PRELIMINARY REPORT ON CHEMICAL ANALYSIS OF AEROSOLS COLLECTED AT OKTYABR'SKY, KAMCHATKA, RUSSIA

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INTRODUCTION

Mineral dust containing iron from the Asian continent is transported eastward over the North Pacific, especially spring (Uematsu et al., 1983). The air-borne iron is considered to be the only one source of input in the central part of the northern North Pacific. In fact, it was found that a near doubling of biomass production was observed in the mixed layer in the North Pacific over a 2-week period after the passage of a cloud of Gobi desert dust (Bishop et al., 2002). The Amur-Okhotsk Project propose that main source of dissolved iron in the Sea of Okhotsk associated with marine product is the Amur River. However, the contribution of the air-borne iron to the marine product in the Sea of Okhotsk cannot be negligible. Therefore, we have to precisely evaluate the contribution of air-borne iron deposited on the Sea of Okhotsk. In order to estimate flux of air-borne iron transported from the Asian continent to the Sea of Okhotsk, We carried out aerosol sampling at Oktyabr'sky, Kamchatka, Russia from Octorber 2005. Here we report the preliminary data of aerosol sampling and chemical analysis.

AEROSOL SAMPLING

Oktyabr'sky, where aerosol sampling was conducted, is in the southwestern part of the Kamchatka Peninsula (Fig1). It is in a middle of sandspit which faces the Sea of Okhotsk on the west side, and the Bolshaya River and wet land on the east side. An aerosol sampler system (ACS-21: Kimoto Electric Co., LTD.) was installed in a small house facing the Sea of Okhotsk in the middle of Oktyabr'sky in October 2005. The sampler was established on the 2nd floor of the house, and connected a polyvinyl chloride pipe which was penetrated through a roof of the house. Ambient air was inhaled through the pipe by the aerosol sampler (Fig 2). The sampler system has a computer to record data of sampling condition (flow rate, running time and so on) and meteorological condition which is monitored by an aerovane and a thermometer installed on the roof of the house during sampling. The sampler also has a control unit to confine the meteorological condition when the sampler runs. There were two chimneys of factory or power station in Oktyabr'sky, and we could see them on the roof of the house. To prevent from contaminating emission from their chimneys, aerosol was sampled only when wind direction was within 170-340° and wind speed was more than 1.0m·s^{-1} (Fig. 3).

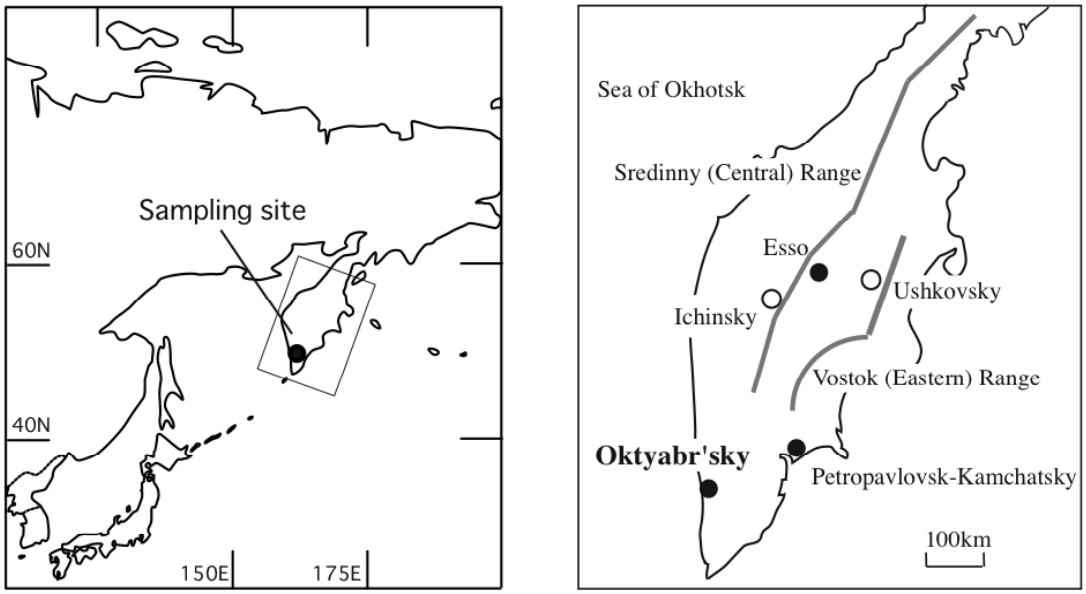

Fig 1. Location of Oktyabr'sky

Aerosol was aerodynamically classified into coarse particle (>2.5μm) and fine particle (<2.5μm) by an impactor attached onto the filter unit, and was collected on Teflon filters (PF040, 90mm diameter: Toyo Roshi Kaisha, Ltd). Coarse particle and fine particle were concentrically collected on the central part and outer part of the filters, respectively. The filter was settled in a plastic cassette case. The cassette case was automatically changed once every one week. The filters was refrigerate after sampling.

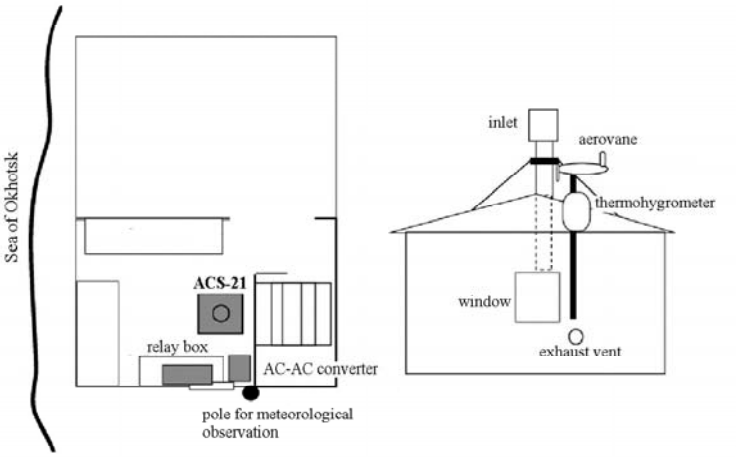

Fig 2. Scematic view of the aerosol sampler

The aerosol sampling was conducted from 19 October 2005 to 15 May 2006. During the sampling period, electric power failure sometimes occurred, and the plastic cassettes were not exchanged in scheduled date. The aerosol sampler was damaged by

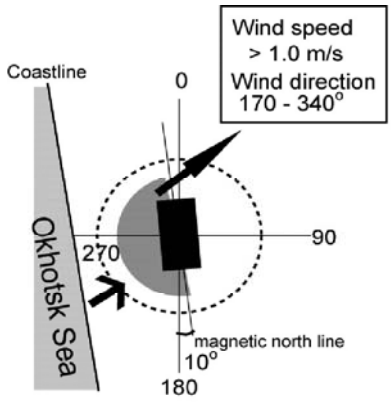

Fig 3. Confine of wind direction to operate aerosol sampling

300V of electrical current when electrical surging occurred at Oktyabr'sky on 15 May. The sampler has not been repaired yet, though we tried to repair it at several times.

The aerosol sampling was managed by ROSHYDROMET (Russian Federal Service For Hydrometeorology and Environmental Monitoring).

CHEMICAL ANALYSIS

The filters were divided into several fragments for chemical analysis of water-soluble substances and of total amount of chemical substances. Water-soluble components in the aerosol were extracted by 10 min ultrasonication with ultrapure water. The concentration of chemical component (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) was determined by an ion chromatography. To facilitate the measurement of the total component, the samples were digested in mixed acid (HNO_3, HF, and $HClO_4$) by a microwave device. The concentration of chemical elements (Al, Fe, Ca, Mg, Mn, Na, Ti, Zn, Sr, Cr, and Ba) was determined by an inductively coupled plasma atomic emission spectrometry. All chemical analysis was done in Hokkaido Tokai University.

RESULT

On water-soluble anion species, dominant species was Cl^- from sea-salt. Mass content of Cl^- was 57-90 %, 43-89 %, and 66-87 % in coarse particle, fine particle, and total of them, respectively. Secondary species was SO_4^{2-}. Mass content of SO_4^{2-} was 7-42 %, 11-52 %, and 12-32%, in coarse particle, fine particle, and total of them, respectively. Mass content of NO_3^- was less than 5 % in whole samples. On water-soluble cation species, dominant species was Na^+ from sea-salt and secondary and tertiary was Mg^{2+} and Ca^{2+} mainly from terrestrial source. Mass content of Na^+ was 80-100 %, 55-100 %, and 78-100 % in coarse particle, fine particle, and total of them, respectively. Mass content of terrestrial elements (Mg^{2+} and Ca^{2+}) was 0-20 %. 0-22 %, and 0-20 % in coarse particle, fine particle, and total of them, respectively. Remarkable differences of chemical composition of water-soluble species between coarse and fine particle were not observed.

On acid-digested elements, dominant element was Na. The mean concentration of Na was 1.1 $\mu g \cdot m^{-3}$ and 2.7 $\mu g \cdot m^{-3}$ in coarse and fine particle, respectively. The mean mass content of Na was 79%, 85%, and 82 % in coarse and fine particle, and total of them, respectively. The mean concentration of Fe was 0.024 $\mu g \cdot m^{-3}$ and 0.025 $\mu g \cdot m^{-3}$ in coarse and fine particle, respectively. The mean mass content of Fe was 1.7 %, 0.8 %, and 1.1 % in coarse and fine particle, and total of them, respectively. Remarkable differences of chemical compositions of acid decomposed element between coarse and fine particle were not observed. Concentrations of all elements but Zn and Cr show high correlation ($r > 0.8$) with Al. Therefore, it estimates that these elements are terrestrial dust, and Zn and Cr are from anthropogenic emission.

Fig.4 shows the variations of concentrations of some chemical species in aerosols at Oktyabr'sky. Concentrations of sea-salt (Na^+, Cl^-) in winter (December, January, and

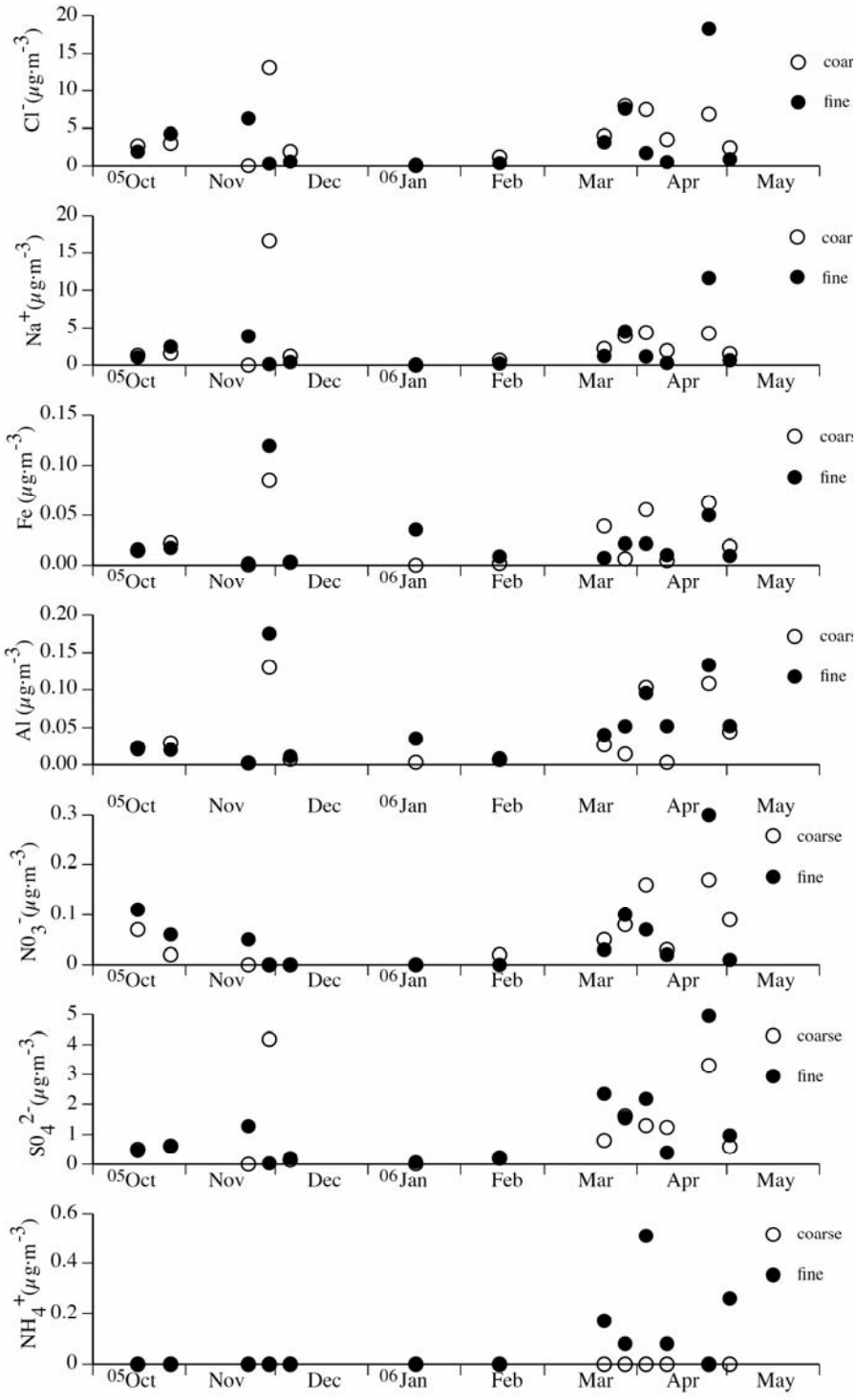

Fig 4. Concentrations of chemical species in aerosols at Oktyabr'sky

February) were lower than in the other months. Because the surface of the Sea of Okhotsk along Oktyabr'sky was open in winter, low concentration of sea-salt in aerosol in winter was not caused by freezing of sea-surface. Frequency of westerly wind in winter was less than 10 % while frequencies of westerly wind in October, and that in March, and April were more

than 50 % and 25%, respectively. Therefore, the variation of sea salt concentration is reflected in the variation of meteorological condition at Oktyabr'sky.

Concentrations of terrestrial dust (Fe and Al) were rather high from March to May, and showed sporadic peaks at the end of November and in April. Moreover, Fe showed a peak in March. Coarse/fine ratio of the concentration of Fe increased at the sporadic peaks in March and April. On the other hand, coarse/fine ratio of the concentration of Al did not show any significant trends, however in general coarse particle concludes 90 % of total Al at Japan when Asian dust is transported (Narita et al., 2005). We estimate that the sporadic peaks of Al and Fe result from Asian dust event, and the concentration of Al and Fe at other period is background level, in spite of uncertainness of Al behaviors.

On anthropogenic species, SO_4^{2-} and NO_3^- showed the different behaviors. Concentrations of NO_3^- increased in both of coarse and fine particles in autumn and spring. Concentration of SO_4^{2-} increased only in fine particles in spring. These behaviors seem to be reflected in emission source of them. The increasing in the concentration of NH_4^+ in fine particles in spring could be reflected in forest fire occurring in Siberia.

ESTIMATION OF IRON FLUX FROM ASIAN CONTINENT TO THE SEA OF OKHOTSK

In order to evaluate the contribution of air-borne Fe to marine product at the Sea of Okhotsk, it is needed to estimate Fe flux to the Sea of Okhotsk. Fig. 5 shows the variation of Fe in aerosol at Oktyabr'sky and Sapporo, Hokkaido, Japan from October 2005 to May 2006. Aerosol at Sapporo was collected at the rooftop of Hokkaido Tokai University, and was analyzed as that from Oktyabr'sky was done (Minami unpublished data). Two peaks of Fe in Sapporo were observed on 10-17 April and on 24 April to 1 May. According to the Lidar observation of National Institute for Environmental Studies, dust concentration increased on 11 April and on 25 April at Sapporo. (http://www-lidar.nies.go.jp/). Around the same time, Fe concentration at Oktyabr'sky increased on 5-12 April and on 26 April to 3 May. Therefore, we assume that these peaks of Fe result from Asian dust events, and after observing at Sapporo on 11 and 25 April, Asian dust was transported to Oktyabr'sky around 12 and 26 April, respectively.

Tsunogai et al. (1985) revealed the exponential relationship between atmospheric concentration of Asian dust and the transport distance from Asian continental coast. Mori et al. (2002) also showed the exponential relationship between atmospheric concentrations of crustal elements and the

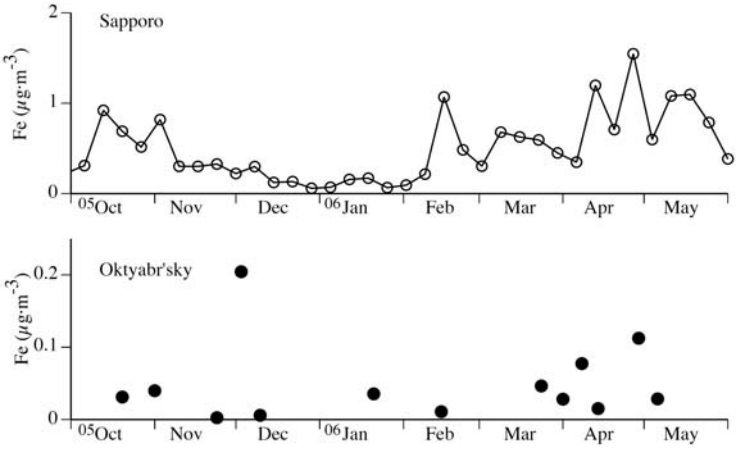

Fig 5. Fe concentration in aerosol at Sapporo and Oktyabr'sky

distance from the source region of Asian dust. Both of these estimations show that the atmospheric concentration of dust or crustal element at certain location exponentially decreases with the transport distance. Therefore, we use the following formula to estimate the concentration of Fe at certain point over the Sea of Okhotsk (C):

$$C = a \exp (b X)$$

where X is the distance from Sapporo, a is the concentration of Fe at Sapporo, and b is constant. Table 1 shows the concentration of Fe at Sapporo and Oktyabr'sky, constant b, and the distance at which concentrations diminish by half (half-concentration distance) at the event on 11 and 25 April. Because the half-concentration distances are equal to the value (330 km for Fe) reported by Mori et al. (2002) and the value (490 km for dust) by Tsunogai et al. (1985), it is possible to estimate the approximate concentration of Fe in relation to the distance from Sapporo.

Uematsu et al. (2003) calculated the total deposition velocity of dust of 0.5 cm· s^{-1} at Sapporo based on the annual deposition flux and the annual mean atmospheric dust concentration. We adopt this value of total deposition velocity, and assume that the high concentration of Asian dust continues for half a day according to the Lidar observation described as above, we estimate the Fe flux over the Sea of Okhotsk (Fig. 6).

For the next step, we are going to investigate the solubility and related behaviors of Fe in seawater in order to estimate how much air-borne Fe can be used for marine production.

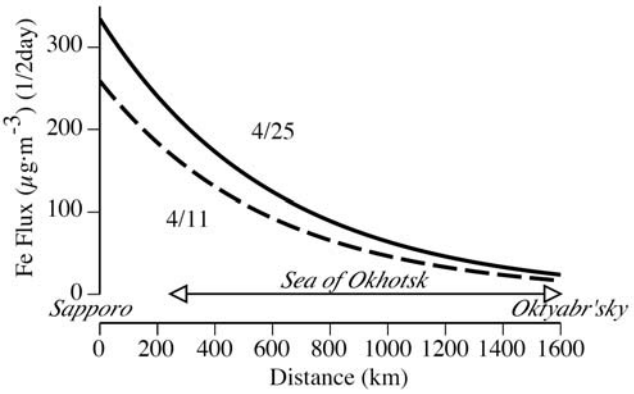

Fig 6. Estimation of Fe flux during half day of Asian dust event observed on 11 and 25 April at Sapporo

ACKNOWLEDGEMENTS

We are grateful to RUSHYDROMET for their management of the aerosol sampling. We are also grateful to the Red Cross at Kamchatka for their kind support of installing of the sampler. We thank Sergei Stephanovich at Okytabr'sky who actually cared the sampling system. We thank Nataria Homich for her kind support and interpretation.

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