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Seasonal variation of natural radionuclides and some elements in plant leaves

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Leaf and aerosol samples were monthly collected in Mt. Sefuri (Fukuoka Prefecture). Radioactivities of ^{7}Be, ^{210}Pb and ^{40}K were determined with gamma-ray spectrometry. The concentrations of some elements in the leaf samples were determined by neutron activation analysis. Similar seasonal variation of ^{7}Be and ^{210}Pb was observed between leaf and aerosol samples, high in spring and winter and low in summer. Correlation factors for trace elements contained in the leaf show large variations. This indicates that the contribution of two sources (atmospheric deposition and uptake from soil) is very variable.

Introduction

The use of plants as a biomonitor has become a well-established technique to estimate atmospheric aerosol or trace element depositions on a geographical basis.[1–6] The relative ease of sampling, the absence of any need for complicated and expensive technical equipments, and the accumulative and time-integrative behavior of the monitor organism makes that the biomonitoring of the atmospheric deposition will be continued for the foreseeable future, especially in large scale surveys.

A plant species to be used for biomonitoring of atmospheric pollution should fulfill several criteria. Most importantly, element uptake should not depend on conditions other than the level of the metal to be monitored.

The purposes of this work are: to measure the accumulation and seasonal variations of the activities of three natural radionuclides (^{7}Be, ^{210}Pb and ^{40}K) in the leaf samples and to compare with those of the deposition and aerosol. To investigate the differences of capture capability of radionuclides among eight leaf plants samples. To investigate the relationship of these natural radionuclides with other elements and to evaluate the feasibility of leaf samples as biomonitor relative to the more frequently used pine needles.

Experimental

Sampling

The sampling site was Mt. Sefuri (height 1055 m) located 20 km southern of Fukuoka city, Japan. Leaves of eight species of plants were collected routinely every month during the period of Dec. 2000–June 2003. The names of the samples: *Quercus acuta*, *Petasitos japonicus*, *Sasa veitchii*, *Miscanthus sinensis*, *Entodon challengeri*, *Ilex crenata*, *Pinus thunbergii*, and *Lycopodium clavatum*. Sampling height was about 1–2 m above ground for *Quercus acuta* and *Pinus thunbergii*, and near the surface (0–50 cm) for other plants. In the laboratory the fresh leaf samples were dried at 130 °C and ashed at 550 °C in an oven.

The deposition samples including rain and atmospheric deposition (wet and dry) were collected at Mt. Sefuri routinely with two bulk collectors. Each collector consisted of a funnel with diameter of 30 cm and a plastic container. The collected depositions were evaporated to dryness in a Teflon beaker.

Aerosol samples were collected at Mt. Sefuri monthly by aspiration of air through 0.04 m^2 glass fiber filter paper (Advantec, GB-100R) using a high-volume air sampler (Sibata, HV-1000F (1 m^3/min)) at 1 m above ground-level for 8 hours. The volume of the filtered air was about 480 m^3. The filters were pressed with a cylindrical container.

Analysis

The radioactivity of the natural radionuclides ^{210}Pb, ^{7}Be and ^{40}K were assayed at 46.5 keV, 477.7 keV and 1462 keV for all samples using a gamma-ray spectrometer with a HPGe semiconductor detector (GMX23190-P, GMX30200; EG&G ORTEC) for about a day. The gamma-ray spectra were analyzed with the gamma studio software (Seiko EG&G). The activities of these three natural radionuclides were decay corrected to the time of sampling.

The concentrations of trace elements in the leaf samples were determined by neutron activation analysis using the nuclear research reactor, JRR-4 JAEA, Tokai, Japan. Two types of irradiation were carried out, short-time (10 seconds) and long-time (3 hours). The concentrations are determined by a comparative method using JB-1 as a reference material. The samples of the short-time irradiation were measured immediately after irradiation and those of the long-time irradiation were measured at 10 days and 30 days after irradiation using

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the gamma-spectrometry system. The elements determined by the short-time irradiation were Mg, Na, Cl, Ca, Mn and Ti, while those by the long-time irradiation were Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Sb, Sc, Se, Sm, Tb, and Yb. The neutron activation analysis has been carried out at the Inter-University Laboratory for the Joint use of JAEA Facilities.

Results and discussion

Seasonal variations

The seasonal variation of ^{7}Be (Fig. 1) and ^{210}Pb of the leaf samples shows that it is generally high in spring season (April/May) and in late autumn or early winter (Oct.–Dec.) and low in summer (from Jun.–Sep.). The low activities of ^{7}Be and ^{210}Pb during summer season are due to the increase of rainfall in this period. Decrease of the activities of ^{7}Be and ^{210}Pb on the leaf samples by rainfall through washout process suggests that the most part of the aerosol deposited just on the surface of the leaf and can be easily detached from the surface. Only small amount of the aerosol enters to the pore of the leaf. It may depend on the size of aerosol particles.

Activity in depositions (Fig. 2) also shows seasonal variations, high and low, in accordance with the activity of the leaf sample. Spring peak of ^{7}Be is well known, resulted from the increase of vertical transport rate of ^{7}Be from stratospheric and upper troposphere to the middle and low troposphere. It is considered that the winter peak of ^{7}Be and ^{210}Pb is due to seasonal variations in the horizontal transport of tropospheric air masses from high latitude into middle latitude, i.e., continental Siberian air mass.[7] It is considered that there is fairly good relationship among the activities of these two radionuclides accumulated on the leaf and the depositions.

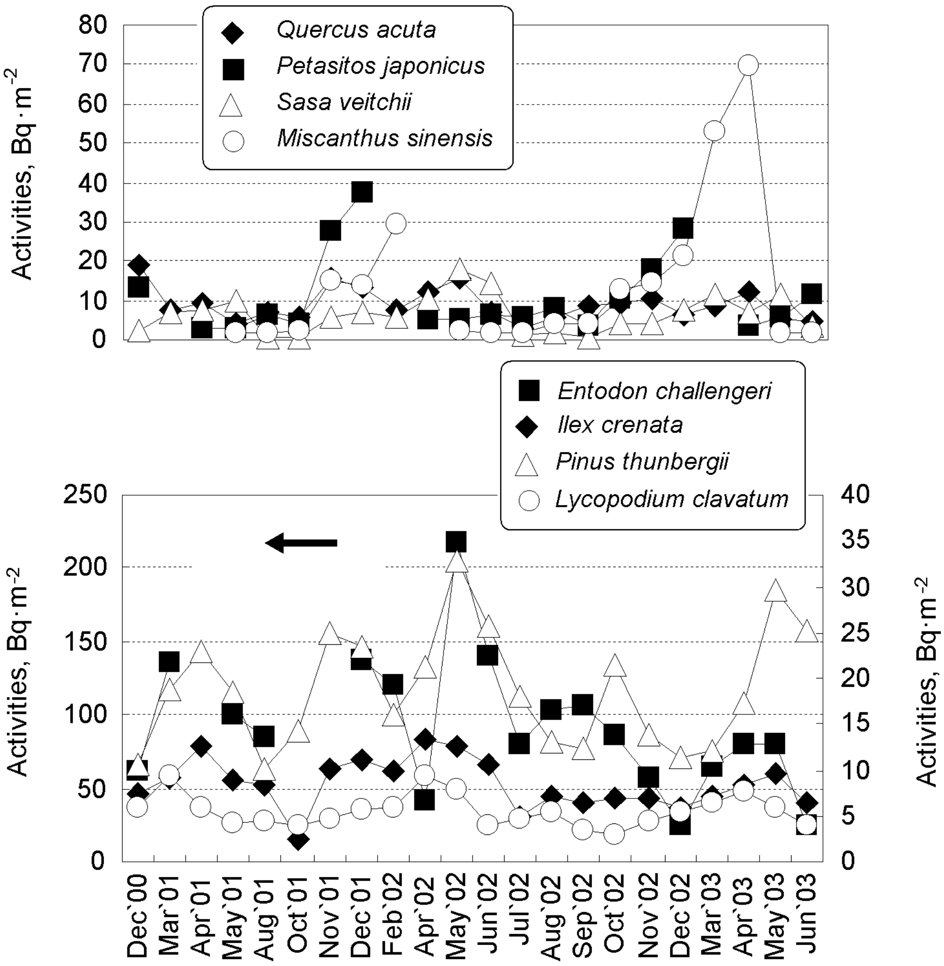

Fig. 1. Variations of ^{7}Be activities in leaf samples

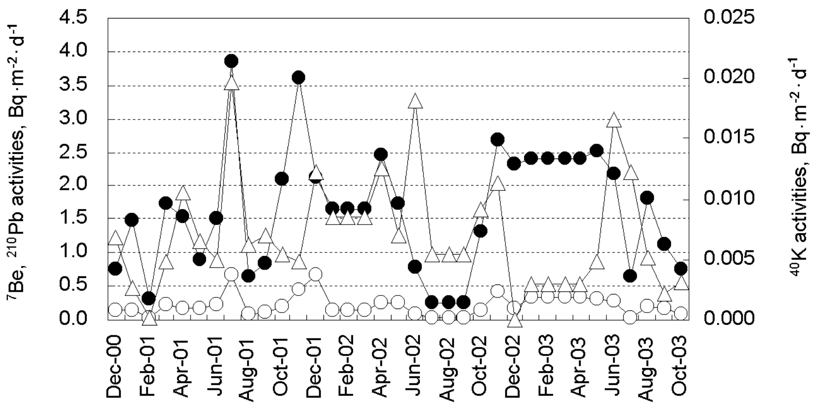

Fig. 2. Variations of ^{7}Be, ^{210}Pb and ^{40}K activities in deposition samples

^{40}K in some species such as *Petasitos japonicus* and *Miscanthus sinensis* show a different pattern from ^{7}Be and ^{210}Pb where the activities of these radionuclides are high in early spring and gradually decrease until the lowest activities at the end of winter. This pattern is readily understood because K is an essential element and necessary during all stages of growth of plants. In early spring *Petasitos japonicus* and *Miscanthus sinensis* will grow-up, during this period these plant samples require more K. For the other species, the activities of ^{40}K are almost constant through a year. Consequently the ^{40}K in the leaf samples is not originated from deposition of atmospheric aerosol (as external source), but contained in plant itself and taken through the roots from the soil (internal source).

Absorption capability

The activities of ^{7}Be, ^{210}Pb and ^{40}K in *Entodon challengeri* are about 4–16 times higher than those in other species, these results agree with the previous works in which the mosses showed great capacity on retaining elements,[1,2] beside that it would depend on living environment of the sample. The *Entodon challengeri* has grown on the bark of other plants. Therefore, we could not separate the moss from the bark and soil completely at the sampling. Incompletion in separation could be affecting to the radioactivity contained in *Entodon challengeri*.

The activities of ^{7}Be in the deposition and aerosol were higher than that of ^{210}Pb. Opposite with the deposition and aerosol was observed for plants that the activities of ^{210}Pb in the leaf samples were higher than those of ^{7}Be. This may indicate that ability/affectivity of leaves to retain or to absorb ^{210}Pb is relatively higher compared with that of ^{7}Be. This result agrees with the previous study that the efficiency for a kind of moss (*Hylocomium splendens*) to retain Pb is almost close to 100%.[1] Factor of ^{7}Be and ^{210}Pb attached in different particles of aerosol could be included to this observation.

The activities of ^{40}K were low in the depositions and not detected in the aerosol samples. This is one of the reasons why the source of ^{40}K is not from aerosol but from biologically uptake of the leaf. The windblown soil dust (local source) would be a source of ^{40}K in depositions.

In the vascular plants, *Pinus thunbergii* has highest ability to retain the aerosol from the atmosphere, about 94% for ^{210}Pb and 19% for ^{7}Be was retained relative to depositions at unit area basis. The 7.4 Bq/m^{2} for ^{210}Pb and 6.7 Bq/m^{2} for ^{7}Be (Table 1) were compared with that of the deposition at Mt. Sefuri. There are three factors which influence the high capability. First, this plant has epicuticular wax or resin on the leaf surface that can retain aerosols or natural radionuclides tenaciously. Second, higher ability of this plant to retains rain water, because the wet deposition was major process to remove the aerosol from the atmosphere. Owing to these factors *Pinus thunbergii* has been always used as biomonitor and standard in the previous works.[1,2,5] It is important to have in mind the possibility of the other factors influencing this observation such as size of aerosol particles and pore of leaf, and the saturation of the leaf to absorb aerosol.

The different order of ability to retain between ^{7}Be and ^{210}Pb in each leaf samples indicates that ^{7}Be and ^{210}Pb probably attached on different particle aerosols. It also could be seen on correlation factor that the samples have a positive correlation between ^{7}Be and ^{210}Pb, but not so strong in some leaf sample like as *Ilex crenata* ($r = 0.59$) and *Pinus thunbergii* ($r = 0.66$) (Table 2).

In all season, the retain of ^{40}K on all samples is more than 100% relative to the depositions. This result proves that ^{40}K does not come from aerosol depositions.

Table 1. Average activities (in Bq/m^2) of ^{7}Be, ^{210}Pb and ^{40}K in leaf samples

Isotope	*Quercus acuta*	*Petasitos japanicus*	*Sasa Veutcguu*	*Miscanthus sinensis*	*Entodon challengeri*	*Ilex crenata*	*Pinus thunbergii*	*Lycopodium clavatum*
^{7}Be	2.1	3.2	1.7	3.8	18.4	3.0	6.7	4.4
^{210}Pb	2.3	0.9	1.1	1.7	15.1	3.7	7.4	4.6
^{40}K	6.2	10.4	1.7	4.9	2.6	5.0	7.7	7.7

Table 2. Correlation factors between ^{210}Pb and ^{7}Be, ^{40}K and some other elements

Sample	^{7}Be	^{40}K	Ce	Co	Cr	Cs	Eu	Fe	Hf	La	Na	Mn
Quercus acuta	0.8	–0.51	0.25	0.14	0.05	–0.42	0.29	0.52	0.13	0.01	0.63	0.27
Petasitos japonicus	0.89	–0.83	–0.12	0.53	0.64	–0.47	–0.07	0.42	–0.04	–0.06	0.81	0.34
Sasa veitchii	0.95	–0.47	0.29	0.2	–0.58	0.31	0.81	0.36	0.03	0.42	0.38	0.6
Miscanthus sinensis	0.94	–0.83	–0.17	–0.11	0.23	–0.38	–0.16	0.2	–0.15	–0.13	0.43	0.3
Entodon challengeri	0.71	0.43	–0.3	0	0.02	0.55	0.24	0.37	–0.47	0.18	–0.36	0.04
Ilex crenata	0.59	–0.32	0.46	0.58	–0.36	–0.23	0.35	0.56	–0.04	0.52	0.74	0.2
Pinus thunbergii	0.66	–0.4	0.36	0.52	0.05	–0.08	0.48	0.35	0.07	0.55	0.68	–0.12
Lycopodium clavatum	0.82	0.1	0.27	0.35	0.2	0.08	–0.03	–0.03	–0.43	–0.21	0.25	0.55

Elemental concentration

The correlation factors on ^{210}Pb with elements for the eight leaf samples are presented in Table 2 showing similar correlation patterns in each plant species. Table 2 shows that Na has a strong correlation with ^{210}Pb and ^{7}Be, this observation indicates that Na comes from the same source as ^{210}Pb and ^{7}Be; Na comes from natural process, mainly atmospheric transport of sea-salt from the marine environment.[1]

The lack of correlations of elements with ^{210}Pb indicates that the leaf samples can hardly be used as reliable biomonitors of the atmospheric depositions of the trace metals.

For the others element (Ce, Co, Cs, Eu, Fe, Hf, La, Mn) correlations of inter-element in the leaf samples seem not to be consistent or to be opposite in each leaf sample. For example, the correlation factors of ^{7}Be and Cr in leaf of *Petasitos japonicus* are relative high but with other leaf samples have low correlation. This is not easily explained. In other studies these elements almost enter to the leaf by root uptake in vascular plants (Mg, Ba, Mn , Ca, Cs, Hf) or come from mineral particle, mainly wind-blown dust from local soil (Al, Sc, La, V, Cr, Co, Sm, Fe, Yb).[1,2] But the source of the elements from atmospheric deposition possibly influences this process. Owing to this source it could be understand, why the correlations of element in the leaf samples were so poor. That may indicate that these leaf samples are hardly considered to be a biomonitor for trace metals from atmospheric depositions.

Conclusions

Seasonal variation of ^{7}Be and ^{210}Pb are observed in the leaf samples and total deposition, high in spring and winter and low in summer.

The ability of the leaf samples to retain aerosol depends on some factors such as surface area of the leaf, physical conditions of the leaf (epicuticular wax/resin on the surface) and intensity/total rainfall. *Pinus thunbergii* has the highest capability to absorb/retain ^{7}Be and ^{210}Pb. We suggest selecting other leaf samples that contain resin on surface to compare with *Pinus thunbergii* sample.

Correlation factors for trace elements contained in the leaf samples show large variations. This indicates that the contribution of two sources (atmospheric deposition and uptake from soil) in leaf samples is very variable.

References

1. T. BERG, E. STEINNES, Environ. Pollut., 98 (1997) 61.
2. T. BERG, O. ROYSET, E. STEINNES, Atmos. Environ., 29 (1995) 353.
3. B. WOLTERBEEK, Environ. Pollut., 120 (2002) 11.
4. C. BRANQUINHO, F. CATARINO, D. H. BROWN, M. J. PEREIRA, A. SOARES, Sci. Total Environ., 232 (1999) 67.
5. D. CEBURNIS, E. STEINNES, Atmos. Environ., 34 (2000) 4265.
6. H. F. VAN DOBBEN, H. TH. WOLTERBEEK, G. W. W. WAMELINK, C. J. F. TER BRAAK, Environ. Pollut., 112 (2001) 163.
7. E. STEINNES, J. P. RAMBAK, J. E. HANSSEN, Chemosphere, 25 (1992) 735.