

## Atmospheric phosphorus deposition in Ashiu, Central Japan – source apportionment for the estimation of true input to a terrestrial ecosystem

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**Abstract.** Atmospheric bulk depositions of soluble reactive phosphorus (SRP), soluble unreactive phosphorus (SUP), particulate inorganic phosphorus (PIP), particulate organic phosphorus (POP), total phosphorus (TP) and some other dissolved and particulate components were monitored for 3 years in Ashiu, Central Japan. The mean bulk depositions of SRP, SUP, PIP, POP, TP, dissolved components (Na, Mg, nss-Ca, K, V, Mo, nss-SO<sub>4</sub>) and particulate components (Al, Fe, Ti, Ca, Mg, Mn, Ba, Sr, Zn) were 175, 76, 136, 397, 783, 156,000, 10,900, 7450, 5470, 10.3, 1.52, 40,100, 13,200, 3590, 2630, 576, 624, 42.3, 30.2, 17.4, 8.2  $\mu\text{mol m}^{-2} \text{ year}^{-1}$ , respectively. The value for TP deposition was in the lower range of previous literature. The low P deposition probably reflected the method applied to reduce the contribution of local particles, including (1) placement of samplers off the ground surface, (2) installation of multiple samplers, and (3) rejection of contaminated samples. Al data suggested that  $15 \pm 5\%$  of TP was brought by lithogenic dust from East Eurasia. Nss-SO<sub>4</sub> and Mo data and air-mass backward trajectories suggested that  $39 \pm 4\%$  of TP was derived from coal combustion in China. It was speculated that the rest ( $47 \pm 6\%$ ) of the TP deposition might be predominantly attributed to the contribution of local biogenic particles. Net atmospheric TP input (lithogenic dust and fossil fuel combustion) was almost equal to the TP outflow from Japanese forests on granitic soils.

### Introduction

Phosphorus is one of the most important elements on earth, and it controls many of the biogeochemical processes occurring in the biosphere (Jahnke 2000). It has long been suggested that the atmosphere plays a significant role in supplying P to various ecosystems including lakes and forests (Gardner 1990; Jassby et al. 1994; Campo et al. 2001). In order to evaluate the role of the atmosphere in the P budget of ecosystems, the amount of atmospheric P input needs to be determined accurately and properly. However, values reported in

the previous literature fall within a wide range (Newman 1995; Redfield 1998). In addition, the origin of such heterogeneity has not yet been fully resolved.

If we are to understand the nutrient budget of a particular ecosystem, information on the sources of deposition is crucial. If the source lies outside the target ecosystem, it constitutes a genuine part of the atmospheric input. If the source lies inside, it should be considered as a contamination source (Ahn and James 1999). It depends on the nature of the target ecosystem whether a certain source should be regarded as a true input or as part of intra-system recycling. If the targets are lakes or estuaries, local particles, such as insects, plant debris, or bird droppings, should be regarded as part of true atmospheric input. On the other hand, if targets are terrestrial ecosystems, such as forests or watersheds, only particles transported over a long distance, such as sea-salt particles, continental dust or soot, should be considered as true atmospheric input, while local particles are rather a part of intra-system recycling.

The goal of this study is to quantify the amount of true atmospheric P input to terrestrial ecosystems. Our previous studies (Tsukuda et al. 2004, 2005) have shown that P deposition data are much more susceptible to the influence of local particles than other components. It was suggested that local material could be reduced when appropriate measures are applied, including replicated sampling on a tall tower and rejection of contaminated samples. It was also argued that even after such precautionary methodologies are taken, local particles could not be eliminated completely. A considerable part (11–41%) of soluble total phosphorus (STP) deposition was estimated to be attributable to local material. In order to evaluate atmospheric P input accurately, the effect of local particles should be quantified via some formula for source apportionment. Understanding the relative importance of each atmospheric P sources is also important for water quality management to control eutrophication of lakes or estuaries.

The examination of the spatial variability of P deposition over a wide area might give an insight into the emission sources of atmospheric P. Unfortunately, however, there is a strong preponderance of previous total-P (TP) deposition measurement from North America and Europe, with a few exceptions concerning several tropical sites (Newman 1995). There is no report found in the international literature that uses competent methodology to specify TP deposition rates in the Asian region.

It is not difficult to find studies providing information on the sources of P in the atmosphere. Kopacek et al. (1997) compared data from two sites in Czech Republic and reported that P deposition was higher in an agricultural/industrial area. They also pointed out that the correlation between rainfall and P deposition was low, suggesting that a large part of atmospheric P was of local origin. Hendry et al. (1984) studied P deposition in a forest near Turrialba, Costa Rica, and argued that weak correlation of rainfall and P deposition data argues for the local origin of P. Jassby et al. (1994) measured P deposition on a transect over Lake Tahoe, California and Nevada, USA. They found that P deposition decreased with increasing distance from the lakeshore, and

suggested that the P deposition was of a terrestrial nature. Carlisle et al. (1966) and Jordan et al. (1995) argued that synchronicity of P deposition and flowering showed that pollen can be an important P source at Grizedale Forest, UK and on the shore of the Chesapeake Bay, Maryland, USA, respectively. Shaw et al. (1989) and Sober and Bates (1979) found that P deposition has its peak during the spring, and argued that biogenic material (e.g. pollen and insects), or farming activities (e.g. fertilization and plowing), might be major P sources for Narrow Lake, Alberta, USA and for Lake Carl Blackwell, Oklahoma, USA, respectively. Eisenreich et al. (1977) also mentioned that biological and agricultural activities could be major atmospheric P sources over Lake Michigan, USA, while higher values from urban sites might be reflecting different anthropogenic P sources. Lewis (1981) examined the seasonal variation of P deposition at Lake Valencia, Venezuela, and concluded that high particulate P during rainy season is related to organic material, while high soluble P during the dry season can be traced to plant ash from fires in farmlands. Bergametti et al. (1992) studied atmospheric deposition at Corsica Island, Italy, and suggested that soil particles from arid regions and anthropogenic activities in urban areas are major P emission sources. Newman (1995) reviewed various articles on P deposition and concluded that wind erosion of soil, pollen, burning of plant material, coal and oil, and occasionally volcanic eruptions might play important roles in providing P to terrestrial ecosystems. Even though the discussion is far from uncommon in the literature, most studies discuss P sources only qualitatively or semi-quantitatively, and truly quantitative discussion is rarely found.

Although previous literature has not yet attempted very vigorously to do so, there are possible methods for the source apportionment of P deposition. Soil derived P deposition might be estimated using soil-specific elements (e.g. Al or Ti) as indicators (Bergametti et al. 1992). Tsukuda et al. (2005) suggested that soluble-P from fossil fuel combustion can be evaluated using dissolved Mo and  $\text{nss-SO}_4$  deposition data. The method might be useful for total-P as well. P from pollen, or other biogenic particles, might be estimated through fractionation of P in deposition samples (soluble/particulate or organic/inorganic) using methods of soil analysis (see Kuo 1996 for example).

In this study, atmospheric P deposition was monitored for 3 years in Ashiu, Central Japan. Replicated sampling on a 6-m tower and choosing the least contaminated samples were applied in an attempt to obtain a dataset with the least possible influence of local particles. The result might be the first contribution concerning TP deposition from the Asian region. Seasonal variation of deposition was measured for each P fractions (*soluble reactive P: SRP, soluble unreactive P: SUP, particulate inorganic P: PIP, particulate organic P: POP*) and other components including  $\text{SO}_4$  and metals. Relations among P, Al,  $\text{SO}_4$  and Mo data were analyzed to estimate P from lithogenic dust or fossil fuel combustion. Contribution of local material was evaluated and its influence on atmospheric P deposition was discussed. P deposition value was compared with

river runoff data to evaluate the role of atmosphere in the P budget of terrestrial ecosystems.

### Materials and methods

A detailed description of our sampling site and sampling methodology is available in our previous report (Tsukuda et al. 2005) and thus only briefly mentioned here. The study site was an opening area at Hitsukura in Ashiu Forest Research Center, Field Science Education and Research Center of Kyoto University, which is located in Central Japan (Figure 1). Bulk (wet + dry) samples were obtained after each rain event. Sampling was conducted for about 3 years from 3 November 2000 to 31 November 2003. Samplers were placed on a 700 mm table in the beginning and on a 6 m tower after 25 April 2001. In this study, two types of bulk samplers were used; a rain sampler and a snow sampler. The rain sampler consisted of a polyvinyl chloride tube of 154 mm diameter and 510 mm height, a piece of 1 mm mesh polypropylene net attached 65 mm below the tube opening with a silicon bond, and a polyethylene funnel of 150 mm diameter, attached just below the net with a silicon bond. The upper half of the tube was detachable, and a 2 l polyethylene bottle was placed below the funnel as a reservoir. The snow sampler was a polyethylene bucket of 286 mm diameter and 375 mm height that can be sealed with a cover during transportation. Multiple samplers (5–9 rain samplers through spring to autumn and 2–3 snow samplers during the winter) were

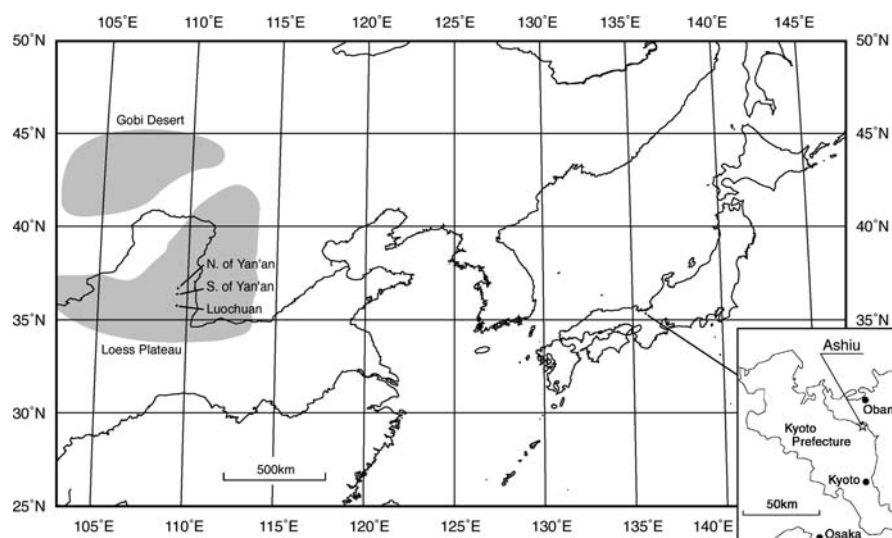


Figure 1. Location map of the sampling sites for atmospheric deposition (Ashiu) and for Chinese loess (North of Yan'an, South of Yan'an, and Luochuan).

installed, and samples were separately retrieved, filtered (0.2  $\mu\text{m}$  polycarbonate membrane) and stored (filtrates were frozen and filters were air-dried).

The analytical methods for the dissolved components were described in Tsukuda et al. (2005). The measured components include SRP (molybdenum blue method), STP (persulfate decomposition),  $\text{SO}_4$  (ion-chromatography), Na, K (acetylene-flame AAS), Ca, Mg (ICP-AES), V and Mo (ASCFA).

Particulate components analyzed were PIP, POP, PTP (particulate total phosphorus) using sequential extraction based on Williams et al. (1976) and Kuo (1996), and Al, Fe, Ti, Ca, Mg, Mn, Ba, Sr, Zn using  $\text{HNO}_3$ – $\text{HF}$ – $\text{HClO}_4$  decomposition (Sugiyama 1996). The details of the analytical procedures were as follows.

Sequential extraction: Each filter was placed in a 10 ml polypropylene centrifuge tube with 4 ml of 0.3 M NaOH. The tube was sealed with a cap and shaken for 17 h at 25 °C. The sample was centrifuged and supernatant was transferred using a pipette to a glass test tube having a 20 ml line. Two milliliter of distilled water was added to the residue, mixed, centrifuged and supernatant was transferred to the test tube. 4 ml of 1 M HCl was added to the residue and shaken for 17 h at 25 °C. The sample was centrifuged and supernatant was transferred to the test tube. Two milliliter of distilled water was added to the residue, mixed, centrifuged and supernatant was transferred to the test tube. four milliliter of 0.5 M NaOH was added to the residue and heated to 85 °C in an aluminium heating block for 9 h. The sample was cooled to room temperature, centrifuged and supernatant was transferred to the test tube. Two milliliter of distilled water was added to the residue, mixed, centrifuged and supernatant was transferred to the test tube. Finally, the test tube was filled up to 20 ml with distilled water and mixed well to obtain an extract mixture. For PTP measurement, 5 ml of each extract mixture was transferred to a test tube having a 10 ml line. 0.5 ml of saturated  $\text{MgCl}_2$  solution, one drop of concentrated  $\text{SO}_4$  and 1 ml of 60%  $\text{HClO}_4$  were added to each test tube. The tube was heated in an aluminium heating block at 205 °C for 90 min after a gradual temperature increment. Samples were cooled to room temperature, dissolved with distilled water, neutralized with a drop of 1% *p*-nitrophenol solution and 2 M NaOH and determined for P with ascorbic acid method using a colorimeter (UV-1200, Shimadzu Co. Ltd.). For PIP measurement, each extract mixture was filtered through 0.45  $\mu\text{m}$  cellulose acetate membrane filter. Five milliliter of filtrate was transferred to a test tube having a 10 ml line, neutralized with a drop of 1% *p*-nitrophenol solution and 2 M NaOH and determined for P with ascorbic acid method using the same colorimeter. POP content was calculated as difference between PTP and PIP. All reagents were of analytical grades purchased from Wako Pure Chemical Industries, Ltd. Relative standard deviation (RSD) of triplicate analysis was measured for filter samples of the extraction experiment (see below). For all fractions, the results were lower than 5%, with a few exceptions of very low concentrations (e.g. PIP for pollen), which showed a maximum 20% RSD.

$\text{HNO}_3$ – $\text{HF}$ – $\text{HClO}_4$  decomposition: Each filter was placed in a 30 ml PTFE vessel and hydrolyzed with 1 ml of 28%  $\text{NH}_3$  solution by sealing tightly with a cap and allowing it to stand for 24 h. The cap was removed and the vessel was kept at 150 °C until its content was evaporated to dryness. One milliliter of 61%  $\text{HNO}_3$ , 0.3 ml of 60%  $\text{HClO}_4$  and 1 ml of 49%  $\text{HF}$  were added to each vessel, which was loosely covered with a cap and heated at 120 °C for 2 h, 150 °C for 2 h and 170 °C for 4 h. The cap was removed and the vessel was heated at 170 °C until its content was evaporated to dryness. After cooling, 1 ml of 61%  $\text{HNO}_3$  and 0.5 ml of 60%  $\text{HClO}_4$  were added to each vessel. The vessel was heated at 170 °C until its content was evaporated to dryness. After cooling, 4 ml of 0.1 M  $\text{HNO}_3$  was added to the vessel. The vessel was sealed tightly with a cap and placed in an ultrasonic bath for 90 min for complete dissolution. The final solution was determined for metallic components via ICP-AES (ICAP-96-953, Nippon Jarrell-Ash). All reagents were of ultra-pure grades purchased from Kanto Kagaku. Each heating was conducted on a hot plate in a clean box, into which air was pumped through a 0.1  $\mu\text{m}$  air filter.

Three filter blanks were prepared by filtering 1 l of distilled water through each of three unused filters and analysing them for dissolved and particulate components. The mean content of each component in the filter blanks was subtracted from the content measured for every deposition sample. Analytical error was normally lower than 5%, but in some cases, under lower concentrations the error could be as high as about 10%.

TP was calculated as sum of STP and PTP. Seasalt-derived sulfate and calcium were calculated using the seawater molar ratio (Murray 1992) and Na data. Non-seasalt sulfate (nss- $\text{SO}_4$ ) and calcium (nss-Ca) were calculated as the difference between total and seasalt derived  $\text{SO}_4$  and Ca. Sample contents of each component were calculated multiplying concentrations by sample volumes, which were then divided by sampler opening area to obtain bulk depositions ( $\mu\text{mol m}^{-2}$ ). Daily bulk depositions ( $\mu\text{mol m}^{-2} \text{ day}^{-1}$ ) were calculated through dividing the bulk depositions by sampling intervals (days). Rainfall and air temperature were measured through an electronic thermometer and a tipping bucket rain gauge with a data logger at a meteorological station located 2 km south of the sampling site (Mr. Hosomi, Mr. Ohashi and Mr. Okabe, personal communication).

An extraction experiment was conducted to understand how particular emission sources (lithogenic dust from East Eurasia, local soil and pollen) are detected in terms of chemical P fractions. Arid regions in East Eurasia, including Gobi and Taklimakan, generate large amounts of aeolian lithogenic dust (*Kosa*), which is often observed in Japan during the spring (Inoue and Naruse 1987). It is well established that the Chinese Loess Plateau (CLP) was generated by deposition of lithogenic dust from the same region (Pye 1987). In order to represent lithogenic dust from East Eurasia, loess was sampled at three sites in CLP (North of Yan'an 36°42' N 109°27' E, South of Yan'an 36°23' N 109°25' E, Luochuan 35°46' N 109°25' E: Figure 1). Local soil and

pollen (*Carpinus laxifolia*, *Chamaecyparis obtusa*, *Cryptomeria japonica*, *Fagus crenata*, *Pinus densiflora*, and *Quercus monogolica*) were sampled in the surrounding area of the study site in Ashiu. Two loess/soil samples were taken at each site, from the surface (0–9 cm) and from the bottom (18–45 cm), to elucidate the magnitude of vertical redistribution (e.g. salt accumulation) that might bring P to the soil surface. 10–50 mg of each sample was placed in a 50 ml polypropylene centrifuge tube. 40 ml of distilled water was added to each tube. The tube was gently shaken several times and allowed to stand still for 24 h. The sample was then vigorously shaken for 10 s and filtered through a 0.2  $\mu\text{m}$  polycarbonate filter. The procedures were designed to mimic the sampling and processing steps for actual deposition samples of this study. Filtrate was determined for SRP, SUP, STP, Al, Fe, Ti, Mn, Ca and Mg. Particulate matter trapped on the filter was determined for PIP, POP, PTP, Al, Fe, Ti, Mn, Ca and Mg. Analytical methods were the same as the ones for the deposition samples described above.

## Results and discussion

### *Annual rainfall and annual deposition*

Annual rainfall and annual deposition of the measured components are shown in Table 1. The large values for Na and Mg indicate the significant influx of seasalt particles. The high nss-SO<sub>4</sub> value shows that the site also received a considerable amount of acid deposition. Values for particulate Al and Fe were also large, suggesting a significant deposition of crustal material (e.g. soil and continental dust). If P fractions are compared, depositions were the largest for POP, followed by SRP, PIP and SUP. TP deposition was  $783 \pm 68 \mu\text{mol m}^{-2} \text{ year}^{-1}$ .

TP depositions reported in the previous literature are compiled in Table 2. The values are distributed over a wide range ( $226\text{--}5430 \mu\text{mol m}^{-2} \text{ year}^{-1}$ ) within which the results of this study fall at a relatively lower level. As shown in Tsukuda et al. (2004) and Tsukuda et al. (2005), P deposition data are very susceptible to the influence of local particles. The low TP deposition obtained in this study probably reflected the methodology applied to reduce local particles (Tsukuda et al. 2005) including: (1) placement of the samplers off the ground surface, (2) installation of multiple samplers, and (3) rejection of contaminated samples.

There are various emission sources of P in the atmosphere discussed in the literature including: fossil fuel or biomass combustion, farming (plowing, fertilization, burning etc.), local biogenic particles (pollen, insects, plant debris etc.), resuspension of local soil, lithogenic dust from arid regions and volcanic activity. In Ashiu particularly, there was no farmland or active volcano in surrounding area, so that one can disregard effects from farming and volcanic activity. As discussed in Tsukuda et al. (2005), local biogenic

Table 1. Annual rainfall and annual deposition of measured components in Ashiu Forest Research Center.

Rainfall and P fractions		Rainfall	SRP	SUP	STP	PIP	POP	PTP	TP	
15 Nov. 2000 to 14 Nov. 2001		2554	217	72	288	167	403	570	858	
15 Nov. 2001 to 14 Nov. 2002		1910	176	78	254	142	330	471	725	
15 Nov. 2002 to 14 Nov. 2003		2506	131	80	211	98	458	556	767	
Mean		2323	175	76	251	136	397	532	783	
STD of annual values		359	43	4	39	35	64	54	68	
Dissolved components		Na	Mg	Ca	nss-Ca	K	V	Mo	SO <sub>4</sub>	nss-SO <sub>4</sub>
15 Nov. 2000 to 14 Nov. 2001		164,000	11,500	10,200	6570	5520	10.7	1.53	55,300	45,900
15 Nov. 2001 to 14 Nov. 2002		140,000	10,100	9600	6560	5470	8.4	1.49	42,000	33,600
15 Nov. 2002 to 14 Nov. 2003		165,000	11,100	12,900	9240	5430	11.7	1.56	50,600	40,700
Mean		156,000	10,900	10,900	7450	5470	10.3	1.52	49,300	40,100
STD of annual values		14,000	800	1700	1550	50	1.7	0.03	6700	6200
Particulate components		Al	Fe	Mg	Ti	Ca	Mn	Zn	Ba	Sr
15 Nov. 2000 to 14 Nov. 2001		16,300	4470	3470	702	732	50.5	28.9	22.0	9.7
15 Nov. 2001 to 14 Nov. 2002		16,000	4230	3070	706	733	48.3	36.4	21.2	10.0
15 Nov. 2002 to 14 Nov. 2003		7300	2070	1360	320	407	28.1	25.4	9.0	4.8
Mean		13,200	3590	2630	576	624	42.3	30.2	17.4	8.2
STD of annual values		5100	1320	1120	222	188	12.4	5.6	7.2	2.9

Unit:  $\mu\text{mol m}^{-2} \text{ year}^{-1}$  except for rainfall ( $\text{mm year}^{-1}$ ).



Table 2. TP depositions reported in previous literature.

Site	Rainfall	TP	Reference
Lake Valencia, Venezuela	750	5430	Lewis (1981)
Crown Estate, Berkshire, UK	882	3940	Alcock and Morton (1985)
Lake Thunderbird, Oklahoma, USA	862	3460	Johnson and Risser (1974)
Merlewood, UK	1050	3230	Allen et al. (1968)
Abbot's, UK	400	2580	Allen et al. (1968)
Silpho, UK	700	2580	Allen et al. (1968)
Lake Carl Blackwell, Oklahoma, USA	–	1950	Sober and Bates (1979)
Walker Branch, Tennessee, USA	1530	1780	Swank and Henderson (1976)
Pitt County, North Carolina, USA	1050	1580	Brinson et al. (1980)
Lake Stechlin, Germany	–	1460	Mothes et al. (1985)
Grizdale Forest, UK	1710	1390	Carlisle et al. (1966)
Rhode River, Maryland, USA	1098	1320	Jordan et al. (1995)
Southen Basin, Lake Michigan, USA	568	1170	Eisenreich et al. (1977)
Piburger See, Austria	–	1160	Psenner (1984)
Grizdale Forest, UK	1710	1130	Allen et al. (1968)
Lake Tahoe, California, USA	976	1050	Jassby et al. (1994)
Loch Ard Forest, Scotland, UK	2050	1050	Harriman (1978)
Rawson Lake, Ontario, Canada	790	1050	Schindler et al. (1976)
Lake O'Woods, West Virginia, USA	–	988	Havens and DeCosta (1984)
Rimov Reservoir, Czech Republic	502	775	Kopacek et al. (1997)
Parkgate, Ireland	1000	743	Jordan (1987)
Northen Basin, Lake Michigan, USA	442	713	Eisenreich et al. (1977)
Cottage Hill, UK	1934	710	Gore (1968)
Loughgrave, Ireland	1661	710	Gibson et al. (1995)
Narrow Lake, Alberta, USA	503	655	Shaw et al. (1989)
Kerloch, UK	750	646	Allen et al. (1968)
Silent Valley, Ireland	990	646	Jordan (1987)
Turrialba, Costa Rica	–	613	Hendry et al. (1984)
Slapy Reservoir, Czech Republic	510	484	Kopacek et al. (1997)
Altnaheglish, Ireland	1438	420	Jordan (1987)
Lake Gardsjon, Sweden	974	255	Persson and Broberg (1985)
Narragansett, Rhode Island, USA	–	226	Graham and Duce (1979)
Ashiu, Japan	2323 ± 359	783 ± 68	This study*

\*Mean and standard deviation of three-year data.

Unit: mm year<sup>-1</sup> for rainfall and  $\mu\text{mol m}^{-2} \text{ year}^{-1}$  for TP.

particles and fossil fuel combustion might be major P sources. In addition, lithogenic dust from East Eurasia is often observed in Japan during the spring (Ishii 1979), which might also act as a P source. Resuspended local soil should also be considered. Each of these sources will be evaluated separately in a later section.

### Seasonal variation

Seasonal variation of rainfall and atmospheric deposition is shown in Figure 2. While rainfall showed no clear pattern, atmospheric deposition of

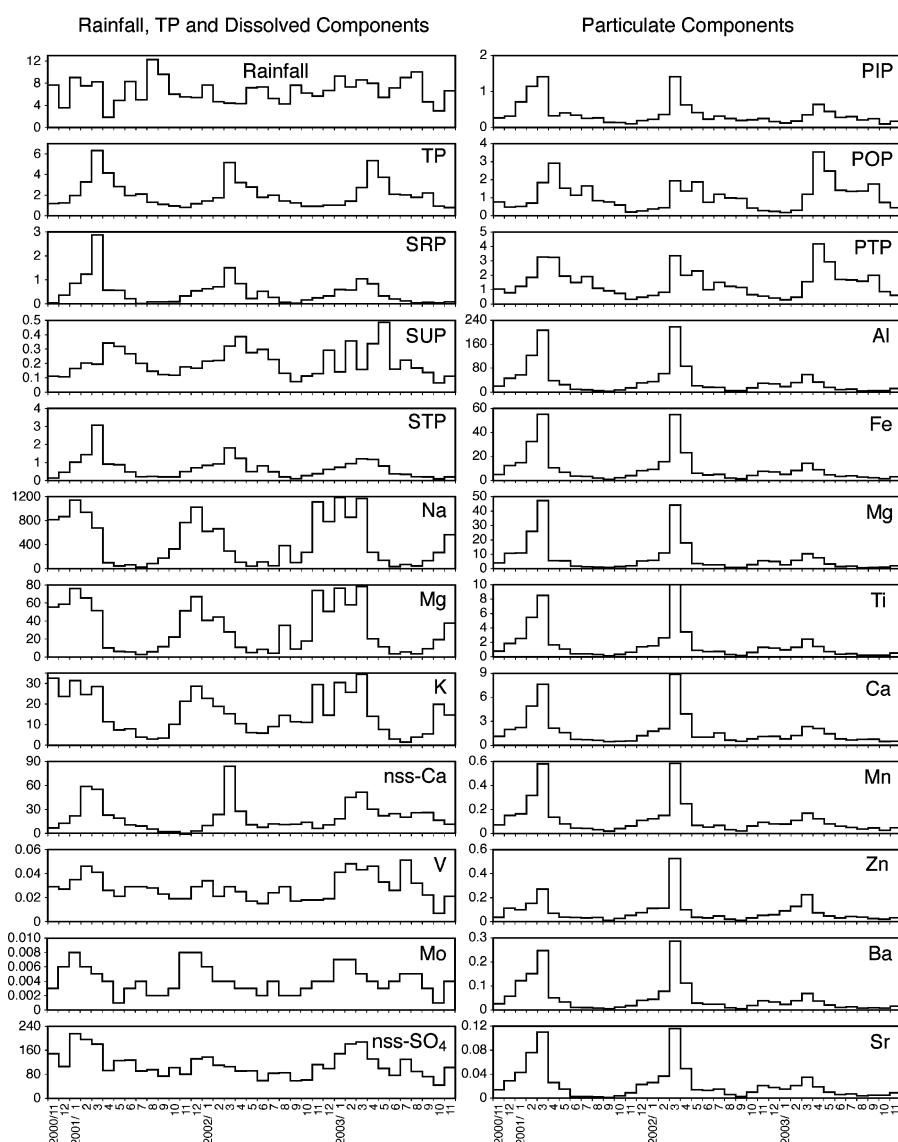


Figure 2. Seasonal variations of monthly averaged rainfall ( $\text{mm day}^{-1}$ ) and atmospheric bulk depositions ( $\mu\text{mol m}^{-2} \text{day}^{-1}$ ).

each component showed distinct seasonal variation. The components seemed to be divided into four groups. The first group had a broad peak during the winter and the spring (P fractions). The second group had a horizontal peak during the winter (Na, Mg, and K). The third group had two peaks during the winter and the summer (V, Mo, and nss-SO<sub>4</sub>). The fourth group had a

strong peak during the spring (dissolved nss-Ca and particulate metals). Within the first group of P fractions, the patterns were not identical: SRP and PIP deposition dropped to almost zero during the summer, while considerable deposition of POP and SUP was found during the summer. The above seasonal patterns might have reflected the nature of emission sources for each component.

#### *Extraction experiment*

The result of the extraction experiment is shown in Table 3. When compared with pollen, loess contained relatively large amount of PIP and particulate metals (Al, Fe, Ti, Mn, Ca and Mg), but the leachable P (SRP and SUP) content was very low. P content of loess varied among sampling sites, but the proportion was similar (PIP ~80%, POP ~20%, SRP and SUP ~0%). No systematic variation was found with regard to the sampling depth; thus vertical P redistribution through the soil profile was not evident. Though basically similar to loess, Ashiu soil was relatively enriched in POP (>60% of TP) but depleted in Ca and Mg. Pollen was generally rich in SRP, SUP and POP but poor in PIP or metals. The distinct characteristics of chemical composition and P forms can be useful for apportioning the sources of P.

#### *Chemical forms of P as a clue to source apportionment*

As sampling and analytical procedures were identical during the entire sampling period, the seasonal pattern of chemical P forms (SRP/SUP/POP/PIP) might reflect variation of emission sources. As shown in Figure 3, the proportion of soluble-P was large during the winter (November–February) but small during warmer seasons (March–October). It is also remarkable that SRP decreased almost to zero during the summer (July–September). The variation might be reflecting the seasonal change in P sources.

Another possible factor affecting the annual pattern is the transformation of P forms by microbial activity. It is well known that P forms in natural water samples can be seriously affected by microbial activity within a few hours (Maher and Woo 1998). In this study, samples were retrieved after each rain event, and the intervals between the end of rain and sample retrieving and filtration were normally 12–24 h, during which some microbial activity might have taken place. It is also plausible that such activity might occur in the sample bottle not only after rain but also during rain. In this study, no preservative (acids, chloroform etc.) was added to samplers because preservatives could disturb chemical analysis. It is thus plausible that microbial uptake could have transformed certain proportion of the soluble-P to particulate-P. Microbial activity is generally enhanced under higher temperatures, and the PTP/TP molar ratio actually showed a positive correlation with air tempera-

Table 3. Result of the extraction experiment.

Dissolved components	SRP	SUP	STP	Al	Fe	Ti	Mn	Ca	Mg
<i>Chinese loess</i>									
North of Yan'an, 0–2 cm	0.0	0.0	0.1	4	0	0	0.0	99	6
North of Yan'an, 18–25 cm	0.0	0.0	0.0	6	0	0	0.0	96	8
South of Yan'an, 0–2 cm	0.1	0.0	0.1	2	0	0	0.0	89	3
South of Yan'an, 48–55 cm	0.0	0.0	0.0	9	0	0	0.0	103	4
Luochuan, 0–5 cm	0.5	0.0	0.6	4	0	0	0.0	90	4
Luochuan, 40–45 cm	0.1	0.0	0.2	3	0	0	0.0	97	4
<i>Japanese soil</i>									
Ashiu, 5–9 cm	0.2	1.0	1.2	9	0	0	4.4	6	2
Ashiu, 23–27 cm	0.0	0.1	0.1	6	0	0	2.0	2	1
<i>Pollen</i>									
<i>Cryptomeria japonica</i>	19.7	7.5	27.1	3	0	0	0.0	0	0
<i>Chamaecyparis obtusa</i>	41.3	3.4	44.7	2	0	0	0.7	4	8
<i>Pinus densiflora</i>	55.1	4.7	59.8	–3	0	0	0.7	–2	17
<i>Carpinus laxifolia</i>	105	7.8	113	1	0	0	1.0	14	14
<i>Fagus crenata</i>	99.3	41.0	140	16	0	1	0.8	5	42
<i>Quercus monogolica</i>	125	88.8	214	–7	0	0	0.6	3	39
Particulate components	PIP	POP	PTP	Al	Fe	Ti	Mn	Ca	Mg
<i>Chinese loess</i>									
North of Yan'an, 0–2 cm	15.8	3.4	19.2	2060	477	94	9.4	1143	491
North of Yan'an, 18–25 cm	16.2	3.6	19.8	2000	476	93	9.1	1129	490
South of Yan'an, 0–2 cm	16.3	3.2	19.5	2110	489	97	9.6	1119	486
South of Yan'an, 48–55 cm	17.5	2.9	20.5	2100	500	96	9.6	1115	493
Luochuan, 0–5 cm	22.8	5.8	28.6	2150	526	98	10.1	830	459
Luochuan, 40–45 cm	19.2	4.3	23.4	2070	516	95	9.6	924	459
<i>Japanese soil</i>									
Ashiu, 5–9 cm	21.0	31.8	52.8	2760	668	105	40.2	2	230
Ashiu, 23–27 cm	18.3	34.2	52.5	2980	722	119	43.5	1	247
<i>Pollen</i>									
<i>Cryptomeria japonica</i>	1.5	26.3	27.9	0	1	0	0.4	35	40
<i>Chamaecyparis obtusa</i>	1.6	29.4	31.0	7	2	0	4.9	38	58
<i>Pinus densiflora</i>	1.8	18.5	20.3	9	3	0	0.8	4	16
<i>Carpinus laxifolia</i>	1.7	45.3	46.9	9	3	0	0.8	11	7
<i>Fagus crenata</i>	1.1	42.5	43.6	6	2	0	0.2	3	7
<i>Quercus monogolica</i>	1.6	82.7	84.3	20	7	1	0.9	11	26

ture (Figure 4). It is noteworthy that adsorption and desorption of soluble-P onto particles could also affect PTP/TP ratio (Maher and Woo 1998). Therefore, it is quite likely that a significant part of leached P (e.g. soluble-P from pollen) had been transformed into particulate P by the time of sampling and filtration. The magnitude of such transformation is difficult to determine as it can only be measured by varying the sampling conditions. These facts seem to suggest that chemical P form data might not be readily useful for source apportionment.

Table 3. Continued.

Total	SRP + PIP	SUP + POP	TP	Al	Fe	Ti	Mn	Ca	Mg
<i>Chinese loess</i>									
North of Yan'an, 0–2 cm	15.9	3.4	19.3	2060	477	94	9.4	1242	498
North of Yan'an, 18–25 cm	16.2	3.6	19.8	2000	477	93	9.1	1224	498
South of Yan'an, 0–2 cm	16.4	3.2	19.6	2110	489	97	9.6	1208	489
South of Yan'an, 48–55 cm	17.6	2.9	20.5	2110	500	96	9.7	1218	497
Luochuan, 0–5 cm	23.3	5.9	29.2	2160	526	99	10.1	919	462
Luochuan, 40–45 cm	19.3	4.3	23.6	2070	516	95	9.6	1021	463
<i>Japanese soil</i>									
Ashiu, 5–9 cm	21.2	32.8	54.0	2770	668	105	44.7	8	232
Ashiu, 23–27 cm	18.3	34.3	52.6	2990	722	119	45.4	4	248
<i>Pollen</i>									
<i>Cryptomeria japonica</i>	21.2	33.8	55.0	3	1	0	0.4	36	40
<i>Chamaecyparis obtusa</i>	42.9	32.8	75.8	9	2	0	5.6	42	65
<i>Pinus densiflora</i>	56.9	23.2	80.2	6	3	0	1.5	2	33
<i>Carpinus laxifolia</i>	107	53.0	160	10	3	0	1.8	25	21
<i>Fagus crenata</i>	100	83.4	184	22	3	1	1.0	8	48
<i>Quercus monogolica</i>	127	171	298	13	7	1	1.5	14	65

Unit: mmol kg<sup>-1</sup>.

In order to identify P sources via chemical P form dataset, samples should be protected from microbial activity by automation of samplers (filtration, freezing etc.) or by the addition of preservatives to samplers. It must be kept in mind, however, that certain preservatives might seriously alter the chemical forms of P (Maher and Woo 1998).

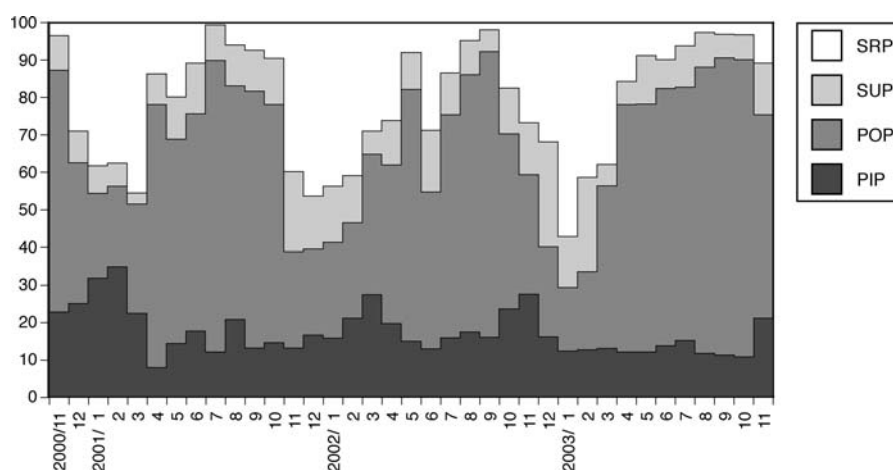


Figure 3. Seasonal variation of deposited P fractions (in % TP).

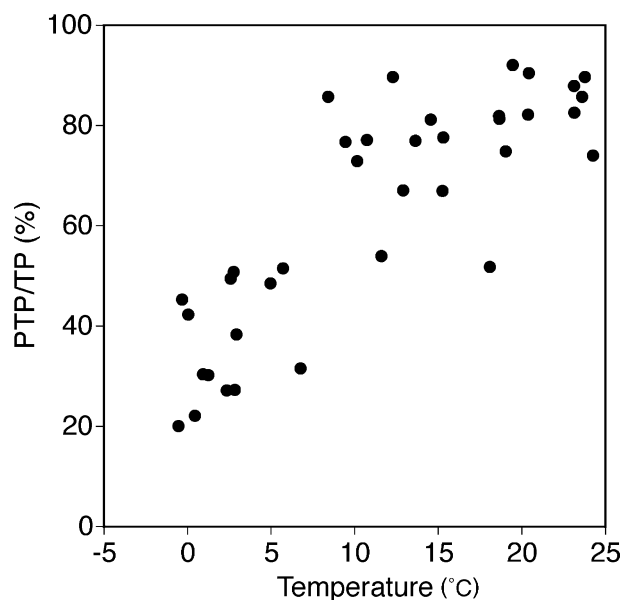


Figure 4. Correlation between monthly averaged air temperature and PTP/TP molar ratio.

#### *Lithogenic dust as a P source*

As Al, Fe, Ti and Mn are the major component of loess or soil but their concentration in pollen is low (Table 3), they might be useful as indicators of lithogenic dust P. Al and Ti deposition flux showed very clear and strong correlation to each other (Figure 5a), with Ti/Al molar ratio 0.0437. The value is close to that of Chinese loess (0.0380–0.0398: Table 3), Ashiu soil (0.0456–0.0465: Table 3) or literature values for loess of East Eurasia (0.0329–0.0339: Pye 1987; Gallet et al. 1996). The similarity in Ti/Al ratio suggests that Al deposition was predominantly derived from local soil or lithogenic dust from East Eurasia.

Several pieces of evidence imply that lithogenic dust from East Eurasia, rather than the local Ashiu soil, is more important as Al source. Total nss-Ca (sum of dissolved nss-Ca and particulate Ca)/Al molar ratio of atmospheric deposition in Ashiu was 0.368 (Table 1). The value was much higher than that of Ashiu soil (0.001–0.003: Table 3) but closer to Chinese loess (0.43–0.61: Table 3) or the literature values for loess of East Eurasia (0.653–1.09: Pye 1987; Gallet et al. 1996).

On the other hand, Mn/Al molar ratio was 0.00280 (Table 1). The ratio was much lower than that of Ashiu soil (0.0152–0.0161: Table 3), but closer to Chinese loess (0.00454–0.00469: Table 3) or the literature values for loess of East Eurasia (0.00484–0.00637: Pye 1987; Gallet et al. 1996).

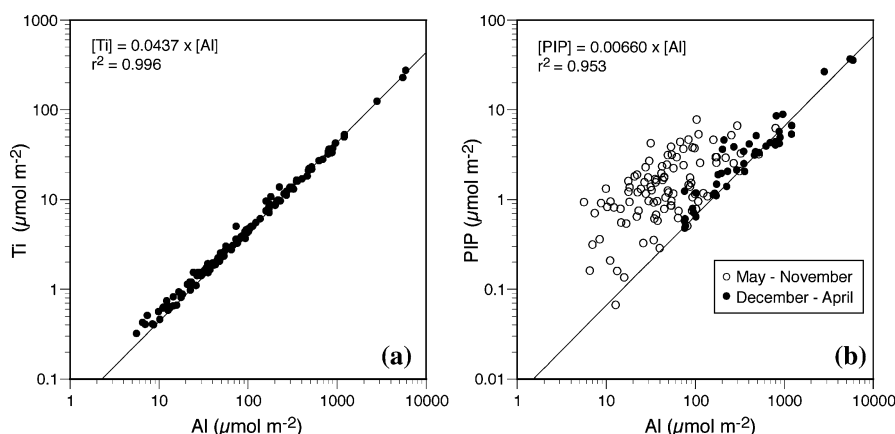


Figure 5. Correlations between atmospheric bulk depositions: (a) Al versus Ti, (b) Al versus PIP. Regression lines are for (a) all data, and (b) data through December to April.

Some other facts further support the hypothesis that the contribution of local soil to Al deposition in the Ashiu area is small. Rainfall was distributed throughout the year (Figure 2) and the ground was almost always wet with vegetation coverings. Deposition samples of this study were obtained on a 6-m sampling tower. Al deposition peaks were found in February and March (Figure 2), when the ground was covered with snow. The period is also known to be the season for major deposition of lithogenic dust from East Eurasia (Ishii 1979). These facts, together with Ca/Al and Mn/Al ratio, all suggest that lithogenic dust from East Eurasia is the major source of Al deposition in Ashiu area.

A scatter diagram for Al and PIP was examined and it was found that the correlation was high through December to April (winter), and the correlation was low, and PIP was relatively enriched, through May to November (spring–autumn) (Figure 5b). High PIP/Al ratio through May to November might be explained via the transformation of P as discussed above. During warmer seasons, microbial activity might transform soluble-P to labile-POP, and labile-POP can be detected as PIP via sequential extraction (Kuo 1996). Adsorption of orthophosphate to the surface of mineral particles (Maher and Woo 1998) might also cause a high PIP/Al ratio.

The high correlation between Al and PIP through December to April (PIP/Al molar ratio = 0.00660,  $r^2 = 0.953$ ) suggests that PIP during this season was predominantly brought by lithogenic dust from East Eurasia. The PIP/Al molar ratio for the period was slightly lower than the ratio for loess obtained from the extraction experiment (0.0077–0.011: Table 3). The difference in PIP/Al, Ti/Al, Ca/Al and Mn/Al ratios might be reflecting variations in the source region or in grain-size fractionation.

Overall, it can be concluded that PIP from lithogenic dust may be calculated using particulate Al as an indicator:

$$[\text{PIP from lithogenic dust}] = 0.00660 \times [\text{particulate Al}]$$

Other fractions of lithogenic dust P can also be estimated using molar ratio of P fractions in Chinese loess (Table 3).

#### *Fossil fuel combustion as a P source*

Tsukuda et al. (2005) showed that soluble-Mo or soluble-nss-SO<sub>4</sub> can be used as indicators for STP derived from fossil fuel combustion. They have also used backward air-mass trajectory data and the chemical composition of various fuels, and speculated that most of the fossil fuel-derived P was from coal combustion in China. In order to elucidate if these components could also be used as indicators for fossil fuel-derived TP (not STP), the correlation of excess-TP (TP minus lithogenic dust P) with Mo (Figure 6a) and nss-SO<sub>4</sub> (Figure 6b) were examined. It was found that the correlation was high through October to February (Mo: P/Mo molar ratio = 182,  $r^2 = 0.457$ ; nss-SO<sub>4</sub>: P/nss-SO<sub>4</sub> molar ratio = 0.00817,  $r^2 = 0.595$ ), and the correlation was low, and TP was relatively enriched, through March to September. According to the backward air-mass trajectories computed via HYSPLIT4 (Draxler and Rolph 2003), the high correlation period was part of the time when Chinese air-mass was passing over Ashiu, which extended through late autumn to early summer (October–June). During that time, fossil fuel (predominantly coal) combustion in China might have been the major TP source. The time through late winter to early summer (March–June) in Ashiu is the flowering season with significant pollen emission, which might explain TP enrichment during the time. It is thus reasonable to conclude that Mo and nss-SO<sub>4</sub> could also be used as indicators for TP from fossil fuel combustion.

As Migon and Sandroni (1999) argued, it might be possible that plant biomass combustion emits considerable P to the atmosphere. Nevertheless, the excess-TP/ SO<sub>4</sub> molar ratio of deposition (0.00817) fell between that of coal (0.0206) and that of crude oil (0.00276), but much smaller than that of plants (1.2). The excess-TP/Mo molar ratio of deposition (182) was also between those of coal (450) and crude oil (15), but much smaller than that of plants (15,000) (the element contents of fuels are taken from Table 3 in Tsukuda et al. 2005). The similarity in molar ratio seems to favor fossil fuel rather than plant biomass as the source of P in Ashiu.

#### *P from the other sources*

P from the other sources than lithogenic dust and fossil fuel combustion is discussed in this section. Based on the above discussion, lithogenic dust derived



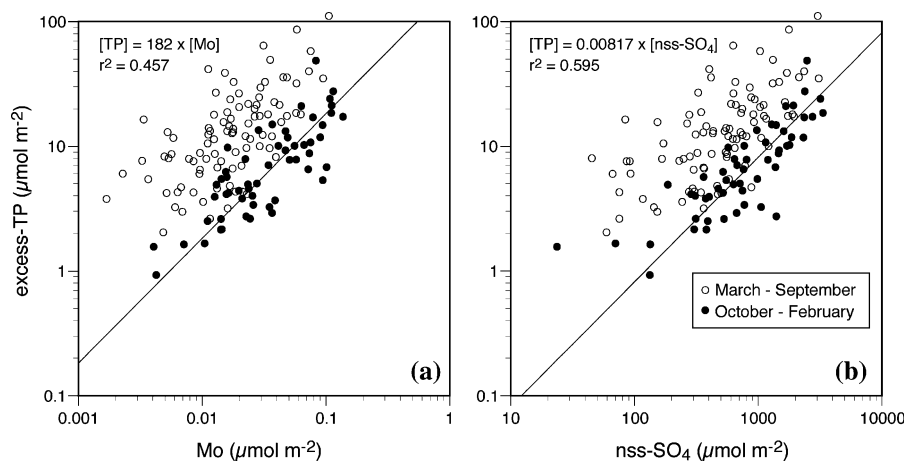


Figure 6. Correlations between atmospheric bulk depositions: (a) Mo versus excess-TP, (b) nss-SO<sub>4</sub> versus excess-TP. Both regression lines are for data through October to February.

P can be estimated using particulate Al as an indicator:

$$[\text{lithogenic dust P}] = 0.00660 \times [\text{particulate Al}] \times [\text{TP/PIP molar ratio of Chinese loess}]$$

which was calculated to be  $106 \pm 41 \mu\text{mol m}^{-2} \text{ year}^{-1}$  ( $15 \pm 5\%$ ). Fossil fuel derived P can be estimated using dissolved Mo as an indicator:

$$[\text{fossil fuel P}] = 182 \times [\text{dissolved Mo}]$$

or using dissolved nss-SO<sub>4</sub> as an indicator:

$$[\text{fossil fuel P}] = 0.00817 \times [\text{dissolved nss-SO}_4]$$

which was calculated using Mo data to be  $277 \pm 6 \mu\text{mol m}^{-2} \text{ year}^{-1}$  ( $35 \pm 1\%$ ) or calculated using nss-SO<sub>4</sub> data to be  $327 \pm 50 \mu\text{mol m}^{-2} \text{ year}^{-1}$  ( $42 \pm 6\%$ ). The mean value was  $302 \pm 28 \mu\text{mol m}^{-2} \text{ year}^{-1}$  ( $39 \pm 4\%$ ). P from the other sources was then calculated by subtraction of lithogenic dust and fossil fuel contribution from total deposition to be  $374 \pm 45 \mu\text{mol m}^{-2} \text{ year}^{-1}$  ( $47 \pm 6\%$ ).

Sea spray is considered here as the first candidate for the other sources. Sea salt-derived P can be estimated using Na deposition data and seawater P/Na molar ratio ( $4.3 \times 10^{-6}$ ; Murray 1992). The resultant value was less than  $1 \mu\text{mol m}^{-2} \text{ year}^{-1}$ . TP flux after exclusion of lithogenic dust P and fossil fuel P showed no correlation with Na flux ( $r = -0.0556$ ,  $N = 149$ , unit:  $\mu\text{mol m}^{-2}$ ). It can be concluded safely that sea spray plays only a negligible role as a P source in Ashiu.

Another remaining possibility as a P source is biogenic particles. The seasonal variation of TP after subtraction of the contribution from lithogenic dust

and fossil fuel combustion showed its peak during the spring (March–May), decreased gradually through summer to autumn (June–October) and dropped to nearly zero during the winter (November–February). The pattern seems to synchronize with biological activity in the field. Spring is the flowering season in Ashiu with significant emission of pollen from trees. During the summer and the autumn, plant debris or insect fragments were commonly found on samplers. These facts all suggest that biogenic particles are the third and the last predominant P source.

If biogenic particles originate within the terrestrial ecosystem, they should not be considered as part of the true atmospheric input. It is difficult to determine their actual source region, because the nature of the particles is very diverse. Nevertheless, pollen has a relatively large ( $\sim 20 \mu\text{m}$ ) diameter and its deposition rate decreases exponentially according to the distance from the source (Sugita 1993; Newman 1995). This fact makes the influence of long-range transport of pollen smaller. It is also plausible that if the target ecosystem has identical vegetation and climate as those of the surrounding areas, import and export of P via insects or plant debris should be roughly balanced over the boundary. It is thus speculated that most of the biogenic particles could be regarded as of local origin. From the calculation above, local biogenic particles may account for as much as  $47 \pm 6\%$  of the measured TP deposition. Local sources might contribute true input to waterbodies, but not to watersheds or forests. It is thus concluded that one should take considerable care when interpreting P deposition values as net atmospheric input to terrestrial ecosystems.

#### *The role of atmospheric deposition in the P budget of terrestrial ecosystems*

River run-off of TP from watersheds is comprehensively reviewed in Dillon and Kirchner (1975). According to their review, TP outflow is the lowest from forests developed over igneous parent material ( $23\text{--}284 \mu\text{mol m}^{-2} \text{ year}^{-1}$ ). The flux increases when the parent material is sedimentary, or when the vegetation contains pasture. However, the references reviewed in Dillon and Kirchner (1975) are mostly from North America and Scandinavia and do not necessarily represent values worldwide. In Japan, Kunitatsu (1995) measured TP output from forest stands on granitic parent material and reported slightly higher values ( $142\text{--}581 \mu\text{mol m}^{-2} \text{ year}^{-1}$ ; Table 4).

As discussed in the previous paragraphs, the major P sources for Ashiu are expected to be lithogenic dust and fossil fuel combustion. As both materials are transported over a long distance (from China or East Eurasia), it might be speculated that atmospheric P input should not differ much throughout the Japanese archipelago. TP deposition flux obtained in this study was  $783 \pm 68 \mu\text{mol m}^{-2} \text{ year}^{-1}$ , largely exceeding outflow values in Table 4. If local contributions are excluded, however, net atmospheric input decreases to  $409 \pm 46 \mu\text{mol m}^{-2} \text{ year}^{-1}$ . The value is in the range of TP outflow in Table 4. The result seems to suggest that atmospheric input makes a significant con-

Table 4. The P budget of terrestrial ecosystems.

Item	TP flux ( $\mu\text{mol m}^{-2} \text{ year}^{-1}$ )	Reference
<i>Output</i>		
Igneous parent material		
Forested		
North America, Scandinavia	152 (23–284)	Dillon and Kirchner (1975)
Aburahi-S, Japan	142	Kunimatsu (1995)
Myokoji, Japan	268	Kunimatsu (1995)
Kutsuki-R, Japan	326	Kunimatsu (1995)
Aburahi-N, Japan	581	Kunimatsu (1995)
Forested and Pasture	329(191–517)	Dillon and Kirchner (1975)
Sedimentary parent material		
Forested	378 (216–591)	Dillon and Kirchner (1975)
Forested and Pasture	752(358–1195)	Dillon and Kirchner (1975)
<i>Input</i>		
Atmospheric deposition (32 sites)	1434 (226–5425)	24 References
Atmospheric deposition in Ashiu, Japan	$783 \pm 68$	This study*
Lithogenic dust ( <i>Kosa</i> )	$106 \pm 41$	This study*
Fossil fuel combustion	$302 \pm 28$	This study*
Local biogenic particles	$374 \pm 45$	This study*

\*Mean and standard deviation of 3-year data.

tribution to the P budget of Japanese forested watersheds on igneous parent material.

## Conclusion

- (1) TP deposition in Ashiu was measured as  $783 \pm 68 \mu\text{mol m}^{-2} \text{ year}^{-1}$ . The value was relatively low in the range of reported values. The lower TP deposition probably reflected the method applied to reduce the contribution of local particles (Tsukuda et al. 2005) including: (1) placement of samplers off the ground surface, (2) installation of multiple samplers, and (3) rejection of contaminated samples.
- (2) Using Al, Mo and  $\text{nss-SO}_4$  as indicators, the contribution of lithogenic dust and fossil fuel was estimated to be  $15 \pm 5\%$  and  $39 \pm 4\%$  of total TP deposition, respectively. The rest ( $47 \pm 6\%$ ) was proposed to be predominantly associated to local biogenic particles. Local sources may be a part of true input to waterbodies, but do not contribute true atmospheric input to terrestrial ecosystems. One must take considerable care when interpreting P deposition values as atmospheric input to terrestrial ecosystems.
- (3) The net atmospheric P input (lithogenic dust and fossil fuel combustion) in Ashiu area was estimated to be  $409 \pm 46 \mu\text{mol m}^{-2} \text{ year}^{-1}$ . The P was presumably derived from East Eurasia. The value was almost equal to the

TP outflow from Japanese forests on granitic soil. It is possible that atmospheric deposition plays an important role in supplying P to forest ecosystems developed on igneous parent material in Japan.

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