Science of the Total Environment 408 (2010) 1932–1942

Contents lists available at ScienceDirect

Science of the Total Environment

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

Pollution of montane soil with Cu, Zn, As, Sb, Pb, and nitrate in Kanto, Japan

Takejiro Takamatsu [a,b], Mirai Watanabe [b,*], Masami K. Koshikawa [b], Tomoyoshi Murata [b], Shigeki Yamamura [b], Seiji Hayashi [b]

[a] Center for Water Environment Studies, Ibaraki University, 1375 Ohu, Itako, 311-2402 Ibaraki, Japan
[b] Water and Soil Environment Division, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, 305-8506 Ibaraki, Japan

ARTICLE INFO

Article history:
Received 14 August 2009
Received in revised form 27 November 2009
Accepted 10 January 2010
Available online 11 February 2010

Keywords:
Anthropogenic elements
Enrichment ratios
Forest pollution
Air pollution
Cumulative input of NO_3^-
Cryptomeria japonica

ABSTRACT

Soil cores and rainwater were sampled under canopies of *Cryptomeria japonica* in four montane areas along an atmospheric depositional gradient in Kanto, Japan. Soil cores (30 cm in depth) were divided into 2-cm or 4-cm segments for analysis. Vertical distributions of elemental enrichment ratios in soils were calculated as follows: $(X/Al)_i/(X/Al)_{BG}$ (where the numerator and denominator are concentration ratios of element-X and Al in the i- and bottom segments of soil cores, respectively). The upper 14-cm soil layer showed higher levels of Cu, Zn, As, Sb, and Pb than the lower (14–30 cm) soil layer. In the four areas, the average enrichment ratios in the upper 6-cm soil layer were as follows: Pb (4.93) ≥ Sb (4.06) ≥ As (3.04) > Zn (1.71) ≥ Cu (1.56). Exogenous elements (kg/ha) accumulated in the upper 14-cm soil layer were as follows: Zn (26.0) > Pb (12.4) > Cu (4.48) ≥ As (3.43) ≥ Sb (0.49). These rank orders were consistent with those of elements in anthropogenic aerosols and polluted (roadside) air, respectively, indicating that air pollutants probably caused enrichment of these elements in the soil surface layer. Approximately half of the total concentrations of As, Sb, and Pb in the upper 14-cm soil layer were derived from exogenous (anthropogenic) sources. Sb showed the highest enrichment factor in anthropogenic aerosols, and shows similar deposition behavior to NO_3^-, which is a typical acidic air pollutant. There was a strong correlation between Sb and NO_3^- concentrations in rainfall (e.g., in the throughfall under *C. japonica*: $[NO_3^-] = 21.1$ [dissolved Sb], $r = 0.938$, $p < 0.0001$, $n = 182$). Using this correlation, total (cumulative) inputs of NO_3^- were estimated from the accumulated amounts of exogenous Sb in soils, i.e., 16.7 t/ha at Mt. Kinsyo (most polluted), 8.6 t/ha at Mt. Tsukuba (moderately polluted), and 5.8 t/ha at the Taga mountain system (least polluted). There are no visible ecological effects of these accumulated elements in the Kanto region at present. However, the concentrations of some elements are within a harmful range, according to the Ecological Soil Screening Levels determined by the U.S. Environmental Protection Agency.

1. Introduction

Human activities such as mining, industry, agriculture, waste treatment, and transportation release substantial amounts of trace elements into the environment (Nriagu and Pacyna, 1988; Nriagu, 1990a). In particular, smelting, incineration, and transportation release pollutants into the atmosphere. Worldwide, annual emissions are approximately 332 Gt of Pb, 132 Gt of Zn, 35 Gt of Cu, 19 Gt of As, and 3.5 Gt of Sb (Nriagu and Pacyna, 1988). Recently, emissions from point sources such as smelters and incinerators have decreased, but emissions from transportation remain significant. Transportation emits trace elements from fuel combustion (Huang et al., 1994; Wang et al., 2003) and abrasion of brakes and tires (Weckwerth, 2001; Iijima et al., 2007). Thus, the air around roads with dense traffic in Tokyo contains more than 50 μg/m^3 of particulate matter that is rich in trace elements (Mizohata et al., 2000). Size distribution of the particulate matter is bimodal, with the trough at 1–2 μm. The course particulate fraction contains mainly crustal elements, whereas the fine (<2 μm) fraction contains anthropogenic elements such as Cu, Zn, As, Sb, and Pb (Mizohata et al., 2000; Iijima et al., 2007). The fine particulate matter is suspended in air for several weeks and is often transported over large distances. In fact, particulate matter collected at remote sites contained Zn, As, Sb, and Pb with enrichment factors exceeding 100 (Hashimoto and Otoshi, 1984; Takamatsu et al., 2000; Otsuka et al., 2002). The particulate matter is eventually deposited to soil either directly or via deposition onto vegetation (Takamatsu et al., 2000; Sakata et al., 2006). Therefore, pollution of soil by trace elements progresses gradually, even in montane forests far from urban areas. Such pollution has been reported in many countries including the United States (Friedland et al., 1984; Grigal and Ohmann, 1989; Miller and Friedland, 1994; Johnson et al., 1995; Weathers et al., 2000), France (Saur and Juste, 1994; Hernandez et al., 2003), Sweden (Johansson et al., 1995), Norway (Steinnes et al., 1997), Poland (Kabala and Szerszen, 2002), and Slovakia (Lobe et al.,

* Corresponding author. Tel.: +81 29 850 2469; fax: +81 29 850 2576.
E-mail address: watanabe.mirai@nies.go.jp (M. Watanabe).

0048-9697/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2010.01.016

1998). Pollution affects organisms within forest ecosystems, and inhibits decomposition of organic matter on forest floors, which disrupts nutrient cycles (Cotrufo et al., 1995). A synergistic effect of pollution and acid precipitation is also possible (Vogelmann, 1982). Anthropogenic elements deposited to forest soils accumulate in the surface layers of the soil (Corwin et al., 1999; Hou et al., 2005a; Ruan et al., 2008), and are usually immobilized there for a long time (e.g. Friedland and Johnson, 1985; Hawkins et al., 1995). However, such accumulations are considered as “chemical time bombs” (Kabala and Szerszen, 2002), because they will eventually leach into waterways. For instance, in montane forests of the northeastern United States, Pb leaching is expected to begin in about 2050 (Miller and Friedland, 1994).

Although there are no rules or guidelines on montane soil pollution in Japan, it is important to analyze current levels of anthropogenic elements in montane forest soils, and to determine potential effects of pollution. However, such studies have rarely been carried out in Japan. In this study, we analyzed soil pollution at several mountain sites located around the Tokyo Metropolitan area, which has the largest population (ca. 31 million) in the world.

Transportation is the major emission source of trace elements and nitrogen oxides (Kannari et al., 2007). Emission of excessive nitrogen has many adverse effects on montane soil, including soil acidification, deficiency in alkaline nutrients, increases in metal toxicity, and nitrate leaching into stream water (e.g. Aber et al., 1989). To evaluate these effects, we must determine current loads and total (cumulative) loads of nitrogen. This is because the above effects progress slowly, and there is a latent period before effects become visible. However, there is no appropriate technique to estimate the total nitrogen input to montane soil. Antimony, which is a typical traffic-origin element, behaves similarly to nitrogen oxides during aerial transportation and deposition processes (Takamatsu et al., 2000). After deposition, nitrogen oxides in the soil form NO_3^-, which is highly mobile. However, Sb is immobile and accumulates in surface soils (Ainsworth et al., 1990; Bossew et al., 2004; Hou et al., 2005a; Steely et al., 2007). Thus, Sb may be an appropriate indicator of the total input of nitrogen oxides. In this study, therefore, we propose a method to estimate the total (cumulative) inputs of NO_3^- to montane forest soils from the amounts of exogenous (anthropogenic) Sb accumulated in soils.

2. Materials and methods

2.1. Soil sampling

The sampling areas were located at the foot (160–600 m a.s.l.) of Mt. Kinsyo, Mt. Tsukuba, and in the northern and southern parts of the Taga mountain system. All study areas were located in the Kanto region. The geology at these areas is a plutonic association including granite and diorite, and the soil species is Cambisol (brown forest soil). The vegetation is plantation forests of *Cryptomeria japonica* or natural mixed forests of *C. japonica* and broad-leaved trees (Fig. 1 and Table 1). Area-1 appears to be the most polluted (Watanabe et al., 2006), because it is located northwest of the Tokyo Metropolis (population: ca. 13 million) and lies under the route through which polluted air masses from Tokyo flow frequently, especially in summer (Chang et al., 1989). The emissions of NOx and particulate matter from Tokyo were 56,300 and 3920 metric tons in 2005, respectively. About half of the total levels of pollutants are derived from transportation, and the rest are derived from industry, households, and construction machinery (Bureau of the Environment, TMG, 2009). Saitama Prefecture, which is adjacent to Tokyo, also emits comparable amounts of NOx and particulate matter (49,780 and 2941 metric tons, respectively, in 2004). Area-2 appears to be moderately polluted (Watanabe et al., 2006, 2008). It is not situated on the main route of

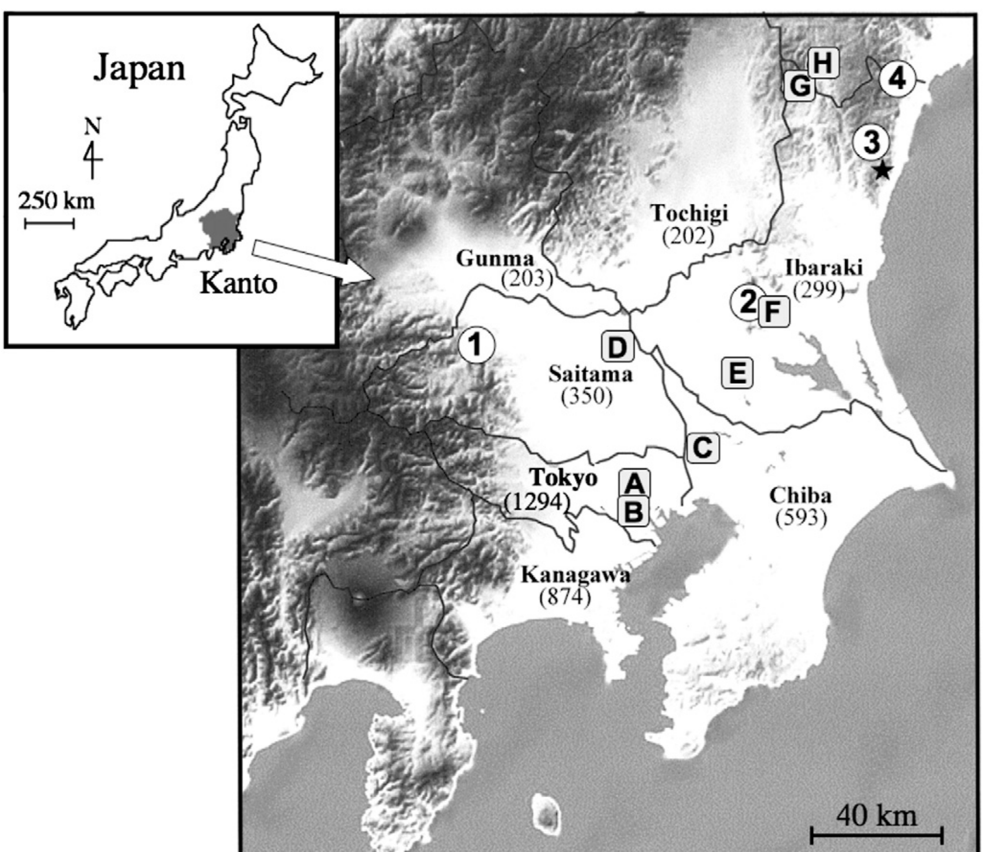

Fig. 1. Map showing sampling locations of soils (1–4) and rainwater (A–H). ★: Old Hitachi mine. Numbers in parentheses show population (×10,000) in each prefecture.