

Selected Article

Non-Filterable Metals (NFM) in the Atmosphere

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A new air sampler, the Mist-UV sampling system, has been developed to trap and detect metals and metal compounds present in atmospheric samples, as non-filterable metal (NFM). NFM includes metal compounds which are contained in or on fine particulate in an air sample, as well as volatile compounds. The Mist-UV system is based on the combination of two ideas, mixing the filtrated air sample with nitric acid mist and simultaneous ultraviolet irradiation of the mist. Atmospheric NFM in the introduced air samples, which were first passed through a 0.2 μm filter, were oxidized by UV irradiation and dissolved in the nitric acid mist. The trapped metals resulting from the NFM in nitric acid were quantitatively determined using ICP-MS. As a result of measuring of the NFM concentration in the atmosphere using this method, five metals (magnesium, aluminum, barium, strontium, and copper) were detected. The NFM concentrations were found to be significantly higher than concentrations of particulate metals, therefore the atmospheric importance and role of NFM cannot be ignored in the estimation of global metal circulation and budgets.

Introduction

The concentration of metal compounds in the atmosphere can be generally obtained by measuring metals that constitute or adhere to the particulates known as aerosol particulates¹ suspended in the atmosphere. The airborne particulates are classified into comparatively large particulates of several μm or more generated from minerals, soil, and seasalt, and the secondary particulates with small diameters created by coagulation and condensation of gases and volatile compounds through photo-oxidation. The former has been considered as a major source of atmospheric metals. Therefore, atmospheric concentration of the metals present in the airborne particulates captured by means of filters or inertial impactors² have been measured to study compositions, behaviors, and atmospheric circulation of metals. The metal concentration in ice and snow from polar areas, such as the South Pole and Greenland, and their compositions were successively reported from the 1980s. Metals in the natural or non-polluted atmosphere can be the main source of them since it was considered that polar snow was not influenced by artificial metal contamination, however, metal compositions in polar snow were considerably different from those in airborne particulates. This result implies that other natural emission sources of atmospheric metals exist. As in the results of the measurement in the atmosphere over the open ocean, the metal concentration extracted from the small particulates (0.5 μm or less) that cannot be captured by the aerosol filter is found to be significantly higher than that from the larger particulates. The metals of submicron particulates passed through the filter are considered to control the atmospheric metals on the earth,

because of the metal concentration and compositions in the atmosphere in the polar area and over the open ocean are largely different from the metal compositions in the natural airborne particulates.

In this research, a new technology for measuring the concentration of metal compounds passed through the aerosol filter (Non-filterable metal: NFM) were developed. The metal concentrations in the atmosphere were observed to measure their seasonal and diurnal variation, and their sources were estimated. Additionally concentrations of NFM and airborne particulate metals were compared to clarify the importance of atmospheric NFM.

*1: A suspension of fine liquid or particulates in the air is the aerosol. The aerosol is called dust, fumes, mist or smoke from the difference in its generation process, or from a meteorology view point, it may be also called fog, mist, haze, or smog from the difference in visibility and color (From Japan Association of Aerosol Science and Technology website).

*2: This is the method that utilizes the inertia power of particulates, which separates particulates from fluid by changing the flow of fluid suddenly. The collecting plate, which counters the flow velocity, captures particulates (From Fluid engineering handbook (Nikkankogyo Shimbun, Inc.)).

Development of the Mist-UV Method

Atmospheric samples passed through the airborne particulate filter contains particulates and gases, therefore, it is required for a simple method to capture the air sample using a method to quantify total concentration of atmospheric metals by directly introducing air sample to the analyzer (ICP-MS). However, because of the low concentration of atmospheric metals, it is necessary to concentrate metal compounds before their analysis. For

example, volatile metal compounds represented by methylated metals or metalloids (Arsenic and selenium) are generally separated and quantified by gas chromatography - mass spectrometry (GC-MS) after concentrating them by passing the air sample through the cryotrapping using cold media (e.g. liquid nitrogen). However, these methods have some problems, for example, the difficulty of handling and ice clogging due to condensation of water vapor in the cryotrapping tube. Besides, the method can be applied only to the chemical species analysis of specific metal compounds, which readily condensed in cryotrapping tube. On the other hand, a gas washer or impinger has been applied to achieve the purpose, however, optimizing the trapping efficiency and diffusion velocity have a limitation. Therefore those methods may not be available to measure atmospheric concentration of NFM with high trapping efficiency.

In this study, new and original sampling method, Mist-UV method, was developed for trapping the NFM efficiently. The outline of the Mist-UV system is shown in Figure 1.

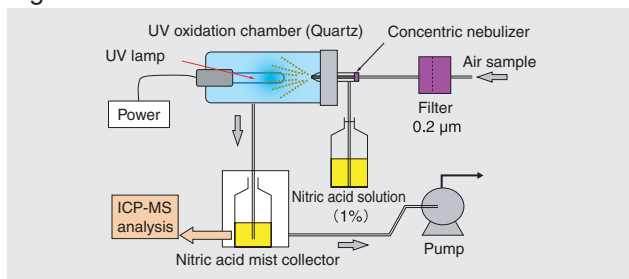


Figure 1 Mist-UV System

This system comprise a particulate filter, a polyethylene nitric acid supply bottle, UV oxidation chamber with a mist generator, mist collector, vacuum air pump, and tubing/connections. Air samples were drawn into the system and passed through a 0.2 µm particulate filter to remove major airborne particulates. The filtered air was then introduced into a concentric nebulizer (mist generator), where it was mixed with the 1% nitric acid which was spontaneously sucked up from the nitric acid supply bottle. The nitric acid mist containing the NFM was then exposed to UV irradiation as it passed through the UV oxidation chamber. The mist was collected in a polyethylene bottle placed below the UV chamber. The concentration of NFM in the atmosphere was subsequently determined by inductively - coupled plasma mass spectrometry (ICP-MS) analysis of the metals dissolved in the nitric acid. These results can be converted into the NFM concentration in the atmosphere using the ratio of the volume of the air sample passed through the Mist-UV system and that of the nitric acid solution. It is possible to identify metals that are just dissolved/absorbed in nitric acid with this sampling system, by operating the Mist-UV sampler with the UV lamp switched off. Metals detected in this way are characterized as “metals dissolved/absorbed in nitric acid (MDA)”. In other words, the difference in the concentration between the NFM and MDA comes from the metallic compounds that can be readily oxidized by UV irradiation (e.g., reduced metals

or organic metals), and the larger deference in the concentration is presumed as being more largely influenced by other than particulates of the mineral, soil, and salt of seawater. The advantages of the Mist-UV method are listed as follows:

- (1) The oxidization and dissolution of the NFM that are not captured by the filter can be performed simultaneously without contamination by external factors (e.g. artifacts of sampling operation).
- (2) Sampling operation can be performed safely and easily because no cold media (e.g. liquid nitrogen) is used.
- (3) The captured nitric acid solution can be directly introduced into the analyzer such as the ICP-MS without performing a pretreatment procedure.
- (4) Almost all metal compounds can be collected and detected.

Annual variation of NFM concentration in the ambient air was measured, and magnesium, aluminum, strontium, barium, and copper were mainly detected. For these detected metals, trapping efficiencies of the Mist-UV method were carried out by comparing with the cryotrapping method that uses liquid nitrogen. It was confirmed that a trapping efficiency of 70% or more could be attained compared to the cold trap method. Limits of quantitation were, magnesium: $0.1 \mu\text{g} \cdot \text{m}^{-3}$, aluminum and barium: $0.05 \mu\text{g} \cdot \text{m}^{-3}$, copper: $0.01 \mu\text{g} \cdot \text{m}^{-3}$, and strontium: $0.005 \mu\text{g} \cdot \text{m}^{-3}$.

NFM Concentration in Ambient Air

Seasonal Change

In order to observe seasonal variations of NFM concentrations, annual ambient air sampling was undertaken between September 2000 and August 2001 in a suburb of Auckland, New Zealand. NFM concentration of four to seven air samples were measured every month. Five metals (Mg, Al, Cu, Ba and Sr) were detected as NFM in ambient air and their annual variation of concentrations are shown in Figure 2.

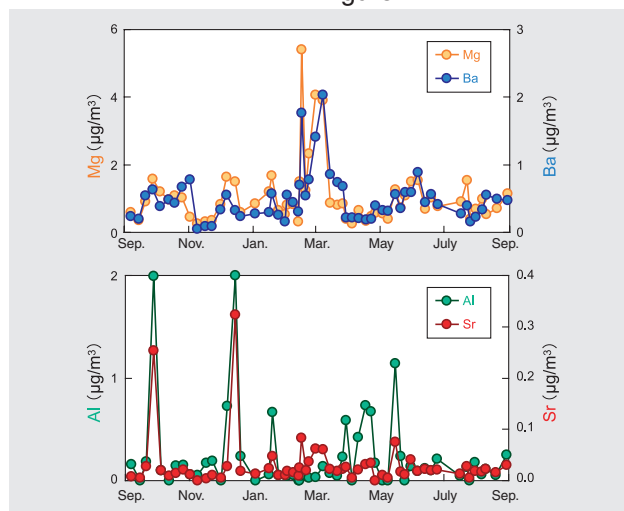


Figure 2 Seasonal Change of the NFM Concentration

Elevated atmospheric concentrations of Mg and Ba were detected in midsummer (February to March). More importantly, clear differences between NFM and MDA concentrations were observed in all seasons. This suggests that the UV oxidized fraction in NFM dominated and NFM is enriched with reduced metals or organic metals. It was probable that such compounds were released from natural sources, such as microorganisms in soil and plants, with their concentrations being enhanced by rising the air temperature in summer. In contrast, remarkably high concentrations of Al and Sr as NFM were discovered in several air samples. Aluminum showed extremely high concentration peaks that reached $2 \mu\text{g} \cdot \text{m}^{-3}$. Since no big difference from the MDA concentration was observed in these metals, they were dominated by the non-oxidisable compounds. This implies that the sources of Al and Sr were mainly from inorganic or oxidized metals associated with fine particulates ($<0.2 \mu\text{m}$).

Copper showed a very unique seasonal variation of concentration as NFM. A single large Cu concentration peak of NFM was observed only in the summer (January to February). Copper as MDA was not detected from all samples, which implies that reduced or organic copper compounds were due to high Cu concentration as NFM. It has been discussed that mineral dust, soil, and seasalt particulates are predominant sources of atmospheric copper, however, these results prove that other emission sources are responsible for atmospheric Cu. It is likely that these emissions are promoted by periodic variation of the natural environment, for example, spring bloom which occurs in early summer.

Comparison with PM_{10}

Airborne particulate sampling using a high volume sampler was carried out in the same period of NFM sampling, and metal concentration of PM_{10} (particulate diameter $<10 \mu\text{m}$) were measured. Table 1 gives a comparison of the geometric mean values of NFM and PM_{10} metals. Since the range of the NFM particulate diameters ($<0.2 \mu\text{m}$) detected using the Mist-UV method is narrower than that of PM_{10} ($<10 \mu\text{m}$), the NFM concentration was predicted to be lower than the PM_{10} concentration. However, it is clear that the concentrations of the NFM (with the exception of Al) were substantially higher, by a factor of 3-15, than those found for PM_{10} . This means that atmospheric concentrations of metals detected with the Mist-UV sampling system were higher than those detected in PM_{10} using a quartz filter. These results show that the metal compounds that cannot be captured by the filter exist in the atmosphere as the volatile phase in extremely high concentration. These metal compounds probably attribute to submicron particulate metals enriched with organic metal compounds easily decomposed by UV irradiation.

Table 1 Comparison of the Metal Concentrations between NFM and PM_{10} Samples ($\mu\text{g}/\text{m}^3$)

| Metal | Geometric mean concentration (Range) | |
|-----------|--------------------------------------|--------------------------------------|
| | NFM ($<0.2 \mu\text{m}$) (n=12) | PM10 ($<10 \mu\text{m}$) (n=10) |
| Magnesium | 1.1 (0.3-4.9) | 0.4 (0.1-0.7) |
| Aluminum | 0.06 (<0.05 -0.65) | 0.08 (0.01-0.17) |
| Copper | 0.12 (<0.02 -0.20) | 0.006 (<0.003 -0.017) |
| Strontium | 0.020 (0.010-0.080) | 0.003 (0.002-0.006) |
| Barium | 0.45 (0.15-1.7) | <0.03 |

Diurnal and Nocturnal Variations

During the annual observation, air sampling over 12 hours was carried out for 4 - 6 days in each season to see diurnal and nocturnal differences of NFM. Daytime concentrations of magnesium, strontium, and barium were higher than those observed during nighttime in summer (February) and autumn (May). These results suggest that atmospheric concentrations of NFM are influenced by meteorological factors, particularly light irradiation and subsequent increasing air temperature during day light hours. Meanwhile, high nocturnal concentrations of Al in winter were observed, which suggests emissions of Al as NFM occur most commonly during the night in winter. Because there were many residences that are using wood burning as domestic heating system in the vicinity of the sampling site, it is suggested that emission and residence of atmospheric fine particulates of soot or smoke, enriched with Al, took place during the night. Accordingly the aluminum that adheres to fine particulates originated from combustion may have been detected as the NFM Al. Mineral particulates have also been considered as emission sources of atmospheric aluminum. It is interesting that human activities are another major emission source of NFM in discussions about human health hazards.

Emission Sources of NFM

The following facts related to the NFM are revealed from above observation:

- (1) Magnesium, barium, strontium, and copper have specific generation sources in that the sunlight and temperature rise promote their emission into the atmosphere. They contain the reduced or organic metal compounds readily oxidized by UV irradiation.
- (2) Aluminum and strontium are very likely detected as oxidized metals with fine particulates.

It is considered that seasalt particulates, vehicle exhaust gas, and soil are important contributors for atmospheric NFM detected at the observation location. Seasalt particulates, originated from sea spray due to the destruction of air bubbles on the surface seawater, include alkali metals and alkali-earth metals in high concentrations; therefore, they may have been the main

generation sources of the NFM. However, NFM were not ever detected that could explain atmospheric NFM concentration when measuring metal concentration of the air sample passed through seawater. Additionally it is hard to consider that the fine particulates detected as the NFM are emitted from the generation process of the seasalt particulates. Further, the composition ratio of metals differs largely from the dissolved compositions in seawater. Consequently seasalt and seawater were not the direct origin of the NFM.

Vehicle emission gas can be the largest generation source of combustion gases throughout the year around observation point. The exhaust gas emitted from gasoline and diesel engines were collected and measured NFM concentration, respectively. Figure 3 shows the results.

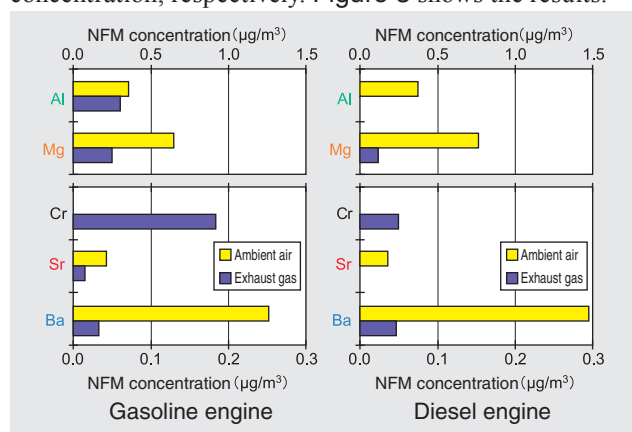


Figure 3 NFM Concentration in Exhaust Gas Emitted from Vehicle Engines

Unexpectedly, the concentrations of the atmospheric major metals (Mg, Al, Sr, Ba) as NFM were lower in concentration in the automobile emissions than those measured in ambient air. It was likely that the NFM was oxidized during the combustion process inside the engine, and oxidized metals were adsorbed by the comparatively large particulates, such as soot, and captured by the filter of Mist-UV sampler. Another notable result was that Chromium as NFM was detected in remarkably high concentrations in all emission gas samples, particularly those from the petrol engine. Although the causes and mechanism of generating the chromium are not yet clear, Cr can be an indicator of NFM emissions from automobiles especially from petrol engines.

Emission gases or particulates from soil can be another important contributor for atmospheric NFM detected in this study. Mg and Ba concentrations in the air from wet soil clearly exhibited higher concentrations than those in ambient air samples. Air in wet soil can be an important natural source of the atmospheric Mg and Ba as NFM. Biogenic activities, such as microorganisms and invertebrates, are possibly involved in NFM generation and emission from soil in wet condition. In contrast, the NFM concentrations of Al and Sr in the air passed through dry soil were significantly higher than those in ambient air. Fine soil particulates that pass through the filter of Mist-UV sampler are considered to be the potential origins of airborne particulate matter detected

as NFM.

Conclusion

In this study, the NFM concentrations were found to be significantly higher than concentrations of particulate metals. If higher concentrations of NFM are observed in natural air samples obtained from other locations around the world, the current measurement can result in an underestimation of atmospheric metal concentration. This implies that role of NFM cannot be ignored in the restructuring of the budget of metals on the earth's surface and the global metal circulation. Furthermore, revealing chemical species is necessary to discuss their emission sources and atmospheric behaviors. It is probable that NFM is a major precursor of particulate metals through photochemical reactions and condensation or coagulation process in the atmosphere, and it may be closely related with the atmospheric aerosol formations and their particulate size distributions.

The Mist-UV system could also be useful to determine the air quality in the cleanroom widely used in semiconductor industries. The cleanroom air is set up to eliminate airborne particulates by using an air filtration system, however, non-filterable compounds and gases could not be trapped by filters and be suspended in the cleanroom air. It is known that metal contamination on the surface of an integrated circuit (IC) can be responsible for shorting the electric circuit, therefore NFM concentration needs to be monitored in cleanroom air for further development of semiconductor.

Reference

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