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AMBIENT PARTICLE LOSSES  
IN THE SK SAMPLING SYSTEM

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1 INTRODUCTION

Particle losses in sampling systems, such as the KK or SK, are known to occur and may be due to a combination of gravity settling, turbulent and electrostatic deposition, diffusion, and inertial impaction. Furthermore, particles deposited in the sampling lines may also become reentrained by particle bouncing, turbulence, mechanical vibrations, and particle collisions. Each of the above "mechanisms" may in turn depend on a number of variables, such as flow Reynolds number, curvature of the lines, properties of the materials of the lines, and the characteristics of the particles (e.g., size, density, wet, dry, sticky).

Because of the large number of possible deposition/reentrainment mechanisms and variables involved in these processes, the total problem of particle transport and deposition is very difficult to analyse theoretically. Empirical data, therefore, must be relied upon in practical situations to assess the extent of net losses in the system, as well as possible deviations in measured concentrations from representative concentrations in the atmosphere from which the sample is drawn. Such data can also serve as a guide for designing sampling systems with a minimum of particle losses.

Swedish experiments with ambient aerosols (1) have revealed substantial differences in measured concentrations of several chemical components of the particles, when measurements were made with and without sampling lines. Particle losses generally increased with higher sampling rates, thus increased turbulence in the sampling line.

The SK system has been extensively used by NILU both in urban and rural areas. It is also one of the two recommended systems for obtaining particulate samples (for subsequent chemical composition determinations) for the EMEP network. Although some comparison sampling with the SK system and the EMEP medium volume sampler has been done (2), no evaluation of possible aerosol losses in the SK sampling train is available. A series of measurements were conducted at NILU during late 1980 and early 1981 to obtain such information for certain chemical species in ambient aerosols.

## 2 EXPERIMENTAL

Forty-four ambient aerosol sampling runs were conducted on the roof of the NILU building in November and December 1980, and January, February and March 1981. Except for one (due to power failure), all sampling runs were of approximately 24-hour duration. The sampling schedule was irregular, and no runs were conducted on weekends and holidays.

### 2.1 Experimental design

Duplicate, simultaneous samples of the "true" and SK-collected aerosols were obtained during each run. Four SK-type sampling inlets (vertical elutriator/inverted funnel) aspirated ambient air simultaneously just outside the south wall of the ca. 3 m high eastern penthouse on the roof of the NILU building, with their downward-facing openings about 2 m above the flat roof of the building. The penthouse wall is about 10 m from the southern roof edge of the NILU building. The inlets were arranged within  $< 1 \text{ m}^2$  area, as shown in Figure 1.

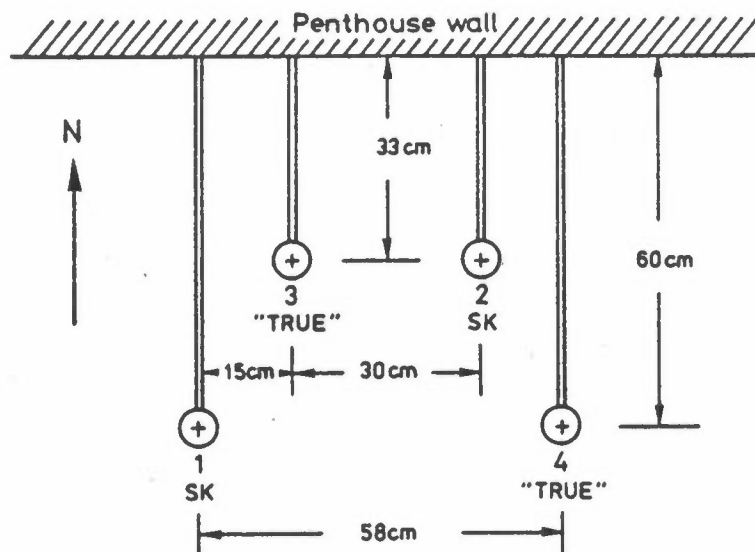


Figure 1: Arrangement of SK and "true" sampler inlets outside the NILU penthouse (looking down on the inlets).

Two of the sampling trains - considered to represent the "true" aerosol sample - drew air through a filter in an open-face filter holder\* inserted directly in the funnel of the inlet. The other two inlets functioned as the sample air intakes of the normal SK system (where the filter in an "in-line" filter holder\* is preceded by a semi-rigid plastic tubing sampling line and a bees wax coated metal distribution manifold). All four sampling trains aspirated ambient air at approximately the "standard" SK sampling rate of  $2.5 \text{ L min}^{-1}$ .

Beginning in early January 1981 an EK-type sampler was also operated in parallel with the other 4 sampling trains (about 2 m west of Sampler 1 and ca. 80 cm from the wall). The EK system also uses an open-face filter holder directly in a radiation-shielded vertical elutriator inlet, but aspirates air at 6-7 times higher rate than the SK.

Although it is known, that the vertical elutriator-type inlets (such as the one used with the SK system) are sensitive to wind speed changes, for purposes of this study it was assumed that for

\*NILU-design models, for 42 mm dia. filters.

a given test both systems had the same sampling effectiveness, and any differences in measured particle concentrations were due to particle transmission losses within the SK system.

Because of the inclement wintertime weather conditions, no attempt was made during the sampling program to clean portions of the SK sampling train to assess the effect of particle accumulation.

After the completion of the sampling program, optical reflectance of the deposited particles on the filters was measured, and the filter sets were analysed for  $\text{SO}_4$ , Pb, Mg and Ca.  $\text{SO}_4$  has been the main chemical species in aerosols of interest to NILU, OECD and EMEP programs. Pb can be considered to represent a "dry" anthropogenic aerosol, while Mg a "wet" and Ca a "dry" natural aerosol. Because Pb requires acid extraction sample pretreatment, to avoid analytical uncertainties due to filter splitting, Pb analysis was performed on filter sets from alternate sampling runs. Representative blank filters from the same batches as the sample filters were selected and analysed for the same components.

## 2.2 Sampling equipment and components

The SK sampling trains (3) were slightly modified NILU models (the first seven outlets of the sample manifold were plugged, and the in-line filter holder used only on the last). Because of some uncertainties about the actual sample volumes obtained by before-and-after flowrate measurements with rotameters (the current SK procedure), all volumes were measured with air volume-integrating dry gas meters (DGM).

For the "true" sample trains, the open-face filter holders in the SK inlets were directly connected with semi-flexible tubing to the inlets of the DGMs. In all 4 sampling trains, the inlet gauge



pressure to the DGMs\*\* was measured (from a T-connection) with a H<sub>2</sub>O-manometer, and the sampling rate was regulated with a flexible plastic tubing/pinch clamp bleed valve on the meter outlet. The appropriate flowrate was adjusted by timing the meter dial readings with a stopwatch. A diaphragm-type vacuum pump\*\*\* concluded each sampling train.

The DGMs in the four sampling trains were calibrated (at 4 flowrates, 5 runs each) immediately before and after the sampling program with a laboratory wet test meter. The calibrations were performed with the fully assembled sampling train, i.e., with the inlet, sampling line, filter/filter holder, DGM and vacuum pump in place, and thus at realistic sampling pressure drops.

In the EK setup (Sampler 5) the vacuum pump preceded the DGM\* in the sampling train, so that the meter operated at essentially atmospheric pressure. This DGM was not, however, calibrated because no standard having appropriate capacity for the flowrate of the EK system was available. With the exception of Sampler 5 (EK, always run at full capacity of the pump), the sampling rates of all four samplers were individually adjusted at the start of each run, and the DGM inlet pressure measured. The flowrates and the inlet pressures were re-measured at the end of each sampling run.

### 2.3 Concentration calculations and data processing

The concentrations of "smoke", SO<sub>4</sub>, Pb, Mg and Ca were calculated for each of the sample filters from the reflectance measurements, the chemical analyses results, and from the DGM indicated sample volumes. The blank amount were then assumed to represent the interfering levels due to filter impurities, and were used to adjust the calculated concentrations. In calculating the concentrations of smoke, in µg/m<sup>3</sup>, the International Standard Calibration curve (4) was used for converting measured reflectance to gravimetric units.

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\* 10 L rev. <sup>-1</sup> model, Wilhelm Ritter KG, Bochum-Langendreer.

\*\* Model G4, Dehm & Zinkeisen GmbH, Dreieich b. Frankfurt a.M.

\*\*\* Model DOA-121-BG, Gast Mfg. Comp., Benton Harbor, MI.

The calculated values were then plotted for visual assessment of any differences between the measured "true" and SK-sampled concentrations. Student's t-tests were employed to ascertain if statistically significant differences in measured concentrations of the various components existed.

First, the equality of mean concentrations from Samplers 1 and 2, and then Samplers 3 and 4 was tested for each component (cf. Tables 6 and 7). Then, the t-test was performed on the differences between the average concentration values from Samplers 1 and 2 and Samplers 3 and 4 to test whether long-term averages are the same for both types of samplers (cf. Table 8). Finally, the concentration averages from the SK and "true" samplers were compared with the concentration values measured with the EK sampler, for the period the latter was run (cf. Tables 9 and 10).

If it is assumed that  $x(=y-z)$  is normally distributed with a mean  $\mu$ , then it follows that the statistic

$$t = \frac{\bar{x} - \mu}{\hat{s}} \sqrt{N}$$

is Student's t-distributed with  $N-1$  degrees of freedom.

$y$  and  $z$  = observed concentrations or mean concentrations from identical samplers.

$\bar{x}$  = arithmetic mean of the  $x$ 's for all runs for a given component

$\hat{s}$  = estimated standard deviation of the  $x$ 's

$N$  = number of sampling runs for a given component

The null-hypothesis is:

$H_0$ : there is no difference between  $y$  and  $z$ , i.e.,  $\mu = 0$ .

From this it follows that

$$t = \frac{\bar{x}}{\hat{s}} \sqrt{N}$$

and  $H_0$  is accepted, at a chosen confidence level, if:

$$|t| = \left| \frac{\bar{x}}{\hat{s}} \sqrt{N'} \right| < t_c,$$

where:

$t_c$  = confidence coefficient obtained from Student's t-distribution with N-1 degrees of freedom.

### 3 DATA AND RESULTS

The calculated concentration data are presented in Tables 1-5 and Figures 2-6. The results of the statistical tests are shown in Tables 7-10.

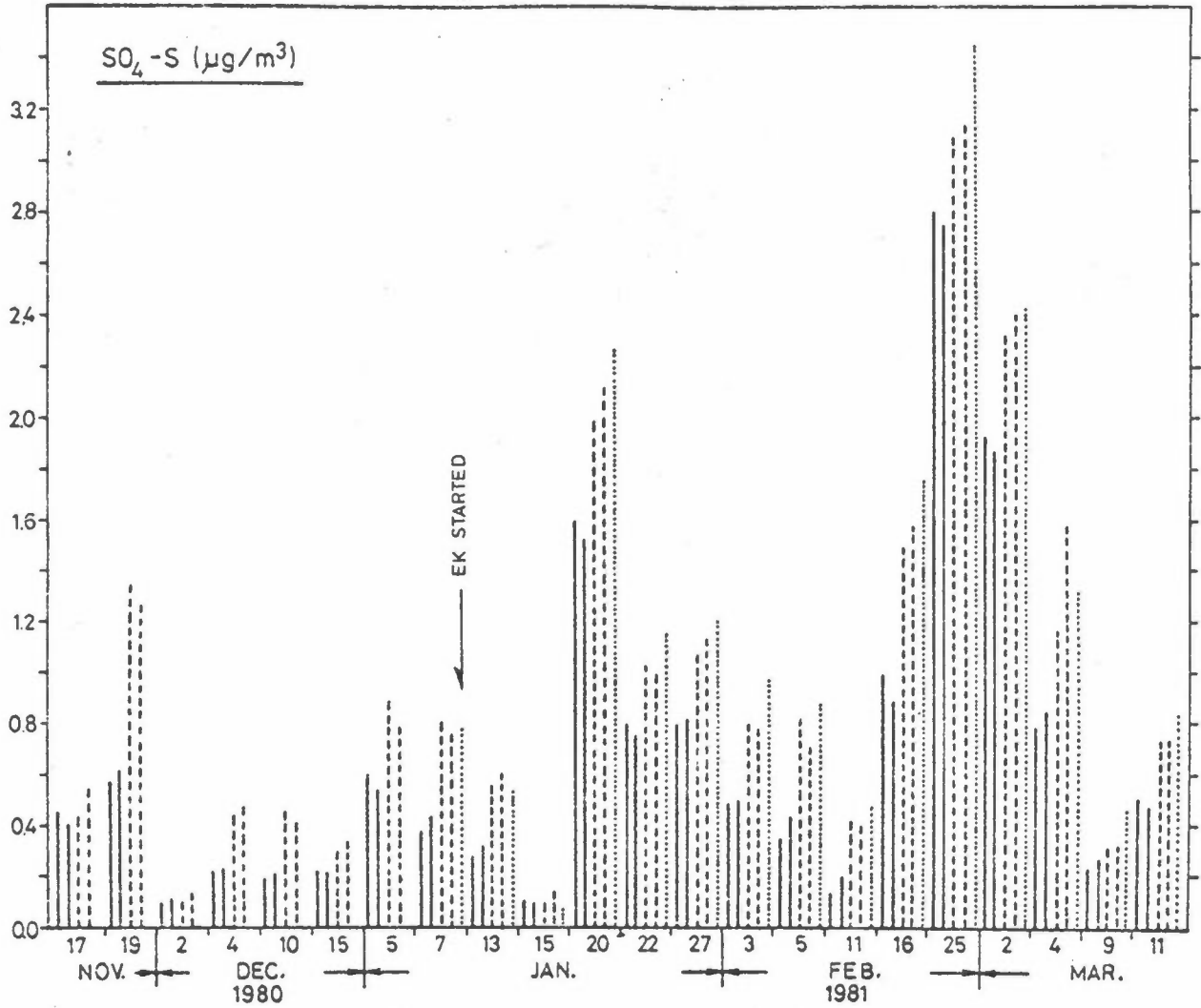


Figure 2: Sulphate (SO<sub>4</sub>-S) concentrations, in µg m<sup>-3</sup>, as measured by the five samplers on alternate sampling days.

- SK 1 and 2
- - - "True" 3 and 4
- .... EK

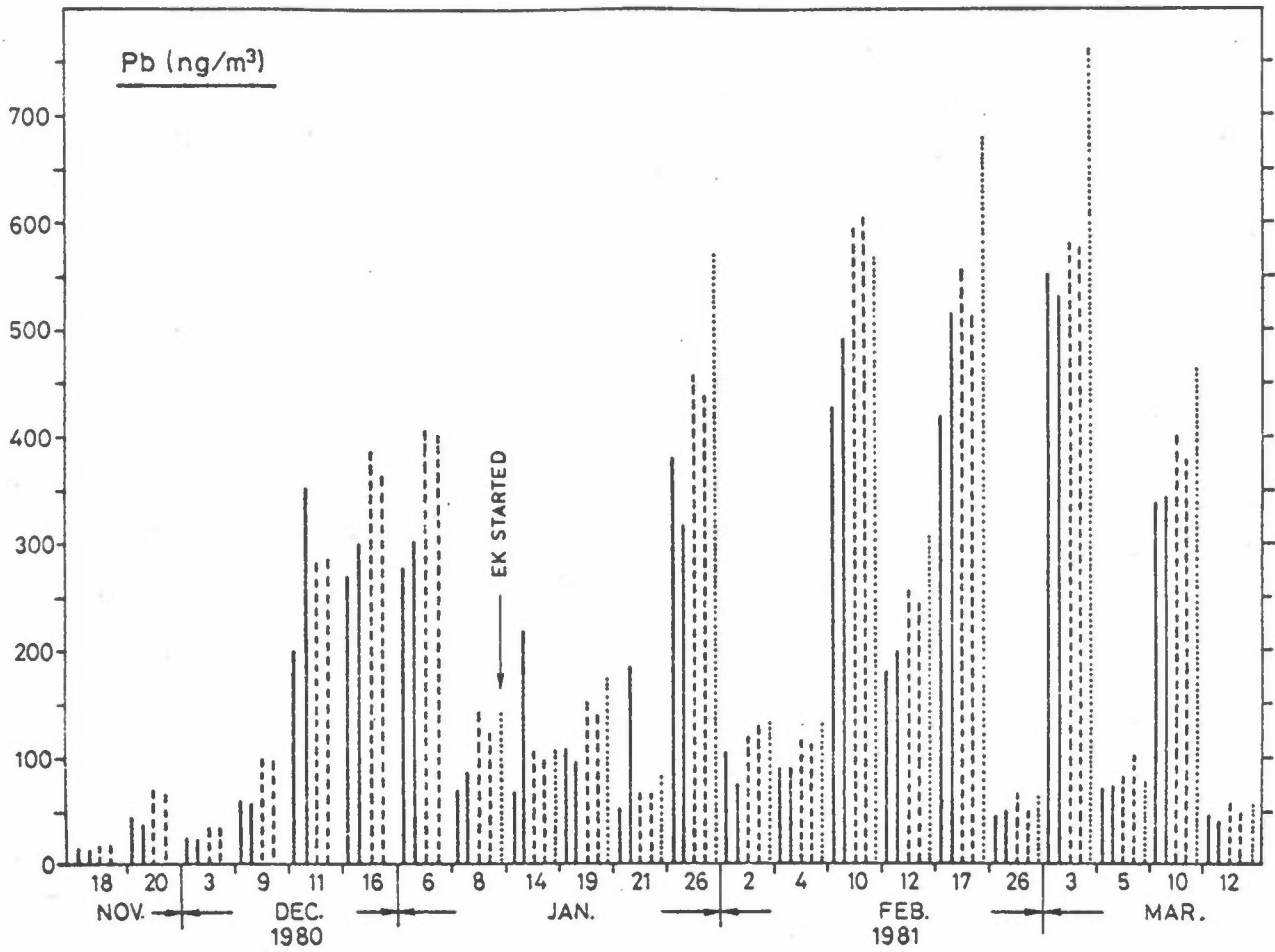


Figure 3: Lead (Pb) concentrations, in  $\text{ng m}^{-3}$ , as measured by the five samplers on alternate sampling days.

- SK 1 and 2
- - - "True" 3 and 4
- .... EK

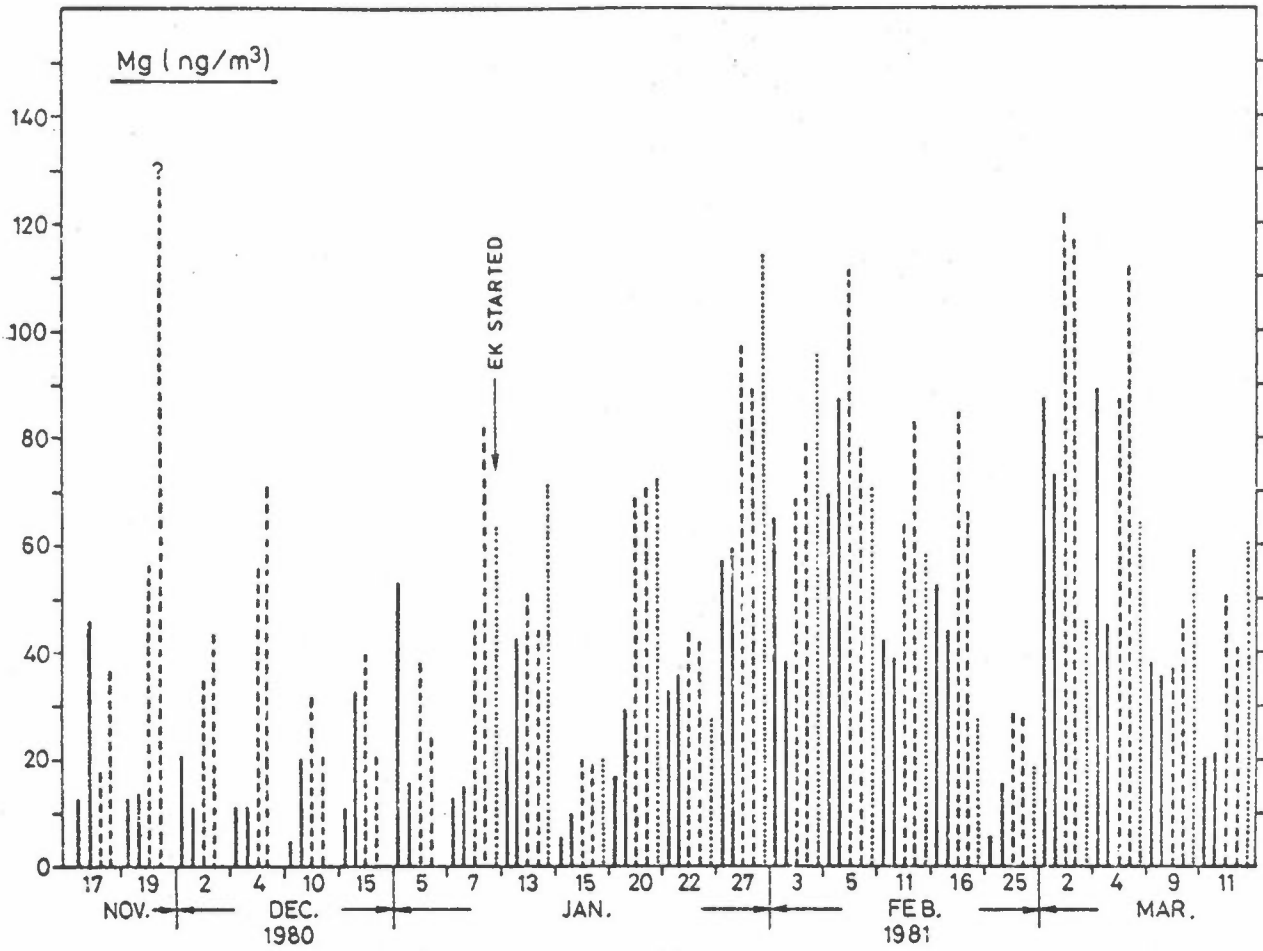


Figure 4: Magnesium (Mg) concentrations, in  $\text{ng m}^{-3}$ , as measured by the five samplers on alternate sampling days.

- SK 1 and 2
- - - "True" 3 and 4
- .... EK

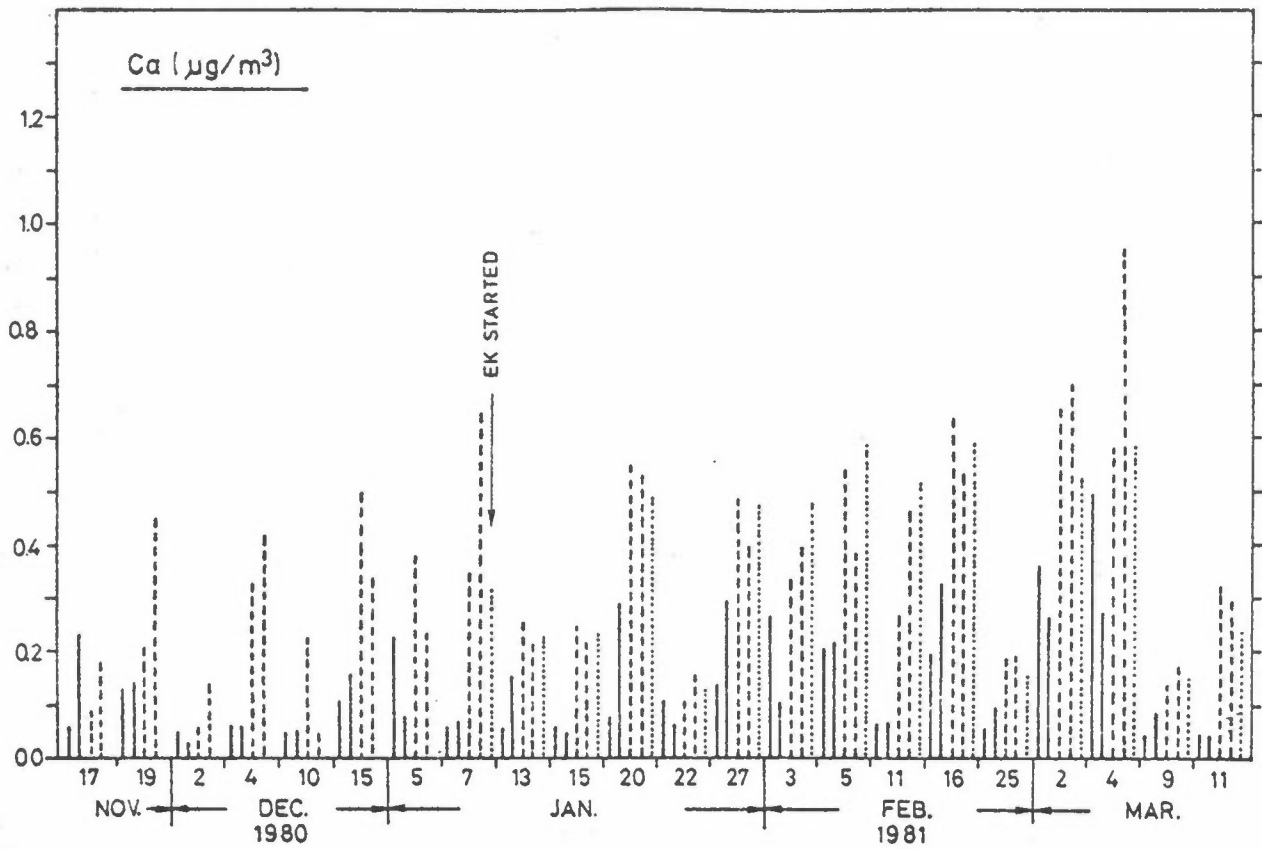


Figure 5: Calcium (Ca) concentrations, in  $\mu\text{g m}^{-3}$ , as measured by the five samplers on alternate sampling days.

- SK 1 and 2
- - - "True" 3 and 4
- .... EK

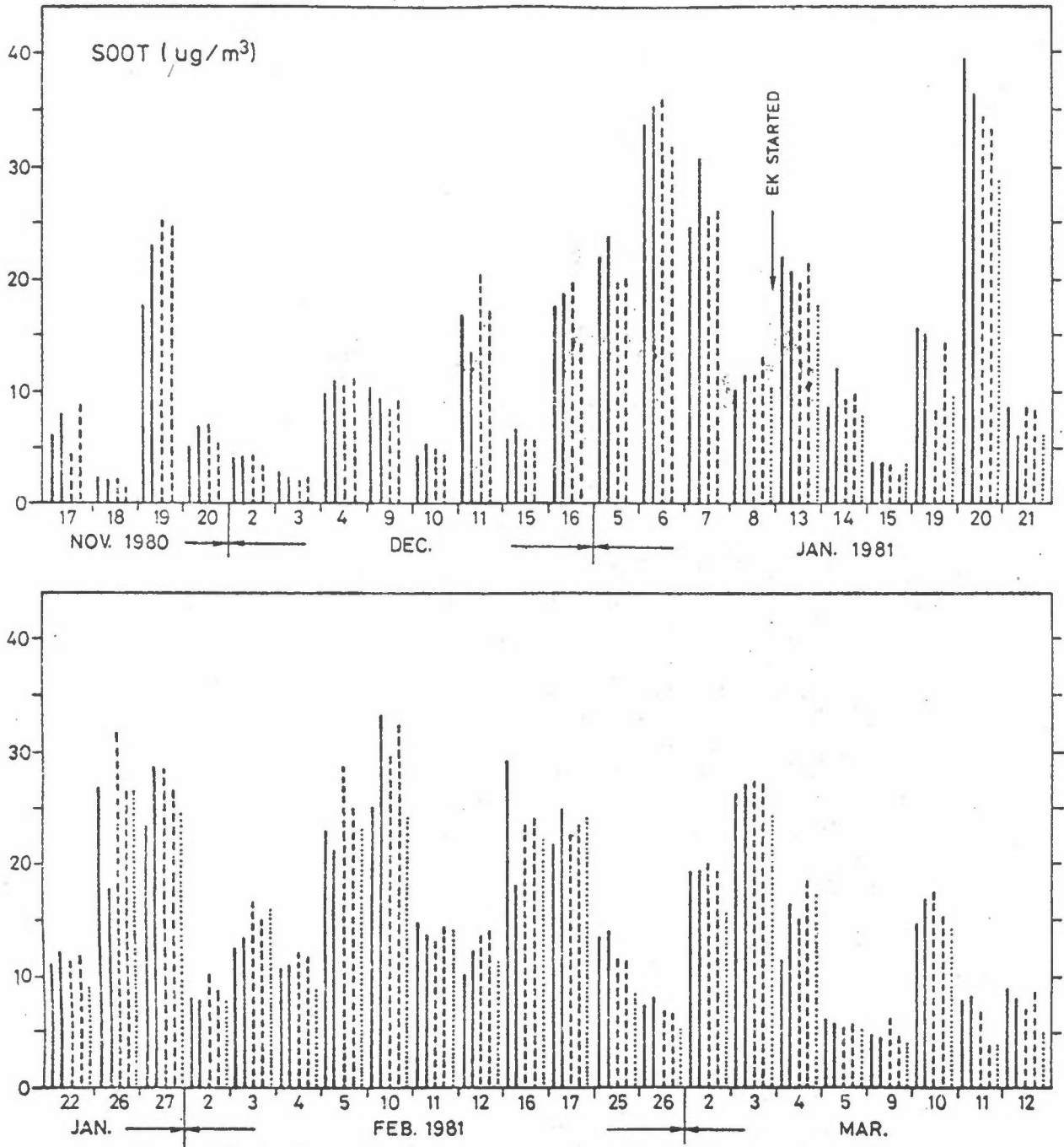


Figure 6: Soot concentrations, in  $\mu\text{g m}^{-3}$  (by the reflectance method), as measured by the five samplers.

- SK 1 and 2
- - - "True" 3 and 4
- .... EK



Table 1: Airborne water-soluble sulphate ( $SO_4-S$ ) concentrations (in  $\mu g m^{-3}$ ), as measured simultaneously at NILU, November 1980 - March 1981.

Run No.	Date	Sampler number*				
		1	2	3	4	5
		$SO_4-S$ concentration, $\mu g m^{-3}$				
1	17-18.11.80	0.45	0.40	0.44	0.65	(-)
3	19-20.11.80	0.57+	0.62	1.34	1.27	(-)
5	2-3.13.80	0.10	0.11	0.12	0.14	(-)
7	4-5.12.80	0.23	0.23	0.45	0.47	(-)
9	10-11.12.80	0.19	0.21	0.46	0.41	(-)
11	15-16.12.80	0.22	0.22	0.30	0.34	(-)
13	5-6.1.81	0.60	0.54	0.89	0.79	(-)
15	7-8.1.81	0.38	0.44	0.81	0.76	0.78
17	13-14.1.81	0.28	0.32	0.56	0.61	0.53
19	15-16.1.81	0.11	0.10	0.10	0.14	0.08
21	20-21.1.81	1.60	1.53	1.99	2.12	2.27
23	22-23.1.81	0.81	0.76	1.04	1.00	1.16
25	27-28.1.81	0.79	0.82	1.08	1.14	1.22
27	3-4.2.81	0.49	0.50	0.80	0.79	0.98
29	5-6.2.81	0.35	0.44	0.83	0.71	0.88
31	11-12.2.81	0.14	0.20	0.42	0.41	0.48
33	16-17.2.81	0.99	0.89	1.49	1.58	1.76
35	25-26.2.81	2.80	2.75	3.08	3.14	3.45
37	2-3.3.81	1.93	1.87	2.33	2.40	2.43
39	4-5.3.81	0.79+	0.85	1.16	1.57	1.32
41	9-10.3.81	0.23	0.27	0.32	0.32	0.45
43	11-12.3.81	0.51	0.48	0.73	0.74+	0.85

\* cf. Figure 1

(-) sampler not operated

+ possible filter holder leakage

Table 2: Airborne lead (Pb), soluble in 1:1 HNO<sub>3</sub>, concentrations (in ng m<sup>-3</sup>) as measured simultaneously at NILU, Nov. 1980-March 1981.

Run No.	Date	Sampler number*				
		1	2	3	4	5
		Pb concentration, ng m <sup>-3</sup>				
2	18-19.11.80	16.6	15.0	21.3	21.6	(-)
4	20-21.11.80	45.1	39.5	70.7	66.2	(-)
6	3- 4.12.80	25.3	24.0	36.2	36.0	(-)
8	9-10.12.80	61.0	57.9	98.5	98.8	(-)
10	11-12.12.80	200	353	284	287	(-)
12	16-17.12.80	271	300	388	367	(-)
14	6- 7. 1.81	280	305	406	402	(-)
16	8- 9. 1.81	71.0	87.0	143	122	142
18	14-15. 1.81	67	220**	106	99.0	109
20	19-20. 1.81	110	97	153	141	175
22	21-22. 1.81	54.0	187**	67.0	66.0	84.0
24	26-27. 1.81	381	319	453	437	570
26	2- 3. 2.81	106	75.0	119	130	131
28	4- 4. 2.81	91.0	89.0	116	113	131
30	10-11. 2.81	430 <sup>+</sup>	490	596	605	568
32	12-13. 2.81	180	200	257	243	308
34	17-18. 2.81	420	516	557	515	679
36	26-27. 2.81	45.0	49.0	57.0	48.0	61.0
38	3- 4. 3.81	552	531	580	576	762
40	5- 6. 3.81	72.0	73.0	82.0	101	78.0
42	10-11. 3.81	339	343	399	376	463
44	12-13. 3.81	47.0	42.0	57.0	48.0	54.0

\* cf. Figure 1.

\*\* value excluded from statistical tests.

(-) sampler not operated

+ possible filter holder leakage

Table 3: Airborne water-soluble magnesium (Mg) concentrations (in  $\text{ng m}^{-3}$ ), as measured simultaneously at NILU Nov 1980-March 1981.

Run No.	Date	Sampler number*				
		1	2	3	4	5
		Mg concentration, $\text{ng m}^{-3}$				
1	17-18.11.80	12.9	45.8	17.4	35.3	(-)
3	19-20.11.80	12.7 <sup>+</sup>	13.8	56.3	12.7	(-)
5	2- 3.12.80	20.9	11.0	34.8	43.4	(-)
7	4- 5.12.80	11.5	11.5	55.7	71.2	(-)
9	10-11.12.80	4.8	20.5	36.9	20.7	(-)
11	15-16.12.80	11.0	32.5	39.6	28.9	(-)
13	5- 6. 1.81	52.8	15.4	38.0	24.2	(-)
15	7- 8. 1.81	12.8	14.8	46.1	82.1	63.0
17	13-14. 1.81	22.6	42.7	51.0	44.3	71.6
19	15-16. 1.81	5.3	9.9	19.8	19.0	19.5
21	20-21. 1.81	16.8	29.2	68.7	70.6	72.2
23	22-23. 1.81	32.4	35.1	43.8	42.1	27.7
25	27-28. 1.81	57.3	59.7	96.4	88.9	114
27	3- 4. 2.81	65.2	38.6	69.0	79.3	96.0
29	5- 6. 2.81	69.7	87.6	111	77.7	70.7
31	11-12. 2.81	42.3	39.1	63.8	82.4	58.2
33	16-17. 2.81	52.8	44.6	85.1	65.4	53.9
35	25-26. 2.81	6.0	15.7	28.4	28.1	18.9
37	2- 3. 3.81	87.2	73.6	112	117	46.0
39	4- 5. 3.81	89.1 <sup>+</sup>	45.6	87.2	112	64.7
41	9-10. 3.81	37.5	36.0	36.4	45.5	58.9
43	11-12. 3.81	20.3	21.3	50.1	41.0 <sup>+</sup>	60.6

\* cf. Figure 1.

(-) sampler not operated

+ possible filter holder leakage

Table 4: Airborne water-soluble (Ca) concentrations (in  $\mu\text{g m}^{-3}$ ) as measured simultaneously at NILU, Nov. 1980-March 1981.

Run No.	Date	Sampler number*				
		1	2	3	4	5
		Ca concentration, $\mu\text{g m}^{-3}$				
1	17-18.11.80	0.06	0.23	0.09	0.18	(-)
3	19-20.11.80	0.13 <sup>+</sup>	0.14	0.21	0.45	(-)
5	2- 3.12.80	0.05	0	0.06	0.14	(-)
7	4- 5.12.80	0.06	0.06	0.33	0.42	(-)
9	10-11.12.80	0.05	0.05	0.23	0.05	(-)
11	15-16.12.80	0.11	0.16	0.50	0.34	(-)
13	5- 6. 1.81	0.23	0.08	0.38	0.24	(-)
15	7- 8. 1.81	0.06	0.07	0.35	0.65	0.32
17	13-14. 1.81	0.06	0.16	0.26	0.22	0.23
19	15-16. 1.81	0.06	0.05	0.25	0.10	0.05
21	20-21. 1.81	0.08	0.29	0.55	0.53	0.49
23	22-23. 1.81	0.11	0.06	0.11	0.16	0.13
25	27-28. 1.81	0.14	0.30	0.48	0.40	0.48
27	3- 4. 2.81	0.27	0.11	0.34	0.40	0.39
29	5- 6. 2.81	0.21	0.22	0.55	0.39	0.59
31	11-12. 2.81	0.07	0.07	0.27	0.47	0.52
33	16-17. 2.81	0.20	0.33	0.64	0.54	0.59
35	25-26. 2.81	0.06	0.10	0.19	0.19	0.16
37	2- 3. 3.81	0.37	0.27	0.66	0.70	0.53
39	4- 5. 3.81	0.50 <sup>+</sup>	0.28	0.58	0.95	0.59
41	9-10. 3.81	0.05	0.09	0.14	0.18	0.15
43	11-12. 3.81	0.05	0.05	0.32	0.30 <sup>+</sup>	0.24

\* cf. Figure 1

(-) sampler not operated

+ possible filter holder leakage

Table 5: Airborne "smoke" concentrations (in  $\mu\text{g m}^{-3**}$ ), as measured simultaneously at NILU, Nov. 1980-March 1981.

Run No.	Date	Sampler number*				
		1	2	3	4	5
		"Smoke" concentration, $\mu\text{g m}^{-3**}$				
1	17-18.11.80	6.5	7.8	4.4	8.9	(-)
2	18-19.11.80	2.2	2.0	2.2	1.4	(-)
3	19-20.11.80	17.6 <sup>+</sup>	22.8	25.3	24.5	(-)
4	20-21.11.80	5.1	6.7	6.9	2.2	(-)
5	2- 3.12.80	3.7	3.9	4.1	3.4	(-)
6	3- 4.12.80	2.8	2.2	2.1	2.2	(-)
7	4- 5.12.80	9.6	10.7	10.4	11.1	(-)
8	9-10.12.80	10.2	9.3	8.4	9.1	(-)
9	10-11.12.80	4.2	5.2	4.7	2.2	(-)
10	11-12.12.80	16.7	13.4	20.2	17.0	(-)
11	15-16.12.80	5.7	6.5	5.7	5.6	(-)
12	16-17.12.80	17.4	18.6	19.5	14.2	(-)
13	5- 6. 1.81	21.8	23.7	19.6	19.9	(-)
14	6- 7. 1.81	33.6	35.2	35.9	31.8	(-)
15	7- 8. 1.81	24.6	30.6	25.5	26.0	25.3
16	8- 9. 1.81	10.1	11.4	11.4	13.0	10.1
17	13-14. 1.81	21.8	20.5	19.6	21.3	17.6
18	14-15. 1.81	8.5	11.9	9.3	9.7	7.8
19	15-16. 1.81	3.7	3.6	3.5	2.6	3.4
20	19-20. 1.81	15.6	15.3	8.3	14.3	9.6
21	20-21. 1.81	39.5	36.5	34.4	33.2	28.8
22	21-22. 1.81	8.7	6.1	8.5	8.4	6.0
23	22-23. 1.81	11.2	12.1	11.4	12.0	9.2
24	26-27. 1.81	26.8	17.9	31.8	26.5	26.5
25	27-28. 1.81	23.6	28.7	28.3	26.3	24.5
26	2- 3. 2.81	8.3	8.1	10.1	9.0	7.6
27	3- 4. 2.81	12.4	13.4	16.6	15.0	16.0
28	4- 5. 2.81	10.6	10.9	12.0	11.7	8.5
29	5- 6. 2.81	22.9 <sup>+</sup>	21.1	28.7	24.9	22.9
30	10-11. 2.81	24.8 <sup>+</sup>	33.0	29.5	32.2	24.1
31	11-12. 2.81	14.6	13.5	12.9	14.3	14.0
32	12-13. 2.81	10.0	12.1	13.5	14.0	11.3
33	16-17. 2.81	29.2	18.3	23.6	24.1	22.2
34	17-18. 2.81	21.7	24.8	22.6	23.4	24.1
35	25-26. 2.81	13.5	13.9	11.5	11.4	8.4
36	26-27. 2.81	7.3	7.8	6.8	6.7	5.3
37	2- 3. 3.81	19.2	19.3	19.9	19.2	15.4
38	3- 4. 3.81	26.0 <sup>+</sup>	26.7	27.3	27.1	24.1
39	4- 5. 3.81	11.3 <sup>+</sup>	16.4	14.9	18.4	17.2
40	5- 6. 3.81	6.2	5.8	5.4	5.6	5.2
41	9-10. 3.81	4.7	4.5	6.2	4.6	3.9
42	10-11. 3.81	14.7	16.7	17.4	15.3 <sup>+</sup>	14.3
43	11-12. 3.81	7.7	8.1	6.9	3.8 <sup>+</sup>	5.0
44	12-13. 3.81	8.8	8.0	7.0	8.5	4.9

\* cf. Figure 1  
 \*\* from reflectance measurements (4)  
 (-) sampler not operated  
 + possible filter holder leakage

Table 6: Statistics for concentration differences between the two SK samplers (Samplers 1 and 2).

Component	$\bar{x}$	$\hat{s}$	t	$t_c$ at 95%
SO <sub>4</sub> -S	0.00045	0.051	0.041	2.080*
Pb	- 13.1	45.0	1.30	2.093**
Mg	0.0046	18.1	0.0012	2.080*
Ca	-0.0077	0.10	0.35	2.080*
Smoke	-0.45	3.2	0.93	2.020***

\*N = 22; \*\*N = 20; \*\*\*N = 44.

Table 7: Statistics for concentration differences between the two "true" samplers (Samplers 3 and 4).

Component	$\bar{x}$	$\hat{s}$	t	$t_c$ at 95%
SO <sub>4</sub> -S	-0.03	0.10	1.44	2.080
Pb	7.0	13.4	2.34	2.093
Mg	1.21	18.1	0.31	2.080
Ca	-0.023	0.15	0.72	2.080
Smoke	0.29	2.2	0.86	2.020

N: As in Table 6.

Table 8: Statistics for averaged concentration difference between the SK samplers (Samplers 1 and 2) and the "true" samplers (Samplers 3 and 4), as explained in text.

Component	$\bar{x}$	$\hat{s}$	t	$t_c$ at 95%
SO <sub>4</sub> -S	-0.3	0.2	7.7	2.080
Pb	-44	36	5.6	2.093
Mg	-23	15	7.1	2.080
Ca	0.21	0.12	8.3	2.080
Smoke	-0.3	2.1	0.9	2.020

N: As in Table 6.

Table 9: Statistics for concentration differences between the average of the two SK samplers (Samplers 1 and 2) and the EK sampler (Sampler 5).

Component	$\bar{x}$	$\hat{s}$	t	$t_c$ at 95%
SO <sub>4</sub> -S	-0.43	0.21	8.0	2.145*
Pb	-95	76	4.5	2.179**
Mg	-19	25	3.0	2.145
Ca	-0.20	0.12	6.5	2.145

\*N = 15; \*\*N = 13.

Table 10: Statistics for concentration differences between the average of the two "true" samplers (Samplers 3 and 4) and the EK sampler (Sampler 5).

Component	$\bar{x}$	$\hat{s}$	t	$t_c$ at 95%
SO <sub>4</sub> -S	-0.10	0.11	3.5	2.145
Pb	-46	64	2.6	2.179
Mg	6.1	25	0.93	2.145
Ca	0.031	0.098	1.23	2.145

N: As in Table 9.

#### 4 DISCUSSION OF RESULTS

Visual examination of Figures 2-6 alone reveals differences between the concentrations of the various components measured simultaneously by the three types of samplers. Indeed, for a given run there are differences in the pairs of values from each type of sampler noticeable. The latter are more pronounced for the "coarse" elements Mg and Ca. The results of Student's t-tests, in Tables 6 and 7, show, however, that despite this occasional variability the long-term averages (i.e., the arithmetic means for the entire study period in Table 11) for the components from the SK samplers and for the "true" samplers can be considered "the same" (t values <  $t_c$  at

Table 11: Mean concentrations of the various aerosol components, as measured simultaneously at NILU, November 1980 - March 1981.

Components	Units	Sampling period	Sampler number														
			1		2		3		4		5						
			$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s					
SO <sub>4</sub> -S	μgm <sup>-3</sup> "	17.11.80-12.03.81	0.66	0.65	0.66	0.63	0.94	0.72	0.98	0.75	(-)	(-)	(-)	(-)			
		07.01.81-12.03.81	0.81	0.73	0.81	0.70	1.12	0.78	1.16	0.80	1.24	0.87					
Pb	ngm <sup>-3</sup> "	18.11.80-12.03.81	166	146	191	173	229	199	223	185	(-)	(-)	(-)	(-)			
		08.01.81-13.03.81	198	169	224	183	249	202	241	196	296	248					
Mg	ngm <sup>-3</sup> "	17.11.80-12.03.81	34	26	34	20	57	27	56	29	(-)	(-)	(-)	(-)			
		07.01.81-12.03.81	41	27	40	21	65	28	66	28	61	26					
Ca	μgm <sup>-3</sup> "	17.11.80-12.03.81	0.14	0.12	0.14	0.10	0.34	0.18	0.36	0.21	(-)	(-)	(-)	(-)			
		07.01.81-12.03.81	0.15	0.13	0.17	0.10	0.37	0.18	0.41	0.23	0.36	0.18					
"Smoke"	μgm <sup>-3</sup> "	17.11.80-13.03.81	14.2	8.8	14.7	9.0	14.9	9.4	14.5	9.0	(-)	(-)	(-)	(-)			
		07.01.81-13.03.81	15.6	8.5	15.9	8.6	16.2	8.8	16.1	8.5	14.1	7.9					

(-) sampler not operated

$\bar{X}$  = arithmetic mean concentration for the period

s = estimated standard deviation of concentration



95% confidence level). One possible exception is the average value from the "true" samplers for Pb.

All calculated t values for the SK vs "true" comparisons in Table 8 indicate significant differences in the measured mean concentrations of all components (t values > t<sub>c</sub> at both 95% and 99% significance levels), with the exception of smoke. The two samplers SK (with filters mounted in-line after a sampling line and manifold) and "true" (open-face filter holder mounted outside) thus seem to be equivalent as far as the determination of smoke by the reflectance method is concerned (5,6).

A comparison of the arithmetic means of the average concentrations over the test period from the SK and the "true" measurements show that the SK samplers collected consistently only a fraction of the amount sampled by the "true" samplers, with the exception of smoke. If the calculated fractions for each run are considered as independent realizations from a normal distribution, with unknown mean and variance, then the confidence limits of the mean value of the fraction for each of the measured components can be estimated.

The confidence interval, at a given confidence level, is:

$$\bar{X} \pm \frac{t_c s}{\sqrt{N-1}}$$

where:

$\bar{X}$  = the estimated fractional collection, e.g., in %,

s = the estimated standard deviation, e.g., in %,

N = number of samples,

t<sub>c</sub> = the confidence coefficient for Student's t distribution, with N-1 degrees of freedom

At the 95% level, the estimated confidence intervals (in %) of the various components, collected by the SK samplers relative to the "true" samplers, are:

SO<sub>4</sub>-S : 66.0 ± 6.7%  
Pb : 77.2 ± 4.9%  
Mg : 59.7 ± 11.2%  
Ca : 42.3 ± 8.8%

From the above, it is clear that there can be substantial line losses for the SK system, which appear to vary with particle size - assuming that other influences (e.g., wind speed fluctuations) are the same for both types of samplers. Thus, Pb (for which car exhaust in the NILU parking lot was at least a partial source), probably contained in the finer particles, has the lowest line losses, while Ca (a soil-derived element) has the highest. Mg (expected to be mainly of marine origin) is lost to a lesser extent than Ca, perhaps, because the largest of the sea salt particles are lost in transport from their salt-water sources in the area. Because of such possible fractionation, the extent of line losses for "wet" vs "dry" coarse particles could not be assessed.

It is interesting to note that there is no systematic difference apparent in the smoke measurements by the two types of samplers. The smoke determinations give an indication of the concentration of black particles (soot) in the air. These are mostly generated by combustion processes. In an urban atmosphere the soot particles are mainly submicron. Heintzenberg (7) reports mass mean diameters in the vicinity of 0.2 μm from measurements in Stockholm. Thus, they are generally larger than Pb particles (0.05-0.1 μm) and probably smaller than the sulphate particles (~0.5 μm). It would be interesting to study whether the particle diameter differences can account for the fact that soot particles do not seem to experience loss in the sampling line, while sulphate and lead particles do.

The results of Student's t-tests for the averaged SK and "true" samplers vs the EK sampler are shown in Tables 9 and 10. Because of the much higher flowrate than recommended for smoke sampling, EK-measured smoke concentrations are not included. At the 95% confidence level, the SK concentrations of the various components

are significantly different from those measured by the EK sampler (cf. Table 9). The average "true" values for SO<sub>4</sub>-S and Pb are also different, while Mg and Ca are not (cf. Table 10).

The corresponding confidence intervals (in %) for the fractions collected by the SK and "true" samplers, relative to the EK sampler, are:

	SK	"True"
SO <sub>4</sub> -S	64.7 ±22.6%	107.9 ± 9.1%
Pb	71.2 ±10.3%	113.0 ± 8.4%
Mg	71.4 ±40.3%	96.2 ±18.7%
Ca	47.7 ±20.7%	90.8 ±25.3%

In the light of the findings from the SK and "true" comparisons above, undersampling by the SK samplers was to be expected, but the apparent undersampling of the coarser Ca-containing particles by the EK sampler is surprising. Although of the same diameter, the inlet of the EK sampler has about 5 times higher intake velocity than the "true" (and SK) sampler, which should result in a more efficient collection of the aerodynamically coarser particles (8). Similarly the reason for the slight oversampling of the fine SO<sub>4</sub>- and Pb-containing particles by the EK sampler is not clear, although such behaviour has been observed with other types of sampler inlet at high wind speeds (9).

The sampling effectiveness of vertical elutriator type inlets, used by all three sampling systems in this study, is known to suffer from wind speed variations (5). All sampling inlets (except for EK) were quite closely spaced, so that wind effects (if any) should have been similar. The placement of the inlets near the penthouse wall, however, undoubtedly exposed them to unpredictable turbulence conditions. An examination of the pairs of concentration values from each run for the "near-the-wall" (SK 2 and "true" 3) and "away-from-the-wall" (SK 1 and "true" 4) inlets failed to point to any consistent bias in the measured concentrations.

5 CONCLUSIONS

- (a) The SK aerosol sampler undersamples ambient aerosols, due to unavoidable sampling line losses;
- (b) the extent of aerosol loss from the sample appears to be particle size related, and can exceed 50% for the coarse fraction particles;
- (c) sampling systems which expose the aerosol collection substrate directly to the sampled air stream are to be preferred, but require relatively wind speed-independent inlets for representative sampling;
- (d) For the measurements of smoke by the reflectance method, which is correlated to the concentration of carbonaceous particles in the air, the SK sampler seem to be equivalent to the "true" sampler.

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