C-1.3.2 Determination of Dry-deposited Pollutants and their Behavior in the Forest Ecosystem

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Abstract

About 200 leaf samples of *Cryptomeria japonica* D. Don (and some other conifers) were collected from various areas in Japan (urban, suburban and rural areas, remote island, etc.). Aerosols deposited on the leaves were separated by dissolving the epicuticular wax with chloroform, and collected on quartz wool. They were then analysed for 29 elements by neutron activation analysis. Deposition of aerosols on the leaves began just after leaf expansion (in May or June), and its amount increased with time to reach a maximum and steady level in winter. The amounts of aerosols per unit leaf weight (or area) were larger in conifers than in broad-leaved trees. Although elements in the aerosols had various origins (fossil fuels, sea-salts, volcanic gases and soils), more than 90% of Au, Ag, Sb, Cl, Se and I, 80-90% of Br, Zn and As, 40-60% of Cr, Cs, Co and V, and ca. 30% of Fe and Na were non-soil fractions, whereas Th, Hf, Rb, Ta, Ti, Mn, Al and rare earth elements originated mostly from soils. Sb, which originated mainly from combustion of fossil fuels, was highly enriched in the aerosols (enrichment factor vs. soils: >100), in spite of its low natural abundance. Since Sb accumulates on leaves and subsequently in surface soil due to washing-down, it is a good indicator for evaluating the load of atmospheric pollutants in soil and vegetation. For instance, the amount of Sb deposited on 1-year leaves of *C. japonica* reached more than 100 ng/g-fresh leaves in heavily polluted areas of Saitama Prefecture (cf. ca. 10 ng/g-fresh leaves on Yakushima Island, Kagoshima). Since the origin of Sb and the mechanism of its atmospheric transport are expected to be similar to those of S and N compounds, the load of acidic pollutants may be estimated from the amount of Sb that accumulates in the environment.

Key Words Aerosol, Dry-deposition, Japanese cedar (*Cryptomeria japonica*), Sb, Neutron activation analysis

1. Introduction

Acidic pollutants, discharged into the atmosphere by human activities, acidify the water and soil environment via deposition on vegetation and soil surfaces. The deposition occurs through two processes: wet and dry deposition. In the former, the pollutants are contained in rain, snow or fog, and in the latter, soil and vegetation absorb and/or adsorb gaseous and particulate pollutants directly. Dry deposition is significantly affected by many environmental factors; that on vegetation is influenced by plant species and microclimate, and that on soil by the taxonomy and physico-chemical properties of the soil. Therefore, the process of dry deposition is very complex and more difficult to analyse than that of wet deposition.

Dry deposition in forest ecosystems has been evaluated mainly on the basis of differences in the compositions of elements and ions between precipitation and stemflow plus throughfall. However, as well as releasing some basic cations and organic substances into the stemflow and throughfall, plants also take up some ions (e.g. nitrate) as nutrients from the pollutants (Takamatsu et al., 1997). This plant contribution changes seasonally. Therefore, it is difficult to differentiate quantitatively between the components originating from the pollutants and those originating from plant bodies in stemflow and throughfall, sometimes resulting in erroneous conclusions.

The final goal of this study was to evaluate the deposition of acidic pollutants using bio-inert indicator elements (e.g. Sb) whose origin and atmospheric transport mechanism are similar to those of acidic pollutants. For this purpose, leaves of *Cryptomeria japonica* (and some other conifers) were collected from various areas of Japan, and aerosols deposited on the leaves were quantified by neutron activation analysis. The elemental compositions of the aerosols were characterized in relation to the local environment of the sampling sites. The effects of aerosols on tree physiology were also discussed (Takamatsu et al., 1992, 1996, 1997, 1999; Sase et al., 1998b).

2. Materials and Methods

2.1 Collection of leaf samples and separation of aerosols

About 200 leaf samples of *C. japonica* (and some other conifers) were collected from trees more than 30 years old mainly in the Kanto and Tohoku districts, and on Yakushima Island, Kagoshima. The sampling height varied from 2 to 30 m (top, middle and bottom positions of trees for investigating the effect of branch height; 2-5 m for others). The leaves were collected together with branches (weight: > 1 kg; length: ca. 30 cm) in a plastic bag containing damp tissue paper and brought to the laboratory, where they were kept in a chilled darkroom (at 5 °C) until analysis. The leaves (together with ca. 5-cm stems in the case of *C. japonica*) were washed in distilled water using an ultrasonic cleaner (Branson, 80W), dried in an oven below 50 °C for 30 min, and then allowed to dry at room temperature. Since the water content of the leaves remained approximately constant throughout the whole pretreatment process, including storage and washing, the weight of the prepared leaves was regarded as the fresh mass. Five grams of the prepared leaves (0-year or 1-year) was shaken for 15 s with 20 ml chloroform to dissolve the epicuticular wax and consequently separate aerosols from the leaf surface. The aerosols suspended in chloroform were then collected on quartz wool by filtration. Six batches were prepared for each sample; two of the batches were subjected to the following neutron activation analysis and the remainder were kept for future analysis by ICP-AES and ion chromatography (Sase et al., 1998a, 1998b).

2.2 Neutron activation analysis (Koyama and Matsushita, 1980; Takamatsu et al., 1982)

Determination of semilong- and long-lived nuclides: The aerosol sample (together with quartz wool) was double-heat-sealed in a small clean polyethylene bag. Fifteen samples were packed in an irradiation capsule together with a neutron flux monitor (Co, 30 μg) impregnated in a Millipore filter (HAWP, 25 mm i.d.). Irradiation was carried out for 50 min in a pneumatic tube (Pn-2; thermal neutron flux: 2.75 x 10^{13} n/cm^2/s) at Kyoto University Reactor (KUR). The irradiated samples were then cooled for 4-5 days. After renewing the outer polyethylene bags enclosing the samples, the γ-ray spectra were measured for 8,000 s using a Ge(Li) diode detector coupled to a 4K-channel pulse height analyzer, and then analysed for semilong-lived nuclides using the computer program developed by Koyama and Matsushita (1980). After the samples had been cooled for ca. 1 month, the γ-ray spectra were measured again for 100,000 s to analyse long-lived nuclides. The elements determined included Sm, Ce, Yb, Lu, Se, Th, Cr, Au, Hf, Br, As, Sb, Ag, Cs, Sc, Rb, Fe, Zn, Co, Ta, Na, Eu and La.

Determination of short-lived nuclides: Each sample was sealed in polyethylene bags as described above, then 2 or 3 samples were packed in a capsule together with a neutron flux monitor (Mn, 10 μg). Irradiation was carried out for 20 s in Pn-3 (2.34 x 10^{13} n/cm^2/s). Just after irradiation, the outer bag enclosing the sample was renewed, and the γ-ray spectra were measured for 100-200 s to determine short-lived nuclides. In this procedure, Si in quartz wool produced ^{28}Al through the ^{28}Si(n, p)^{28}Al reaction, and interfered with the analysis of Al. In order to correct this, the weight of the quartz wool was kept constant (25 mg; corresponding to 32 μg Al after irradiation). The elements determined included Ti, I, Mn, V, Al and Cl.

3. Results and Discussion

3.1 General characteristics of the aerosol elemental compositions

When the elemental compositions of aerosols deposited on the leaves were compared with those of soil and other crustal materials (Bowen, 1979), the aerosols were found to be rich in Se, Cr, Au, Br, As, Sb, Ag, Zn, I and Cl. Fig. 1 shows the non-soil fractions (i.e. those from human activities, sea-salts and volcanic gases) of elements in the aerosols. Sc was used as a standard element to estimate the soil fractions of elements based on the typical median concentrations of elements in soil (Bowen, 1979), because Sc was analysed in all samples with high precision (deviation in γ-ray counting: < 2%) and the non-soil fraction of Sc in the aerosols was very small (e.g. Sc concentrations in vehicle exhaust dust were less than 1 ppm). On average for ca. 200 samples, more than 90% of Au, Ag, Sb, Cl, Se and I (Ag and Se: not shown in Fig. 1, because these elements were analysed in only a limited number of samples, i.e. 20-30% of total), 80-90% of Br, Zn and As, 40-60% of Cr, Cs, Co and V, and ca. 30% of Fe and Na were identified as non-soil fractions. These included elements which combine strongly with chloride (Au: pK_1=8.5; Ag: 9.8) and produce chloride compounds with relatively low boiling points (Sb: b.p.=223 °C ($SbCl_3$); Se: 178 °C ($SeOCl_2$); As: 130 °C ($AsCl_3$); Cr: 117 °C (CrO_2Cl_2)). Since the concentration of Cl was also high in the aerosols (2.0±1.1 μg/g-fresh leaves), these elements may have been occluded in the aerosols as chloride compounds when being released into the atmosphere by combustion of fossil fuels, spraying of sea-salts, and/or evolution of volcanic gases (volcanic gases are usually rich in chloride). Among the above elements, Sb seems to have originated mainly from combustion of fossil fuels (especially oil), because the soot deposited on vehicle exhaust pipes had extremely high concentrations of Sb (4.3 ppm, n=6; Sb/Sc=11.3, cf. the ratio in soil: 0.14; Bowen, 1979). Sb was accumulated on the leaf surface (as described below) and subsequently immobilized in surface soil due to washing down (Takamatsu, unpublished). In addition, the analytical precision of Sb in the neutron activation analysis (deviation in γ-ray counting: < 5%) was considerably high, in spite of its relatively low concentration (X-X00 ng/g-fresh leaves). Therefore, Sb appears to be a promising indicator element for evaluating the long-term input of atmospheric pollutants into the environment. The elements deposited on leaves as aerosol components are partly washed down by precipitation, and this phenomenon may have been significant for alkali metals (Na and Cs; Rb: scarcely contained as non-soil fractions) and anionic elements (Cl, Br and I).

As shown in Fig. 1, elemental compositions (especially non-soil fractions) of the aerosols were sometimes affected by the specific sources in the local environment. For instance, the aerosols on *C. japonica* leaves from Osorezan (Shimokita, Aomori) were rich in As, which originated from volcanic gases (108±50 ng/g-fresh leaves, n=3; cf. average: 19+27 ng/g-fresh leaves, n=116; non-soil fractions on 1-year leaves). The samples on *C. japonica* leaves near an electrochemical plant (Yakushima Denko, Co., Ltd.) on Yakushima Island, which uses ca. 670 kl of heavy oil and 1,000 t of coal per year to produce silicon carbide and ferrosilicon, had extremely high concentrations of Co, V and Mn (17±28, 126±114, and 342±288 ng/g-fresh leaves, respectively, n=4; cf. average: 4±6, 36±40, and 0±150 ng/g-fresh leaves, respectively, n=116; non-soil fractions on 1-year leaves). In addition, the samples from Osorezan and Yakushima, which are both located near the sea, were clearly affected by sea-salts, having relatively high concentrations of I, Cs and Na, compared with the inland samples.

3.2 Effects of tree species and branch height

Figure 2 compares the amounts of elements, deposited on leaves as aerosol components, among several tree species. All the species, when compared on the basis of leaf dry weight or area, showed a similar trend (data, not shown). The deposited amounts of elements were usually larger on leaves of conifers (especially *C. japonica*) than those of broad-leaved trees. Although deposition of aerosols on leaves may be influenced by many factors including leaf type, morphology, the chemical properties of epicuticular wax, and static electricity induced on the leaf surface (in winter) (Takamatsu, unpublished), etc., further investigation of the mechanisms involved will be necessary.

Figure 3 shows the effect of branch height on the amount of Sb in aerosols on leaves, which were retrieved from single stands of *C. japonica* growing in various environments. The samples free from the direct effects of vehicles (except for the sample from Tsukuba, Ibaraki) had approximately constant amounts of Sb, irrespective of branch height, implying that the single stands of *C. japonica* had been exposed to air pollution of the same magnitude at the top, middle

and bottom positions. However, on the roadside tree (Tsukuba), the amount of Sb increased significantly from top to bottom due to the direct effect of vehicle exhaust fumes. In the case of *C. japonica* trees located within the stand (data, not shown), the treetop leaves extending above the canopy were often loaded with a larger amount of aerosols (Sb) than those under the canopy. A similar tendency was also seen for other conifers (*Pinus densiflora*, *Thujopsis dolabrata* var. *hondai*, and *Chamaecyparis obtusa*).

3.3 Accumulation of aerosols with leaf aging

Figure 4 shows changes in the amounts of Sb deposited as aerosol components on leaves of *C. japonica* and *C. deodara* with leaf aging. Deposition of the aerosols (Sb) began just after expansion of the current leaves (in late May or early June), and the amount increased gradually with time (the deposition rates increased slightly in late autumn and winter), reaching maximum and approximately constant levels in winter. Therefore, annual changes in the amounts of Sb on 1-year leaves were small (although a slight and temporary increase was sometimes observed in winter), probably because an equilibrium between deposition and washing-out was attained. Most of the other elements showed accumulation profiles similar to those of Sb, but the deposited amounts of some soluble elements (e.g. Na) tended to reach steady levels somewhat rapidly and sometimes varied irregularly, due probably to precipitation just before sampling.

3.4 Evaluation of atmospheric pollution

As described before, the amounts of aerosols on 1-year leaves remained almost constant throughout the year, and appeared to depend on the degree of atmospheric pollution at each sampling site. Figure 5 compares the amounts of Sb on 1-year leaves of *C. japonica* among areas differing in their degree of pollution. The samples from Saitama had extremely large amounts of Sb, followed in decreasing order by the plains area of Ibaraki (including NIES in Tsukuba), urban areas in Tohoku district, mountainous areas in Ibaraki, mountainous areas in Tohoku district, Shimokita in Aomori, and Yakushima Island. In Saitama, the deposition rate was about 10 times that on Yakushima. Figure 6 shows the amounts of Sb on 1-year leaves of *Abies mariesii* from mountainous areas in Kanto and Tohoku. The deposition rate of Sb was less than 20 ng/g-fresh leaves at all sites, but slightly higher at Nenbutsudaira (Nikko, Tochigi), Konsei Pass (Nikko, Tochigi), the southeastern slope of Mt. Nantai (Nikko, Tochigi), and Mt. Oga (Nasu, Tochigi) than in the other areas, due probably to the influence of pollutants from Tokyo and its suburbs. Figure 7 shows the amounts of Sb on 0-year and 1-year leaves of *C. japonica* at various points around the coast of Yakushima. The deposition rates were clearly larger on the north side of the island than on the south side, suggesting transport of pollutants from Kyushu (and probably East Asia).

3.5. Effects of aerosols on tree physiology

The aerosols deposited on tree leaves were rich in several toxic elements such as Sb, As, Se and Cr, and may have contained some toxic organic compounds (e.g. pesticides); thus, some negative effects exerted by such chemicals may be significant. Aerosols increase the leaf wettability and also accelerate the degradation and erosion of epicuticular wax on the leaf surface, resulting in an increase of cuticular transpiration, leaching of nutrients, and invasion by pollutants and pathogens (Percy, et al., 1994; Sase et al., 1998; Sase and Takamatsu, 1998). In addition, a proportion of the aerosols penetrate into the stomata. Since conifers usually have depressed stomata, aerosols are easily trapped there and are difficult to wash out. Aerosols that have penetrated into stomata often cause their incomplete closure, thus disturbing the control of transpiration and gas-exchange. In fact, in 1-year leaves of *C. japonica* from Saitama, which bore large mounts of aerosols, 42±18% (n=4) of the stomata had been damaged (cf. : 2.8±0.5%, n=4, for 1-year leaves from mountainous areas in Ibaraki). Increased cuticular transpiration rates (1.01±0.24 %/h, n=4; cf. 0.63±0.05 %/h, n=4, for 1-year leaves from mountainous areas in Ibaraki, according to the desiccator method of Sase et al., 1998b) and leaching of basic cations from the leaf surface (157±53 μg/g-fresh leaves, n=4; cf. 80±12 μg/g-fresh leaves, n=4, for 1-year leaves from mountainous areas in Ibaraki; amounts of Na+K+Mg+Ca leached into dilute sulfuric acid (pH=3) for 2 h), both of which were

probably the result of stomatal damage, were also observed. These physiological changes may have imposed some significant stress on the trees (Takamatsu et al., 1996; Sase et al., 1998a, 1998b).

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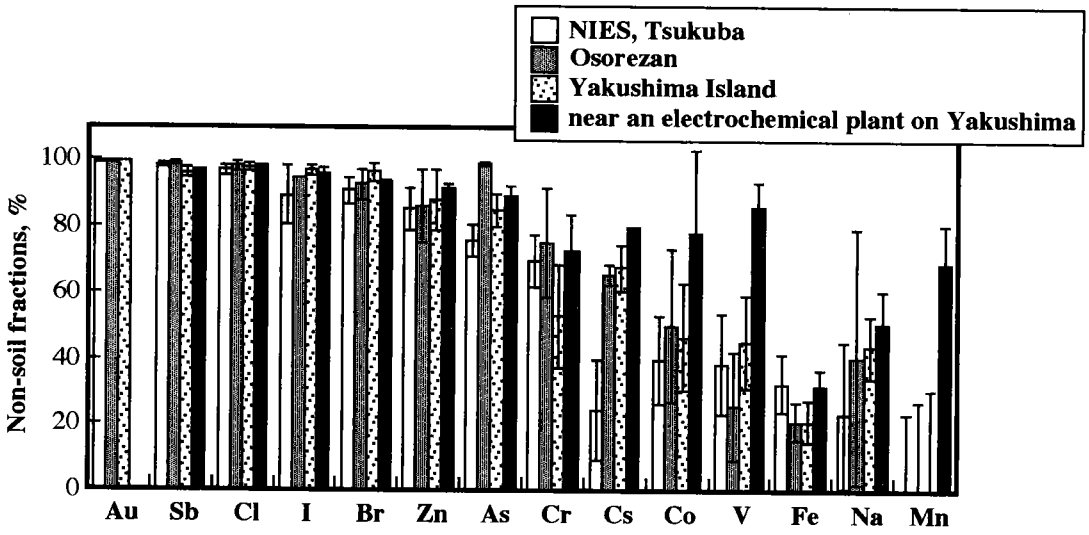


Fig. 1 Non-soil fractions of elements in aerosols deposited on leaves

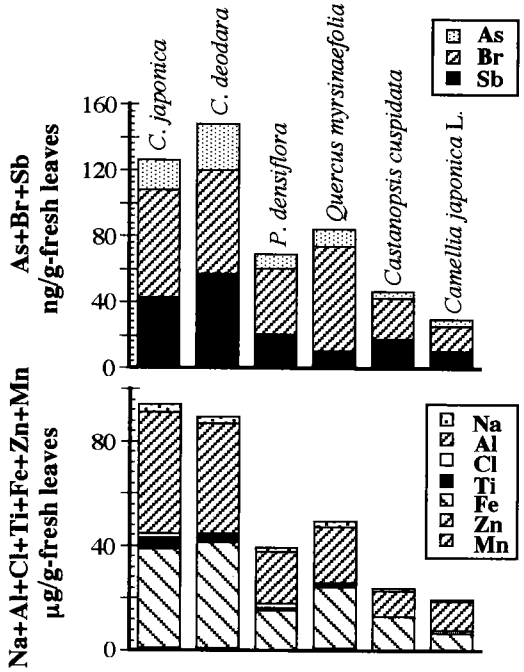


Fig. 2 Amounts of elements in aerosols deposited on the leaves of different tree species
Sampling: at NIES, Tsukuba; 0-year leaves in winter

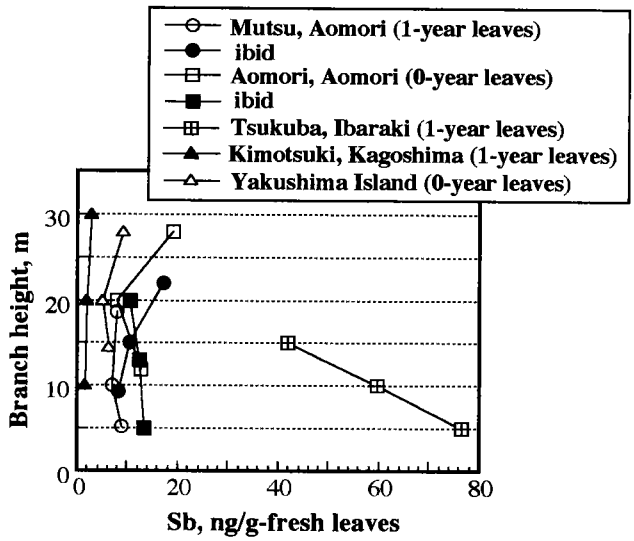


Fig. 3 Amounts of aerosols (Sb) on *C. japonica* leaves at different branch heights

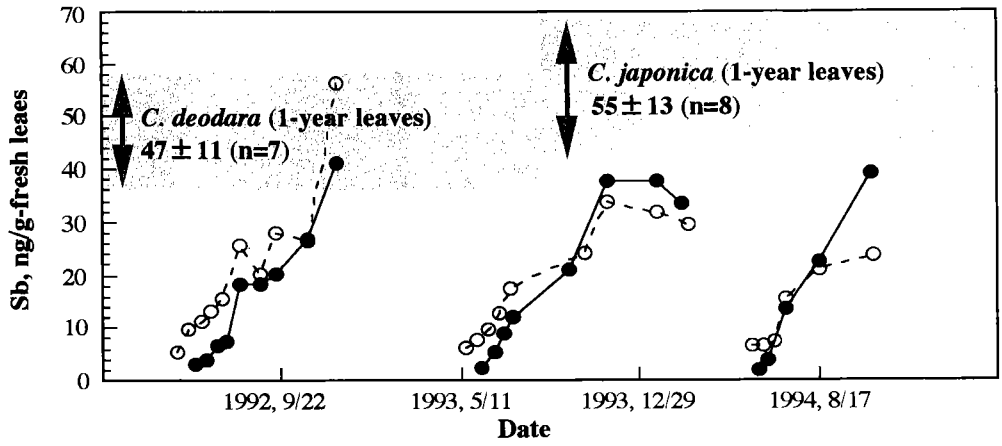
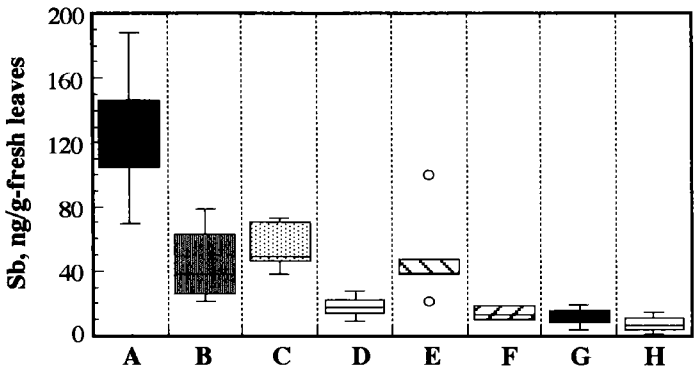


Fig. 4 Accumulation of aerosols (Sb) on leaves with leaf aging
Observation site: NIES, Tsukuba. (●) *C. japonica*, (○) *C. deodara*



A: Saitama; B: Plains in Ibaraki; C: NIES, Tsukuba; D: Mountainous areas in Ibaraki; E: Urban areas in Tohoku; F: Mountainous areas in Tohoku; G: Shimokita, Aomori; H: Yakushima Island.

Fig. 5 Amounts of aerosols (Sb) on 1-year leaves of *C. japonica* from various areas differing in their degree of air pollution

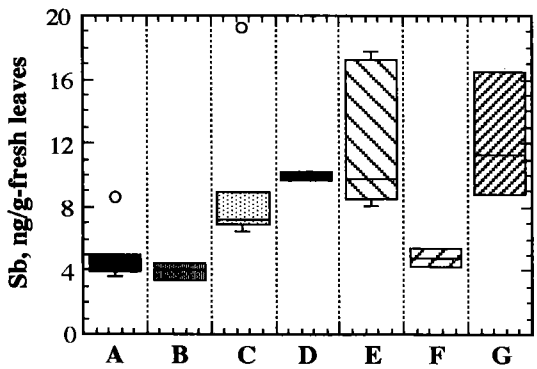


Fig. 6 Amounts of aerosols (Sb) on 1-year leaves of *Abies Mariesii* from mountainous areas in Kanto and Tohoku districts
A: Shizu-rindo (woodland path), Nikko; B: Northeastern slope of Mt. Nantai, Nikko; C: Nenbutsudaira, Nikko; D: Konsei Pass, Nikko; E: Southeastern slope of Mt. Nantai, Nikko; F: Hachimantai, Iwate: G: Mt. Oga, Nasu.

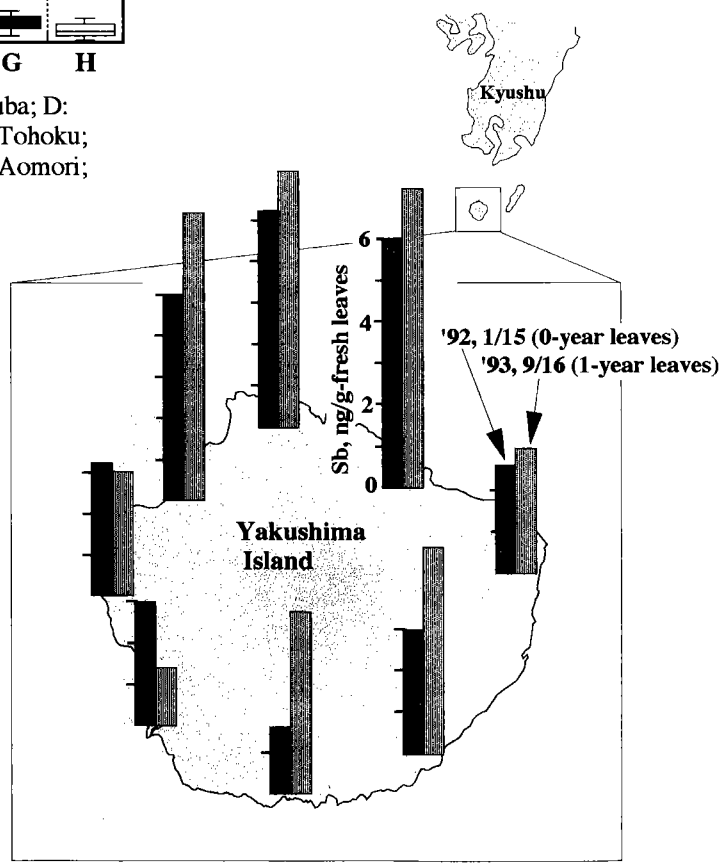


Fig. 7 Amounts of aerosols (Sb) on *C. japonica* leaves taken from around the coast of Yakushima Island