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AN ANALYSIS OF HELSINKI AIR 1962 TO 1977 BASED ON TRACE METALS AND RADIONUCLIDES

by

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Abstract

High average concentrations of lead (0.5 $\mu g/m^3$) and cadmium (2 ng/m^3) were typical of the air in central Helsinki throughout the '60s, but after 1970 they decreased to around 0.15 $\mu g/m^3$ for lead and 0.4 ng/m^3 for cadmium in 1977. The earlier lead and cadmium values were most likely due mainly to small on-site refuse incinerators, which numbered 1300 or so in 1967 but fell to about a tenth of that figure by 1973. Significant amounts of lead came from lead smelters in Tikkurila, 15 km NNE of central Helsinki. Since 1970, lead from origins other than motor traffic has gradually decreased in quantity.

The concentrations of ^{212}Pb during winter were much higher in urban than in rural areas. This is evidently due to ventilation of buildings. The wind direction pattern of stable lead was found to approach that for ^{212}Pb when vehicular exhaust became the main source of lead in the later '70s.

Other observed mean concentrations: Cu:70, Zn:172, Br:49, and Sb:6, all ng/m^3. Antimony decreased in the '70s, the other three displayed no trends.

Concentrations of suspended particulates in central Helsinki have diminished greatly since 1970. The yearly average observed on the roof of the Meteorological Institute in central Helsinki 21 m above street level, was 39 $\mu g/m^3$ in 1977, compared to 65 $\mu g/m^3$ in 1970. Besides the decreasing number of on-site incinerators, the steady changeover to district heating has

evidently been a primary factor in this healthy development. The situation in 1977, therefore, was such that, often during southerly winds, incoming air already contained quantities of particulates and smoke as large as those added by its passage over central Helsinki. But being on low ground almost surrounded by water, Helsinki is also vulnerable to pollution from local emissions. Due to the stabilizing effect of the cold sea surface during the summer months the difference between winter and summer in air concentrations of copper, lead, suspended particles, etc., is small.

1. *Introduction*

In 1970 we determined lead concentrations in the air on the roof of the Meteorological Institute in Helsinki during different wind directions. After supplementary measurements of lead in snow samples at ten sites in and around Helsinki, and analyses of fly-ash samples from trash incinerators, we concluded that, besides motor traffic, the lead contents of the air were due to lead smelters 15 km north of Helsinki, and to trash burning in the urban area (MATTSSON & JAAKKOLA 1970).

As our results seemed to bear no relation to subsequent measurements made by the air-pollution authorities, we were especially pleased when the Nessling Foundation granted us funds in 1977 to expand our original one-year project to cover the period from 1970 to 1977 and to add new components.

As will be seen below, these new measurements, especially those for 1974 to 1977, gave an interesting picture of the changes in lead pollution in Helsinki. By 1977 the general level had decreased and we found no abnormally concentration in any wind direction.

We remeasured a number of air filters used in the 1970 project. Originally we had wet-ashed a half of each filter; now we used up another quarter. The new Pb determinations confirmed our earlier results so it seemed that a rapid change in lead concentration had taken place since 1970.

As a third stage, in 1978 we wet-ashed and analyzed a quarter of every weekly air filter exposed in 1962, 1963, 1964, 1967, 1970, 1973 and 1977. This gave an even clearer picture of the development of air pollution. The components analyzed now were Pb, Cd and Cu. It became apparent that both Pb and Cd were actually decreasing at the beginning of the '70s.

The main object of the present study is therefore to seek possible explanations for the conspicuous features of the partly intercorrelated lead and cadmium concentrations in the air, especially during the '60s.

In addition to the above projects, the cadmium contents of weekly air filters from five rural stations were determined for the winter season of 1976/77. This period was selected mainly owing to observations of high concentrations of cadmium in the

snow cover at six sampling stations in Western Finland. These findings, which our measurements failed to support, were made by the National Water Board in 1977. Nevertheless our measurements at the rural stations provided useful background information for the study in the Helsinki area.

We also studied air reaching Helsinki from the Gulf of Finland. During warm southerly winds the lowest air layer is stabilized by the cold seasurface, providing ideal conditions for low-level transport of air pollution. For further information we placed an extra air sampler on Harakka, a small island immediately south of central Helsinki. Parallel sampling here revealed that the air arriving from the open sea is not very clean. Sometimes it contains more TSP (total suspended particulates) than the air 40 km inland.

In Chapter 7 we report on the use of some natural and artificial atmospheric radionuclides, which can be measured with higher precision than many of the pollutants studied here. These radioactive tracers, which come either from the surface of the earth or from stratospheric heights, offer valuable information on the origin and stability conditions of the air mass under observation. As determinations of radioactive nuclides were made both from the original intact air filters and from the final solution, the radioactive tracers also served a useful function as a check on the reliability of the sampling and wet-ashing methods.

2. *Earlier Observations and Questions Arising from them*

As typical values for 1961, LAAMANEN [11] presents the following metal concentrations at street level, at a point with heavy traffic near the Helsinki Railway Terminus: Cu:40, Mn:40...50, Ni:not detectable, Zn:210...220, and Pb:60...70, all in ng/m^3.

Ten years later in 1971–72 LAAMANEN [12] measured the following daily averages at the same site: Cu:45, Ni:50, Zn:150, and Pb:1260 ng/m^3. Except for the low Pb value of 1961, which was evidently erroneous, these values do not much differ from average values in the vast majority of other cities. WARK and WARNER [20] mention the following average concentrations obtained from biweekly (*sic*) samplings at 300 urban stations in the U.S.A. between 1960 and 1965: Cu:90, Mn:100, Ni:34, Zn:670, and Pb 790 ng/m^3. In the same study the mean values were 105 μg/m^3 for total suspended particulates (TSP), 2 ng/m^3 for Cd, and 1 ng/m^3 for Sb. These components are mentioned as they are of interest in the present study.

DEMUYNCK *et al.* [5] report the following highest observed daily mean concentrations in Ghent, Belgium, during a period of unusually high particulate levels in

September 1972: Pb 3010, Cd: 22, Cu: 200, Mn: 460, Ni: 120, Zn: 1018, Sb: 88 ng/m^3, and TSP: 366 μg/m^3. The particulates were sampled on the roof of the Institute of Nuclear Science, 5 km south of the center of Ghent. 80 μg/m^3 was reported as the normal level TSP, i.e. the increase during the stagnant anticyclonic conditions in question was roughly five-fold. The TSP and the metal concentrations under normal conditions did not differ much from the U.S.A. averages mentioned above.

The Helsinki data given above were largely confined to ground-level sampling close to motor traffic. Thus they reflect the pattern of exhausts and rising dust in the immediate vicinity of the sampler and are not specific for a larger area; the same pattern can be found in any city.

But in LAAMANEN's [12] study, which includes a comprehensive review of all observations made in Helsinki up to 1972, our interest was caught by a comparison between the data from the heavy-traffic station area mentioned above, and a much quieter sampling point in Pohjois-Haaga 6 km NNW of it. At this point 8 of the 19 components determined were of equal of higher average concentrations i.e. Cu, Fe, Cr, Ti, K, Rb, P, and Si. The two-year average Pb concentration was also conspicuously high, 960 ng/m^3, but even more so was the minimum of the daily averages, which was 600 ng/m^3 compared to 530 at the Railway Station site. At both sites the Br concentrations varied in the ratio of 1:50 whereas Pb varied as 1:5, which seemed to indicate lead originating from sources other than motor traffic.

ASIKAINEN and BLOMQVIST [1] found high concentrations of lead in the air 1 km NW of Helsinki-Vantaa Airport in January and February 1969. The air filters, covering 3 to 5 days, yielded average concentrations of around 4 μg/m^3 when the wind had been blowing from the direction of lead smelters at Tikkurila 3,5 to 4 km SE of the airport.

In a study for 1970 we found that lead from the smelters could clearly be observed in central Helsinki as could be anticipated from Asikainen and Blomqvist's measurements (MATTSSON and JAAKKOLA, [13]).

We also found high lead concentrations in incinerator fly ash and we concluded that incinerators should be considered seriously in combatting lead pollution. In the case of the high lead level at Pohjois-Haaga air, for instance, a district incinerator lying less than 1 km from the sampling site and two large smelters within 10 km had to be taken as potential sources in addition to traffic. The incinerator would also explain the high concentrations of the other components, Cu, Fe, Cr, etc., mentioned above.

3. *Collection and Storage of Aerosol Samples*

Exception in 1977, all the aerosol samples used in the present study were air filters originally collected for the purpose of measuring artificial and natural radionuclides in the air and subsequently stored in the basement of the Meteorological Institute.

After assessment of its radioactivity, each filter had been inserted in a folder of thin paper. Some 30 folders were packed in a paper envelope, and 10 to 20 envelopes were stored in a heavy cardboard box.

In 1977 a half of each air filter for the days in which we were interested was wet-ashed and analyzed immediately. The other half was used for non-destructive measurements of radioactivity and then stored. In 1977 we also established a new sampling station on the island of Harakka, directly south of central Helsinki. Figures 1 and 12 and the lower part of Fig. 13 show the location and surroundings of this new temporary station.

The aerosol collectors and sampling location of these old air filters from Helsinki, Nurmijärvi and Sodankylä are described elsewhere (MATTSSON [14]).

The collection period for the daily samples was from 8^h on the date indicated to 8^h the next day. Weekly samples were mostly collected between 8^h on Monday and 8^h the following Monday. In Table 2 the weekly samples are indicated by the date of last full day, which was usually a Sunday.

For the daily sampling we used Whatman GF/A glass-fibre filters, and for the weekly sampling Whatman grade 42 paper-fibre filters.

The collection site for the weekly samples from Helsinki before 1967 was Hämeentie 31 (Fig. 9).

The main collection site in Helsinki Kaisaniemi: The principal conclusions in the present study are closely connected with the location of our main aerosol sampler on the roof of the Meteorological Institute in Kaisaniemi (Fig. 2). This site therefore calls for a detailed description:

The distance to the nearest major traffic route is 150 m to the SE. Two hundred metres away to the ESE a small local oil-heating system was in use till summer 1975. The railway station yard lies 300...400 m to the SW. Since 1969 electric trains have gradually superseded diesel trains, especially in local traffic.

The main industrial area is 2 to 10 km north-east of the sampler and the nearest stack, belonging to Helsinki's biggest power station, which is coal-fired, lies NE at a distance of 1600 m. Another smaller industrial area lies about 3 km to the south-west.

The distribution of total suspended particulates (TSP) by wind direction (Fig. 3)

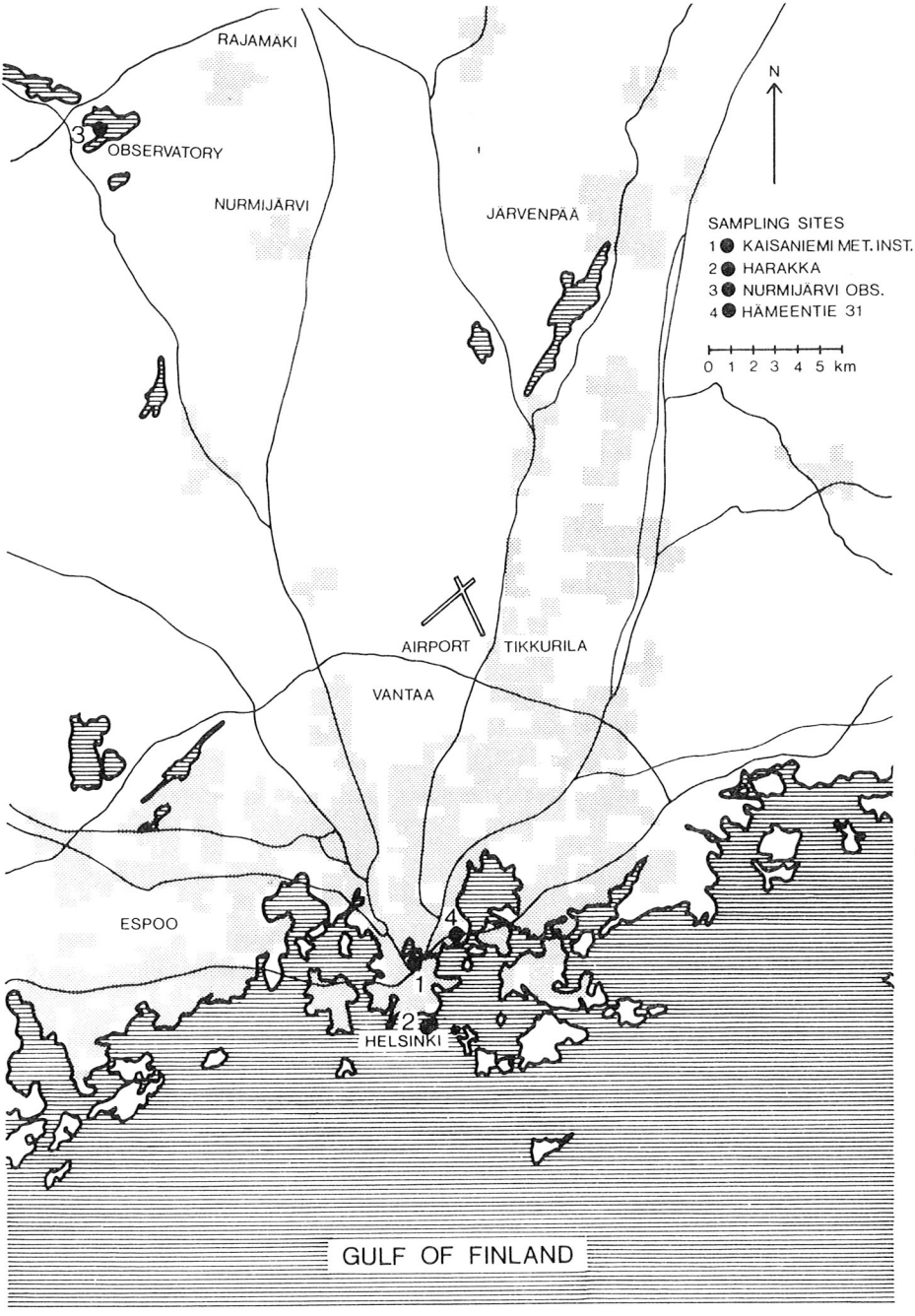

Fig. 1. Sampling points in Helsinki (1, 2, and 4) and Nurmijärvi (3).

Table 1. Determinations by AAS (atomic absorbtion spectrophotometry) of Pb, Cu, Cd, Mn, and Ni in daily aerosol samples, 1969...1977. The Helsinki samples were selected, basing on original wind recording graphs, to include only days when the wind had been blowing from a single direction (±45°) during the 24-hour period in question. For 1969 and 1970, however, the samples were chosen to verify results in an earlier publication (MATTSSON and JAAKKOLA [13]). The sampling period was 8^h on the date noted to 8^h the following day. The table contains all the determinations made for the present study.

SAMPLE DATE	LOCATION	TSP	METAL CONCENTRATION (ng/m³)					WIND
		μg/m³	Pb	Cu	Cd	Mn	Ni	DIRECTION
1969 Aug 6,	Helsinki		317	55	0.4	75	18	60°
» » 7,	»		242	24	0.2	259	13	45
» » 13,	»		187	42	0.5	71	12	270
» » 14,	»		208	66	0.2	101	11	60
» Sep 23,	»		107	21	ND	25	22	315
» » 25,	»		289	45	1.2	44	22	315
» Dec 12,	»		1470	30	1.2	–	–	–
» » 22,	»		1420	49	3.4	–	–	–
1970 Jan 12,	Helsinki	130	318	21	2.1	–	–	70°
» » 22,	»	79	307	25	3.5	–	–	–
» » 29,	»	244	891	81	2.5	–	–	–
» Feb 12,	»	209	1070	34	2.5	–	–	–
» » 17,	»	185	1530	32	2.2	–	–	–
» » 18,	»	265	2550	76	4.2	–	–	–
» Apr 9,	»	159	3460	186	10.3	–	–	30
» Jun 8,	»	37	227	67	0.4	–	–	105
1971 Jan 28,	Helsinki		260	99	6.5	37	31	30°
» Feb 15,	»		154	23	0.9	41	119	100
» » 17,	»		130	27	2.0	73	63	110
» » 18,	»		60	16	0.6	37	90	125
» Mar 1,	»		92	14	1.2	26	21	70
» » 3,	»		136	19	0.3	38	23	45
» » 4,	»		131	42	2.5	37	29	45
» » 11,	»		125	22	0.2	29	39	330
» Apr 6,	»		80	20	0.3	38	35	90
» » 13,	»		47	6	ND	19	26	330
» » 14,	»		142	12	1.9	27	22	350
» » 16,	»		278	90	1.5	57	88	130
» » 19,	»		186	30	0.8	31	29	225
» » 22,	»		429	30	4.6	48	18	10
» May 25,	»		88	18	0.3	27	28	90
» » 31,	»		233	46	1.0	46	34	90
» Jun 1,	»		293	51	0.8	69	21	–
» » 8,	»		266	18	1.3	25	6	350
» Jul 14,	»		220	20	ND	35	5	210
» » 28,	»		239	24	1.2	28	12	250
» Aug 25,	»		225	31	0.4	31	6	250
» Nov 9,	»		164	14	0.2	17	37	285
» » 23,	»		203	53	2.0	310	36	45
» » 29,	»		310	44	0.5	30	29	180
» Dec 1,	»		346	32	0.5	19	28	180
» » 2,	»		827	106	2.9	70	62	180
» » 28,	»		293	98	3.9	263	23	45

cont.

cont.

SAMPLE DATE	LOCATION	TSP	METAL CONCENTRATION (ng/m³)					WIND
		µg/m³	Pb	Cu	Cd	Mn	Ni	DIRECTION
1972 Jan 27,	Helsinki		124	41	1.6	64	49	90°
» Feb 23,	»		224	27	0.3	28	48	300
» Apr 5,	»		70	308	0.3	36	40	140
» » 20,	»		215	42	0.2	37	38	220
» Jul 3,	»		59	19	ND	32	4	90
» » 27,	»		103	14	ND	16	11	30
» Aug 2,	»		144	49	0.2	96	4	140
» » 9,	»		210	35	0.2	47	10	180
» » 29,	»		310	128	3.4	28	9	20
» Sep 28,	»		292	38	1.0	50	38	35
1973 Jan 8,	Helsinki		117	18	ND	25	16	315°
» » 8,	»		188	20	0.1	26	25	260
» » 12,	»		242	46	0.3	39	23	160
» » 13,	»		167	306	0.2	14	22	160
» » 15,	»		151	135	0.2	22	42	100
» Feb 22,	»		354	38	2.0	45	28	40
» Mar 1,	»		126	35	0.1	50	52	100
» » 15,	»		243	58	0.4	48	24	250
» Apr 2,	»		203	35	0.1	37	36	210
» May 30,	»		242	36	ND	30	3	120
» Jul 3,	»		155	27	ND	28	5	175
» » 26,	»		191	56	0.6	28	6	60
» Aug 13,	»		110	18	0.4	21	4	330
» » 23,	»		136	35	ND	22	3	260
» » 29,	»		494	67	0.3	53	8	150
» Sep 18,	»		293	21	0.2	18	12	270
» » 24,	»		266	31	ND	18	10	135
» Oct 18,	»		458	136	0.5	25	46	320
» » 22,	»		147	24	0.7	20	15	340
» Nov 1,	»		329	37	0.3	44	31	270
» » 20,	»		165	50	1.1	24	13	340
» » 30,	»		1041	216	3.0	108	128	45
» Dec 14,	»		185	46	1.6	26	44	80
1974 Jan 8,	Helsinki	92	210	39	1.1	37	18	135°
» » 9,	»	123	264	52	0.2	51	28	170
» » 10,	»	139	288	50	0.2	57	40	190
» Apr 4,	»	174	231	78	0.2	88	38	255
» » 23,	»	56	198	36	3.3	32	15	20
» May 7,	»	50	116	1094	1.8	34	34	45
» » 29,	»	43	184	68	0.2	16	14	165
» Jun 6,	»	61	151	32	0.3	35	15	195
» » 12,	»	46	178	211	ND	19	9	20
» Aug 6,	»	19	60	186	ND	10	5	315
» » 8,	»	9	71	117	ND	11	1	285
» Sep 2,	»	65	147	26	ND	33	27	105
» Oct 9,	»	111	76	615	1.0	78	15	45
» Nov 28,	»	51	120	212	0.4	22	53	135

cont.

cont.

SAMPLE DATE	LOCATION	TSP	METAL CONCENTRATION (ng/m³)					WIND
		µg/m³	Pb	Cu	Cd	Mn	Ni	DIRECTION
1975 Jan 1,	Helsinki	18	112	189	0.3	12	33	260°
» » 28,	»	138	153	42	0.1	52	14	150
» Apr 2,	»	61	133	20	ND	45	27	200
» » 14,	»	23	186	12	0.7	30	12	360
» May 22,	»	46	125	31	ND	23	10	200
» » 26,	»	34	110	23	0.4	21	3	360
» Jun 3,	»	51	144	19	ND	22	3	110
» Jul 24,	»	65	156	19	ND	30	3	120
» » 28,	»	38	61	28	ND	18	ND	360
» Aug 9,	»	22	141	3	ND	15	1	40
» » 10,	»	74	68	3	ND	20	2	185
» Oct 16,	»	70	164	20	0.5	61	8	145
» Nov 21,	»	16	70	1	ND	12	7	330
1976 Mar 4,	Helsinki	138	220	54	3.9	46	31	30°
» Jun 16,	»	49	104	22	1.2	26	26	20
1977 Mar 28,	Helsinki	81	107	37	0.9	49	9	50°
» » 29,	»	65	66	27	0.2	45	25	360
» Apr 12,	»	21	111	19	0.2	17	5	100
» » 13,	»	20	181	23	ND	16	–	150
» » 14,	»	54	198	28	0.3	52	–	100
» May 2,	»	45	91	30	0.4	64	12	80
» » 3,	»	45	115	25	0.4	36	8	120
» » 4,	»	80	121	37	0.3	49	11	100
» » 5,	»	153	301	81	0.3	140	19	220
» » 9,	»	37	110	39	0.3	22	12	240
» » 20...22,	»	31	71	25	0.9	22	7	–
» » 24,	»	11	52	11	ND	17	5	350
» Aug 31,	»	45	152	29	0.6	10	8	230
» Sep 6,	»	44	146	28	0.1	23	–	220
» » 19,	»	20	190	20	0.4	14	4	300
» May 3,	Harakka	19	17	3	0.2	28	1	120
» » 4,	»	57	11	1	0.2	39	8	100
» » 5,	»	86	11	4	0.2	110	10	220
» » 24,	»	49	68	141	0.9	21	26	350
» Aug 31,	»	48	20	13	0.7	26	–	230
» Sep 6,	»	27	13	12	1.0	5	–	220
1977 Mar 28,	Nurmijärvi		~7	ND	ND	~6	ND	–
» » 29,	»		68	ND	ND	~6	ND	–
» Apr 11,	»		21	152	ND	64	6	–
» » 12,	»		38	573	ND	29	–	–
» May 2,	»		7	3	ND	46	0	–
» » 3,	»		23	9	0.2	29	1	–
» » 4,	»		24	63	0.5	20	2	–
» » 5,	»		~7	7	0.3	51	5	–
» » 9,	»		11	ND	0.2	18	1	–
» » 22,	»		–	ND	0.0	11	–	–
» » 23,	»		17	13	0.3	12	1	–
» Aug 31,	»		74	8	0.4	17	3	–

cont.

cont.

SAMPLE DATE	LOCATION	TSP	METAL CONCENTRATION (ng/m^3)					WIND
		$\mu g/m^3$	Pb	Cu	Cd	Mn	Ni	DIRECTION
1977 Sep 6,	»		14	53	ND	4	–	–
» » 17,	»		ND	0	0.5	2	ND	–
» » 18,	»		29	25	0.7	2	ND	–
1976 May 29,	Sodankylä		2	23	ND	77	2	–
1977 May 22,	Sodankylä		15	ND	ND	9	ND	–
» » 24,	»		–	ND	ND	14	ND	–
» Sep 5,	»		ND	6	ND	ND	–	–
» » 6,	»		ND	9	ND	ND	–	–
» » 16,	»		11	1	0.1	2	2	–
» May 22,	Ivalo		–	ND	ND	3	ND	–
» » 23,	»		14	ND	ND	8	3	–
» Sep 16,	»		ND	3	ND	3	ND	–
» » 17,	»		4	ND	ND	3	–	–

Table 2. Pb, Cd, Cu, Ni, and Zn content of two fly ash samples. The first sample »Kyläsaari» was taken on December 17, 1973 from the cyclon separator of the Helsinki main incinerator. The second sample »Haaga 3» is ash from the lowest part of the stack of a Power station that uses 90 per cent oil and 10 per cent refuse. The metals were determined by the National Board of Water Laboratory and by the Department of Radiochemistry, University of Helsinki.

SAMPLE	METAL CONCENTRATION (parts per million)				
	Pb	Cd	Cu	Ni	Zn
Kyläsaari Incinerator	9600	256	890	155	22500
Haaga 3 Power Station	1930	39	520	1110	4200

does not imply any major nearby source. Instead the TSP configuration reflects average air stability as indicated by radon, absolute humidity distribution, etc. The three components presented in Fig. 3, especially when observed during non-stagnant atmospheric conditions, as they were here, originate from widely distributed source areas not confined to the urban area. The slightly accentuated concentration of TSP compared to radon in the east may be due to the nearby traffic route mentioned above. In the NE a local component from coalfulled power stations is probably significant (*cf.* Fig. 8 for manganese).

Even more interesting is a comparison of the TSP configuration with that for ^{212}Pb (ThB) (Fig. 4) measured during the winter season, when its sources are

Fig. 2. The Meteorological Institute adjacent to Kaisaniemi Park, viewed from the NW. The sampling point shown in Fig. 1 is on the roof.

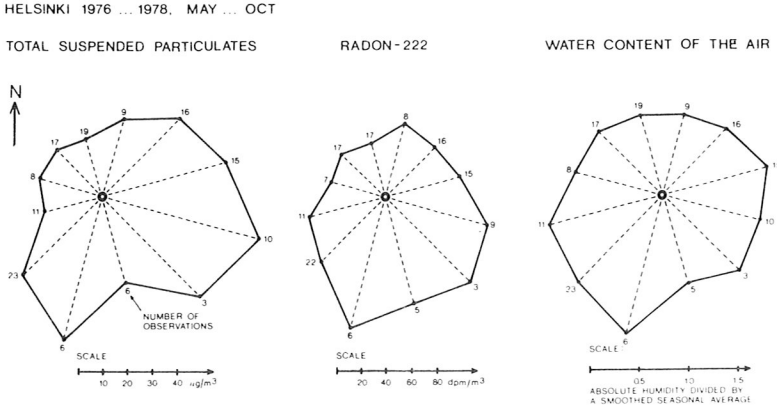

Fig. 3. Observations on the Meteorological Institute roof of three air components, broken down by wind direction (the direction from which the wind was blowing). These components, which are characterized by large source areas not confined to the urban area, are: total suspended particulates (TSP), ^{222}Rn, and water content of the air relative to a smoothed seasonal average. Radon activity is denoted by its momentary value at 13.30 ^{h} local time, and TSP and absolute humidity are shown in 24-hour averages. (North is up in the diagram).

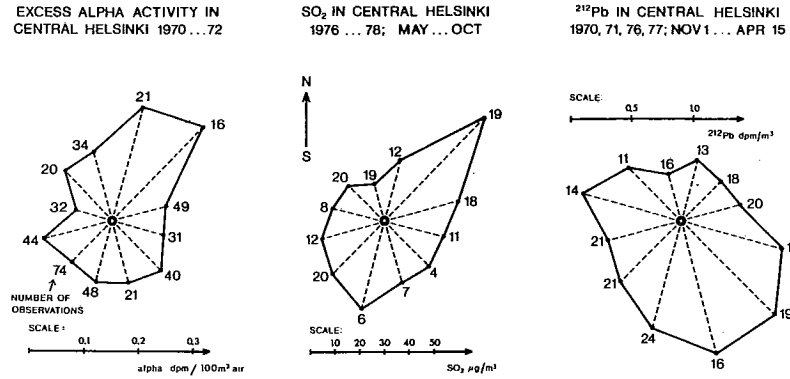

Fig. 4. Observations on the Meteorological Institute roof of three components with specific sources within the city area. »Excess alpha radioactivity» represents the difference in alpha radioactivity between the aerosol samples from Helsinki and the Nurmijärvi Observatory, both as measured five days after the end of the sampling. These configurations, with additional comments, have been published earlier by MATTSSON [14]. The daily averages for the SO_2 configuration were taken from the Meteorological Institute's monthly weather review (Kuukausikatsaus Suomen ilmastoon).

almost solely within the urban area, evidently due to ventilation of buildings (the simultaneous concentrations at the Nurmijärvi Observatory in a rural area 40 km to the north, were about a fifth of those in central Helsinki). As there can only be very little thoron (^{220}Rn) exhalation in parks during winter, the ^{212}Pb configuration thus reflects the vicinity of the sampler to Kaisaniemi Park (Fig. 2) and water areas in the north. Consequently we can expect that other components of mainly urban origin, such as lead, should lead to similar configurations.

The other two components in Figure 4, »excess alpha radioactivity» and SO_2, are examples of air pollution with distinct sources in the urban area. These sources, particularly power stations in the NE, become more conspicuous when we take into consideration the differences in average air stability between NE and SE winds. A more realistic picture of the relative impact of the local sources can thus be obtained by inscribing the wind configuration for a tracer with widely distributed source areas, say ^{222}Rn, in the configuration for the component in question and observing the differences between the areas.

4. *Pb, Cd, Cu, Ni, and Mn in daily air filter 1971...77*

Between March and October 1977 we determined Pb, Cd, Cu, Ni, and Mn in 151 selected daily air filters from the years 1969...1977 (Table 1). 104 of these were

old archive aerosol samples, all collected on the roof of the Meteorological Institute in Helsinki (Fig. 2). The other 47, including air filters from collection sites elsewhere in Finland, were treated as soon as they arrived at the laboratory.

The air filters dating from 1969 and 1970 were measured for the purpose of verifying the results of an earlier study on lead in the Helsinki air (MATTSSON and JAAKKOLA [13]).

The other archive filters were selected basing on recorded wind diagrams and weather maps, so as to take only sampling periods with wind directions staying within an angle of 90°. But thanks to the wide choice, at our disposal most of the selected air filters actually represent periods when the wind directions fell within a narrower sector.

The above method of selection means that many weather types were left unrepresented, so the result does not give the average levels of the measured components. Another limitation is that the Helsinki daily samples had only been taken on the weekdays Monday to Thursday. All the same, the broader project presented in the next chapter covers complete years of sampling and thus fills in the gaps left by the above limitations.

In 1977 the sampling periods were chosen to cater for the case studies reported in Chapter 7.

Chemistry: All the aerosol samples dealt with in this chapter were taken on Whatman GF/A glass-fibre filters. A half of each sample was leached and wet-ashed with nitric-acid by a procedure described by MATTSSON [14] on pages 25 to 28. In addition to the metals of main interest here, we also wished to analyze the ^{210}Pb, ^{210}Bi, ^{210}Po, and ^{106}Ru especially in the case studies. As the same sample extracts had to be used, this affected the choice of procedure.

The sample solutions obtained from the wet-ashing were adjusted to 1 M with HCl. The lead, copper, manganese and nickel concentrations of most of the air-filter samples were determined using an ordinary flame-atomic absorption spectrophotometer (Perkin-Elmer 303). In some samples the concentrations of these elements were below the detection limit of the flame-atomic absorption method. In these cases the determinations were made by flameless atomic absorption spectroscopy. In this method, a heated graphite furnace atomizer (Perkin-Elmer, HGA 72) is used instead of a flame burner-atomizer. The detection limits for Pb, Cu, Mn, and Ni are about one to two orders of magnitude lower in the flameless method than in ordinary flame-atomic absorption spectroscopy. All the cadmium concentrations were determined by the graphite-furnace method. To control the reproducibility of the atomic absorption analyses, four to five parallel determina-

tions were made from every sample solution. The standard deviation of the mean varied between ±0.5 and ±10 % for the flame-atomic absorption method and mostly between ±5 and ±10 % for the flameless method, depending on the metal concentrations in the sample solution.

In addition to the detection limits of the atomic absorption spectrometer system used, the lowest detectable metal concentrations in air-filter samples depend on the reagent background. This »blank» value was mainly due to the metal content of the filter material and the nitric acid used for wet-ashing. When half of a Whatman GF/A glassfibre filter (diameter 24 cm) was wet-ashed and leached with concentrated nitric acid, the reagent background values for Pb, Cd, Cu, Mn, and Ni were 18, 0.9, 20, 3, and 9 μg, respectively. Half of the air filter corresponded to an air volume of 1750 m^3. Thus the reagent-background concentrations which had to be subtraced from the total metal concentrations of the air were 10, 0.5, 10, 1.6 and 5 ng/m^3 for Pb, Cd, Cu, Mn and Ni, respectively.

In Table 1, metal concentrations under the detection limit are marked ND (not detectable). In these cases the difference between the total concentration of the sample obtained and the blank concentration was less than the standard deviation of the mean (1 δ) for the reagent background determinations.

Fly ash analyses: Analyses of fly ash trapped in cyclon separators or electrostatic precipitators or even taken from the stack, do not give us the ultimate information, which would be the knowledge of the composition of the escaping suspended particles. Much basic research has, however, been done in this field and we have by now a rather good qualitative picture of the fractionating phenomena that occur. So for example COLES *et al.* [3] reported in an investigation on coal fired power plants that in particular ^{210}Pb showed a definitive depletion in the bottom ash and in the electrostatic precipitator fly ash. GREENBERG *et al.* [6] found in a study on particles released in refuse incinerators, for the volatile metals cadmium, lead, and zinc, enrichment factors from fly ash to suspended particles ranging 10...25. In a later study GREENBERG *et al.* [7] came to the conclusion that 90 per cent of the metals lead, cadmium, and zinc entering the plant leaves via the stack.

The Helsinki main incinerator differs from the three incinerators studied by Greenberg et al. in that the former uses part of its generated heat for power production. This means that the fly ash here is more efficiently cooled, which favours a shift of the volatile metals towards larger particles and better removal by mechanical filters.

The relative distribution of the metals in the two fly ash samples presented in Table 2 is of some interest. The ratio Cd/Pb in the incinerator fly ash sample

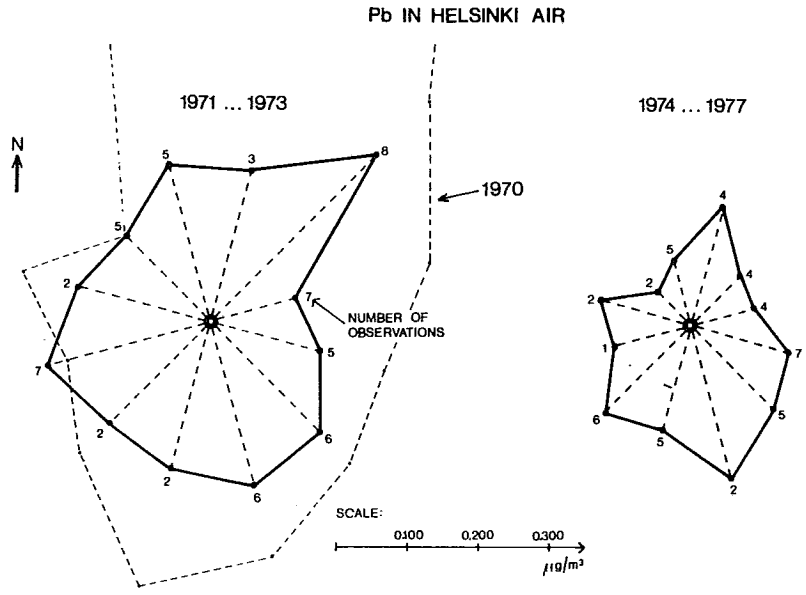

Fig. 5. Daily averages of lead concentrations in Helsinki air, broken down by wind direction (the directions from which the wind was blowing). The results of an earlier study for 1970 (MATTSSON and JAAKKOLA [13]) are enclosed by a dash line: the full contour is shown in the inset for Fig. 10.

taken from the cyclon separator was 0.027, which also is the ratio of Cd to Pb estimated to enter the plant (HELSINGIN KAUPUNKI [8]). From the data for the power station Haaga 3 we note that nickel may be usable as a trace metal for oil fuelled power.

In the following discussion on possible sources for observed metals in the air, we shall base our conclusions on wind direction analyses, seasonal variations etc. and not on the scarce emission values available. Only the relative distribution of the metals in the fly ashes will be referred to.

Comments on the results. Lead: A conspicuous decrease in the air concentration of lead appears to have taken place after 1970. In Figure 5 the results of our earlier study for 1970 are enclosed by a dashed line; the full 1970 configuration is shown in the inset of Fig. 10. Here in addition to remeasuring the old solutions, we leached wet-ashed and measured the other of the two quarters remaining in the original air filters. All the new measurements agreed with the results published earlier.

If the lead had originated from traffic alone we could have expected a configuration like the one for winter ^{212}Pb in Fig. 4. In fact, the lead configuration for 1974 to

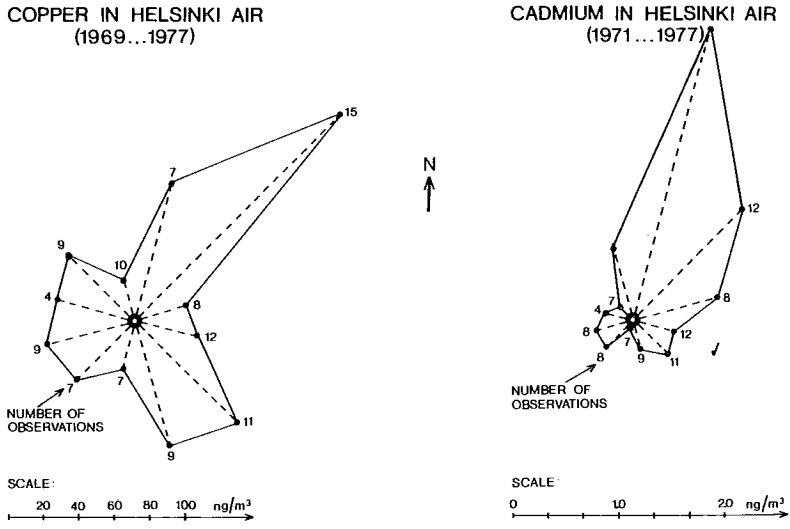

Fig. 6. Daily averages of copper and cadmium concentrations in central Helsinki air, broken down by wind direction.

1977 (Fig. 5) comes quite close to the ^{212}Pb in Fig. 4. The biggest difference between the 1971–73 and 1974–77 configurations was a remarkable decrease of lead concentrations during NE (45°) winds. One reason for this may have been that a bridge (Pitkäsilta) 500 metres NE of the sampler has been closed to private-car traffic during rush hours since 1974. This has reduced the gasoline-powered traffic on the bridge by roughly 40 % (HAATAJA [9]).

Copper: The only significant feature in the copper variation was that the winds from the direction of the main power station, 48°, brought higher concentrations. A smaller peak can be seen from the SE (Fig. 6).

High copper concentrations were not restricted to the Helsinki area; Table 1 includes values from the Nurmijärvi Observatory that were often higher than in central Helsinki.

Cadmium: NRIAGU [17] estimates that waste incineration is a primary source of anthropogenic cadmium in the air in addition to metal production. Most of the airborne cadmium we observed came from 0...30°, which is in fact the direction or the main incinerator in Helsinki, lying 3 km from the aerosol sampler in the direction 28°. In 1974 the ash from the cyclon separator of the incinerator was found to contain 256 ppm of Cd and 9,650 ppm of Pb, i.e. the cadmium amounted

to 2.65 % of the lead. We estimated that at that time (MATTSSON and JAAKKOLA [13]) the incinerator could cause a lead concentration of 0.8 $\mu g/m^3$ in central Helsinki during the most unfavourable weather conditions. As cadmium and lead, both highly volatile metals, are enriched to an equal extent in the suspended particles leaving an incinerator stack (GREENBERG *et al.* [7]) one could expect that a similar »worst» situation would produce a cadmium concentration of 2.65 % of 0.8 $\mu g/m^3$, *i.e.* 21 ng/m^3 in central Helsinki. Our higherst daily Cd average measured after 1970 was 10.3 ng/m^3 (Table 1), on a day when the wind was mostly at 30°.

Air concentrations of cadmium and particle-bound mercury were also measured by the Department of Radiochemistry (Helsinki University) in June 1971 (MIETTINEN [15]). 27 daily samples, each representing 3500 m^3 of air, were collected on the roof of the Department of Biochemistry building located 300 metres in the direction 100° from our main sampler on the Meteorological Institute of Kaisaniemi. The only two days with winds from the main incinerator were 13th and 14th June. The cadmium concentrations on those days were 3.2 and 2.2 ng/m^3, and the particle-bound mercury 1.0 and 0.7 ng/m^3. These values were the highest in the whole of that project, during which the average was 1.0 ng/m^3 for cadmium and 0.28 ng/m^3 for particle-bound mercury. A further analysis of concentrations versus wind directions revealed that a slight increase in mercury also occurred during NE winds, but cadmium rose significantly only during more northerly winds (30°). Miettinen's cadmium configuration thus agree with our Fig. 6.

Table 3. Average air concentrations, ng/m^3, of Cd at five rural stations in winter 1976. The locations and descriptions of the sampling sites will be found in the YEARBOOK [21]. ND = not detected.

Sampling period	Nurmijärvi	Vaasa	Joensuu	Tikkakoski	Kajaani
1976–10–11...12–26	0.61	0.45	0.27	0.28	0.19
1976–12–27...1977–02–28	0.82	0.20	0.26	0.43	0.26
1977–03–01...05–02	0.17	0.59	0.10	0.09	ND

Cadmium in rural areas: On the whole, cadmium has been low in the Helsinki air since 1970, originating almost exclusively from the direction of Helsinki's main incinerator. Cadmium concentrations from southerly and westerly directions were often so low that they approached our detection limit.

As mentioned in the Introduction, high cadmium concentrations in snow were reported for the winter of 1976/77. We therefore determined Cd in weekly air

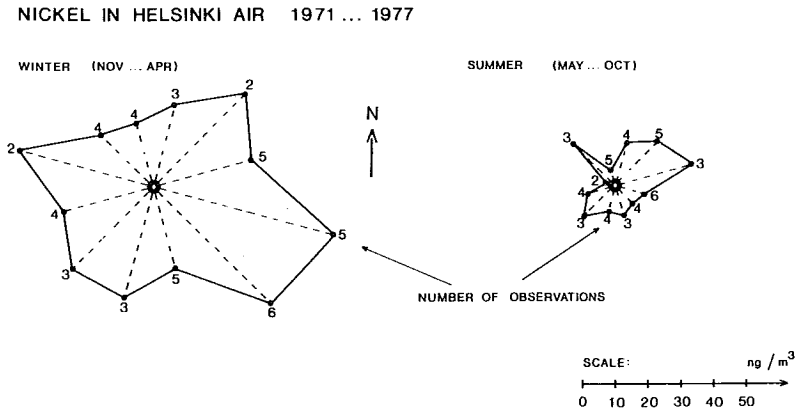

Fig. 7. Daily averages of nickel concentrations in central Helsinki air broken down by wind direction. The colder half of the year November to April, is shown separately from the warmer half, May to October.

filters for the whole of the snow period at a number of rural stations (Table 3). The levels were found to be low, and close to the values measured in Helsinki during winds other than N...NE (Fig. 6).

Nickel: Nickel is the only one of the five metals determined that showed a clear seasonal variation (Fig. 7). Oil combustion is the main source of anthropogenic nickel (NRIAGU [17]). See also Table 2. Winter and summer oil consumption in Helsinki vary in the ratio of 70:30. The resultant difference in emissions is a plausible explanation for seasonal variation of nickel.

Manganese: Manganese comes from a wide variety of sources. In summer, soil-derived Mn plays an important role, and the wind configuration (Fig. 8, right) is fairly similar to that for TSP (Fig. 3). In winter the coal-fired power stations in the NE and SW evidently contribute significantly, and Fig. 8, left, is more like Fig. 4 for SO_2.

On the whole, manganese correlated with the smoke shade of the air filter and with TSP, but much less so with the other metals measured.

5. *Levels of Pb, Cd, and Cu before 1971*

The rapid decrease of airborne lead after 1970 noted above naturally raises the question of whether 1970 was an exceptional year or just the last year of a period of higher pollution. During the '60s only weekly sampling was made in Helsinki,

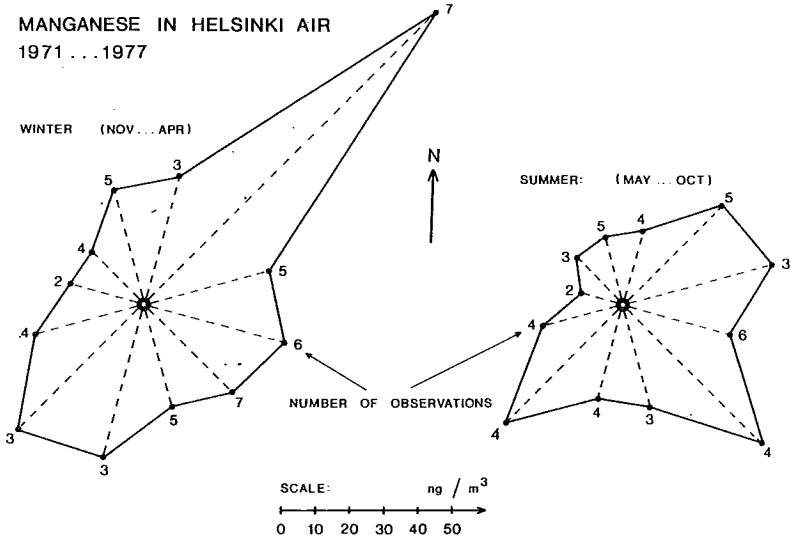

Fig. 8. Daily averages of manganese concentrations in central Helsinki air broken down by wind direction. The colder half of the year, November to April, is shown separately from the warmer half, May to October.

so a full analysis of lead by wind direction was not possible. Instead, we divided the weekly groups as follows:

»NE» – weeks during which there had been winds blowing from the sector 0...30°

»W» – weeks with winds mainly in the sector 150°...360°

»E» – all other weeks, notably with winds from the sector 30°...150°, but also with 150°...360° winds

Each year was further divided into four periods of three months each.

For wind data we used the 2^h, 8^h, 14^h, and 20^h observations, which was available from magnetic data tape.

All the weekly air samples were taken on Whatman 42 paper-fibre filters. This new project comprises the years 1962, '63, '64, '67, '70, '73, and '77. The years 1973 and 1977 were included for the sake of comparability to the results in Chapter 4. Before 1967 the sampling site was at Hämeentie 31 (Fig. 9), 1820 m NE of the present site in Kaisaniemi (Fig. 2).

Chemistry: Quarter pieces of each weekly air filter were grouped according to the above scheme and then wet-ashed with concentrated nitric acid, hydrogen peroxide and hydrochloric acid.

Fig. 9. Collecting point at Hämeentie 31 for weekly aerosol samples in Helsinki from 1962 to 66. The arrow shows the air inlet of the sampler 30 metres above street level. The location is viewed from the West.

The air filters were dissolved completely and the resulting solution was diluted for atomic-absorption spectrometric determination. Owing to the low metal concentrations in the Whatman 42 filter material and the small amount of nitric acid required for dissolving the sample, the reagent background for lead and copper was negligible and only a slight correction for cadmium was needed. The concentrations of lead were determined with both the flame and the flameless method, cadmium only with the latter.

A complete list of the groups measured and the results is given in Table 4.

Comments on the results: Except for a few cases of higher concentrations during periods of winter inversion, no systematic seasonal variation was found in any of the three components. Significantly higher quantities of lead and cadmium were noted for the sector 0...30° in the yearly means, except for 1977 (Pb and Cd) and 1963 (Cd).

In an effort to illustrate the results diagrammatically, we proceeded as follows: basing on the above four-observations-a-day wind data we estimated that the wind had been in the 0°...30° sector for an average of 24 hours in each »NE» week. Therefore one day with the unknown concentration, C, from the 0°...30° sector,

Table 4. Determinations by AAS of Pb, Cu, and Cd in complete series of weekly aerosol samples for the years 1962, 63, 64, 67, 70, 73, and 77. These weekly samples have been grouped according to season and prevailing winds by a method described in Chapter 6. The sampling site was Hämeentie 31 (Fig. 9) until 1967, and Vuorikatu 24 in Kaisaniemi since then (Fig. 2).

YEAR	SAMPLE	SAMPLE INCLUDES WEEKS ENDING:	AIR m^3	Pb ng/m^3	Cu ng/m^3	Cd ng/m^3
1962	Winter »NE»	Jan28, Feb18, Feb25, Mar04, Mar11, Mar18	1121	379	120.4	3.17
	Winter »E»	Jan21, Feb04, Mar25, Apr01	846	340	118.2	2.96
	Winter »W»	Jan14	166	231	170.2	21.49
	Spring »NE»	Apr29, May06, Jun08	560	268	95.5	2.54
	Spring »E»	Apr15, Apr20, May13, May20, Jun03	1146	299	90.8	2.73
	Spring »W»	Apr08, May27, Jun17, Jun24, Jul01	1137	200	76.5	2.07
	Summer »NE»	Jul15, Jul29, Aug26, Sep02, Sep23, Sep30	1079	395	101.9	1.85
	Summer »E»	Jul22, Aug19, Sep09	660	254	79.5	2.39
	Summer »W»	Jul08, Aug05, Aug12, Sep16	901	200	72.6	1.89
	Autumn »NE»	Nov11, Nov25, Dec16, Dec23, Dec30	1018	695	74.7	4.17
	Autumn »E»	Oct21, Nov04, Dec02, Dec09	818	452	94.7	2.93
	Autumn »W»	Oct07, Oct14, Oct28, Nov18	806	233	71.3	1.98
1963	Winter »NE»	Jan13, Jan20, Feb03, Mar17, Mar31	1056	341	85.2	2.27
	Winter »E»	Jan06, Jan27, Feb10, Mar03, Mar24	1035	589	87.0	2.56
	Winter »W»	Feb17, Feb24, Mar10	616	414	63.4	2.03
	Spring »NE»	Apr28, Jun03, Jun09	636	291	91.3	1.42
	Spring »E»	Apr07, May05, Jun16, Jun23	818	281	88.1	1.59
	Spring »W»	Apr15, Apr21, May12, May19, May26, Jun30	1154	243	78.0	1.99
	Summer »NE»	Jul07, Aug19	356	435	43.5	1.33
	Summer »E»	Jul28, Aug04, Aug11, Sep15, Sep22	1040	207	64.4	1.35
	Summer »W»	Jul14, Jul21, Aug25, Sep01, Sep08, Sep29	1196	230	78.6	2.42
	Autumn »NE»	Nov10, Dec08, Dec15, Dec22	891	893	84.2	2.02
	Autumn »E»	Oct20, Nov03, Nov17, Nov24, Dec01	1076	325	62.3	1.67
	Autumn »W»	Oct06, Oct13, Oct27, Dec29	848	271	74.3	1.65
1964	Winter »NE»	Feb16, Feb23, Mar08, Mar15, Mar22, Mar30, Apr05	1644	654	56.3	1.98
	Winter »E»	Jan19, Jan26, Feb02, Feb09	997	211	55.7	1.43
	Winter »W»	Jan12, Mar01	437	206	78.9	1.37
	Spring »NE»	Apr26, May24	421	315	43.9	2.67
	Spring »E»	Apr12, May10, May18, May31, Jun07	1186	234	60.7	1.35
	Spring »W»	Apr19, May04, Jun14, Jun21, Jun28, Jul05	1371	160	44.9	2.17
	Summer »NE»	Jul19, Aug09, Aug16	699	486	34.3	1.75
	Summer »E»	Aug30, Sep06, Sep13, Sep27, Oct04	1111	362	54.0	1.83
	Summer »W»	Jul12, Jul26, Aug02, Aug23, Sep20	1141	213	52.8	2.45
	Autumn »NE»	Nov22, Nov29, Dec06, Dec20	837	597	62.7	2.30
	Autumn »E»	Oct18, Nov08, Dec27	657	400	51.8	1.92
	Autumn »W»	Oct11, Oct25, Nov01, Nov15, Dec13	1118	306	44.7	2.68
1967	Winter »NE»	Jan08, Jan29, Feb05, Feb26	955	586	116.2	3.14
	Winter »E»	Jan15, Feb19, Mar05, Mar19	965	477	127.5	1.92
	Winter »W»	Jan22, Feb12, Mar12, Mar26	965	373	108.8	1.81
	Spring »NE»	Apr09, Apr16, May07, May28, Jun18	1149	505	96.6	1.35
	Spring »E»	Apr23, Apr30, May14, May21	1231	374	95.5	1.14
	Spring »W»	Apr02, Jun11, Jun25	689	312	100.1	0.94

cont.

cont.

YEAR	SAMPLE	SAMPLE INCLUDES WEEKS ENDING:	AIR m^3	Pb ng/m^3	Cu ng/m^3	Cd ng/m^3
	Summer »NE»	Aug27, Sep10, Sep17, Sep24	987	760	81.1	1.98
	Summer »E»	Jul09, Jul30, Aug06	713	281	129.0	0.77
	Summer »W»	Jul02, Jul16, Jul23, Aug20	1427	308	103.7	1.05
	Autumn »NE»	Nov05, Dec10, Dec17, Dec26	998	561	95.2	1.70
	Autumn »E»	Oct01, Oct22, Nov12, Nov19	1213	379	56.1	1.20
	Autumn »W»	Oct08, Oct15, Oct29, Dec03	1000	360	55.0	1.50
1970	Winter »NE»	Jan18, Feb01, Feb22	599	639	41.7	1.59
	Winter »E»	Jan11, Jan25, Feb15, Mar01, Mar22, Apr05	1426	389	46.3	1.74
	Winter »W»	Feb08, Mar08, Mar15, Mar30	881	227	46.0	1.29
	Spring »NE»	Apr12, Apr19, May03, May10, Jun21	1096	598	56.1	1.19
	Spring »E»	May31, Jun07, Jun14	700	257	43.6	1.02
	Spring »W»	Apr26, May18, May24, Jun28, Jul05	1209	190	43.4	0.65
	Summer »NE»	Aug02, Aug16, Aug23, Aug30, Sep27, Oct04	1336	251	35.6	0.58
	Summer »E»	Jul19, Aug09	484	170	62.0	0.46
	Summer »W»	Jul12, Jul26, Sep06, Sep13, Sep20	1212	247	33.4	0.78
	Autumn »NE»	Nov08, Nov15, Dec20, Dec27	1055	358	28.0	1.00
	Autumn »E»	Oct11, Oct18, Nov01, Nov29, Dec06	1306	331	48.2	0.74
	Autumn »W»	Oct25, Nov22, Dec13	788	279	31.7	0.65
1973	Winter »NE»	Feb04, Feb25, Mar04	716	328	102.0	1.33
	Winter »E»	Jan14, Jan21, Feb11, Mar11, Mar18, Apr01	1407	178	91.0	0.68
	Winter »W»	Jan07, Jan28, Feb18, Mar25	919	163	84.9	1.55
	Spring »NE»	May20, May27, Jun03, Jun17, Jun24	1299	231	158.0	0.50
	Spring »E»	Apr08, May01, May06, Jul01	956	157	61.7	0.47
	Spring »W»	Apr15, Apr23, May13, Jun10	1069	187	80.4	0.61
	Summer »NE»	Jul08, Jul29, Sep02, Sep16, Sep23	1115	184	39.5	1.30
	Summer »E»	Jul22, Aug12, Aug19, Sep09	880	170	67.0	0.80
	Summer »W»	Jul15, Aug05, Aug26, Sep30	941	186	129.6	0.80
	Autumn »NE»	Nov04, Nov25, Dec02, Dec09	1010	297	69.3	1.24
	Autumn »E»	Oct07, Oct14, Nov18, Dec23	1165	206	34.3	0.43
	Autumn »W»	Oct21, Oct28, Nov11	693	173	57.7	0.65
1977	Winter »NE»	Jan23, Jan30, Feb13, Apr03	933	193	65.4	0.86
	Winter »E»	Feb06, Feb20, Feb27, Mar20, Mar27	1145	135	114.4	0.74
	Winter »W»	Jan09, Jan16, Mar06, Mar13	951	163	91.5	0.68
	Spring »NE»	May08, May29, May22, Jun19	955	47	18.3	0.10
	Spring »E»	Apr11, Apr17, May01, Jun05, Jun12	1225	102	34.7	0.37
	Spring »W»	Apr24, May15, Jun26, Jul03	971	82	33.5	0.21
	Summer »NE»	Jul10, Aug07, Aug14, Aug21	945	116	30.2	0.26
	Summer »E»	Jul17, Jul31, Sep11, Sep18, Sep25, Oct02	1447	114	30.8	0.24
	Summer »W»	Jul24, Aug28, Sep04	710	134	33.1	0.21
	Autumn »NE»	Oct09, Dec11, Dec26	695	129	40.3	0.29
	Autumn »E»	Oct16, Oct23, Nov20, Nov27	968	155	42.4	0.62
	Autumn »W»	Oct30, Nov06, Nov13, Dec06, Dec18	1289	124	30.6	0.47

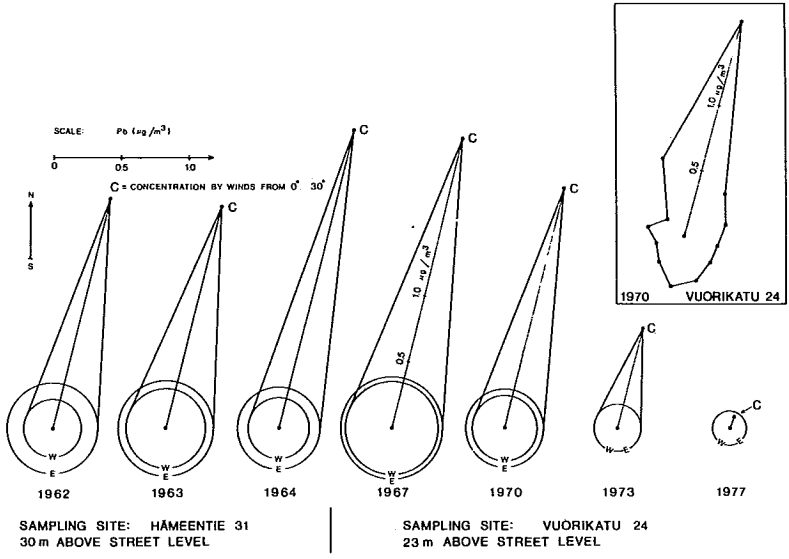

Fig. 10. Interpretation of data in Table 2 on average weekly lead concentrations in the air. The distance to point C represents the yearly average lead concentration when the wind was blowing from the sector 0°...30°. The radius of the circle »W» represents the average concentration during winds mainly from the sector 150°...360° with no winds from the sector 0...30°. The radius of the circle »E» represents the yearly average lead concentration in all the other weeks i.e. during winds frequently from the sector 30°...150°, but also from the sector 150°...360°. Inset: the results of an earlier study for 1970 (MATTSSON and JAAKKOLA [13]), in which daily sampling was practised, drawn to scale.

plus six day with the concentration »W» (or »E»; we used the smaller of the two) should equal seven days of the observed concentration »NE», i.e.

$$C = 7\ \text{»NE»} - 6\ \text{»W»}$$

In Figures 10 and 11, the radii of the circles represent the yearly average concentrations »W» and »E». The concentration C in the above equation was plotted as a dot in the direction 15°, and tangents of the »W» and »E» circles, respectively, were drawn to this dot.

The reulting Pb configuration for 1970 resembles that in our earlier study (MATTSSON and JAAKKOLA [13]), which is drawn to scale in the inset of Figure 10. The fact that even the calculated concentration peak from the direction 15° is almost the same (1.82 μg Pb/m³ here and earlier 1.68) must be fortuitous because, in our earlier study the wind was from that direction on only three of the 47 observed days.

Cadmium displays a less pronounced but still significant peak during 0°...30° winds (Fig. 11). Here again a comparison with earlier measurements from daily

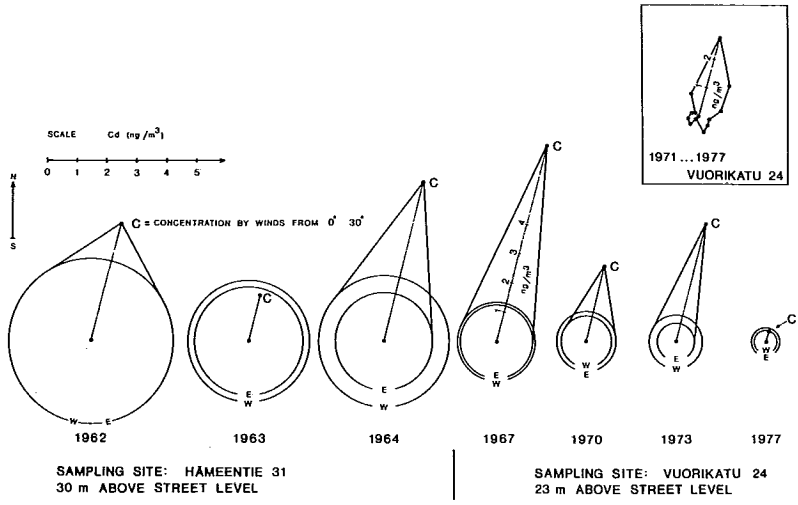

Fig. 11. Interpretation of data in Table 2 on average weekly cadmium concentrations in central Helsinki air. The distance to point C represents the yearly average cadmium concentration during winds from the sector 0°...30°. The radius of the circle »W» represents the average concentration during winds mainly from the sector 150°...360° with no winds from the sector 0°...30°. The radius of the circle »E» represents the yearly average cadmium concentration in all the other weeks, i.e. during winds frequently from the sector 30°...150° but also from the sector 150°...360°. Inset: cadmium configuration from Figure 6 drawn to scale for comparison's sake.

air filters (Chapter 5) offers no contradictions. Neither does Figure 11 contradict our assumption that the airborne cadmium comes mostly from trash burning; the high level of cadmium in the air regardless of wind direction before 1967 may have been due to on-site trash burners, which numbered 1300 or so in 1967, but were reduced to roughly 1/10 of that figure by 1973. Thus the effect of the Helsinki main incinerator, lying in the direction 28°, gradually became relatively greater.

The same features are found for lead (Fig. 10), but here the incinerator accounted for only a small fraction of the high concentrations coming from the 0°...30° sector. Most of it evidently came from lead smelting works at Tikkurila 15 km away in the direction 5°...15°. In 1973 the average Cd concentration in the air from the direction 0°...30° was 4 ng/m^3. The Cd/Pb ratio in the fly ash from the cyclon separator of the incinerator was 0.026 (Table 2). So one could expect a lead concentration of 4/0.026 = 154 ng/m^3, which is only a fifth of the average, 750 ng/m^3, observed in 1973.

The high average Cd-concentration, 21.5 ng/m^3, during the week 8...14th January 1962 (Table 2) is conspicuous. As we had pieces left of both air filters

collected in parallel during that week, the value was checked by renewed determinations of Cd in both filter pieces separately. Both samples were high in Cd and the earlier result was confirmed. We have found no explanation for this anomalously high level in that week; the difficulty, of course, is that the weather and wind direction changed a good deal during the long sampling period.

Neither have we found any systematicity for the apparently stochastic fluctuation of the copper values in Table 4. The evident reason for this is that the sources of airborne copper are numerous and none of them especially superior to the other. Important sources are waste incineration, coal and wood combustion, and industrial applications (NRIAGU [17]).

The copper data did not correlate with the high lead values, which up to 1970 were connected with the wind sector 0...30°. This agrees with the assumption that lead came from the smelters. The lack of correlation also eliminates possible hypotheses that the high lead concentrations could have been connected to particularly stable weather conditions.

6. *Instrumental Neutron-Activation Analyses of Br, Sb, and Zn*

In November 1979 we sent 22 weekly aerosol samples taken on Whatman 42 paper-fibre filters, together with six reference samples, for irradiation by the Triga Mark II reactor at the Technical Research Centre of Finland. One quarter of each air filter was used. The samples were irradiated for 10 to 15 hours in a neutron flux of 1.2×10^{12} neutrons $\times$ $cm^{-2} \times s^{-1}$. Bromine and antimony were determined gammaspectrometrically 2...3 days after the irradiation and zinc and antimony (second measurement) about four weeks after it. In January 1980 we irradiated another 13 weekly samples this time one eight of each air filter was used. Four of the samples were check-ups of the earlier analyses so altogether 33 weeks were studied. In the January series zinc was not determined. All results are given in Table 5.

Table 5. Determinations of Br, Sb, and Zn by instrumental neutron activation analysis in 33 selected weekly air filters from Helsinki. The sampling site was Hämeentie 31 in 1964 (Fig. 9) and Vuorikatu 24 in 1967 and after (Fig. 2). The mean lead values for the groups have been taken from Table 4. Lead was determined separately for the two 1970 samples. The table includes all the measurements of Br, Sb, and Zn carried out for the present study. For an explanation of WIND GROUP, see Chapter 5. NM= not measured, ND = not detected.

LAST WHOLE DAY OF SAMPLING WEEK		METAL CONCENTRATIONS (ng/m³) Br	Pb	Br/Pb	Sb	Zn	WIND GROUP
1964	Jan 12	38	206	0.17	ND	165	»W»
	Mar 01	33			ND	144	
	Apr 19	36			4	183	

cont.

cont.

LAST WHOLE DAY OF SAMPLING WEEK		METAL CONCENTRATIONS (ng/m³) Br	Pb	Br/Pb	Sb	Zn	WIND GROUP
1964	Nov 22	55			2	153	»NE»
	Nov 29	40	597*	0.085	1	140	
	Dec 06	57			9	237	
1967	Apr 02	62			5	NM	»W»
	Jun 11	55	312	0.16	5	NM	
	Jun 25	33			2	NM	
	Aug 27	49			15	111	»NE»
	Sep 10	55	760	0.088	17	116	
	Sep 17	91			18	201	
	Sep 24	73			3	NM	
	Jul 09	42			8	128	»E»
	Jul 30	44	281	0.15	6	138	
	Aug 06	43			24	120	
1970	Jan 18	67	405	0.17	8	NM	»NE»
	Feb 08	46	278	0.17	3	NM	»W»
AVERAGE »NE»		61	655	0.09	9.1	160	»NE»
AVERAGE »W»		43	271	0.16	2.7	164	»W»
AVERAGE 1964...70		51	453	0.11	7.2	153	
1973	Jan 07	36			ND	138	»W»
	Jan 28	59	163	0.30	2	218	
	Feb 18	46			2	NM	
	Mar 25	55			7	206	
	Feb 04	48			5	251	»NE»
	Feb 25	60	328	0.22	12	307	
	Mar 04	111			11	288	
1977	Jan 23	87			5	206	»NE»
	Jan 30	48	198	0.26	6	219	
	Feb 13	51			6	290	
	Apr 03	15			1	NM	
	Apr 24	32			ND	NM	»W»
	May 15	29	82	0.29	ND	87	
	Jun 26	8			ND	45	
	Jul 03	26			ND	42	
AVERAGE »NE»		60	251	0.24	6.6	260	»NE»
AVERAGE »W»		36	123	0.29	1.4	123	»W»
AVERAGE 1973+1977		47	182	0.26	3.8	191	
AVERAGE 1964...77		49	326		5.7	172	

*average value for a period which, in addition to the three weeks in this table, included the week ending February 9.

Selection of samples: The purpose was to compare weeks with no wind from the direction 0...30° to weeks with maximum winds from that direction. We also wished to compare 1964 and 1967, years of high average lead concentration, with 1973 and 1977 (see Fig. 10).

Bromine lead ratios: KING *et al.* [10] report average Br/Pb ratios from 16 different sites in or adjacent to the City of Cleveland as ranging from 0.21 to 0.32. PACIGA and JERVIS [19] observed the following Br/Pb ratios in Toronto in the summer of 1974: urban site: 0.29, expressway site: 0.34, industrial sites: 0.13 and 0.18. The two last values were accompanied by high Sb concentrations of 45 an 17 ng/m^3 respectively. The authors mention a battery recycling plant in the neighbourhood as an explanation for the high Sb value and the low Br/Pb ratio, 0.13.

CONNOR *et al.* [4] point out that bromine has a tendency to escape from Pb salts both in the air and on air filters during storage. The decomposition of Pb-Br salts is speeded up by photons and X-rays. Higher Br/Pb ratios can thus be expected in winter than in summer, and low ratios could be a result of losses during X-ray fluorescence spectrometry.

The ethyl fluid mixture of tetraethyllead, ethylene dibromide, and ethylene dichloride, used as a lead additive in motor petrol in Finland, has the weight ratio Br:Pb of 0.386.

LAAMANEN [12] measured a Br/Pb ratio of 0.14 as a two-year average, in central Helsinki close to heavy traffic, and a ratio of 0.10 on the outskirts of Helsinki, in 1971–72.

Br/Pb was also observed in the present study. The ratio was conspicuously low in 1964 and 1967 especially in the groups with 0...30° winds. This observation supports the assumption that much of the airborne lead at that time was of other than traffic origin. The possibility of bromine escape during storage suggested above by Connor et al. must be allowed for. But quite apart from this, the Br/Pb ratio was lower in weeks when there were also winds from the direction of the Tikkurila factory area.

Antimony: The negative plates of an ordinary automobile battery contains antimony as a hardener. Lead emitted by a lead smelter for such batteries is therefore accompanied by Sb. ASIKAINEN [2], for instance observed an Sb/Pb-ratio of 0.06 in the smoke coming from one of the smelters in Tikkurila. In our study, too, antimony concentrations were found to be higher when the wind was from the direction of the smelters.

The precision of the antimony concentrations in Table 5 is low. This was due to the relatively high antimony concentration found in the radiated »blank» samples.

As the number of determinations was also small, no convincing conclusions can be drawn concerning the variation of the antimony. All the same, it appears that up to 1970, antimony was accompanied by rather high lead concentrations and low Br/Pb-ratios, but it did not correlate with zinc. A plausible explanation would thus be that antimony originated from the lead smelters. After 1970, however, the pattern is not quite the same, because zinc now correlated with high antimony values whereas the Br/Pb-ratio decreased only slightly. This indicates a possibility that both antimony and zinc may have originated at least in part from incineration.

Zinc concentrations: In addition to primary metal production industries and wood combustion, which can be excluded both here, trash incineration is a main source or anthropogenic airborne zinc (NRIAGU [17]). It is therefore interesting to note features in the zinc data that resemble those for cadmium, which is also a trash-incineration product. In 1964 and 1967, when there were still a large number of on-site incinerators spread around central Helsinki, the zinc values were fairly uniform and did not depend on wind directions, whereas in 1973 and 1977 the highest zinc concentrations were found during weeks when the wind had been blowing from the direction of the main incineration plant. During other wind directions the zinc concentrations were lower in the '70s than in the '60s (Table 5).

7. *Case Studies of Air Components in Central Helsinki Simultaneously with Observations Made outside the Urban Area*

We have seen above that, in addition to pollution sources within Helsinki, lead from the Tikkurila smelters contributed remarkably to the lead level in the city, at least from 1962 to 70. In April 1977 we set up a new aerosol sampling station on the island of Harakka, immediately to the south of Helsinki (Figures 1 and 12), in order to analyse air coming in from the open sea before it reached the urban area.

During selected weather periods we simultaneously collected aerosol samples from this new site, our main sampling site on the roof of the Institute building, at the Nurmijärvi Observatory located 40 km inland (Fig. 1). In addition to the metals in Table 1, a number of radionuclides were determined in part non-destructively from the surface of the air filter (^{212}Pb, ^{210}Pb and total long-lived beta-activity), and in part from the solubilized part of the aerosol sample (^{210}Po, ^{210}Bi, ^{210}Pb, and ^{106}Ru). Major purpose of these measurements was to confirm that neither the sampling nor the wet-ashing was causing non-real differences between the three stations. For example, the long-lived ^{210}Pb and ^{106}Ru concen-

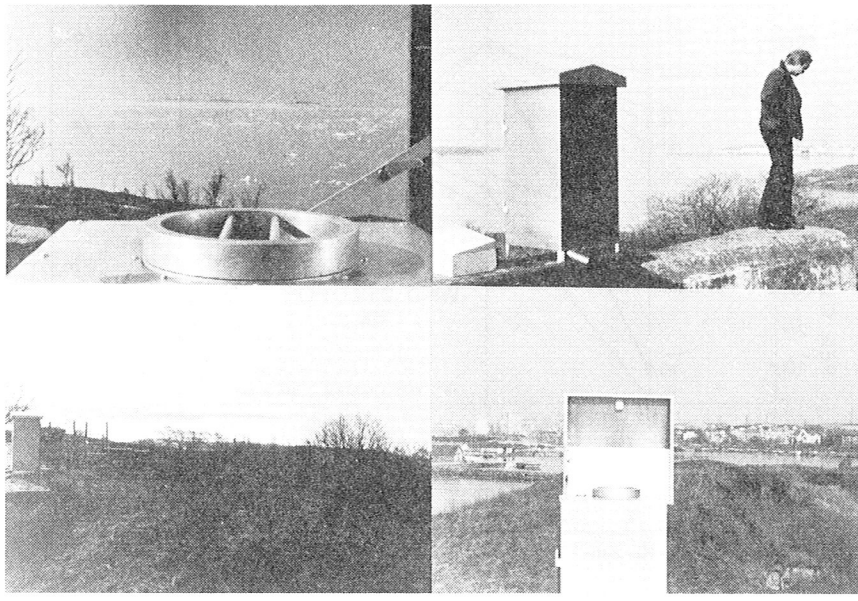

Fig. 12. Aerosol sampler on Harakka, a small island directly south of central Helsinki. The four photographs are views from the NE (upper left), E, NW, and SE (lower right).

trations should be almost the same at Harakka as at the Meteorological Institute.

The first period chosen included 3 May, 4 May, and 5 May 1977. A moist, stable air mass was coming in from the SE over the cold open sea, on which lumps of ice could still be seen (Fig. 12). A high-pressure centre originating over Lake Ladoga was moving slowly towards Moscow and the wind was turning slowly from SE to S and at the same time dying down. Owing to conductive cooling by the cold sea, a shallow inversion layer developed, affecting the coastal belt for 10...15 km inland. From a diagram of the relative concentration of a number of trace components on 4 May, (Fig. 13) we can see that the quantity of old fission products descending from the stratosphere was smaller in Helsinki than in Nurmijärvi. This is a common phenomenon, especially during stable onshore winds in early summer when vertical exchange in the coastal area is decreased by an intense uninterrupted inversion layer, which disappears about 20 km inland.

Another notable feature in the diagram is that smoke shade, Mn, and Ni were lower at Nurmijärvi than Harakka, even though the air at Nurmijärvi came from the direction in industrial areas whereas the Harakka air came from the open sea. The ^{212}Pb (ThB) concentration on that day in Nurmijärvi was high, averaging 4 dpm/m^3. This is a higher-than-average value for May, as measured at several stations in South Finland, and it does not seem likely that the mean concentra-

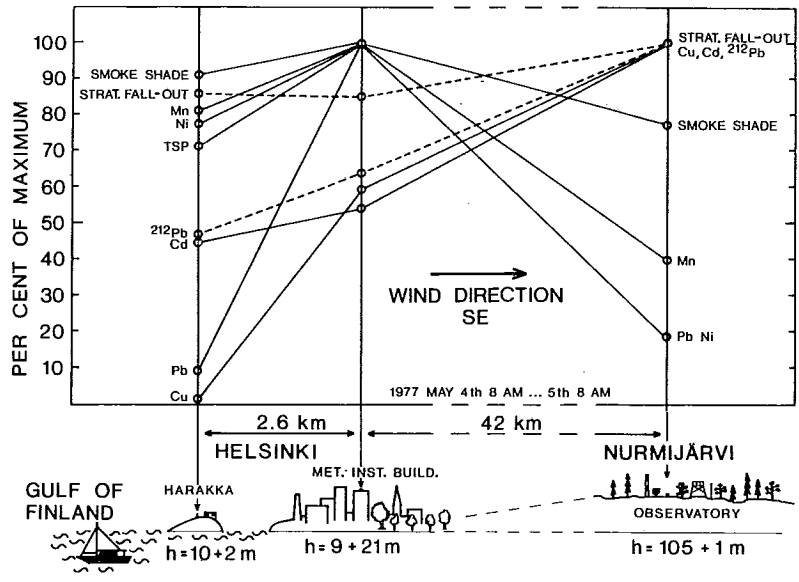

Fig. 13. Simultaneous relative (highest value = 100) average concentrations of a number of air components at Harakka, on the roof of the Meteorological Institute, and the Nurmijärvi Observatory between 8^h and 8^h on 4 and 5 May 1977.
The absolute values corresponding to the index 100 were Cu: 63, Pb: 121, Cd: 0.50, Ni: 10.8, Mn: 48.8, all in ng/m^3; TSP: 80 µg/m^3, smoke shade: 3.3 (in an index range of 0...6), ^{212}Pb: 4.12 dpm/m^3, stratospheric fall-out: 0,27 dpm/m^3.

tions south of the Gulf of Finland were much higher that day. The average surface-wind speed was around 15 km/h, which means that the air had been travelling for roughly ten hours over the sea before reaching Harakka. As the radioactive half-life of ^{212}Pb is 10.6 hours, decay alone reduced the activity concentration to 50 % during its passage over the Gulf of Finland. The high ^{212}Pb concentration at Harakka seems to imply that concentrations decrease very slowly in the stratified layer above the sea.

On the next day, 5 May (Fig. 14), the wind was weaker, the air hazy, and insolation resulted in fumigation of the lowest part of the inversion layer. Weather of the kind occurring on 5 May, is the most detrimental in its effect on the quality of the air in Helsinki. At Nurmijärvi, too the surface air was more stable, which resulted in a roughly two-fold rise in the daytime ^{222}Rn concentration. In common with 4 May, when the wind was stronger, we find that the air was cleaner at Nurmijärvi than at Harakka. On both days, too, the air arriving at Harakka was low in copper and lead but rather high in ^{212}Pb, smoke shade, and TSP (total suspended particulates).

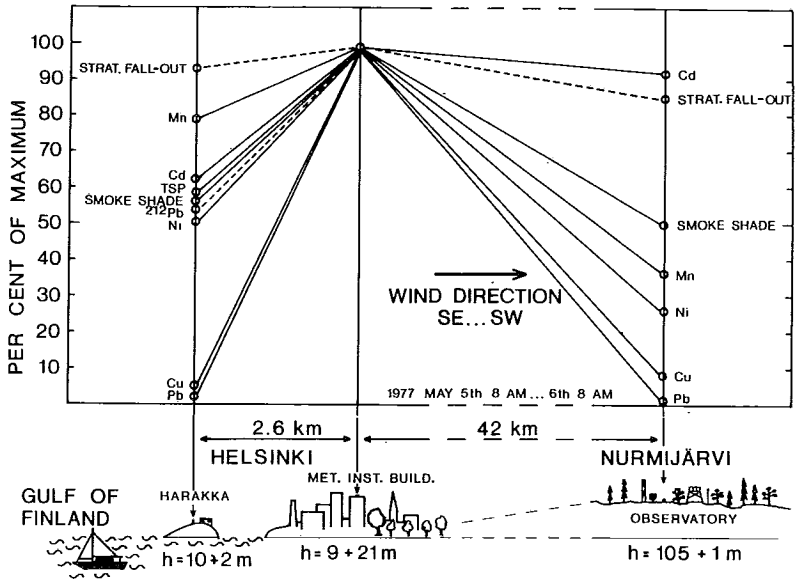

Fig. 14. Simultaneous relative (highest value = 100) average concentrations for a number of air components at Harakka, at the roof of the Meteorological Institute, and at the Nurmijärvi Observatory, from 8^h to 8^h on 5 and 6 May 1977. The absolute values corresponding to the index 100 were: Pb: 301, Cu: 81.3, Ni: 18.9, Cd: 0.32, Mn: 140, all in ng/m^3; TSP: 153 μg/m^3, smoke shade: 5.5 (in an index range of 0...6), ^{212}Pb: 2.8 dpm/m^3, stratospheric fall-out: 0.71 dpm/m^3.

Figures 16 and 17 show two more situations in which a southerly wind was crossing the sea to Harakka. On 31 August, a warm moist air mass was moving slowly over South Finland and on 6 September, a strong cyclonic wind from the SW was blowing. The general features were nearly the same here as in Figures 13 and 14. The only puzzling aspect was the higher concentration of long-lived radionuclides at Harakka on 31 August. We have found no explanation for this and the difference remains an uncertainty factor in these two samples.

Only one case of a land wind was studied (Fig. 15), because a coke heating plant 100 m NW of the sampler feeds it abnormal amounts of fly ash. Measurements of the three simultaneous aerosol samples revealed that the ^{212}Pb activity, which was determined from the surface of the undivided filters, was the same at all three stations. This was expectable because the northerly wind was turbulent and strong. The ^{106}Ru-activity, which was measured from the solubilized half of the sample, was also the same allowing for the errors inherent in the method. Quite expectably, the lead concentration increased as the air moved downtown from the Meteorological Institute to Harakka, but the excessive increase of the other components must be

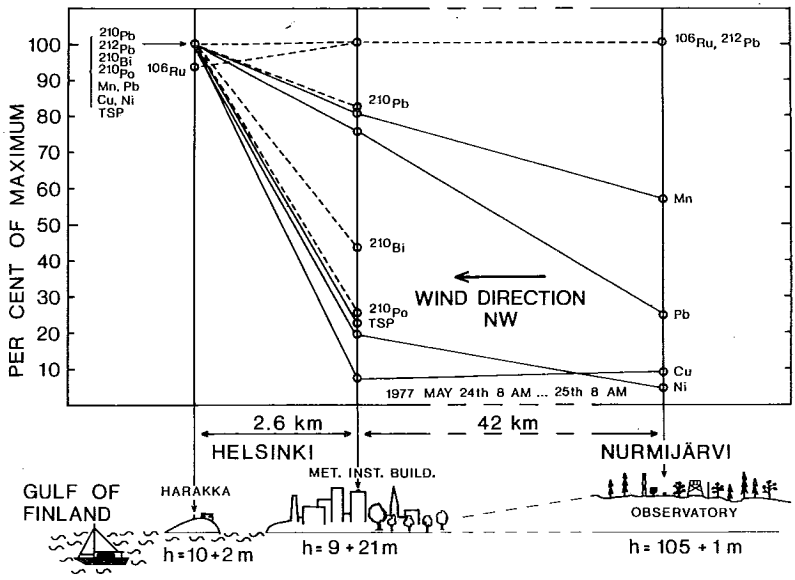

Fig. 15. Simultaneous relative (highest value = 100) average concentrations for a number of air components at Harakka, at the roof of the Meteorological Institute, and at the Nurmijärvi Observatory from 8^h to 8^h on 24 and 25 May 1977. The absolute concentrations corresponding to index 100 were: Cu: 141, Ni: 26, Mn: 21, Pb: 68, all in ng/m^3; TSP: 49 μg/m^3, ^{106}Ru: 0.97 dpm/100 m^3, ^{210}Po: 0.199 dpm/100 m^3, ^{210}Bi: 0.74 dpm/100 m^3, ^{210}Pb: 0.60 dpm/100 m^3, ^{212}Pb: 1.31 dpm/m^3.

attributed to fly ash from the adjacent heating plant. TSP, Ni and Cu increased almost in parallel as could be expected. Both ^{210}Po and ^{210}Pb increased by around 0.17 dpm/100 m^3, whereas ^{210}Bi, grew by 0.42, i.e. three times more. This points to a fractionation phenomenon observed earlier in the ^{210}Pb radionuclide series (COLES *et al.* [3]): the highly volatile ^{210}Po and ^{210}Pb condense on finer particles and are carried farther away by the wind, whereas ^{210}Bi is enriched in heavier fly-ash particles.

Change in pollution with air stability: We found above that the air arriving in Helsinki from the sea after traversing 800 to 2000 m of almost pure residential area, doubled or tripled its concentration of TSP and some of the metals determined.

DEMUYNCK *et al.* [5] in Ghent, Belgium used another method of distinguishing local from advective pollution: they watched relative changes in aerosol composition with varying stability conditions and found that they could divide the components into five groups. For example, they discovered a local anthropogenic group including metals such as Cu, Cd, Sb, In, Ag, and Hg, which displayed a pronounced peak under

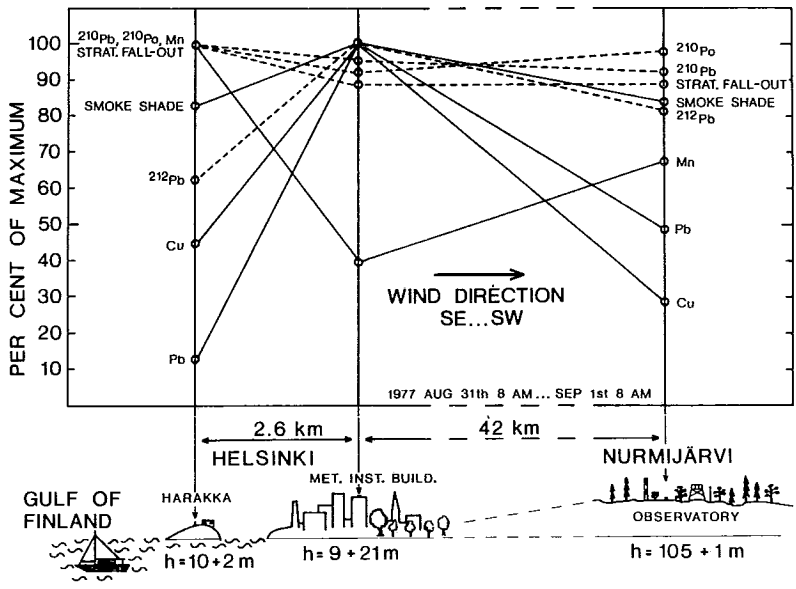

Fig. 16. Simultaneous relative (highest value = 100) average concentrations for a number of air components at Harakka, at the roof of the Meteorological Institute Building and at the Nurmijärvi Observatory from 8^h to 8^h on 31 August and 1 September 1977. The absolute concentrations corresponding to the index 100 were: Pb: 152, Cu: 29, Mn: 26, all ng/m^3; smoke shade: 3.0 (in an index range of 0...6), ^{212}Pb: 2.14 dpm/m^3, stratospheric fall-out: 0.33 dpm/m^3, ^{210}Po: 0.178 dpm/100 m^3, ^{210}Pb: 2.21 dpm/100 m^3.

stable conditions. Another group – F, V, Cr, Zn, Cs, I, SO_4^{2-}, NH_4^+, NO_3^- and benzene-extractable organics – correlated with TSP and were classed as »elements with mainly distributed pollution sources». Sodium and chlorine were found to increase with stronger winds from the west and north, indicating a marine influence.

In applying the above method, we ran into the difficulty of finding a period with changing wind speed and/or stability conditions, but with essentially the same wind direction. In Helsinki, land and sea breezes make such periods rare.

April 12th to 15th case: In our first period under study, 12 to 15 April, the above requirements were not quite fulfilled and we were faced with the expectable difficulties of interpretation. The period began with a warm, moist SE wind, which periodically caused rains when it met with a colder cyclonic stream from SW. The mean wind speed then decreased resulting in fog with light drizzle at the end of the period. A high ^{210}Pb-concentration was typical of the continental air mass brought in from the SE by a high pressure centre over northern Russia.

From 12th to 13th April, when the mean wind speed decreased, Pb, Cu and ^{210}Po increased, but there was almost no change in ^{212}Pb, TSP and Mn (Fig. 18).

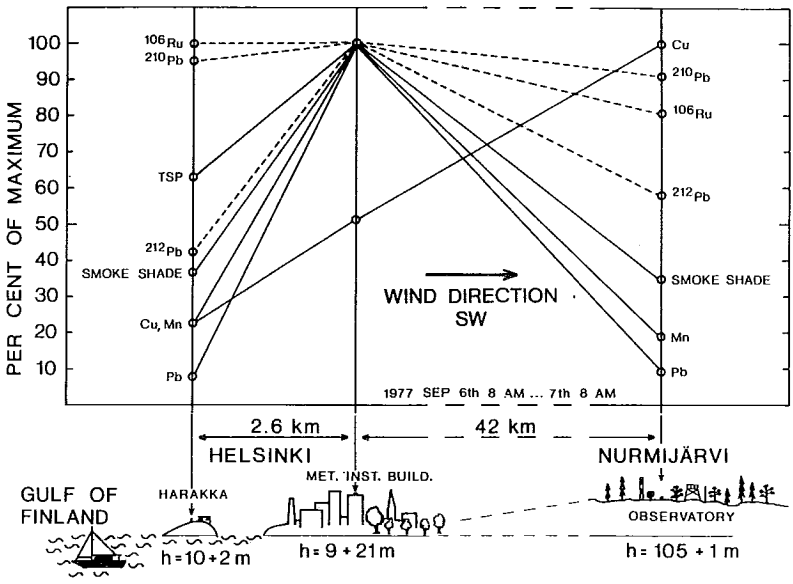

Fig. 17. Simultaneous relative (highest value = 100) average concentrations for a number of air components at Harakka, at the roof of the Meteorological Institute building, and at the Nurmijärvi Observatory from 8^h to 8^h on 6 and 7 September 1977. The absolute concentrations corresponding to the index 100 were: Pb: 146, Cu: 53, Mn: 23, all in ng/m^3; smoke shade: 2.8 (in an index range of 0...6), TSP: 44 µg/m^3, ^{212}Pb: 1.34 dpm/m^3, ^{210}Pb: 0.86 dpm/100 m^3, ^{106}Ru: 1.39 dpm/100 m^3.

^{222}Rn, which is often used as an index of stability, decreased. The slight change in wind direction towards the S and SW on 13th April probably indicated a temporary intrusion of westerly maritime air with lower concentrations of soil-derived components such as ^{222}Rn, ^{212}Pb, and Mn. This is borne out by an increase in the ^{210}Bi/^{210}Pb ratio.

On 14th April a high pressure ridge had developed with greater subsidence and stability, accompanied by a sharpish increase of ^{106}Ru descending from upper air layers. The concentration of all the components measured rose, except for ^{212}Pb. The reason for the decrease in the latter was a lack of local ^{220}Rn (Tn) exhalation during this season. Substantial exhalation does usually not start before the end of April, when the snow melts and the ground begins to dry out.

Wash-Out Ratio: The dimensionless ratio, concentration in rain (ng/kg) divided by concentration in air (ng/kg), can be expected to be higher for elements more dispersed in altitude – for example, when the source is distant – than for local pollution. This wash-out ratio for 12th and 13th April was 260 for Pb, 1,100 for

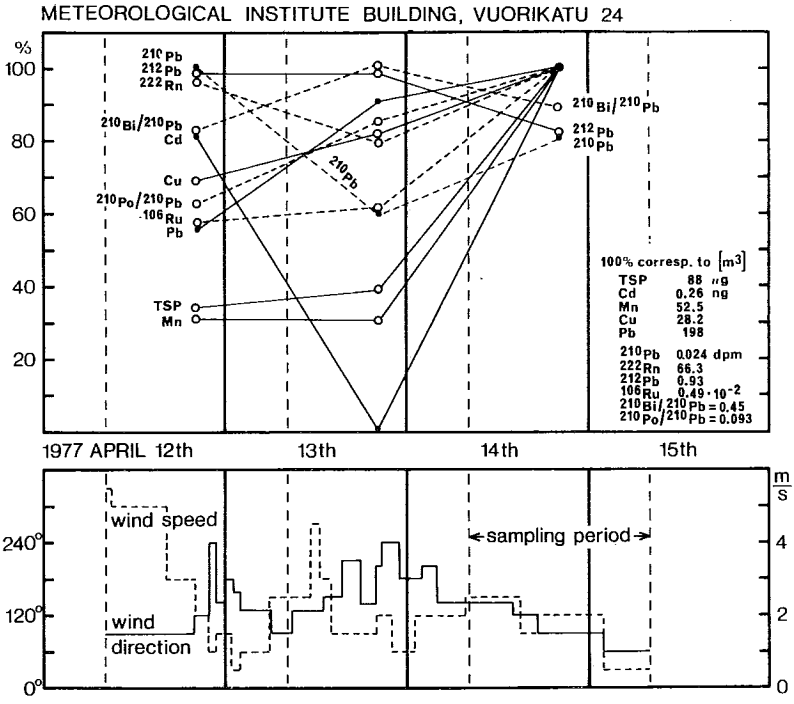

Fig. 18. Daily relative average concentrations of a number of air components observed on the roof of the Meteorological Institute, Vuorikatu 24, Helsinki between 8^h and 8^h on 12th to 15th April 1977. The highest daily average of each component during this period was indexed at 100 % for comparability.

Mn, 1,000 for ^{210}Pb, 2,700 for old fission products, and 10,000 for Cu. On the third day of the period, April 14th, which was stable with fog and drizzle, all the values were higher: Pb: 1,900, Mn: 8,000, ^{210}Pb: 3,800, and Cu: 16,000. The reason was apparently that the rain was now forming in a much lower air layer. However, we do not understand why the copper values were so abnormally high.

The May 2nd to 6th case: During the above period in April even the highest concentrations of each component in central Helsinki were relatively low, so we realized that it was almost impossible to judge to what extent the air components had already increased with the growing stability of the air before reaching the urban area. Between 2nd and 6th May, therefore, we also studied the simultaneous situation at Harakka, which lay upwind of the urban area during that period.

The weather on 2nd to 6th May, (Fig. 19) was similar to the April period. A critical difference was that the sea was now ice-free and conductive cooling had

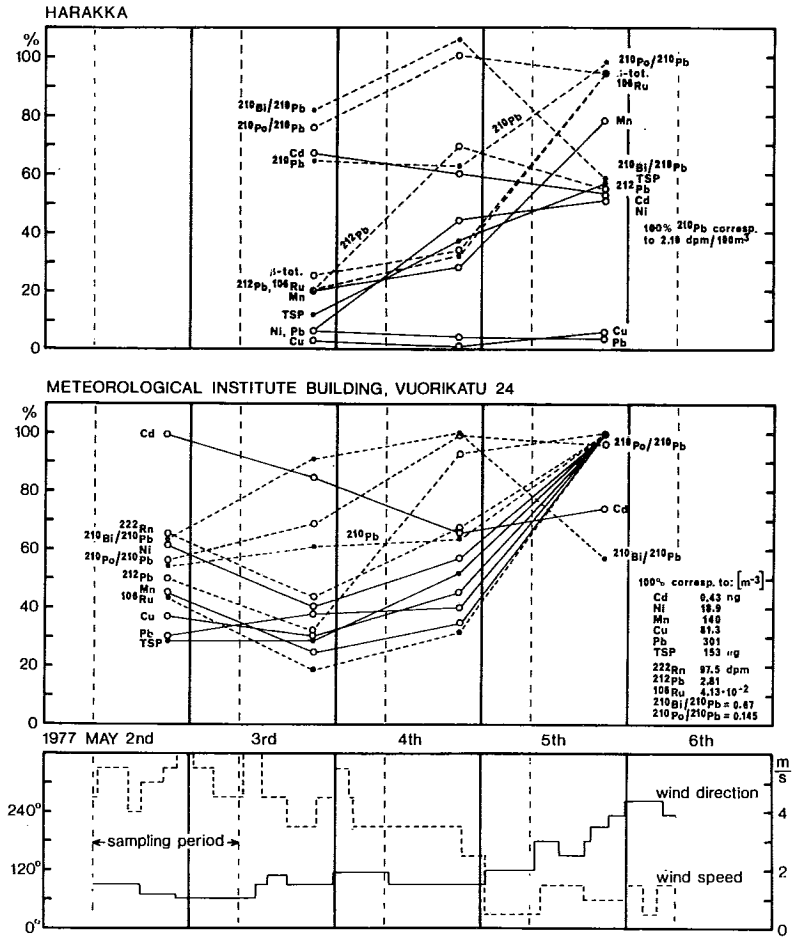

Fig. 19. Daily relative average concentration of a number of air components observed simultaneously at Harakka and the Meteorological Institute roof between May 2nd 08^h... 6th 08^h 1977. The highest daily average of each component at the Institute during this period, was indexed at 100 for comparability.

caused an intense shallow inversion layer over the urban area. The concentrations of most components on the last day of the May period were now double or triple the maxima in the April period.

The relevance of the information offered by the radioactive components measured here is apparent. Since both ^{106}Ru determined from the solubilized part of the aerosol sample and long-lived beta activity counted from the non-destructed half of the air filter were the same at Harakka as at the Institute, we could be

sure that sampling and chemical treatment had not caused differences. Ni, and to a great extent Mn, Cu, Pb and TSP, followed the variation of ^{222}Rn at the Institute. On comparing this with Harakka (Fig. 19, upper part) we find that nearly all the Cu and Pb and roughly 50 % of the Ni and TSP, but only a minor part of the Mn had come from the urban area.

The clear decrease in all the non-local components except ^{210}Pb on 3 rd May was caused by a temporar influx of arctic air. The slight increase of ^{210}Pb despite the ^{222}Rn decrease reflects the arctic origin of the air. In the north ^{222}Rn decreases owing to lack of sources, whereas long-lived ^{210}Pb accumulates. The high ^{210}Pb/^{222}Rn ratio therefore denotes a long residence time for both the radioactive lead and the adherent aerosol. The same applies to the highish ^{210}Bi/^{210}Pb and ^{210}Po/^{210}/Pb.

On the following day, 4th May, the age indicators ^{210}Bi/^{210}Pb and ^{210}Po/^{210}/Pb displayed even higher values but now evidently for another reason. The anticyclonic character of the air mass with its stability and subsidence was enhanced, as can also be seen from the increased concentration for the old fission product ^{106}Ru, descending from upper air layers. But it is no paradox that the next day, 5th May, when the concentration of ^{106}Ru was even higher, the age indicators now pointed to a lower age. The difference was that on 5th May the subsiding part of the ^{210}Pb and the aerosol constituted only a small fraction of the total in the ground-surface air. In fact the aerosol and ^{210}Pb samples were young on the average.

The behaviour of ^{212}Pb (ThB) is informative. Only a small part of its rapid increase on 5th May was local in origin, as can be seen from the Harakka diagram. The next day, when the wind almost died out, the ^{212}Pb activity at Harakka decreased, apparently due to radioactive decay during its passage over the Gulf of Finland, which now lasted longer. At the same time, Mn, Ni and TSP continued to increase, indicating that their average residence time was longer than the average radioactive life of ^{212}Pb, which is 15.4 hours. The ^{212}Pb at the Institute was slightly higher on May 5th but half of it was now of local origin.

8. *Discussion and conclusions*

We have determined a number of metals in the central of Helsinki air retrospectively between 1962 and 1977. Our first sampling site was at a height of 30 m near a street with heavy traffic (Hämeentie 31). At the beginning of 1967 the site was moved to the roof of the present Meteorological Institute building, at Vuorikatu 24, which was 21 m above the street level, but slightly further away from the main traffic thoroughfare. We feel that the latter site is fairly well suited to

the requirements of a downtown background station for monitoring long-term variations in airborne pollutants.

The limitations of working mainly with a single station are obvious. We have therefore tried to confirm and supplement our observations with wind-direction analyses, comparisons with a temporary station at another site, and a study of the variation of different components with changes in air stability. We have also carried out simultaneous measurement of a number of natural radionuclides, whose air concentrations are only slightly affected by human activity. The latter measurements illustrate and document the average air stability conditions for the sampling period, and often they helped to classify the air mass.

The backbone of our study concisted of measurements of Pb, Cd, Cu, Mn, and Ni in 126 selected daily air filters from Helsinki between 1969 an 1977. The filters were chosen basing on weather maps and original wind-recording graphs. As they were limited to days during which the wind had been blowing from a single direction, the results do not represent average conditions. This deficiency was at least partly compensated by analyzing Pb, Cd, and Cu in complete series of weekly samples for a number of full years. Three of the years selected – 1970, 1973, and 1977 – also served as an unbiased check for the first stage of our project because the weekly air samples were collected on the same roof as the daily samples, but the filter material, chemical wet-ashing procedure and the chemist doing the routine work were not the same. After rearranging the data, we found that the results of the separate projects agreed adequately (Figs. 10 and 11).

High lead concentrations in central Helsinki up to 1970 are the most conspicuous finding. We consider it beyond doubt that the highest concentration, which came from the sector 0...30°, were caused by lead smelters at Tikkurila and not by the main incinerator in Helsinki or other sources. As proof of this statement, we present the following findings:

- In all the cases of high lead concentrations (100...580 ng/m^3) measured at the Nurmijärvi Observatory the wind was found to have come from the direction of the lead smelters in the Tikkurila area. In several of these cases, the wind could not even temporarily have come from the direction of the Helsinki area or its incinerator (MATTSSON and JAAKKOLA [13]).
- ASIKAINEN and BLOMQVIST [1] (1969 and 1970) found very high average Pb concentrations, ranging from 1000 to 4000 ng/m^3 in the air during 3 to 5 day sampling periods when the wind had mainly been from the direction of the Tikkurila lead smelters 3.5 to 4 km SE of their sampler.
- The shape of the concentration-versus-wind-direction configuration for lead (Fig. 10, inset) is not quite the same as for cadmium (Fig. 6 right). The Pb

configuration displays a bulge to the west, whereas the Cd pattern bulges to the east of the sector 0...30°. The lead smelters lie in the sector 5...15°, and the main incinerator in the direction 28°.

After 1970, the lead smelters continued to contribute to the airborne lead in Helsinki, but to a much smaller degree (Fig. 10). In spring 1972 we collected samples of 2.5-month-old snow from ten different areas in and around Helsinki. The only sample with a conspicuously higher-than-average lead content came from the Tikkurila area (MATTSSON and JAAKKOLA [13]).

But in the '60s the lead concentration was also high in all other wind directions. We have found no explanation to this, other than what we suggested in an earlier paper – namely that daily household trash incinerated on-site contained lead in amounts comparable with or higher than that emitted by gasoline-fuelled vehicles (MATTSSON and JAAKKOLA, [13]). The change from on-site to municipal incineration would thus explain the gradual decrease of lead in downtown Helsinki: There were 1300 on-site incinerators in central Helsinki in 1967; ten years later there were less than 100.

It is true the lead content of gasoline was higher in the '60s – approximately 0.7 g per litre, whereas it in the Helsinki area in the '70s has decreased to 0.45 (1978) – and that gasoline-fuelled traffic has decreased rather than increased in central Helsinki since 1970 (HAATAJA [9]), but these differences are too small to explain the radial changes that have occured since 1970.

Other figures may be of equal interest: at the beginning of the '70s some 10 million wine bottles with lead capsules weighing about 7.6 grammes each, were sold annually in the Helsinki area (wine-bottle lead capsules were abolished after 1975). This means a »production» of about 9 kg of lead trash per hour, most of which ended up in on-site or municipal incinerators. This amount is roughly the same as the quantity of lead in gasoline sold per hour in the same Helsinki area. As lead is a very volatile metal, its dispersion into the air by trash burning may be more effective than that due to gasoline combustion.

Our findings with regard to lead give rise to the thought that a series of simple measurements 15 to 20 years ago would have led to actions resulting in a much lower lead level in Helsinki with much less economic stress than changing over to low-lead or lead-free gasoline.

Cadmium concentrations during the '70s were low in central Helsinki. Values of 5 to 10 ng/m^3 were observed only during NNE winds. In the '60s the concentrations were higher and occurred in all wind directions. We have concluded that the Cd came mainly from refuse incineration and thus decreased when on-site trash burning was almost abolished. The cadmium did not come from the lead smelters.

The decrease of airborne cadmium in the 1970s was also due to the fact that industries using cadmium replaced it with other metals or compounds. This substitution took place when the »Itai-Itai» disease in Japan during '60s revealed high environmental toxicity of cadmium.

Of the metals determined, copper displayed the smallest systematic variations. From daily samples taken since 1970 it seems, though, that winds from the direction of the coal-fuelled power stations in the NE have brought significantly higher-than-average Cu concentrations.

Nickel was the only metal found to have an unquestionable seasonal variation: High in winter and low in summer. We concluded that its air concentration correlates with oil consumption.

Manganese correlates with TSP and smoke shade in summer. Probably it is a largely soil-derived component, so not a typical urban pollutant. During the winter season coal-fired power stations also appear to be a potential source.

We also carried out a much more limited study on bromine, antimony, and zinc in weekly samples, half of which were from the '60s, and half from the '70s. We found the bromine air concentration to be fairly constant during the periods studied in 1964, 1967, 1973, and 1977. (The possibility of bromine escape from the air filters during storage must be allowed for).

In the case of antimony we concluded that much of it came from the lead smelters at Tikkurila.

The zinc data series appear to indicate that incineration is a significant contributor in addition to generally distributed sources like windblown dust and vegetation.

But quite apart from lead and cadmium, the air in Helsinki became much cleaner in the '70s. Average TSP values around 1960 were roughly 100 $\mu g/m^3$ (LAAMANEN [11]); the average for 1970 was 65 $\mu g/m^3$ and for 1977 39 $\mu g/m^3$. The last two values were determined for the present study from air filters on the roof of the Meteorological Institute.

The cleaner air was due mainly to the abolition of on-site incinerators but also to the change from local to district heating. The situation now is that many advective components play an important role among the pollutants of central Helsinki. Southerly winds frequently bring in air that is warmer than the sea surface. In the resulting stratified lowest air layer, dispertion is minimal, and we found that up to 50 % of the TSP and a number of other components measured on the Institute roof were already in the air above the sea before they reached the urban area.

The vicinity of water, however, is even more important as a stabilizer of the air inside the city. Being almost surrounded by water and low-lying, Helsinki is

extremely vulnerable to pollution from local emissions. The detrimental effects on air quality of land and sea breeze have been analyzed by OLSSON [18] in the case of Lake Michigan, which is almost as big an area of water as the Gulf of Finland. But in any onshore wind, a shallow layer of unstable air capped by a lid of stable air frequently results when the air is first cooled by conduction above the sea and then mixed from the bottom by the city's own heat, insolation, and the surface roughness in the urban area.

To sum up the levels of several components such as Cd, Cu, Sb and TSP in central Helsinki during the '60s did not differ much from average levels in many other cities in Europe or the U.S.A. They only appear high when compared to the levels in Helsinki in 1977. One exception was lead which up to 1971 was anomaously high, especially considering that the high concentrations were not confined to areas close to traffic routes, but affected a much greater part of the population than lead from automobile exhausts does.

Acknowledgements: We are grateful to the Nessling Foundation for supporting this work financially.

We are especially indebted to Mrs. Maija-Liisa Kohtala who did all the chemical work, including determinations of the metals during the first stage of this work in 1977 and 1978.

Our sincere appreciation goes to Miss Soili Tiainen and Mrs. Säde Lauren, who made the atomic-absorption spectrophotometric analyses during the later stage of our study.

We are indebted to Mrs. Pirkko Karlsson and Mrs. Mirja Savolainen, who treated most of the observational data and to Mrs. Tuula Suortti, who made the drawings, graphs and diagrams.

We are obliged to Mr. R.J. Milton for revising the English Language of our manuscript.

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