Atmospheric Environment 95 (2014) 334–343

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Water-soluble organic nitrogen in the ambient aerosols and its contribution to the dry deposition of fixed nitrogen species in Japan

Kiyoshi Matsumoto [a, *], Yuya Yamamoto [a], Hiroshi Kobayashi [a], Naoki Kaneyasu [b], Takashi Nakano [c]

[a] Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-4-37, Takeda, Kofu, 400-8510, Japan
[b] Atmospheric Environment Study Group, National Institute of Advanced Industrial Science and Technology, 16-1, Onogawa, Tsukuba, 305-8569, Japan
[c] Mt. Fuji Research Institute, Yamanashi Prefectural Government, 5597-1, Kenmarubi, Kamiyoshida, Fujiyoshida, 403-0005, Japan

HIGHLIGHTS

- Large portions of the WSON were found in the fine-mode aerosols.
- The fine-mode WSON are mainly derived from secondary reactions of its precursor gases.
- Vegetation source is an important source of the coarse-mode WSON.
- The significant part of the WSON was deposited by coarse-mode aerosols.
- Adsorption of organic gases on the filter had little effect on the WSON measurement.

ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form
26 May 2014
Accepted 18 June 2014
Available online 19 June 2014

Keywords:
Water-soluble organic nitrogen
Water-soluble total nitrogen
Fixed nitrogen
Aerosol
Dry deposition

ABSTRACT

Measurements of the water-soluble organic nitrogen (WSON) in the aerosols were conducted over three years at two sites; an urban site in Kofu and a forested site in Fujiyoshida, Japan. Our preliminary experiment demonstrated that the adsorption of organic gases on the filter had little effect on the measurement of the WSON. The mean concentration of the WSON in the aerosols at the urban site was 0.221 μg m^{-3}, which was higher than that of 0.101 μg m^{-3} at the forested site. Large portions of the WSON were found in the fine-mode range; 90.3% at the urban site and 86.4% at the forested site. The WSON constituted a significant fraction of the water-soluble total nitrogen (WSTN) in the aerosols; 11.1% and 16.2% of the WSTN in the coarse and fine particles, respectively, at the urban site, and 11.5% and 13.1% in the coarse and fine particles, respectively, at the forested site. The fine-mode WSON would be derived from the reaction of its basic precursor gases with particulate or gaseous acidic species. Photochemical reactions and combustion emissions could also be important sources of the fine-mode WSON. In the coarse-mode range, on the other hand, vegetation sources could be an important source of the WSON. The mean concentration of urea in the aerosols at the urban site was 1.7 ngN m^{-3}. A large portion (87.2%) of the urea was partitioned into the fine-mode range. Urea is a minor compound in the particulate WSON in this region with contributions to about 1% of the WSON. Approximately 26% of the dry deposition of the WSTN was attributed to the WSON in the cold season. The significant part (96.5%) of the WSON was deposited by coarse aerosols. Coarse-mode WSON is important for discussing the dry deposition fluxes of the WSON and fixed nitrogen.

1. Introduction

The deposition of atmospheric fixed nitrogen species to the earth's surface is an important source for bioavailable nitrogen both in aquatic and terrestrial ecosystems (Aber et al., 1989; Duce et al., 1991; Jassby et al., 1994; Cornell et al., 1995). Increases in the fixed nitrogen species in the atmosphere due to recent human activities, such as fossil fuel burning and fertilization, have significant impacts on global environments through their deposition; for example, nitrogen saturation in terrestrial ecosystems, eutrophication and decreased water quality in aquatic ecosystems, and chemical and climatic perturbation in the atmosphere (Aber et al., 1989;

* Corresponding author.
E-mail address: kmatsumoto@yamanashi.ac.jp (K. Matsumoto).

http://dx.doi.org/10.1016/j.atmosenv.2014.06.037
1352-2310/

Bytnerowicz and Fenn, 1996; Galloway and Cowling, 2002; Duce et al., 2008).

Organic nitrogen species have been reported to be significant components in the atmosphere, mainly based on deposition chemistry studies. Many previous studies have demonstrated that organic nitrogen contributes about 10–50% of the total nitrogen in the atmospheric deposition (e.g., Eklund et al., 1997; Scudlark et al., 1998; Cornell et al., 2001, 2003; Zhang et al., 2008; Bencs et al., 2009; Karthikeyan et al., 2009; González Benítez et al., 2009). Because the bioavailability of the organic nitrogen species in the atmospheric deposition was verified from bioassay results (Peierls and Paerl, 1997; Seitzinger and Sanders, 1999), these organic nitrogen species should be included in the fixed nitrogen pool and would act as bioavailable nitrogen in the terrestrial and aquatic ecosystems.

Recently, investigations of organic nitrogen species in the ambient aerosols have been conducted at many areas in the world including urban, suburban, rural, forested, and marine sites (e.g., Cornell et al., 2001; Zhang et al., 2002; Mace et al., 2003a, 2003b; 2003c; Nakamura et al., 2006; Calderón et al., 2007; Duan et al., 2009; Lin et al., 2010; González Benítez et al., 2010; Violaki and Mihalopoulos, 2010; Miyazaki et al., 2011). Many of these previous studies have found that about 10–60% of the water-soluble nitrogen in the aerosol is of an organic form. Size-segregated investigations of water-soluble organic nitrogen (WSON) in the aerosols demonstrated that its size distribution significantly varied among the studies; dominance in the fine-mode range (Violaki and Mihalopoulos, 2010), dominance in the coarse-mode range (Mace et al., 2003b), and a bi-modal distribution (Cornell et al., 2001). Nakamura et al. (2006) reported that dominance of the WSON in the fine-mode range was often found in the polluted air masses over the East China Sea, whereas its size shifted to the coarse-mode range during the Asian dust event with a heavy loading of coarse dust particles.

The chemical components and sources of the WSON in the ambient aerosols have been little understood. The WSON in the aerosols can be broadly separated into two categories; reduced organic nitrogen species and oxidized organic nitrogen species. Reduced organic nitrogen species include urea, alkyl amines, and amino acids that have been reported to originate from various sources, such as the ocean, terrestrial vegetation, organic litter, microorganisms, biomass burning, agricultural activity, animal husbandry, anthropogenic combustion processes, waste treatment, and various industries (Gorzelska et al., 1992; Milne and Zika, 1993; Zhang and Anastasio, 2001; Neff et al., 2002; Ge et al., 2011). Oxidized organic nitrogen species would mainly consist of organic nitrate from the reactions between hydrocarbons and nitrogen oxides both from natural and anthropogenic sources (Neff et al., 2002; Atkinson, 2007). In addition, a further portion of the WSON could be macromolecular compounds from primary biogenic and soil particles, and nitrogenated soot from combustion processes (Cornell et al., 2003 and references therein).

Although a wide variety of organic nitrogen species have been measured in the atmospheric condensed phase, amino acids, amines, and urea have been detected as major compounds. Zhang et al. (2002) showed that free and combined amino compounds contributed 23% of the WSON in the ambient aerosols at a site surrounding agricultural and urban areas in northern California. Low-molecular weight aliphatic amines have been detected in the ambient aerosols with comparable concentrations to these amino acids (Gorzelska and Galloway, 1990; Zhang and Anastasio, 2003). Urea has also been reported to contribute to a large fraction of the WSON in the ambient aerosols, for example, it accounted for 20–46% of the WSON (Cornell et al., 2001; Violaki and Mihalopoulos, 2011), but sometimes it is not a major compound with <1% of the WSON (Cornell et al., 1998; Mace et al., 2003a).

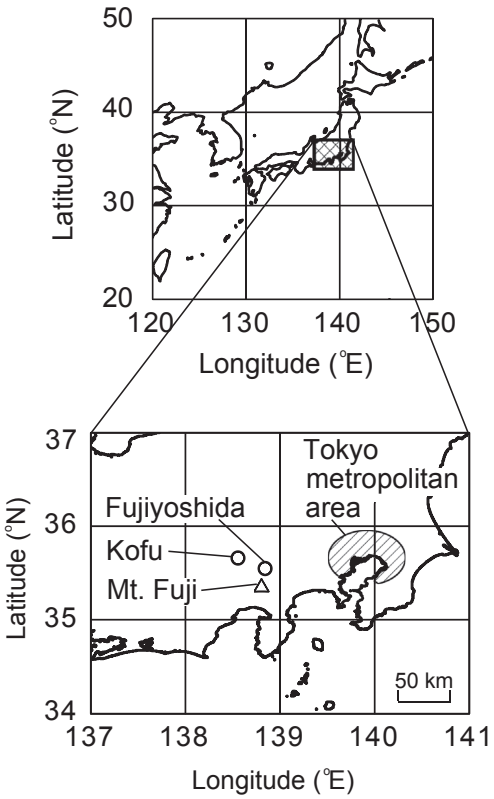

Fig. 1. The locations of Kofu and Fujiyoshida.

Although the measurements of the WSON in the ambient aerosols have gradually increased in the recent studies, they are still scarce compared to those of the inorganic nitrogen species. In particular, very little is known about the size distribution, chemical composition, and source of the WSON in the ambient aerosols, which are important for discussing the atmospheric behaviors and environmental impacts of the WSON. In addition, the estimate of dry deposition amount of the WSON and its contribution to the deposition of the fixed nitrogen have been quite insufficient both in observational and numerical studies.

In order to evaluate the contribution of the WSON to the fixed nitrogen in the ambient aerosols and their deposition, and to discuss the sources of the WSON in the aerosols, observations of the WSON in the size-segregated aerosols were conducted over three years at two sites with different atmospheric environments, i.e., urban and forested sites. In addition, the concentrations and size distribution of urea in the ambient aerosols, and its contribution to the WSON were also investigated in order to clarify the chemical components of the WSON in the aerosols.

2. Experiment

2.1. Sample collection

Air samplings were conducted at two sites; an urban site in Kofu and a forested site in Fujiyoshida, both in Yamanashi Prefecture, Japan. Kofu is the capital city of Yamanashi Prefecture located in the Kofu basin, about 100 km from the Tokyo Metropolis central, with a population of about 200,000. The sampling site in Kofu is located on the building roof of the University of Yamanashi (about 18 m above