

NILU OR : 64/85  
REFERENCE: O-8510  
DATE : NOVEMBER 1985

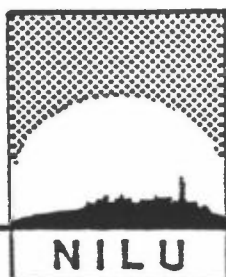
**CHEMICAL COMPOSITION OF AEROSOLS  
AT BP PROJECT GROUND STATIONS**

by

Jozef M. Pacyna

Val Vitols

Jan Erik Hanssen



**NORWEGIAN INSTITUTE FOR AIR RESEARCH**

---

ROYAL NORWEGIAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

NILU OR : 64/85  
REFERENCE: O-8510  
DATE : NOVEMBER 1985

*CHEMICAL COMPOSITION OF AEROSOLS  
AT BP PROJECT GROUND STATIONS*

by

Jozef M. Pacyna

Val Vitols

Jan Erik Hanssen

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



**ABSTRACT**

Aerosol measurement results are presented for all BP Project ground stations and all intensive measurement campaigns, as well as tentative speculation and discussion on the possible source (s) of the arctic aerosol. The main emission sources, likely contributing to the high concentrations of trace elements and major ions at the arctic island stations during the winter half-year, appear to be located in northern and western USSR. The Norwegian mainland stations (except for Vardø) were exposed to pollutants transported mainly from central Europe and the British Isles. These two regions and the emission areas in the USSR seem to be important for long-range transport of air pollutants to the Arctic during the summer half-year as well. During some periods, emission regions on the North American continent can be a suspected cause of enhanced air pollutant concentrations at the arctic island stations. Since the mainland station Vardø is located quite near the copper-nickel smelter complex on the Kola Peninsula, the increased metal and ion concentrations at the station were often related to the Kola source area emissions.



**CONTENTS**

	Page
ABSTRACT .....	
1 INTRODUCTION .....	
2 EXPERIMENTAL .....	
2.1 Sampling equipment .....	
2.1.1 Remarks on filtration characteristics .....	
2.2 Chemical analyses .....	
2.2.1 Major ions and trace elements .....	
2.2.2 Carbonaceous constituents of aerosols .....	
3 MEASUREMENT RESULTS .....	
3.1 Time series of trace elements .....	
3.1.1 Comments on Hi-Vol vs. EXTRA measurements .....	
3.2 Time series of major ions .....	
3.2.1 Comments on Hi-Vol vs. EK measurements .....	
3.3 Carbonaceous content of aerosols .....	
3.3.1 Comments on black carbon measurements .....	
3.4 Meteorological data .....	
4 DISCUSSION OF RESULTS .....	
4.1 Origins of trace elements in aerosols .....	
4.1.1 August/September 1982 campaign .....	
4.1.2 March 1983 campaign .....	
4.1.3 August/September 1983 campaign .....	
4.1.4 February/March/April 1984 campaign .....	
4.1.5 June/July 1984 campaign .....	
4.1.6 Seasonal variations at Ny Alesund .....	
4.1.7 Trace element concentrations by various sampling and analytical methods .....	
4.2 Ionic balances for aerosols .....	
5 CONCLUDING REMARKS .....	
6 ACKNOWLEDGEMENTS .....	
7 REFERENCES .....	



## CHEMICAL COMPOSITION OF AEROSOLS AT BP PROJECT GROUND STATIONS

### 1 INTRODUCTION

This report presents aerosol measurement results for all BP Project ground stations and all intensive measurement campaigns, as well as tentative speculation and discussion on the possible source(s) of the sampled aerosols in the Norwegian Arctic.

The bulk of the aerosol chemical composition data are shown in time series graphs of trace element (Pb, Cd, Zn, Ni, V and Mn) and major ion ( $\text{SO}_4^{2-}$ -S,  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{H}^+$ ) mean concentrations over 2- or 3-day sampling periods. The chemical data for the time series plots come from the analyses performed at the Chemical Laboratory, Norwegian Institute for Air Research (NILU).

Limited comparisons of results, obtained by different sampling and analytical techniques are discussed. Preliminary results of determinations of carbonaceous content of the arctic aerosol are also included.

### 2 EXPERIMENTAL

#### 2.1 SAMPLING

Arctic aerosols at all BP Project ground stations (see Figure 1) were sampled in two aerodynamic size fractions by a high-volume (Hi-Vol) filter sampling method (Vitols and Wasseng, 1985). An impactor-type particle size fractionator, incorporated in the Hi-Vol sampling head, enabled the collection of ca.  $>2.5 \mu\text{m}$  equivalent aerodynamic diameter (EAD) "coarse" fraction on glass filter substrates, and  $<2.5 \mu\text{m}$  EAD "fine" fraction on 20 x 25 cm Whatman 41 cellulose-type filters (Whatman 541 was used during Fall 1982 campaign).



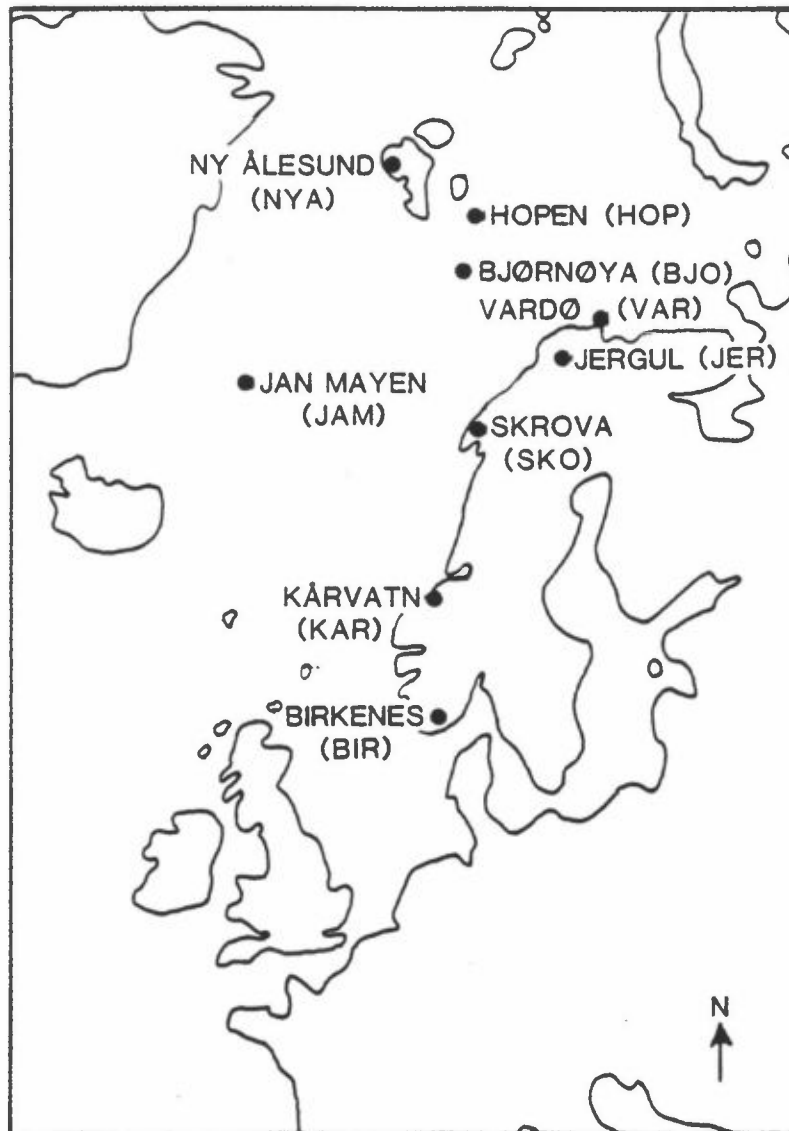


Figure 1: Locations of BP Project ground stations.

In general, the fine fraction ( $<2.5 \mu\text{m}$  EAD) particles are representative of long-range transported anthropogenic aerosols. Thus, due to cost and available time restraints, only the fine fraction particles (on Whatman filters) were analysed for trace elements and major ions, and in some cases for carbonaceous materials as well.

The air volumes, sampled by the Hi-Vols over the 2- and 3-day sampling runs, were ca.  $3300 \text{ m}^3$  and  $4900 \text{ m}^3$ , respectively. The sample volumes, used for aerosol concentration calculations, were at "sampling conditions", except for the NYA reference station, where they were converted to "standard" volumes at 1013 mb and  $25^\circ\text{C}$ . Wintertime measurements at NYA of pressure and temperature of air reaching the flow metering device (an orifice meter) of the sampler indicated, however, that differences between air volumes at sampling and standard conditions never exceeded 10%, even under the ambient air temperature and pressure extremes encountered during NYA winters.

#### 2.1.1 Remarks on filtration characteristics

Although Whatman 41 cellulose fibre filters have low flow resistance and are advantageous for analytical purposes (relatively low blank values of most trace elements and ions), this type of filter has a pronounced filtration efficiency minimum for submicrometre aerosols (e.g., Lindeken et al., 1963; Marple and Liu, 1983). This implies that there is some particle size- and filter face velocity-dependent penetration (at least at the outset of sampling) of these fine particles. Filtration efficiency has been shown to increase with sampling time (Lindeken et al., 1963), which is believed to be due to "loading" of the filter fibres with collected aerosol particles. This effect, however, may not be significant at the relatively low aerosol levels in the Arctic.

Dolske et al. (1984) evaluated trace element penetration through cellulose filter media under actual field sampling conditions, using a 2-stage impaction fractionator/afterfilter setup\*. Their results indicate that fine particle penetration was somewhat R.H. dependent, and ranged from ca. 10% for Fe to 38% for Zn and 43% for Pb.

---

\* Essentially similar to the BP Project Hi-Vol sampler, except that their fractionator's (Sierra Model 235, Stages 1 + 3)  $d_{50}$  was  $1.0 \mu\text{m}$  EAD (at  $1.1 \text{ m}^3 \text{ min}^{-1}$ ).

During wintertime episodes, some particle penetration through the Hi-Vol Whatman 541 and 41 filters was evident. In a limited number of sampling runs at NYA, two Whatman filters, placed in series in the filter holder, were used as the Hi-Vol afterfilter, to obtain some estimate of the extent of penetration. The results showed about 10% penetration, with no particular dependence on chemical composition. It is, of course, understood, that with two filters (with identical collection characteristics) in series, the second would not collect all the particles penetrating the first.

The foregoing then makes it clear, that the concentrations of trace elements (as well as some ions) in fine fraction particles are, collected by Hi-Vol samplers, could likely be underestimated. Depending on the element in question, the measured concentrations in the worst case may constitute anywhere from ca. 60 to 90% of "true" airborne concentrations.

## 2.2 CHEMICAL ANALYSES

The routine analyses of major ions in the Hi-Vol filter samples by the Chemistry Laboratory of NILU were preceded by extractions of major ions in distilled water, and of trace elements in 1N nitric acid solution. In both cases, one quarter of the sample filters was extracted in 50 ml of the relevant solution for 30 minutes at room temperature in a mechanical shaker. Before the analyses, the extracts were filtered through a Whatman 41 filter.

The concentrations of major ions in the extracts were determined by the analytical methods listed in Table 1.

Table 1: Analytical methods used at NILU for major ions in water extracts of Hi-Vol filter samples.

Ion	Method
$\text{SO}_4^{2-}$ -S	Ion chromatography (Dionex)
$\text{NO}_3^-$	" " "
$\text{Cl}^-$	" " and the spectrophotometric iron-thiocyanate method (Auto Analyzer)
$\text{NH}_4^+$ -N	Spectrophotometric indophenol method (Auto Analyzer)
$\text{Na}^+$	Flame emission
$\text{K}^+$	} Atomic absorption spectrometry
$\text{Mg}^{2+}$	
$\text{Ca}^{2+}$	
$\text{H}^+$	pH-meter with combined electrode, calibrated against standard buffers. Calculation of $\text{H}^+$ from $\text{H}^+ = 10^{-\text{pH}}$
	} with addition of $\text{Cs}^+$ and $\text{La}^{++}$ to the solutions

The trace elements were all analysed by atomic absorption spectrometry (AAS), using an air/acetylene flame for Zn, and the graphite furnace technique (Perkin Elmer HGA 400) for Pb, Cd, Ni, V, and Mn. The standard procedures specified by the manufacturer were followed. In the case of Ni and V, pyrolytically-coated graphite tubes were used. Calibrations were performed with solutions containing known concentrations of the elements in 1N nitric acid solution, to match the sample extracts. Field blanks (filters returned unexposed from the sampling stations) were extracted and analysed in the same manner. Table 2 gives the detection limits (in the extracts) of the various analytical methods, and the range of the blank values (ng/filter and  $\text{ng/m}^3$  for a  $4000 \text{ m}^3$  sample) for the different major ions and trace elements.

In the case of Cl and Na, blank corrections were made. Because of the relatively large range of blank values of the filters used during the BP programme, no corrections have been made for the other components. This means that the lowest concentrations measured are somewhat uncertain, especially for samples with low sample volumes.

Table 2: Detection limits ( $\mu\text{g}/\text{l}^{-1}$ ) of the analytical methods used at NILU, and the range of field blanks, given as  $\mu\text{g}/\text{filter}$  and  $\text{ng}\cdot\text{m}^{-3}$  for a  $4000\text{ m}^3$  sample (approximate volume of a 2-day sample).

Component	Detection limit $\mu\text{g}/\text{l}^{-1}$ (in the extract)	Filter blank (range)	
		$\mu\text{g}/\text{filter}$	$\text{ng}\cdot\text{m}^{-3}$ ( $4000\text{ m}^3$ )
$\text{SO}_4^{-\text{S}}$	10	2-30	0.5-7.5
$\text{NO}_3^{-\text{N}}$	10	<2-22	<0.5-5.5
$\text{NH}_4^{-\text{N}}$	40	<8-24	<2-6
$\text{Cl}^{-}$	10	90-354	22.5-88.5
Na	50	28-160	7-40
K	10	2-32	0.5-8
Mg	10	<2-8	<0.5-2
Ca	10	<2-28	<0.5-7
$\text{H}^{+}$	-	0.8-10	0.2-2.5*
Pb	1	<0.2	<0.05
Cd	0.05	<0.01-2	<0.0025-0.005
Zn	5	1-3	0.25-0.75
Ni	2	<0.4	<0.1
V	3	<0.6	<0.15
Mg	0.25	0.05-0.6	0.025-0.15

\*  $\text{neq}\cdot\text{m}^{-3}$ .

### 2.2.1 Remarks on possible sampling artifacts

The airborne concentrations of  $\text{NO}_3^{-\text{N}}$ ,  $\text{NH}_4^{-\text{N}}$ ,  $\text{Cl}$ , and  $\text{H}^{+}$  were determined from the analysis results of water extracts of the Whatman 41 filters. Due to the relatively long (2- and 3-day) sampling runs and subsequent storage, chemical reactions among the various collected aerosols, as well as with gaseous species in sample air under the reduced pressure conditions in the filter holder, are possible (Brice et al., 1982). Thus, the concentrations determined from the analyses of the filter extracts may not necessary reflect the true airborne concentrations of the ions in the fine fraction aerosols. Gaseous nitric acid ( $\text{HNO}_3$ ), hydrochloric acid ( $\text{HCl}$ ) and ammonia ( $\text{NH}_3$ ) in the air may be adsorbed on the cellulose filter, or on the particles already collected on the filter. In this case the analysis can not

distinguish between particulate and gaseous nitrate, chloride and ammonium. Obviously these species may undergo reactions in the ambient air as well, but during the relatively long sampling period the equilibrium between the gas and aerosol phases may be substantially changed.

The opposite effect, i.e., loss of airborne aerosol nitrate, chloride, ammonium and  $H^+$  may also occur because of chemical reactions or volatilization, caused by changes in air temperature, pressure and humidity during sampling. The magnitude of these effects is not easily estimated. One way of estimating, for example, the loss of chloride (possibly as HCl) (Larssen and Hanssen, 1980) would be to look at the measured ratios between chloride, magnesium and sodium, under the assumption that all these sampled ions originate from airborne seasalt, and that the original seawater ratios are preserved in the aerosol. Such calculations are performed in Section 5.2.

### 2.2.2 Carbonaceous constituents of aerosols

The various analytical methods for determination of carbonaceous material in ambient particles are mainly based on thermal combustion, optical transmittance and absorption, photoacoustics, nuclear excitation (Raman spectroscopy), and wet chemical oxidation principles.

Selected Hi-Vol and EK filters from various BP Project campaigns and ground stations were analysed for graphitic "black carbon" in a cooperative study with Lawrence Berkeley Laboratory (LBL)\* by optical attenuation measurements (Rosen et al., 1980).

The optical attenuation,  $A$ , is defined as:

$$A = -100 \ln (I/I_0),$$

when  $I_0$  is the intensity of light (wavelength = 0.63  $\mu\text{m}$  in this case) transmitted through a blank filter, and  $I$  is the intensity through a

---

\* Dr. H. Rosen, Applied Science Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA, U.S.A.

particle-loaded sample filter. Assuming fixed optical constants, 'A' should be proportional to the graphite content of the aerosol. Quantitative correlation, however, depends on the properties of the filter medium used for the collection of the aerosol sample and has to be established empirically.

### 3 MEASUREMENT RESULTS

For quick reference, all intensive campaign periods are listed in Table 3.

Table 3: Periods of intensive measurement campaigns at all BP Project ground station.

Station	Measurement campaign				
	1982	1983		1984	
	Fall	Spring	Fall	Spring	Summer
NYA, NILU I NYA, NILU II	1982-08-15 to 09-13 —	1983-03-01 to 04-06 —	— 1983-08-08 to 09-14	— 1984-02-27 to 04-09	— 1984-06-18 to 07-18
BJO	1982-08-16 to 09-11	1983-02-28 to 03-30	1983-08-08 to 08-19	1984-02-29 to 03-30	1984-07-09 to 07-16
HOP	1982-08-16 to 09-11	1983-02-28 to 04-01	1983-08-08 to 09-12	1984-02-27 to 04-12	1984-06-18 to 07-16
JAM	1982-08-16 to 09-11	1983-02-28 to 04-01	1983-08-08 to 09-12	1984-02-27 to 04-02	1984-06-18 to 07-18
VAR	1982-08-30 to 09-11	1983-02-28 to 03-30	1983-08-08 to 09-12	1984-02-29 to 04-02	1984-06-18 to 07-16
JER	1982-09-01 to 09-11	1983-03-18 to 03-30	1983-08-10 to 08-12 1983-08-29 to 09-12	1984-02-27 to 04-02	1984-06-18 to 07-20
SKO	—	1983-02-28 to 03-30	1983-08-08 to 09-12	1984-02-27 to 04-12	1984-06-18 to 07-18
KAR	—	1983-03-10 to 03-30	1983-08-12 to 09-12	1984-03-07 to 04-02	1984-06-22 to 07-18
BIR*	1982-08-27 to 09-11	1983-03-02 to 03-30	1983-08-08 to 09-12	1984-03-07 to 04-02	1984-06-18 to 07-16

\* Not a BP Project station

The results of trace element and major ion measurements by Hi-Vol samplers are presented in the form of time series plots for all BP Project intensive measurement campaigns at all ground stations in Figures 2 through 45. Preliminary results of determinations of carbonaceous matter on selected Hi-Vol filters and EK prefilters are presented in Table 4.

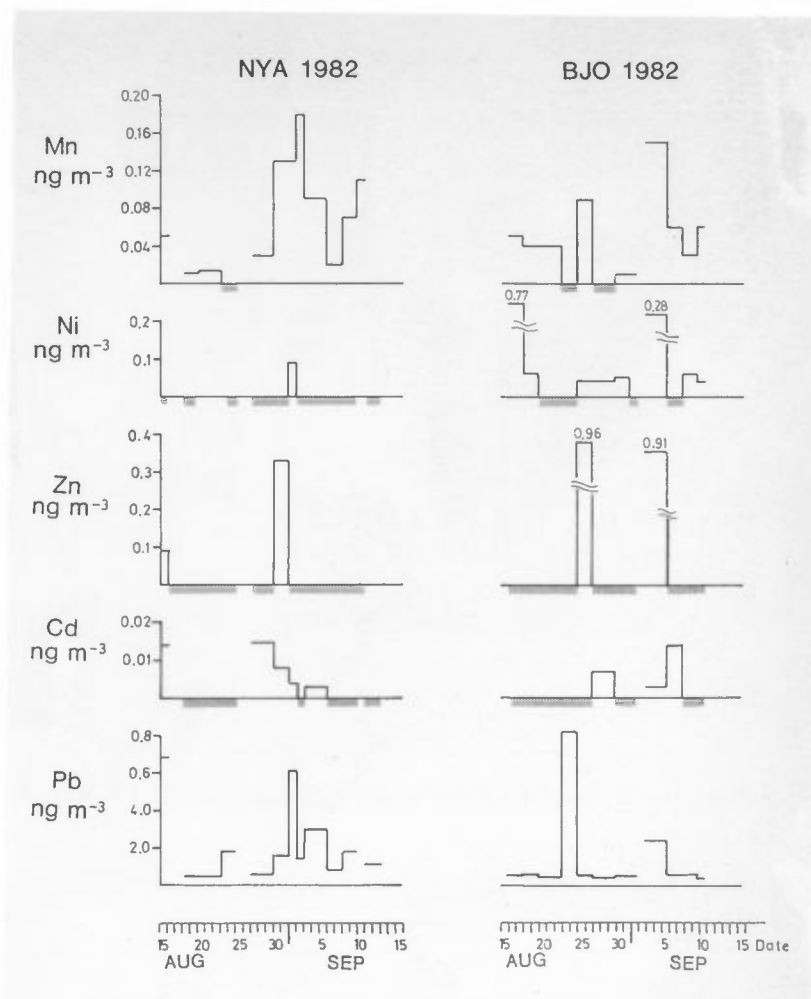


Figure 2: Time series of 2- and 3-day mean concentrations of trace elements from high-volume (Hi-Vol) filter sampling at Ny Alesund (NYA) and Bjørnøya (BJO) during the Fall 1982 campaign.

▨ indicates concentrations below detection limit (b.d.l.).



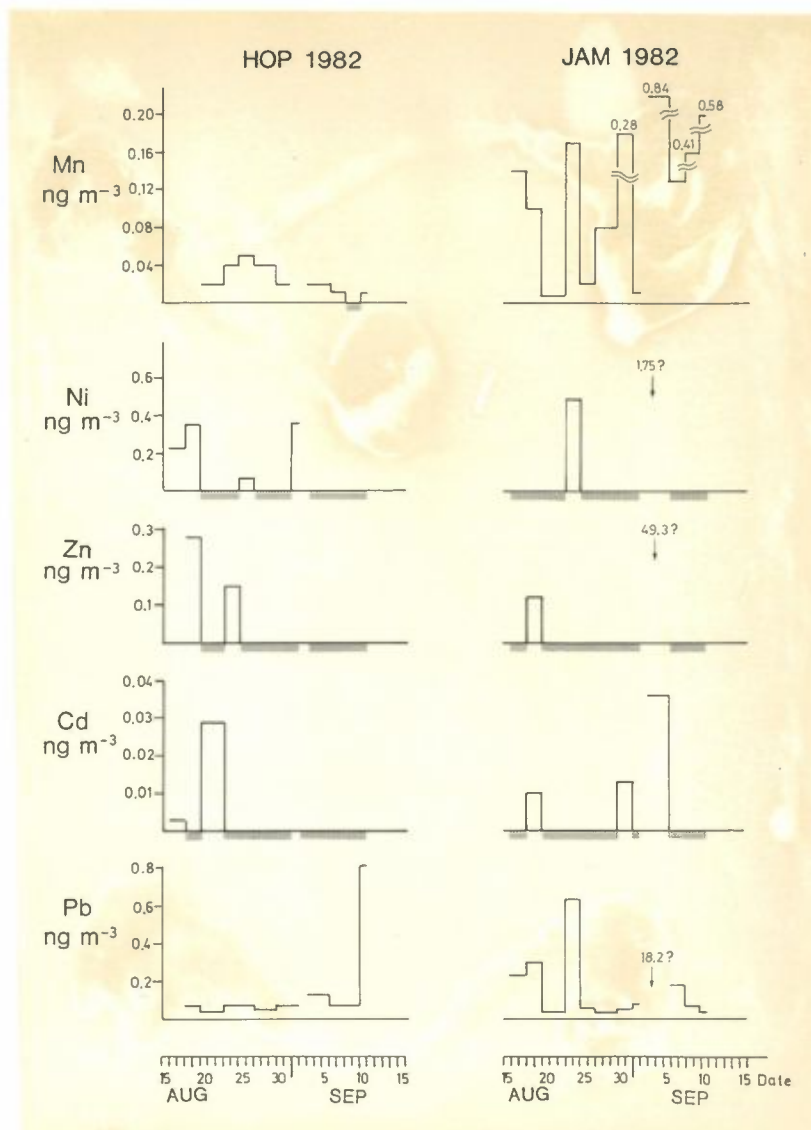


Figure 3: Time series of 2- and 3-day mean concentrations of trace elements from high-volume (Hi-Vol) filter sampling at Hopen (HOP) and Jan Mayen (JAM) during the Fall 1982 campaign.

▨ indicates b.d.l.

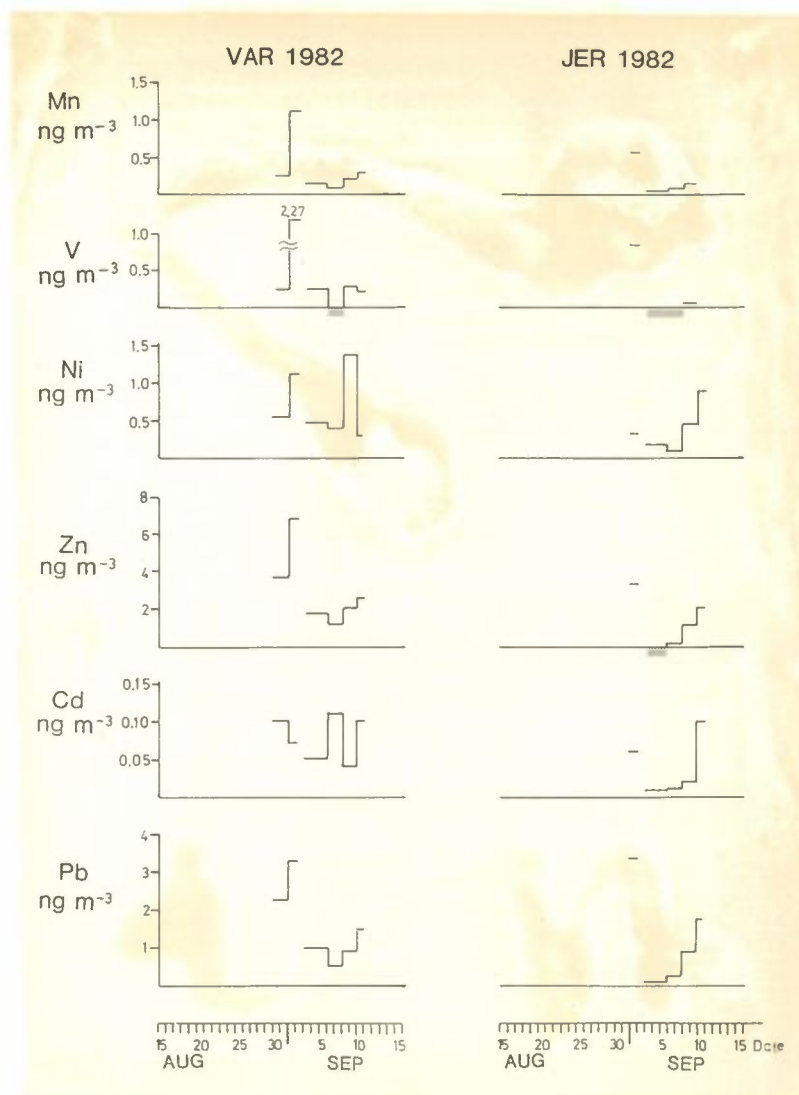


Figure 4: Time series of 2- and 3-day mean concentrations of trace elements from high-volume (Hi-Vol) filter sampling at Vardø (VAR) and Jergul (JER) during the Fall 1982 campaign.

▨ indicates b.d.l.

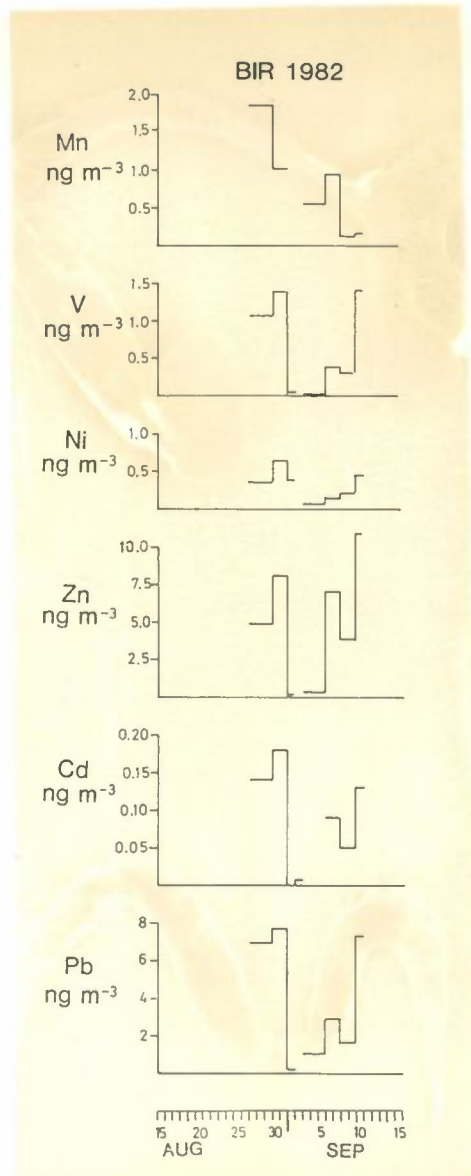


Figure 5: Time series of 2- and 3-day mean concentrations of trace elements from high-volume (Hi-Vol) filter sampling at Birkenes (BIR) during the Fall 1982 campaign.

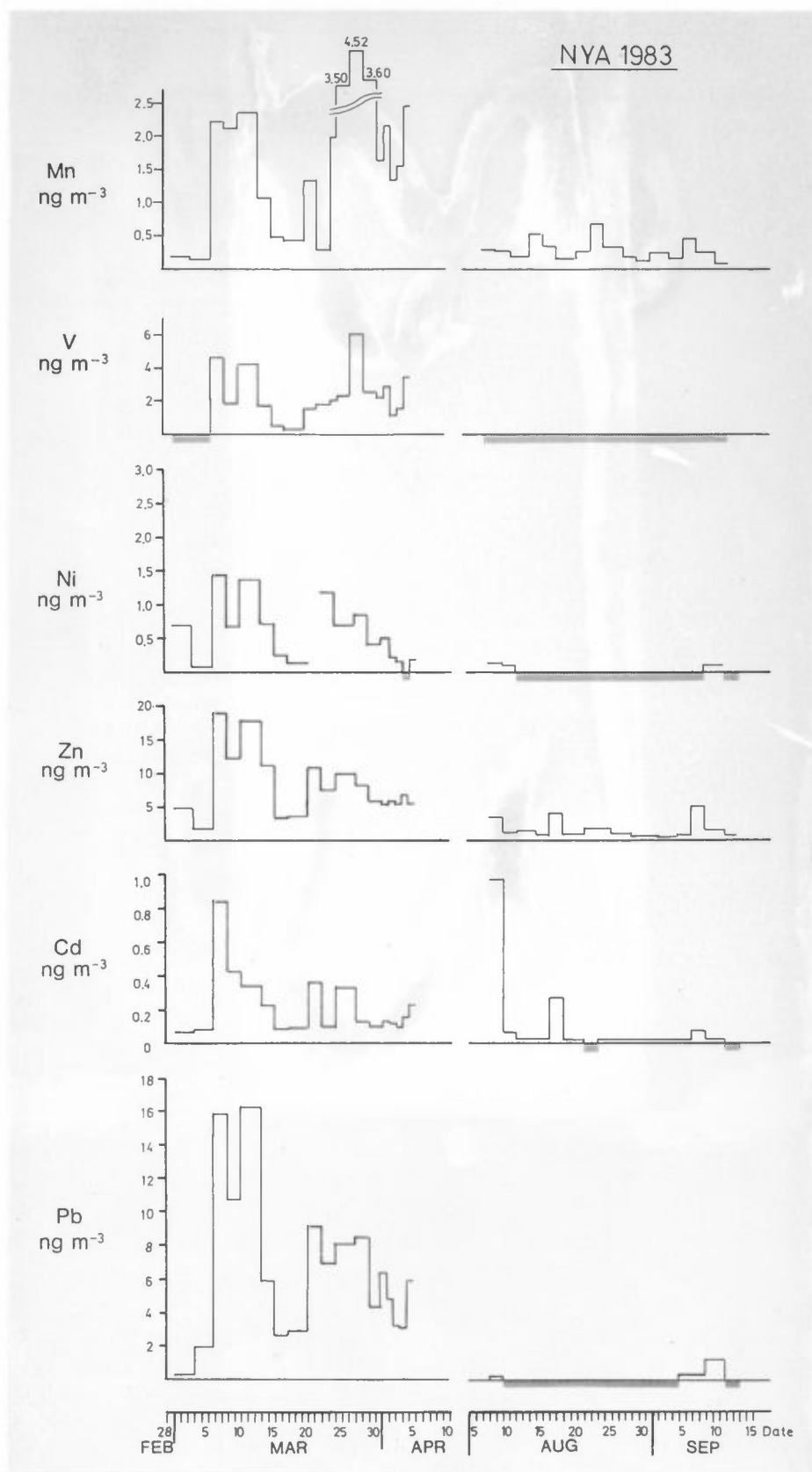


Figure 6: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at NYA during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

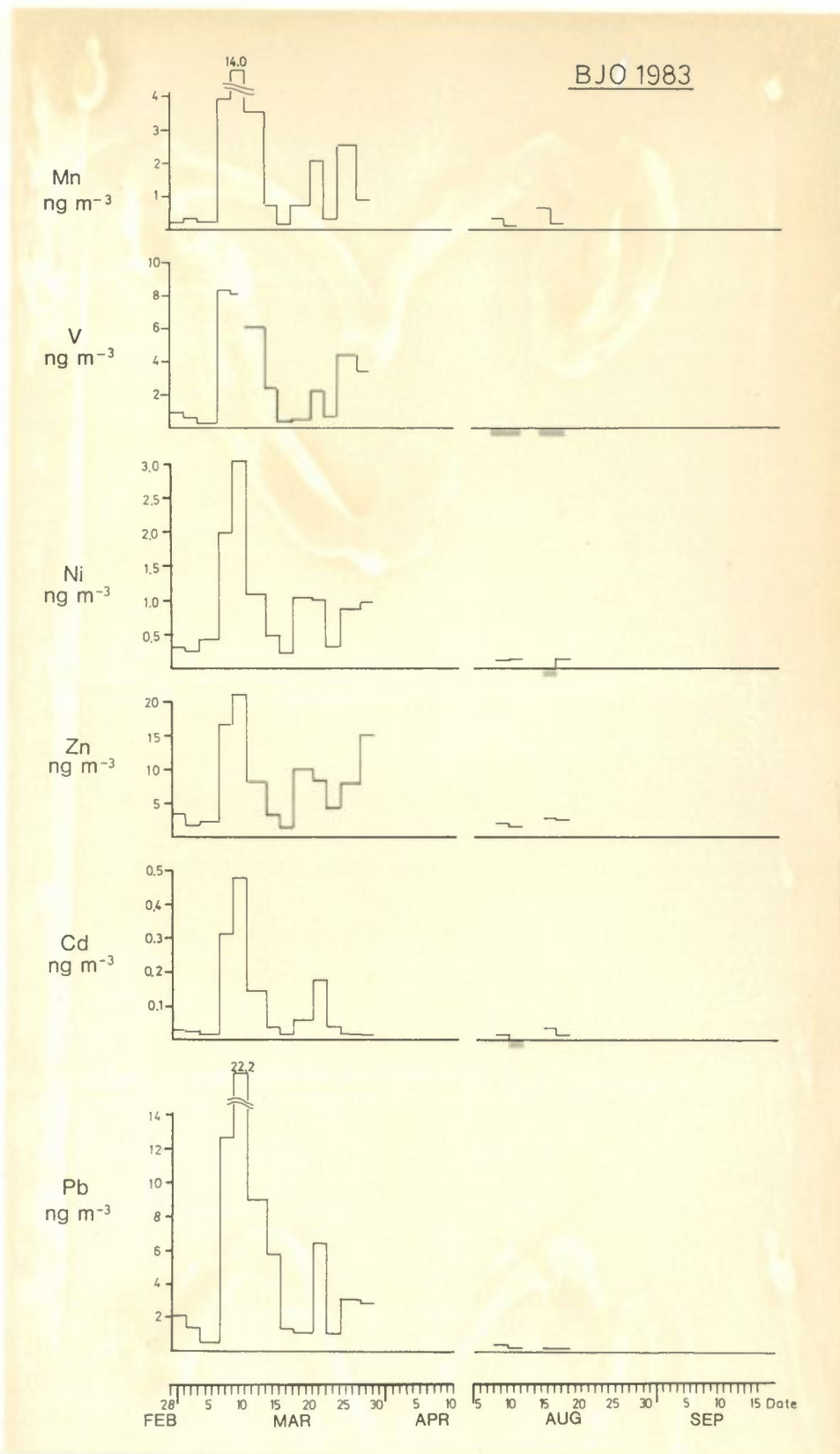


Figure 7: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at BJO during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

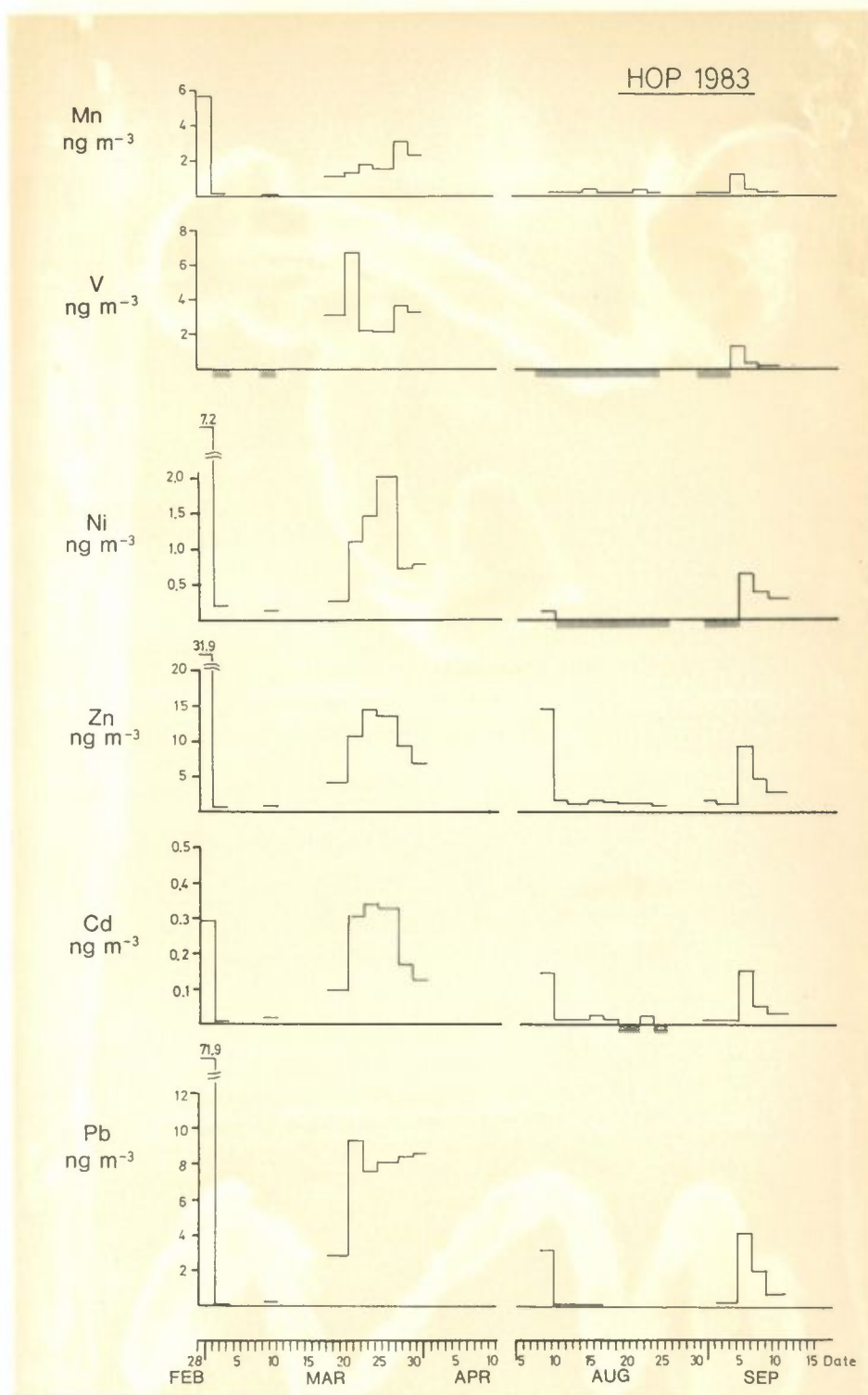


Figure 8: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at HOP during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

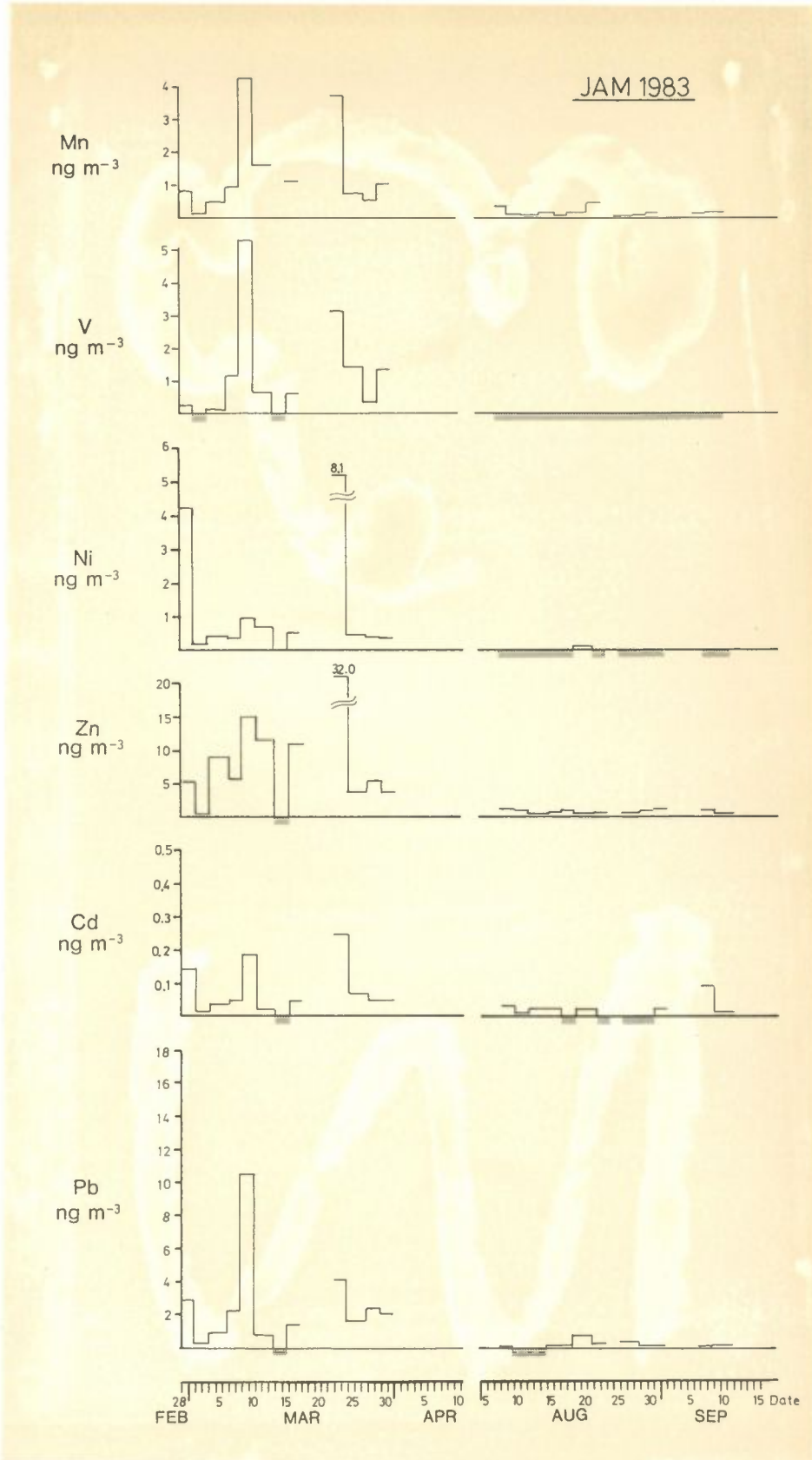


Figure 9: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at JAM during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

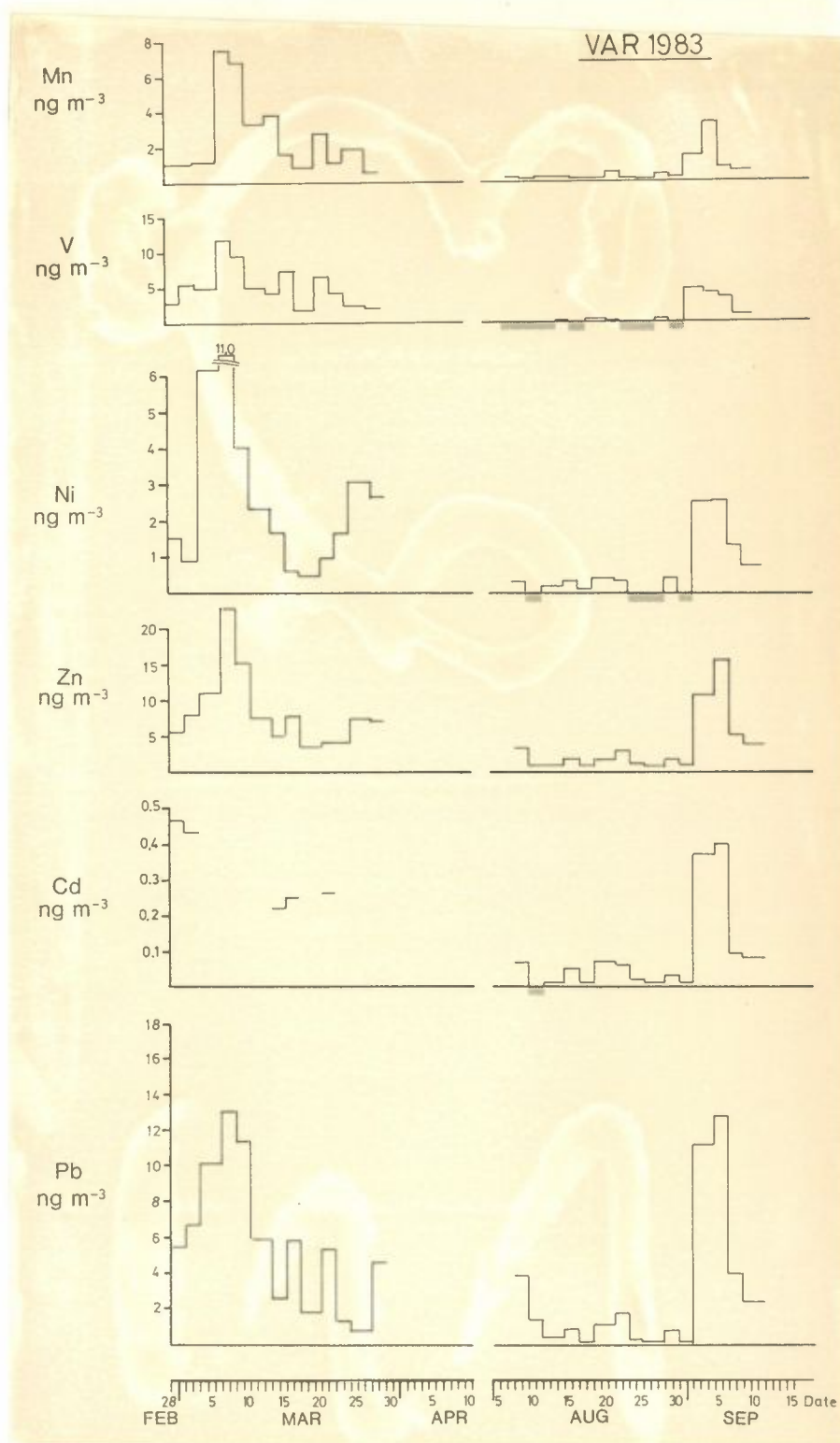


Figure 10: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at VAR during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.



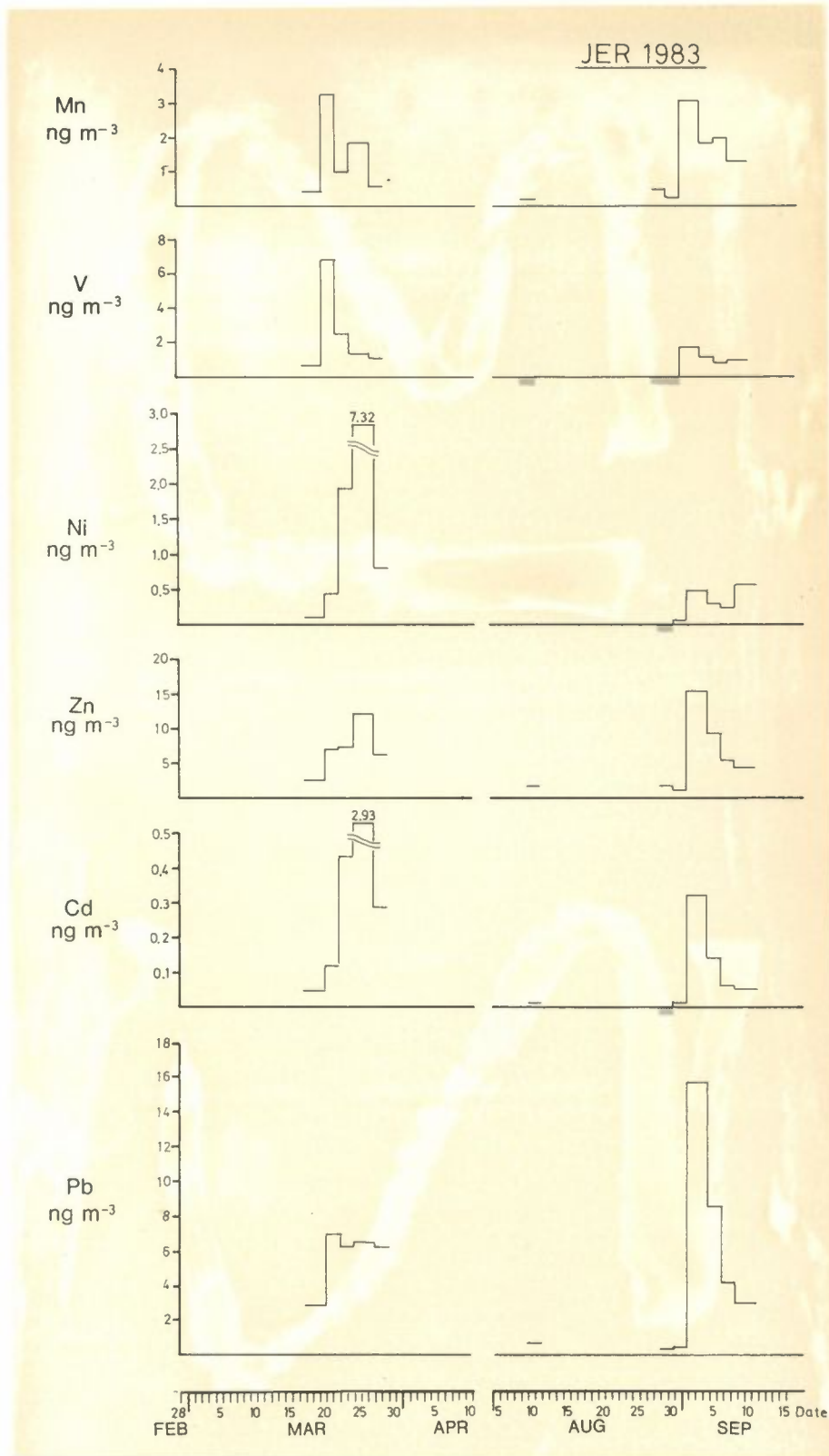


Figure 11: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at JER during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

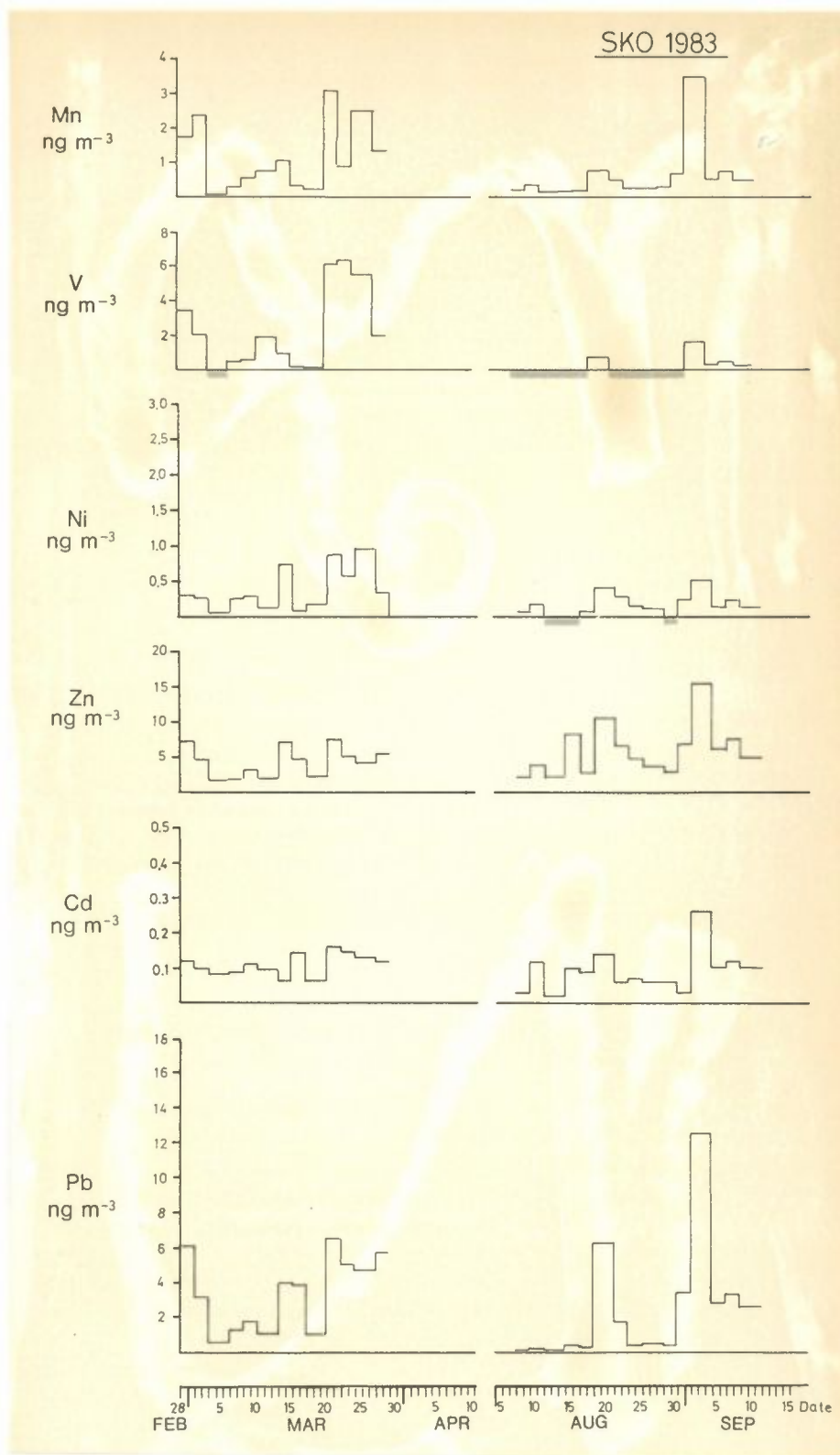


Figure 12: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at SKO during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

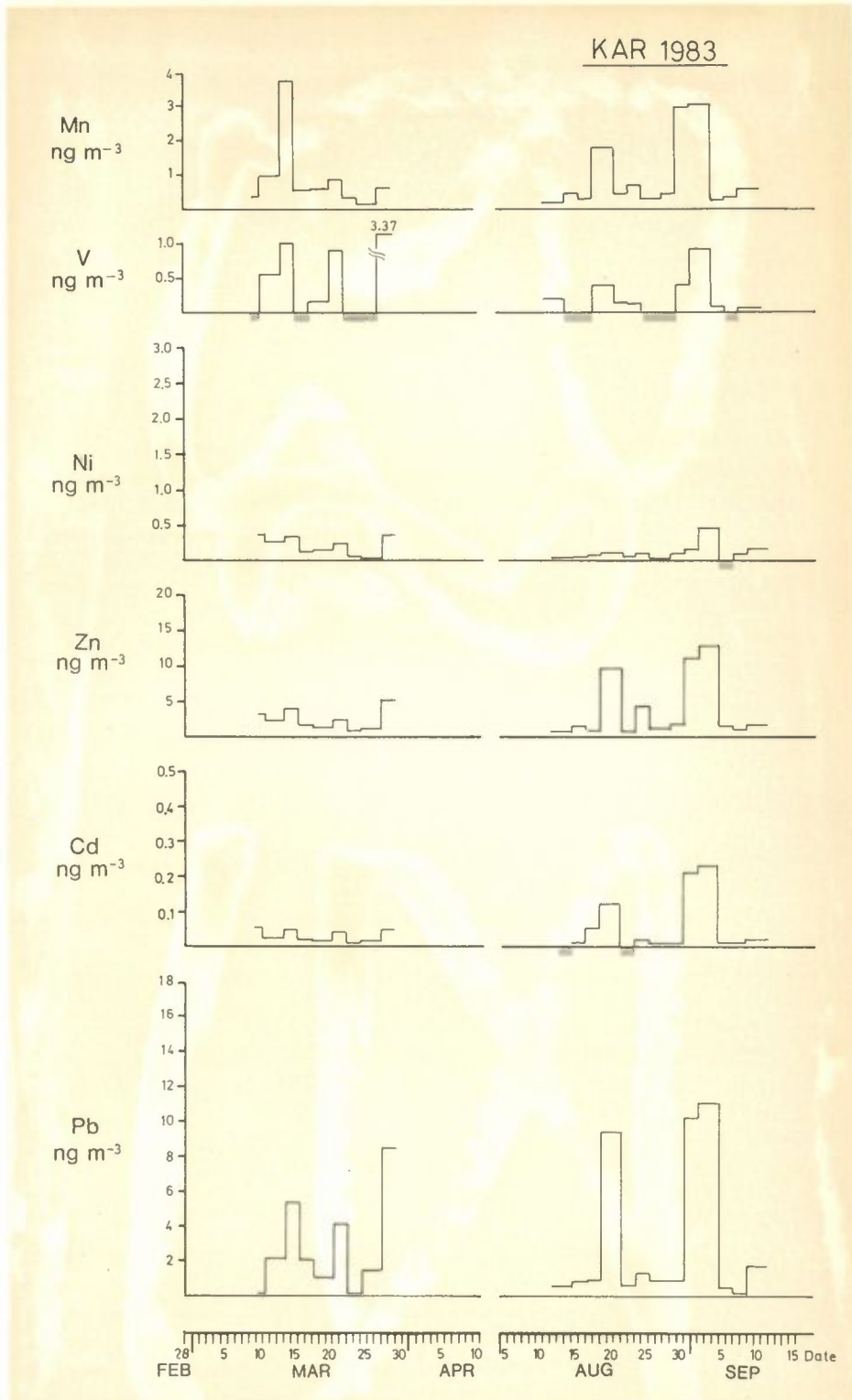


Figure 13: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at KAR during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

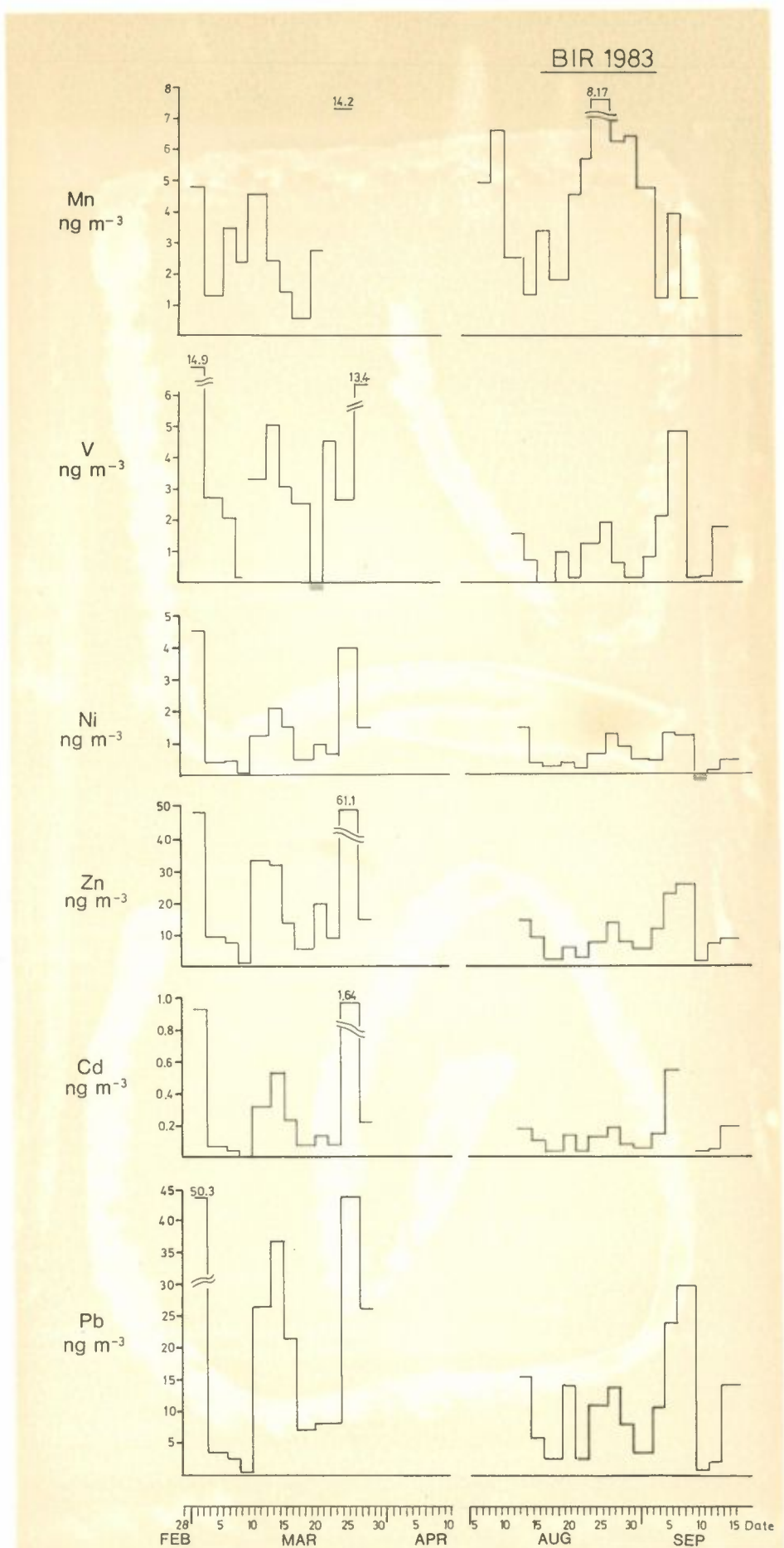


Figure 14: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol filter sampling at BIR during the Spring 1983 and Fall 1983 campaign.

▨ indicates b.d.l.

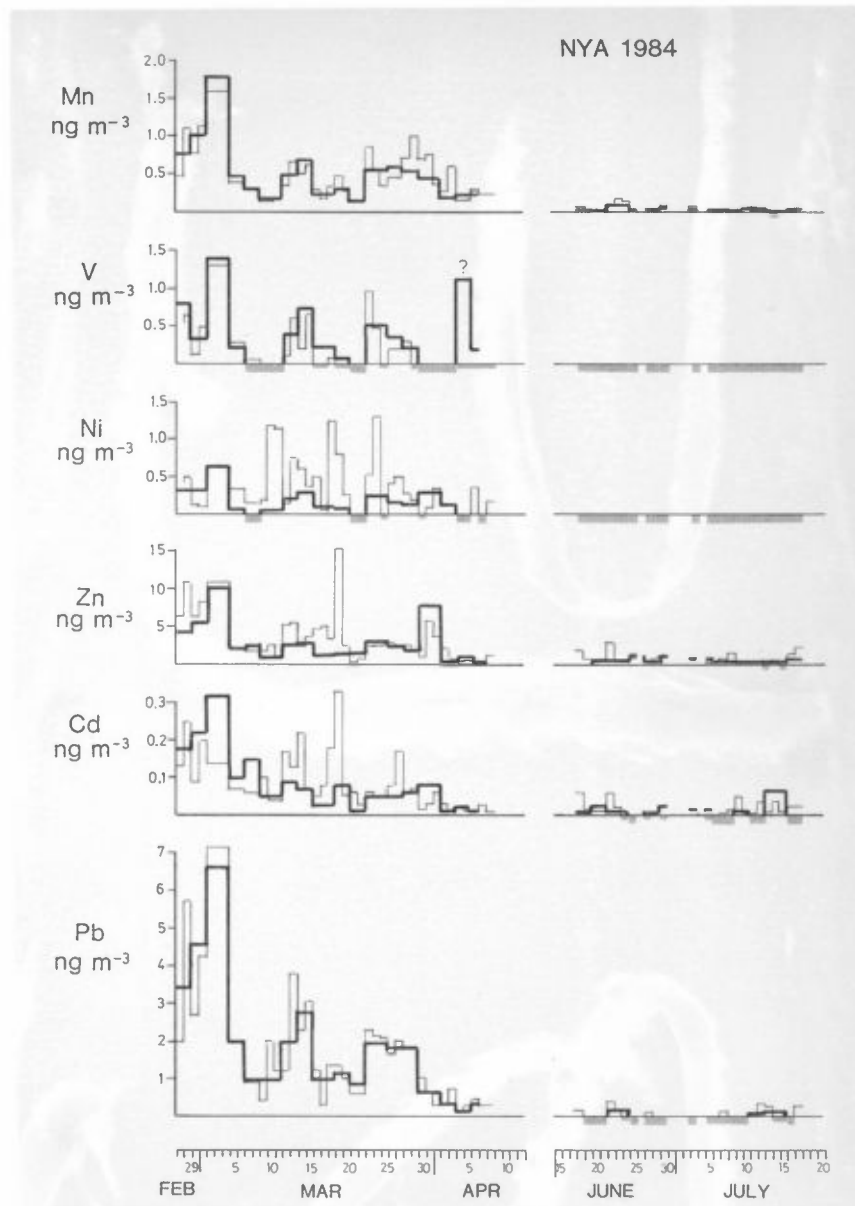


Figure 15: Time series of 2- and 3-day mean concentrations of trace metals from Hi-Vol (—) and EXTRA (—) sampling at NYA during the spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.  
 ▩ indicates EKSTRA concentrations b.d.l.

The missing sampling periods in Summer 1984 are due to persistent local sources influences.

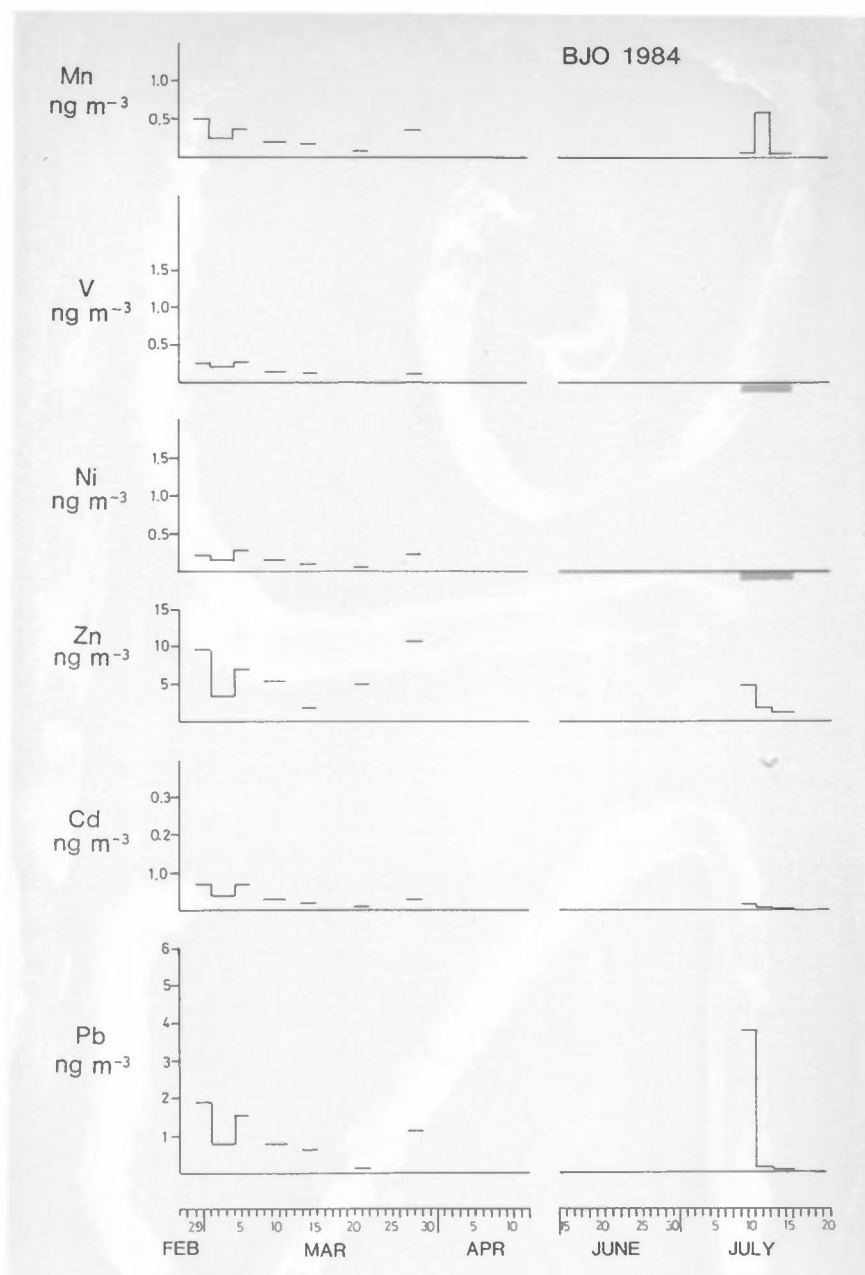


Figure 16: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at BJO during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.

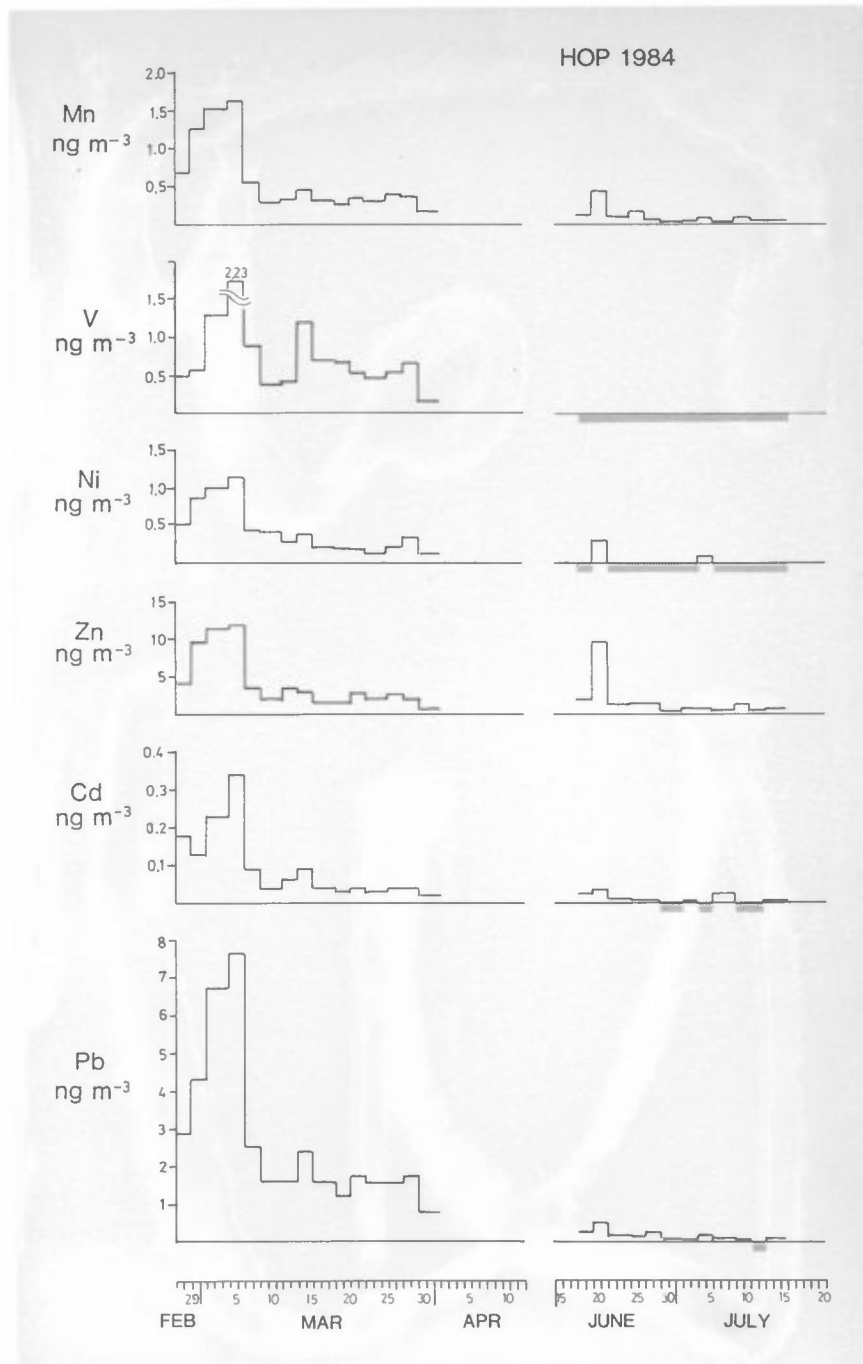


Figure 17: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at HOP during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.

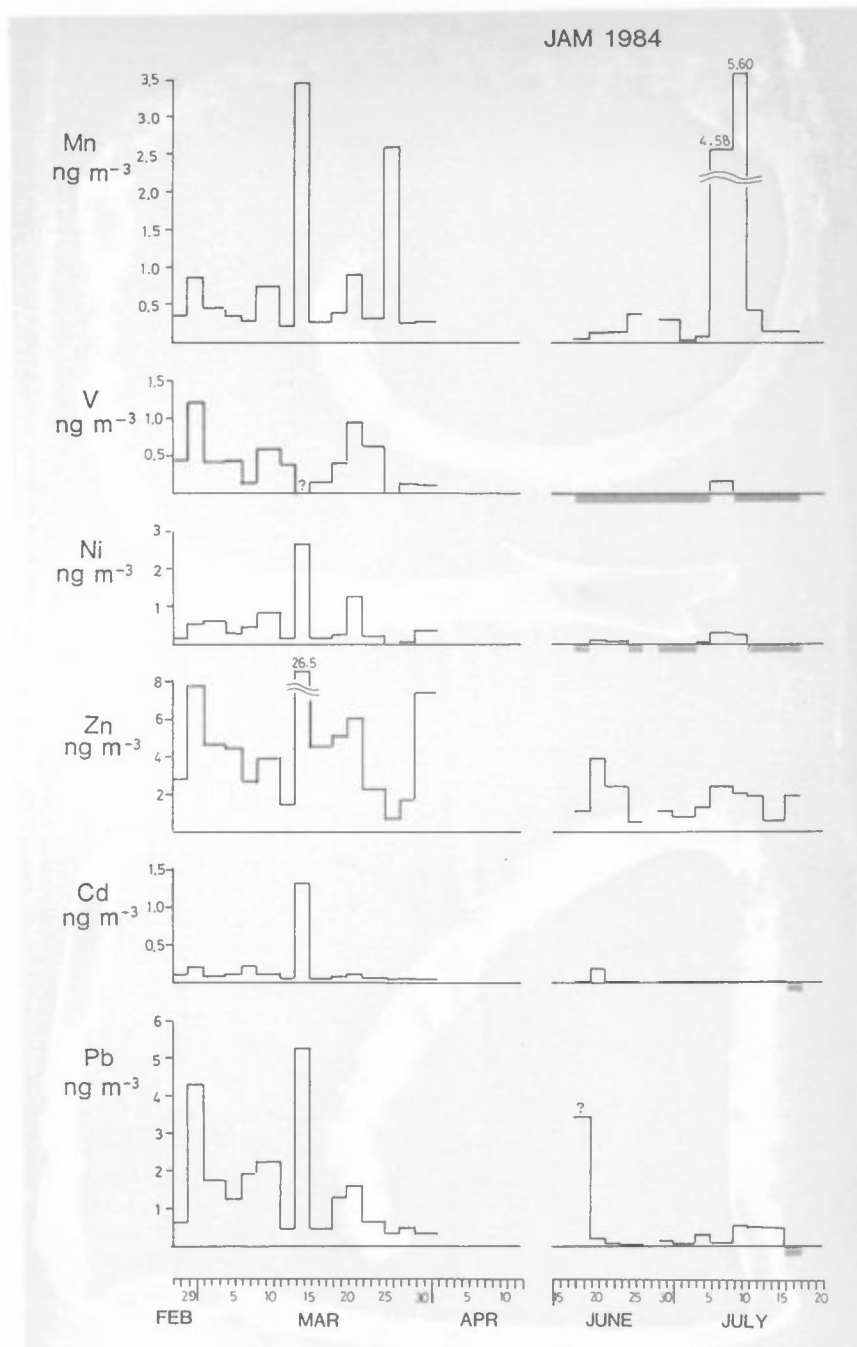


Figure 18: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at JAM during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.



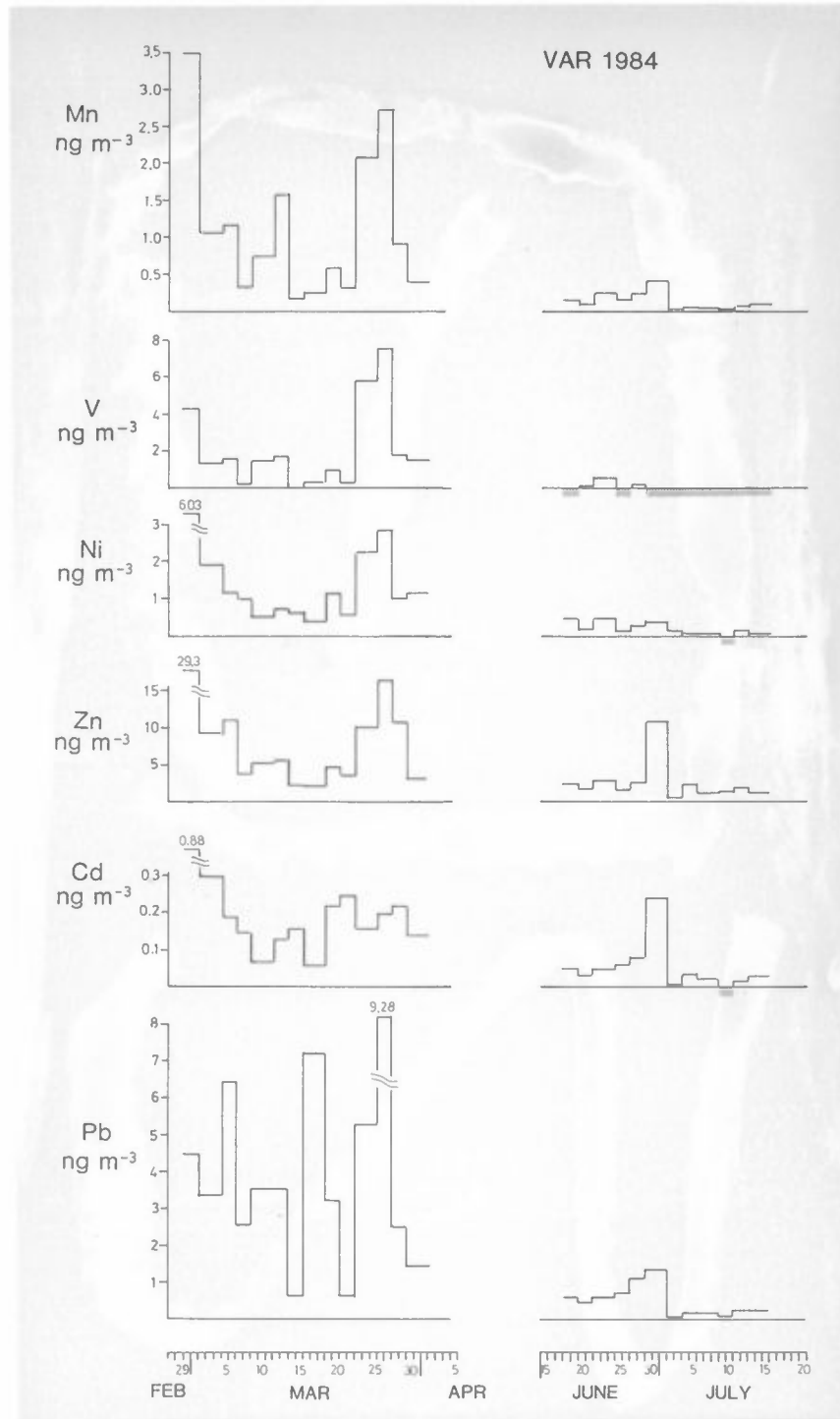


Figure 19: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at VAR during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.

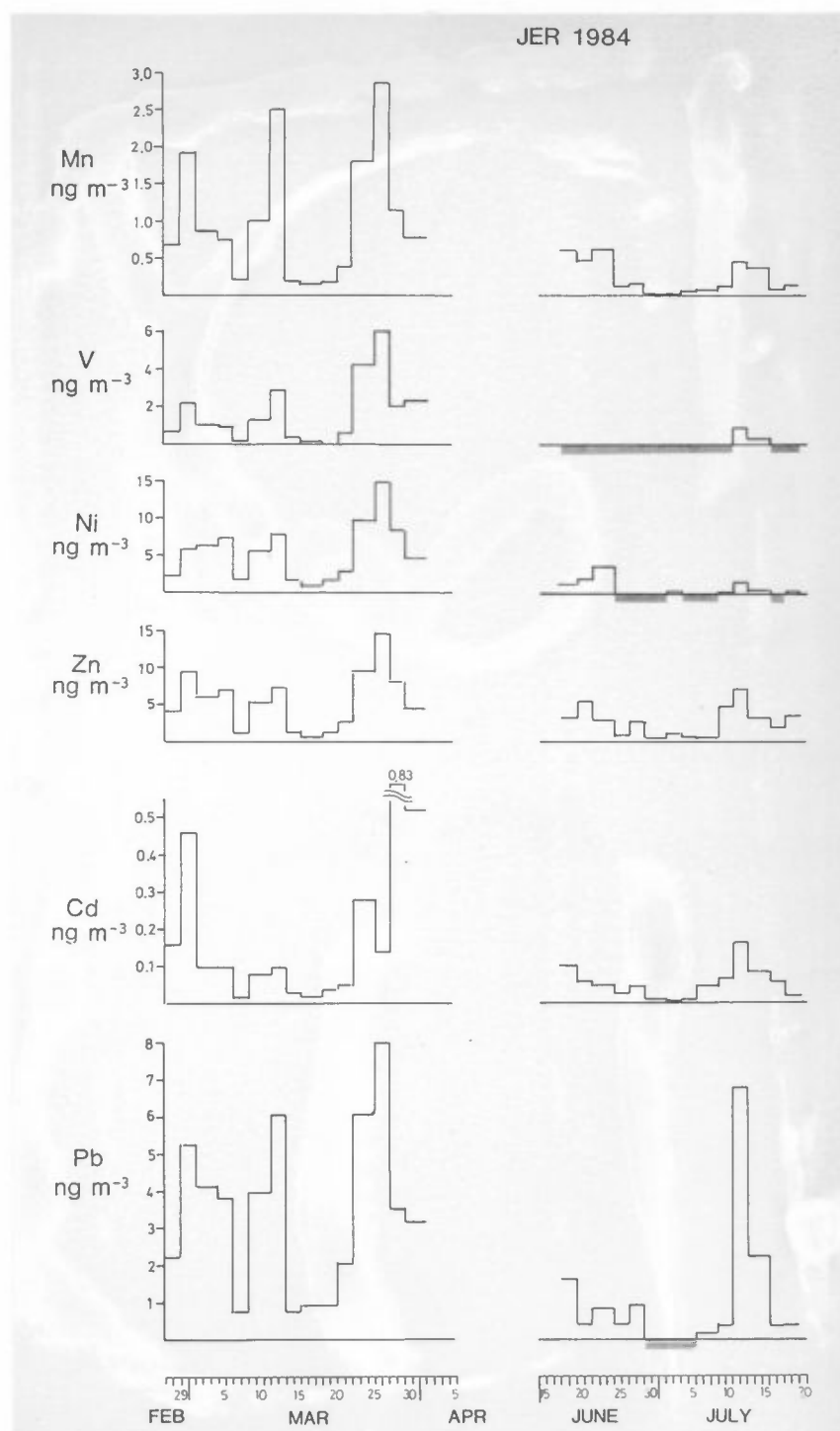


Figure 20: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at JER during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.

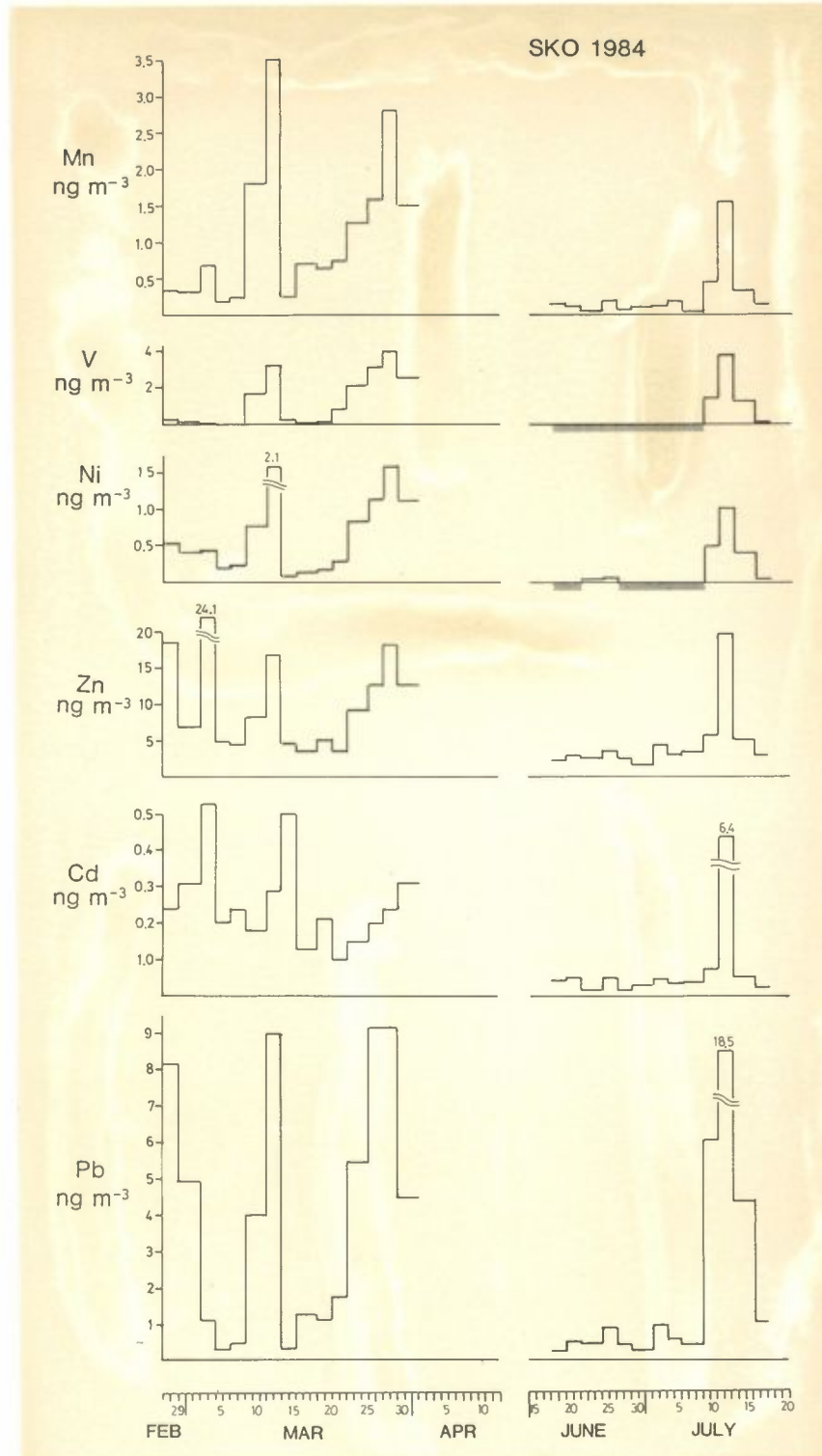


Figure 21: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at SKO during the Spring 1984 and Summer 1984 campaigns.

indicates Hi-Vol concentrations b.d.l.

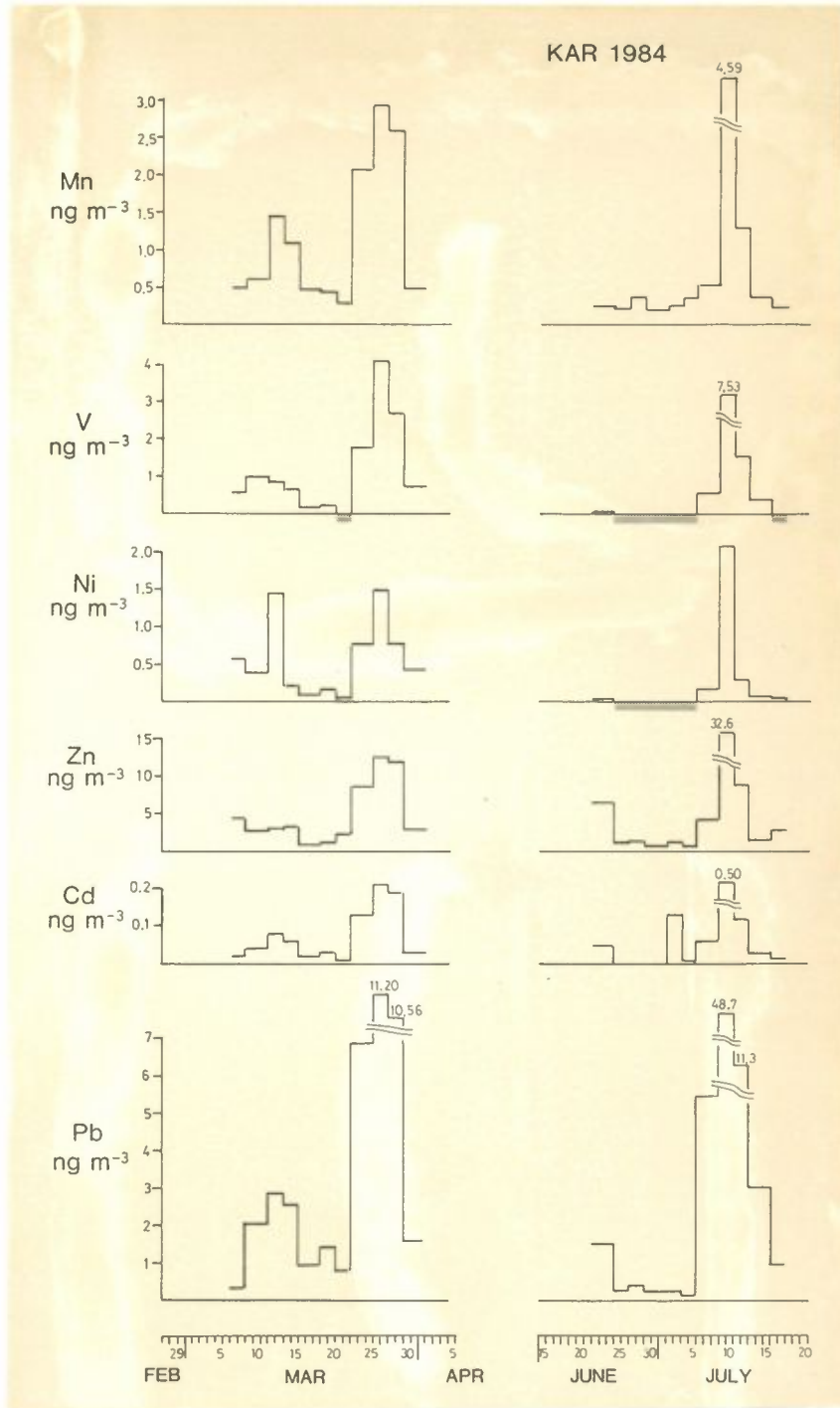


Figure 22: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at KAR during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.

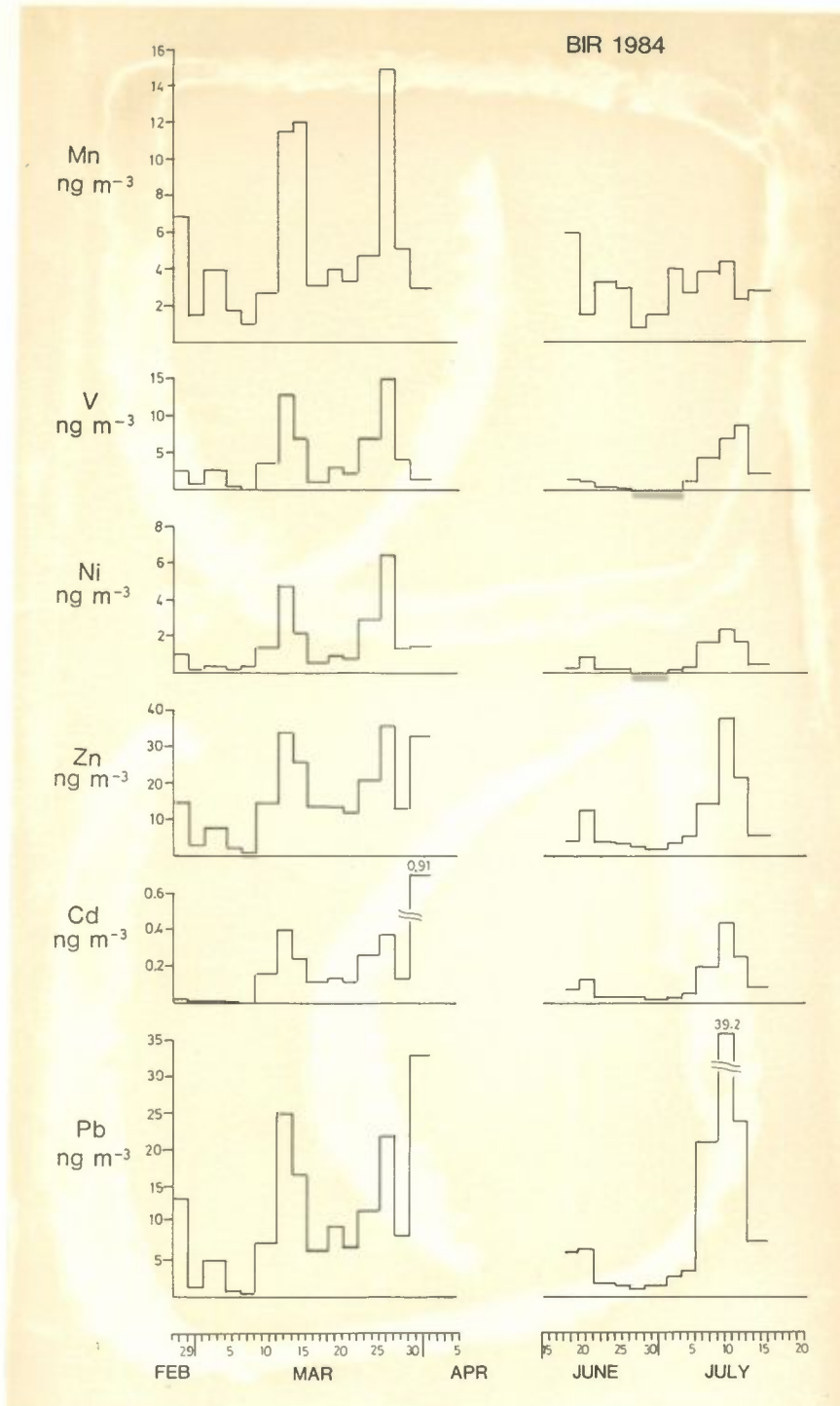


Figure 23: Time series of 2- and 3-day mean concentrations of trace elements from Hi-Vol sampling at BIR during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.

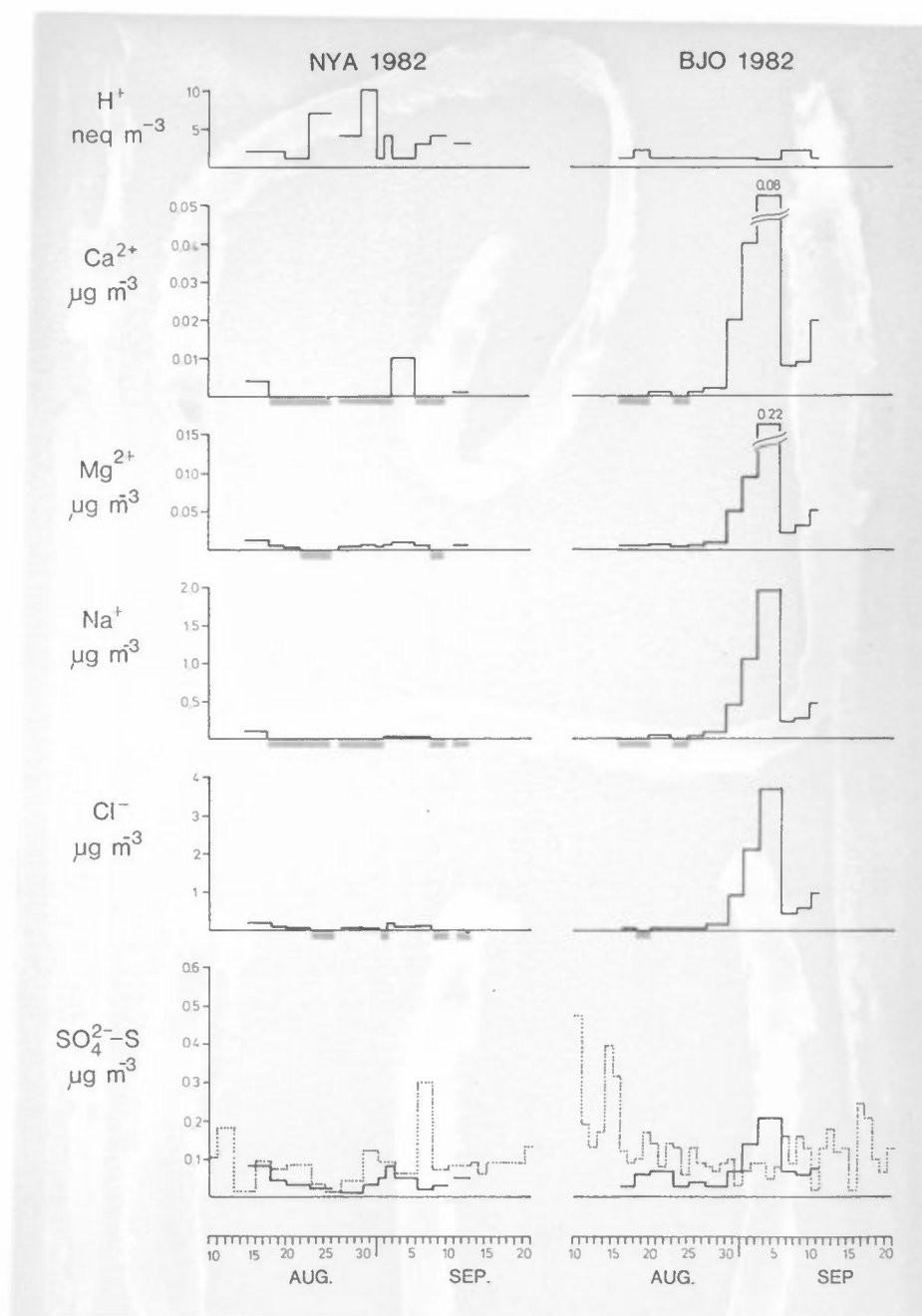


Figure 24: Time series of 2- and 3-day mean concentrations of major ions from high-volume (Hi-Vol) filter sampling at NYA and BJO during the Fall 1982 campaign.

▨ indicates concentrations below detection limit (b.d.l.).

For  $\text{SO}_4^{2-}\text{-S}$ , (.....) indicates 2- and 3-day mean concentrations at NYA, and 24-h concentrations at BJO from low-volume (EK) sampling.

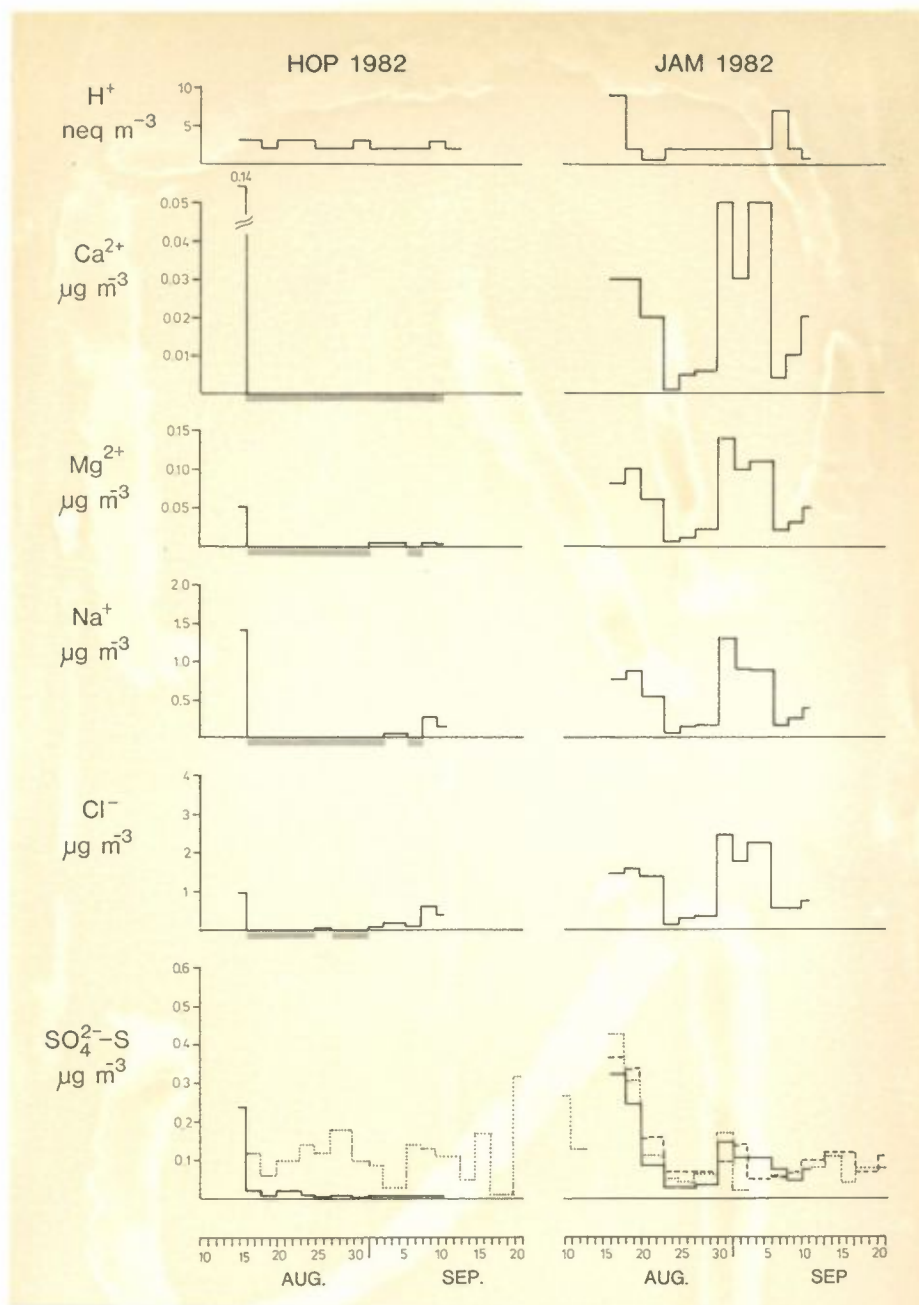


Figure 25: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling at HOP and JAM during the Fall 1982 campaign.

▨ indicates b.d.l.

For SO<sub>4</sub><sup>2-</sup>-S at HOP (.....) indicates 2- and 3-day mean concentrations from EK sampling;  
 for SO<sub>4</sub><sup>2-</sup>-S at JAM, (.....) indicates 2- and 3-day mean concentrations from EK sampling at Jan Met, and (----) from EK at Båtvika.

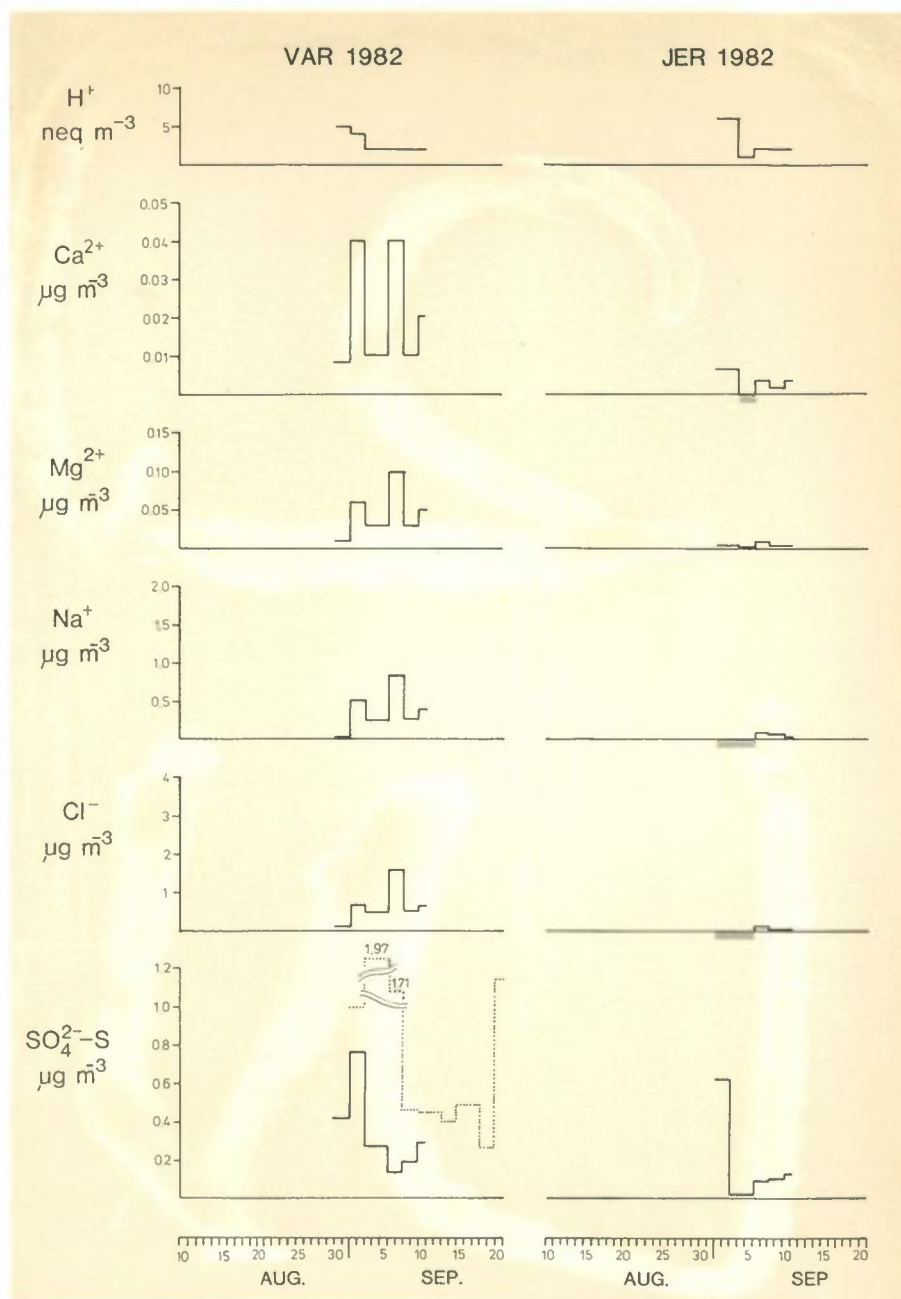


Figure 26: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling at VAR and JER during the Fall 1982 campaign.

▨ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$  at VAR, (.....) indicates 2- and 3-day mean concentrations from EK sampling.



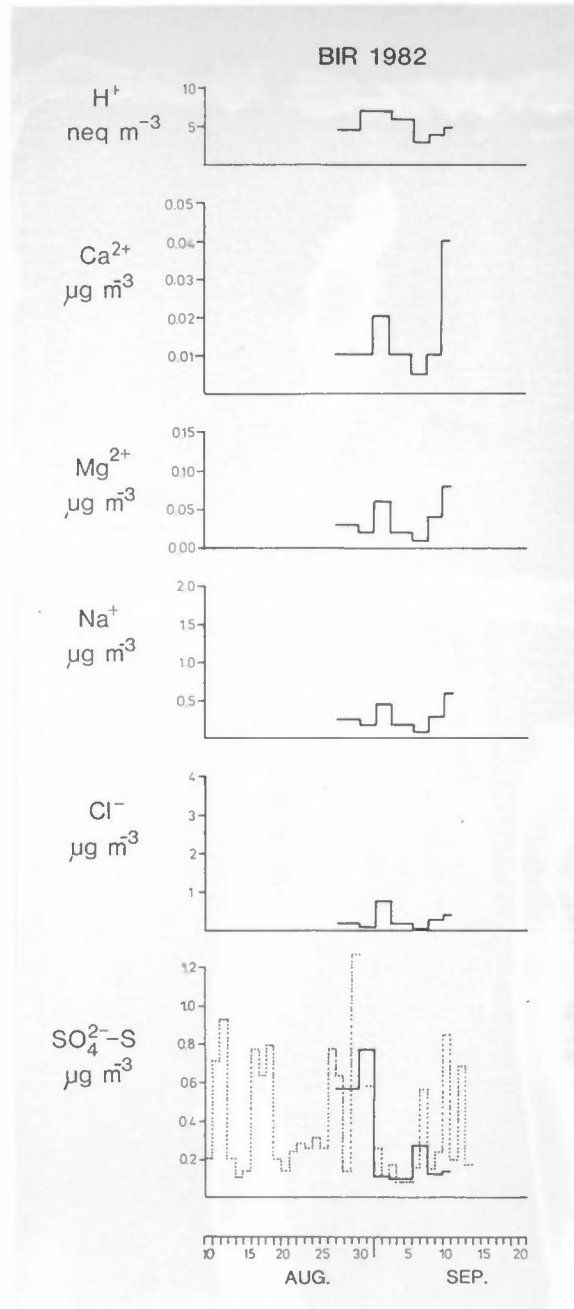


Figure 27: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling at BIR during the Fall 1982 campaign.

For  $\text{SO}_4^{2-}\text{-S}$ , (.....) indicates 24-h concentrations from EK sampling.

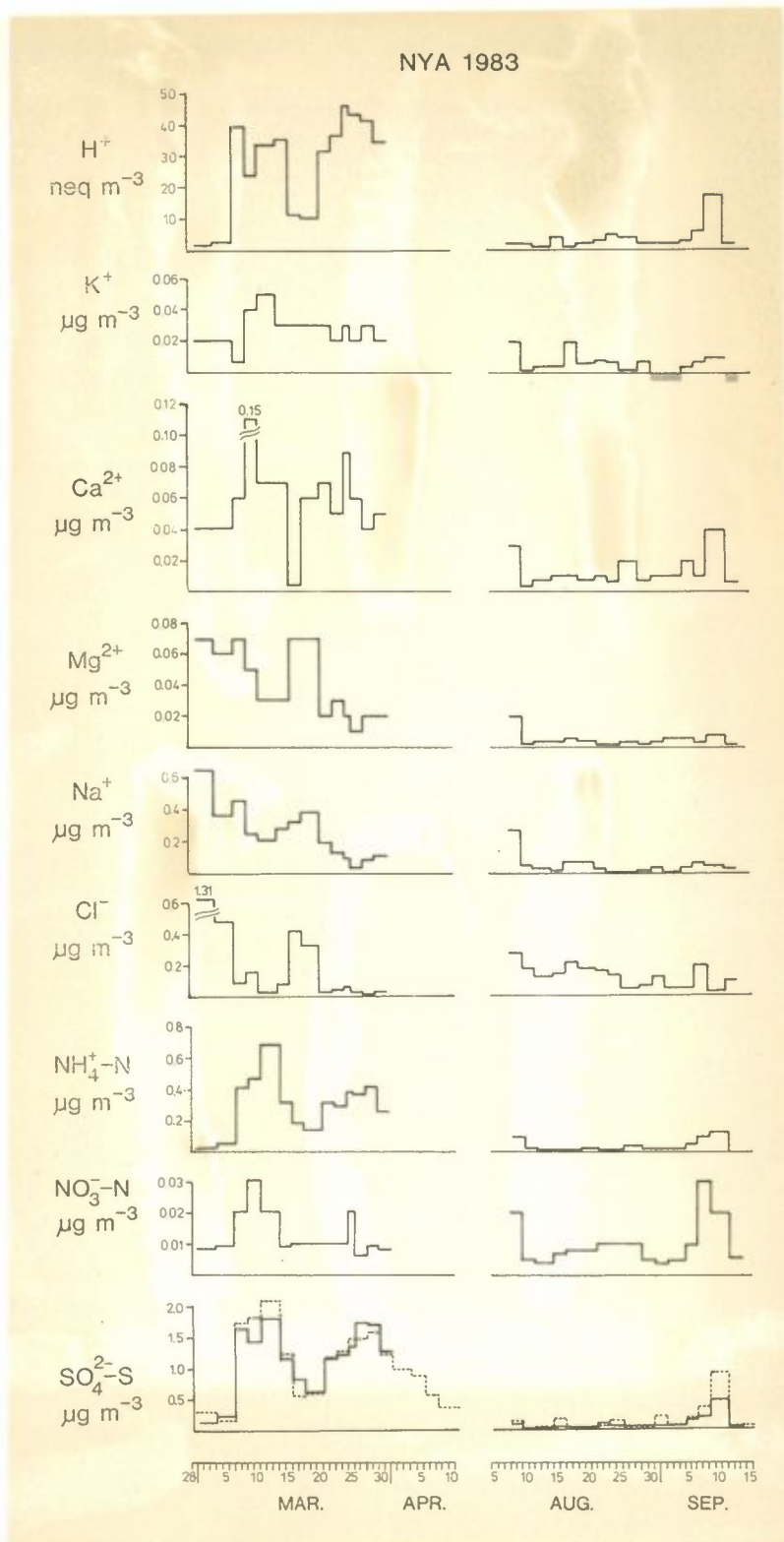


Figure 28: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling at NYA during the Spring 1983 and Fall 1983 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (.....) indicates 24-h concentrations from EK sampling.

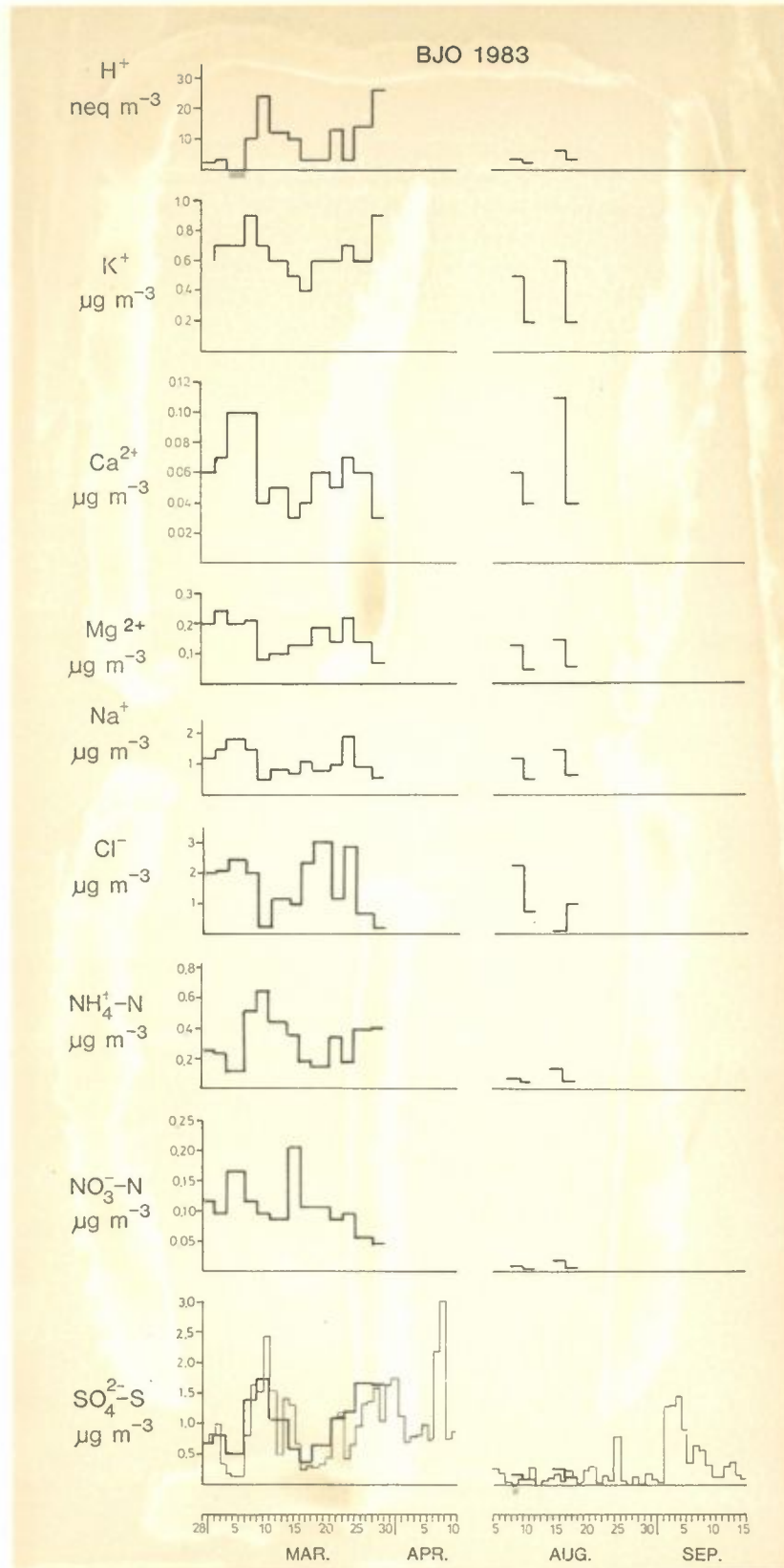


Figure 29: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at BJO during the Spring 1983 and Fall 1983 campaigns.

■■■■ indicates b.d.l.

For SO<sub>4</sub><sup>2-</sup>-S, (—) indicates 24-h concentrations from EK sampling.

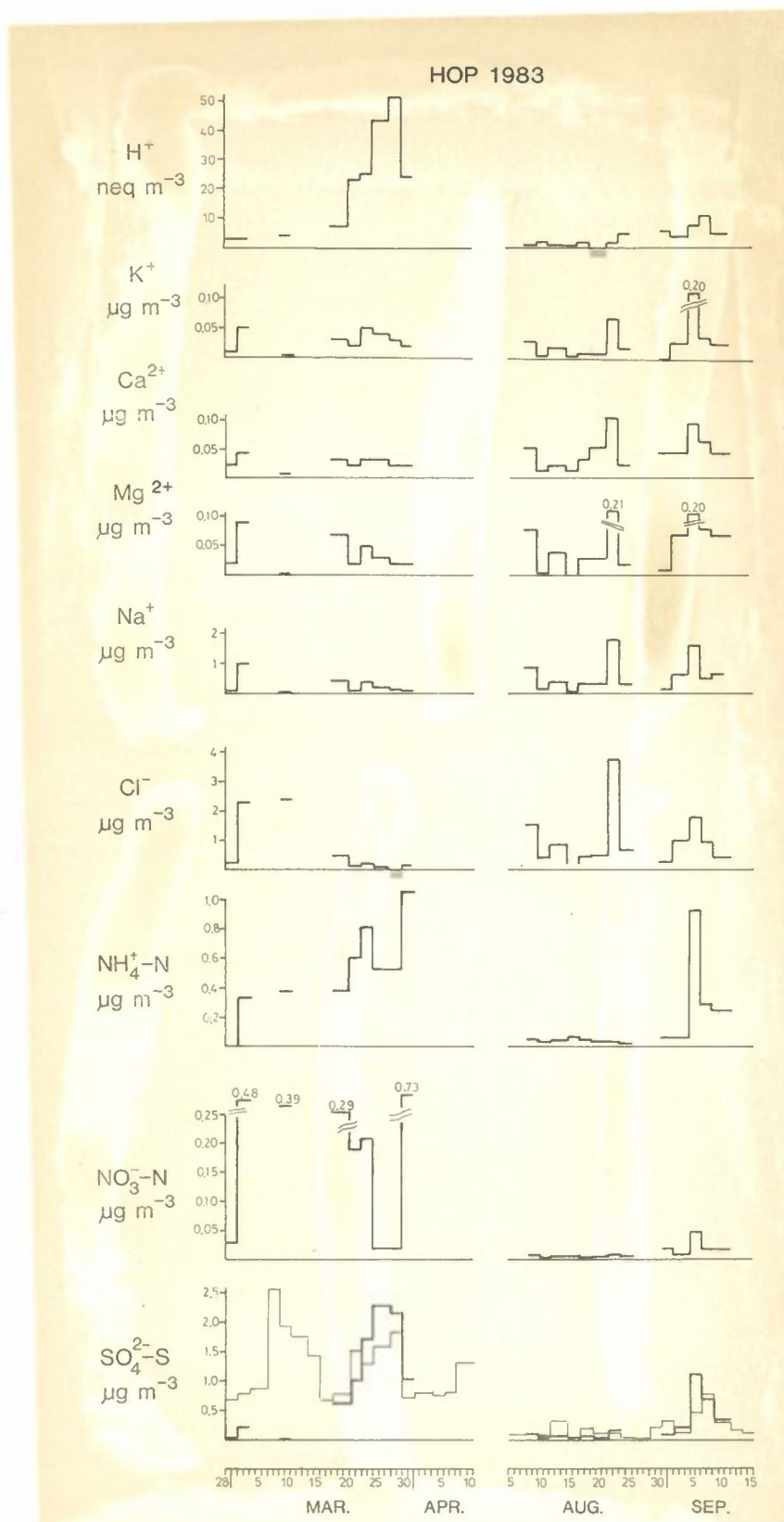


Figure 30: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at HOP during the Spring 1983 and Fall 1983 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (---) indicates 24-h concentrations from EK sampling.

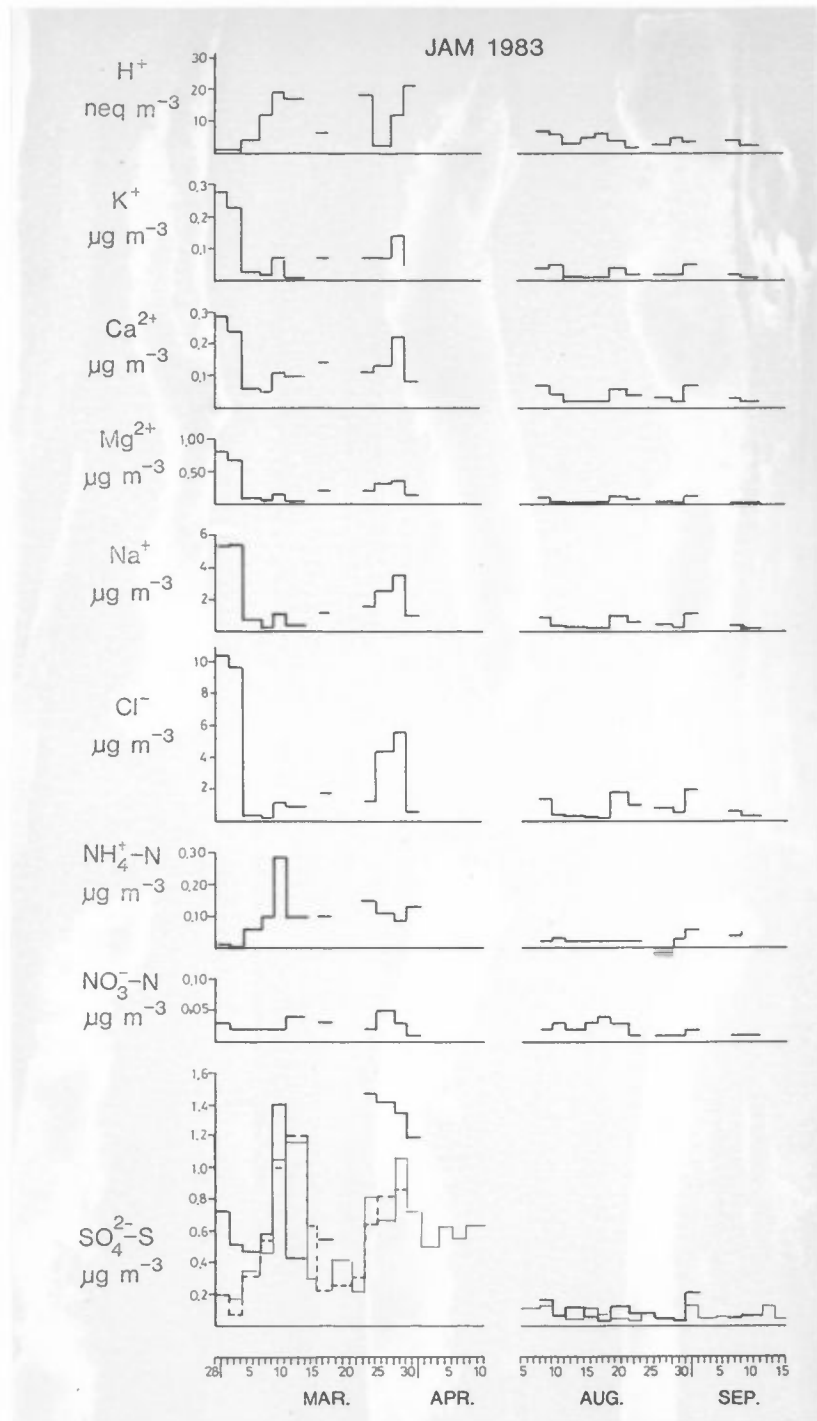


Figure 31: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at JAM during the Spring 1983 and Fall 1983 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (—) indicates 24-h concentrations from EK sampling at Jan Met and (----) at Båtvika.

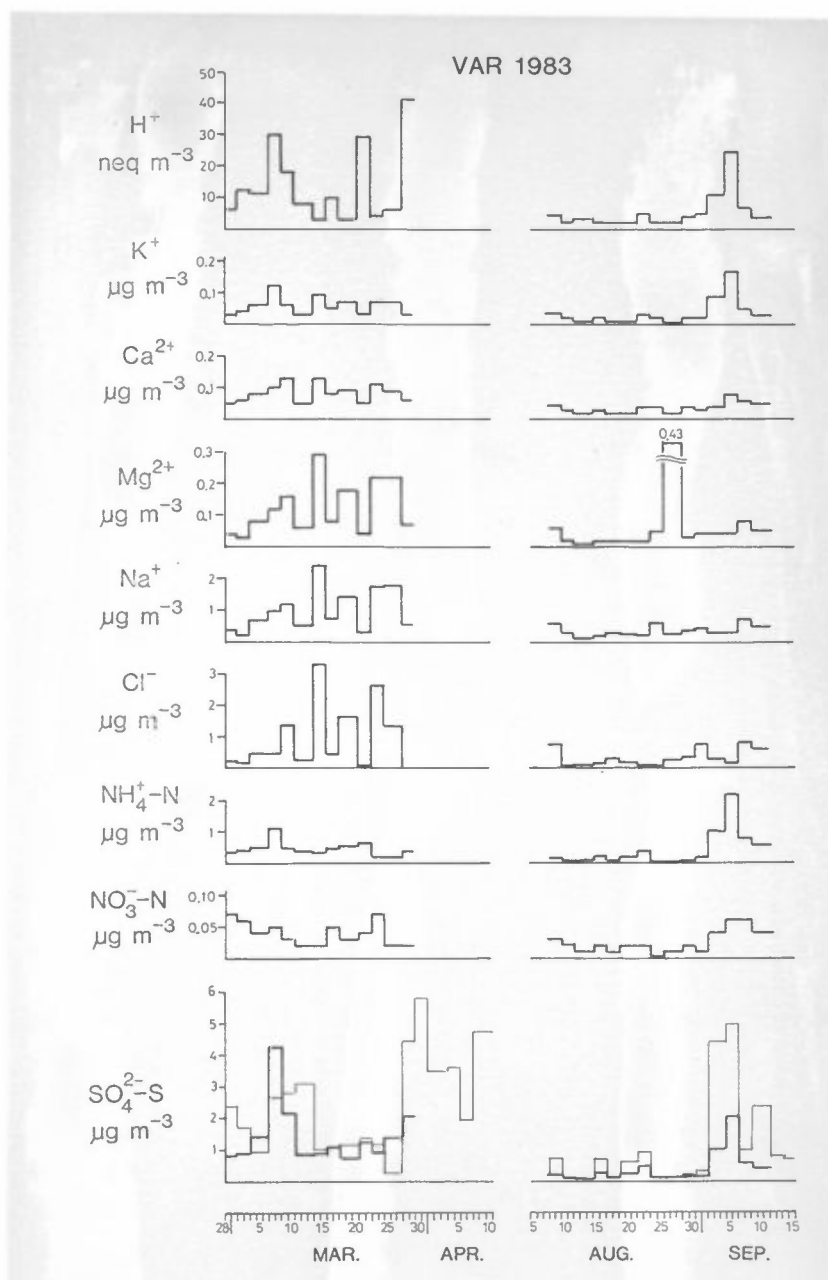


Figure 32: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at VAR during the Spring 1983 and Fall 1983 campaigns.

For SO<sub>4</sub><sup>2-</sup>-S, (—) indicates 24-h concentrations from EK sampling.

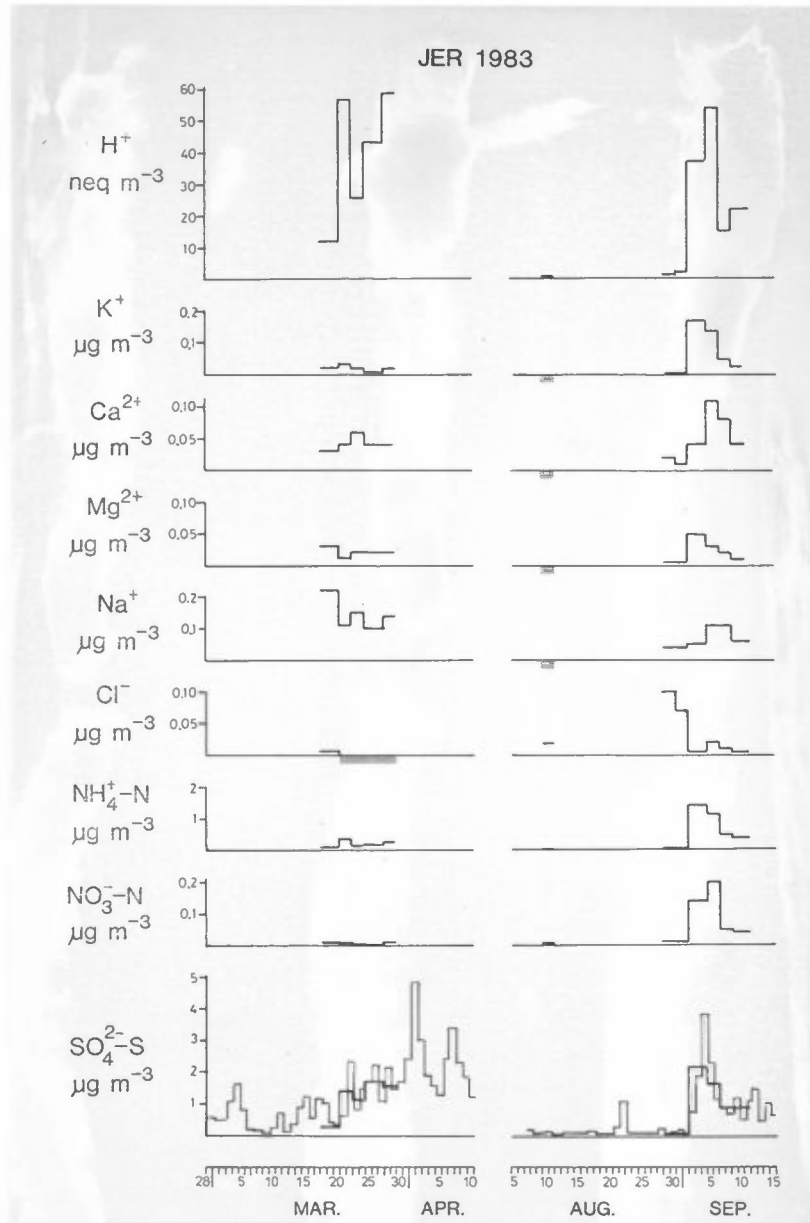


Figure 33: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at JER during the Spring 1983 and Fall 1983 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2--}\text{S}$ , (—) indicates 24-h concentrations from EK sampling.

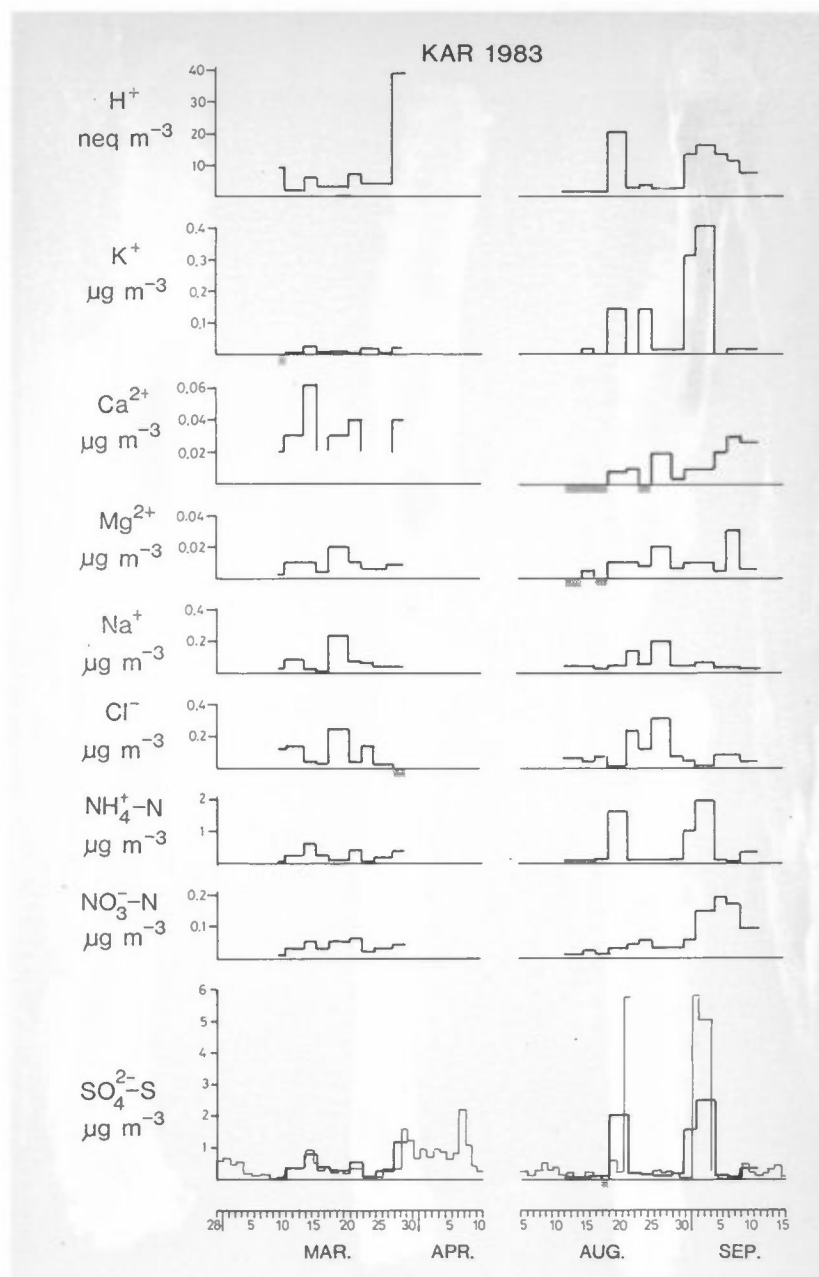


Figure 34: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at KAR during the Spring 1983 and Fall 1983 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2--}\text{S}$ , (—) indicates 24-h concentrations from EK sampling.



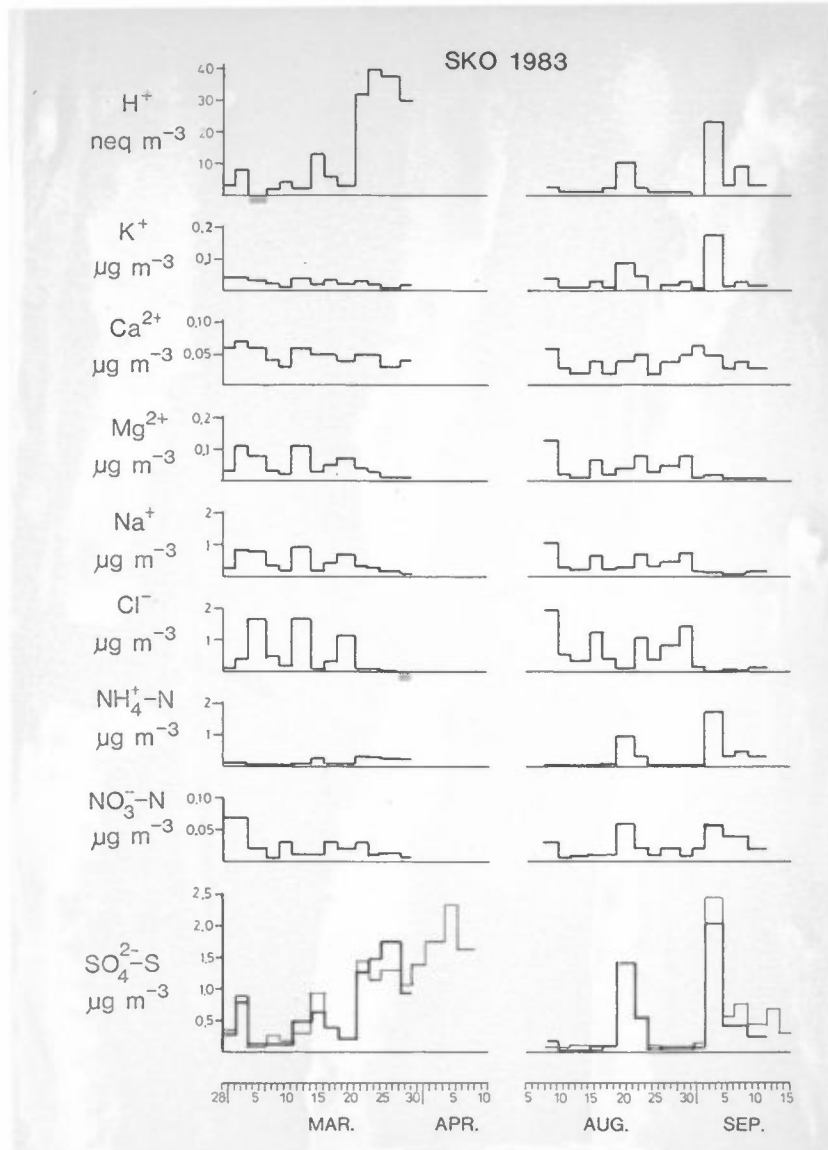


Figure 35: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at SKO during the Spring 1983 and Fall 1983 campaigns.

▨ indicates b.d.l.

For  $SO_4^{2-} - S$ , (—) indicates 24-h concentrations from EK sampling.

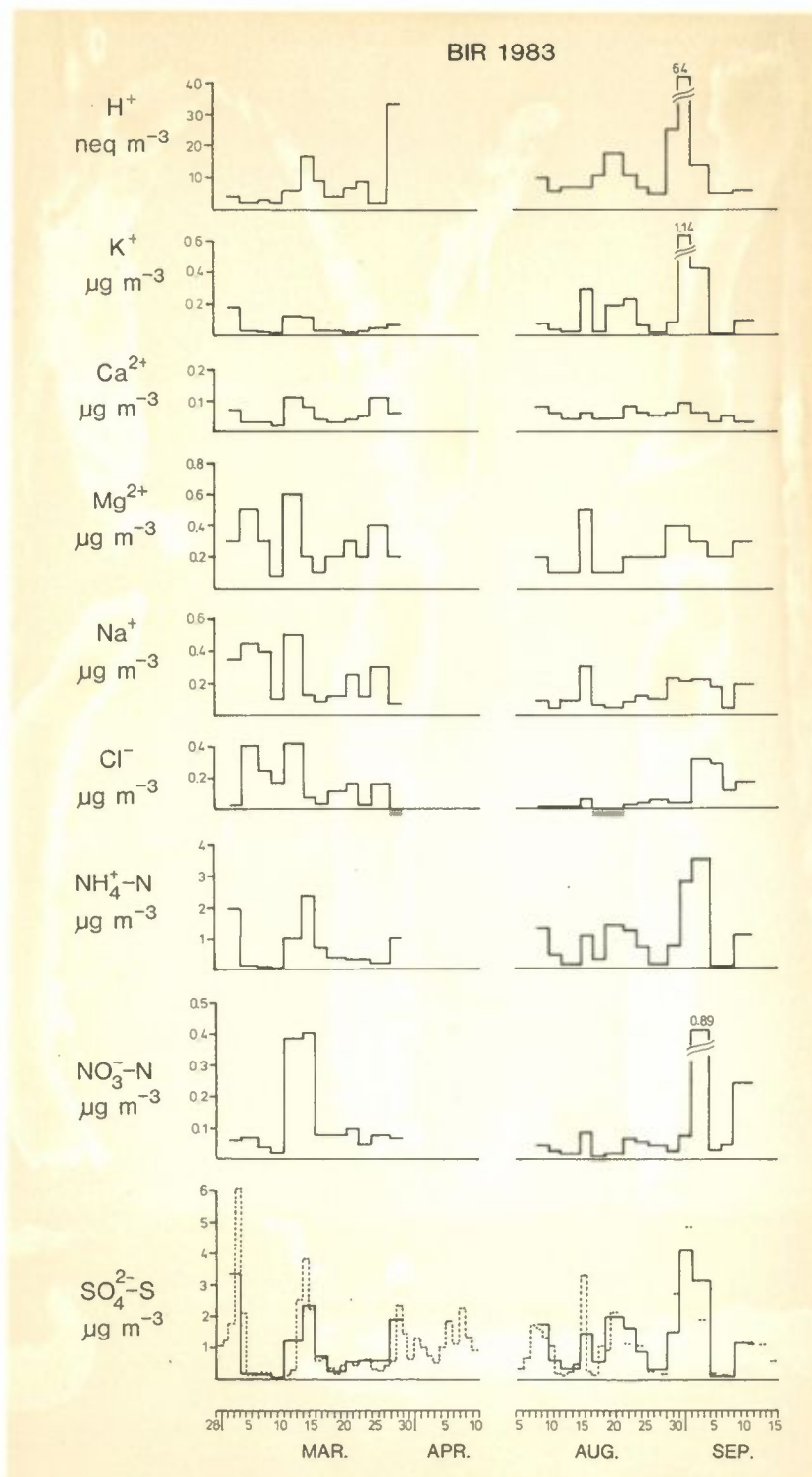


Figure 36: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at BIR during the Spring 1983 and Fall 1983 campaigns.

For  $SO_4^{2-} - S$ , (.....) indicates 24-h concentrations from EK sampling.

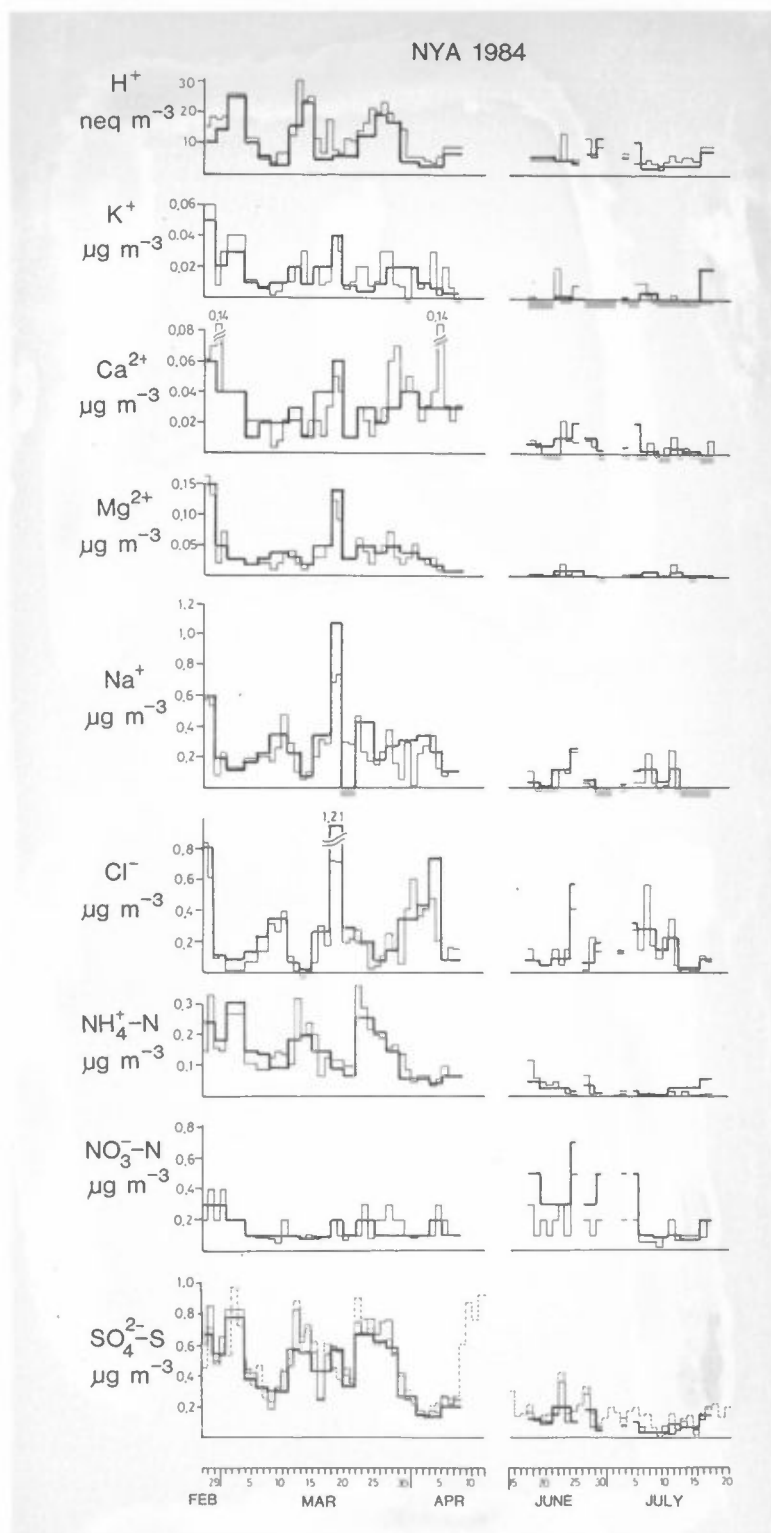


Figure 37: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol (—) and 24-h EXTRA (---) sampling at NYA during the Spring 1984 and Summer 1984 campaigns.

▨ indicates Hi-Vol concentrations b.d.l.

▩ indicates EXTRA concentrations b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (.....) indicates 24-h concentrations from EK sampling.

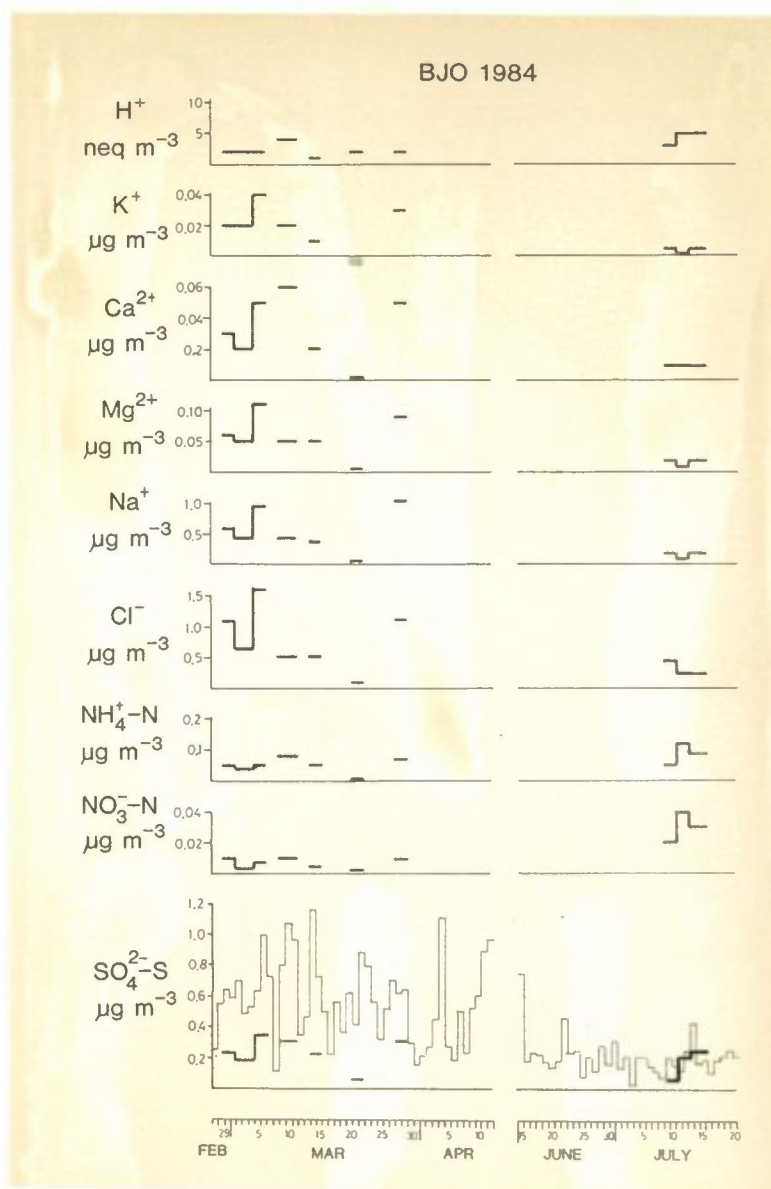


Figure 38: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at BJO during the Spring 1984 and Summer 1984 campaigns.

▣ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (—) indicates 24-h concentrations from EK sampling.

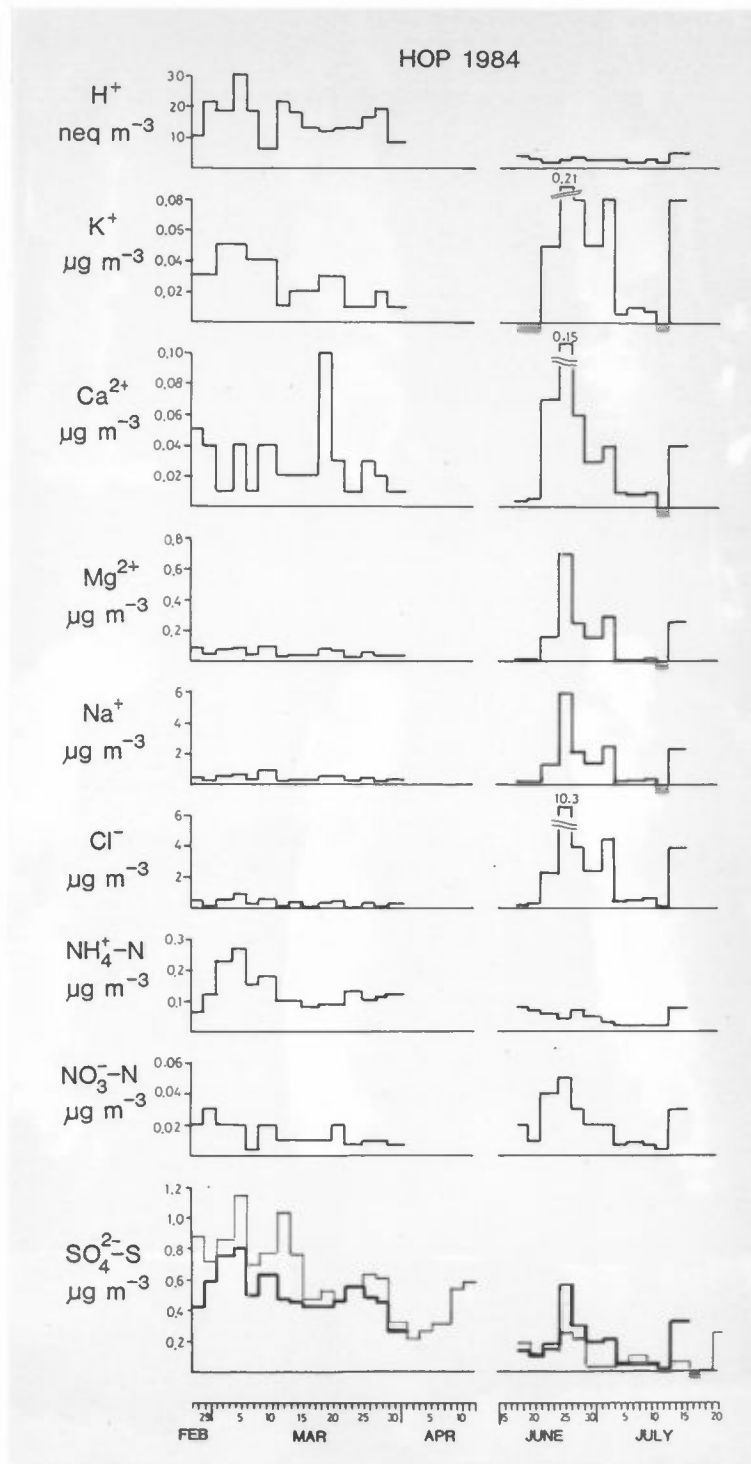


Figure 39: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling at HOP during the Spring 1984 and Summer 1984 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (—) indicates 24-h concentrations from EK sampling.

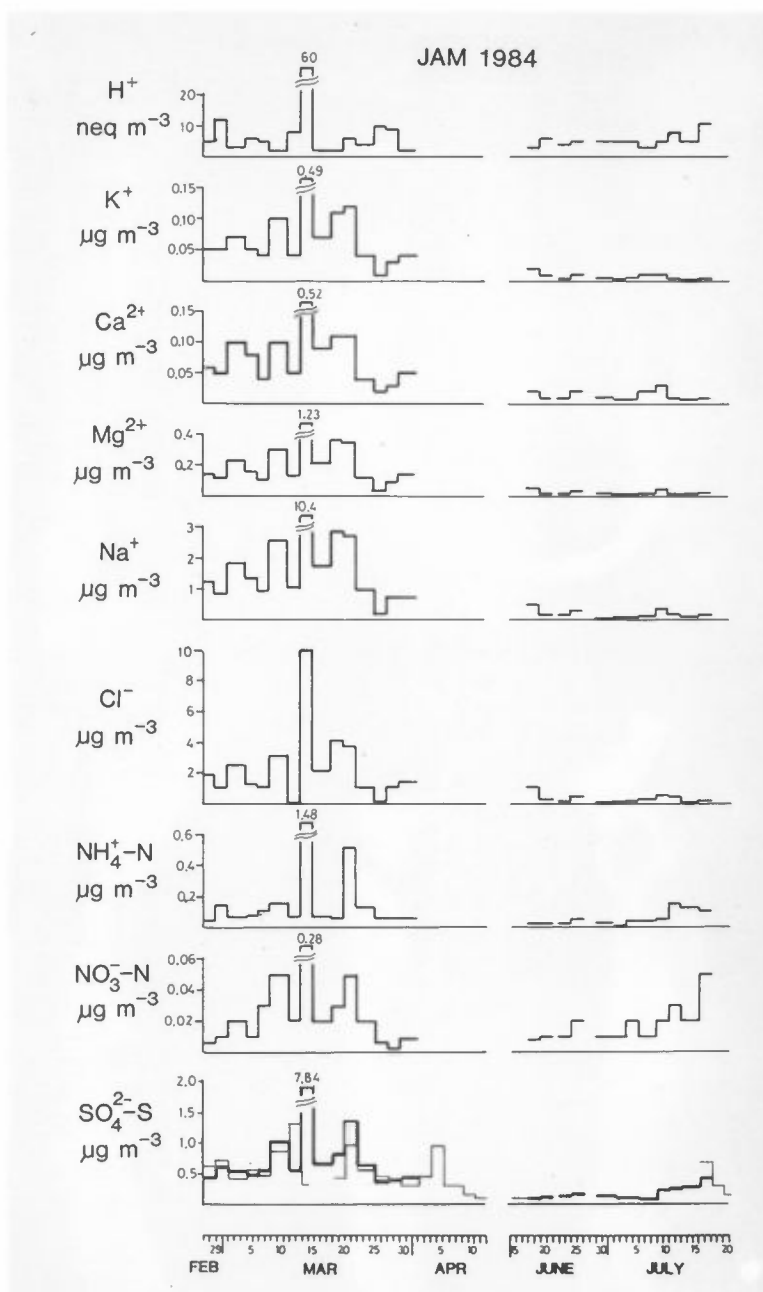


Figure 40: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling at JAM during the Spring 1984 and Summer 1984 campaigns.

The Hi-Vol sample between 1984-03-14 and 16 was of very short duration (<2 h), and thus not representative for the period.

For  $\text{SO}_4^{2-}\text{-S}$ , (—) indicates 24-h concentrations from EK sampling.

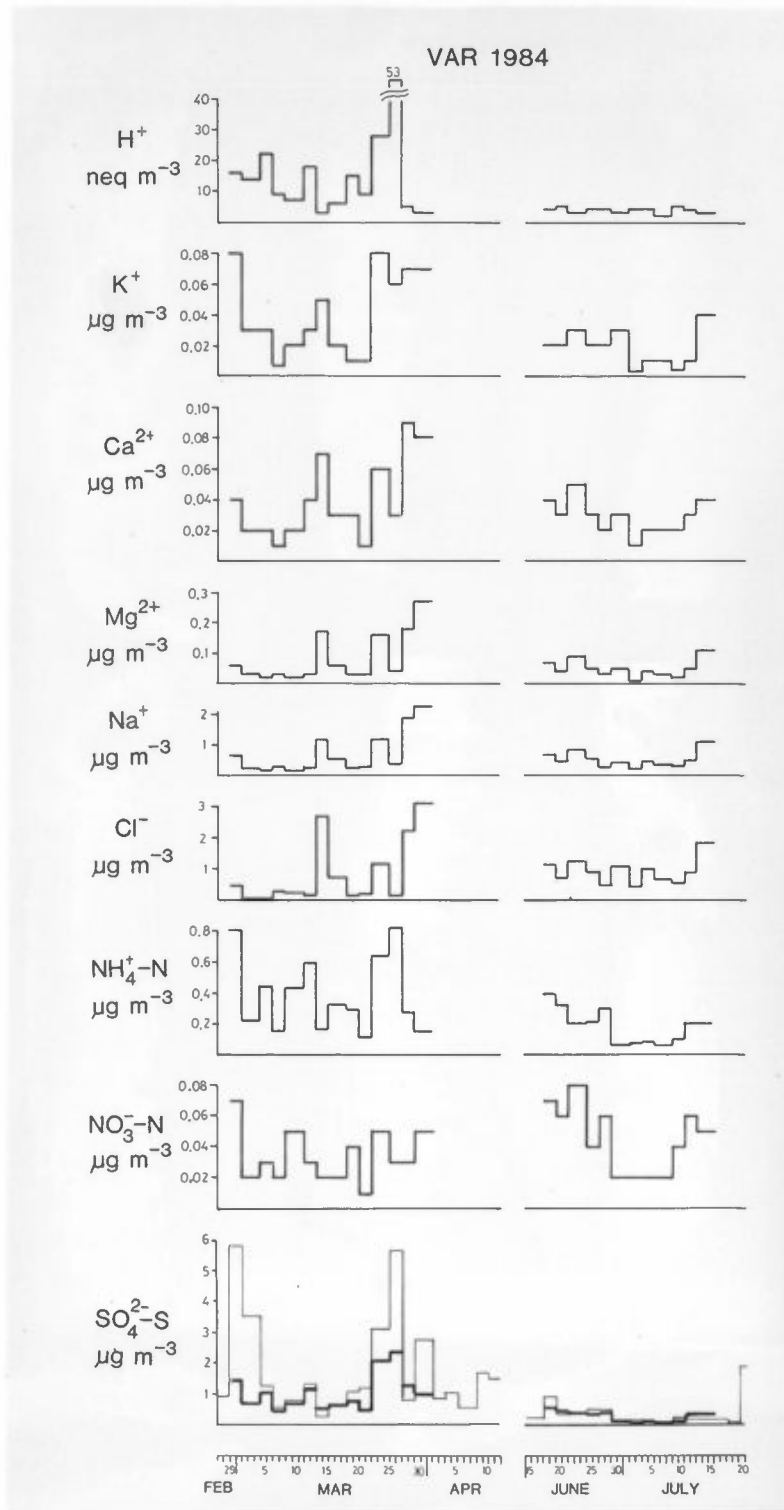


Figure 41: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at VAR during the Spring 1984 and Summer 1984 campaigns.

For  $\text{SO}_4^{2-}\text{-S}$ , (---) indicates 24-h concentrations from EK sampling.

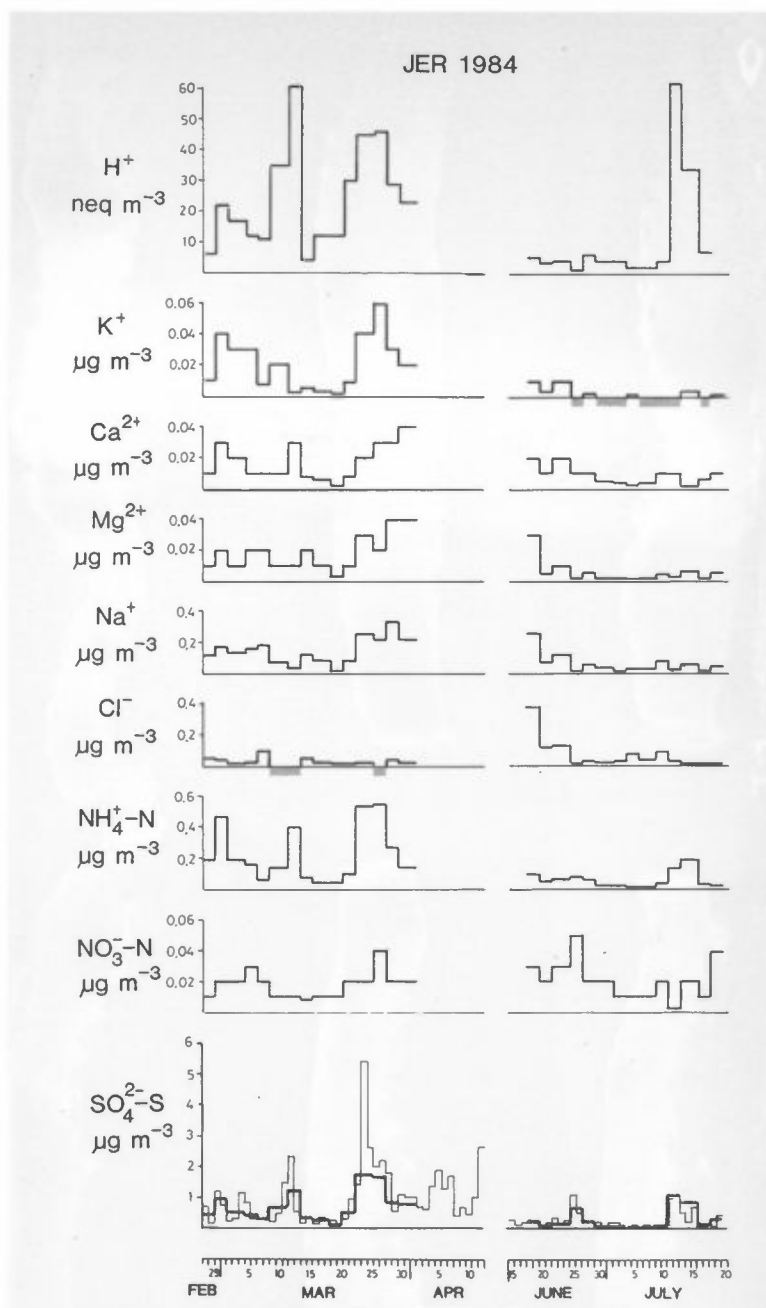


Figure 42: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at JER during the Spring 1984 and Summer 1984 campaigns.

▨ indicates b.d.l.

For  $SO_4^{2-} - S$ , (—) indicates 24-h concentrations from EK sampling.



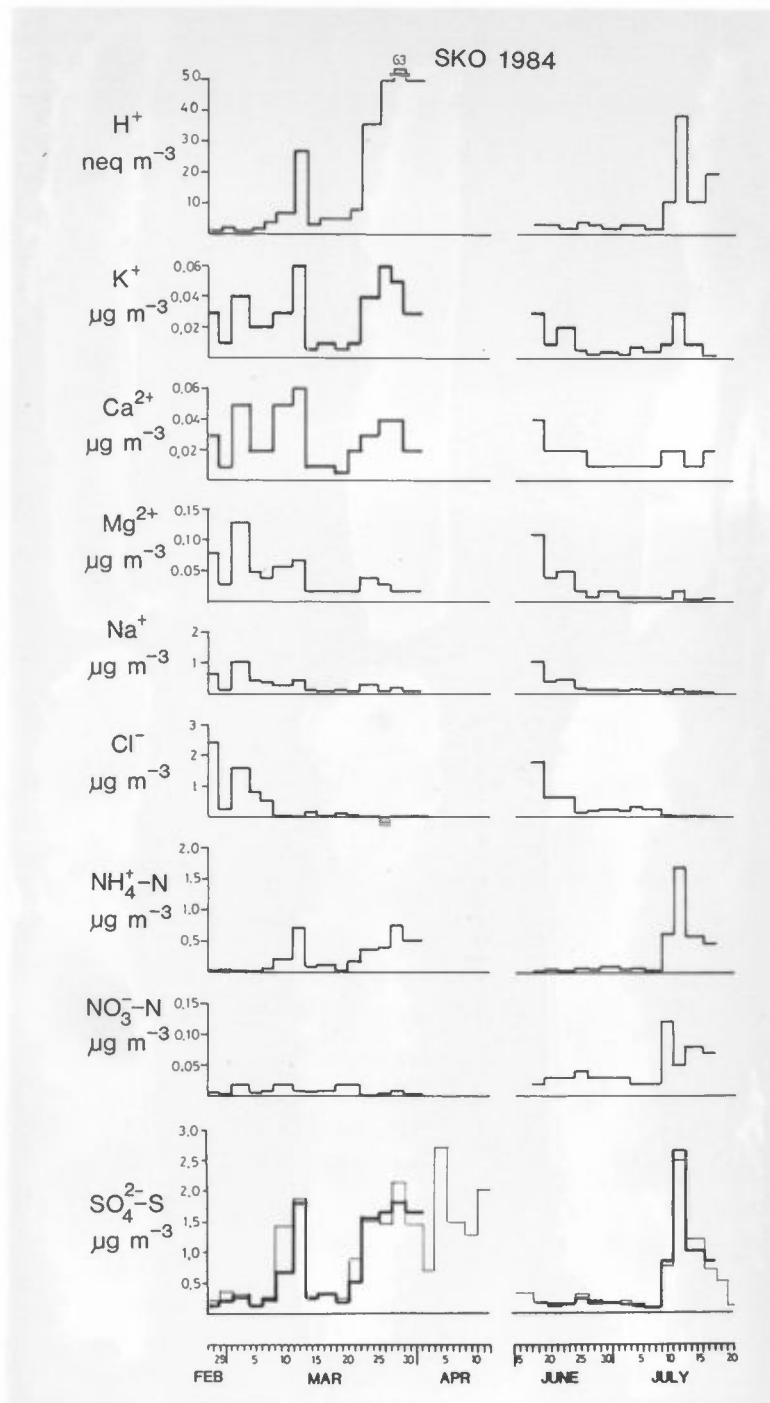


Figure 43: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at SKO during the Spring 1984 and Summer 1984 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (—) indicates 24-h concentrations from EK sampling.

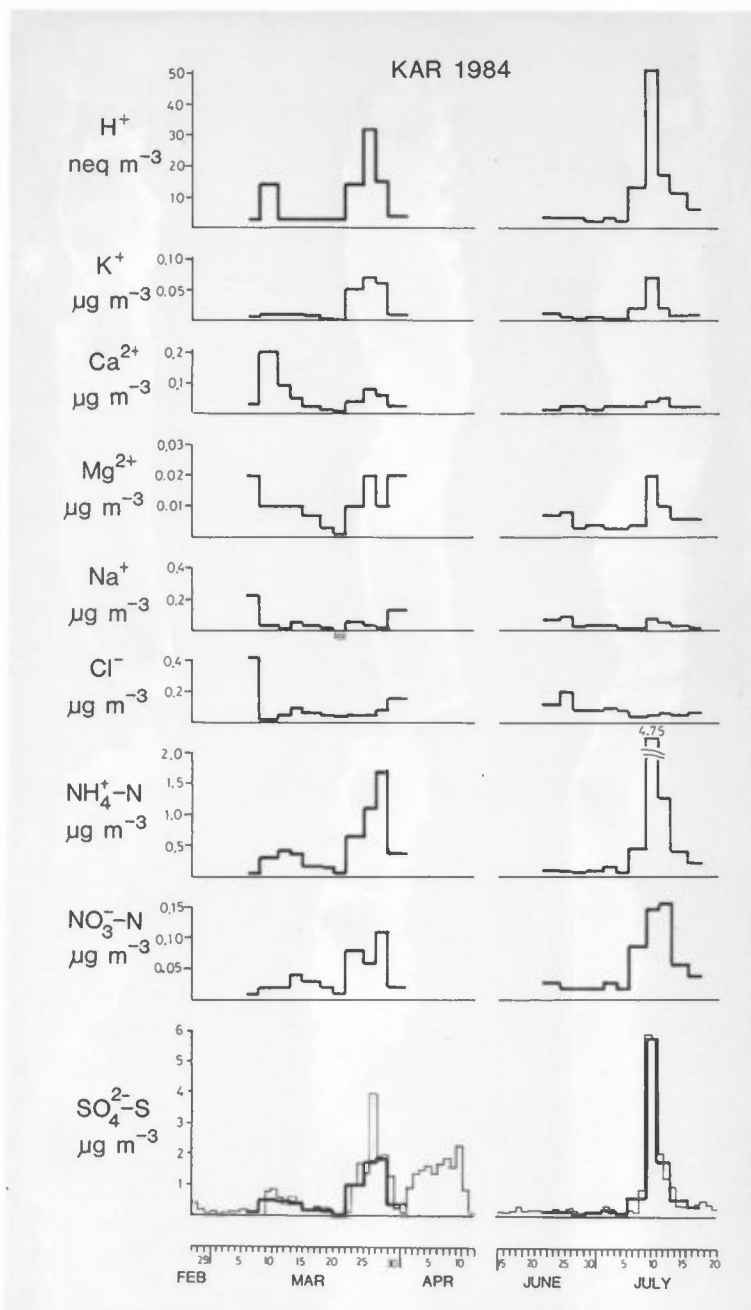


Figure 44: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at KAR during the Spring 1984 and Summer 1984 campaigns.

▨ indicates b.d.l.

For  $SO_4^{2-} - S$ , (—) indicates 24-h concentrations from EK sampling.

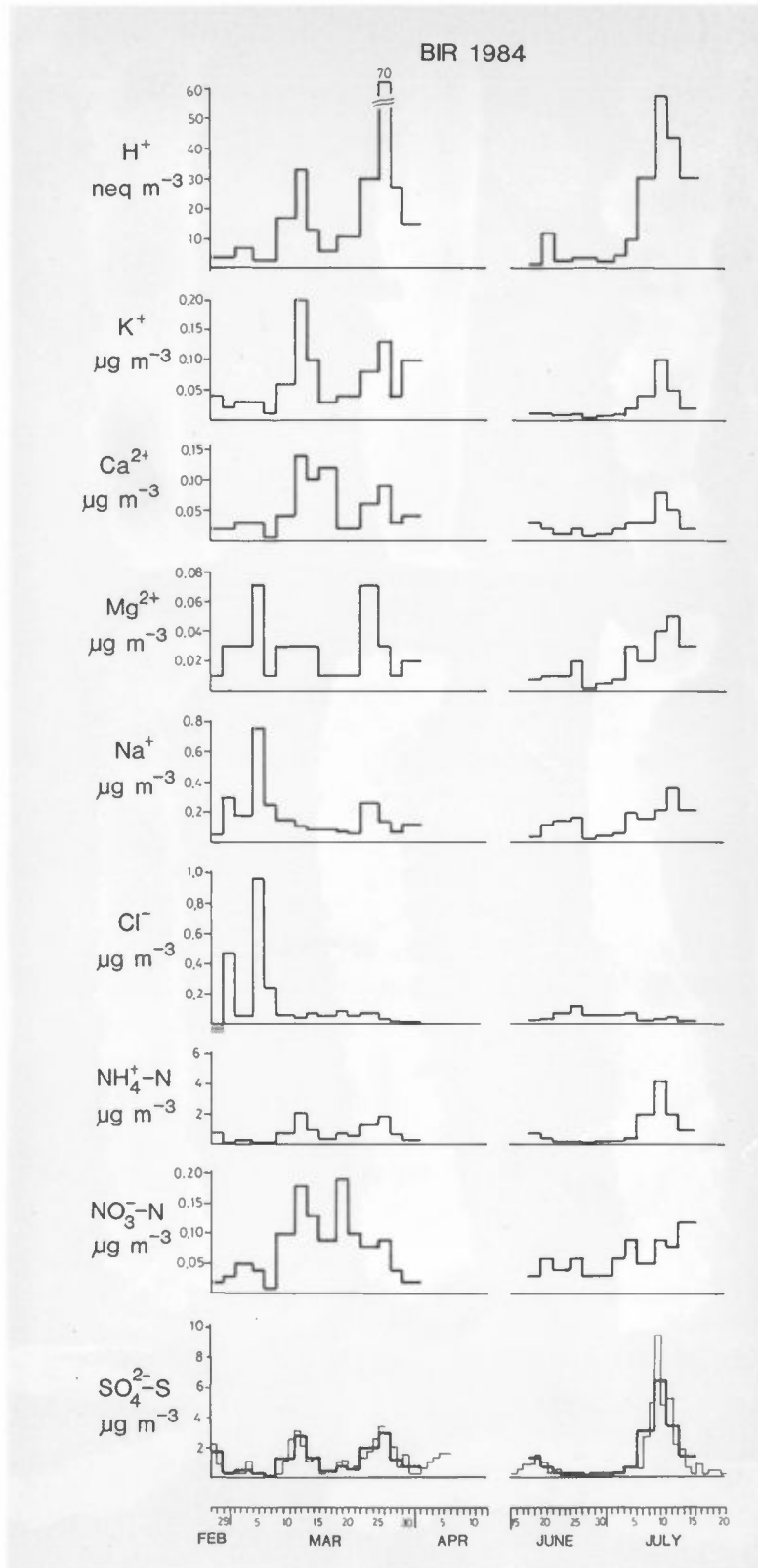


Figure 45: Time series of 2- and 3-day mean concentrations of major ions from Hi-Vol sampling (—) at BIR during the Spring 1984 and Summer 1984 campaigns.

▨ indicates b.d.l.

For  $\text{SO}_4^{2-}\text{-S}$ , (—) indicates 24-h concentrations from EK sampling.

All Hi-Vol sampling runs were conducted on a 2 + 2 + 3 day schedule, with the first 2-day run normally starting on a Monday morning, and the last 3-day run ending on Monday morning between 0800 h and 0900 h MET.

### 3.1 TIME SERIES OF TRACE ELEMENTS

The 2- and 3-day mean concentrations of Pb, Cd, Zn, Ni, V, and Mn, measured by Hi-Vol filter samplers, are shown in Figures 2 through 23. For Spring 1984 campaign at NYA, the trace metal results from 24-h sampling runs of the EXTRA filter sampler (Vitols and Wasseng, 1985) are included for comparison with the Hi-Vol results (Figure 15).

NB the different vertical (concentration) scales in the figures.

#### 3.1.1 Comments on Hi-Vol vs. EXTRA measurements

As seen in Figure 15 and Figure 37 in Section 3.2, there are disagreements between the concurrently measured trace element and major ion concentrations in the samples collected by Hi-Vol and EXTRA samplers\* during the 1984 BP Project campaign at NYA. Some of the apparent differences are clearly exaggerated by the expanded vertical (concentration) scales, when the plotted concentrations are near the detection limit of the analytical methods for a given constituent. In general, however, such differences may be due to sampling, sample handling and treatment, and analytical factors.

As seen in Figure 15, the disagreements are particularly pronounced for Ni, Cd and Zn during the Spring 1984 campaign. Sampling factors, that could have conceivably caused the disagreements include differences in sampling rates (and thus filtration face velocities and efficiencies), fine/coarse fraction cut points, filter "loading" effect, and duration of sampling runs. Neither of these, however, could explain consistently the substantial disagreements for these trace elements. Re-examination of the analytical laboratory records, on the other hand, revealed considerable blank variability and the

---

\* For sampler descriptions see Vitols and Wasseng (1985).

possibility of contamination of the EXTRA filter extracts. Since the Hi-Vol and EXTRA sample comparisons for the ionic species (Figure 37, Section 3.2) show fair agreement, the anomalous EXTRA results for these 3 trace elements must be regarded as a measurement "accident". Thus, the Hi-Vol concentrations in Figure 15 for Ni, Cd and Zn should be taken as the more accurate ones.

21 Figursider

### 3.2 TIME SERIES OF MAJOR IONS

The 2- and 3-day mean concentrations for  $\text{SO}_4^{2-}\text{-S}$ ,  $\text{NO}_3^- \text{-N}$ ,  $\text{NH}_4^+ \text{-N}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{H}^+$ , measured by Hi-Vol filter samplers, are shown in Figures 24 through 45.

NB the different vertical (concentration) scales in the figures.

The  $\text{SO}_4^{2-}\text{-S}$  results from the low-volume EK samplers are included for comparison with those from Hi-Vol samplers (for EK-sampler description see Vitols and Wasseng, 1985). For the BP stations, which also serve the EMEP Programme (i.e., BJO, JER, KAR and BIR), the EK measurements represent 24-h means. Beginning with the Spring 1984 campaign, the EK at NYA was also operated on a 24-h schedule. Furthermore, note that where sulphate (as sulphur) concentrations ( $\text{SO}_4^{2-}\text{-S}$ ) from Hi-Vol and EK samplers are superimposed, the former represent total while the latter "excess" (or non-marine) concentrations of the ion. The excess sulphate concentrations are taken to represent that portion of the ion in the aerosol which is of non-seasalt origin. The adjustment of total to excess sulphate assumes that sea water is the only source of Mg, and seasalt-derived S and Mg in the aerosol exist in the same ratio as in sea water (i.e.,  $\text{S/Mg} = 0.695$ ). Thus, if desired, the Hi-Vol total  $\text{SO}_4^{2-}\text{-S}$  concentrations can be converted to excess sulphate by subtracting from the total the marine component,  $\text{SO}_4^{2-}\text{-S}_{\text{marine}} = 0.695 \text{ Mg}^{2+}_{\text{aerosol}}$ , where  $\text{Mg}^{2+}_{\text{aerosol}}$  is the concentration in the aerosol sample.

### 3.2.1 Comments on Hi-Vol vs. EK measurements

Even at a glance, there are obvious differences in the superimposed time series of  $\text{SO}_4^{2-}$ -S concentrations from Hi-Vol and EK sampling. As in the case for trace elements (Section 3.1.1), some of the differences appear exaggerated because of expanded concentration scales.

The two sampling systems\* are different in several respects, including sampling rates and durations, cut-off diameters, filter efficiencies, and sampling control.

For the most part (but not entirely) the EK concentrations are higher. The EK filter undoubtedly collects more coarse particles than in the Hi-Vol fine fraction, which at the island stations (with the possible exception of HOP in wintertime) would be largely sulphate-containing airborne seasalt. These particles have a mass mode in the coarse particle range (Blanchard and Woodcock, 1980). The EK results, however, have been corrected for marine sulphate (as noted earlier), and thus should have all seasalt contribution removed, which is not the case of the Hi-Vol samples. Anthropogenic  $\text{SO}_4^{2-}$ -S should be largely found in accumulation mode particles (Whitby, 1978; Hoff and Trivett, 1984, Pacyna et al., 1984) and it is likely that the more efficient Whatman 40 prefilter of the EK sampler collects proportionately more of the aerosol than the Whatman 41 of the Hi-Vol. The filtration efficiency difference alone, however, cannot explain the concentration discrepancies consistently.

The EK prefilter and the KOH-impregnated afterfilter are not physically separated from each other in the filter holder. Thus, it is conceivable that under wet and humid conditions the impregnation could spread to the aerosol prefilter, converting at least some of the ambient  $\text{SO}_2$  to sulphate. Since the EK samplers were operated uncontrolled at all BP Project ground stations, such an effect should be most pronounced at locations, where Hi-Vol sampling was controlled and the ambient  $\text{SO}_2$  levels were relatively high (e.g., VAR), and/or the stations were near sulphur-containing fuel combustion (e.g., BJO, HOP and VAR). Figures 26 and 41 seem to confirm this for VAR, but Figure 32 shows an inconclusive trend. For BJO, Figures 24 and

---

\* For sampler description and sampling characteristics see Vitols and Wasseng (1985).

29 also permit no firm conclusions, in some cases showing higher Hi-Vol concentrations. Beginning with the Fall 1983 campaign, usable data recoveries from BJO were too poor for comparisons (Figures 29 and 38). In case of HOP (Figures 25, 30 and 39), the differences go both ways. The much higher higher Hi-Vol  $\text{SO}_4^{2-}$ -S concentrations at JAM during the last week in March 1983 (Figure 31) seem to be at least partly due to seasalt sulphate, because uncorrected (total) EK concentrations are at about the same level, although not consistently so.

Thus, there does not seem to be an entirely satisfactory explanation of the differences in the Hi-Vol and EK measurements, and a combination of factors - both sampling and analytical - lies behind the observed disagreements.

### 3.3 CARBONACEOUS CONTENT OF AEROSOLS

As of this writing, the quantitative calibration of the Whatman 40 and 41 filter media was not yet completed at LBL. The already available attenuation measurements, however, may be used to indicate the relative "blackness" of black carbon deposits on the selected Hi-Vol and EK filters. Since the primary purpose of the pilot study was to evaluate the feasibility of the optical attenuation method for fibrous filter media application, the filters were selected entirely arbitrarily according to their darkened appearance.

The "blackness" values (in arbitrary units) listed in Table 4, were obtained by normalizing the measured attenuation to sample volume ( $\text{m}^3$ ) per unit area ( $\text{cm}^2$ ) of filter.

Table 4: Relative "blackness" of selected Hi-Vol, EXTRA and EK filter samples at the various BP Project ground stations (1983-84).

Ground station	Sampling period	Sampler	Attenuation, A	Sample $\text{m}^3 \text{cm}^{-2}$ filter	"Blackness" (arbitrary) units)
NYA	1983-03-07 to 09	EXTRA	30	6.4	4.7
"	1983-03-13 to 14	"	24	4.0	6.0
"	1983-03-22 to 23	"	34	4.2	8.0
"	1983-03-25 to 26	"	25	3.8	6.6
"	1983-03-30 to 31	"	22	4.0	5.6
"	1983-04-02 to 03	"	11	2.6	4.3
"	1983-09-09 to 12	Hi-Vol	21	10.5	2.0
"	1983-09-09 to 12	EK	38	11.0	3.5
"	1984-02-28 to 29	EXTRA	15	3.7	4.1
"	1984-03-01 to 02	"	28	4.9	5.8
"	1984-03-02 to 05	"	83	15.0	5.5
"	1984-03-02 to 05	Hi-Vol	45	9.9	4.6
BJO	1983-03-07 to 09	Hi-Vol	7	7.8	0.9
"	1983-03-09 to 11	"	20	8.7	2.3
"	1983-03-11 to 14	"	17	8.8	1.9
HOP	1983-03-18 to 21	Hi-Vol	5	13.4	0.4
"	1983-03-23 to 25	"	4	9.7	0.3
"	1983-03-25 to 28	"	26	14.1	1.9
"	1983-03-28 to 30	"	10	9.5	1.1
"	1983-08-19 to 22	"	110	12.3	8.9
"	1983-08-31 to 09-02	"	100	8.7	11.5
"	1984-03-12 to 14	"	72	10.1	7.1
"	1984-03-16 to 19	"	118	14.3	3.7
JAM	1983-03-07	Hi-Vol	23	8.2	2.8
"	1983-03-09 to 11	"	18	6.3	2.9
"	1983-03-23 to 25	"	24	8.7	2.8
"	1983-03-30 to 04-01	"	19	7.2	2.6
"	1984-02-29 to 03-02	"	29	9.9	2.9
"	1984-03-02 to 05	"	27	13.4	2.0
VAR	1983-09-02 to 05	Hi-Vol	52	13.2	3.9
"	1983-09-02 to 05	EK	77	9.5	8.1
"	1983-09-05 to 07	Hi-Vol	66	8.5	7.8
"	1983-09-05 to 07	EK	72	6.7	10.7
"	1983-09-07 to 09	Hi-Vol	55	8.6	6.4
"	1983-09-09 to 12	"	49	12.9	3.7
"	1984-02-29 to 03-02	"	57	8.6	6.6
"	1984-03-02 to 05	"	38	14.3	2.7



Table 4: Cont.

Ground station	Sampling period	Sampler	Attenuation, A	Sample $m^3 cm^{-2}$ filter	"Blackness" (arbitrary units)
JER	1983-03-21 to 23	Hi-Vol	38	10.6	3.7
"	1983-03-23 to 25	"	47	10.3	4.6
"	1983-03-25 to 28	"	53	15.5	3.4
"	1983-03-28 to 30	"	35	10.3	3.4
"	1983-09-02 to 03	EK	28	3.5	8.1
"	1983-09-03 to 04	"	34	3.7	9.2
"	1983-09-04 to 05	"	33	3.5	9.5
"	1983-09-02 to 05	Hi-Vol	82	12.8	6.4
"	1983-09-05 to 07	"	55	8.9	6.2
"	1983-09-07 to 09	"	40	8.2	4.9
"	1983-09-09 to 12	"	65	14.6	4.5
SKO	1983-03-14 to 16	Hi-Vol	28	8.6	3.3
"	1983-03-21 to 23	"	26	8.4	3.1
"	1983-03-23 to 25	"	24	8.6	2.8
"	1983-03-25 to 28	"	48	12.8	3.8
"	1983-09-02 to 05	"	71	12.9	5.5
"	1983-09-02 to 05	EK	49	9.3	5.3
"	1983-09-05 to 07	"	28	7.2	3.9
"	1983-09-07 to 09	Hi-Vol	32	9.4	3.4
"	1983-09-09 to 12	"	31	13.5	2.3

Hi-Vol = high-volume filter sampler;

EXTRA = high-volume filter sampler, deployed at NYA only for special measurements;

EK = low-volume filter sampler.

### 3.3.1 Comments on black carbon measurements

Interest in carbonaceous aerosols and their possible effects on visibility, health and climate has been on the rise in recent years. Specifically in the Arctic, optical absorption of graphitic "black carbon" (BC) (also referred to as soot, and elemental carbon) appears to be large enough to cause significant perturbations of solar radiation balance (e.g., Porch and MacCracken, 1982).

Aerosol particles from combustion sources contain a variety of carbonaceous compounds, but BC can only be produced by incomplete combustion. It is inert to transformations in the atmosphere, and thus a good "tracer" substance for the mostly anthropogenic combustion emissions.

LBL has developed methods for chemical and optical determination of BC content of aerosol samples on filters, allowing the correlation of optical attenuation of filter deposit with BC concentrations in the air (Gundel et al., 1984). A successful calibration of fibrous filter media, such as Whatman 40 and 41, is very desirable since it would enable a relatively simple assessment of the important BC component of arctic aerosol from routine Hi-Vol and EK measurements, without the need to resort to specialised sampling and analytical procedures.

In the few instances where "blackness" data in Table 4 are available from parallel sampling with both Hi-Vol and EK samplers, the EKs usually give higher values than the Hi-Vols. This again may reflect the better filtration efficiency of Whatman 40 filters (used for EK sampling) for collection of very fine particles (see Section 2.1.1). The preliminary nature of the "blackness" determinations and the sparseness of data for comparisons, however, do not justify any firm conclusions on either correlation of "blackness" with trace element and/or ion concentrations, or sampler variability.

#### 3.4 METEOROLOGICAL DATA

The BJO, HOP and JAM ground stations were located at the Norwegian Meteorological Institute (DNMI) weather stations. Meteorological data, relevant to the BP Project measurements, are also compiled by DNMI from Ny Ålesund, Svalbard (Airport) Radio (at Longyearbyen), Vardø Radio, and Skrova. The availability of the DNMI data is listed in Table 5. The data can be obtained by special request from DNMI\*, or (for the BP Program campaign periods only) from NILU\*\*.

Wind data summaries, specific to the various NYA sampling station locations, for MISU and BP campaign periods are presented in Vitols and Pacyna (1985). Wind speed and direction recordings at the Båtvika JAM station on Jan Mayen are available only for the periods 1982-06-17 to 1982-07-31, and 1983-03-01 to 1983-03-31.

---

\* DNMI, Klimaavdeling, P.b. 230, Blindern, 0314 Oslo 3, Norway.

\*\* Contact Forsker E. Joranger, NILU, P.b. 130, N-2001 Lillestrøm, Norway.

Table 5: Availability of relevant meteorological data from the Norwegian Meteorological Institute (DNMI).

Station	Frequency and time of day, h (MET) of observations	Processed data available for time of day h (MET)	Continuous recordings available			
			Wind speed	Wind direction	Temp	Rel. humidity
Svalbard Radio	Every 3 hours	01, 07, 13, 19	X	X	X	X
Bjørnøya	" " "	" " " "	X	X	X	X
Jan Mayen	" " "	" " " "			X	X
Vardø Radio	" " "	" " " "	X			
Skrova	" " "	" " " "				
Hopen	" " "	" " " "			X	X
Ny Ålesund	(except 22 h) 07h, 13h, 19h	07, 13, 19	X			

MET = mean European time (GMT + 1h)

#### 4 DISCUSSION OF RESULTS

##### 4.1 ORIGIN OF TRACE ELEMENTS IN AEROSOLS

###### 4.1.1 August/September 1982 campaign

From the two- and three-day mean concentrations during this BP Project campaign, summarized in the time-series in Figures 2-5 for trace elements and in Figures 24-27 for ions, several instances with peaks in the concentration of various elements and ions at the Norwegian arctic island and mainland stations are apparent. Concentrations of almost all trace element peaked first during the period 1982-08-18 to 1982-08-19 at HOP and JAM. Similar peaks in cation and anion concentrations were observed only at JAM. The 850 mb wind trajectories, shown in Figure 46, seem to indicate transport of air masses from Great Britain and Central Europe over Scandinavia to JAM and HOP. The two other arctic island stations, NYA and BJO, were bypassed by the air masses. No measurements were carried out at BIR, JER, and VAR until 1982-08-27, and presence of the pollution load at

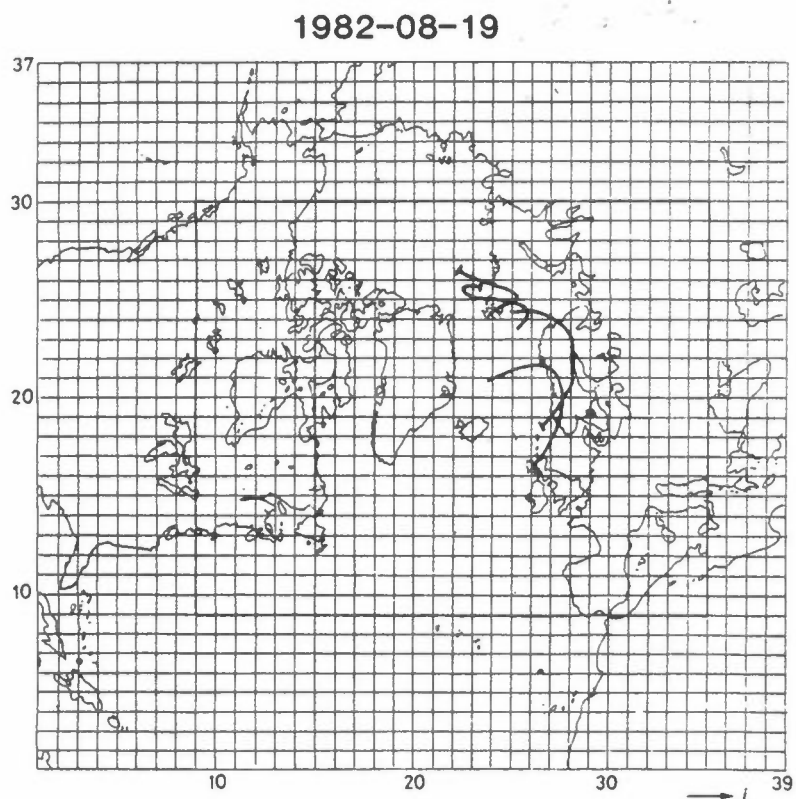
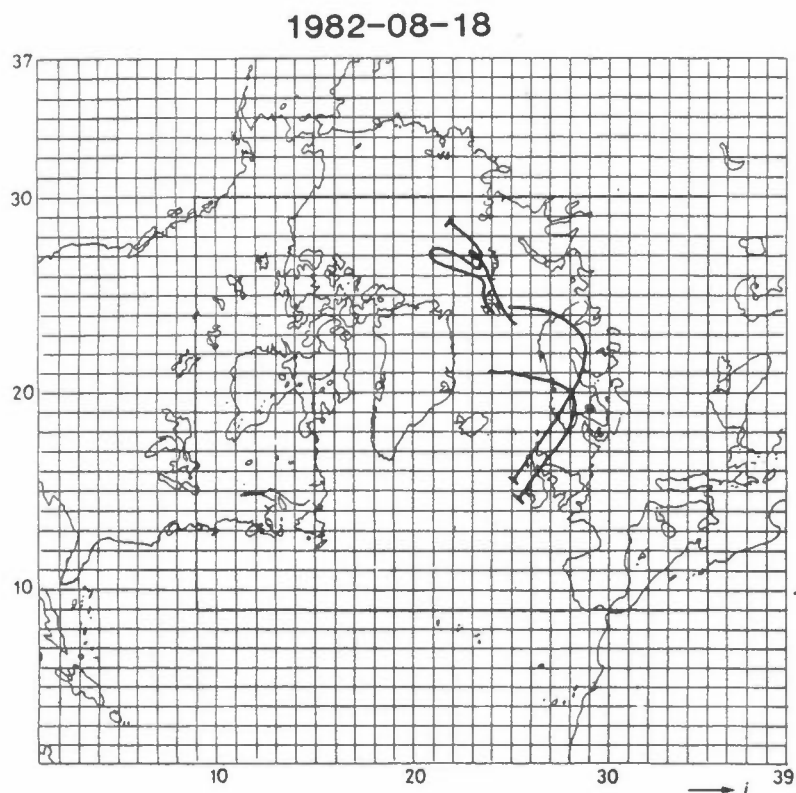


Figure 46: Daily 850 mb trajectories for JAM, BJO, HOP and NYA during the period 1982-08-18 to 1982-08-19.

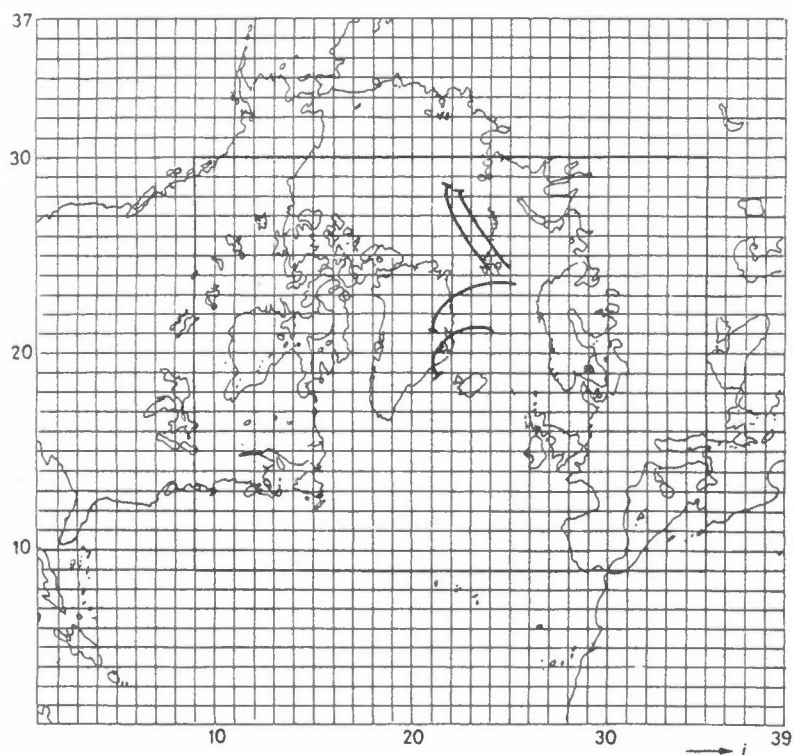
the mainland stations could not be verified. After this 2-day episode, the trajectories at the arctic stations indicated transport of rather clean air from northern North American continent. The enhanced concentration of Cd at HOP, in sample collected between 1982-08-20 and 1982-08-22, is difficult to explain. Since there were no coincident peaks in concentrations of any of the other anthropogenic trace elements, sampling/analytical artifact can be suspected.

Enhanced concentrations of trace elements were observed at JAM and BJO between 1982-08-23 and 1982-08-26. The 850 mb wind trajectories in Figure 47 indicate transport from eastern part of Greenland. The air mass, however, could have originated on the North American continent, since the trajectories trace back only 2-3 day transport. Clean air masses, circulating over the Arctic Ocean, prevailed over NYA and HOP (see Figure 47).

The next increase in pollutant concentrations was observed between 1982-08-29 and 1982-09-01 at NYA, HOP and JAM. The trajectories in Figure 48 indicate long-range transport from source areas in the USSR to the Norwegian Arctic. During this period, simultaneous high concentrations of all measured trace elements and ions were observed at BIR, JER and VAR. The 850 mb trajectories indicate possible transport from Great Britain and Central Europe to the mainland stations, but no mixing with the above "Soviet" air mass during 1982-08-29 to 1982-09-01. However, the "European" air mass moved northward two days later, when the arctic island stations seemed to be exposed to polluted air (see 850 mb trajectories in Figure 48 and 49). As a result, high concentrations of all metals and ions were observed at NYA, JAM and BJO between 1982-09-03 and 1982-09-05. On the other hand, low concentrations were observed at the mainland stations, which were bypassed by this air mass. The only slightly elevated Pb concentration during low levels of other trace elements and ions at HOP is somewhat surprising, since the trajectories in Figure 48 and 49 indicate, that this station was in the path of pollutant transport.

The possible origins of the 1982-08-29 to 1982-09-01 and 1982-09-03 to 1982-09-05 episodes in the Norwegian Arctic suggested here are confirmed by the findings of the BP Project study on the meteorological conditions conducive to air pollutant transport to the Norwegian Arctic by Iversen (1985).

1982-08-23



1982-08-24

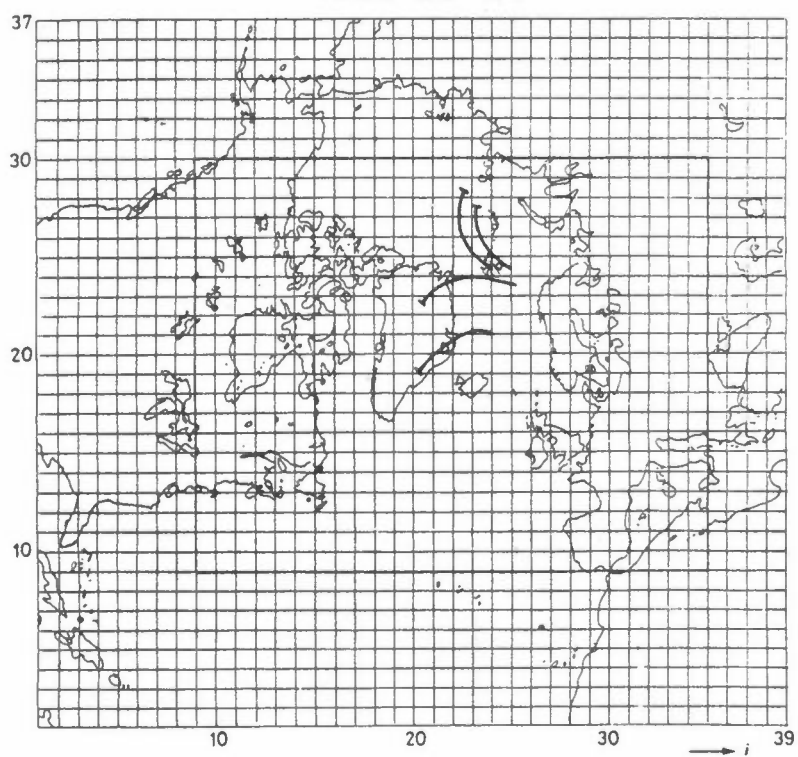
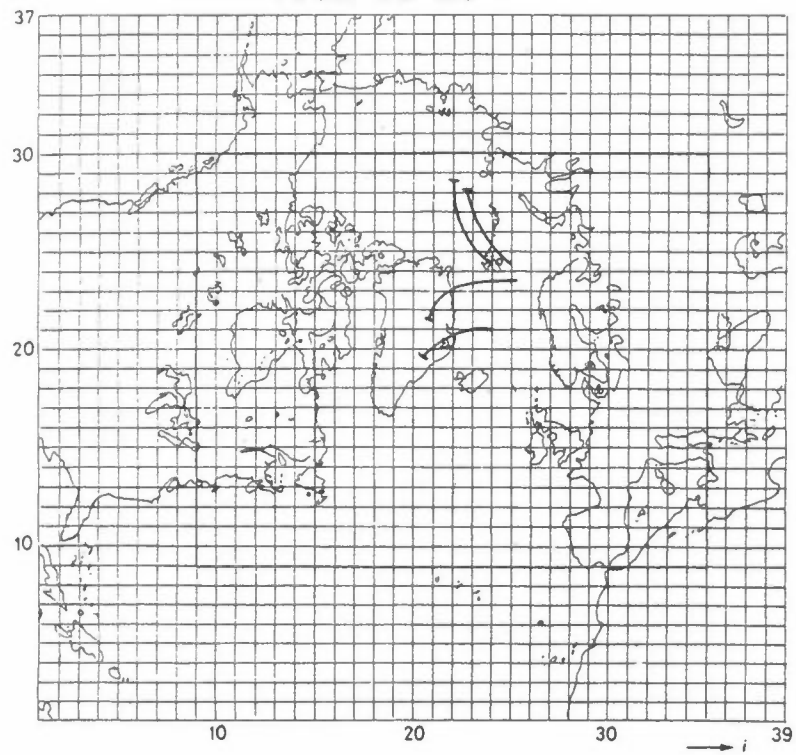


Figure 47: Daily 850 mb trajectories for JAM, BJO, HOP and NYA during the period 1982-08-23 to 1982-08-26.

1982-08-25



1982-08-26

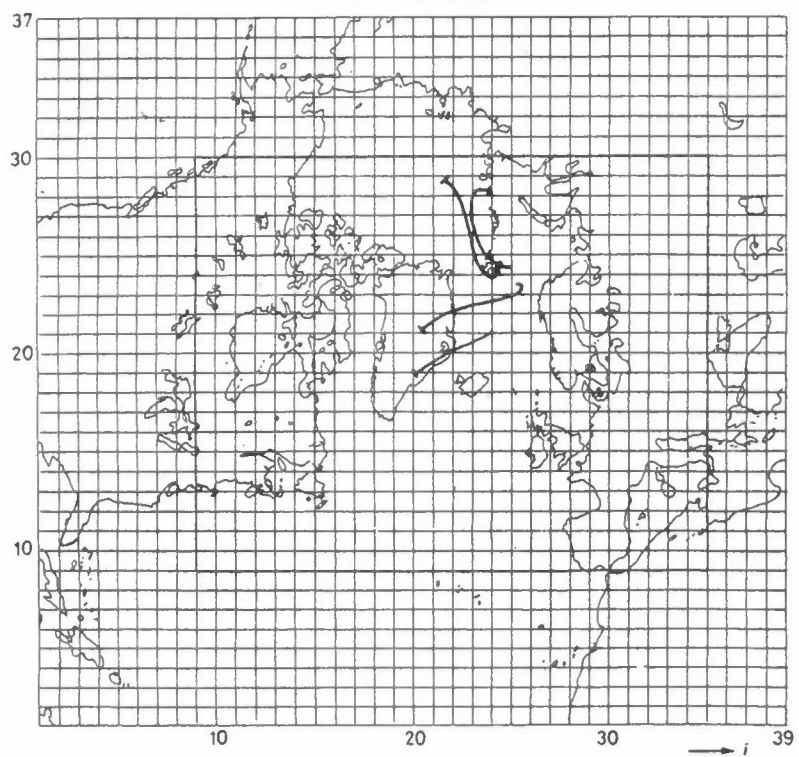


Figure 47: Cont.

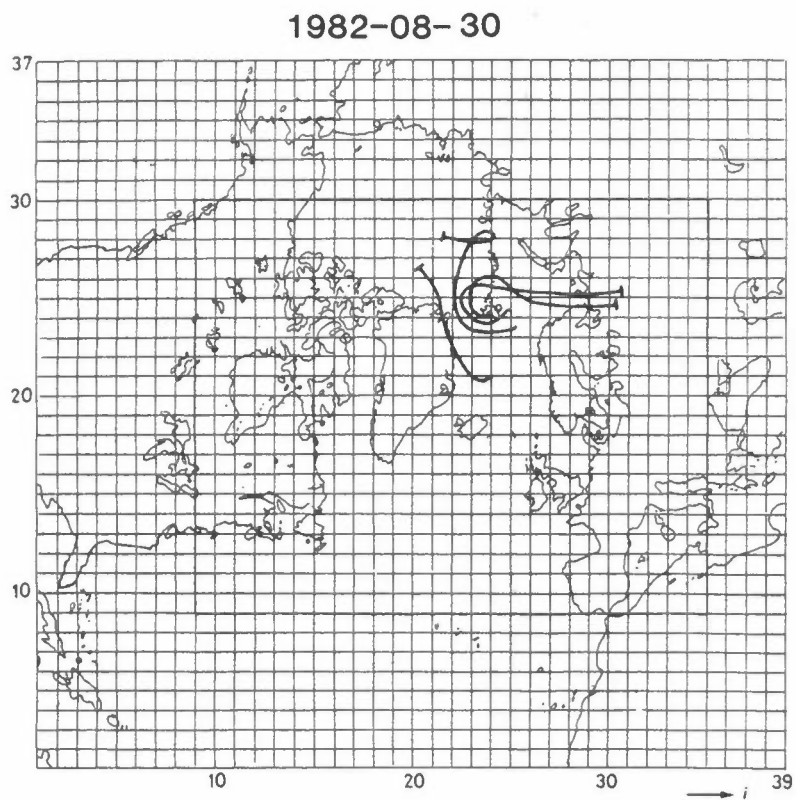
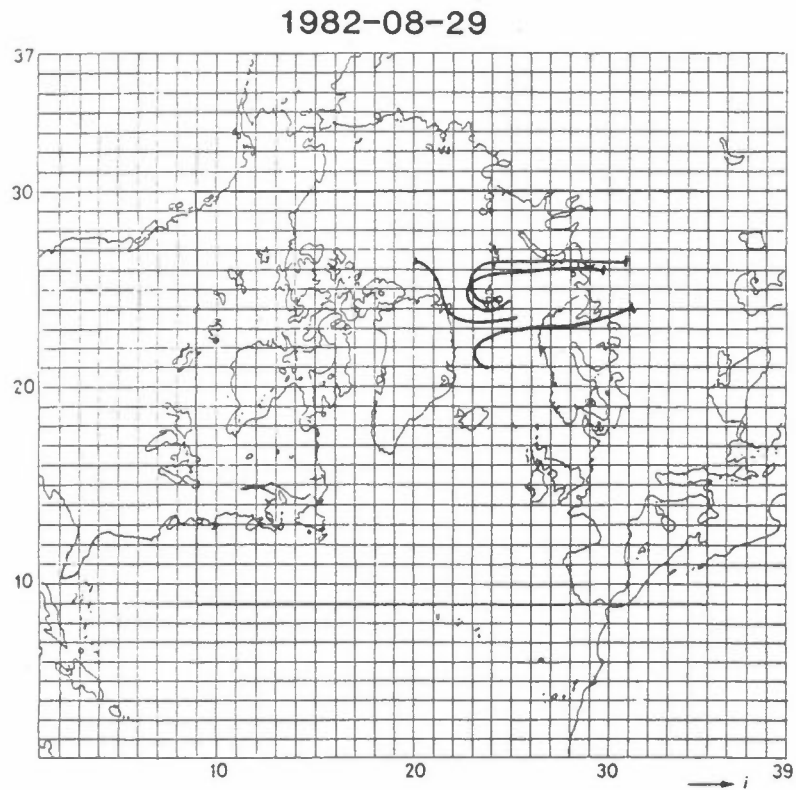
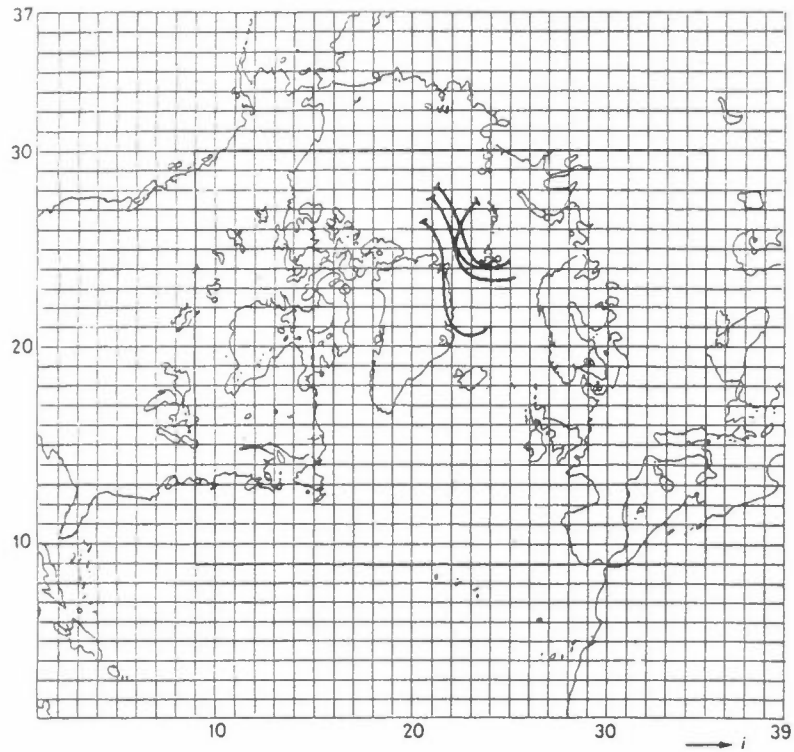


Figure 48: Daily 850 mb trajectories for JAM, BJO, HOP and NYA during the period 1982-08-29 to 1982-09-01.



1982-08-31



1982-09-01

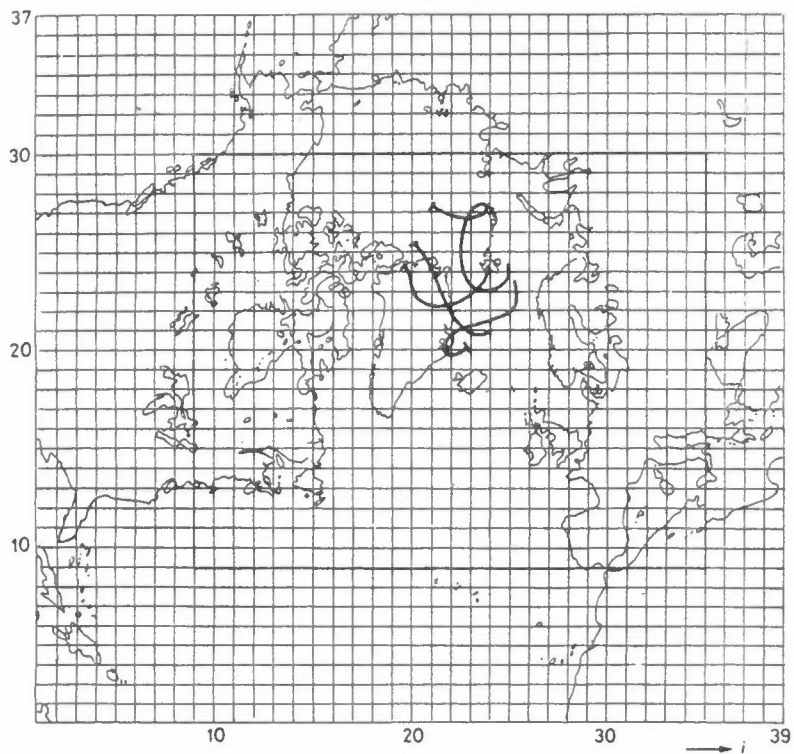


Figure 48: Cont.

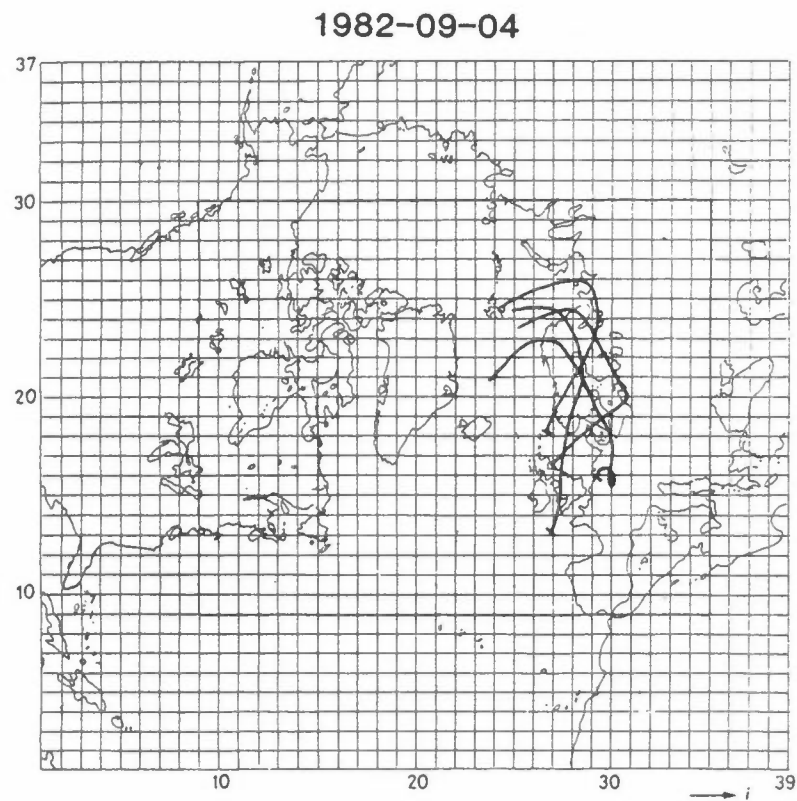
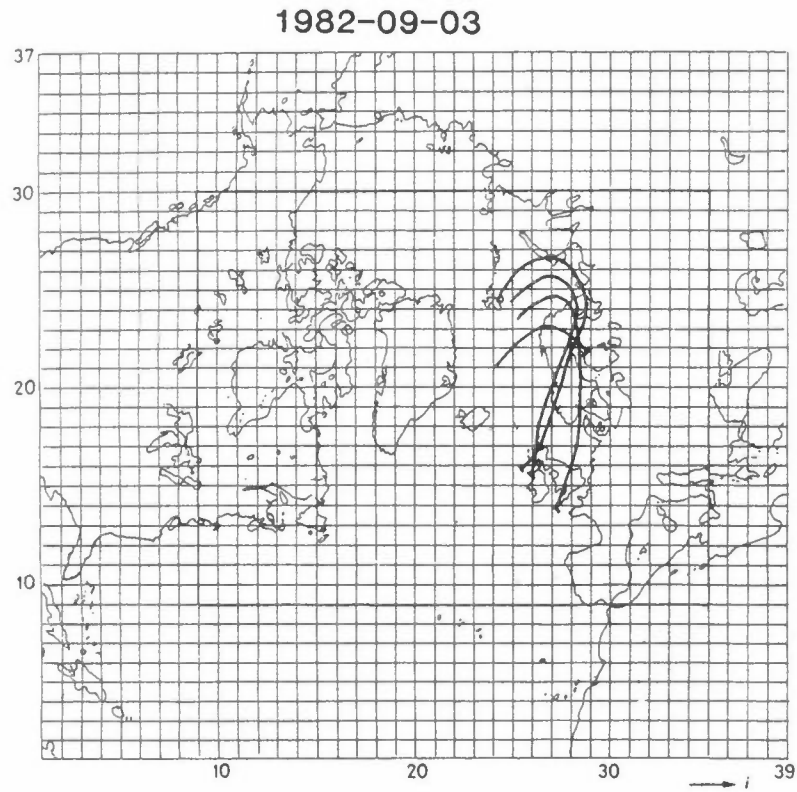


Figure 49: Daily 850 mb trajectories for JAM, BJO, HOP and NYA during the period 1982-09-03 to 1982-09-05.

1982-09-05

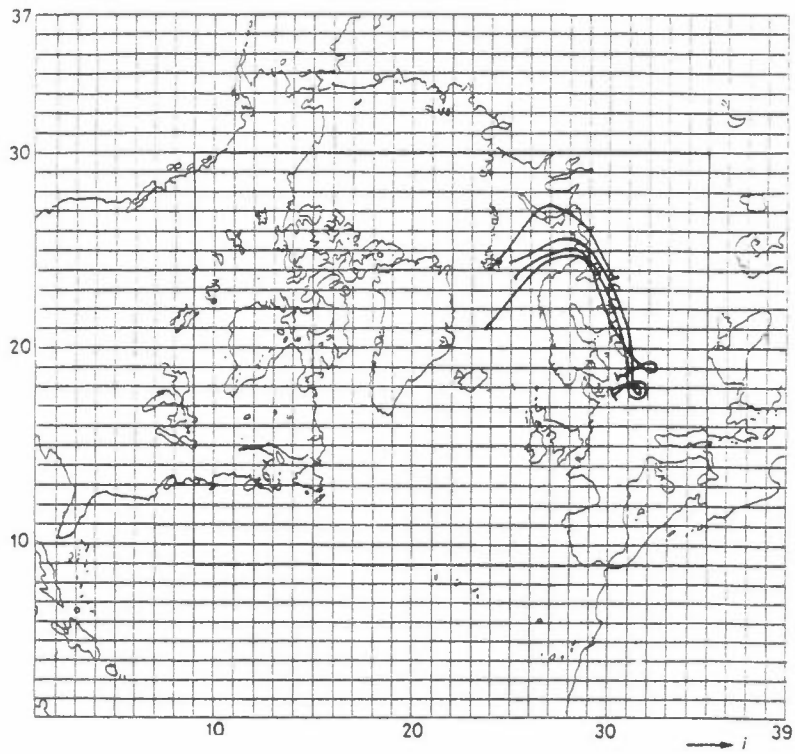


Figure 49: Cont.

1982-09-10

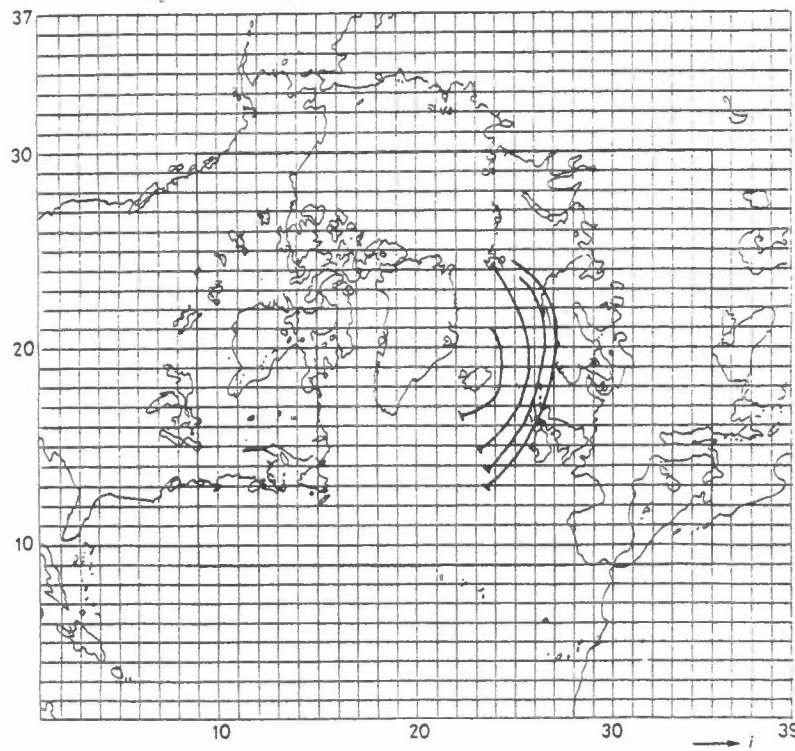


Figure 50: 850 mb trajectories for JAM, BJO, HOP and NYA on 1982-09-10.

The Pb concentrations were elevated at HOP after 1982-09-10, when 850 mb trajectories in Figure 50 indicate northward advection of air masses over northern Scotland and along the west coast of Scandinavia. Since motor vehicle traffic is the main source of Pb pollution in the more urbanised regions, the increase in Pb could be expected. No enhanced trace metal concentrations were observed at the other arctic island stations, for which air masses had different origins (Figure 50). A strong pollutant transport episode is indicated at the three mainland stations BIR, VAR and JER in early September, 1982.

During the Fall 1982 campaign, the NYA ground station appears to have been bypassed by the main pollution transport episodes. Only condensation nuclei (CNC) measurements were available at NYA for this campaign (Heintzenberg et al., 1983), and without corresponding aerosol light scattering ( $\sigma_{sp}$ ) data, the occurrence of transport episodes cannot be independently verified.

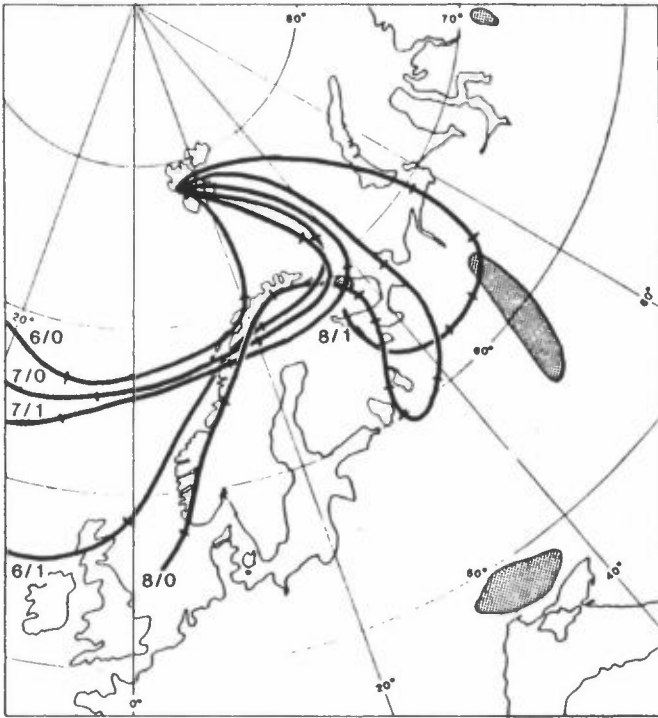
Results from size-differentiated aerosol chemical composition measurements at NYA during Fall 1982 are not available at this time.

#### 4.1.2 March 1983 campaign

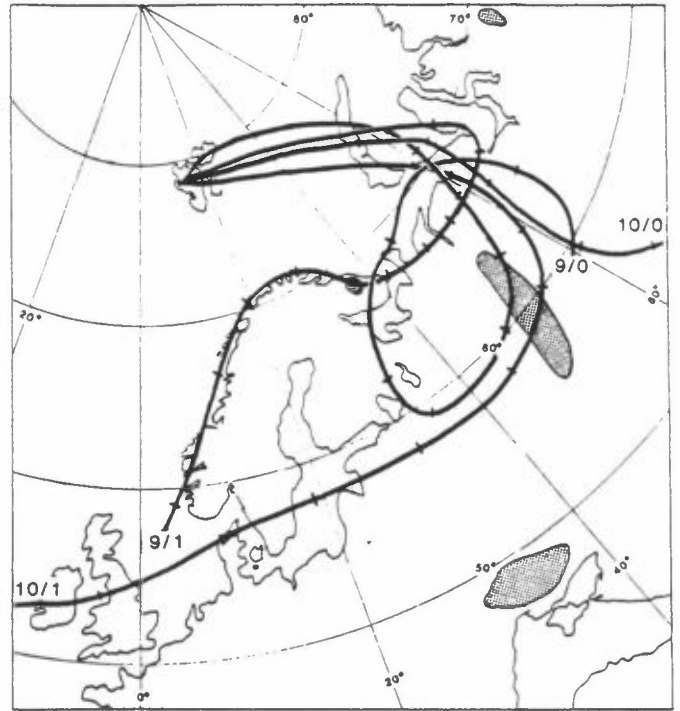
The two- and three-day mean concentrations are summarized in the time-series in Figures 6-14 for trace elements, and Figures 28-36 for cations and anions. There were well-defined concentration peaks of Mn, V, Ni, Zn, Cd, Pb, as well as  $H^+$ ,  $K^+$ ,  $Ca_4^{2+}$ ,  $NH_3^+-N$ ,  $NO^- -N$ , and  $SO_4^{2-} -S$  at NYA between 1983-03-06 and 1983-03-13. One day later, on 1983-03-07, enhanced concentrations were also observed at BJO and JAM. Data are missing for this period from HOP, the remaining arctic island station. While during this time the trace element concentrations at the Norwegian mainland stations BIR, KAR, and SKO were low, elements and ions at VAR station, the most easterly on the mainland (see Figure 1), showed the same pattern as the arctic island stations during 1983-03-04 to 1983-03-11.

In Figure 51 the 850 mb wind trajectories to NYA (Harris, 1984) are reproduced. They indicate that the main sources of pollutants, likely enhancing concentrations of anthropogenic trace elements and ions, were the industrial complexes on the Kola Peninsula and along the Urals in the USSR. The apparent transport time for the pollutants between VAR and NYA, was 2

1983-03-06/08



1983-03-09/10



1983-03-11/13

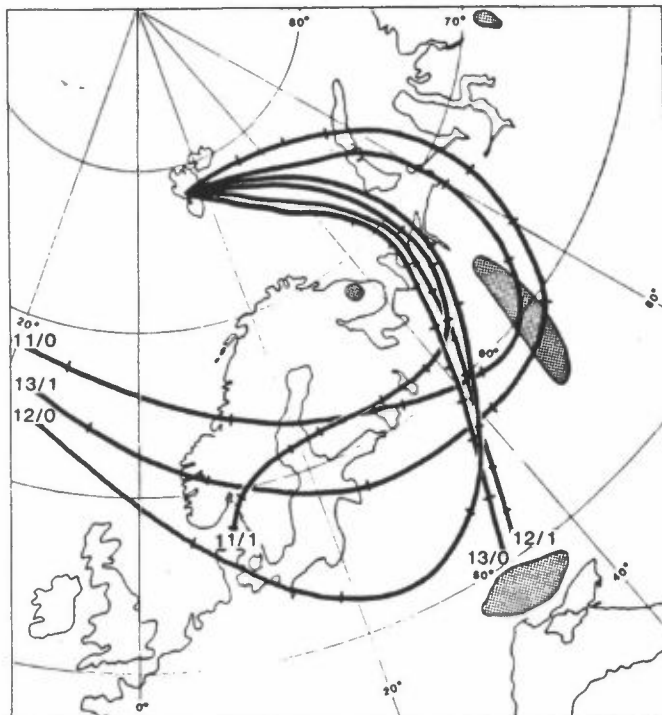


Figure 51: Daily 850 mb trajectories to NYA during the period 1983-03-06 to 1983-03-13, at 00 00 UT (indicated by 0 after the slash) and 1200 UT (1 after slash). Daily marks are provided on each trajectory

The shaded areas represent main emission regions in the USSR.

days, and 1 day between NYA, and BJO and JAM. Unfortunately, no wind trajectories are available for BJO and JAM, but it can be speculated, that the polluted air masses reached NYA first, and then turned over Spitsbergen to JAM and BJO.

The very high concentrations of Ni at VAR indicate transport from the large copper-nickel smelter at Nikel, USSR, just across the Norwegian border, only ca. 120 km to SSW from the VAR station. The wind trajectories indicate that this source area in early March 1983 was upwind of the VAR station. The Ni emissions from this metallurgical complex are estimated to ca.  $535 \text{ t a}^{-1}$ , based upon available information on smelting capacities and processes used, metal concentration in the ore, and type and efficiency of air pollution control devices (NILU, 1984).

Two other important source areas with copper-nickel smelters in the USSR are located in southern Urals, and at Norilsk. Compared to the smelter at Nikel, both have larger smelting capacities and presumably higher atmospheric emissions of the metal (NILU, 1984). As indicated by the trajectories in Figure 51, the Ni emissions from the Urals smelters probably contributed to the total amount of Ni transported into the Arctic between 1983-03-06 and 1983-03-13. The emissions from Norilsk, the world's largest copper and nickel smelter complex (ANR, 1982), did not seem to contribute to the pollution load reaching NYA at that time.

The Norilsk smelter complex was probably the main source of anthropogenic pollutants measured at NYA and HOP between 1983-03-21 and 1983-03-29, and at JAM between 1983-03-23 and 1983-03-25. Daily 850 mb trajectories for NYA from 1983-03-20 to 1983-03-24 are shown in Figure 52.

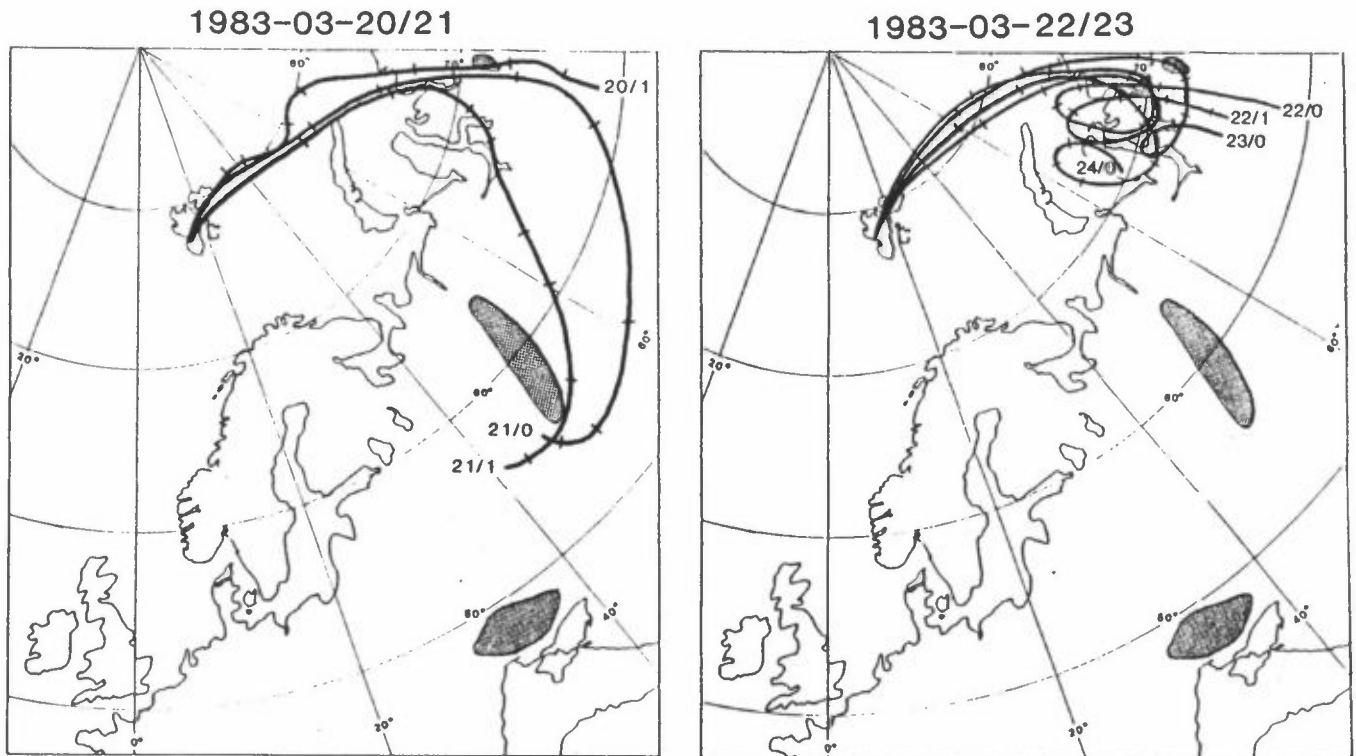


Figure 52: Daily 850 mb trajectories to NYA during the period 1983-03-20 to 1983-03-24, at 0000 UT (indicated by 0 after the slash) and 1200 UT (1 after slash). Daily marks are provided on each trajectory.

The shaded areas represent main emission regions in the USSR

Fossil fuel combustion is the second important source of anthropogenic trace elements in the arctic atmosphere during the episodic periods in 1983-03. Oil and coal burned by electric utilities, industry, and commercial and domestic boilers, particularly west of the Urals, have contributed to enhanced concentrations of Mn, V and Ni during the episodes in this period (Ottar and Pacyna, 1984). The Zn and Cd concentrations behaved similarly to Ni concentrations, decreasing from VAR to the arctic island stations.

The  $H^+$  concentrations are very enhanced in the Arctic during these long-range transport episodes. This may be due to the high concentration of  $SO_4^{2-}$ -S, although  $NO_3^-$ -N was also enhanced. The  $Cl^-$  and  $Na^+$  concentrations were quite insignificant during these episodes. One explanation for the Cl decrease during an episode is that the ion is driven off from the particles as hydrochloric acid by sulphuric acid. Indeed, the  $SO_4^{2-}$  concentrations in samples collected during this episode were high. The increased

concentrations of  $K^+$  and  $Ca^{2+}$  are likely due to emissions of K and Ca from coal combustion by electric utilities, since both K and Ca have been identified in stack emissions from coal-fired power plants (Tomza, 1985).

A further clue to the origin of the long-range transported air pollutants in the Arctic in 1983-03 is provided by the size-differentiated chemical composition of the arctic aerosol, and enrichment factors calculated for various size fraction of particles collected at NYA (Pacyna et al., 1984a). During both episodes in March 1983, increased concentrations of several elements in the  $<0.5 \mu\text{m}$  EAD and  $1.0\text{-}2.0 \mu\text{m}$  EAD particle fractions were observed, while the concentrations in the in-between,  $0.5\text{-}1.0 \mu\text{m}$  EAD, range remained unchanged from non-episodic periods. A detailed discussion on the size-differentiated chemical composition of the arctic aerosol at NYA is presented elsewhere (Vitols and Pacyna, 1985). The fact, that the episodes added particles mainly the  $< 2.0 \mu\text{m}$  EAD range points to an anthropogenic origin, and suggests contributions from oil and coal combustion, and the high-temperature processes of copper-nickel smelters. The very similar shape of the mass-size distribution plots for trace elements, specific to non-ferrous metal production (Vitols and Pacyna, 1985), suggests that this source category may have dominated over fuel combustion in enhancing the anthropogenic aerosol concentrations during the March 1983 episodes in the Arctic.

Increased enrichment factors of certain trace elements in the  $<0.5 \mu\text{m}$  EAD particle fractions during the March 1983 episodes verify transport of pollutants over and from portions of the USSR (Pacyna et al., 1984a; Vitols and Pacyna, 1985). Further confirmation of the anthropogenic origin of these episodes in the Norwegian Arctic comes from a comparison of concentration peaks (in Figures 6-10, and Figures 28-31) with peaks in 12-h medians of aerosol light scattering coefficient,  $\sigma_{sp}$ , and condensation nuclei (CN) concentrations during March 1983 at NYA (see Figure 5 in Vitols and Pacyna, 1985). The variations in concurrent  $\sigma_{sp}$  and CN counts follow each other closely, and peak at the same time as the episodic concentrations of anthropogenic elements and some ions. The very similar shape of the  $\sigma_{sp}$  and CN medians indicates the existence of particles in the  $0.02\text{-}1.0 \mu\text{m}$  dia. range, including long-rang transported "aged aerosol".



The suggested origins of the March 1983 episodes in the Norwegian Arctic are in very good agreement with the findings of the statistical analysis of pollutant transport to the Norwegian Arctic, based by large scale atmospheric flows by Iversen (1985).

During March 1983, the highest concentrations of several trace elements and ions were observed at the Norwegian mainland station BIR. This southern-most "background" station (see Figure 1) is mainly affected by long-range transport from Great Britain and Central Europe (Pacyna et al., 1984b). The concentrations further north on the mainland at KAR and SKO, on the other hand, were significantly lower than at the arctic island stations, supporting the suggestion that a "clean" zone off the western coast of Norway in the Norwegian Sea is normally by-passed by long-range transport (Joranger and Ottar, 1984).

#### 4.1.3 August/September 1983 campaign

The time series of two- and three-day mean concentrations from the Fall 1983 campaign are shown in Figures 6-14 for trace elements, and Figures 28-36 for major ions. Very high concentrations of Cd and Zn at NYA, and Cd, Zn, and Pb at HOP were observed during the first days of the measurement campaign (1983-08-08 to 1983-08-10). The 850 mb wind trajectories in Figure 53 indicate air mass transport from the North American continent around the southern end of Greenland, and then to JAM, NYA, HOP and BJO. These air masses could have been contaminated by pollutants from various sources in north-eastern North America, but the very low concentrations at JAM eliminate mineral extraction and processing on Greenland as a possible cause.

The 12-h medians of both  $\sigma_{sp}$  and CN concentration at NYA were elevated at that time (See Figure 6 in Vitols and Pacyna 1985) confirming the anthropogenic origin of the transported particles. The ion concentrations were also increased at the other arctic island stations (except  $SO_4^{2-}$ -S and  $H^+$ ), indicating a substantial influence of seasalt, as would be expected with over-the-sea-trajectories. Size-differentiated composition of the aerosol during this period (Pacyna and Ottar, 1985) suggests that seasalt was also the major source of K in the  $>1 \mu g$  EAD particles, and S and Ca in the  $>8 \mu m$  EAD particles. After 1983-08-10, wind trajectories indicated transport of clean air from the Arctic Ocean to the Spitsbergen area.

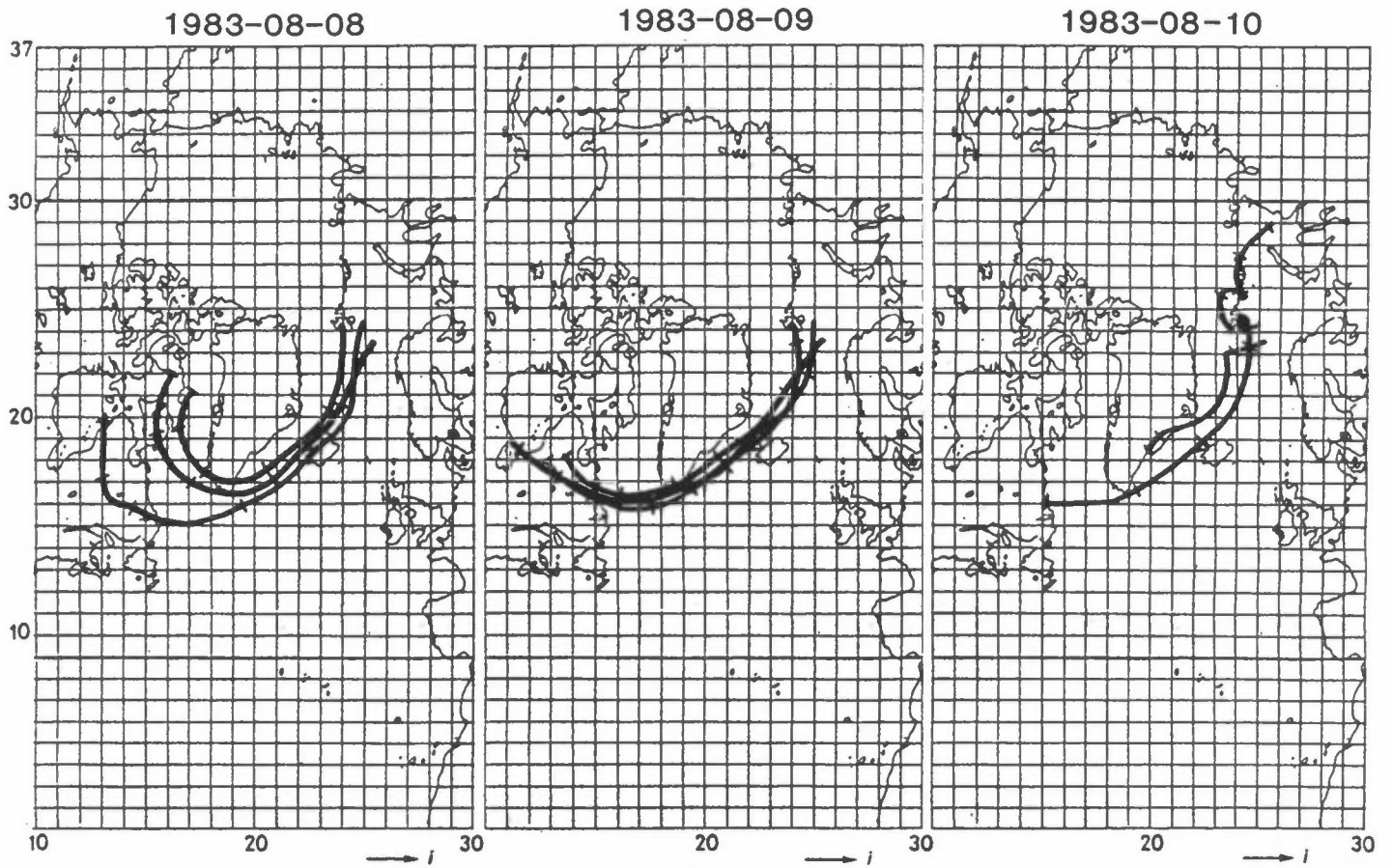


Figure 53: Daily 850 mb trajectories to HOP, BJO and NYA during the period 1983-08-08 to 1983-08-10. Daily marks are provided on each trajectory.

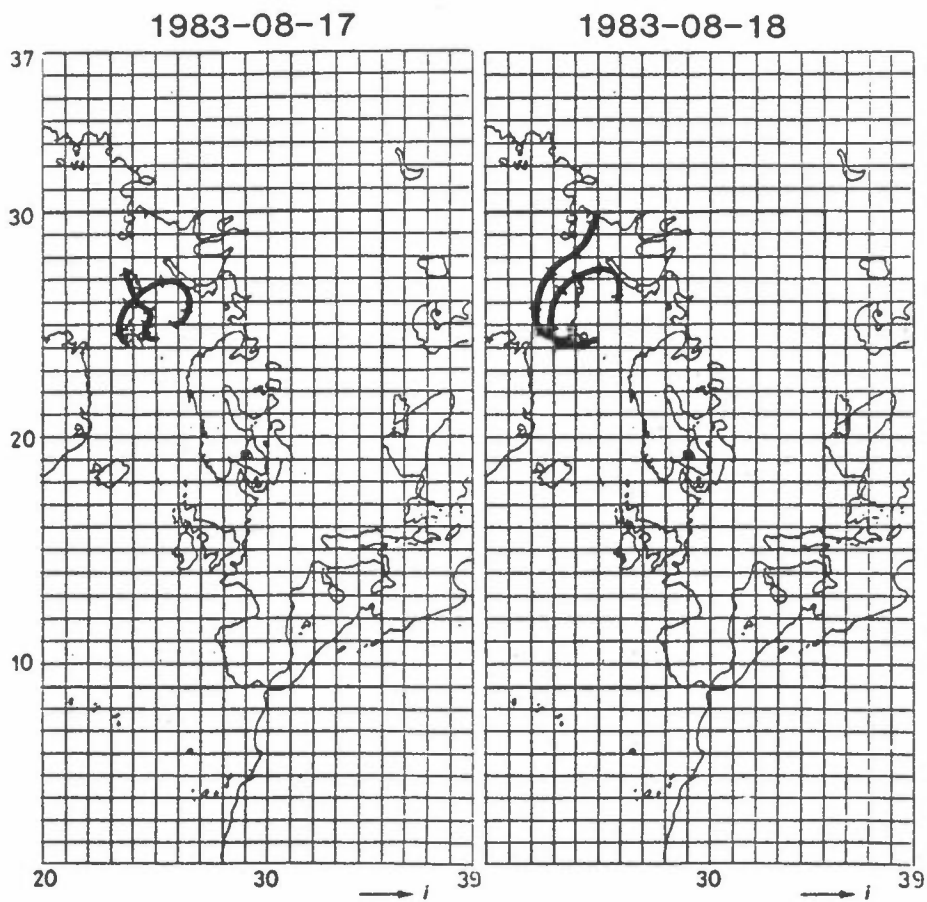


Figure 54: Daily 850 mb trajectories to HOP and NYA during the period 1983-08-17 to 1983-08-18. Daily marks are provided on each trajectory.

Due to its several unusual features, the period between 1983-08-14 and 1983-08-24 at NYA has been examined in detail by Vitols and Pacyna (1985). High peaks in 12-h CN concentration medians occurred on several occasions, while  $\sigma_s$  remained sub-detectable at the same time. This suggests the presence of fresh nucleation mode (or Aitken range) particles, possibly the result of relatively local gas-to-particle conversion from biogenic process emissions over the sea. On 1983-08-18, however, 850 mb back trajectories (Figure 54) indicated transport of air from eastern USSR, which was confirmed by NILU aircraft measurement on 1983-08-18 (Flight B-3, Pacyna et al., 1985c). A well defined aerosol layer between 2500 m and 45000 m (with peak particle concentration at 3600 m) was observed over Spitsbergen.

Weather maps for 700 and 500/1000 mb levels (Europäischer Wetterbericht, 1983) suggest that a lifting of the airmass during transport from the USSR by the polar front was feasible, which would explain the aloft polluted layer. The 12-h CN medians at NYA for 1983-08-18 were low and  $\sigma_s$  subdetectable, which suggests that no downward mixing of the transported <sup>sp</sup> pollutants over Spitsbergen had occurred. Trace element and ion concentrations at HOP and JAM (no data for BJO) were also low, so that the distinct concentration peaks in Cd and Zn at NYA, without a corresponding increase in the other elements (as seen in Figure 6) are quite baffling. The NYA station log does record a Hi-Vol pump motor fire on the afternoon of 1983-08-18, which may have generated the measurable quantities of Cd and Zn.

High concentrations of all elements and ions were measured at HOP and NYA (except for V at the latter) between 1983-09-05 and 1985-09-09. Substantially increased concentrations were first observed at NYA (1983-09-07 to 1983-09-9), when the 850 mb trajectories, shown in Figure 55, trace transport of air masses from western Europe. High concentrations of all trace elements and ions were also observed at BIR, SKO and KAR between 1983-08-31 and 1983-09-02, and at JER and VAR between 1983-09-02 and 1983-09-05. The peak concentrations of trace elements and ions at HOP, from 1983-09-05 to 1983-09-07, were evidently due to air mass passing across England, western Europe and Scandinavia. The trajectories for NYA started more to the west than those for HOP, which probably explains the lower anthropogenic constituent concentrations measured at NYA.

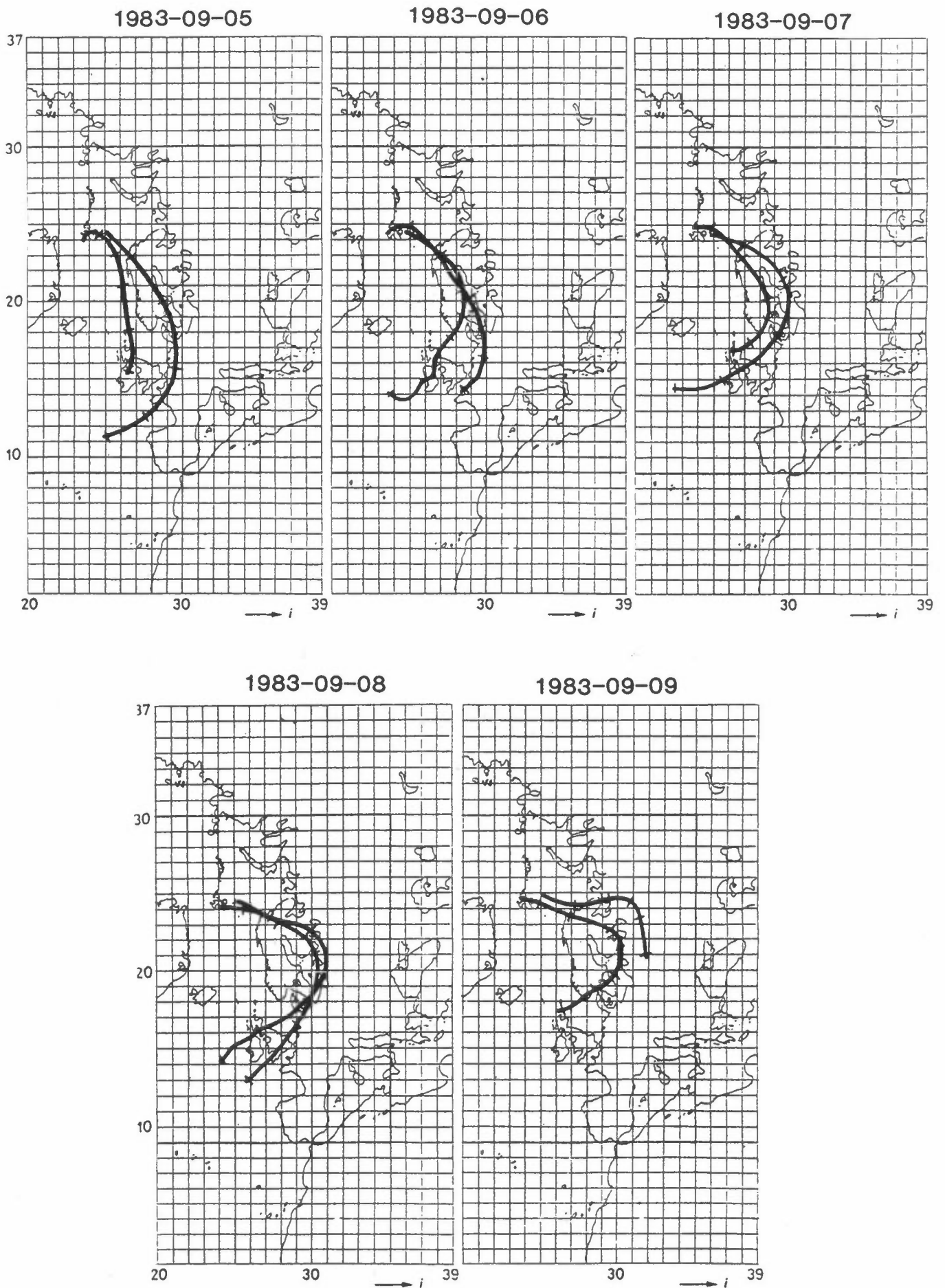


Figure 55: Daily 850 mb trajectories to HOP and NYA during the period 1983-09-05 to 1983-09-09. Daily marks are provided on each trajectory.

During 1983-09-07 to 1983-09-09, the trajectories to HOP started over the European continent and the Kola Peninsula. Trajectories to NYA passed more to the west. As a result, Ni concentrations at NYA were significantly lower than those at HOP. The high concentrations observed at VAR from 1983-09-05 to 1983-09-07 were due to emissions from sources in the Kola Peninsula. VAR was outside the air mass moving from Europe to the Norwegian Arctic in this period. With the arrival of relatively clean Atlantic air masses after 1983-09-11, the concentrations of all elements and ions at HOP and NYA decreased substantially.

The anthropogenic origin of aerosols measured during the early September episode at NYA is confirmed by the size-differentiated trace element composition reported elsewhere (Vitols and Pacyna, 1985). The particle mass-size distributions for several trace elements showed maximum abundance in the 0.5-1.0  $\mu\text{m}$  EAD fraction, while the concentrations were lower in the 0.25-0.5  $\mu\text{m}$  EAD fraction, and below detection limits in the  $<0.25$   $\mu\text{m}$  EAD fraction. This is consistent with the assumption of "aged aerosols". The high-temperature processes, which are the probable main sources of trace elements, produce particles predominantly  $<0.5$   $\mu\text{m}$  EAD, which grow during the long-range transport in summer to accumulation mode particle sizes.

The very high enrichment factors for S, Cd, Pb and Zn in aerosols at NYA during the Fall 1983 episodes (see Vitols and Pacyna, 1985) also indicate long-range transport of pollutants from industrial areas in Eurasia and perhaps North America, while the elements Ni and Mn have partly anthropogenic and partly crustal origins.

#### 4.1.4 February/March/April 1984 campaign

The two- and three-day mean concentrations for this campaign are summarized in the time-series in Figures 15-23 for trace elements, and in Figures 37-45 for ions.

There were several instances of elevated concentrations of trace elements and ions at the Norwegian arctic island and mainland stations. Concentrations of almost all trace element peaked during the period 1984-02-29 to

1984-03-04 at NYA, and from 1984-02-29 to 1984-03-06 at HOP. During this time there were also corresponding concentrations peaks in  $H^+$ ,  $Ca^{2+}$ ,  $NH_4^+$ -N and  $SO_4^{2-}$ -S at both stations. An examination of weather maps (Europäischer Wetterbericht, 1984) for the period 1984-02-29 to 1984-03-02 indicates two low pressure centres over Scandinavia and Novaya Zemlya island, off the northern coast of USSR mainland. The 850 mb trajectories are shown in Figures 56 and 57 for NYA and HOP, respectively. The increased pollution levels measured at NYA and HOP are probably due to sources in northern USSR, particularly from the Norilsk metallurgical processes with their high emissions of Ni, Zn, Cd, and Pb. Fossil fuel combustion may have also contributed to the Mn and V concentrations. The chemical composition of size-differentiated aerosols at NYA (Vitols and Pacyna, 1985) shows significant As, Ni, Pb, Cu, Br, S, V, Zn concentrations and enrichment factors, for samples collected during 1984-02-29 to 1984-03-05. These chemical signatures further implicate transport of anthropogenic air pollutants from northern USSR to NYA. The  $\sigma_{sp}$  and CNC 12-h medians at NYA during the above period (Vitols and Pacyna, 1985) peaked as well, thus indicating the presence of long-range transported "aged aerosol". The explanation for an increase in the ion concentrations during this period is likely the same, as for the episodic periods in March 1983.

The trace element and ion concentrations at BJO were much lower than those at NYA and HOP, suggesting that the episode missed BJO. Indeed, the relevant weather maps indicate that BJO, VAR, JER and SKO were all in different air masses circulating over Scandinavia. JAM was probably affected by the same air mass as NYA, since enhanced Mn, V, Zn and Pb concentrations were observed there from 1984-02-29 to 1984-03-01. The 850 mb trajectories in Figure 58 seem to confirm this. These values, as could be expected, were lower at NYA, due to downward mixing into the unstable lower air layers during the lengthy passage over the open ocean.

An increase in pollutant concentrations at NYA was observed again during 1984-03-13 to 1984-03-15, when a high pressure centre was dominating Scandinavia and western USSR (see also 850 mb trajectories in Figure 59). Emission sources in industrial regions of western USSR seemed to be responsible for the elevated concentrations at NYA, a supposition supported by, e.g., the size-differentiated chemical composition of aerosols, enrich-

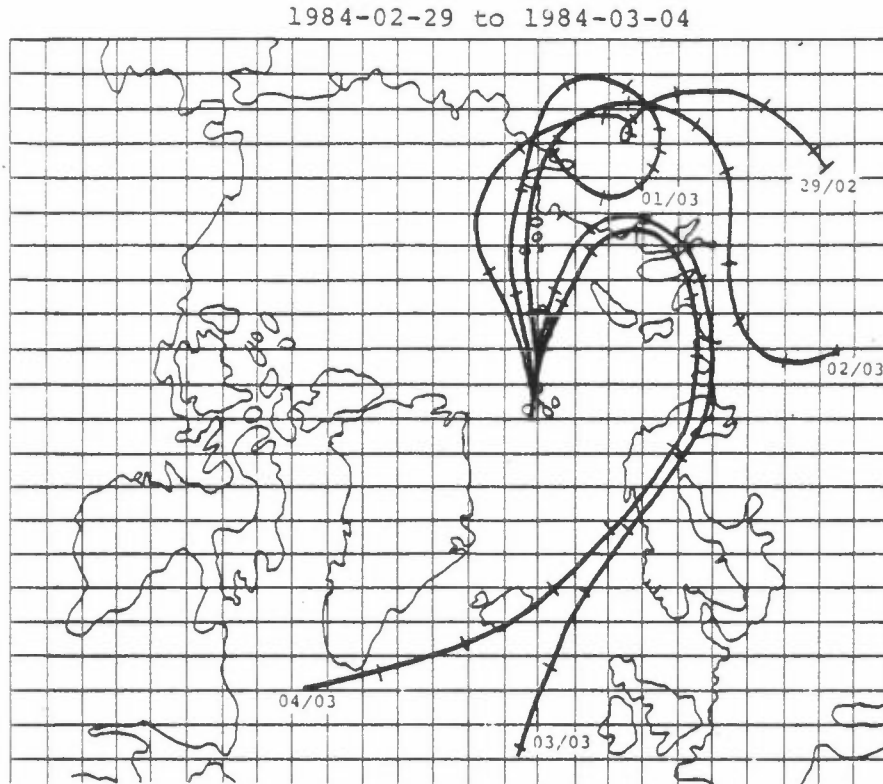


Figure 56: Daily 850 mb trajectories to NYC during the period 1984-02-29 to 1984-03-04. Daily marks are provided on each trajectory.

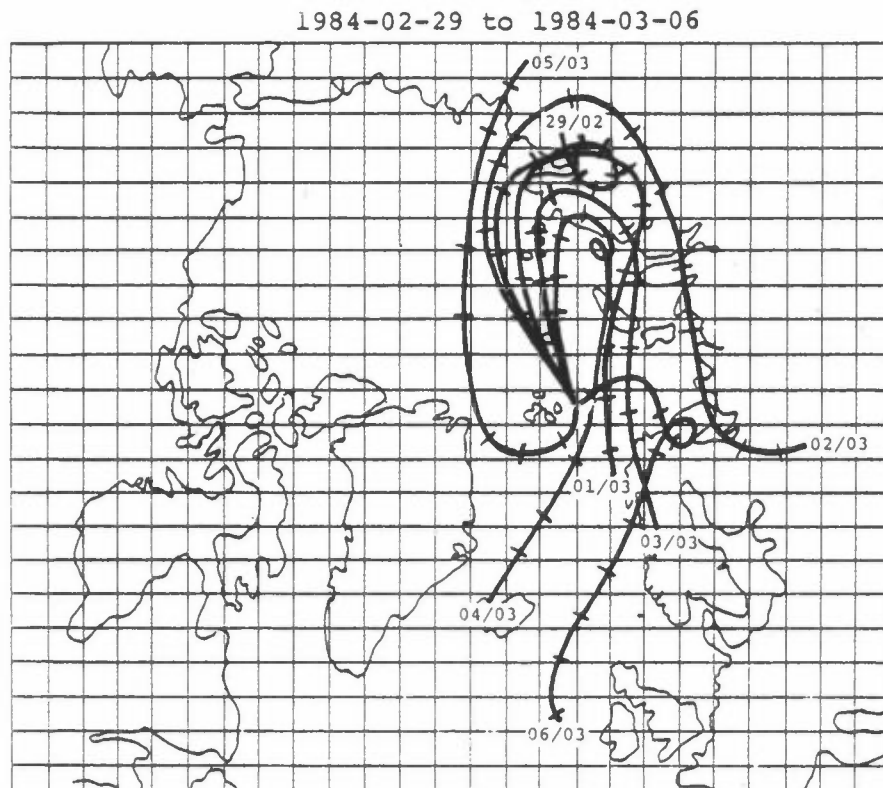


Figure 57: Daily 850 mb trajectories to HOP during the period 1984-02-29 to 1984-03-06. Daily marks are provided on each trajectory.



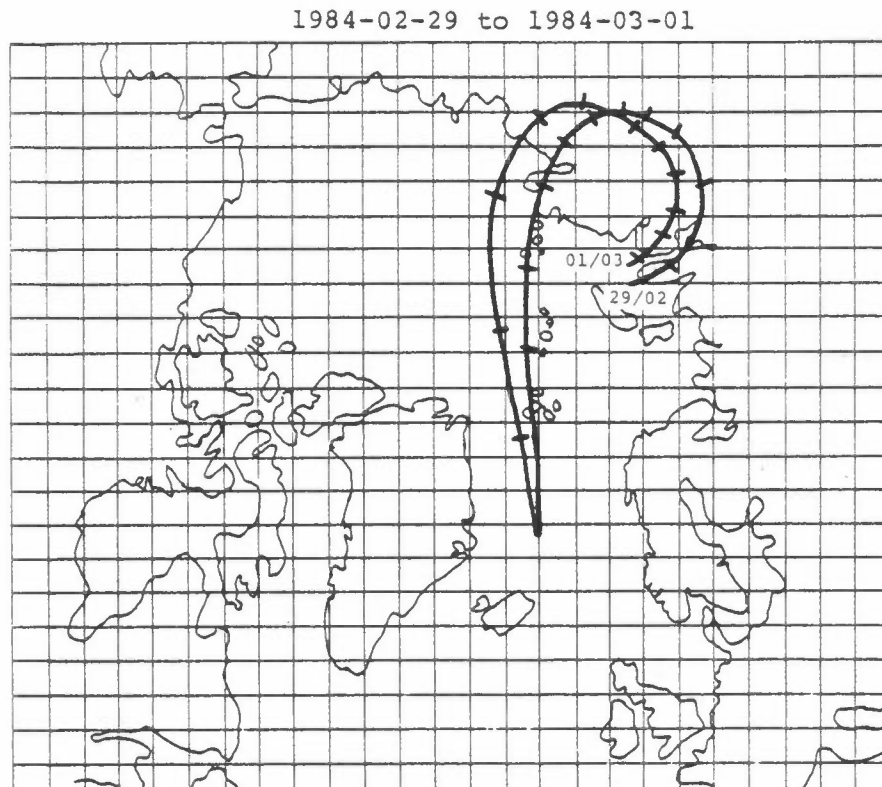


Figure 58: Daily 850 mb trajectories to JAM during the period 1984-02-29 to 1984-03-01. Daily marks are provided on each trajectory.

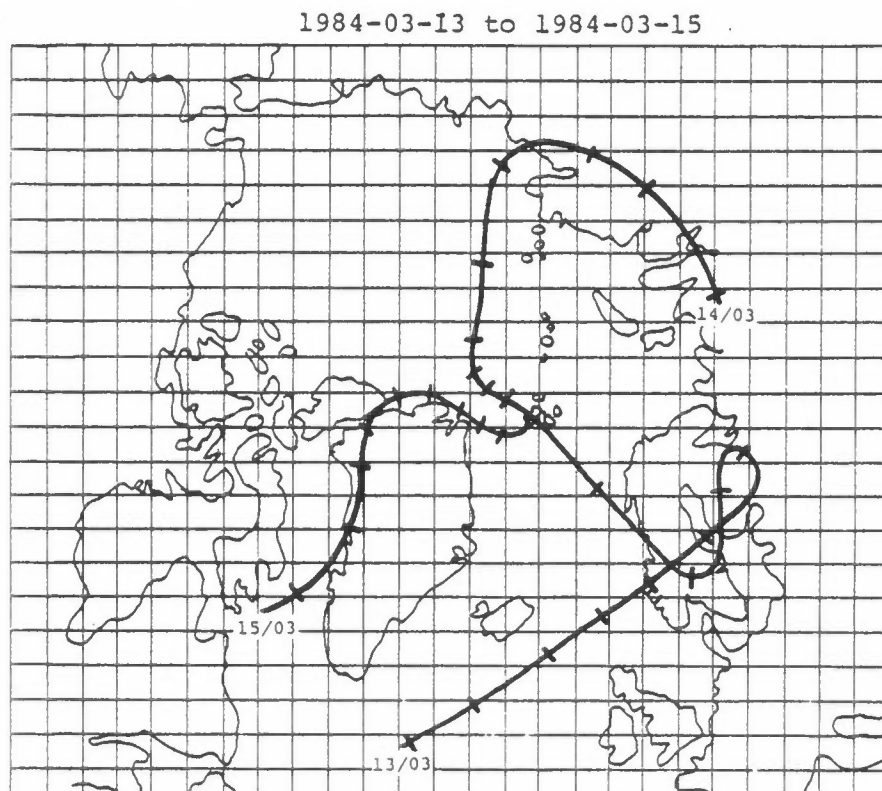


Figure 59: Daily 850 mb trajectories to NYA during the period 1984-03-13 to 1984-03-15. Daily marks are provided on each trajectory.

ment factors of trace elements, and  $\sigma_{sp}$  and CNC measurements at NYA (Vitols and Pacyna, 1985). During the same period, HOP and BJO appear to have been affected by another air mass, since no significant concentration increases were observed there. Sharp concentration peaks for all trace element and ions (except  $Mg^{2+}$ ,  $Na^+$ , and  $Cl^-$ ) were observed at JER, SKO, KAR, BIR, and to some extent at VAR, from 1984-03-12 to 1984-03-14, and at JAM from 1984-03-13 to 1984-03-15, when the weather maps indicated air mass passage over western USSR.

The concentrations of all trace elements and ions peaked at JAM from 1984-03-20 to 1984-03-22. The concentrations peaks for  $Na^+$  and  $Cl^-$  were likely due to airborne seasalt at this island site. A low pressure centre over Iceland and Jan Mayen probably caused the air mass to pass over England. The 850 mb trajectories are available in Figure 60. No other BP stations were apparently affected by this air mass.

Near the end of this campaign, trace elements and ions were enhanced between 1984-03-23 and 1984-03-25 at NYA, and from 1984-03-25 to 1984-03-26 at VAR, JER, KAR, SKO and BIR. Weather maps for these periods indicate an high pressure area over Scandinavia and western USSR. As a result, various emission sources in Central Europe and western USSR could have contributed. The 850 mb trajectories in Figure 61 seem to confirm this hypothesis. It should be noted, that the postulated origins of the February/March 1984 episodes at NYA are again in good agreement with the findings of Iversen (1985).

#### 4.1.5 June/July 1984 campaign

The two- and three-day mean concentrations from this campaign are summarized in the time-series in Figures 15-23 for trace elements, and Figures 37-45 for ions. Measurement data from BJO are available only after 1984-07-09.

The concentrations of all elements, except V, were enhanced at HOP and JAM from 1984-06-20 to 1984-06-21. Only slightly elevated concentrations of Cd were observed at NYA at that time. Weather maps for the period show a low pressure centre over Spitsbergen. The pollutants measured at the arctic island stations were probably transported from sources in North America and

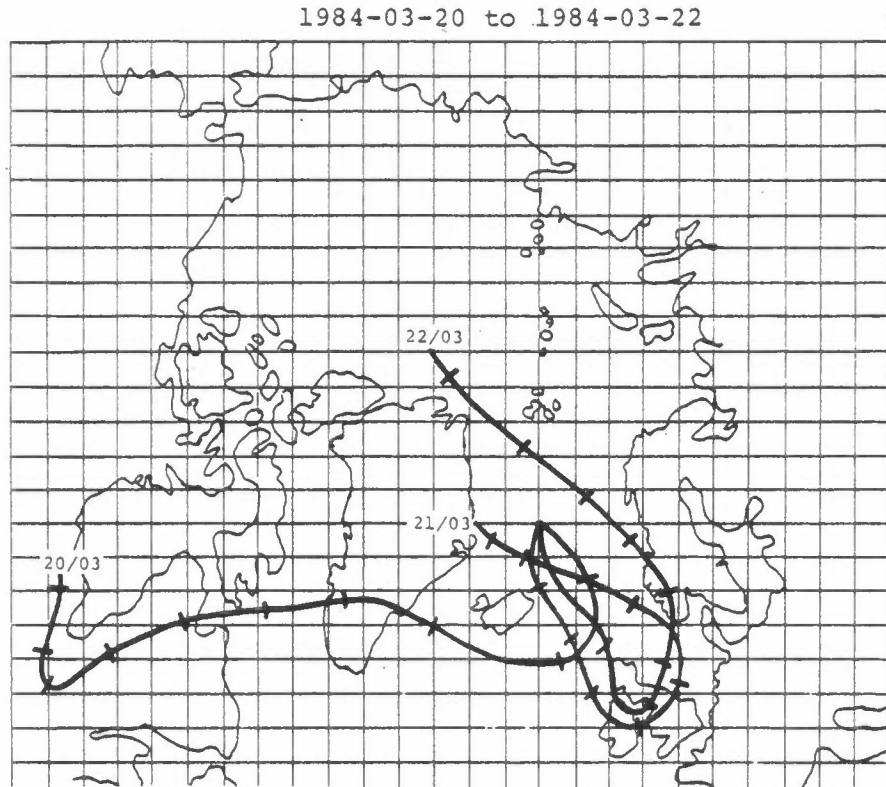


Figure 60: Daily 850 mb trajectories to JAM during the period 1984-03-20 to 1984-03-22. Daily marks are provided on each trajectory.

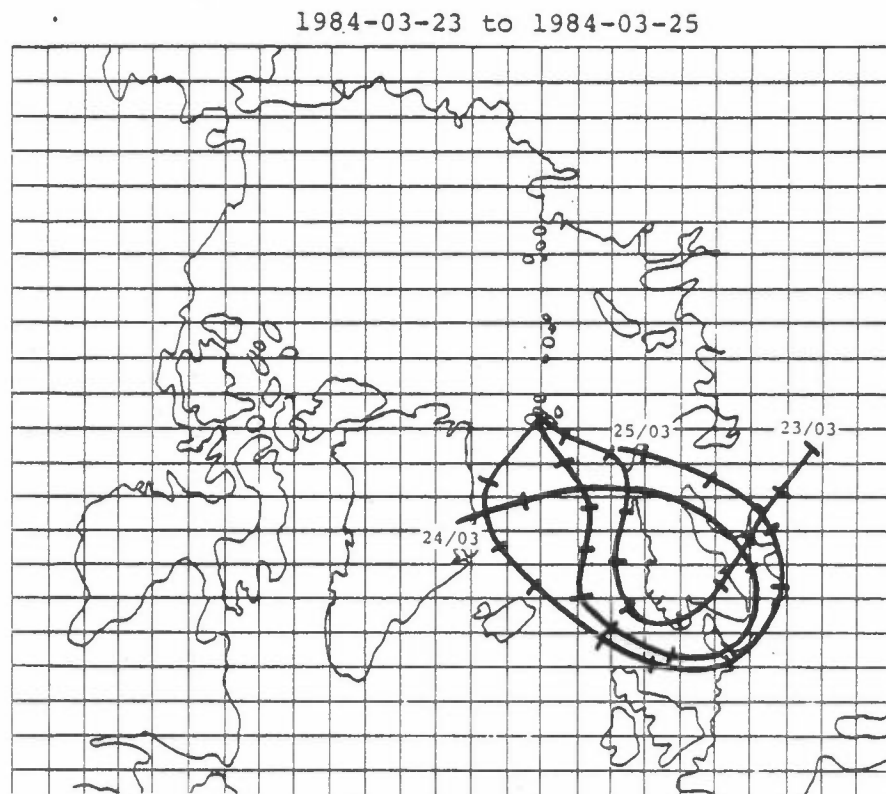


Figure 61: Daily 850 mb trajectories to JAM during the period 1984-03-23 to 1984-03-25. Daily marks are provided on each trajectory.

Scandinavia, as can be deduced from the 850 mb trajectories in Figures 62 and 63. In the same period, increased concentrations of all trace elements and  $\text{SO}_4^{2-}$ -S,  $\text{NO}_3^-$ -N and  $\text{H}^+$  were observed at BIR, likely caused by anticyclonic circulation over source areas in Central Europe. From 1984-06-22 to 1984-06-24 enhanced concentrations of all trace elements, except V, occurred at VAR, JER, and KAR, when a low pressure centre was located over the Norwegian Sea, directing emissions from the Kola Peninsula towards the BP Project mainland stations.

The very high Cd pulse at NYA on 1984-06-26 at NYA is very likely a measurement artifact, since no other element showed similar behaviour.

Very high concentrations of Zn, Cd and Pb were observed at VAR from 1984-06-29 to 1984-07-01, although the concentrations of these aerosol constituents were not increased at the neighboring JER. Elevated ions, particularly  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$  at NYA and HOP, during this period, can be attributed to airborne seasalt, since the ratios of  $\text{SO}_4^{2-}/\text{Na}^+$  and  $\text{SO}_4^{2-}/\text{Mg}^{2+}$  were close to those in sea water.

During the period 1984-07-06 to 1984-07-12 enhanced concentrations of all trace elements and  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N and  $\text{SO}_4^{2-}$ -S were measured at all Norwegian mainland stations, except VAR. At the beginning of the period, anticyclonic circulation dominated Central Europe. The concentrations peaked between 1984-07-09 and 1984-07-10, when a low pressure centre was situated over the area west of the British Isles. Thus, the increased pollution loads, measured at the Norwegian mainland stations, were probably transported from various source areas in Europe.

A second high pressure area over northern Scandinavia from 1984-07-09 to 1984-07-10 may explain the very high concentrations of Mn, V, Ni, Zn and Pb at JAM, since the air mass reaching this station could have carried emissions from sources in northern USSR (see the 850 mb trajectories in Figure 64). The same polluted air mass was probably also affecting BJO on 1984-07-10, when high Mn, Zn, Cd and Pb concentrations were measured.

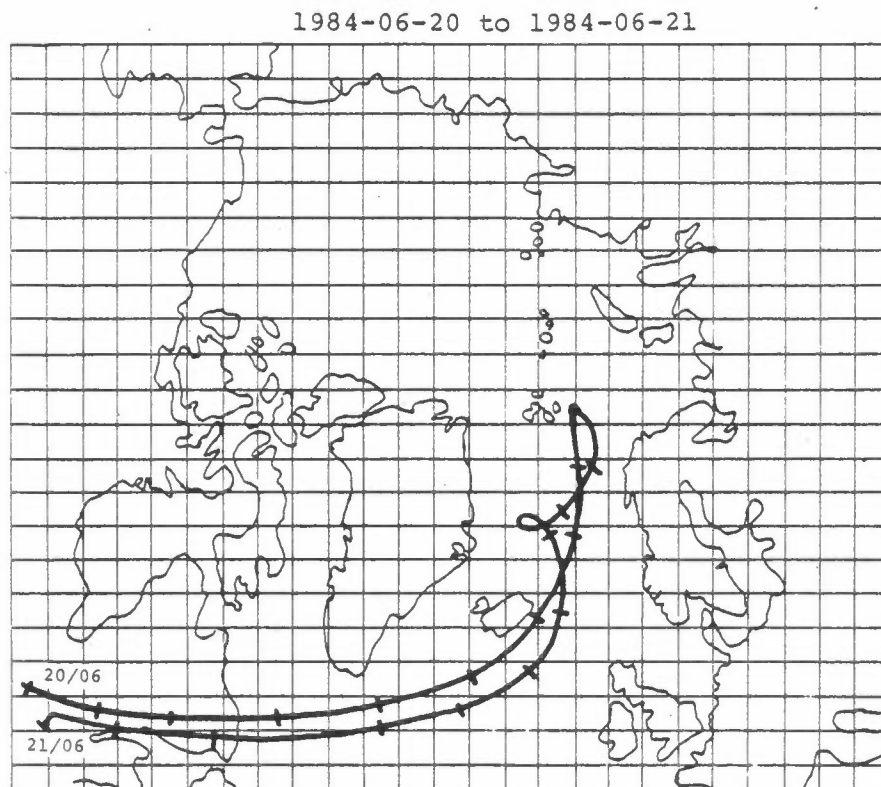


Figure 62: Daily 850 mb trajectories to HOP during the period 1984-06-20 to 1984-06-21. Daily marks are provided on each trajectory.

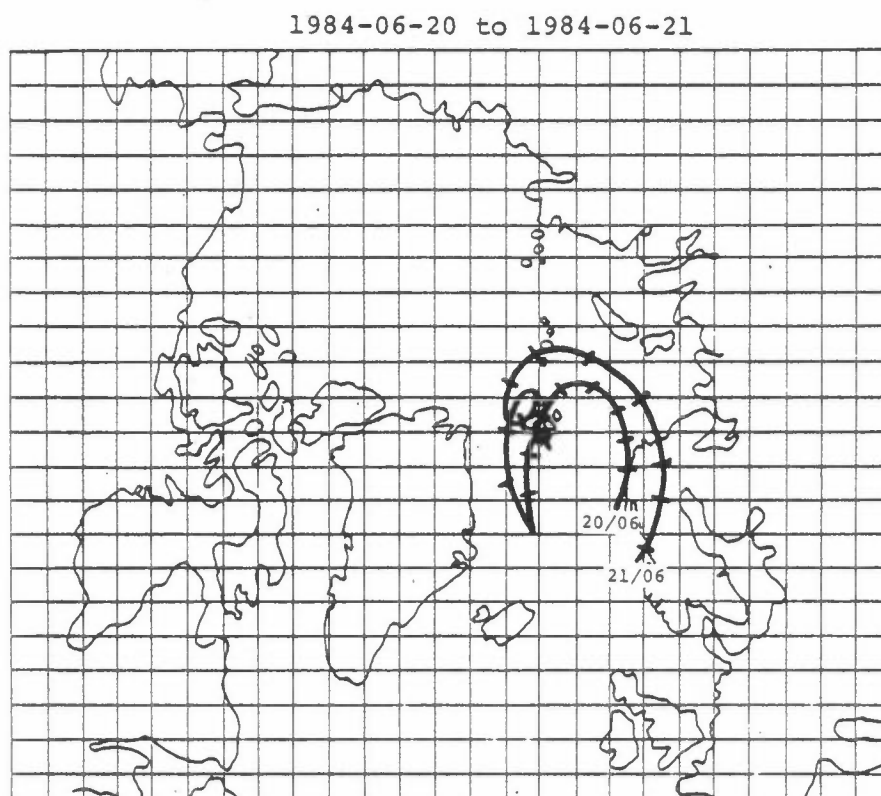


Figure 63: Daily 850 mb trajectories to JAM during the period 1984-06-20 to 1984-06-21. Daily marks are provided on each trajectory.

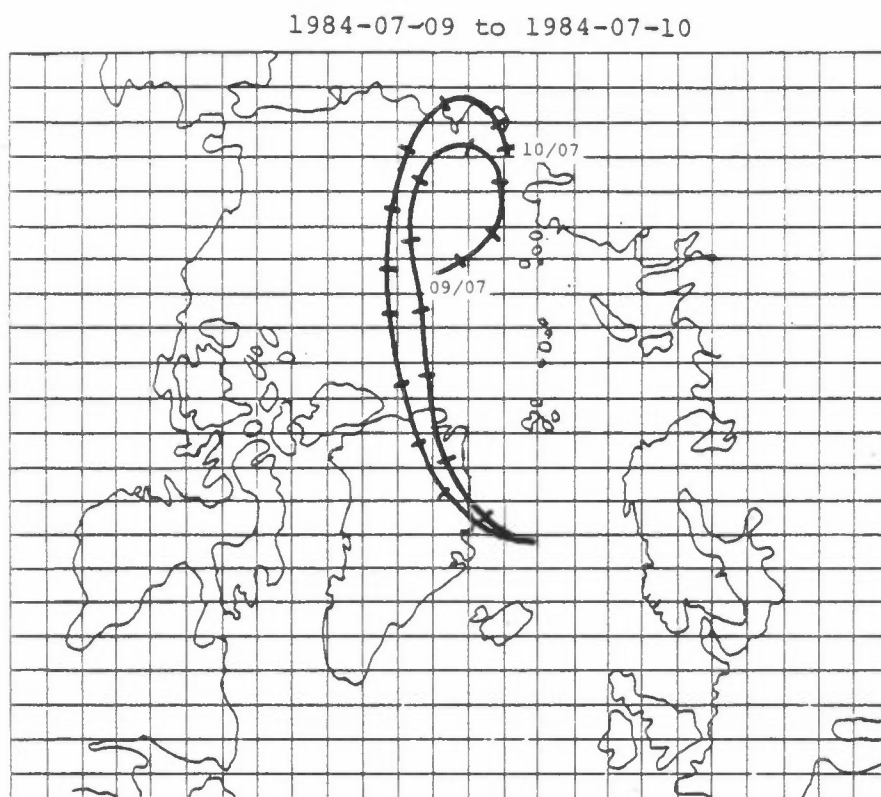


Figure 64: Daily 850 mb trajectories to JAM during the period 1984-07-09 to 1984-07-10. Daily marks are provided on each trajectory.

In summary, the NYA ground station appears to have been bypassed by the main air pollutant transport episodes during the Summer 1984 campaign. The results of size-differentiated chemical composition analyses of the arctic aerosol (Vitols and Pacyna, 1985) support this conclusion. Except for a few occasions, clean air prevailed at the other arctic island stations as well. Norwegian mainland stations appear to have been episodically affected by sources in Western and Central Europe, and from the Kola Peninsula in the USSR.

#### 4.1.6 Seasonal variations at Ny Alesund

Seasonal variations in the chemical composition of the arctic aerosol at NYA are apparent, when the available monthly mean concentrations of Zn, Pb, Cd, Cl and  $\text{SO}_4^{2-}$ -S for August and September in 1977, 1978, and 1979 (Larssen and Hanssen, 1980; and unpublished data\*) are compared, in Figure 65, to the measurement results from the Fall 1983 campaign (Pacyna and Ottar, 1985). The decrease in  $\text{Cl}^-$  concentrations in 1983 can be related to an increase in the  $\text{SO}_4^{2-}$ -S and H concentrations at the same time. This could not, however, be taken as an indication of any general trends, because the monthly mean values of Pb, as well as reduced  $\text{Cl}^-$ , are too dependent on the occurrence of episodic long-range transport. Interestingly, the lower Pb/S ratios in 1983 imply that the reductions in lead additives in petrol, imposed in several European countries in the early 1980's, have indeed resulted in lower Pb concentrations, even in the Arctic.

No general conclusion can be drawn about Cd, since the increased Cd concentrations in early August 1983 were likely caused by only one strong episode of long-range transport from the USSR to the Norwegian Arctic.

The Zn concentrations shown in Figure 65 are also difficult to interpret. Possibly the wind sector sampling controller during 1977 -1979 may not have

---

\*Courtesy of S. Larssen, NILU

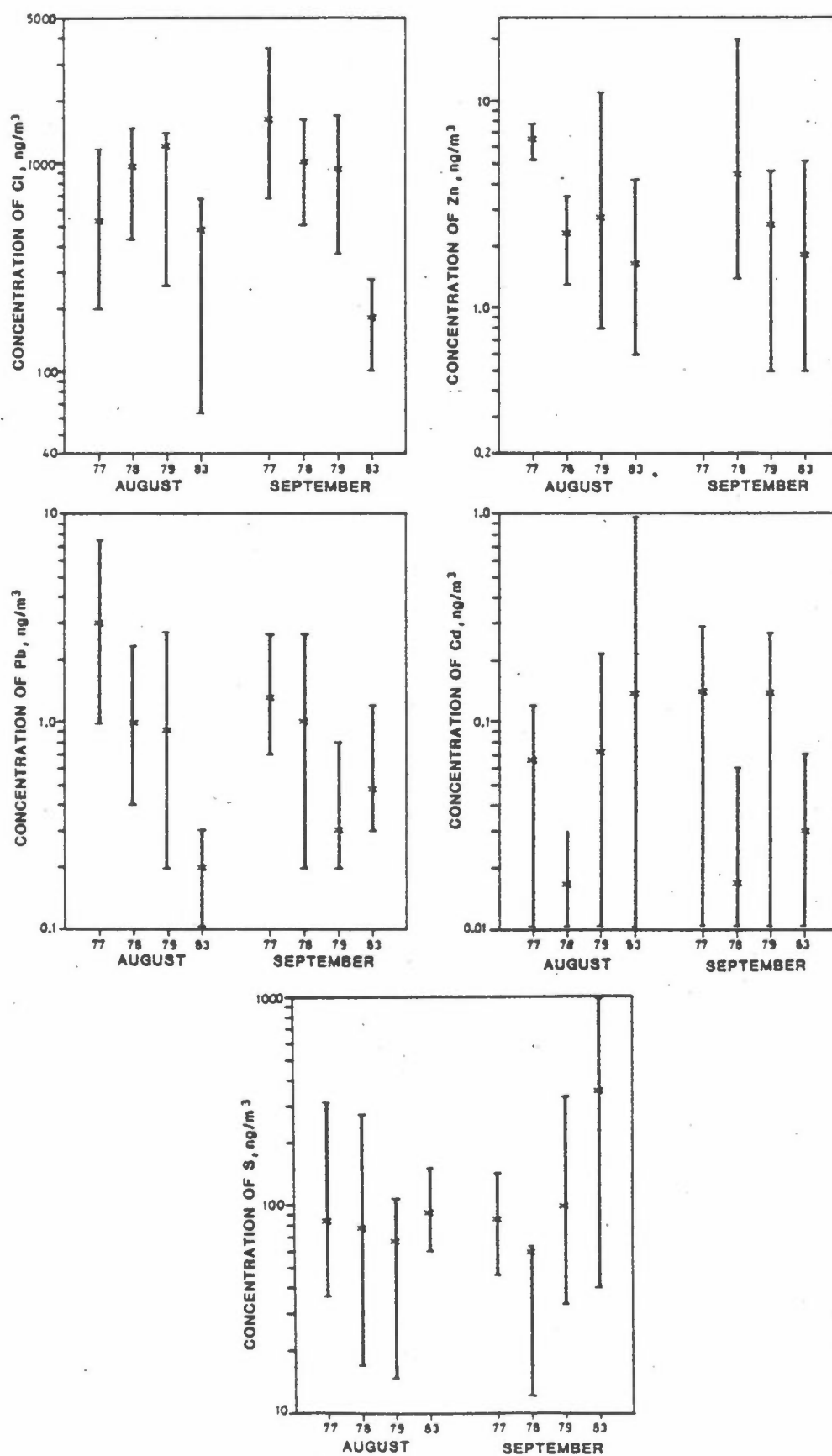


Figure 65: Range of observed aerosol concentrations at NYA during summer/fall 1977, 1978 and 1983. The monthly mean values are indicated by x (Pacyna and Ottar, 1985).



prevented the diesel engine effluents from the Ny Alesund power plant from reaching the sampling site.

Trace element concentrations from the March 1983 and February/March 1984 campaigns at NYA can be compared to the independent measurements by MISU in March 1981 (Heintzenberg et al. (1983), as shown in Table 6. The element concentrations in March 1983 were generally higher than those in 1981 and in 1984, due to the very strong episodic long-range transport of air pollutants from sources areas in northern USSR in the beginning of March, 1983. Some minor differences might be conceivably due to the somewhat different aerosol

Table 6: Concentration ranges ( $\text{ng m}^{-3}$ ) of trace elements at NYA measured in March 1981 (Heintzenberg et al., 1983) and from Hi-Vol sampling during the Spring 1983 and Spring 1984 BP Project campaigns.

Period Element	March 1981 (Heintzenberg et al., 1983)*	March 1983 (this work)**	February/March 1984 (this work)**
Mn	<0.525-1.56	0.35-4.52	0.16-1.77
V	<0.776-<2.38	0.24-5.86	0.07-1.38
Ni	0.383-1.39	0.08-1.44	0.05-0.62
Zn	<0.548-5.42	2.1-19.2	0.23-10.02
Pb	<1.00-4.97	0.30-16.0	0.16-6.56

\* in aerosols  $< 2 \mu\text{m}$  EAD.

\*\* in aerosols  $< \text{ca } 2.5 \mu\text{m}$  EAD.

fractions analysed. Heintzenberg et al. (1983) reported trace element concentrations for particles nominally  $< 2.0 \mu\text{m}$  EAD, while the BP Project Hi-Vol sampler separated particles at about  $< 2.5 \mu\text{m}$  EAD. Even if the aerosol segregation had been exactly at the 2.0 and 2.5  $\mu\text{m}$  EAD cut points (which is doubtful), the additional mass of the 2.0 to 2.5  $\mu\text{m}$  particles could not have had any significant effect, because normally aerosol mass exhibits a minimum in this size range. During Spring 1984, when only minor long-range transport episodes were observed, trace element concentrations, with few exceptions, were lower than in 1981 and 1983 (see Table 7).

#### 4.1.7 Trace element measurement by various sampling and analytical methods

In order to assess the possible influence of analytical methods on the reported Pb, Ni, Cd, V, Mn, and Zn concentrations, selected Hi-Vol samples, collected at NYA and VAR during Spring 1983 campaign, were analysed by instrumental neutron activation analysis (INAA-1) as well as by particle induced X-ray emission (PIXE-1) at the University of Gent, Belgium, and by instrumental neutron activation analysis (INAA-2) at the University of Rhode Island, U.S.A. These results, together with those from the AAS analyses at NILU, are shown in Table 8 for NYA, and Table 9 for VAR.

Table 7: Concentration ranges ( $\text{ng m}^{-3}$ ) of trace elements at NYA measured during August-September 1982 (Heintzenberg et al., 1983) and concentration ranges reported in this work from Hi-Vol sampling.

Period	August-September 1982 (Heintzenberg et al., 1983)*	August-September 1982 (this work)**	August-September 1983 (this work)**	June-July 1984 (this work)**
Element				
Mn	<0.02-0.3	0.01-0.18	0.07-0.66	0.02-0.11
V	<0.05-0.3	b.d.l.	b.d.l.	b.d.l.
Ni	0.02-0.1	b.d.l. -0.09	b.d.l. -0.11	b.d.l.
Zn	0.08-0.6	b.d.l. -0.33	0.50-5.10	0.25-1.25
Pb	<0.08-0.5	0.05-0.68	b.d.l. - 0.30	b.d.l.-0.16

b.d.l.: Below detection limit.

\* in aerosols <2  $\mu\text{m}$  EAD.

\*\* in aerosols <ca 2.5  $\mu\text{m}$  EAD.

To ascertain the possible influence of the sampling and analytical method, the NYA Hi-Vol results were also compared with the independently measured size-differentiated trace element concentrations from the low-volume cascade impactor (BTL C.I.). The BTL C.I. (a 6-stage cascade impactor (plus after filter) of Battelle-design) separated aerosol particle mass into 7 aerodynamic size ranges, which were analysed by particle induced x-ray emission method (PIXE-2) at the University of Lund, Sweden. (For more details on the BTL C.I. measurements, see Vitols and Pacyna, 1985.)

Three important factors should be considered when comparing the results of trace element concentrations (shown in Tables 8 and 9) obtained by the different sampling and analytical methods. The BTL C.I. impacted the aerosol particles in the size range  $<0.25 \mu\text{m}$  to  $>8 \mu\text{m}$  EAD on six 0.25 mm diameter polyethelene glycol-coated glass discs, followed by a Nuclepore (NP) after-filter. The Hi-Vol samples were collected on the large (20 cm x 25 cm) Whatman 41 cellulose filters. The flowrate for the BTL C.I. was  $1 \text{ l min}^{-1}$ , while about  $1 \text{ m}^3 \text{ min}^{-1}$  for the Hi-Vol sampler. The element mass concentrations obtained by BTL C.I. and analysed by PIXE-2 can be somewhat underestimated because, in the first place, they represent trace element amounts in particles  $<2.0 \mu\text{m}$  EAD, whereas the Hi-Vol fine fraction cut is at  $<2.5 \mu\text{m}$  EAD. Secondly the BTL C.I. concentrations for these comparisons were obtained by simply summing the individual stage collections (plus after-filter), so that any possible internal sample losses in the BTL C.I. are not included.

Judging from these rather limited comparisons, it appears that the AAS and PIXE methods are about equally satisfactory for Pb, Zn and Ni analyses (the latter method even for aerosol samples collected on fibrous filters), AAS and INAA are best for V, AAS for Cd, and INAA for Mn.

Table 8: Pb, Ni, Cd, V, Mn, and Zn concentrations ( $\text{ng m}^{-3}$ ) at NYA, Spring 1983, as determined by various analytical methods. (Except for the PIXE-2 samples (sum of 6 BTL C.I. substrates and afterfilter) all other methods analysed portions of Hi-Vol samples on Whatman 41 filters.)

Sample	Pb		Ni		Cd		V			Mn			Zn						
	AAS	PIXE-1 PIXE-2	AAS	PIXE-1 PIXE-2	AAS	INAA-1	AAS	INAA-1	INAA-2	PIXE-2	AAS	INAA-1	INAA-2	PIXE-2	AAS	INAA-1	INAA-2	PIXE-2	
N-1	0.3	<0.9	b.d.l.	<0.20	b.d.l.	0.061	<1.07	b.d.l.	0.32	0.02	b.d.l.	0.22	0.30	0.22	0.10	5.0	1.0	0.85	0.38
N-2	1.9	2.2	2.0	0.08	<0.20	0.076	4.30	b.d.l.	0.20	0.14	b.d.l.	0.20	0.28	0.23	0.64	2.1	2.4	1.66	1.11
N-3	15.6	22.0	16.1	1.44	2.10	0.828	<1.3	4.5	4.90	4.26	1.90	2.20	3.80	3.30	2.24	19.2	23.0	18.9	13.7
N-4	10.6	16.0	9.7	0.68	1.50	0.415	1.04	1.9	2.70	7.72	0.68	2.10	3.70	3.42	1.58	12.5	16.0	15.2	10.2
N-5	16.0	19.1	16.8*	1.37	2.30	0.330	0.74	4.4	5.40	4.04	2.50*	2.40	4.90	3.99	3.23*	17.9	23.0	22.0	17.7*
N-6	5.8	9.6		0.72	0.93	0.219	<1.1	1.8	2.30	1.87		1.10	2.11	1.66		11.3	8.3	7.0	
N-7	2.6	2.7	3.6*	0.24	<0.40	0.080	<1.29	0.3	0.76	0.62	0.27*	0.50	1.27	0.75	0.69*	3.6	5.0	3.5	3.8*
N-8	2.8	4.8	4.3*	0.14	0.30	0.083	<1.6	0.2	0.52	0.46	b.d.l.*	0.4	1.00	0.82	0.65*	3.7	4.9	3.8	3.4*
N-9	9.0	10.2	9.2*	-	0.95	0.355	<1.3	1.7	2.18	1.93	1.75*	1.3	2.35	2.00	1.69*	10.9	11.8	10.7	9.5*
N-10	6.9	7.7		1.17	1.04	0.098	<0.99	1.8	1.90	1.68		0.4	1.80	1.77		7.6	9.3	9.1	
N-11	8.0	8.1	8.0*	0.69	1.10	0.322	<1.4	1.9	2.30	1.91	1.33*	1.9	3.40	2.75	2.21*	10.0	13.4	10.8	8.7*
N-12	7.0	8.9		-	1.39	0.125	<1.3	2.0	2.07	1.81		3.5	3.02	2.52		8.2	15.0	9.1	
N-13	8.4	9.0		0.84	0.95	0.127	<0.9	2.1	1.92	1.53		4.5	2.30	1.88		8.3	9.9	9.1	
N-14	4.3	5.3	6.3*	0.40	0.78	0.097	<1.55	2.0	1.19	3.72	0.24*	3.6	1.44	1.09	1.30*	5.9	5.3	4.6	5.2*

\*<sup>1</sup> not for the full period.

b.d.l.: below detection limit.

AAS : Chemical Laboratory, NILU

PIXE-1 : University of Gent, Belgium

INAA-1 : University of Gent, Belgium

PIXE-2 : Lund Institute of Technology, Lund, Sweden

INAA-2 : University of Rhode Island, Narragansett, RI, U.S.A.

Table 9: Pb, Ni, Cd, V, Mn, Zn concentrations ( $\text{ng m}^{-3}$ ) at VAR, Spring 1983, by AAS and PIXE analyses.

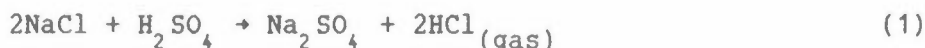
Sample	Pb		Ni		Cd		Zn		Mn		V	
	AAS	PIXE-1	AAS	PIXE-1	AAS	INAA-1	AAS	INAA-1	AAS	INAA-1	AAS	INAA-1
V-1	5.5	5.2	1.49	1.20	0.472	<2.0	5.8	6.6	1.1	0.8	2.8	1.6
V-2	6.7	9.1	0.83	1.20	0.440	<2.0	8.2	10.9	1.0	0.8	5.5	2.8
V-3	10.2	13.5	6.20	4.70		<1.5	11.2	18.0	1.1	2.0	4.8	4.8
V-4	13.1	21.3	11.0	7.10		<3.2	23.1	23.6	7.6	7.4	11.7	15.0
V-5	11.4	13.5	4.07	2.10		<2.6	15.5	15.9	6.8	2.6	9.4	2.3
V-6	5.9	7.5	2.32	2.00		<1.9	7.8	9.4	3.3	1.8	4.9	2.0
V-7	2.6	5.1	1.16	0.91	0.221	<4.4	5.2	5.4	3.8	1.4	4.1	1.2
V-8	5.8	9.0	0.58	0.96	0.253	<3.6	7.9	10.1	1.6	2.0	7.3	2.1
V-9	1.8	5.8	0.43	0.36		<2.9	3.7	4.5	0.9	0.8	1.8	0.8
V-10	5.3	5.9	0.93	0.82	0.266	<1.9	4.3	5.1	2.8	1.1	6.5	2.1
V-11	1.3	3.0	1.63	1.65		<3.8	4.3	3.2	1.1	0.5	4.1	1.3
V-12	0.8	2.4	3.09	1.00		<3.0	7.5	5.8	1.8	0.7	2.3	0.9
V-13	4.6	5.8	2.67	2.90		<3.0	7.4	9.4	0.5	0.9	2.0	2.0

AAS : Chemical Laboratory, NILU  
 PIXE-1: University of Gent, Belgium  
 INAA-1: University of Gent, Belgium

#### 4.2 ION BALANCES FOR AEROSOLS

The sums of the analysed anions and cations (as equivalents) in the water extracts have been calculated, and the agreement was for the most part within 10%. For most of the samples, the sum of anion-equivalents was higher than of the cation-equivalents, which may indicate that some of the metals, which were not analysed in the water extracts, were in a water soluble form. Since the water extracts for most of the samples were quite acidic, this could obviously be the case.

As mentioned under Chemical Analysis in Section 2.2., the sampling artifact leading to the loss of chloride may be quantified. If the ratios of main components in seasalt are assumed to be preserved in the fine fraction of aerosol, the Cl/Na ratio found would indicate the degree of chloride loss. In Figure 66 this ratio is plotted against  $H^+$  concentrations, calculated from the pH values in the water extracts for the NYA samples from the Winter 1983 campaign. Although there are no quantitative relationships between them, it is clearly seen that the Cl/Na ratio decreases when the  $H^+$  concentration increases. Possibly most of the chloride is lost by the reaction:



which means that  $H^+$  is lost as well. It is possible to calculate the amount of chloride lost by assuming that the Cl/Na ratio should have been 1.8. If all the chloride were lost as HCl, it can then be calculated how much the  $H^+$  concentration was reduced.

## 5 CONCLUDING REMARKS

The results of the various BP Project campaigns, presented in this report, show that airborne trace elements in aerosols are useful indicators of episodic long-range transport of air pollutants to the Norwegian sector of the Arctic. On many occasions during the Spring 1983 and Winter/Spring 1984 campaigns, the concentrations peaks for either all, or some of the trace elements were observed. Very often concentrations of some ions, particularly  $H^+$ ,  $NO_3^-$ ,  $SO_4^{2-}$ -S,  $K^+$  and  $Ca^{2+}$ , showed a similar pattern. The elevated anthropogenic Pb, Cd, Ni, and V concentrations clearly trace air pollution episodes.

In order to assess the origin(s) of aerosols measured during episodes, their chemical composition was examined, together with relevant information from weather maps and/or wind back-trajectories for the periods. The main emission sources, likely contributing to the high concentrations of trace elements at the BP Project arctic island stations during the winter half-year, appear to be located in northern and western USSR. Emissions from

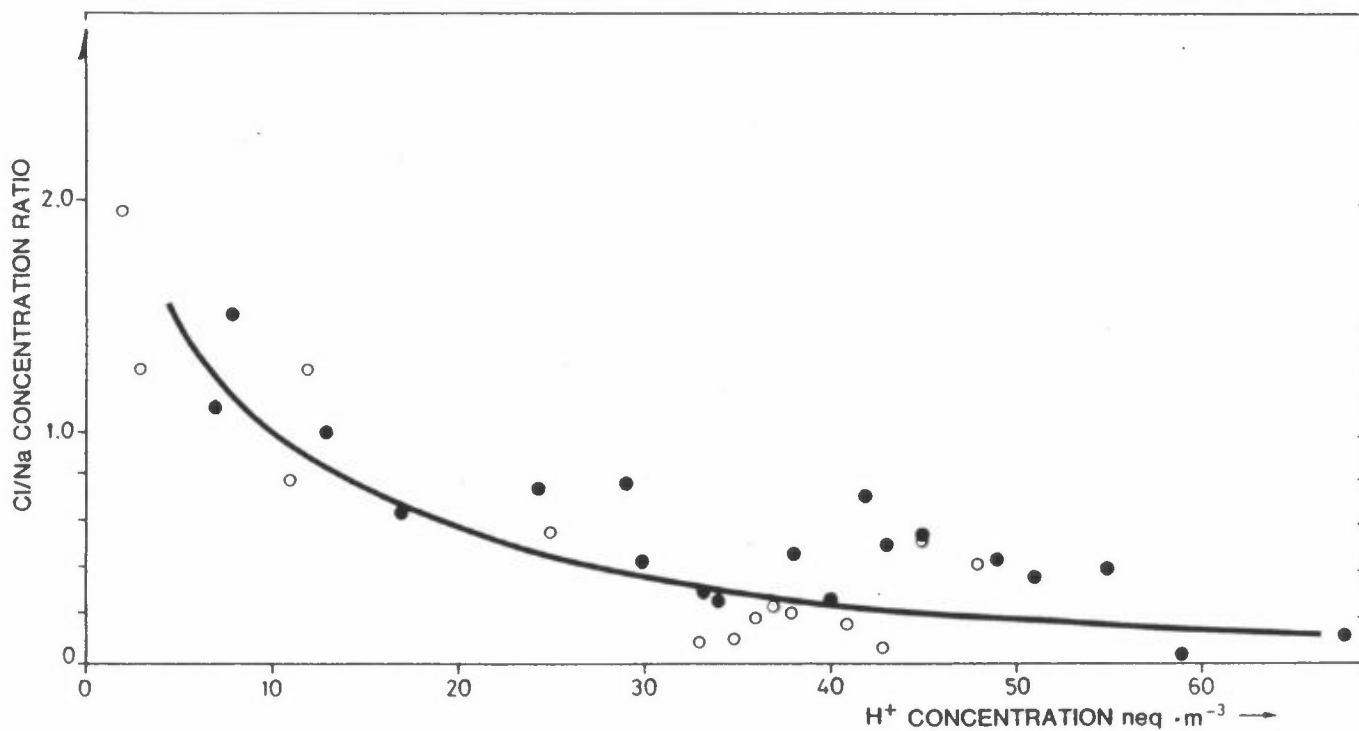


Figure 66: Cl/Na ratio vs. H<sup>+</sup> concentrations calculated from the pH values in the water extracts for the NYA samples from the Winter 1983 campaign.

copper-nickel smelting on the Kola Peninsula were often implicated as major contributors of Pb, Cd, Ni and Zn at NYA, HOP and BJO stations. Since the mainland station VAR is located quite near this major USSR smelter complex, the increased metal concentrations at VAR were often related to the Kola source area emissions, e.g., during the period 1983-03-06 to 1983-03-13. This episode of long-range transport, clearly detected at NYA, BJO and JAM, was a major one during the Spring 1983 campaign in the term of high trace element concentrations.

The Norwegian mainland stations (except for VAR) were exposed to pollutants transported mainly from central Europe and the British Isles. These two regions and the emission areas in the USSR seem to be important for long-range transport of air pollutants to the Arctic during the summer half-year (June to September) as well, (e.g., the episode from 1983-09-05 to 1983-09-09). During several other periods, (e.g., 1983-08-08 to 1983-08-10), emission regions even on the North American continent can be a suspected cause of enhanced air pollutant concentrations at the arctic island stations. In general, the USSR emission sources are the likely major contributors of particulate air pollutants in the Norwegian Arctic both during the winter (February to April) and the summer half-years, while the European and possibly North American sources appear to contribute only during the summer half-year.

The relatively limited number of trace elements measured in Hi-Vol samples during the BP Project campaigns does not permit effective use of receptor modeling to identify more precisely the emission regions, and to differentiate between emissions from Eastern and Western Europe. For this, information on size-differentiated chemical composition and enrichment factors for a larger number of trace elements in aerosol is required. Such information at this time is only available for the NYA reference station (Vitols and Pacyna, 1985; Pacyna, 1986). Nevertheless, it can be safely speculated that the aerosol Pb, Cd, Ni and Zn at the arctic island stations are due to emissions from metallurgical processes, while V and Mn come from fossil fuel combustion. Some of the Mn and Zn is likely of natural origin.



These conclusions are in good agreement with the findings reported from other BP Project studies, e.g., on the origin of aerosols aloft (Pacyna et al., 1985), size-differentiated chemical composition of the arctic aerosol (Vitols and Pacyna, 1985), and statistical analysis of aerosol sulphate in the Norwegian Arctic and large-scale atmospheric flows (Iversen, 1985).

## 6 ACKNOWLEDGEMENTS

This work was funded by British Petroleum International Ltd.

The authors thank Dr. Willy Maenhaut, University of Gent, Belgium and Dr. Urszula Tomza, Silesian University, Katowice, Poland for INAA and PIXE analyses, and Dr. Kenneth A. Rahn, University of Rhode Island, Narragansett, RI, USA for INAA analysis of Hi-Vol samples collected at NYA and VAR during the March 1983 measurement campaign; and Dr. Hal Rosen, Lawrence Berkeley Laboratory, University of California (at Berkeley), for carbonaceous particle work.

## 7 REFERENCES

- ANR (1982) Soviet arctic developments. Norilsk expands. Arctic News Record, Annual 1982, 8-9.
- Blanchard, D.C. and Woodcock A.H. (1980) The production, concentration and vertical distribution of the sea-salt aerosol. In: Aerosols: anthropogenic and natural sources and transport. Ed. by T. Kneip and P. Liroy. New York (N.Y. Acad. Sci., Annals. 338). 330-347.
- Brice, J., Lux, J.E. and Stevens, R.D.S. (1982) The measurement of filter collection efficiencies of atmospheric reactive gases at low temperatures. Downsview, Ont. Concord Scientific Corporation, (CSC. 110-107).
- Dolske, D.A., Schneider, J. and Sievering, H. (1984) Trace element pass-through for cellulose filters when used for aerosol collection. (Technical Note). Atmos. Environ., **18**, 2557-2558.
- Europäischer Wetterbericht (1983) Amtsblatt des Deutschen Wetterdienstes, Offenbach am Main.
- Europäischer Wetterbericht (1984) Amtsblatt des Deutschen Wetterdienstes, Offenbach am Main.

- Gundel, L.A., Dod, R.L., Rosen, H. and Novakov, T. (1984) The relationships between optical attenuation and black carbon concentration for ambient and source particles. Sci.Total Environ., 36, 197-202.
- Harris, J. (1984) Trajectories during AGASP, Geophys.Res.Lett., 11, 453-456.
- Heintzenberg, J., Bischof, W., Odh, S.-A., and Moberg, B. (1983). An investigation of possible sites for a background monitoring station in the European Arctic. Stockholm. (Department of Meteorology, University of Stockholm, Rept. AP-22).
- Hoff, R.M. and Trivett, N.B.A. (1984) Ground-based measurements of Arctic haze made at Alert, N.W.T., Canada, during Arctic Gas and Aerosol Sampling Project (AGASP). Geophys.Res.Lett., 11, 389-392.
- Iversen, T. (1985) On air pollution transport to the Norwegian Arctic. Lillestrøm, Norwegian Institute for Air Research (NILU OR 59/85).
- Joranger, J. and Ottar, B. (1984). Air pollution studies in the Norwegian Arctic. Geoph.Res.Lett., 11, 365-368.
- Larssen, S. and Hanssen, J.E. (1980) Annual variations and origin of aerosol components in the Norwegian arctic - subarctic region. In: WMO technical conf. on regional and global observation of atmospheric pollution relative to climate. Boulder 1979. Papers. Geneva (WMO Spec. Environ. Report, 14).
- Lindeken, C.L., Morgan, R.L. and Petrock, K.F. (1963) Collection efficiency of Whatman 41 filter paper for submicron aerosols. Health Physics, 9, 305-308.
- Liu, B.Y.H., Pui, D.Y.H. and Rubow, K.L. (1983) Characteristics of air sampling filter media. In. Aerosols in the Mining and Industrial Work Environments. Vol. 3: Instrumentation. Ed. by Marple, V.A. and Liu, B.Y.H. Ann Arbor, MI Ann Arbor Science.
- NILU (1984) Emission sources in the Soviet Union. Lillestrøm, Norwegian Institute for Air Research (NILU TR 4/84).
- Ottar, B. and Pacyna, J.M. (1984). Sources of Ni, Pb and Zn during the arctic episode in March 1983. Geophys.Res.Lett., 11, 441-444.

- Pacyna, J.M., Vitols, V. and Hanssen, J.E. (1984a). Size-differentiated composition of the arctic aerosol at Ny-Alesund, Spitsbergen. Atmos. Environ., 18, 2447-2459.
- Pacyna, J.M., Semb, A., and Hanssen, J.E. (1984b). Emission and long-range transport of trace elements in Europe. Tellus, 36B, 163-178.
- Pacyna, J.M. and Ottar, B. (1985). Transport and chemical composition of summer aerosol in the Norwegian Arctic. Atmos. Environ., 19, 2109.
- Pacyna, J.M., Ottar, B., Vitols, V. and Arnesen, K. (1985) Aircraft measurements of air pollutants in the Norwegian Arctic. Appendices A, B, C and D. Lillestrøm, Norwegian Institute for Air Research (NILU OR 66/85).
- Pacyna, J.M. (1986) Source-receptor relationships for air pollutants in the Arctic. Lillestrøm, Norwegian Institute for Air Research (NILU OR 3/86).
- Porch, W.M. and MacCracken, M.C. (1982) Parametric study of the effects of arctic soot on solar radiation. Atmos. Environ., 16, 1365-1371.
- Rosen, H., Novakov, T. and Bodhaine, B.A. (1981) Soot in the Arctic. Atmos. Environ., 15, 1371-1374.
- Salzman, E.S., Savoie, D.L., Zika, R.G. and Prospero, J.M. (1983) Methane sulfonic acid in the marine atmosphere. J. Geophys. Res., 88, 10897-10902.
- Vitols, V. and Wasseng, J.H. (1985) BP Project ground station descriptions. Lillestrøm, Norwegian Institute for Air Research (NILU OR 63/85).
- Vitols, V. and Pacyna, J.M. (1985) Special measurements at Ny Alesund: physical and chemical properties of the arctic aerosol. Lillestrøm, Norwegian Institute for Air Research, (NILU OR 65/85).
- Whitby, K.T. (1978) The physical characteristics of sulfur aerosols. Atmos. Environ., 12, 135-159.

117  
NORSK INSTITUTT FOR LUFTFORSKNING (NILU)  
NORWEGIAN INSTITUTE FOR AIR RESEARCH

(NORGES TEKNISK-NATURVITENSKAPELIGE FORSKNINGSRÅD)

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

RAPPORTTYPE Oppdragsrapport	RAPPORTNR. OR 64/85	ISBN-82-7247-635-5	
DATO December 1985	ANSV. SIGN. <i>J. Schjoldager</i>	ANT. SIDER 106	PRIS NOK 90.-
TITTEL Chemical composition of aerosols at BP- Project ground stations		PROSJEKTLEDER J.M. Pacyna	
		NILU PROSJEKT NR. 0-8510	
FORFATTER(E) Jozef M. Pacyna Val Vitols Jan Erik Hanssen		TILGJENGELIGHET* A	
		OPPDRAKSGIVERS REF.	
OPPDRAKSGIVER (NAVN OG ADRESSE) BP International Ltd., ECC Britannia House, Moore Lane London, EC 24 9BV, England			
3 STIKKORD (à maks. 20 anslag) Arctic                      Air quality measurement                      Ground station data			
REFERAT (maks. 300 anslag, 7 linjer)			

TITLE Chemical composition of aerosols at BP-Project ground stations
ABSTRACT (max. 300 characters, 7 lines) Aerosol measurement results are presented for all BP Project ground stations, as well as tentative speculation on the possible source(s). In general, the USSR emission sources are the likely major contributors of particulate air pollutants in the Norwegian Arctic both during the winter and the summer half-year, while the European and possibly North American sources appear to contribute only during the summer half-year.

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