C-1 International Co-operative Survey to Clarify the Trans-boundary Air Pollution Across the Northern Hemisphere (Abstract of the Final Report)

Contact Person Kentaro Murano
Team Leader
Atmospheric Environment Research Division
National Institute for Environmental Studies
Onogawa 16-2, Tsukuba, Ibaraki, 305-8506 Japan
Tel:+81-29-850-2537 Fax:+81-29-850-2579
E-mail: murano@nies.go.jp

Budget for FY2002-2004 62,858,000 Yen (**FY2004**; 19,788,000 Yen)

Key Words East Asia, Acid Rain, Ground-based Observation, Emission Inventory
Source-receptor Analysis,

1. Introduction

To tackle the trans-boundary air pollution across the continent is urgent issues over the world. Air pollutants emitted in Europe and North America bring the air pollution over the North Pole and both continents, and these issues are common ones both Europe and North America. Not only Europe and North America are involved to tackle these issues individually, but also they are co-operating to tackle these issues. It is necessary to conduct ground-based observation to monitor air pollutants such as sulfur and nitrogen comounds, heavy metals and POPs in Siberia to clarify the trans-boundary air pollution from Europe to Asia. These observations provide the basic data as upstream of East Asia for the trans-boundary air pollution in East Asia.

The quantification of trans-boundary air pollution between China, Korea and Japan is high priority issues for the administration. It is necessary to revise or to compile the emission inventory of air pollutants such as VOC, ammonia and heavy metals in East Asia. New generation source-receptor matrix of air pollutants including multi-components with smaller grid sizes can provide the quantitative data on trans-boundary air pollution between China, Korea and Japan, contribute to administrative policy. The restricted deposition data compiled with Acid Deposition Monitoring Network in East Asia(EANET) activities can be analyzed with acid deposition transport model to clarify the distribution of acid precipitation, contribute to the EANET activities.

2. Reseach Objectives

Clarification of trans-boundary air pollution in the Northern Hemisphere is research objective in this project. The trans-boundary air pollution from Europe to Asia is evaluated with the research to evaluate the atmospheric environment at East Siberia. Gas, particulate matter concentration measurement and collection of precipitation and deposition of mercury and lead as well as the lead isotope determination are conducted at remote site (Mondy), rural site (Listvyanka), urban site (Irkutsk) in East Siberia and Primorskaya (PR) in Primorsky region in Russia.

According to the start of full monitoring activity by EANET from 2001, model verification is possible using many monitoring data in the East Asia region. The development of latest emission inventory of air pollutants such as SO_2, NOx, NMVOC and NH_3 with 0.5 degrees spatial resolution covering China, Taiwan, Republic of Korea, North Korea and

Mongolia are the research objective.

Detailed new generation source-receptor analysis of nitrogen oxides including multi-components with smaller grid sizes is developed. The analysis of restricted deposition data compiled with EANET activities with acid deposition transport model can provide the distribution of acid precipitation over East Asia. Since July 2000 till now, Miyakejima volcano, which is located 200km south from Tokyo, has erupted with substantial emission of sulfur dioxide. SO_2 emission was 9 Tg for 1 year from the beginning of the eruption. The amount was comparable to the anthropogenic emission from whole China and 10 times as the emission from Japan. Sulfate concentration increased by 2 times in the PBL over Far East Asia as the result of sulfate production from the volcanic SO_2 in the air. We estimated acidification of precipitation by the volcanic sulfate using a numerical model.

3. Research Method

Russian East Siberia and Primorsky region are located in northeastern part of Eurasian continent. Their atmospheric environment may be influenced by European sources of pollution and affect air quality in Japan. Therefore, it is important to clarify atmospheric environment in these regions in order to evaluate long-range transportation of air pollutants. For these reasons, wet deposition and gas/aerosol concentration were determined at 3 sites (Irlutsk, Listvyanka, and Mondy) in East Siberia and 1 site (Primorskaya) in Primorsky region from 2002 through 2004. Mercury and lead concentration and lead isotopic composition of environmental samples were also determined in these regions as tracers of long-range transportation of air pollutants.

Sample collection and analytical methods in the monitoring station in Russia are as follows:

Collection of wet deposition was carried out with Ogasawara US 320 (diameter 357mm). Collection of gas and aerosol was conducted with 4 stages filter-pack method using NILU filter holder and appropriate filters. Chemical analytical method for deposition, gas and aerosol are as follows:

1) Anion (HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-) : HPLC
2) NH_4^+: Nessler's method, UV/Visible spectrophotometry PV8700, 440nm
3) Ca^{2+}, Mg^{2+}, Na^+, K^+: Atomic absorption spectrophotometry
4) pH: pH meter F-21, Horiba
5) Electric Conductivity: EC-meter, CM-14P TOA

Emissions inventory of air pollutants in East Asia, where China, Taiwan, Japan, Republic of Korea(ROK), Democratic People's Republic of Korea(DPRK), Mongolia in the year 2000 is developed. Air pollutants, SO_2, NOx, NMVOCs, NH_3, as precursors of acidification, sulphate and nitrate, and CO as tracer gas of long range transport air pollution, Suspended Particulate Matter (PM_{10}) as an important element to human health risk, and Hg which is one of the important heavy metals in global scale pollution and China is a large source of it.

China is a area where much amount of many air pollutants emitted, and where drastic change and rapid growth of energy demand reflecting recent economic development, and there is regional deference of emission structure between developed coastal area and inland west area in the country, so our inventory work is carried out intensively on China emissions by province.

The atmospheric transport model including air pollutants emission, chemical transformation, and deposition module was applied to conduct detailed(50 areas) source-receptor analysis. We examined the annual concentration and deposition for nitrogen oxides in East Asia using by a regional chemical transport model (HYPACT) coupled with the

Regional Atmospheric Modeling System (RAMS). The model domain covers the 4,800 km (x) × 4,400 km (y) area in East Asia with horizontal grid spacing 80km. Number of grid points are 60(x) x 55(y) x 23(z) and the top of vertical level is 20km. Numerical simulation has been conducted through one year for 1995.

Gaseous compound, particulate matter and precipitation were collected at Mt. Happo and chemical analysis was conducted. MSSP (reagional-scale Eulerian Model System for Soluble Particles) is used for the modeling study. This model consists of three submodel (meteorological model, chemical transport model and thermo-equilibrium model). For the emission of SO2 from Miyakejima volcano, we used the direct measurement data obtained with Meteorological Agency.

4. Results and Discussion

(1) Evaluation of atmospheric environment in East Siberia and Primorsky region in Russia

Wet deposition and gas/aerosol samples were collected annually at 3 sites (Irlutsk, Listvyanka, and Mondy) in East Siberia and 1 site (Primorskaya) in Primorsky region from 2002 through 2003.

Precipitation was acidified mainly by sulfuric acid. Although sulfate concentration in precipitation was higher comparing with Japan, Europe, and United States, their deposition was smaller than that in these regions due to small precipitation amount. On the other hands, since basic substances neutralized precipitation more significantly in comparison with other regions, precipitation acidity was lower than that in other regions. Seasonal variation of concentration and wet deposition of major components in precipitation shows several pattern, however, wet deposition of sulfate, ammonium, and hydrogen ion were large in summer in all sites.

Sulfur dioxide and sulfate aerosol were major components of acidic substances in the atmosphere in these regions. Sulfur dioxide concentration was high in winter in all sites. Ammonia gas and ammonium aerosol were main components of basic substances in the atmosphere. Emission amount of ammonia gas seemed to be large in summer because the concentration was high in summer in spite of large precipitation amount. Annual mean concentration of ozone monitored at remote site, Mondy, ranged from 43 to 44 ppb with no change of annual mean in the period. Annual mean concentration of acidic and basic substances was same level as or lower than that of low concentration sites in Japan except ammonia gas concentration in Primorskaya. Dry deposition amounts of sulfur compounds (sulfur dioxide and sulfate aerosols), ammonia/ammonium aerosols, and nitric acid/nitrate aerosols estimated by inferential method were higher than that in Japan reflecting small precipitation amount.

Since lead isotopic composition of the snow water collected in East Siberia was reasonable in comparison with the composition determined in Japan, close relationship between both regions were confirmed.

The variation of air concentration in Mondy was compared with that in Rishiri located on the leeward to evaluate long-range transportation of air pollutants. Backward and forward air mass trajectories were estimated in Mondy on typical cases of air concentration, wintertime in which high sulfur dioxide concentration was observed (1), early summer in which high concentration of sulfate and ammonium aerosol was observed, late summer in which low concentration of total sulfur and ammonium compounds was observed (2), and so on (Fig. 1). Air masses in wintertime moved long distance. It was found that winter air masses usually moved from Europe to East Siberia within only 3 days and moved from East Siberia to Japan within 3 days. It seemed to be possible to evaluate the relation of air concentration between two sites considering the residence time of sulfur dioxide in the atmosphere. On the other

hands, it was difficult to explain the relation of both sites in the case of high sulfate and ammonium aerosol concentration in early summer. It may be need to trace more long time for evaluating long-range transportation of aerosols. Air masses in late summer moved short distance, therefore, low concentration of total sulfur and ammonium aerosols in the period seemed to be caused by local emission sources and meteorological condition in both sites.

These monitoring results and analytical procedures may be also useful for evaluating EANET monitoring data.

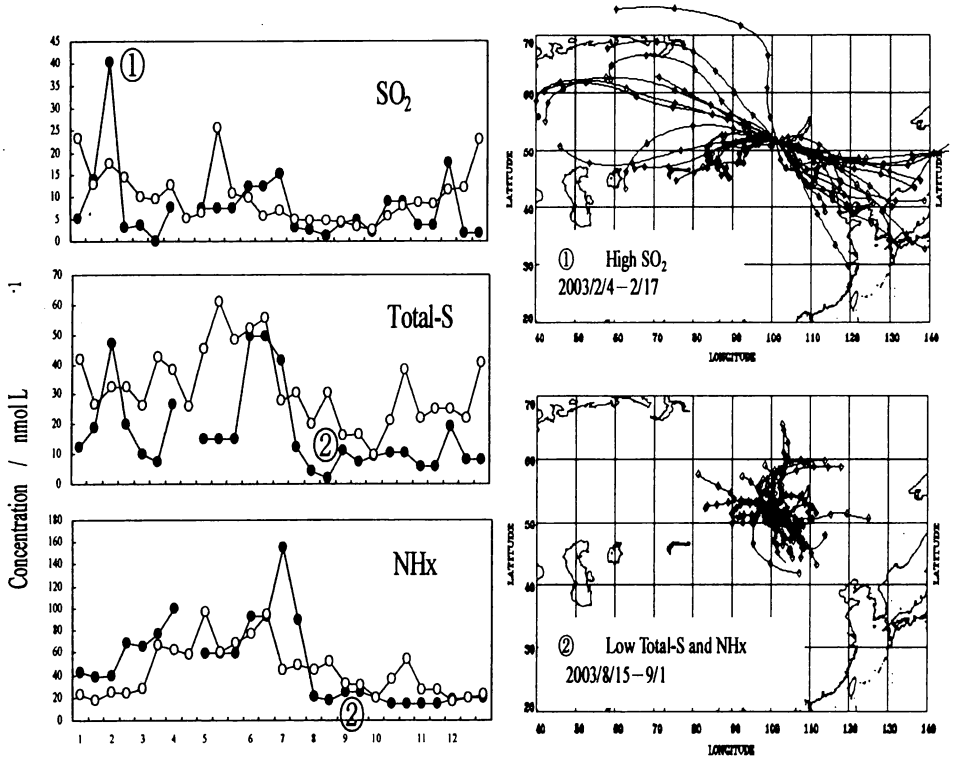

Fig. 1 Comparison of air concentration between Mondy and Rishiri and air mass trajectory at Mondy (2003) ●: Mondy, ○: Rishiri, ①: High SO_2, ②: Low Total-S (SO_2+nss-SO_4^{2-}) and NHx (NH_3+NH_4^+)

(2)Development of air pollutants emission inventory

First step of the emission estimation process is making energy matrix sectored by emission sources and fuel types by province based on the energy statistics of Chinese government. The original energy matrix of energy demand sector splitting into detailed industrial sectors as iron steel, cement, glass, other ceramics and by transportation modes and fuel types including biomass fuels by province is made, and emission factors per unit fuel consumption and by boiler size for coal which would reflect emission levels in China are given to it to estimate emissions of air pollutants from combustion sources. In terms of emission factors setting, recent emission factors applicable to China including small combustion sources and biomass fuels are surveyed, considering the emission control levels of car vehicle vintage by province, and emission observation data of boilers in China is taken into as well. For SO_2 emission estimation, SO_2 removal by the de-SO_x system at large stationary sources, and SO_2 emissions from non combustion sources of industrial processes are taken from the environment yearbook of China. NMVOCs emissions from evaporation sources, petroleum, petrochemical, and solvent are estimated as well.

In case simulation modeling of long range transport of air pollutants coming from East

Asia to Japan, minute analysis by nesting is effective to clarify regional scale influence from local sources in Japan. For this purpose we developed modeling system of high resolution inventory as temporally and regionally for Japan. Emission from open biomass burning of agricultural waste is estimated and temperature modification in cold start of car vehicles is considered as well.

Korean emission data are provided by the Republic of Korea government through international collaboration.

Summary table of country basis emissions in East Asia by this EAGrid 2000 inventory is shown in Table 1. In Table 1 the estimation results are compared with the previous studies. The features of this inventory are SO_2 and NMVOCs emissions in China are larger than previous studies, especially large NMVOCs emission estimation result would need to be checked with the observed concentration data by the dispersion modeling.

Table 1 Emissions Comparison of EAGrid2000 and previous studies

(Unit: Mg/y for Hg and Gg/y for others)

	SO_2	NOx	NMVOC	NH_3	PM_{10}	CO	Hg
China	28,355	11,826	47,243	12,167	16,962	111,084	185
	20,385	11,347	17,432	13,570	10,838	115,749	-
Taiwan	403	515	894	133	356	2,135	5
	376	521	510	152	52	2,127	-
Japan	872	2,371	2,006	443	192	5,016	9
	801	2,198	1,920	352	271	6,806	-
ROK	531	1,004	665	166	71	834	7
	829	1,322	1,161	172	142	2,824	-
DPRK	288	214	290	50	-	-	9
	227	273	234	98	312	3,556	-
Mongolia	70	24	8	87	-	-	1
	84	39	25	117	71	368	-
China, Taiwan, Japan and ROK	30,161	15,715	50,808	12,909	17,580	119,069	206
	22,391	15,388	21,023	14,246	11,302	127,506	-

1)Upper : This EAGrid 2000 result Under : Streets et al.(2003) ,PM_{10} is from Iowa Univ.

2) ROK from I. S. Park, Korean Institute of Environment Sciences

3) Taiwan: from Taipei China Government "25 years Fact of Air quality Control "

4) DPRK, Mongolia extrapolation from 1995 data using energy demand trend. PM_{10} and CO are not estimated.

5)NH_3,Hg all countries data are estimated originally in this study.

(3)Annual source-receptor analysis of acid deposition in East Asia

We examined the annual source-receptor relationships for sulfur and nitrogen oxides in East Asia using by a regional chemical transport model (HYPACT) coupled with the Regional Atmospheric Modeling System (RAMS). Model results are compared with the observation data, which are the daily concentrations of particulate SO_4^{2-} and NO_3^- and the annual SO_4^{2-} and NO_3^- depositions measured by several organizations in the Japanese Islands. The RAMS/HYPACT can reproduce the day-to-day variations of SO_4^{2-} and NO_3^- concentrations and the annual amount of SO_4^{2-} and NO_3^- wet depositions. The annual spatial distributions of the concentration and deposition for sulfur and nitrogen oxides are estimated in East Asia. The general features of distribution for SO_2 concentration is similar to those for SO_4^{2-} and NO_3^-. These concentrations are the highest in the eastern part of China and is moderately higher over the East China Sea and the western part of Japan. NO_2 concentration

is high in some megacities over East Asia (Beijing, Shanghai, Seoul, Pusan, and Tokyo) due to the large emission fluxes in urban area. In contrast, the spatial distributions for the sulfur and nitrogen depositions are completely different from those for gaseous and particulate concentrations, because the wet deposition is strongly influenced by rainfall amount. Source contributions to annual sulfur and nitrogen depositions in the Japanese Islands are shown in Table 2. Annual sulfur deposition in Japan is 49 % from China, 21 % from Japan, 13 % from volcanoes and 12 % from North and South Korea. The contribution of nitrogen deposition is 39 % for Japan, 34 % for China, and 18 % for North and South Korea. Our modeling results suggest that Chinese emission contributes to almost half of sulfur deposition and one third of nitrogen deposition in the Japanese Islands.

Table 2 Source contributions to annual sulfur and nitrogen depositions in the Japanese Islands.

	Authors	Base year	Contribution (%)				
			Volcano	Japan	China	Korea	Others
Sulfur	Ikeda & Higashino (1997)	1990	28	37	25	10	0
	Ichikawa et al. (1998)	1988-89	18	40	25	16	1
	Huang et al. (1995)	1989	94		3	2	1
	Carmichael & Arndt (1995)	1990	45	38	10	7	0
	Ichikawa et al. (2001)	1990	25-31	27-30	24-27	17-19	1-2
		1995	24-32	26-29	29-32	12-13	1-2
	This work	***1995***	***13***	***21***	***49***	***12***	***5***
Nitrogen	Ikeda & Higashino (1997)	1990	—	76	13	11	1
	Holloway et al. (2002)	1990	—	65	18	15	2
	This work	***1995***	—	***39***	***34***	***18***	***9***

(4)Change of atmospheric environment caused by the eruption of the Miyakejia Volcano

At Happo, measured sulfur dioxide and sulfate concentration increased from 0.4ppb to 1.5ppb and 2.5μg m^{-3} to 3.8μg m^{-3} as shown in Table 3. The simulation result shows that aerosols in the volcanic plume were strongly acidified (pH value was around 0) and 80% of sulfate ion was existed as HSO_4^-. The anthropogenic sulfate and the volcanic sulfate in the atmosphere over East Asia were comparable during one year from the onset of the eruption. In winter the volcanic sulfate aerosols were transported to the Pacific Ocean due to the prevailing northwesterly wind. In contrast they were transported over Japan in other seasons. The acidity of precipitation in Japan decreased by 0.1 -0.3 over the area along the Sea of Japan and 0.3-1.0 along the Pacific Ocean on annual average, equivalent to the neutralization by the dust particles (the yellow sand) in spring. The observation has revealed that the abundant volcanic sulfate resulted in the expulsion of non-volcanic nitrate and chloride in aerosols into the gas phase. As the deposition velocities of gaseous nitrate and chloride are much higher than those in aerosols, the deposition of them should be accelerated. This additional deposition is referred to as "indirect acidification", corresponding to "direct acidification" by the deposition of volcanic sulfate. This indirect acidification is estimated quantitatively for the first time using the model and is found to be comparable to the direct acidification (7-210%).

Table 3. Change of air quality before and after the eruption measured at Happo.

	Gas (ppb)		Aerosol (μg m^{-3})					Precipitation (mg L^{-1}) [e]				
	SO_2	O_3	PM10 [f]	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	pH	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+
Annual mean												
Before eruption [b]	0.4	52	8	2.5	0.32	0.05	0.85	4.87	0.81	0.63	0.28	0.14
After eruption [c]	1.5	53	15	3.8	0.33	0.03	1.12	4.81	1.36	0.66	0.36	0.18
2 months mean; from August to September												
Before eruption [d]	0.2	38	14	2.2	0.2	0.02	0.75	5.11	0.25	0.31	0.09	0.06
After eruption [c]	3.3	46	17	6.5	0.24	0.03	1.56	4.50	1.70	0.83	0.17	0.33

a) except pH, b) from Jul. 1999 to Jun. 2000, c) from Aug. 2000 to Jul. 2001,
d) 1999, e) 2000 f) aerosol less than 10 μm in diameter