United Nations Environment Programme

Promoting Minamata Convention on Mercury by making the most of Japan's knowledge and experiences
Interim project progress report

November 2022

Asia Center for Air Pollution Research

Japan Environmental Sanitation Center

1. Objective of the project

This project aims to evaluate the feasibility and challenges for introducing ambient mercury monitoring by gold trap method, which will be included in the monitoring guidance of Minamata Convention, to existing monitoring sites. The pilot monitoring is conducted at the Niigata-Maki Acid Deposition Monitoring station, Japan from 2021 to 2023. The detailed activity is shown as below.

1. Establish and undertake continuous data collection and analysis based on consistent methodology in the region.

Activity 1.1: Evaluate the usefulness and value-add of the existing facilities and learning materials for establishing and implementing new ambient mercury monitoring.

- Examine the existing and available facilities and materials that will be used for ambient mercury monitoring.
- Evaluate the existing training materials and advise the improvement in more comprehensible ways.
- Evaluate the benefits and additional burden of existing monitoring sites in comparison with establishing independent monitoring sites.
- Prepare a report.

Activity 1.2: Undertake continuous data collection based on methodology in the region.

- Set up a mercury monitoring system at an existing ambient monitoring site.
- Undertake continuous sample collection and analyze mercury levels in ambient air.
- Compile data set together with ancillary information including meteorological data.
- Assess and evaluate the effectiveness of the sampling methodology and amend it if necessary.

2. Implementing period

The activities in this report were implemented from August 2021 to October 2022.

3. Implementing agency

Asia Center for Air Pollution Research, Japan Environmental Sanitation Center

4. Results of the project

4.1 Preparation for the pilot monitoring and development of the Standard Operating Procedure (SOP)

Niigata-Maki national acid deposition monitoring station (37°48’33”, 138°51’09”, 52 m altitude) is selected as the mercury pilot monitoring site. It is located at the foot of Mt. Kakuda (482 m a.s.l.), 1 km from the seashore, and 25 km southwest of the center of Niigata City, the capital of Niigata Prefecture, Japan, as shown in Fig. 1. This station was constructed by the Ministry of the Environment, Japan to monitor acid deposition and air pollutant concentration and to investigate acid deposition in rural areas on the coast of the Sea of Japan. There are no industrial sources near Niigata-Maki site, but a small community (approximately 1300 population) is located 2 km northwest of the station, and thus it is classified as a rural station. Air masses reaching the station are dependent on seasonal wind patterns, which are affected by the monsoon circulation: in winter the northwest cold currents prevail, while in summer they are replaced by the hot and humid currents of the Pacific Ocean. At the station, gaseous pollutants such as SO_2, NO, NO_2, O_3, particulate matter concentrations of PM_{10}, $PM_{2.5}$, ionic and metallic components, water soluble organic carbon, and meteorological parameters of wind direction, wind speed, temperature, relative humidity, precipitation amount, solar radiation are monitored.

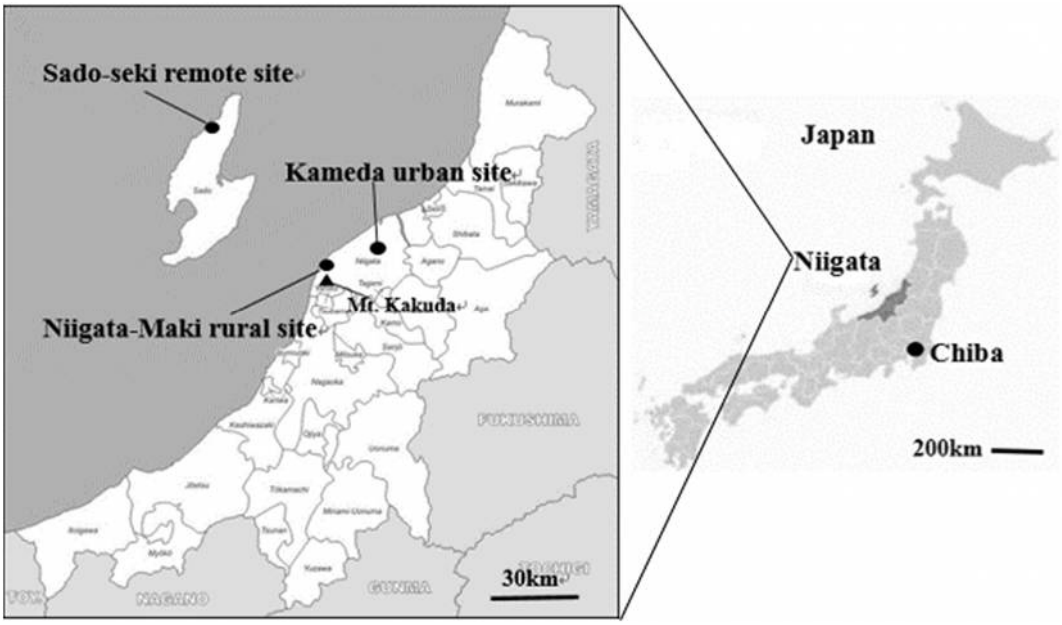


Fig. 1 Location of the Niigata-Maki national acid deposition monitoring station

For the preparation of pilot monitoring, the necessary equipment and analytical instruments for mercury monitoring were obtained, and the applications for use of the Niigata Maki station were submitted to the Ministry of the Environment and Niigata Prefecture, respectively, and were approved in September 2021. Then, the test measurements were conducted on September 21-22, 2021, and it was confirmed that the measurements could be made without any problems.

Fig. 2 Photo of the test measurements during September 21-22. The left one shows sampling through manifold, and the right one shows sampling without manifold.

As shown in Fig.2, the ambient air was sampled through manifold or without manifold. The mercury concentrations for both sampling lines were compared. The results of Fig.3 show that there is no significant difference between the sampling line through manifold and one without manifold. There is good agreement between the mercury concentration at Niigata-Maki and those at near regular mercury monitoring stations in Niigata city. Therefore, we decided the mercury sampling is conducted through air sampling manifold. Then, we developed the Standard Operating Procedure (SOP) of ambient mercury sampling as shown in pages 4 to 8.

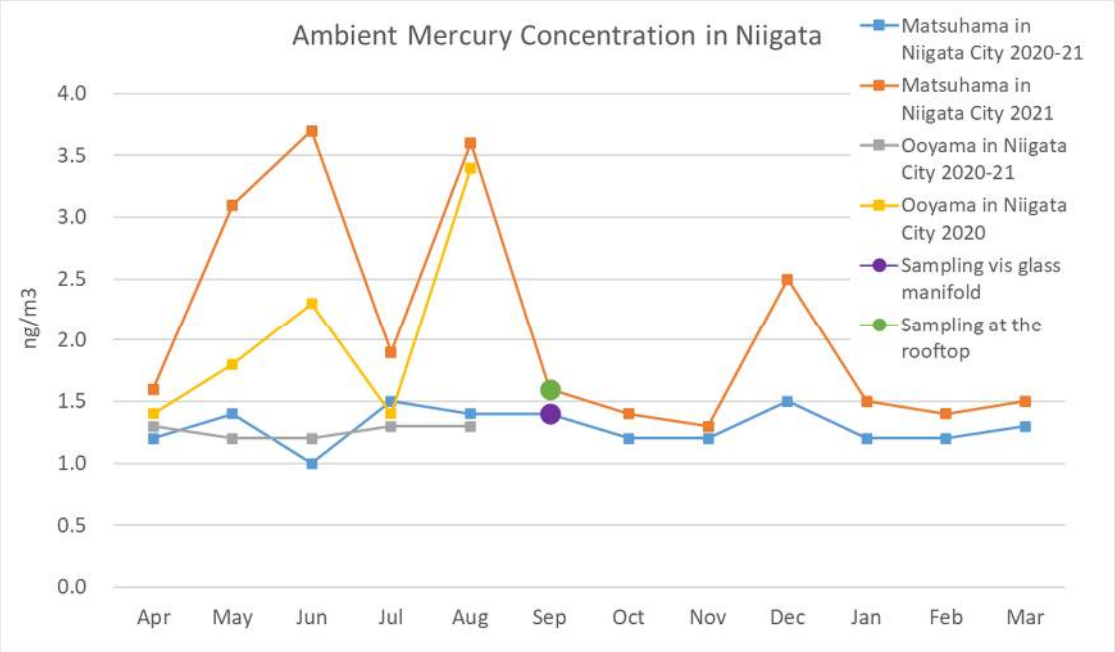


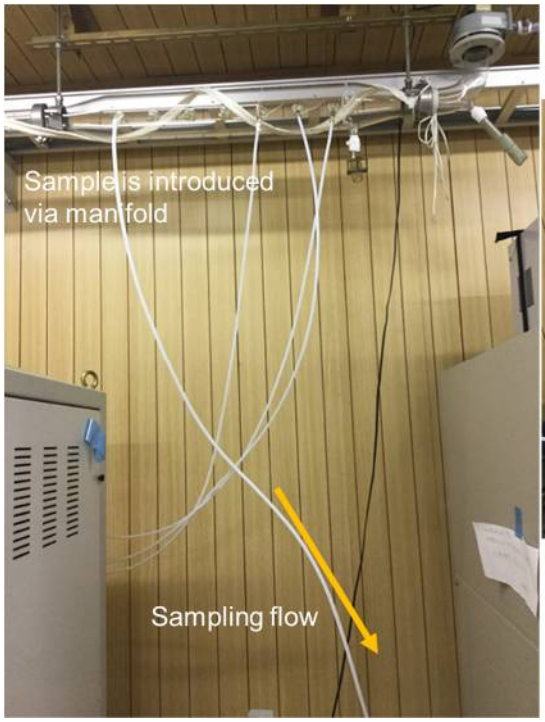
Fig. 3 Mercury concentrations obtained by the test measurements. The mercury concentrations are 24-hour average.

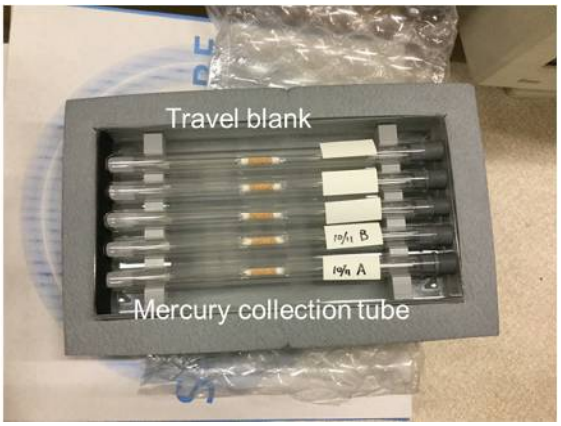
The first regular mercury measurement was conducted on October 11-12, 2021. The photos of regular mercury measurement are shown in pages 4 to 5. The sampling procedure was followed by the SOP shown in pages 6 to 10. The duration of each sampling is 24 hour, and the regular mercury measurement is conducted every two weeks until September 2023. At the initial period of measurement, the following issues are raised.

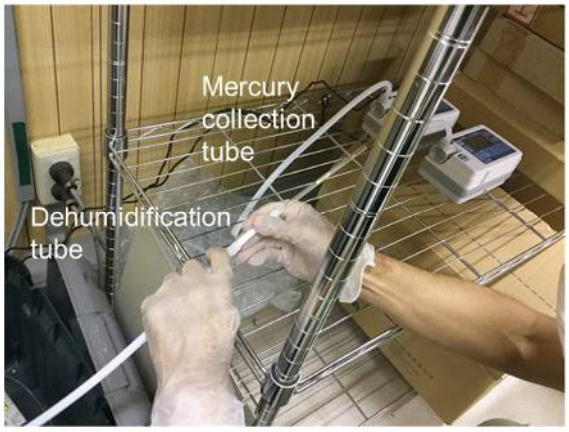
- The quartz wool used to fill the soda lime may shift during sampling, and it may contaminate into the mercury collection tube. The installation of quartz wool is carefully considered.
- The Japanese guideline (Manual of measurement method of hazardous air pollutants-Monitoring of mercury in the Ambient Air) describes that the quartz wool should be treated with silane to prevent adsorption, but this process may be difficult to implement in developing countries because of treatment of hazardous chemical after use.
- The mercury collection tubes are narrow in diameter, which may cause damaged during sampling procedure. The operator requires careful installation work.

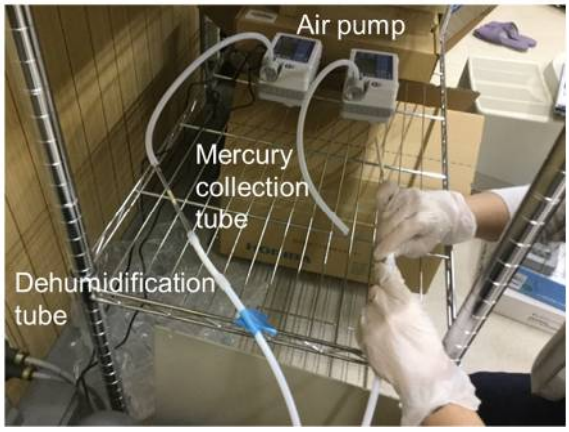
After the sampling, the collection tubes are sent to Japan Environment Sanitation Center at Kawasaki, Japan for analysis. 2 mercury samples and 1 blank sample are analyzed at ever measurement followed by the Japanese guideline. This guideline adopts gold amalgamation trap, thermal desorption and cold vapor atomic absorption spectrometry. The quantity of mercury is measured by the atomic absorption at a wavelength of 253.7nm.

Photos of regular mercury measurement

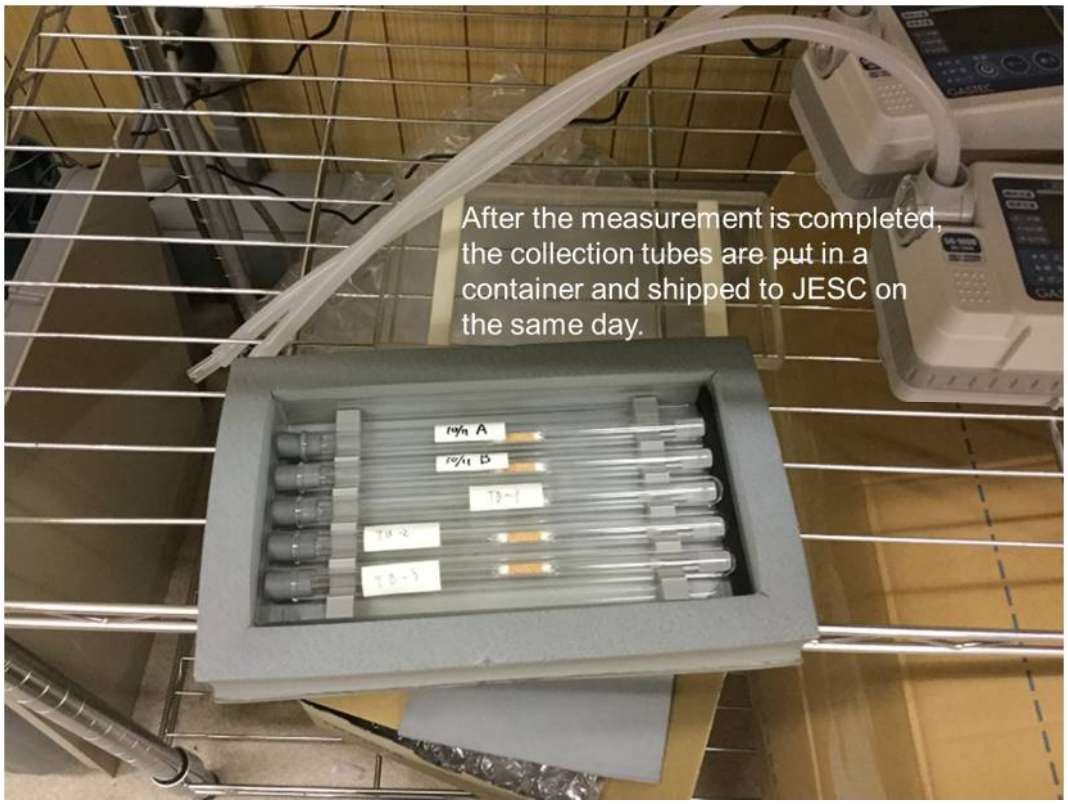









Check the flow rate of 500 mL/min
before starting and ending the measurement


After the measurement is completed,
the collection tubes are put in a
container and shipped to JESC on
the same day.

Standard Operating Procedure (SOP) of Ambient Mercury Sampling

1. Preparation before sampling

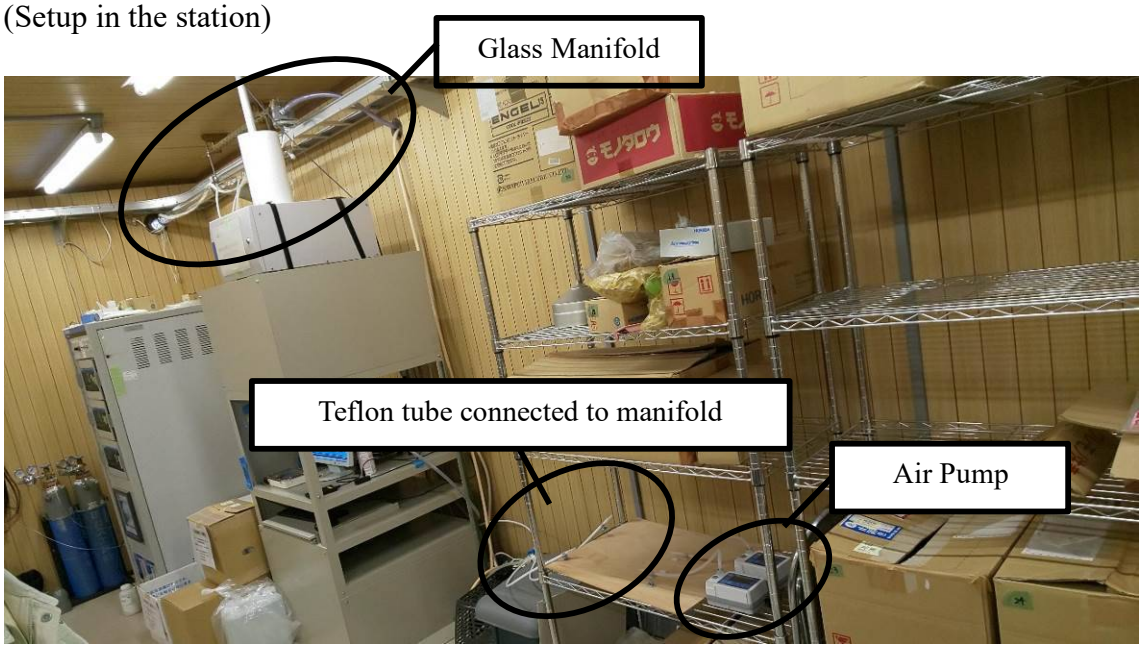
The following items are required for sampling (excluding those installed at the site).

- Mercury collection tubes (sent by JESC East Branch)
- Dehumidifying tubes (Teflon tubes filled with soda lime, prepared by ACAP*)
- Silicone tubes to connect the above two items. (May be stored in a Unipac or a similar bag at the site.)
- A field notebook and writing tools
- Camera (or smart phone)

(Note) Preparation of dehumidifying tubes will be described in the other document.

2. Field work at the start of sampling (Start time is generally 11:30-12:00)

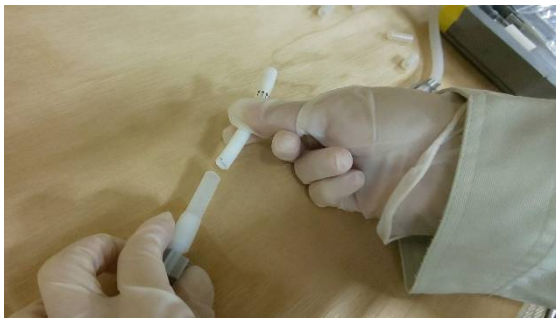
(Setup in the station)



(1) Take a picture of the electric meter and record the amount of electricity used (kwh) in the field notebook. (At the first sampling of the month, press and hold the rate and CO_2 buttons on the meter at the same time to reset the meter.)

The following procedure should be conducted for two flow paths, A and B.

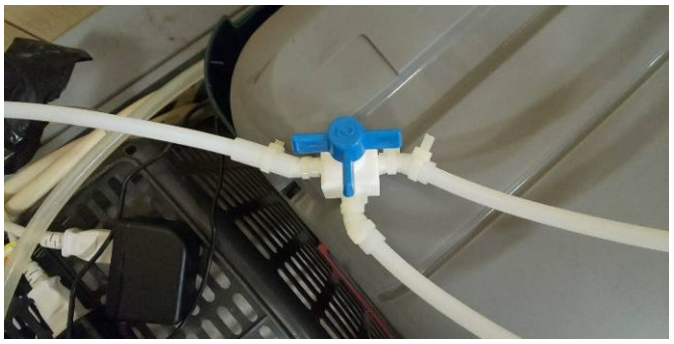
(2) Connect the dehumidification tube to the Teflon tube extending from the manifold. (Note: Connect for the appropriate direction)



(3) Connect the dehumidifying tube to the collection tube with silicone tubing. (Be careful not to damage the collection tube.)

(4) Connect the collection tube to the air pump. (Be careful not to damage the collection tube.)

(5) Open the three-way stopcock
Followed by the picture.
(Note: To prevent backflow of indoor air into the manifold, open the three-way stopcock after completing the step (4).



(6) After confirming that the pump is set to a flow rate of 500 mL/min and a sampling time of 24 hours, press and hold the start/stop button to start the pump. When the pump starts, the pump light will blink.

(7) Record the start time of the measurement (pump start time) and the flow rate after 5 minutes in a field notebook.
(The set of equipment may be left at the station until the next day.)

(8) If there is a sample for the travel blank test, open the stopper of the collection tube container for the travel blank during the step (3) to (6) and close it after starting the measurement.

3. Field work at the end of sampling (End time is after 24 hours. Should arrive at the station before 5 minutes of the end time)

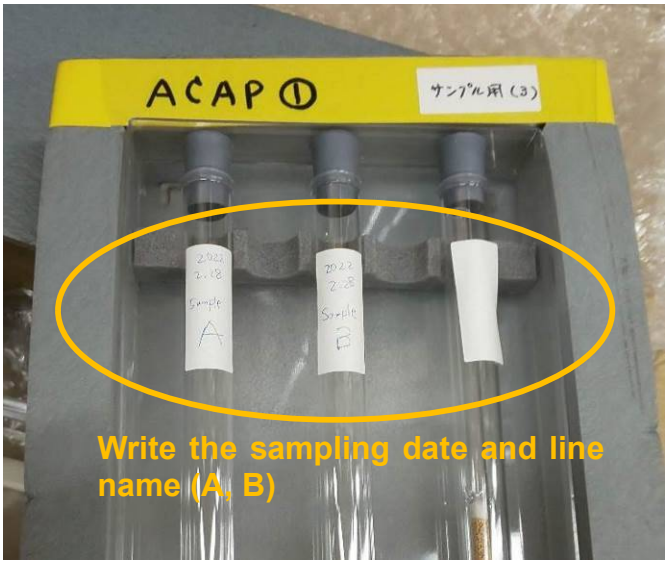
(1) Record the the flow rate before 5 minutes of the end time in a field notebook.

(2) After the pump stopped and the measurement is ended, record the integrating flow volume in the field notebook.

(3) Close the three-way cock. Make sure the manifold side is closed as shown in the photo. (Note: To prevent backflow of indoor air into the manifold, close the three-way stopcock after completing the step (2).

(4) Disconnet the collection tube and the dehumidification tube by the reverse order of installation, and put the collection tube in a container. (Be careful not to damage the collection tube.) Write the sampling date and line name (A, B) on the label.

After removal, cap the Teflon tube extending from the manifold and the silicon tube extending from the pump to prevent contamination.



(5) If there is a sample for the travel blank test, open the stopper of the collection tube container for the travel blank during the step (4), and close it after the work in (4) is completed.

(6) Take a picture of the electric meter and record the amount of electricity used (kwh) in the field note book.

4. Operation after the sampling

(1) Ship the collection tubes to JESC. (Measured by mercury analyzer at JESC)

(2) Photos of the electricity meter will be stored in a server.

(3) Report monthly electricity consumption to Niigata Prefecture office at the end of each month.

4.2 Time variations of mercury concentrations from October 2021 to October 2022

Fig.4 shows time variations of mercury concentrations obtained by the regular measurements at Niigata-Maki and near regular mercury monitoring stations in Niigata city from October 2021 to October 2022, respectively. Monthly averages of meteorological parameters at Niigata-Maki in 2021 is also shown in Table 1 The clear seasonal pattern of mercury concentration was observed. The concentrations during winter (December to April) tend to be higher than those during summer (August to September). This pattern may be associated with long range transportation of mercury that may be contained in coal combustion particle and yellow dust.

There is a precious study of gaseous and particulate mercury and the mercury wet deposition flux measurement at Matsue located in the Sea of Japan site from December 1998 to November 2001 (Marumoto and Sakata, 2007). The particulate mercury concentration and the mercury wet deposition flux during winter and spring were higher than those during summer. Especially during spring, their increase was accompanied with an increase in atmospheric concentrations and wet deposition fluxes of Al, Fe, non-sea-salt Ca and Mn, major components of soil. This suggests the large contribution of the yellow dust. During winter and the yellow dust periods, the Pb/Zn concentration ratio and Pb isotope ratios in air and precipitation observed in Matsue were close to those in the Asian continent. These results implied that during winter in Matsue, long-range transport of particulate mercury from the Asian continent contributes primarily to the Hg wet deposition.

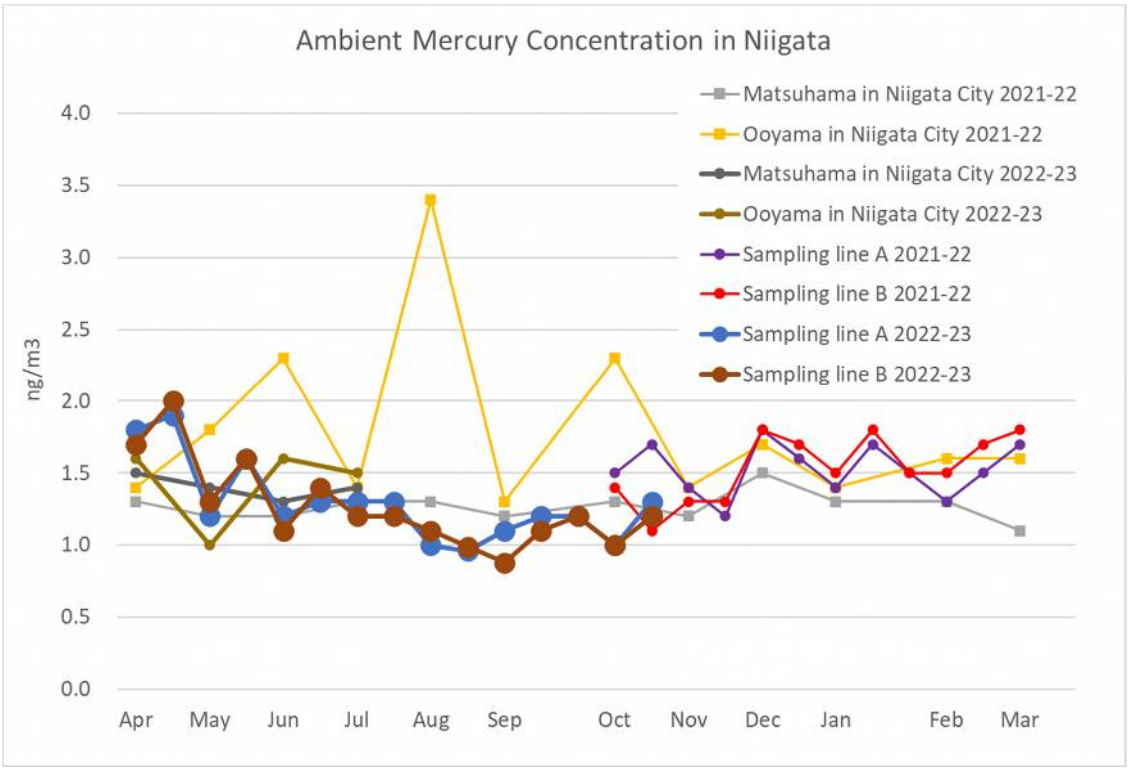


Fig. 4 Mercury concentrations obtained by the regular measurements at Niigata-Maki and near regular mercury monitoring stations in Niigata city from October 2021 to October 2022. The mercury concentrations are 24-hour average.

Table 1 Monthly averages of meteorological parameters at Niigata-Maki in 2021.

Meteorological Statistics : Niigata-maki

2021

Month / Items		1	2	3	4	5	6	7	8	9	10	11	12
Tempera-ture (ºC)	monthly mean	1.6	4.2	8.1	11.0	16.4	21.5	26.1	26.4	21.8	16.8	11.1	5.1
	max.daily mean	6.5	13.5	14.5	16.7	21.8	24.5	28.7	31.6	23.9	23.4	16.3	10.6
	min.daily mean	-2.6	-0.6	1.7	6.2	10.8	16.8	22.1	21.0	17.9	11.7	5.7	-1.6
Relative humidity (%)	monthly mean	80	70	68	66	74	75	78	76	73	75	75	78
	max.daily mean	94	90	83	94	93	89	93	92	89	93	85	92
	min.daily mean	62	52	48	50	57	61	65	60	57	59	59	59
Mean wind speed (m/s)		5.4	6.4	4.1	4.1	4.0	2.6	2.7	3.0	3.3	3.6	5.1	6.3
Most frequent wind direction (bearings)		SE	WNW	SE	SE	WSW	N	SE	SE	SE	SE	SE,SSE	WNW
Precipitation amount (mm/month)		256	96	62	114	104	75	225	195	136	120	197	222
Sunshine duration (hours/month)		--	--	--	--	--	--	--	--	--	--	--	--
Solar radiation (MJ/m^2/month)		154	227	404	539	539	615	640	531	474	321	213	135

5. Summary and future schedule

Since October 2021, the regular mercury measurement at Niigata-Maki station has been conducted without any significant problems. We confirmed that the sampling manifold in the station will not affect measurement values and most of procedures described in the Japanese guideline are applicable of regular measurement. However, the pre-treatment of quartz wool with silane to prevent adsorption is difficult to be conducted. We developed the Standard Operating Procedure (SOP) of ambient mercury sampling. During the period of 2022-2023, the following activities will be highlighted as well as regular activity.

- Preparation of the Standard Operating Procedure (SOP) of mercury sample analysis.
- Trend analysis of ambient mercury concentrations by using meteorological data, air mass back trajectory, trace element concentrations in $PM_{2.5}$ measure by automatic monitor.
- Evaluate the effectiveness of overall procedures of mercury monitoring.
- Recommendation on mercury monitoring to be conducted in developing countries.