Measurement of air pollution in Norilsk

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Abstract: Air pollution, deposition and its accumulation in surface soil were investigated in Norilsk, Russia. Concentrations of SO₂ and NO₂ gas were measured in Norilsk by using passive samplers 29 July-4 August 1993 and 31 July-4 August 1995. SO2 concentrations were more than 100 ppb in downtown Norilsk; the highest value was 260 ppb in 1995. On the other hand, NO₂ concentrations were rather lower than those in Sapporo, Japan. Aerosol chemical species were continuously measured from summer 1993 to summer 1995 at Norilsk Experimental Center in downtown Norilsk. Major components of aerosol chemical species were sulfate $(0.9-16 \mu g m^{-3})$, organics $(1.6-12\mu g m^{-3})$ and elemental carbon $(0.1-4.2\mu g m^{-3})$. The ranges of heavy metal concentrations (ng m³) were Cu, 2-300; Pb, 0.5-83 and Ni, 1-48 with no significant seasonal variations, about ten times more than those in Sapporo. We also collected larch needles, mosses and soil samples to evaluate the deposition and accumulation of the air pollutants. The concentrations of heavy metal and sulfate in larch needles, mosses and surface soil samples decrease with distance from the center of Norilsk. Heavy metal concentrations in deep soil (20-30 cm) were nearly equal to the global mean, whereas the concentrations in surface soil (5-10 cm depth) were several times to hundreds times higher than those in deep soil (20-30 cm depth). This suggests that the emitted pollutant has been deposited and accumulated in surface soil for 40 years, since the nickel-copper smelting companies started operations.

1. Introduction

During more than 70 years, the USSR has developed smokestack industries, which have affected human health and the environment. The complex of nickel-copper smelters in Norilsk (69° N, 89° E) in northwestern Siberia is probably the largest single source of air pollutants in the world. It discharges two million tons of sulfur into the atmosphere per year, along with heavy metals and other hazardous compounds (*e.g.* Green, 1993; Josephson, 1993; Lindene, 1995 and others). It has also been considered to be a major source of Arctic haze (Shaw, 1982). Rahn *et al.* (1983), however, estimated that Norilsk is not a major contributor to Arctic haze. In any case, Norilsk has a large possibility to play an important role in arctic air pollution. Moreover, these air pollutants must eventually be deposited on the ground and cause increase acidity, metal

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and other contaminant concentrations. But, few studies have been done about such problems in Norilsk. The Norilsk nickel complex consists of nickel-copper smelters at Norilsk, copper smelters at Kaierkan and Nadezhda, and coal mine and thermal power plant at Tarnax (Fig. 1). Downtown Norilsk is surrounded with factories. The operations cause that heavy pollution in air, water and soil, forest decline and adverse health effects.

In this study, we first estimated the condition of air pollution in Norilsk by using passive samplers (Okita *et al.*, 1983; Maeda *et al.*, 1994) and continuous aerosol (less than $2 \mu m$) and SO₂ gas samplers. The passive samplers were used for evaluation of distributions of SO₂ and NO₂ concentrations in and around Norilsk for a week. On the other hand, continuous sampling was carried out in the center of Norilsk for evaluation of long-term variation of pollution. We second collected larch needles and mosses as biomonitors for air pollution (*e.g.* Schaug *et al.*, 1990; Berg *et al.*, 1995; Peresedov *et al.*, 1997) to evaluate the deposition of pollutants on the ground and accumulation in surface soil.

2. Experimental procedure

2.1. Measurement of SO_2 and NO_2 concentrations by using passive sampler

The distributions of atmospheric SO₂ and NO₂ concentrations were measured twice by using passive samplers in and around Norilsk from 29 July to 4 August 1993 and from 31 July to 4 August 1995. The sampler consisted of aluminum foil for insulation, POLYFLON filter, reagent soaked paper for absorption of objective gas and two POLYFLON filters in a plastic pot. The absorbent papers were chromatography paper (Advantec TOYO, No. 514 A) in 2×2.5 cm soaked with 2.5% sodium carbonate for SO₂ collection and with 20% triethanol-amine for NO₂ collection. Three passive samplers were simultaneously exposed at each site. After exposure, the soaked paper was unloaded from each sampler and put in distilled-deionized water for extraction. The amount of SO₂ was determined as SO₄²⁻ in the aqueous extract by ion chromatography. And, the amount of NO₂ in the aqueous extract was measured colorimetorically by the NEDA method (Okita *et al.*, 1983).

2.2. Continuous measurement of aerosols and SO_2

The atmospheric aerosols were continuously collected every half-month using filters on the second floor of Norilsk Experimental Center. We used three kind of filters, such as Teflon filters (Sumitomo Fluoropore AF07P) for measurement of water-soluble matter, quartz fiber filters (Palluflex 2500QAST-UP) for carbonaceous particles and Nuclepore filters (Nuclepore co., pore-size $0.4 \,\mu$ m) for heavy metals. Atmospheric aerosols less than $2 \,\mu$ m in diameter were collected on each filter at a flow rate of $5 \,\text{L}$ min⁻¹.

After sampling, the collected aerosols were extracted ultrasonically in distilleddeionized water. We analyzed the concentrations of sulfate $(SO_4^{2^-})$, nitrate (NO_3^-) and chloride (Cl^-) by an ion chromatograph (Yokogawa Electric Works Inc., IC-100, column SAM 3-125), and the concentrations of sodium (Na^+) , calcium (Ca^{2+}) , magnesium (Mg^{2+}) and potassium (K^+) by an atomic absorption spectrometer (Hitachi Inc., 170-30). The ammonium (NH_4^+) concentrations were measured colorimetrically by using the indophenol method (Weatherburn, 1967).

The carbonaceous components on the quartz filters were analyzed by a NC Analyzer (SUMIGRAPH NC-80) and GC-FID (HITACHI 164).

The Nulclepore filters collected atmospheric aerosols which were digested at room temperature in an 1.5 ml HNO₃-0.5 ml HF mixture in a disposable test tube for two days for measurement of metal concentrations (Jalkanen and Hasanen, 1996). After digestion, we analyzed them by inductively coupled plasma-mass spectrometry (ICP-MS: Yokogawa Analytical Systems HP 4500).

2.3. Sampling and analyses of larch needles, mosses and soil

Larch (Larix siberica) needles, mosses (Polytrichum sp., Dicranum sp. and Aulacomiun sp. etc.) and soil samples were collected around Norilsk in the summer of 1996. Some shoots with larch needles were collected in a 20×30 cm polyethylene bag at Moss samples in 20×20 cm in size were also collected in a polyethylene bag at each site. Soils at different depths were sampled in 250 ml polypropylene bottles under each site. the moss. All samples were transported to Japan, and dried and pulverized by a mill (Fritz Pulvurisette 6) to powder less than several tens μ m in diameter at every site. Concentrations of major elements such as Si, Al, Fe and Cu were analyzed by fluorescent X-ray emission analyzer (Horiba MESA-100). For measurements of trace elements, sub-samples (0.1 g) were digested in 3 ml HNO_3 and 0.5 ml HF in TeflonTM pressure decomposition vessels by microwave digester (CEM MDS-2000). After dilution, the concentrations of trace metals in the sample solutions were analyzed by ICP-MS. Relative standard deviations in the analyses were below 5%.

3. Results and discussion

3.1. Distributions of SO_2 and NO_2 concentrations by passive samplers

Figures 1 and 2 show the distribution of mean concentrations of SO₂ and NO₂ from 29 July to 4 August in 1993 in the Norilsk area. Figures 3 and 4 also show the distributions from 31 July to 4 August in 1995. SO₂ concentrations in 1993 were 18 ppb in Tarnax and 21 ppb in Oganer. In downtown Norilsk, SO₂ concentrations in 1993 ranged from 11 to 44 ppb. SO₂ concentrations in 1995 were much higher than those in 1993 due to the stagnant condition. In northern 4 sites in the downtown in 1995, the SO₂ concentrations exceeded 100 ppb, and reached up to 260 ppb. For reference, in Shenyang (China) lead-smelters, SO₂ concentrations measured by using passive samplers ranged from 36 to 137 ppb in 1994 (Kato *et al.*, 1996). As Kato *et al.* (1996) pointed out, SO₂ concentrations in Norilsk depend on the amount of the emission, weather condition and location. In Sapporo, the highest value of SO₂ is at most 20 ppb (Maeda *et al.*, 1994).

On the other hand, NO₂ concentrations were less than 10 ppb in 1993 and 1995, which was rather lower than those in Shenyang (26–39 ppb; Kato *et al.*, 1996) and Sapporo (less than 30 ppb in summer; Maeda *et al.*, 1994).

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Fig. 1. SO₂ and NO₂ concentrations (ppb) in Norilsk area measured by using passive samplers from 29 July to 4 August 1993.



Fig. 2. SO₂ and NO₂ concentrations (ppb) in the center of Norilsk measured by using passive samplers from 29 July to 4 August 1993.



Fig. 3. SO₂ and NO₂ concentrations (ppb) in Norilsk area measured by using passive samplers from 31 July to 4 August 1995.



Fig. 4. SO₂ and NO₂ concentrations (ppb) in the center of Norilsk measured by using passive samplers from 31 July to 4 August 1995.

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Sector Contractor Contractor Contractor										
	E.C.	Org.	SO42	Cl	NO	NH	Na⁺	Caz+	Mg ²⁺	K⁺
1993 AUG.f	1.7	5.6	3.7	0.14	0.19	0.26	0.15	1.6	0.088	-
AUG.s	1.2	2.7	2.1	0.077	0.10	0.65	0.089	0.41	0.041	_
SEP.f	1.9	3,7	3.7	0.17	0.16	0.48	0.099	1.1	0.060	-
SEP.s	1.8	4.0	2.9	0.10	0.16	0.15	0.071	0.42	0.045	
OCT.f	4.2	12	2.8	0.10	0.11	0.60	0.14	0.64	0.045	-
OCT.s	1.1	3.3	4.0	0.24	0.22	0.18	0.25	1.2	0.11	-
NOV.f	2.0	5.9	5.8	0.16	0.49	1.1	0.24	1.1	0.12	-
NOV.s	1.5	3.6	3.3	0.27	0.17	0.79	0.29	0.47	0.082	-
DEC.f	2.3	5.4	4.8	0.044	0.18	1.1	0.12	0.22	0.067	
DEC.s	2.8	4.2	3.1	0.12	0.14	0.76	0.16	0.71	0.074	-
1994 JAN.f	1.0	2.6	2.2	0.011	0.064	0.52	0.090	0.094	0.030	-
JAN.s	2.7	3.8	5.9	0.052	0.20	0.95	0.18	1.9	0.076	-
FEB.f	3.4	4.6	6.9	0.0043	0.13	1.1	0.17	0.65	0.071	-
FEB.s	2.7	4.0	5.0	0.015	0.27	1.2	0.16	0.64	0.061	-
MAR.f	2.0	3.4	6.8	0.046	0.10	1.5	0.17	0.85	0.085	0.24
MAR.s	2.8	3.8	8.1	0.076	0.11	1.5	0.14	2.2	0.082	0.34
APR.f	2.2	3.5	12	0.021	0.050	1.1	0.18	0.53	0.080	0.17
APR.s	3.4	5.1	14	0.016	0.038	1.9	0.18	0.95	0.14	0.30
MAY.f	1.5	2.9	16	0.049	0.022	1.3	0.20	0.62	0.12	0.48
MAY.s	1.3	2.4	15	0.14	0.039	1.5	0.13	0.58	0.11	0.22
JUN.f	0.93	2.9	8.6	0.019	0.045	1.8	0.074	0.25	0.028	0.097
JUN.s	2.5	8.0	9.7	0.11	0.11	1.8	0.14	1.0	0.052	0.23
JUL.f	0.11	1.9	12	0.075	0.094	0.24	0.12	1.3	0.074	0.28
JUL.s	1.8	4.0	0.89	0.028	0.054	0.88	0.040	0.30	0.016	0.086
AUG.	0.59	2.2	5.0	0.025	0.055	-	0.15	0.46	0.040	0.070
SEP.f	1.3	2.4	6.8	0.014	0.042	1.5	-		-	
SEP.s	0.87	2.3	3.2	0.041	0.052	0.99	0.13	0.57	0.054	0.13
OCT.f	0.84	2.4	8.9	0.037	0.050	1.4	0.27	1.0	0.11	0.37
OCT.s	2.5	2.6	3.5	0.073	0.064	0.97	0.21	0.79	0.088	0.15
NOV.	0.98	3.2	9.3	0.13	0.078	1.3	0.56	0.78	0.11	0.21
DEC.	1.8	5.3	13	0.14	0.077	2.4	0.46	1.2	0.087	0.54
1995 JAN.	1.1	1.6	11	0.083	0.061	1.3	0.52	0.62	0.13	0.39
FEB.	2.1	2.5	12	0.0085	0.044	2.2	0.19	0.59	0.11	0.34
MAR.	2.7	3.9	4.5	0.021	0.085	1.8	0.28	0.51	0.11	0.27
APR.f	1.8	2.9	6.4	0.024	0.088	1.1	0.83	0.59	0.10	0.40
APR.s	2.0	3.1	5.3	0.11	0.058	1.2	0.84	0.62	0.14	0.25
MAY.f	1.3	2.6	4.9	0.039	0.14	0.48	0.74	0.74	0.14	0.30
MAY.s	1.5	3.0	7.1	0.034	0.057	0.98	0.50	0.90	0.16	0.59
JUN.f	1.2	3.4	7.1	0.041	0.21	0.66	0.62	0.99	0.17	0.44
JUN.s	1.4	3.3	5.0	0.018	0.047	0.23	0.29	0.71	0.13	0.29
JUL.f	1.7	3.3	6.6	0.046	0.16	0.37	0.27	1.4	0.18	0.40
JUL.s	1.2	2.3	11	0.031	0.033	0.41	0.64	1.3	0.27	0.54
max.	4.2	12	16	0.27	0.49	2.4	0.84	2.2	0.27	0.59
min.	0.11	1.6	0.89	0.0043	0.022	0.15	0.040	0.094	0.016	0.070
mean.	1.8	3.7	6.9	0.07	0.11	1.0	0.27	0.82	0.095	0.30

Table 1. Concentrations of aerosol chemical species collected in Norilsk ($\mu g/m^3$).

- : no data

3.2. Concentrations of SO_2 gas and aerosol chemical species

Table 1 shows the concentrations of aerosol chemical species from August 1993 to July 1995. The mean concentrations in μg m⁻³ were elemental carbon, 1.8; organic carbon, 3.7; SO₄², 6.9; Cl, 0.07; NO₃⁻⁻, 0.11; NH₄⁺, 1.0; Na⁺, 0.27; Ca²⁺, 0.82; Mg²⁺, 0.095 and K⁺, 0.3 with no significant seasonal variations. Sulfate concentration (1–16 μg m⁻³) was occasionally distinctively higher than in Sapporo (monthly mean concentration is 1–3 μg m⁻³), sometimes extremely higher than in Alert in the Canadian Arctic (1–2.5 μg m⁻³) in winter (Barrie and Bottenheim, 1991).

SO₂ concentrations in each half-month from April to December 1995 are shown in Fig. 5. The concentrations were extremely high, up to 111 ppbv in the first half of July and 140 ppbv in the first half of December 1995, consistent with the measurement results by passive sampler. The smelters emit sulfur into the atmosphere primarily as SO₂ (sulfate fraction is less than 2%), and its transformation rate is at most 1% h⁻¹ (Tuovinen *et al.*, 1993), so that there was not enough time to transform sulfur dioxide to sulfate. The concentrations of SO₂ and sulfate in Norilsk were higher than those

1993 AUG.f - NOV.f <
AUG.s. 184 0.018 0.60 11 311 2.1 26 87 9.2 0.49 1.2 0.79 0.49 13 SEP.f. 516 0.073 2.9 37 795 17 73 78 20 0.50 2.1 2.4 0.54 17 SEP.s 765 0.11 0.80 16 834 19 22 85 19 0.44 1.8 3.8 0.46 18 OCT.f. -
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OCT.s 414 0.071 6.2 23 733 9.1 53 50 26 0.56 1.2 1.6 0.59 15 NOV.f 426 0.13 5.5 22 558 20 67 114 33 1.7 3.8 2.6 1.7 51 NOV.s 200 0.17 17 22 657 5.6 55 81 35 0.97 0.49 1.5 1.5 45 DEC.f .
NOV.f 426 0.13 5.5 22 558 20 67 114 33 1.7 3.8 2.6 1.7 51 NOV.s 200 0.17 17 22 657 5.6 55 81 35 0.97 0.49 1.5 1.5 45 DEC.s 223 0.089 2.3 18 312 8.7 59 66 26 1.7 1.2 1.5 1.1 27 JBANS 454 0.32 3.3 2 537 12 55 71 27 4.1 0.54 3.2 0.99 43 FEB.f -<
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JUN.f 259 0.071 * 6.8 309 4.0 29 170 13 0.51 0.29 1.3 0.90 28 JUN.f 259 0.071 * 6.8 309 4.0 29 170 13 0.51 0.29 1.3 0.90 28 JUN.s 648 0.10 0.93 11 739 5.8 29 172 98 0.63 2.2 2.8 1.2 54 JUL.f 697 0.096 3.7 25 785 12 86 339 69 1.4 6.8 2.5 2.0 53 JUL.s 161 0.018 5.3 7.2 443 3.5 20 34 4.7 * 1.5 0.59 0.13 6.4 AUG. - - - - - - - - - - - - - - - - - -<
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<u>La La</u> 317 0.065 2.1 12 270 0.2 40 07 10 0.00 3.0 3.6 0.35 22
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MAD 216 017 0.2 19 007 1.3 97 100 00 1.0 4.4 1.0 1.0 09
ADD f 270 0.057 2.4 11 300 7.1 63 261 24 0.78 8.0 2.1 16 55
APR 177 0.30 11 18 389 7.5 73 261 28 0.80 10 14 13 57
MAY 1 330 0.008 * 8.0 360 71 22 126 92 031 16 42 0.66 25
MATL: 359 0.025 0.0 15 522 12 52 0.01 1.0 4.2 0.00 20 20 20 20 20 20 20 20 20 20 20 20 2
IIIN f 507 0.008 64 42 1137 12 136 570 67 13 66 34 20 66
max 1213 0.32 17 42 1937 20 186 655 98 41 16 51 36 90
min 110 0.018 0.39 68 213 21 20 34 47 0.31 0.20 0.01 64
man 404 011 37 19 608 10 69 180 29 11 42 23 13 38

Table 2. Metal concentrations in atmospheric aerosols collected in Norilsk (ng/m^3) .

- : no data *: no detection

measured by Virkkula *et al.* (1999) in Sevettijärvi, $\sim 60 \text{ km}$ WNW of Nikel, a large pollution source on the Kola Peninsula. The difference is assumed to have been caused by both differences of the amount of emission and distance from the source area.

Table 2 shows atmospheric metal concentrations such as Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Cd and Pb from August 1993 to July 1995. The ranges and mean concentrations of Ni, Cu and Pb in ng m⁻³ were Ni, 20–186, 69; Cu, 34–655, 180 and Pb, 6.4–90, 38. In Sapporo, for reference, annual mean concentrations in ng m⁻³ measured by the National Atmospheric Sampling Network in 1992 were Ni, 2.8; Cu, 27 and Pb, 15. Thus the concentrations of Ni, Cu and Pb in Norilsk were ten times higher than those in Sapporo. Virkkula *et al.* (1999) also measured the concentrations of various elements at Sevettijärvi. The comparison with the result shows that the concentrations of most heavy metals in Norilsk were more than one order higher than those in Sevettijärvi, originated from the Kola Peninsula. The difference was also due to the differences for the amount of emission and distance from the source area.



Fig. 5. Seasonal variation of SO₂ concentration (ppb) in Norilsk from April to December in 1995.

3.3. Deposition and accumulation of air pollutants

Larch needles, mosses and soil samples were collected at 12 sites around Norilsk in summer 1996 to evaluate the deposition and accumulation of pollutants on surface soil (Fig. 6). We collected samples at six sites between Norilsk and Dudinka, about 80 km to the west from downtown, and at six sites between downtown and Lama Lake about 100 km to the east. Figure 7 shows heavy metal concentrations in larch needles at each site. Not only nickel and copper but also lead and cobalt concentrations seemed to decrease with distance from the industrial area. Sulfate showed the same tendency as the heavy metals.

Peresedov *et al.* (1997) reported that heavy metal and rare-earth element concentrations in pine needles and soil tended to decrease with distance from a phosphatic fertilizer factory on the Kola Peninsula. Jaffe *et al.* (1994) showed that a large fraction of emissions from nickel and copper smelting in Monchegorsk on the Kola Peninsula



Fig. 6. Sampling sites around Norilsk.



Fig. 7. Heavy metal concentrations in larch needles at each site ($\mu g/g$).



Fig. 8. Concentrations of ionic species in moss and soil (mg/g-dry soil).

was locally deposited due to sedimentation of large particles (more than $2\mu m$). An other study using a moss technique by Reimann *et al.* (1997) concluded that pollutant emitted from the Russian nickel mining and smelting industry (Monchegorsk and Nikel) reached background levels within about 150 km.

Figure 8 shows amounts of sulfate, nitrate and chloride contained in 1-g of dry soil and moss at different depths at Site 2 and Site 4, as shown in Fig. 6. Sulfate contained in moss at Site 2 was four times higher than that at Site 4. Sulfate concentrations in soil were much less than those in mosses. But the sulfate concentrations in surface soil (5-10 cm depth) were about 5 times higher than those in the deepest soil (20-30 cm depth).

Figure 9 shows the depth profiles of heavy metal concentrations in moss and soil at Site 2, Site 4, Site 7 and Site 12. The metal concentration in ppm was respectively divided by silicon concentration in percent for normalization at each site. The concentrations of copper, nickel and lead in the soil at 5–10 cm depth were more than a few to hundred times higher than those at 20–30 cm depth at Site 2, Site 4 and Site 7. On the other hand, the concentrations of heavy metals in the deep layer (20–30cm) were nearly equal to those in global-mean soil (Bowen, 1966). Thus, we can estimate that the concentrations of metals in soil in Norilsk were the same as those in global-mean soil before industrialization. Thus, the factories started to work in 1960, and the emitted



Fig. 9. Concentrations of heavy metals in moss and soil samples at different depths at Sites 2, 4, 7 and 12 [(ppm)/Si (%)]. G.M. means the ratio in global mean soil by Bowen (1966).

pollutants have been deposited and accumulated in the surface soil for 40 years.

4. Conclusions

Air pollution, deposition and its accumulation in surface soil were investigated in Norilsk. SO₂ concentrations in downtown were more than 100 ppb higher than those in the suburbs, and the highest value was 260 ppb in 1995. On the other hand, NO₂ concentrations were rather lower than those in Sapporo. Major aerosol components were sulfate (0.9–16 μ g m⁻³), organics (1.6–12 μ g m⁻³) and elemental carbon (0.1– 4.2 μ g m⁻³) from summer 1993 to summer 1995. Sulfate concentrations were high in spite of insufficient time to transform sulfur dioxide to sulfate. The ranges of heavy metal concentrations (ng m⁻³) were Cu, 2–300; Pb, 0.5–83 and Ni, 1–48 with no significant seasonal variations, which were about ten times more than those in Sapporo.

We also collected larch needles, mosses and soil samples to evaluate the deposition and accumulation of the air pollutants. Consequently, the emitted pollutants are supposed to have been deposited and accumulated in the surface soil for 40 years, since the nickel-copper smelting companies started to work. So it is necessary to install gas cleaning equipment or improve production processes.

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