

# Aerosol Elements on Tree Leaves

## —Antimony as a Possible Indicator of Air Pollution—

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### Abstract

More than 300 samples of tree leaves (mainly *Cryptomeria japonica*) were collected from urban, suburban, and rural areas in Japan. Aerosols deposited on the leaves (leaf aerosols) were isolated and analyzed by instrumental neutron activation analysis. The amounts of elements in leaf aerosols (aerosol elements) increased with leaf age to reach a steady maximum on one-year-old leaves. Amounts were greater on conifers, especially on *C. japonica*, than on broad-leaved trees, and usually greater on upper leaves. Although the aerosol-elements had various origins, more than 90% of Au, Ag, and Sb, about 80% of Zn and Cr, about 70% of Cl, 30%–50% of As, I, Se, and Br, and 10%–30% of Co, V, and Fe were non-terrestrial, whereas Th, Hf, Rb, Ta, Ti, Mn, Al, and rare earth elements originated mostly from soils. Sb, originating mainly from vehicle exhaust, was highly enriched in leaf aerosols (enrichment factor vs. soil : 2.2–150, av. 38), and its amount correlated with NO<sub>x</sub> concentration and population density in each sampling area. The distribution of *C. japonica* (and also *Pinus densiflora*) everywhere throughout Japan, makes aerosol-Sb on their leaves a good indicator for monitoring air pollution due to daily human activity.

**Key words :** Aerosols, *Cryptomeria japonica*, Neutron activation analysis. Sb, Tree leaf,

### 1. Introduction

Recently, atmospheric concentrations of coarse aerosols (eg., PM 10), discharged mainly from heavy industries, have been decreasing because of the application of efficient air cleaning systems, but those of fine aerosols (eg., PM 2.5) originating mainly from vehicles are still high (Spurny, 1999). Aerosols contain toxic, genotoxic, and carcinogenic substances including elements (As, Cr, Sb, Pb, Se, etc.) and organic compounds (PAHs, oxy-PAHs, nitro-PAHs, etc.) (Kasahara, 1999; Spurney, 1999), and thus have adverse effects on human health (Spurney, 1999). Aerosols also impede plant physiological processes : those deposited on leaves cause deterioration and erosion of epicuticular wax, and thus increase leaf wettability (Cape *et al.*, 1989; Turunen & Huttunen, 1990; Sase *et al.*, 1998b). In addition, some of the aerosols intrude into stomata and block them, disturbing the control of transpiration and gas exchange (Beasley, 1942; Crossley & Fowler, 1986; Farmer, 1993; Beckett *et al.*, 1998; Sase *et al.*, 1998b). These often cause significant water and nutrient stress in plants.

The most widely used methods for sampling aerosols include filtration and diffusion denudation (Kitto & Colbeck, 1999). Although these instrumental techniques are sophisticated and have excellent sampling

yield and precision, they require a power supply, and thus are limited only to areas where they are applicable (i.e. they are difficult to use in remote or mountainous areas). In order to solve this problem, several plants can be effectively used as receptors (natural samplers), including moss (Klumpp *et al.*, 2000), leaves (Beckett *et al.*, 1998), and bark (Fatoki & Ayodele, 1991). Among them, tree leaves appear to be the most promising receptors, for the following reasons : 1) the leaf surface easily adsorbs and accumulates aerosols, especially anthropogenic carbonaceous ones (Wyttenbach *et al.*, 1987a, 1987b; Beckett *et al.*, 1998), because of its hydrophobic nature (Sase & Takamatsu, 1998); 2) the period of exposure is estimable, because leaf ages can be determined precisely; 3) the direct effect of stemflow is not significant; 4) contamination with soil dust flung up from the surroundings is less significant when upper leaves are used.

We isolated aerosols from tree leaves (mainly *Cryptomeria japonica*) collected in remote, rural, and urban areas of Japan, and analyzed them by instrumental neutron activation analysis. The elemental compositions of the aerosols were discussed in relation to both the environment at the sampling sites and the tree properties (species, branch height, leaf age, etc.).

## 2. Materials and Methods

### 2.1 Sampling sites

The sampling sites were in Kanto, Tohoku (including the remote Shimokita), and Yakushima, Japan (Fig. 1). The sites at Osorezan (Aomori) and Yakushima have unusual environments. Osorezan is a typical volcanic area, exposed constantly to acidic volcanic gases (99.7% of sulfur gases occur as  $H_2S$ ; Iwasaki *et al.*, 1962). The *C. japonica* leaves sampled here were exposed to  $H_2S$  at  $5 \pm 3 \mu g S/cm^2/d$  (Sase *et al.*, 1998a). Yakushima is a small mountainous island (about  $500 km^2$ ; highest peak : 1935 m), located about 60 km south of Kyushu in the Pacific Ocean. Human impact on the island is generally low because of the small population (about 14,000); and the main industries are agriculture, forestry, fishing, and tourism. The only heavy industry is an electrochemical plant (Yakushimadenkou Co., Ltd.) near Port Miyaura, in which about 670 kl of heavy oil and about

1,000 t of coal are used per year to produce silicone carbide and ferrosilicon (Sase *et al.*, 1998b).

### 2.2 Leaf samples

More than 300 leaf samples (Kanto : 213, Tohoku : 44, Yakushima : 66 samples) were collected from trees that were isolated or situated on the southern margins of stands. Target species were *C. japonica* (253 samples), other conifers (*Cedrus deodara*, *Pinus densiflora*, *Pinus thunbergii*, *Thujopsis dolabrata* var. *hondai*, *Chamaecyparis obtusa*, *Abies firma*, and *Tsuga sieboldii*) (66 samples), and broad-leaved trees (*Camellia japonica*, *Castanopsis cuspidata*, *Quercus myrsinaefolia*, and *Rhododendron oomurasaki*) (4 samples). Leaves were taken from the top, middle, and bottom of trees (2–30 m above the ground) for investigation of the effect of branch height, and at the bottom (2–5 m; or 1 m for *R. oomurasaki*) for other investigations. Although the total period of sampling extended from October 1991 to April 1997, leaves for the branch height investigation were collected in a single day from the same trees, which had been felled

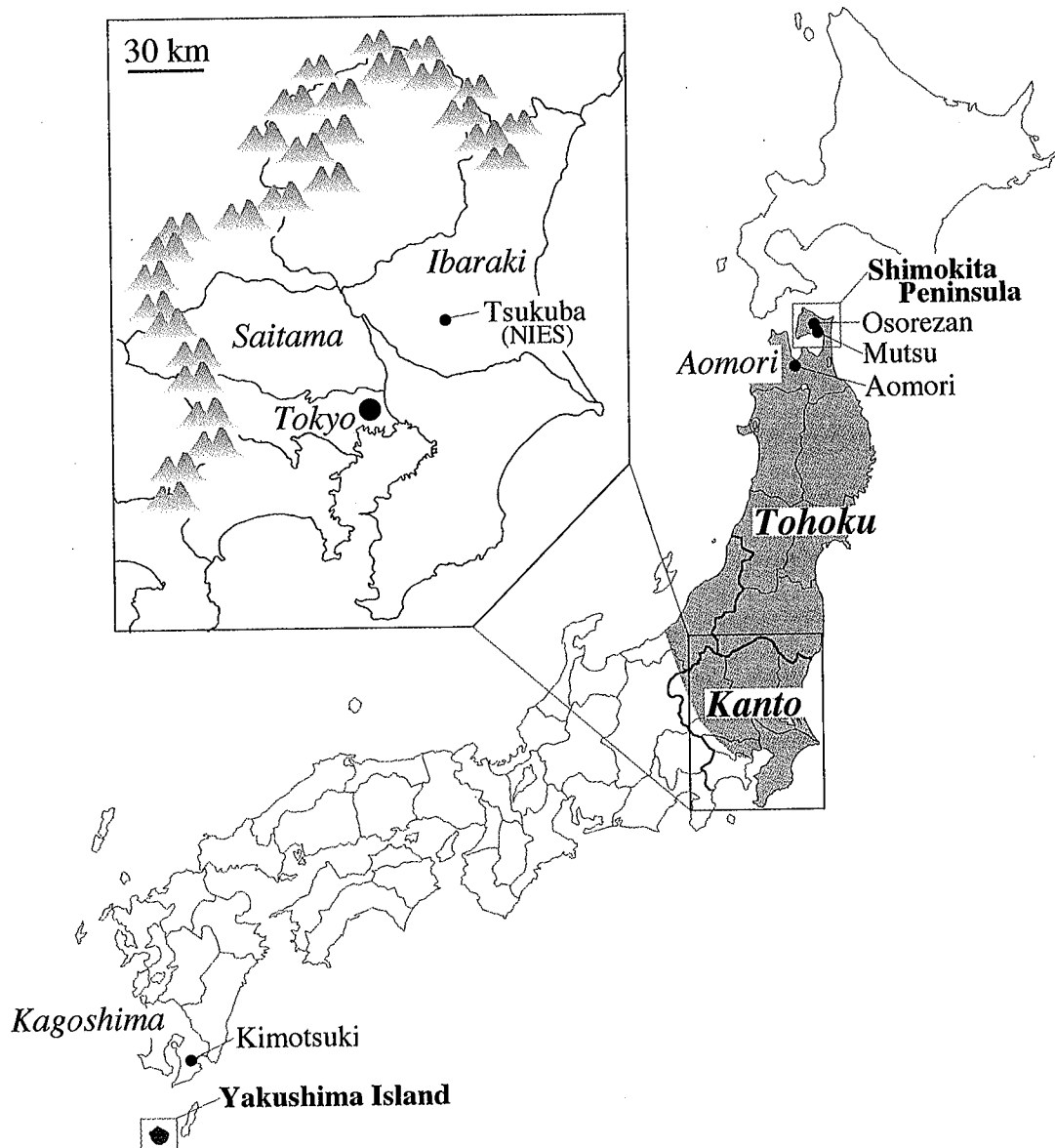


Fig. 1 Locations of sites at which tree leaves were sampled. Most samples were collected in the shaded areas.

for timber and public works (eg., *C. japonica* on Aug. 4, 1993, in Mutsu, Aomori; *C. japonica* on March 17, 1992, in Yakushima; *P. densiflora* on June 15, 1994, at the National Institute for Environmental Studies (NIES), Tsukuba, Ibaraki). Leaves used for investigation of the effect of tree species were collected within about 200 m × 200 m at NIES from October to December, 1992, and within about 50 m × 50 m on Yakushima on September 18, 1993, and at Mutsu, Aomori, on August 4, 1993. Current (0-y) and one-year-old (1-y) leaves (plus about 5 cm of *C. japonica* stems) were sampled separately.

### 2.3 Isolation of leaf aerosols

Leaves were washed in distilled water for 1 min with an ultrasonic cleaner (Branson, 80 W) to eliminate easily removable dust and components of leaf aerosols (thus eliminating any meteorological effect just before sampling), and dried (< 50°C) to remove the adherent water. As the water content of the leaves remained almost constant (especially in *C. japonica*) throughout storage, washing, and drying, the weight of the prepared leaves was regarded as the fresh weight. Five grams of the prepared leaves were shaken for 15 s in 20 ml chloroform to dissolve the epicuticular wax and consequently separate aerosols from the leaf surface (Sase *et al.*, 1998a, 1998b) (no aerosol was found on the leaf surface by SEM observation after this treatment). The aerosols suspended in the chloroform were then collected on a small amount of quartz wool by filtration (Sase *et al.*, 1998b). The amounts of elements in leaf aerosols ("aerosol-elements") were expressed either by fresh weight (ng/g fresh leaves [FL] or  $\mu\text{g/g-FL}$ ) or by leaf surface area (ng/100 cm<sup>2</sup>) (measurement of leaf surface area is described below). The deposition profiles of aerosol elements by dry weight (not shown) were basically the same as those by fresh weight, because the water content of leaves was mostly steady after leaf expansion in August (e.g., *C. japonica*: 58% ± 4%, n=25; *C. deodara*: 58% ± 4%, n=28); and the differences between tree species were small.

### 2.4 Instrumental neutron activation analysis

#### 2.4.1 Determination of semi-long-lived and long-lived nuclides

Each aerosol sample (on quartz wool) and a neutron flux monitor (30  $\mu\text{g}$  Co) were irradiated together for 50 min in Pn-2 (thermal neutron flux:  $2.75 \times 10^{13}$  n/cm<sup>2</sup>/s) (Koyama & Matsushita, 1980) at the Kyoto University Reactor. After the samples were cooled for 4-5 days, the  $\gamma$ -ray spectra of the samples were measured for 8,000 s by a Ge (Li) diode detector coupled to a 4K-channel pulse-height analyzer, and then computer-analyzed for semi-long-lived nuclides. After a month, the  $\gamma$ -ray spectra were measured again for 100,000 s for long-lived nuclides. The elements assayed were Sm, Ce, Yb, Lu, Se, Th, Cr, Au, Hf, Br, As, Sb, Ag, Cs, Sc, Rb, Fe, Zn, Co, Ta, Na, Eu, and La. Relative standard deviations ( $100 (N_B)^{1/2} / N_P$ ; where  $N_B$  and  $N_P$  are counts of background and net peak areas, respectively) of the analytical values

were less than 5% for Sm, Ce, Th, Cr, Br, As, Sb, Cs, Sc, Fe, Zn, Co, Na, and La, 5-10% for Yb, Se, Au, Hf, Ag, Rb, Ta, and Eu, and 10-20% for Lu. Detection limits ( $3(N_B)^{1/2}$ ) of the elements were approximately 0.05 ng for Au, 0.1 ng for Sc, 0.5 ng for Sm, Ta, and Eu, 1 ng for Yb, Lu, Th, Hf, Sb, Cs, and Co, 5 ng for Ce, Se, As, Ag, and La, 10 ng for Cr, Br, Rb, and Zn, 500 ng for Na, and 1  $\mu\text{g}$  for Fe, although they varied depending on the concentrations of coexisting elements (especially Na) and cooling times of the samples.

#### 2.4.2 Determination of short-lived nuclides

Each sample and a monitor (10  $\mu\text{g}$  Mn) were irradiated together for 20 s in Pn-3 ( $2.34 \times 10^{13}$  n/cm<sup>2</sup>/s) (Koyama & Matsushita, 1980). Just after irradiation, the  $\gamma$ -ray spectra were measured for 100-200 s for short-lived nuclides. The Si in the quartz wool produced <sup>28</sup>Al through the <sup>28</sup>Si (n, p)<sup>28</sup>Al reaction, which interfered with the analysis of Al. To correct for this, the weight of the quartz wool was kept constant (25 mg; corresponding to 32  $\mu\text{g}$  Al after irradiation). The elements assayed were Ti, I, Mn, V, Al, and Cl. Relative standard deviations of the analytical values were less than 5% for Mn and Al, 5-10% for V, and 10-20% for Ti, I, and Cl. Detection limits of the elements were approximately 50 ng for I, Mn, and V, 500 ng for Al, 1.0  $\mu\text{g}$  for Cl, and 5.0  $\mu\text{g}$  for Ti, although they varied due to concentrations of coexisting elements (especially Al and Mn) and cooling times of the samples.

### 2.5 Measurement of leaf surface area

Fresh leaves were immersed in chloroform for 0.5-1 min with gentle stirring to remove the epicuticular wax and to make the leaf surface wettable (Sase *et al.*, 1998a). The leaves were next dipped in 0.4% Amido Black 10B dye solution (containing 0.01% Tween 100), shaken to remove excess liquid, and rinsed in 50 ml water to dissolve the dyes. The absorbance of the solution thus obtained was measured at 600 nm. For 12 tree species examined, the amounts of adsorbed dye per unit weight of fresh leaves were almost constant (relative standard deviation: 5.1%-9.0%, n ≥ 5) within samples of the same age. A calibration curve (absorbance at 600 nm = 0.00333 × surface area [cm<sup>2</sup>], r = 0.996 [ $P < 0.01$ ]) was prepared with leaf chips of *Camellia japonica* with known areas, and used to convert the amount of adsorbed dye to the leaf surface area.

### 2.6 Calculation of enrichment factors (EFs)

Elemental concentrations in leaf aerosols were normalized by the concentration of Sc (i.e. X/Sc). Sc was used as a standard element because it was analyzed in all samples with high precision (relative standard deviation < 5%), and anthropogenic Sc in aerosols is very small (e.g. Sc in vehicle exhaust dust is < 1 ppm; from the original data in Table 1). The enrichment factor (leaf aerosol vs. soil) was calculated as  $EF = (X/Sc)_{\text{aerosol}} / (X/Sc)_{\text{soil}}$ . The soil values were averages from surface Brown Forest Soils (Cambisols) from Kanto, Shimokita, and Yakushima (n=18) (procedures used for sampling and NAA, not shown). Aerosols deposited in Japan sometimes contain aeolian dusts (e.g. Kosa aerosols) transported

over a long distance (Nishikawa, 1993 ; Nishikawa *et al.*, 2000), but their elemental compositions may rapidly converge with those of indigenous soil after deposition (Nishikawa *et al.*, 1992). Therefore, the above value is available for soil measurement.

### 2.7 Statistical analysis

Statistical calculations—ANOVA and Fisher's Protected Least Significant Difference—were done with Stat View 4.5j (Abacus Concepts, Inc., Berkeley, CA, USA).

## 3. Results and Discussion

### 3.1 General characteristics

Average (minimum-maximum) amounts of aerosol elements (ng/g-FL), which were determined in more than 80% of the samples, were, in decreasing order : Al,  $26,500 \pm 23,100$  (-133,000) (minimum values omitted : not detected) > Fe,  $22,400 \pm 21,000$  (-130,000) > Na,  $2,560 \pm 2,420$  (172-18,400) > Zn,  $366 \pm 504$  (-3,170) > Mn,  $305 \pm 252$  (-1,340) > Cr,  $87 \pm 94$  (-614) > V,  $73 \pm 57$  (-364) > Br,  $46 \pm 37$  (2.4-290) > Sb,  $31 \pm 52$  (0.58-361) > Ce,  $23 \pm 20$  (-160) > As,  $16 \pm 21$  (-188) > La,  $12 \pm 10$  (-83) > Co,  $6.3 \pm 6.7$  (-61) > Sc,  $5.8 \pm 5.6$  (0.12-34) > Th,  $4.0 \pm 3.1$  (-25) > Cs,  $3.2 \pm 2.3$  (-22) > Hf,  $2.4 \pm 2.1$  (-16) > Sm,  $1.9 \pm 1.7$  (-13). In addition, ranges of amounts (ng/g-FL) of other aerosol elements were : Ti, -17,200 ; Cl, -30,000 ; Rb, -148 ; I, -116 ; Se, -52 ; Ag, -80 ; Yb, -7.2 ; Ta, -4.0 ; Eu, -3.5 ; Au, -3.0 ; Lu, -1.6.

Figure 2 compares the Sc-normalized concentrations of elements in leaf aerosols with those of soil.

The leaf aerosols were rich in Au (average EF=140), Ag (120), Sb (38), Cl (16), Zn (8.7), Cr (6.7), As (3.9), I (3.6), Br (2.9), Se (2.7), Co (1.7), and V (1.5) (Wytttenbach *et al.*, 1987a, 1987b). X/Sc ratios for the elements with EF < 1.5 (Rb, Na, Hf, Th, Ce, Lu, Sm, Ta, La, Cs, Ti, Sc, Yb, Mn, Eu, and Fe) were relatively constant (average standard deviation : about 40%). But ratios for the elements with EFs  $\geq 1.5$  varied greatly (about 125%) and showed regional peculiarity. Figure 3 shows the non-terrestrial fractions (i.e., those from human activities, sea salt, volcanic gases, etc.) of aerosol-elements in several selected areas (balanced with Sc concentrations). On average, for all samples, >90% of Au, Ag, and Sb, about 80% of Zn and Cr, about 70% of Cl, 30%-50% of As, I, Se, and Br, and 10%-30% of Co, V, and Fe were non-terrestrial (not illustrated). These included cationic elements that combine strongly with chloride (e.g., Au :  $pK_1=8.5$ , Ag : 9.8) and produce chloride compounds with low boiling points (e.g.,  $SbCl_3$ , 223°C ;  $SeOCl_2$ , 178°C ;  $AsCl_3$ , 130°C ;  $CrO_2Cl_2$ , 117°C ; Chemical Society of Japan, 1975). As the concentrations of Cl were also high in the leaf aerosols ( $2.0 \pm 1.1$  g/g-FL), 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, or evolution of volcanic gases (usually rich in Cl ; Iwasaki *et al.*, 1962) (Orlic, 1999). However, a proportion of some non-terrestrial elements, which are relatively rich in plant leaves (e.g., Au, Zn, Cl, I, Br, Co ; ratios of abundance in leaves to that in leaf-aerosols > 10 ; Takada *et al.*,

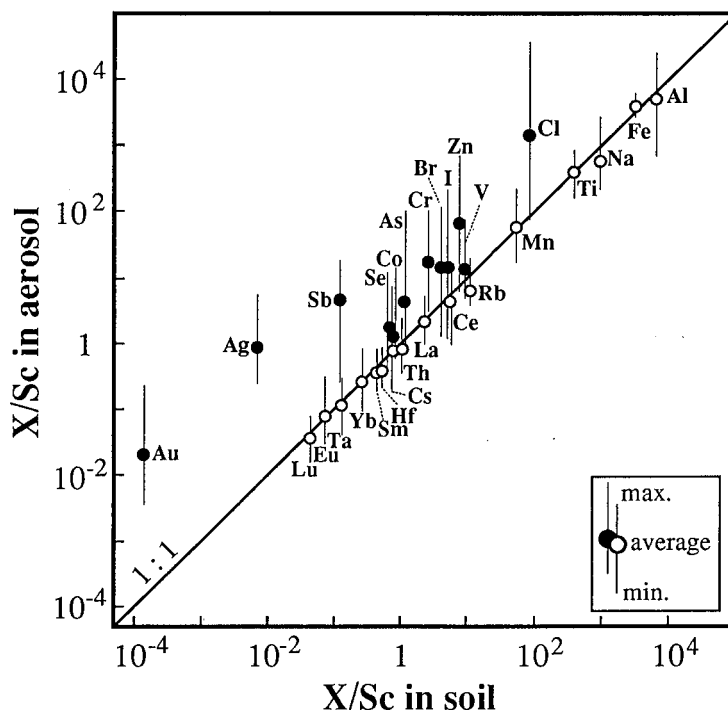


Fig. 2 Relationship between concentrations of elements normalized by concentrations of Sc (i.e. X/Sc) in leaf aerosols and the average ratios of X/Sc in soil. Aerosols : from leaves of 12 tree species, n=242. Soil : Brown Forest Soils (Cambisols), n=18. Closed circles : elements enriched in aerosols (EF  $\geq 1.5$ ), open circles : elements with low EF (< 1.5).

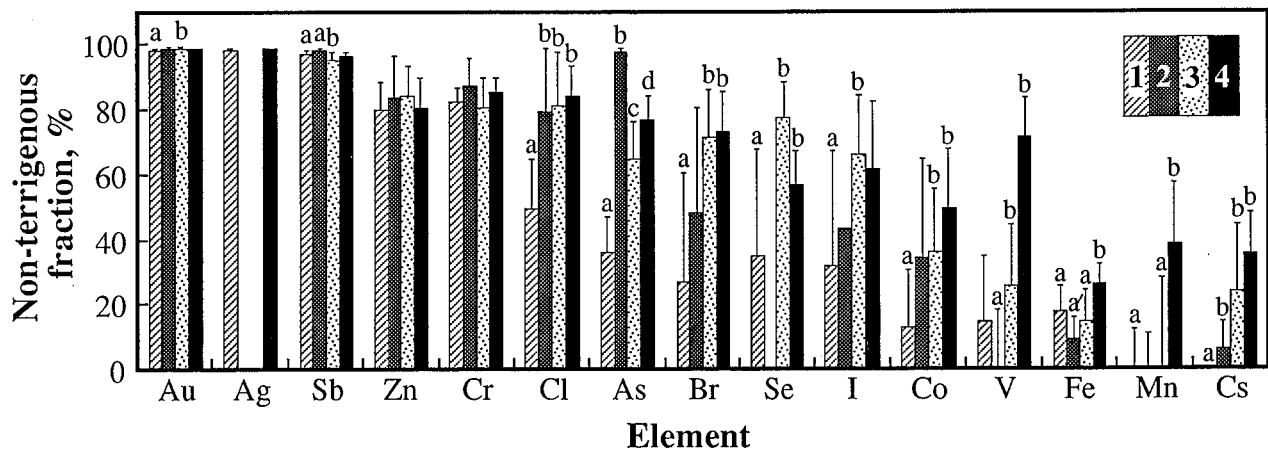
1993), may have originated from the tree itself, because many elements are released from the leaf surface, especially in the physiologically active period of spring and summer (Takamatsu *et al.*, 1997). Among the above elements, Sb seems to have originated mainly from combustion of oil (Huang *et al.*, 1994), because leaching of this element from the leaf surface should be negligible (ratios of abundance in leaves to those in leaf-aerosols : 1-2 ; Takada *et al.*, 1993) and the soot deposited in vehicle exhaust pipes is extremely rich in Sb (4.3 ppm, Sb/Sc : 11.4, n=6 ; cf. Sb/Sc in soil : 0.12 ; from the original data in Table 1). The analytical precision of Sb was high (relative standard deviation < 5%), in spite of its relatively low concentration (0.58-361 ng/g-FL). Sb may thus be a good indicator for evaluating air pollution (described below).

Table 1 shows EFs of elements in aerosols collected by low-volume filtration and by natural deposition on Ti plates (sampling procedures are described briefly in the footnote), and those in vehicle exhaust dusts including NIES CRM No.8 (prepared from precipitates found in ventilators of a highway tunnel ; Okamoto, 1987) and soot deposited in vehicle exhaust pipes (6 samples including 4 from gasoline engines and 2 from diesel engines). The latter samples should have retained the original elemental compositions of vehicle exhaust particles. The EFs of elements other than Na, Zn, Ag, and Au in the leaf aerosols correlated well with those from the other sources (type :  $y = ax^b$  ;  $r > 0.96$ ,  $P < 0.01$ ). This may indicate that the elements enriched in leaf aerosols originated mainly from vehicle exhaust. Although Na, Cl, and Br are abundant in leaves (Takada *et al.*, 1993) and thus may have been

**Table 1** Average enrichment factors of elements in aerosols and vehicle exhaust dust.

Element	Aerosol			Vehicle exhaust dust	
	Leaf*1	Filter*2	Plate*3	CRM*4	Pipe*5
n=	242	12	12	1	6
Rb	0.57		0.47	0.75	
Na	0.58	11	3.0	3.6	1.0
Hf	0.72		0.79	0.69	6.4
Al	0.76	0.71	0.71	0.92	(18)#2
Th	0.77	1.1	0.55	0.60	1.9
Ce	0.79	4.6	0.59	1.0	(64)#3
Lu	0.82			0.87	9.5
Sm	0.84	1.7	0.74	0.85	1.6
Ta	0.84		1.6	1.7	4.7
La	0.94		0.73	0.95	(60)#3
Cs	0.97	1.9	0.48	0.57	
Ti	0.99		(11)#2	1.2	
Sc	1	1	1	1	1
Yb	1.0		0.92	0.80	
Mn	1.1	4.5	1.7	2.4	21
Eu	1.1		1.1	1.3	3.4
Fe	1.2	1.9	1.3	2.8	(46)#2
V	1.5	9.4	1.5	3.4	6.7
Co	1.7	4.3	2.4	8.0	30
Se	2.7	41	1.5	3.6	
Br	2.9	60	10	20	8.2
I	3.6	17		1.3	33
As	3.9	48	1.8	4.3	24
Cr	6.7	25	11	18	(2000)#2
Zn	8.7	(310)#1	17	250	810
Cl	16	290	54	20	30
Sb	38	1300	16	91	95
Ag	120	1200		51	
Au	140		180	32	

Enrichment factor: X/Sc in aerosol or vehicle exhaust dust divided by X/Sc in soil. \*1: leaf aerosols. \*2: aerosols collected on filters (Millipore SSWP, pore size: 3.0  $\mu$ m) using a low volume sampler at NIES (Tsukuba, Ibaraki) (once for 5 days a month from July 1995 to June 1996; flow rate: 15 L/min), Analysis: NAA. \*3: aerosols deposited on Ti-plates (20 cm x 20 cm) sheltered from rain at NIES (retrieved monthly from June 1994 to May 1995), Analysis: NAA. \*4: NIES CRM No. 8 (vehicle exhaust particulates). \*5: Soot deposited in vehicle exhaust pipes (4 from gasoline engines and 2 from diesel engines), Analysis: NAA. #1, #2 and #3: high values due probably to filter blank, contamination of materials, and post-combustion catalysts, respectively.



**Fig. 3** Non-terrigenous fractions of elements in aerosols on *Cryptomeria japonica* leaves. Leaf age : 0-y (after complete expansion of leaves in August) +1-y. Sites : (1) NIES (National Institute for Environmental Studies), Tsukuba, Ibaraki, n=22 ; (2) Osorezan, Aomori, n=6 ; (3) Yakushima, Kagoshima, n=45 ; (4) near the electrochemical plant on Yakushima, n=16. Different lowercase letters above the bars indicate significant differences ( $P < 0.01$ ).

supplied to leaf aerosols due to leaching, their EFs were relatively low in leaf aerosols, due probably to washing out by precipitation. The EF of Zn was also low in leaf aerosols relative to those in vehicle dusts, which may contain tire dust, which is usually rich in Zn (Degobert, 1995). In contrast, the EFs of Au and Ag were somewhat higher in leaf aerosols than in vehicle exhaust dusts. Some of these elements may have been supplied from other sources (e.g., waste incinerators) (Huang, 1994).

Non-terrigenous fractions of the aerosol-elements were sometimes affected by specific sources in the local environment (Fig. 3). For instance, the aerosols on *C. japonica* leaves from Osorezan were rich in As ( $108 \pm 50$  ng/g-FL, n=3; cf. average for all :  $19 \pm 27$  ng/g-FL, n=116; non-terrigenous fractions on 1-y leaves), which originated from volcanic gases. Those from sites near the electrochemical plant on Yakushima had considerably higher concentrations of Fe, Co, Mn, and V (described below). Those from Osorezan and Yakushima, both near the sea, were clearly affected by sea salt, having relatively high concentrations of Cl, Br, I, and Cs compared with the inland samples (e.g., NIES, Tsukuba).

### 3.2 Effect of tree species

Figures 4 and 5 compare the amounts of aerosol elements on leaves among tree species. Sb, As, and Br were chosen to represent non-terrigenous elements, and Sm, Sc, and La (or Th), terrigenous elements. The deposition of aerosols on leaves is likely to have changed depending on the microenvironment around trees, although they were situated within narrow areas (about 200 m  $\times$  200 m at NIES and about 50 m  $\times$  50 m in Yakushima and Mutsu). In addition, the number of samples analyzed here was limited. Therefore, although a strict comparison is difficult (not significant statistically), the following tendencies are indicated : the amounts of aerosol elements were larger on conifers than on broad-leaved trees (Fergusson *et al.*, 1980). For example, the averages (ng/g-FL) at NIES (Fig.4) were  $34 \pm 12$  (conifers) and  $19 \pm 8$  (broad-leaf) for Sb,  $13 \pm 6$  and  $7 \pm 4$ , respectively, for As, and

$53 \pm 23$  and  $35 \pm 21$ , respectively, for Br. Sm, Sc, and La were also deposited more on the conifers (except for *R. oomurasaki*, whose leaves were sampled at 1 m height, and thus bore large amounts from soil dust). The averages (ng/g-FL) were  $1.7 \pm 0.5$  (conifers) and  $0.85 \pm 0.41$  (broad-leaf) for Sm,  $6.4 \pm 2.4$  and  $3.2 \pm 1.6$ , respectively, for Sc, and  $9.8 \pm 3.1$  and  $4.9 \pm 2.1$ , respectively, for La. Among the conifers, *C. japonica* bore the largest amounts of aerosol-elements. This tendency was emphasized in comparisons by leaf area. Although the detailed mechanisms are not clear, the deposition of aerosol elements may be influenced by leaf type, leaf morphology, and the chemical properties of epicuticular wax (Burkhardt *et al.*, 1995).

In addition, comparison of the non-terrigenous fractions of aerosol elements among tree species at NIES (*C. japonica*, *C. deodara*, and *P. densiflora*) indicated species dependency in their depositions, although the mechanism is not understood : aerosol-Br\*, Se, Sb, and Ag tended to be deposited more abundantly on *C. japonica* and *C. deodara* than on *P. densiflora* (\* : different significantly,  $P < 0.05$ ) ; aerosol-Fe\*, Cr, As, Cs\*, Zn, Co, Mn\*, V, and Cl on *P. densiflora* than on the other species ; and aerosol-Au and I on *C. deodara* than on the others.

### 3.3 Effect of branch height

Figure 6 shows the effect of branch height on the amount of aerosol-elements on conifers, using Sb as an indicator. Except for the tree which was situated near a road, and thus was significantly affected by vehicle exhaust (*C. japonica* in Tsukuba : No.8 in Fig. 6 (A1)), the upper leaves, especially top leaves, accumulated more aerosol-Sb than the lower, although such a vehicle effect was also observed to a lesser extent in some other *C. japonica* trees. The abundant aerosol-Sb at the higher position probably occurs because the lower leaves are often sheltered from deposition by other vegetation or artificial structures (Mayer, 1993 ; Beckett *et al.*, 1998). In contrast, on the roadside tree, the amounts of aerosol-Sb increased clearly from treetop to bottom, suggesting the importance of vehicle exhaust as a source of anthropogenic

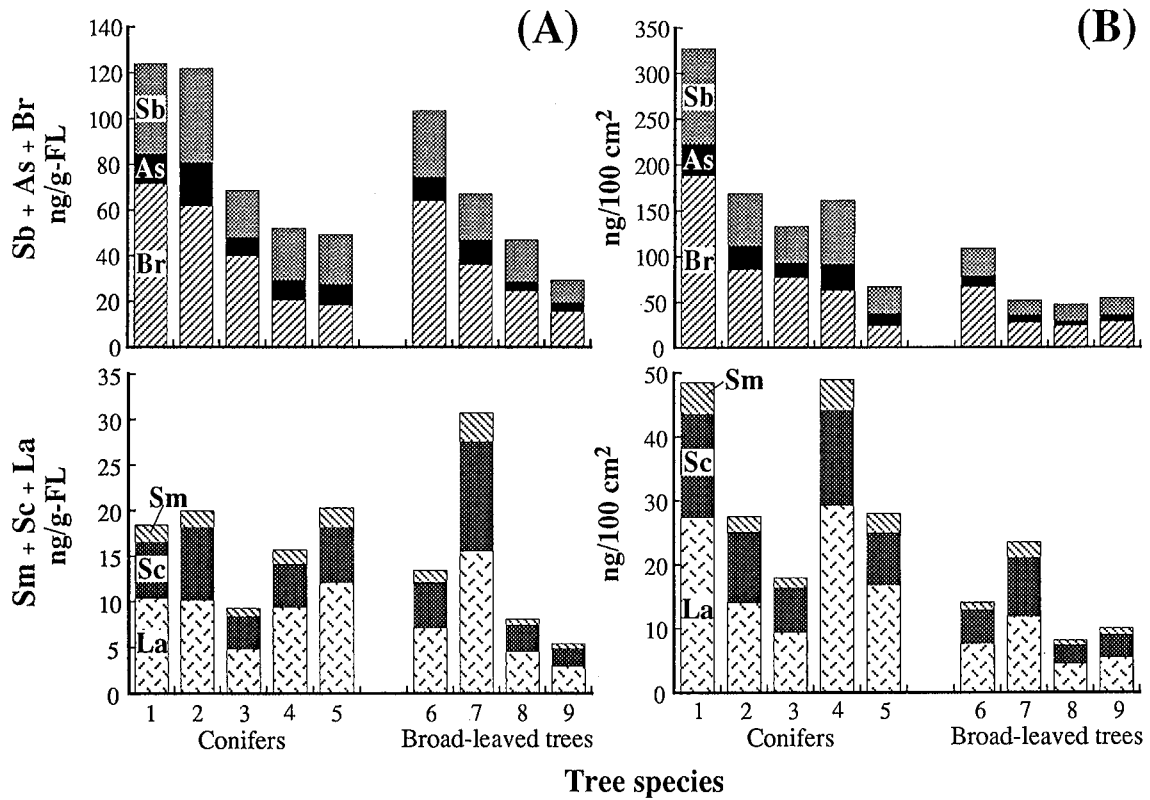


Fig. 4 Amounts of typical terrigenous and non-terrigenous elements in aerosols on leaves of various tree species. Tree species : (1) *Cryptomeria japonica*, (2) *Cedrus deodara*, (3) *Pinus densiflora*, (4) *Pinus thunbergii*, (5) *Chamaecyparis obtusa*, (6) *Quercus myrsinaefolia*, (7) *Rhododendron oomurasaki*, (8) *Castanopsis cuspidata*, (9) *Camellia japonica*. Leaf age : 0-y (from November to December). (A) by fresh weight ; (B) by surface area of leaves. Site : NIES.

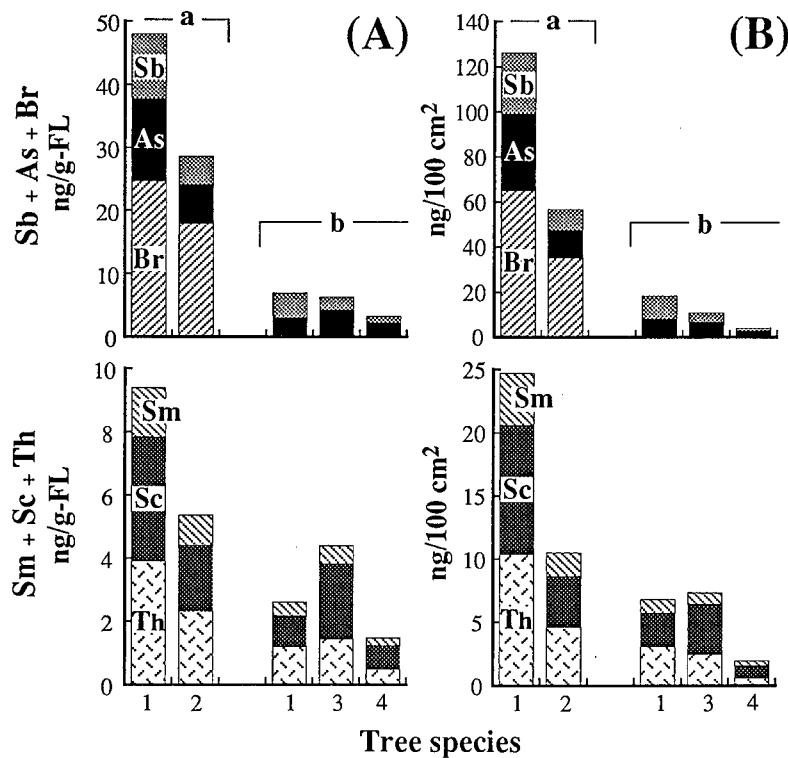
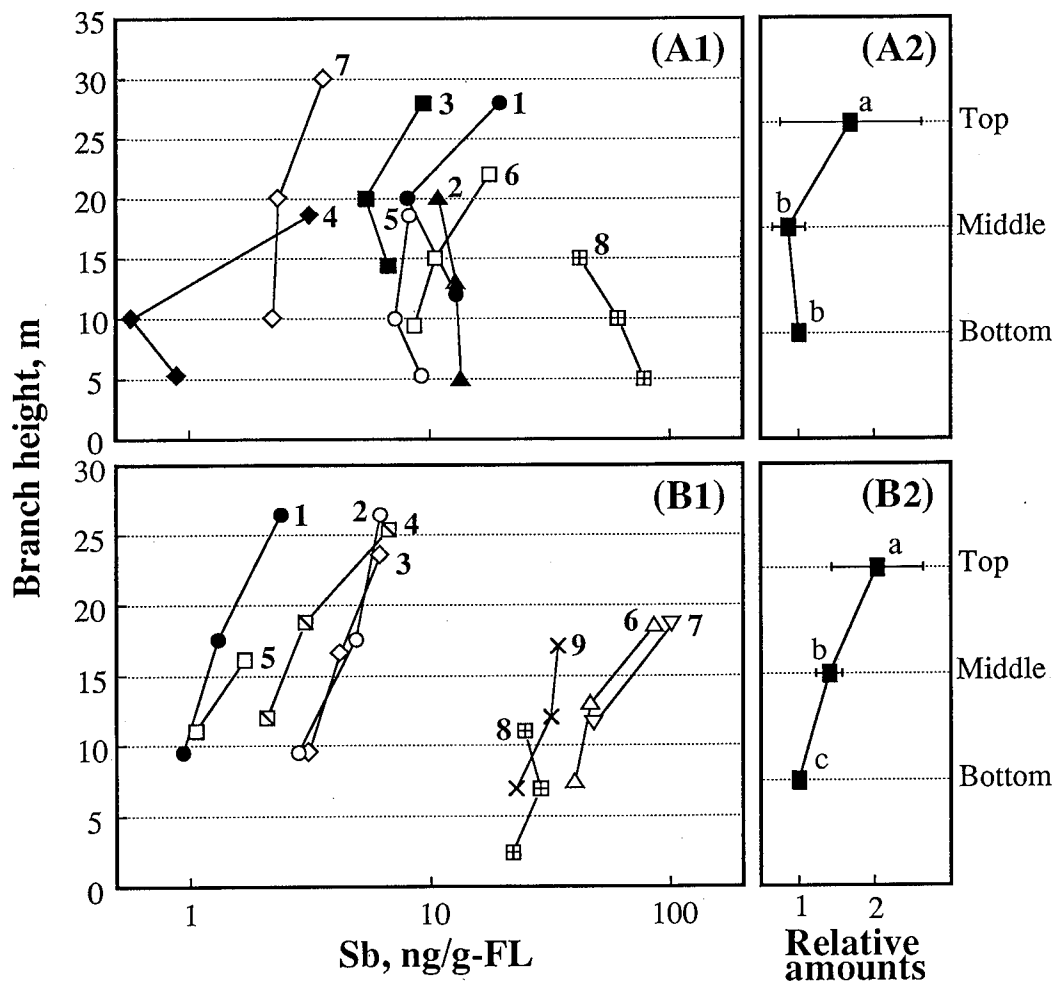


Fig. 5 Amounts of typical terrigenous and non-terrigenous elements in aerosols on leaves of various tree species. Tree species : (1) *Cryptomeria japonica*, (2) *Thujopsis dolabrata*, (3) *Abies firma*, (4) *Tsuga sieboldii*. Leaf age : 1-y. (A) by fresh weight ; (B) by surface area of leaves. Sites : (a) Mutsu, Aomori, (b) Yakushima.



**Fig. 6** Amounts of aerosol-Sb on leaves at different branch heights. (A 1) *Cryptomeria japonica*. Sites and leaf ages : (1, 2) Aomori, Aomori, 0-y in October ; (3) Yakushima, 0-y in March ; (4) Mutsu, Aomori, 0-y in August ; (5, 6) Mutsu, 1-y ; (7) Kimotsuki, Kagoshima, 1-y ; (8) Tsukuba, Ibaraki, 1-y. (A 2) Average relative amounts for *Cryptomeria japonica*, bottom values=1, n=8. (B 1) Tree species, sites, and leaf ages : (1) *Thujopsis dolabrata*, Mutsu, 0-y in August ; (2, 3) *Thujopsis dolabrata*, Mutsu, 1-y ; (4) *Abies firma*, Yakushima, 1-y ; (5) *Tsuga sieboldii*, Yakushima, 1-y ; (6, 7) *Pinus densiflora*, NIES, 1-y ; (8) *Chamaecyparis obtusa*, NIES, 1-y ; (9) *Pinus thunbergii*, NIES, 1-y. (B 2) Average relative amounts for species other than *Cryptomeria japonica*, bottom values=1, n=9. Different lowercase letters above the plots (in A 2 and B 2) indicate significant differences ( $P < 0.05$ ).

aerosol-elements. Other aerosol-elements also showed similar vertical profiles of deposition. For terrigenous elements, however, differences in the amounts between treetop and bottom were less significant than those for Sb (eg., relative amounts of aerosol-Sc : top ( $1.29 \pm 0.66$ ) and middle ( $0.85 \pm 0.28$ ) for *C. japonica* ; top ( $1.72 \pm 0.61^*$ ) and middle ( $1.15 \pm 0.24$ ) for other species ; \* : different significantly,  $P < 0.01$ ), due probably to the contribution of soil dust flung up from the surroundings.

### 3.4 Time-dependent accumulation of aerosol-elements

Figure 7 shows time-dependent changes in the amounts of aerosol-Sb and Na on *C. japonica* and *C. deodara* at NIES. Deposition of the aerosol-elements began just after expansion of 0-y leaves (in late May or early June). The amounts increased almost linearly with time (the rates often increased slightly in late autumn and winter), reaching maximum in winter,

and then staying approximately constant. Therefore, their annual changes on 1-y leaves were small (with a slight and temporary increase in winter), probably because the open surface area of the leaf available for deposition was reduced because of their being covered with aerosols, and/or an equilibrium between deposition and washing out was reached (averages for 1-y leaves of *C. japonica*, Sb :  $59 \pm 12$  ng/g-FL, Na :  $4800 \pm 1200$  ng/g-FL, n=20 ; *C. deodara*, Sb :  $48 \pm 11$  ng/g-FL, Na :  $2500 \pm 300$  ng/g-FL, n=7). In addition, when the changes in Sb/Sc ratios were compared with changes in Na/Sc ratios, the former tended to increase gradually with time (except for the last case from 1997 to 1998), but the latter decreased. Some sparingly soluble elements, such as Sb, which were principally contained in anthropogenic carbonaceous aerosols, appeared to accumulate on leaves, because the carbonaceous aerosols are adhesive and thus more difficult to wash down than soil dust. On the other



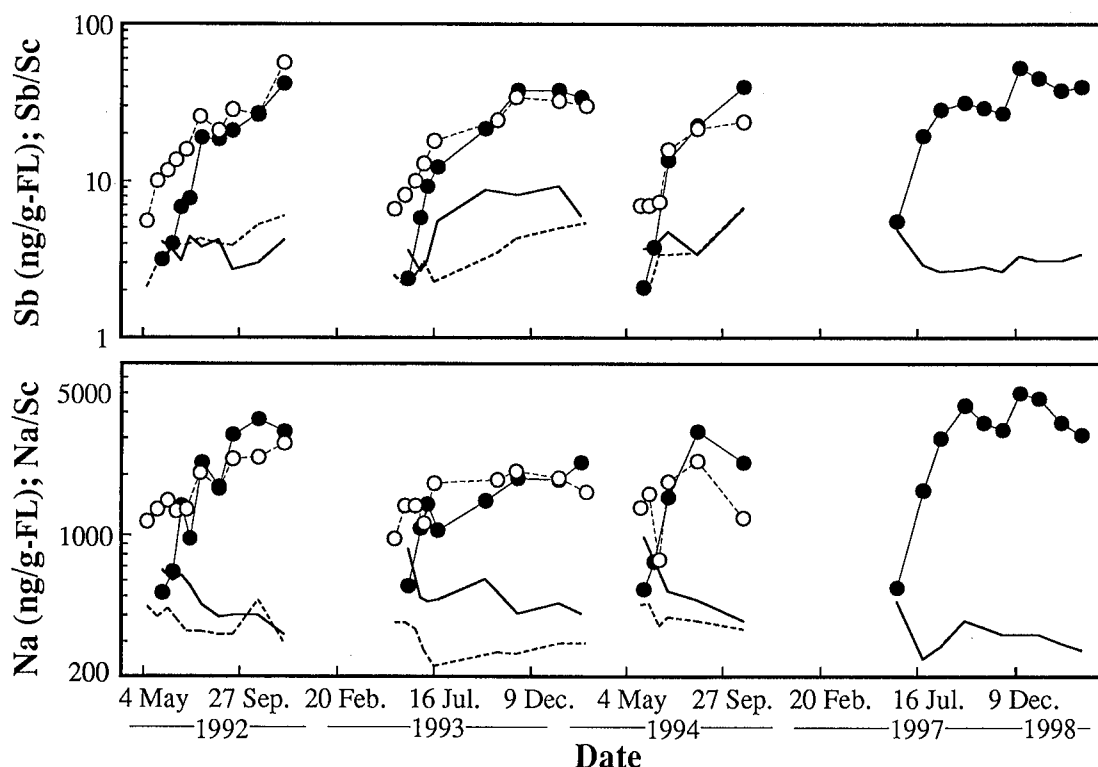


Fig. 7 Time-dependent accumulation of aerosol-Sb and Na on 0-y leaves. Closed circles and solid lines: *Cryptomeria japonica*, Open circles and dotted lines: *Cedrus deodara*. Plots: total amounts (ng/g-FL). Lines: relative concentrations (X/Sc). Site: NIES.

hand, some soluble elements, such as Na, may have easily leached from both the anthropogenic aerosols and soil dust.

### 3.5 Evaluation of air pollution

As described above, the amounts of aerosol-elements on 1-y leaves remained approximately constant throughout the year and appeared to depend on the degree of air pollution at each sampling site. Figure 8 compares the amounts of aerosol-Sb on 1-y 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 those from the plains in Ibaraki (including NIES), urban areas of Tohoku, mountainous areas of Ibaraki, mountainous areas of Tohoku, Shimokita, and Yakushima. In Saitama, the deposition rate ( $135 \pm 75$  ng/g-FL) was about 11 times those of mountainous areas of Ibaraki ( $12.4 \pm 5.2$  ng/g-FL), mountainous areas of Tohoku ( $11.7 \pm 5.5$  ng/g-FL), and Shimokita ( $11.1 \pm 4.8$  ng/g-FL), and about 20 times that of Yakushima ( $6.3 \pm 3.2$  ng/g-FL).

Figure 9 shows the relationships between the amounts of aerosol-Sb on *C. japonica* (using averages of the data in Fig. 8) and the concentrations of  $\text{NO}_x$  (annual averages in 1996: Japan Environment Agency, 1998; average from 3 September to 14 October, 1997, for Yakushima: Kagoshima Prefectural Institute of Environmental Science, 1998), or the population densities (calculated based on data from the Statistics Bureau and Statistics Center, Japan, and Geographical Survey Institute, Japan) in the areas where the leaf samples were collected. Good correlations were obtained in both cases, indicating that

aerosol-Sb (and probably Au, Ag, Zn, Cr, As, etc.) originated from general human activities.

Figure 10 (A) shows the amounts of aerosol-Sb on *C. japonica* leaves from 8 sites around the coast of Yakushima, and Figure 10 (B) shows the amounts of non-terrigenous aerosol-Fe, Co, Mn, and V from the sites near the electrochemical plant. Although the amounts of aerosol-Sb were lower on Yakushima than in other areas (Fig. 8), they were clearly higher on the north side of the island than on the south (average for sites 2-4:  $6.1 \pm 0.9$  ng/g-FL; that for sites 6-8:  $3.1 \pm 1.4$  ng/g-FL;  $P < 0.01$ ). More than 95% of Sb was non-terrigenous on Yakushima (Fig. 3). The island is mostly covered with the same brown forest soils originating from granite and pyroclastic flow deposits, which have fairly constant concentrations of Sb ( $0.76 \pm 0.13$  ppm, Sb/Sc:  $0.10 \pm 0.02$ ,  $n=6$ ). In addition, desorption rates of leaf aerosols by precipitation may be comparable on both sides of the island, because of the almost equal amounts of precipitation (Eguchi, 1984). Therefore, the increased amounts of aerosol-Sb on the north side suggest transport of pollutants from Kyushu (and to a lesser extent from East Asia), since northerly and northwesterly winds a loft become prevalent in winter (Eguchi, 1984).

Near the electrochemical plant, relatively large amounts of non-terrigenous aerosol-Fe, Co, Mn, and V were found on the leaves (cf. those in another rural area, i.e., Shimokita: (Fe)  $1.0 \pm 0.8$   $\mu\text{g/g-FL}$ , (Co)  $0.71 \pm 0.29$  ng/g-FL, (Mn) not detected, (V)  $2.3 \pm 8.1$  ng/g-FL,  $n=18$ ). This is most likely the influence of the gas and soot discharged from the electrochemical plant, because the coal used in the plant is rich in Fe

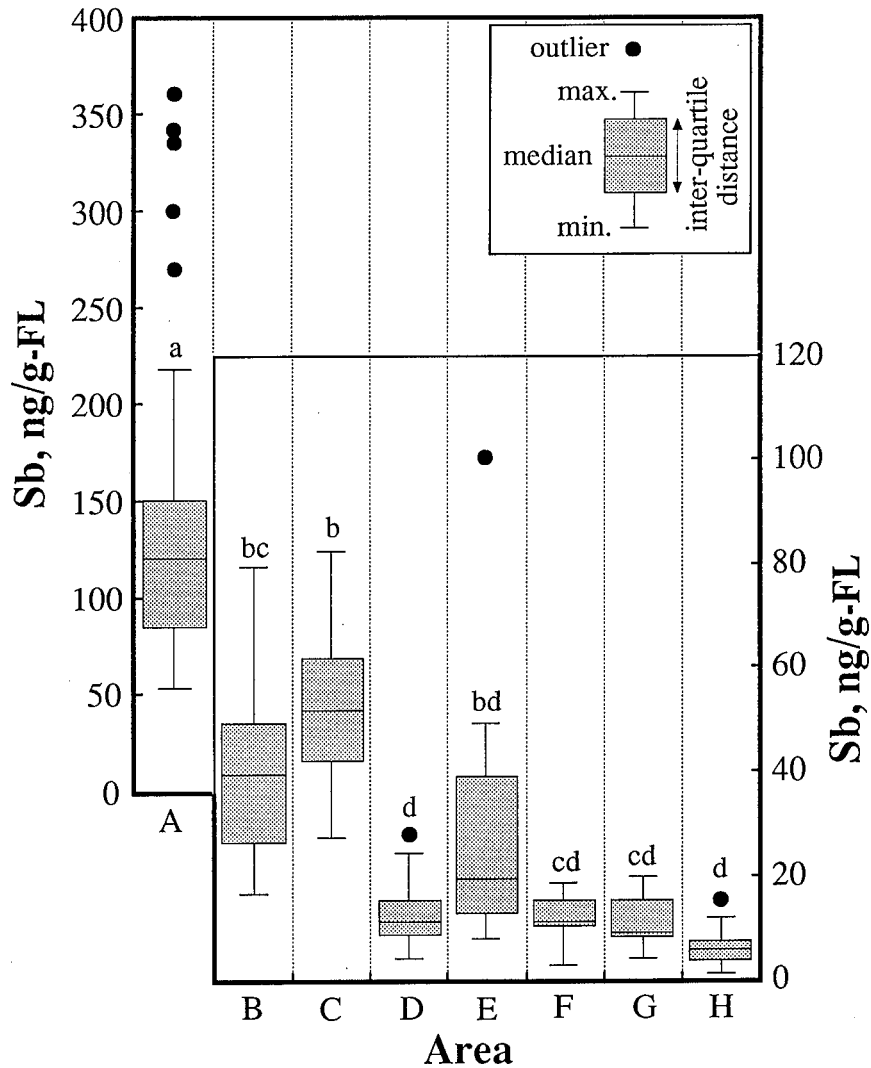


Fig. 8 Amounts of aerosol-Sb on 1-y leaves of *Cryptomeria japonica* from various areas differing in their degree of air pollution. (A) Saitama, n=50; (B) plains in Ibaraki (except NIES), n=33; (C) NIES, n=30; (D) mountainous areas of Ibaraki, n=47; (E) urban areas of Tohoku, n=12; (F) mountainous areas of Tohoku, n=9; (G) Shimokita Peninsula, Aomori, n=11; (H) Yakushima, n=61. Different lowercase letters above the boxes indicate significant differences ( $P < 0.01$ ).

(EF=1.5), Co (3.4), Mn (2.2), and V (95) (from NAA by the authors; heavy oil, not analyzed).

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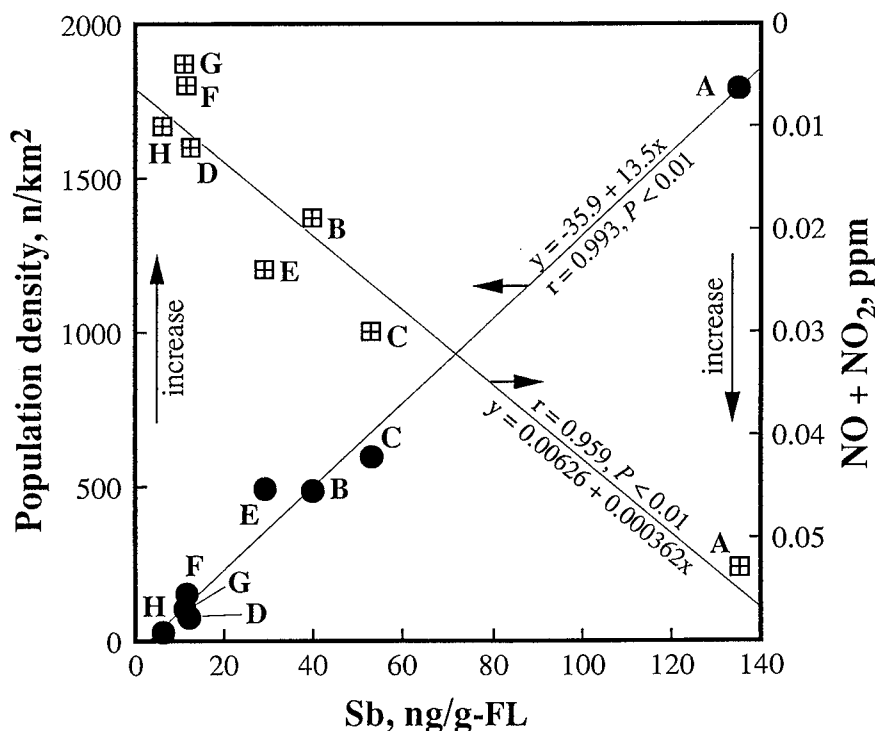


Fig. 9 Relationship between average amounts of aerosol-Sb on 1-y leaves of *Cryptomeria japonica* and population densities or  $\text{NO}_x$  concentrations in the areas where the leaf samples were collected. (A-H) : see legend in Fig. 8.

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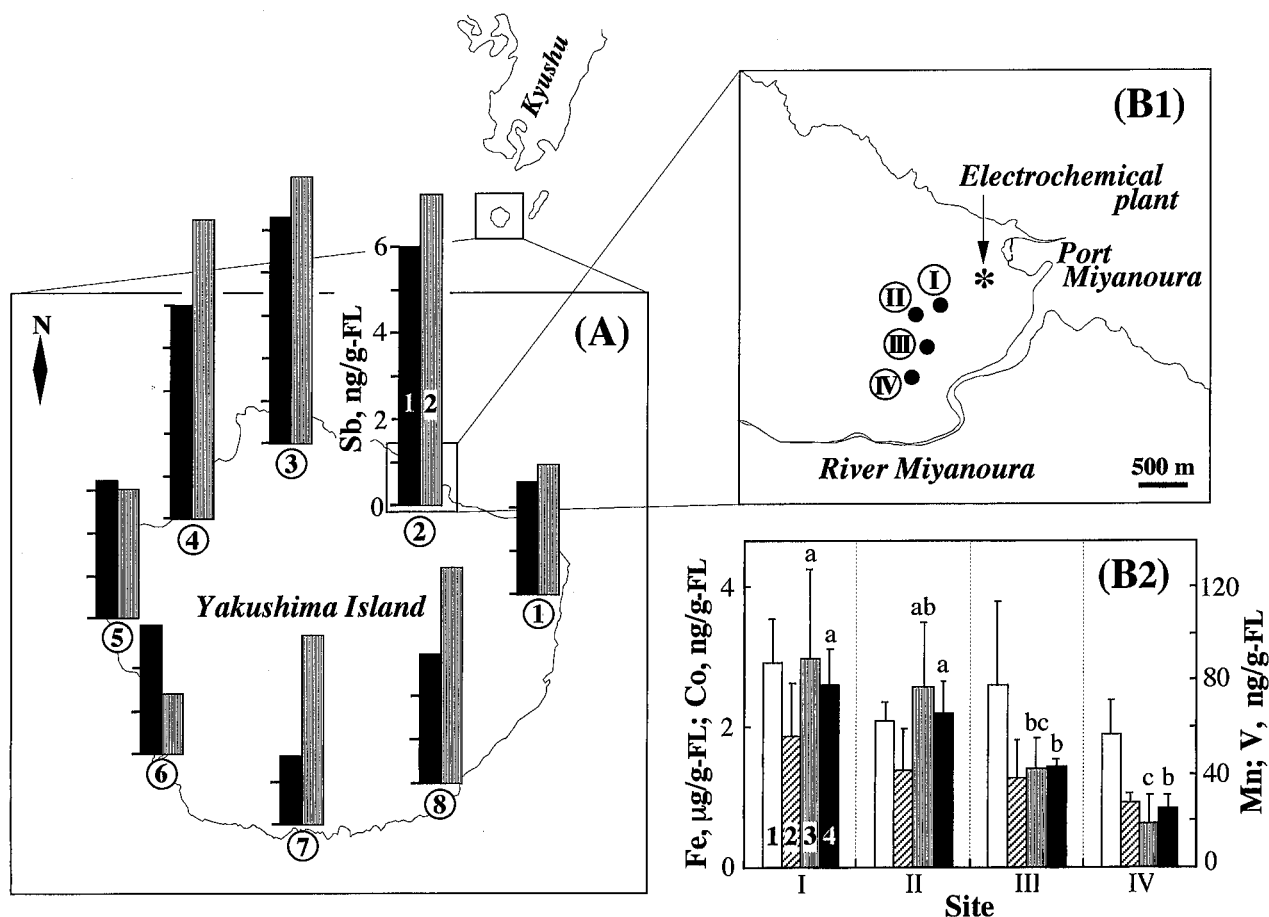
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**Fig. 10** (A) Amounts of aerosol-Sb on *Cryptomeria japonica* leaves from 8 sites around the coast of Yakushima. Samples : (1) 0-y leaves in January, 1992 ; (2) 1-y leaves in September, 1993. (B) Amounts of non-terrestrial Fe, Co, Mn, and V in aerosols on *Cryptomeria japonica* leaves from the sites near the electrochemical plant on Yakushima. Elements : (1) Fe, (2) Co, (3) Mn, (4) V. Samples : 0-y leaves in November, 1996, +1-y leaves in October, 1994, +1-y leaves in November, 1996 ;  $n=3$ . Different lowercase letters above the bars indicate significant differences ( $P < 0.05$ ).

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