Long-term fluctuation and regional variation of nutrient loads from the atmosphere to lakes

T. Kunimatsu* and M. Sudo**

*Department of Ecosystem Studies, School of Environmental Science, University of Shiga Prefecture, Hassaka, Hikone, Shiga 522-8533, Japan (E-mail: *kunimatu@ses.usp.ac.jp*)

**Department of Biological Resources Management, School of Environmental Science, University of Shiga Prefecture, Hassaka, Hikone, Shiga 522-8533, Japan (E-mail: *sudo@ses.usp.ac.jp*)

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Abstract The atmospheric depositions were collected by ordinary bulk-samplers mounted with a glass or polyethylene funnel of 30 cm orifice. A long-term observation was carried out at a site (35°01′30″N, 135°58′07″E) in the urbanized area for 21 years since 1974. The annual volume-weighted average concentrations of total nitrogen (TN) and phosphorus (TP) were 1.02 ± 0.30 and $0.031 \pm 0.015\,mg\,l^{-1}$, respectively, and the loading rates were 14.5 ± 2.8 and $0.43 \pm 0.16\,kg\,ha^{-1}\,yr^{-1}$. The rates neither had a relationship with the precipitation ($1{,}492 \pm 343\,mm\,yr^{-1}$) nor showed any diachronic tendencies. In order to obtain the loading rate of TN and TP within 10% uncertainty under the significant level of 0.01, there is no way but to continue the observation for seven and eleven years or more, respectively. In order to clarify the regional variation of the loading amounts of the depositions, the samplers were set at 12 sites distributing throughout the Kinki District for two years. The distance from northernmost ($2322\,mm\,yr^{-1}$) to southernmost ($1242\,mm\,yr^{-1}$) is about 150 km. The average loading rates of the 12 sites were $16.2 \pm 2.5\,kg\,ha^{-1}\,yr^{-1}$ of TN and $0.730 \pm 0.247\,kg\,ha^{-1}\,yr^{-1}$ of TP. The depositions of NO_3-N, NH_4-N, and TN as well as TP showed tendencies with distances neither from a big city nor from Japan Sea.

Keywords Atmospheric deposition; long term monitoring; nitrogen; phosphorus

Introduction

It has been well documented that atmospheric depositions as well as rivers and the groundwaters play a significant role in supplying nutrients to lake ecosystems. In the case of Lake Biwa, having $27.5\,km^3$ of volume, $675\,km^2$ of surface area and $3{,}144\,km^2$ of catchment area, the amount of the direct deposition on the lake surface was estimated to be 33% of the total load of nitrogen (Kunimatsu, 1998), and 8% of that of phosphorus (Kunimatsu and Kitamura, 1981). In order to study the material balances of the lake ecosystem as well as to decide the priority of measures protecting the lake from eutrophication, it is necessary to evaluate the precise loading rates of nutrients from the atmosphere. Although there have been many studies of the depositions of nitrate and/or phosphate, those of the total nitrogen and/or phosphorus have been restricted. There are at least four major problems in evaluation of the accurate and comprehensive loading rates; first there have not been any standardized sampling devices, namely the material of the sampler, separation of litter and insects, on-site storage, etc., secondly there is no way to separate materials circulating on site, namely, dust, pollen, volatile materials, etc. from the soils, fauna and flora from the bulk deposition (Ahn and James, 1999; Tsukuda *et al.*, 2004), thirdly the problem of how to appreciate the long-term fluctuation of the depositions mainly due to annual changes of meteorological conditions, and fourthly the lack of any criteria to select the observation site to evaluate the true amount of the deposition supplying to a large lake, namely distance from roads, smoke-emitting factories, agricultural fields applied with slurry manure, coast, etc.

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This paper focuses mainly on the latter two problems to protect such a large lake as Lake Biwa against eutrophication, and shows the long-term fluctuations of the loading rates of the total nitrogen and phosphorus as well as their chemical components from the observation for 21 years at a site and the regional variations from the data measured at 12 sites for two years.

Methods

Experimental sites

A long-term experiment to measure the bulk deposition of nutrients was carried out at Site 1 shown in Figure 1, which is located at 35° 01′ 30″ N in latitude, and 135° 58′ 07″ E in longitude. The site is in an urbanized area of Kusatsu City (population; 64,825 in 1975 and 114,009 in 2003, city area; 48.22 km^2) surrounded by paddy fields and forests in the basin of Lake Biwa, which is the largest lake and lies around the central part of the main island of Japan. In the city area, there were neither large factories vomiting thick smoke nor upland fields applied with a lot of manure, compost and/or dairy slurry, which were the anthropogenic sources of nitrogen, sulfur, and chlorine in gaseous and particulate forms. The long-term observation was carried out for 21 years from October 1974 to December 2003 with an interruption for eight years from January 1982 to June 1989. According to the record for the 21 years, the average temperature and precipitation were 11.1°C and 1,492 mm y^{-1}, respectively.

Regional variations of the bulk depositions were investigated by measuring at 12 sites distributed throughout the Kinki District, as shown in Figure 1. Sites 2 and 3 were set in northernmost rural mountain areas and Site 12 in southernmost urbanized areas, namely the Osaka megalopolis area (8.56 million people live in 1,881 km^2). The experiment was carried out for two years from January 1992 to December 1993.

Bulk deposit samplers

A bulk sampling method was used to collect the atmospheric wet and dry deposition. Bulk samplers have been widely used, because they were inexpensive and did not require a power supply (Kopacek *et al.*, 1997; Herut *et al.*, 1999; Campo *et al.*, 2001). Two types of the samplers were used in the study; Type 1 consisting of a glass cylindrical funnel with 30-cm orifice and 15-cm wall height and a light-shielded 20-litre glass reservoir,

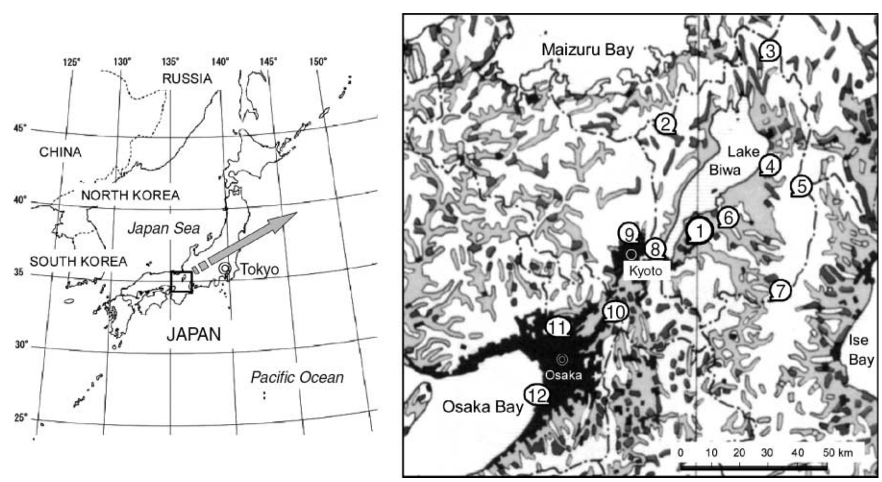

Figure 1 Experimental sites. The numbers typed inside circles show the sampling sites for the observation of regional variation. The site for long-term observation was carried out at Site 1. Areas painted white, gray and black in the right-hand map show mountain areas, agricultural areas and urban areas, respectively

and Type 2 of a conical-shaped polyethylene (PE) funnel with 20 or 30 cm orifice and a 20 L opaque grey PE-reservoir. It is generally recognized that bulk sampling is not always adequate in monitoring the amount of deposition, because substantial biochemical changes and physicochemical aggregation occur inevitably in the reservoirs during the deposition period. In this study, 2 ml of concentrated H_2SO_4 were contained in the reservoir of the sampler of 20-cm orifice to avoid these problems, and the water samples collected by the sampler of 30-cm orifice were used only to analyze pH, EC, and SO_4-S.

Sampling methods

Site 1 was on the roof of a building of four stories in the campus of Junior College of Shiga Prefecture, where the long-term observations were carried out. Before the interruption, Type 1 was used, and water samples were collected once a fortnight. After that, the sampler was changed to a set of Type 2, and water samples were collected monthly for two years. After May 1991, water samples were collected by Type 1 at the same time-interval as before. Water samples were collected monthly in 2-L PE-bottles after measuring the water volumes, from which precipitations were calculated. A rain gauge, as standardized by the Japan Weather Bureau with a 20.3-cm orifice, was placed at the experimental site. Precipitation was also measured at the Otsu station located about 15 km south of the site, which belongs to the Hikone Local Meteorological Observatory. In the regional investigation, a set of Type 2 samplers was set at each site. Sites 2 and 3 were located in an area normally covered with snow from December through early April, where discharge from a rain–snow gauge was pooled in a reservoir during the period.

Water chemistry

A certain volume of a water sample was filtered through a 1-μm pore-size glass-fiber filter with a 45-mm diameter. The total amounts of nitrogen (TN) and phosphorus (TP), and the dissolved components of those (DN and DP) were analyzed in the water sample before filtration and in the filtered sample, respectively. The concentrations of these elements in particulate forms (PN and PP) were obtained from the differences between the concentrations of each of those samples. Chemical analyses were carried out mainly with Japan Industrial Standard Methods (1986), which had been revised for years. So the methods for some items were changed during the long study-period, as follows: Kjeldahl digestion-indophenol blue method for TN and DN changed to basic potassium peroxodisulfate digestion (120°C, 1.5 atm.) – UV absorbance (260 nm) method; HNO_3–$KClO_4$ digestion-molybdenum blue method for TP and DP to acidic potassium peroxodisulfate digestion-molybdenum blue method; sodium salicylate method for nitrate nitrogen (NO_3-N), mercuric nitrate method for chloride ion (Cl^-), flame analysis for sodium ion (Na^+) to suppressed ion chromatographic method (HPLC) using an HIC-6A attached to Shim-pac IC-A1 and IC-C2 (Shimadzu, Kyoto, Japan). Nitrite nitrogen (NO_2-N), ammonium nitrogen (NH_4-N) and phosphate phosphorus (PO_4-P) were assayed with diazonation method, the indophenol blue method and the molybdenum blue method, respectively.

Results and discussion

Fluctuations of loading rates

Seasonal fluctuations. The daily loading rates calculated from data analyzing each sample (every two weeks or month) were plotted with time in Figure 2, in which curves smoothed by the moving average of 5 data were also shown. The curve of TN decreased in winter and increased from summer in autumn every year. The period of the high loading rate coincided with the rainy season and that of the low rate with the dry season in the region. A similar phenomenon was found in the curve of TP. From the result, it

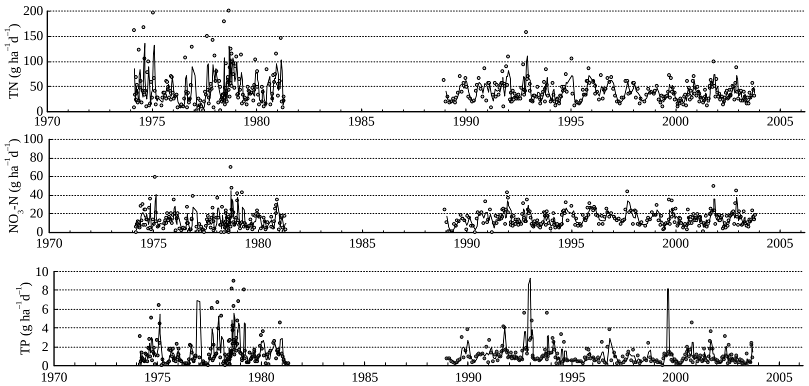

Figure 2 Seasonal changes of depositions of total nitrogen, nitrate nitrogen and total phosphorus at Kusatsu City. Lines were drawn by the moving average of 2 data

should be memorized that we cannot evaluate the annual rate of the atmospheric deposition from observation for less than one year, because the rates of nutrient depositions usually fluctuate more than two times in a year.

Long-term fluctuations. The annual volume-weighted average concentrations were calculated from the long-term data, and plotted with year in Figure 3. No definite tendency was found in the concentrations of TN. As mentioned above, there were no large factories discharging thick smoke and the surrounding agricultural fields were mainly paddy fields, so the changes of the concentrations of NO_3-N and NH_4-N, both of which might be strongly affected by anthropogenic sources, did not show any definite tendency. However, slightly decreasing tendencies were found in the changes of DP and PO_4-P.

The mean values of the annual volume-weighted average concentrations for 21 years and their coefficient of variation are shown in Table 1. The concentrations of TN and TP were 1.02 mg l^{-1} and 0.0310 mg l^{-1}, respectively, of which CV-values were 29 and 47%. The variation of the concentration of phosphorus was greater than that of nitrogen. The ratio of N/P was 33. These results indicate that the sources of nitrogen and phosphorus might be different from each other.

Annual loading rates

The mean values of the annual loading rate for 21 years and its coefficient of variation are also shown in Table 1. The loading rate of TN was 14.5 ± 2.82 kg ha^{-1} yr^{-1}. NO_3-N,

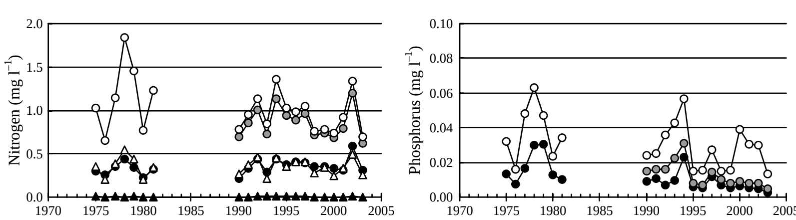

Figure 3 Long-term fluctuations of nitrogen and phosphorus concentrations of atmospheric deposition measured at Kusatsu City. The concentrations were the annual volume-weighted average concentrations calculated from the long-term data obtained once every two weeks before 1982 and once a month after 1989 with the bulk sampler. Nitrogen: ○;TN, ◍;DN, ●; NO_3-N, △; NH_4-N, ▲; NO_2-N. Phosphorus: ○; TP, ◍; DP, ●; PO_4-P

Table 1 Mean values of the annual volume-weighted average concentrations and the annual loads measured at Kusatsu City for 21 years

Items	Concentrations		Loading rates		
	mg l^{-1}	CV (%)	kg ha^{-1} yr^{-1}	CV (%)	Composition (%)
TN	1.02	29	14.5	19	100
DN	0.854	21	12.8	15	88
NH_4-N	0.348	28	4.97	22	34
NO_3-N	0.351	24	5.05	21	35
NO_2-N	0.006	56	0.08	59	1
TP	0.0310	47	0.429	37	100
DP	0.0127	56	0.190	53	44
PO_4-P	0.0112	70	0.155	57	36
Precipitation (mm yr^{-1})	–	–	1,492	23	–

NH_4-N and Org-N occupied about a third of TN each. PN contained only 12%. The variations of each component except for NO_2-N were around 20%, which were almost the same as that of the annual precipitation. The loading rate of TP was 0.429 ± 0.158 kg ha^{-1} yr^{-1}, of which PO_4-P occupied only about one third. The characteristic of phosphorus was that PP contained more than a half, and that the variations were much larger than those of nitrogen. These compositions were not largely different from those measured previously at three different sites in mountain forests in the Lake Biwa basin (Kunimatsu *et al.*, 2001), except that the ratios of NO_3-N (23–31%) were slightly lower and those of PO_4-P (46–57%) were higher than those measured at Kusatsu City. It should be noted from these results that the loading rate measured only inorganic substances largely underestimating the loads of nitrogen and phosphorus from the atmosphere to the lakes.

It was clearly shown from the above investigation that the loading rates of nutrients from the atmosphere changed significantly from season to season as well as from year to year. Changes of important sources for the period may be one of the reasons. The rates, however, did not show any tendencies related with the progress of years in Figure 2. It is also necessary to examine how the yearly changes of precipitation may have affected the rates. The annual loading rates versus the annual precipitations were plotted in Figure 4, in which the average values for 21 years with error spans were also shown. It became clear that any relationships between these parameters were not found on the scatter diagrams of TN or TP.

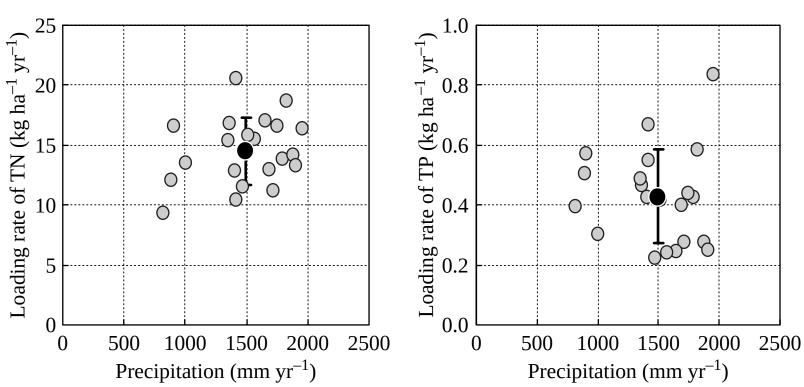

Figure 4 Relationships between the annual loading rates of the atmospheric deposition and the annual precipitations measured at Kusatsu City. The data were the same as those used in Figure 2 and Table 1. ● shows the average value for 21 years with error span

Accuracy of observed annual loading rates

It was left behind as a subject to identify each source, so any suitable methods to obtain reliable loading rates could not be recommended, besides carrying out continuous measurement as long as possible. Then, how long should we continue measuring atmospheric depositions in order to obtain reliable loading rates? Then we examined it using the data measured for 21 years. The data were assumed to be continuous data, although they included an interruption for 8 years from 1981. Suppose that observation was continued for n years and the annual average value x_{n} was obtained. Every continuous n data were picked up from the data as shifting by a year, and a set of $(20 - n + 1)$ averages x_{n} were obtained. On the basis of central limit theorem, x_{n} should distribute the normal distribution around their mean value X_n with the standard deviation s_{n} in spite of the type of the distribution of the original population. So the confidence interval is calculated as following;

$$\mu = X_n \pm t(s_{\mathrm{n}}/n^{0.5}) \qquad (1)$$

where μ and t are the true value and t-value, respectively. t is read in the t-distribution table under a given confidence limit and the degree of freedom ($n - 1$ in this case). The ratios α of $t(s_{\mathrm{n}}/n^{0.5})$ corresponding to 90%- and 95%-confidence limit to X_n were calculated in the long-term data and plotted versus n in Figure 5.

$$\alpha = t(s_{\mathrm{n}}/n^{0.5})/X_n \qquad (2)$$

The curves of TP in the figure were obviously distorted in mid course. This is because an unusually large value obtained in 1985 was contained in the 21 years data, as shown in Figure 4. However any reasons for rejecting such a datum have not been found as yet.

If n gives α_{99} smaller than 0.1, x_n within the confidence interval of X_n (1 ± 0.1) will be obtained under 0.01 significance level. In other words, 99% of the average values obtained by measuring for n years may be included within $\pm$10% of X_n, which is the estimated value of true value of the annual loading rate. The curves of α_{95} and α_{99} in the figure indicate that the mean value of the loading rate of TN satisfying the above condition is obtained by continuous measuring over five and seven years, respectively. The rate of precipitation having the same accuracy may be obtained by measurement over five and six years. It is necessary to continue measuring for more than ten and eleven

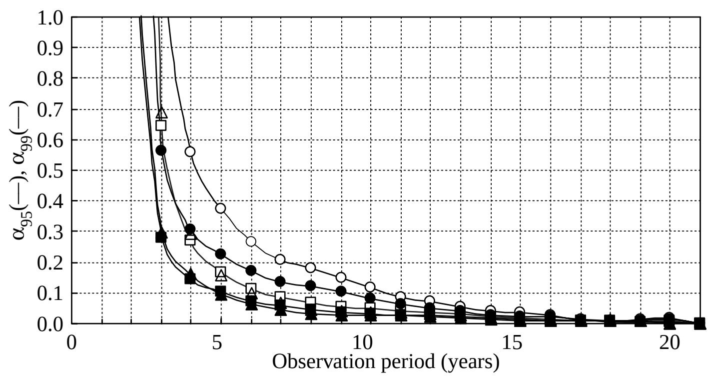

Figure 5 Relationships between the continuous observation periods (n years) and the coefficient of 90% and 95% confidence limits (α_{90}, α_{95}) of the average values. Every n data were picked up from the data obtained for 21 years, and $(20 - n + 1)$ average values x_n were calculated. α is $t(s_n/n^{0.5})/X_n$, where s_n and X_n were standard deviation and mean values of x_n. □; TN, ○; TP, Δ; precipitation

years, respectively, in order to obtain the loading rate of TP satisfying the same condition.

Regional variations

It is well known that the loading rates of the atmospheric depositions are strongly affected by winds blowing across the sea or the different land-use areas. Then, the site effects on the rates were investigated by setting the bulk samplers at 12 sites distributed throughout the Kinki District. As shown in Figure 1, the northern and southern coasts of Kinki District are facing the Japan Sea and the Pacific Ocean, respectively. From the Pacific Ocean, two or three typhoons accompanied by intense winds as well as intense rains usually pass through the district during summer and autumn. During winter, strong monsoon winds often blow from a reverse direction across the Japan Sea accompanied by snow.

First, in order to clarify geographical influence, the average annual depositions were plotted against shortest distances from the Maizuru Bay and from the center of Osaka City in Figure 6. The depositions of Na^+ decreased as the distance from the bay increased, as expected. The seasonal changes of loading rates of Na^+ measured at Site 2 set in a northern rural mountain area and Site 12 at the southern urban area near Osaka City are shown in Figure 7. The deposition of Na^+ obviously increased from November to April at Site 2 every year. However, the seasonal change was found just slightly on the graph of Site 12, although it is located near the sea. The results indicate that the influences of the sea salts are not estimated simply by a function of the distances from the sea. Secondly, it seems to be common knowledge that urbanization strongly affects the deposition of nitrate nitrogen. However, as shown in Figure 6, the effects of the distances from the City Hall of the Osaka megalopolis on the depositions of nss-NO_3-N, which were connected to the supply from the sea salt, were not clear. Moreover, essential differences were not found between Site 2 and Site 12 in Figure 7. Phosphorus also did not show any tendencies.

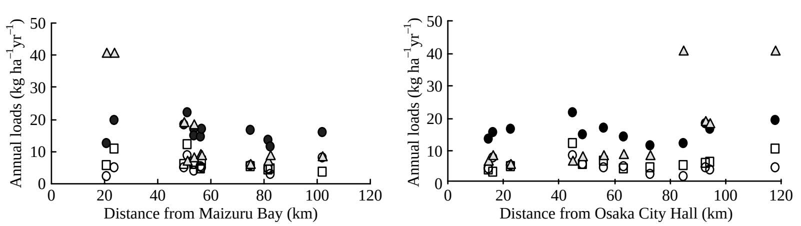

Figure 6 Relationship between the annual loading rates of deposition of nitrogen, phosphorus and Na^+ and shortest distances from Maizuru Bay and from the center of Osaka City. ●; TN, ○; NO_3-N, □; TP (x10), Δ; Na^+

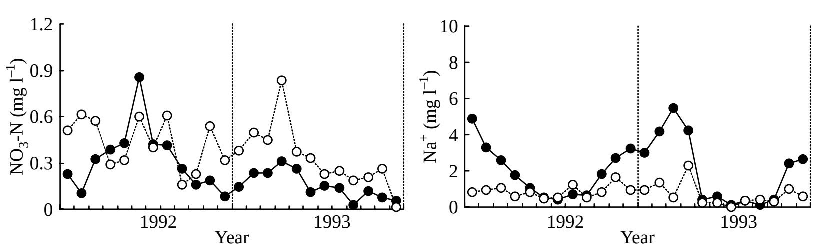

Figure 7 Monthly depositions of NO_3-N and Na^+. Site 2 (●) is located at the northern mountain area, and Site 12 (○) at the Osaka megalopolis area in the southern area of Kinki District

Table 2 Regional variation of the annual loading rates of atmospheric depositions[1] (kg ha^{-1} yr^{-1})

No.	Sites	TN	DN	NH_4-N	NO_2-N	NO_3-N	TP	DP	PO_4-P	Precipitation[3]
1	Kusatsu	18.2	16.9	7.0	0.01	5.4	0.75	0.56	0.42	1678
2	Kutsuki[2]	13.4	11.0	3.8	0.03	3.1	0.85	0.68	0.46	2133
3	Yogo	19.4	17.3	5.5	0.01	4.9	1.10	0.83	0.49	2322
4	Hikone	16.1	15.3	4.8	0.01	4.1	0.52	0.40	0.25	1240
5	Taga[2]	17.0	16.5	4.8	0.00	4.3	0.68	0.60	0.36	2452
6	Yasu	14.0	12.3	4.8	0.02	5.5	0.81	0.63	0.35	1716
7	Koga	12.1	10.3	3.4	0.00	3.0	0.62	0.49	0.35	1737
8	Otsu	18.8	17.7	6.8	0.01	6.0	0.99	0.85	0.62	1660
9	Kyoto	19.4	17.8	7.0	0.02	7.2	1.09	0.97	0.74	1696
10	Hirakata	15.7	13.8	4.9	0.03	5.4	0.57	0.41	0.31	1462
11	Suita	13.5	11.6	3.7	0.02	4.8	0.42	0.28	0.18	1515
12	Sakai	16.7	15.6	6.3	0.04	7.0	0.36	0.25	0.16	1242
Average		16.2	14.7	5.23	0.02	5.06	0.730	0.579	0.391	1738
CV (%)		15.5	18.8	24.7	73.9	26.2	33.9	39.3	43.5	22.2

[1]The bulk depositions were continuously measured once a month from January 1992 to December 1993
[2]Those were measured from January 1993 to December 1993
[3]mm yr^{-1}

The average annual loading rates are shown in Table 2. Precipitations ranged from 1240 mm yr^{-1} at Site 4 to 2452 mm yr^{-1} at Site 5. The average loading rate of TN of all sites was 16.2 kg ha^{-1} yr^{-1} varying from 12.1 kg ha^{-1} yr^{-1} to 19.4 kg ha^{-1} yr^{-1}.The average composition of chemical species was NO_2-N 0.1, NO_3-N 31, NH_4-N 32, Org-N 36 and PN 9 in percent. There were tendencies that the deposition of TN increased in urban areas as well as in high precipitation areas. DIN tended to increase in the urbanized areas. The average loading rate of TP was 0.730 kg ha^{-1} yr^{-1}, varying from 0.36 kg ha^{-1} yr^{-1} to 1.10 kg ha^{-1} yr^{-1}.The average chemical compositions were 54, 46 and 21% for PO_4-P, Org-P and PP, respectively. Phosphorus showed a tendency to decrease in the urbanized areas. These results also indicated that the source of phosphorus was different from that of nitrogen.

Conclusion

From the results of the long-term observation for 21 years at the same site, the loading rates of nutrients from the atmosphere varied significantly from year to year, namely in the cases of TN and TP from 9.37–20.6 kg ha^{-1} yr^{-1} and 0.226–0.838 kg ha^{-1} yr^{-1}, respectively, and had no correlations with annual precipitations. It was shown from the data that in order to obtain the loading rates within 10% of uncertainty under the significant level of 0.01 it was necessary to continue observation for seven and eleven years or more for TN and TP, respectively. It was indicated that the sources of these elements may be different from each other. However, there are so many factors giving more or less annual change to the loading rates, that it was difficult to identify any particular or major factors.

It was also shown that the rates varied from site to site, distributed to not so large an area (150 km from north to south, 60 km from east to west), from 12.1–19.4 kg ha^{-1} yr^{-1} for TN, and from 0.36–1.10 kg ha^{-1} yr^{-1} for TP. However, it was ambiguous whether these variations resulted from anthropogenic pollutions, meteorological conditions, and/or biotic conditions. Thus it seemed difficult to develop any methods or models for predicting the loading rate by using a number of these parameters. In conclusion, there would not be any other way but to make observations at as many sites as possible and to continue for seven years or more in order to obtain accurate and comprehensive loading rates of nutrients from the atmosphere to a lake.

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