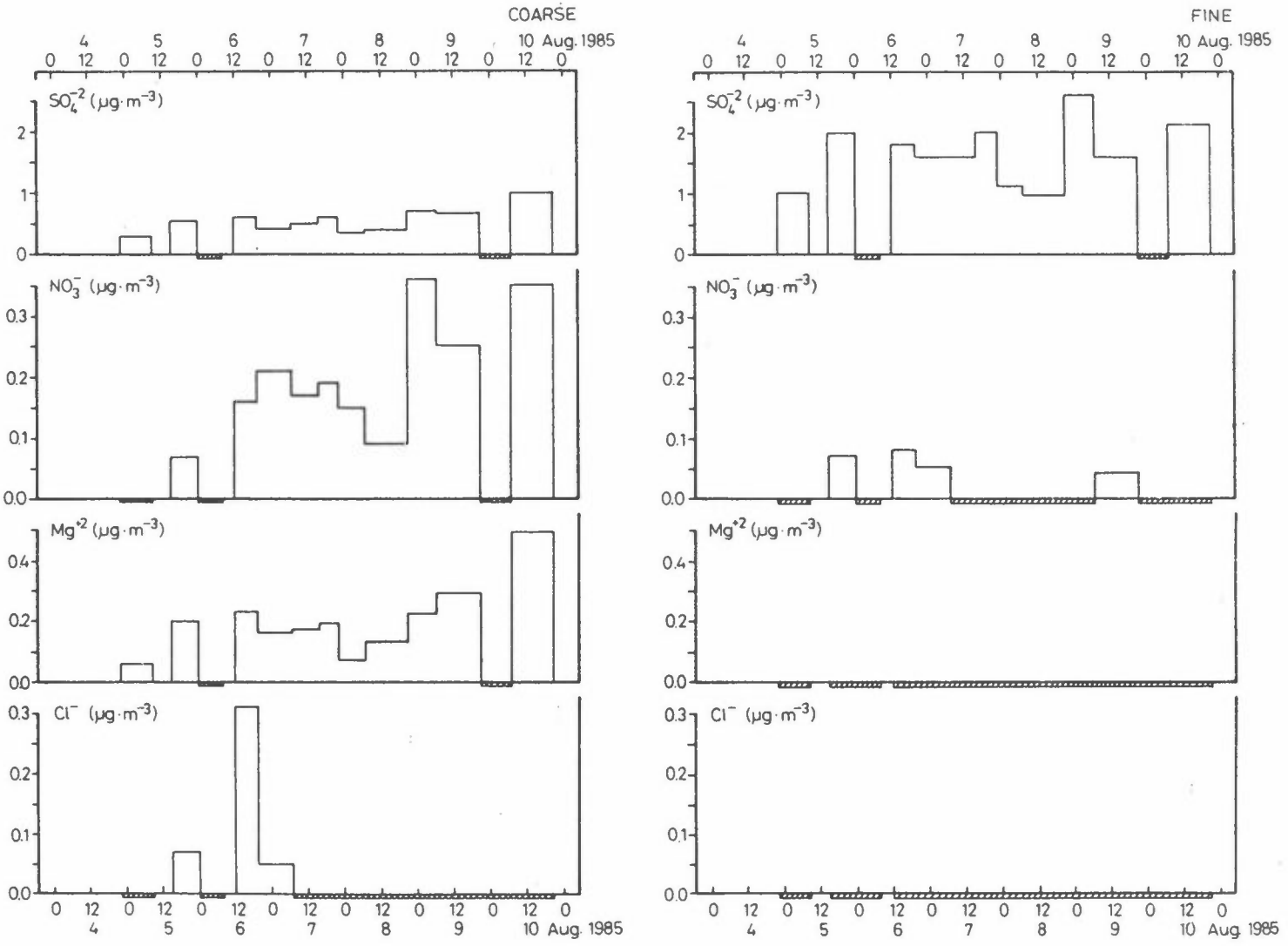

Figure 2: Concentrations of SO_4^{2-}, NO_3^-, Cl^-, and Mg^{2+} in fine and coarse fractions of particles.

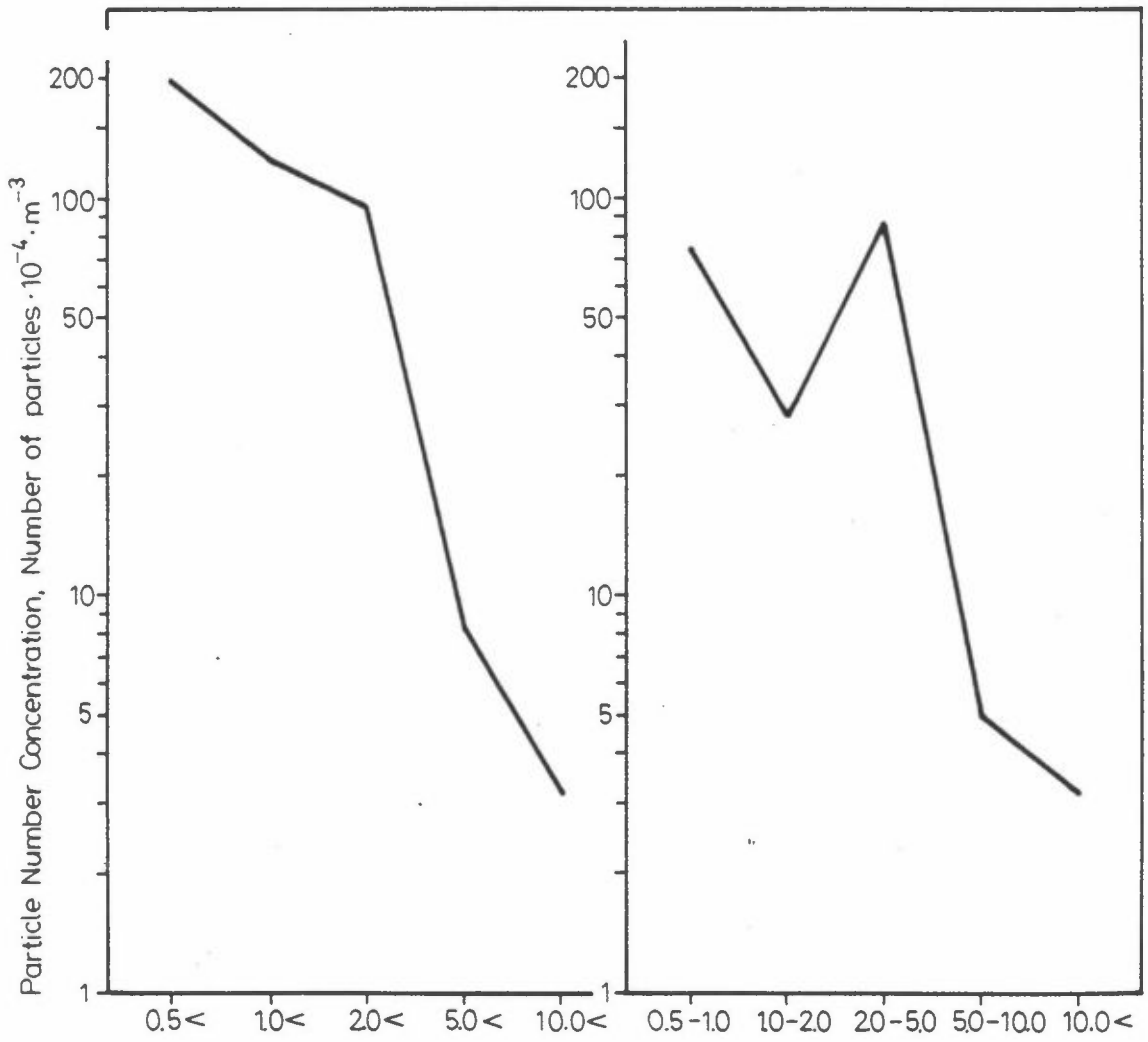

Figure 3: Number-size distribution of particles on 1985-08-07.

NORSK INSTITUTT FOR LUFTFORSKNING (NILU)
NORWEGIAN INSTITUTE FOR AIR RESEARCH

(NORGES TEKNISK-NATURVITENSKAPELIGE FORSKNINGSRÅD)

POSTBOKS 130, 2001 LILLESTRØM (ELVEGT. 52), NORGE

RAPPORTTYPE Teknisk rapport	RAPPORTNR. TR 18/85	ISBN-82-7247-647-9	
DATO November 1985	ANSV. SIGN. H.Dovland	ANT. SIDER 16	PRIS kr.20,00

TITTEL The chemical composition of aerosols in Zabadani Valley, Syria	PROSJEKTLEDER J.M. Pacyna
	NILU PROSJEKT NR. E-8557
FORFATTER(E) Jozef M. Pacyna	TILGJENGELIGHET* A
	OPPDRAGSGIVERS REF.

OPPDRAGSGIVER (NAVN OG ADRESSE)

3 STIKKORD (à maks. 20 anslag)
Aerosol | Trace element | Syria

REFERAT (maks. 300 anslag, 7 linjer)

TITLE

ABSTRACT (max. 300 characters, 7 lines)
The chemical composition of aerosols measured during a short period in 1985-08 in Zabadani Valley, near Damascus, Syria, is presented. Very high concentrations of several anthropogenic elements in some samples indicate transport of air pollutants, likely from industrial sources in the Damascus area, particularly from cement and sugar production, glass, ceramic manufacturing and the textile and sugar production, and motor vehicle traffic. Natural elements due to windblown dust are present in all samples.

*Kategorier: Åpen - kan bestilles fra NILU A
Må bestilles gjennom oppdragsgiver B
Kan ikke utleveres C