

Geoscience studies using by AMS at JAEA-AMS-TONO in the Tono Geoscience Center of the Japan Atomic Energy Agency

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The JAEA-AMS-TONO facility was established in 1997 at the Tono Geoscience Center, Japan Atomic Energy Agency (JAEA). Our AMS system is a versatile system based on a 5MV tandem Pelletron type accelerator (National Electrostatic Corporation, US) and has been made available for ¹⁴C-, ¹⁰Be- and ²⁶Al-AMSs. These multi-nuclide AMSs have been mainly applied to neotectonics and hydrogeology, in support of our research on geosphere stability applicable to the long-term isolation of high-level radioactive waste. Furthermore, the ¹⁴C- and ¹⁰Be-AMSs are used for geoscience, environmental science and archaeology by researchers of universities and other institutes under the JAEA's common-use facility program.

Major contribution of radiocarbon (¹⁴C) dating through our ¹⁴C-AMS to geoscience studies are as follows. Yasue *et al.* identified fault displacement and stratigraphic correlation of black soils based on ¹⁴C ages (presented in this conference). They conducted ¹⁴C dating of the black soil collected from a trench wall of the Atera Fault, Gifu. The results of ¹⁴C date show that the soil age varies from 4,000 to 2,000 y with depth of the sampling points and the soil was deposited at approximately constant rate. Imaizumi *et al.* (2006) estimated the faulting age based on ¹⁴C dating of soils at the Senya Fault in the Toen Fault Zone, Yokote Basin, Akita. It was found that the ages range between 1000 - 1300 y, indicating that the Senya Fault was caused by the Rikuu Earthquake in the year of 1896. Sasaki *et al.* (2006) studied local climate change in an inland basin. Pollen records and ¹⁴C ages of sediments in Ohkute Basin, Gifu were used to reconstruct past climate change. The results suggested that the local climate has been warmer for the last 10000 yBP.

Since the fiscal year of 2013, the ¹⁰Be-AMS has been routinely measured and used to study long-term erosion rates of weathered granitic soil surfaces using cosmogenic ¹⁰Be depth profile under the joint research program with the National Institute of Advanced Industrial Science and Technology (AIST). Recently, we have started development of ²⁶Al-AMS. The system tuning and test measurement have been carried out for routine measurement. The development has so far done well and the routine measurements of the ²⁶Al-AMS will be started in near future. The ¹⁰Be- and ²⁶Al-AMSs will be used to estimate the exposure age of basement rocks as well as the sedimentation rate and the assessment of volcanoclastic material ejected during volcanic eruptions.

Keywords: AMS, Dating, C-14, Be-10, Al-26

Radiocarbon dating of charcoal by the ABOX-SC method

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Charcoal is one of the most important samples for radiocarbon dating. It is necessary to remove contaminants from charcoal sample to obtain the reliable date. ABA (acid-base-acid) method is usually used for chemical pretreatment of charcoal: First, a sample is treated with HCl to remove carbonate contaminant. Next, the sample is treated with NaOH to remove organic contaminants derived from soil during burial. After then, the sample is treated with HCl again to remove absorbed atmospheric carbon dioxide during NaOH treatment. The residue is combusted with CuO at 850°C and graphitized to be ¹⁴C-dated.

However, the ABA treatment often cannot completely remove contaminants from poorly-preserved and/or old charcoals (>about 30 ka). Bird et al. (1999) showed that the ABOX-SC (acid-base-oxidation stepped combustion) method removes organic contaminants more efficiently than the ABA treatment. The age of the charcoal sample treated with the ABOX-SC was reported to be older than that of the charcoal sample treated with the ABA (Brock et al., 2010).

The ABOX-SC method consists of 3 step chemical pretreatments: HCl and NaOH treatments followed by K₂Cr₂O₇-H₂SO₄ treatment in a sealed tube at 60°C for 20 hr (Brock et al., 2010). The mixed solution of K₂Cr₂O₇ and H₂SO₄ removes organic contaminants effectively from charcoal samples, and can extract carbon fraction of oxidation resistant elemental carbon, OREC, which is resistant to oxidation and is less affected by contamination during burial (Bird et al., 1999). After the ABOX chemical treatment, the OREC is heated at 630°C with CuO for 2 hr to remove atmospheric CO₂ contaminants adsorbed during sample treatment and contaminants remained after the ABOX treatment. Finally, the residue of OREC is oxidized completely into CO₂ at 850°C for 1 hr, and the CO₂ is graphitized to be ¹⁴C-dated.

In this study, we apply the ABOX-SC method to some charcoal samples of known age to measure ¹⁴C ages. The charcoal samples, which were excavated from Tang-e Sikan cave in Arsanjan city, Iran, have been dated at about 40 ka and 26 ka by the ABA method, and are considered to be attributed to Upper Paleolithic period. In this study, we confirm the age difference of Paleolithic charcoal samples by the two pretreatment methods of ABA and ABOX-SC.

Keywords: Radiocarbon, Charcoal, ABOX-SC method

AMS radiocarbon dating of Japanese tree rings for regional calibration curve

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Calibration of radiocarbon data can be achieved by comparison of measured radiocarbon age of samples with known calendar age. Tree rings that determined by dendrochronology are one of the important data set for calibration. IntCal13 calibration curve was launched mainly based on trees grown in the northern high latitude. These rings were sampled in ten years each at once to cancel the variation of solar activity, and to obtain sufficient sample size for conventional radiocarbon measurement as well. AMS radiocarbon dating can measure less than 1mg of carbon efficiently and is capable of date annual tree rings. Recent advance in accuracy of AMS radiocarbon measurement reveals that the resolution of IntCal may be insufficient for precise calibration. In particular, regional effect on the calibration curve had turned out to be a major problem. AMS radiocarbon dating of Japanese tree rings with actual age has been carried out to accomplish Japanese regional calibration curve. Tree ring preserves atmospheric ¹⁴C concentration at that time, therefore the offset between radiocarbon age of Japanese tree ring and IntCal should indicate the inhomogeneity in the northern hemisphere.

Keywords: radiocarbon dating, tree ring, calibrated age, atmospheric inventory, regional effect

Radiocarbon dating of archeological remains related with the 13th century Mongol Invasion to Japan

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The shallow sea floor off Takashima, Matsuura, Nagasaki Prefecture, has been investigated archeologically as a potential site where many Mongolian warships exist under the sea sediments. It is historically recorded that more than 4000 Mongolian warships were destroyed by a typhoon during the Mongol invasion to Japan in 1281. The underwater investigations have been performed since 1980, and a lot of archeological remains related with the invasion have been collected there. In 2006, we were allowed to get some archeological remains for 14C dating with AMS. The samples were fragments of palm-bark ropes, lacquer products, bamboo ropes and charred rice. 14C ages for the samples were all consistent with the age of Mongol invasion in 1281.

Recently a body of submerged wrecks most probably originated from Mongolian warship has been discovered in the 1m-deep horizon of the sea sediment off Takashima. During the survey of the new warship, shell samples were collected near the ship. Some shells were recognized to be hull-fouling species, which may have grown up on the bottom of Mongolian warship and preserved along with the broken ship in the sea sediment. We have conducted 14C dating for some shell samples and found out that shells belong to hull-fouling species showed 14C ages consistent with the time of Mongol Invasion. Some other shells not belonging to hull-fouling species showed younger or older dates as compared with the time of Mongol invasion.

Keywords: AMS 14C dating, historical remains, remains from submerged wrecks, Mongol invasion, shell of hull-fouling species

AMS radiocarbon dating of peaty layers in Kimotsuki lowland, southern Kyushu

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Since the middle Holocene, peaty layers have accumulated on the Kimotsuki lowland in south Kyushu, Japan. They can be applied radiocarbon (^{14}C) wiggle-matching for establishing high-resolution chronology. Moreover, several tephra intercalated with the peat bed which originated from Kaimondake, Sakurajima, and the Kirishima volcanoes, and they can certify the reproducibility of ^{14}C dates. On the other hand, the age of the tephra by them can be determined correctly. We present here the results of AMS ^{14}C dating on the core sample, and report the age of each tephra determined from these dates.

Keywords: Kimotsuki lowland, peaty layer, tephra, radiocarbon date

Offset in radiocarbon ages between shell and plant pairs in the Holocene sediments around the Korea

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Since 2009, a research project to evaluate the marine reservoir effects of the coastal sites of Korea has been progressed by KIGAM. Estimating the reservoir effect of this area is difficult because age-known marine samples obtained before AD 1950 are rare. In order to solve this problem, 61 sediment cores were collected with 1 m intervals by a percussion drilling tool from 52 coastal sites in the southern area of the Korean Peninsula. These drilling sites were roughly preselected by the interpretation of modern air photos of internet map services provided by the websites such as Daum and Google. Topographic maps in 1918-1926 with 1/50000 scale and old air photos were also used for the site selection. The length of each core was less than 5 m and the total length was 132 m. Based on analysis of lithology and mollusk assemblages, we selected marine shell and terrestrial plant pairs from same horizons. These samples were cleaned by physical and chemical pretreatments, and reduced by automatic graphitization system in KIGAM. The radiocarbon ages of the samples were measured by the AMS facility of KIGAM. This presentation will report about spatial and historical variation of radiocarbon marine reservoir effect around Korea.

Keywords: Radiocarbon dating, Marine reservoir effect, Coastal sediments, Korea

Estimation for the growth rate of benthic biotic communities in Antarctic lakes

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Antarctica is an ice continent. It has one of the most extreme environments for life in the world. There are very little ice-free regions with life in it, so these regions are sometimes called polar oasis within the polar desert. The ice-free regions are scattered along the coastal regions and around mountainous peaks (Nunataks) in continental Antarctica or concentrated in Antarctic Peninsula in maritime Antarctica. The biota is simple due to lack of remarkable organisms at the top of food webs, and primary producers such as cyanobacteria, algae, lichens, mosses, heterotrophic microorganisms and metazoans dominate the sparse communities. A remarkable diversity of lakes exists in Antarctica, ranging from hypersaline with nearly 10 times the conductivity of seawater, to brackish and freshwater, sub-glacial, permanently ice-covered and seasonally ice-covered lakes. These lakes are unproductive with typical photosynthetic levels of 0.5 — 30 $\mu\text{g-C/L/day}$ from phytoplankton. Phytoplankton cannot bloom and hardly survives in the water column during the best light-available summer around the Syowa region. This results from low annual levels of photosynthetically active radiation and ice cover that attenuate light into the water column or photo-inhibit photosynthetic systems due to continuous low temperatures and the lack of any significant input of inorganic nutrients. Despite such severe situations, one of the most productive ecosystems in continental Antarctica is found in freshwater lakes, where benthic microbes form thick mats, and aquatic mosses can flourish on the lakebeds of the Syowa region. These lakes were exposed by glacial retreat after the Last Glacial Maximum. The benthic mats consist of almost organisms, dominantly cyanobacteria, algae, and mosses in the lakes, because there are a little inorganic particles and organic matters inflow to the lakes from the water catchment, and as pointed out above, almost no phytoplankton in the water column. This negligible level of any sedimentation and turbulence situation is specific to Antarctica, which is suitable to estimate the growth rate of benthic biotic communities in fine-scale. We collected sediment cores from 17 freshwater lakes in Sôya Coast on the south area of Syowa station, continental Antarctica during January-February in 2009 — 2010. The core samples were vertically sliced in each 1 cm as soon as possible after sampling in the field hut, and transported to Japan at -20 °C. Then, we analyzed the samples by using an AMS (accelerator mass spectrometry), and estimated the growth rate of the benthic biotic mats in each Antarctic lake.

Keywords: sediment, AMS, lakes, Antarctic, growth rate

Black SOM dynamics during reforestation of Japanese grassland

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The dynamics of the polyaromatic structures of black humic acids (HAs), which are presumably derived from charred materials, are of significant interest for the global carbon cycle. However, the details of those dynamics are not yet well understood. We investigated differences in the degree of darkness (A600/C values), isotopic ratios ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\Delta^{14}\text{C}$ values), and ^{13}C NMR spectra of size-separated black HAs extracted from Japanese volcanic ash soils in order to estimate the variations in the polyaromatic structures of black HAs during ca. 100 years of natural reforestation of Japanese pampas grassland. For several hundred years, all the study sites were managed similarly as grassland by burning. Subsequently, their management differed: at site G (*Miscanthus sinensis*: C4 plant), maintenance as of the time of this study was still performed by mowing, while at sites P (*Pinus densiflora*: C3 plant) and Q (*Quercus crispula*: C3 plant), maintenance was discontinued ca. 30 and 100 years ago, respectively. Thus, the sites range from grassland (site G) to coniferous forest (site P) to broad-leaved forest (site Q). For all HA size fractions at all sites, we found that $\delta^{13}\text{C}$ values correlate positively with $\delta^{15}\text{N}$ values, although the gradients are much lower for fractions of small to medium molecular size than for fractions of medium to large molecular size (denoted as lower-size and higher-size fractions, respectively). Overall, for the lower-size fractions, the contribution ratio of C4-plant-derived carbon shows a significant positive correlation with A600/C values and a negative correlation with $\Delta^{14}\text{C}$ values, and their aromatic characteristics are greater than those of higher-size fractions within the same black HA. Furthermore, the relative proportion of lower-size fractions decreases with reforestation, especially from site P to Q. The $\delta^{13}\text{C}$ values for all size fractions are similar for sites G and P, but are relatively low for site Q. The aryl C contents of the lower-size fractions are lower and the O-alkyl C contents and the aliphaticity (alkyl C:O-alkyl ratio) are clearly higher for sites P and Q than for site G. These results strongly suggest that stimulation of HA biodegradation might be achievable by continuous input of new plant litter during reforestation, even for lower-size HA polyaromatic structures, despite the fact that lower-size HAs biodegrade more slowly than higher-size HAs.

Keywords: land use, reforestation, soil organic matter, ^{14}C

Potential sink of soil organic carbon in a Japanese cool-temperate forest based on bomb radiocarbon based residence time

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Functional roles of SOC pool for carbon dynamic remains almost unknown. In this study, residence time (RT) based on carbon and radiocarbon (¹⁴C) inventories, was investigated in a Japanese temperate forest (Takayama) under Asian Monsoon climate, and the potential of soil carbon sequestration were also investigated. Soil organic matter was divided to two fractions as low density humified material (LOM) and high density mineral-associated material (HOM). Our results were thoroughly compared with those in a temperate forest (Harvard forest) conducted using a similar approach [Gaudinski et al., 2002]. The LOM was the major part of the SOC (76%) and its contribution was higher even in the deep layer. ¹⁴C contents of LOM in surface layer were similar to those of atmospheric CO₂ and roots, whereas those in deep layer are significantly low (¹⁴C < -200 per mil) as well as HOM fractions, although LOM fraction seems to consist of labile carbon. RTs for low density fractions as derived from their radiocarbon content are 53 ± 330 yrs BP in surface layer and 1760 ± 2780 years BP. Storage of SOC in our site was larger, irrespective of depths and differed considerably from that in Harvard forest. We also measured soil ¹⁴CO₂ profile to determine the rate of CO₂ production from heterotrophic respiration of two SOM fractions. The ¹⁴C values of soil CO₂ profile was constant down to 75 cm depth, which were close to those of atmospheric CO₂ and fine roots, suggesting that most of soil CO₂ is derived from recent photosynthetic fixed C. These results indicate that this forest might be higher sequestering soil carbon as low density fractions semi-permanently, which is also concerned about instability of near future climate change.

Source diagnosis of PAHs using compound class specific ^{14}C analysis and Monte Carlo source apportionment at Kolkata canal

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Atmospheric polycyclic aromatic hydrocarbons (PAHs) originate mostly from incomplete combustion of carbon-based fuels. PAHs account for most (35-82%) of the total mutagenic activity of ambient aerosols. Reduction of air pollution by PAHs is essential for an effective air quality control, which requires reliable source apportionment. It has been reported that atmospheric pollution by PAHs in Indian megacities, such as Kolkata, Mumbai and Chennai, is comparable to the highest levels across the globe and Kolkata air exhibit the highest level among them. Also, our previous survey revealed that sediments from Kolkata city canals have the highest PAHs concentrations (i.e., $15.9 \pm 11.6 \mu\text{g}$ of $\sum 14$ -parent PAHs/g dw, n=12) among the 174 surface sediments from 8 tropical Asian countries.¹ Examining methylated-to parental PAHs ratios of three homologous series and C30-hopane/ \sum PAHs ratios both in sediment samples and in probable source materials, the high level sedimentary PAHs were ascribed to those emitted from combustion sources. However, relative importances of combustion sources were not solved. The present study aimed to apportion sources of combustion to PAHs in highly contaminated sediments from Kolkata, India by using combined approaches of CCSRA technique, molecular fingerprinting and Monte Carlo source apportionment.

Furthermore, three- and four ring PAHs (MW178, 192, 202) in leftover extracts were harvested on PCGC and analyzed for ^{14}C on AMS at NIES-TERRA, NIES (Tsukuba, Japan). PAHs isolated from Kolkata canal sediments showed mostly fossil carbon isotopic signatures, i.e., ^{14}C signal of PAHs with MW178, 202 and those with MW228 were 10.6 ± 0.1 , 5.9 ± 0.4 , 7.6 ± 0.5 pMC (KKNC), 8.4 ± 0.5 , 8.3 ± 0.4 , 8.5 ± 0.3 pMC (KKSC). By using source end-members of MW202 and MW276 isomer pair ratios, Monte Carlo source apportionment² revealed that most of fossil-PAHs were derived from coal combustion, i.e., relative contributions (median) from coal and petroleum combustions were 50% and 11% in KKNC and 13% and 56% in KKSC.

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Keywords: compound class specific radio carbon analysis, PAHs, monte carlo simulation, molecular fingerprinting, source apportionment

Accurate age estimation using ^{14}C in human teeth enamel.

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Radiocarbon (^{14}C) concentration in the atmosphere showed a stable value until 1955. However, as a result of the nuclear bomb testing, modern ^{14}C concentration in the atmosphere dramatically increased during late 1950s and early 1960s. These bomb-produced ^{14}C is then oxidized to form CO_2 , and incorporated into plants by photosynthesis. Then, by eating plants or animals fed by these plants, the ^{14}C concentration in human body reflects the ^{14}C value of atmospheric CO_2 at a certain time. Recent studies insisted that these ^{14}C can play important role for forensic analysis, especially age estimation using ^{14}C in human teeth enamel.

Teeth enamel is such a harder part of the human body that they are hardly destroyed by a natural process. And, the most important is, there is no turnover of enamel after its formation has completed. Although there are previous works which estimate the birth year of individuals by using ^{14}C concentration in enamel, their samples are teeth from Swedish, Scottish and American people, and study areas are mainly at high latitudes of the northern hemisphere. The precision of age estimation using teeth enamel is determined by enamel formation time of teeth and atmospheric ^{14}C concentration in a certain area at a certain year. It is known that teeth formation time of Japanese is different from that of Caucasian. It has been found that ^{14}C concentration in the atmosphere indicates 5 different zones according to different peak ^{14}C concentration of the nuclear bomb testing. These zones are named NH zone1, NH zone2, NH zone3, SH zone3 and SH zone1-2 from north to south. The boundary between NH zone1 and NH zone2 is Ferrel cell - Hadley cell boundary. It is nearly located at 35 °N. So it means that previous works mainly focused on NH zone1 samples, not NH zone2 samples. One of NH zone2 samples, teeth enamels of Japanese have not studied sufficiently. The aim of this study is to clarify whether age estimation using teeth enamels of Japanese can determine the precise year of birth of individuals and to discuss the mechanism of carbon fixation of enamels or other parts of the teeth.

7 of 44 collected tooth samples have been analyzed. They are 5 third molars and 2 second molars. The year of birth of each individual is 1943, 1946, 1951, 1951, 1951 for third molars, and 1933 and 1959 for second molars. In order to get the estimated year of birth, a model age for enamel completion of Japanese was subtracted from the year given by the ^{14}C analysis of samples. The result shows that age estimation using teeth of Japanese gives precise age determination. Needless to say, taking account of the degree of individual variation and possibility of differences in local environment or in diet is important, however, this result seems to be uninfluenced by those effects. Larger number of, more and more various parts of teeth (for example, first molars, anteriors, such as early-completed teeth.) have to be analyzed.

To determine whether an individual is born before or after the peak of atmospheric ^{14}C concentration (in 1964, in NH zone2), root of teeth have to be analyzed. Since root completion age is some years after enamel completion age, it can be easily found that the sample age is whether rising or falling part of the atmospheric ^{14}C curve. We now are preparing for analysis of ^{14}C of root dentine collagen and root inorganic matter. Their results will give more compelling data, now discover what is waiting for you!!

Keywords: human tooth, enamel, ^{14}C , forensic science, nuclear bomb testing, age estimation

Observations of atmospheric radiocarbon in carbon dioxide at Hateruma Island and Cape Ochi-ishi, Japan

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Atmospheric radiocarbon in carbon dioxide ($^{14}\text{CO}_2$) is a powerful tracer for understanding of carbon cycles, e.g. oceanic and biospheric CO_2 exchanges and CO_2 emissions from fossil fuel combustion. Observation sites for radiocarbon concentrations, $\Delta^{14}\text{C}$, are not many enough to evaluate the global and regional carbon flux. We present an analysis of trends, interannual variability (IAV) and seasonal cycle of $^{14}\text{CO}_2$ in background air from July 2004 to December 2012 at two NIES/CGER monitoring stations; Hateruma Island (HAT; latitude 24.06N, longitude 123.81E) and Cape Ochi-ishi (COI; latitude 43.16N, longitude 145.50E). The air samples were collected in 2 L Pyrex glass flasks. The sampling frequency was monthly. CO_2 was extracted from the whole air at NIES and CO_2 samples were converted to graphite and analyzed ratios of $^{14}\text{C}/^{12}\text{C}$ by accelerator mass spectrometry (AMS, National Electrostatics Corp., 1.5SDH) at Paleo Labo Co., Ltd., Japan. Analytical precision in $\Delta^{14}\text{C}$ determined from statistical uncertainty (number of ^{14}C counts) was ± 1.7 - 2.0 ‰ for most samples. The repeatability of measurements using modern reference air was ± 1.9 ‰. A decreasing trend in $\Delta^{14}\text{C}$ was -5 ‰ yr^{-1} in average but large IAV was observed at both stations: large decreases in 2007-2008 and in 2010-2011 (-8 to -9 ‰ yr^{-1}) and almost zero decrease in 2009. We also observed clear seasonal cycle of $\Delta^{14}\text{C}$. The peak-to-peak amplitudes in the seasonal cycle determined from the smooth curve fits were 7 ‰ at both stations and the maximum of $\Delta^{14}\text{C}$ appeared in July and the minimum in January at HAT, and the maximum in September and the minimum in May at COI. The differences in phase of $\Delta^{14}\text{C}$ seasonal cycle between HAT and COI suggested that the atmospheric $\Delta^{14}\text{C}$ at COI was influenced by CO_2 emitted from terrestrial biosphere.

Radiocarbon based source apportioning of PM_{2.5} carbonaceous aerosols at Cape Hedo, Okinawa and Fukue island, Japan

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Radiocarbon (¹⁴C) analysis of the carbonaceous aerosol allows an apportionment of fossil and non-fossil sources of air-borne particulate matter (PM). A chemical separation of total carbon (TC) into its sub-fractions organic carbon (OC) and elemental carbon (EC) refines this powerful technique, as OC and EC originate from different sources and undergo different processes in the atmosphere. Although ¹⁴C analysis of TC, EC and OC has recently gained increasing attention, Nowadays gigantic brownish haze from various burning and combustion processes is also blanketing India and surrounding land and oceans during the winter season. In China and surrounding countries, same kind of atmospheric pollution are widely observed and occurred as well. Additionally this soot-laden Brown Cloud is affecting South and East Asian climate as much or more than carbon dioxide and cause hundreds of thousands of premature deaths annually, yet its sources have been poorly understood. In this study, we investigated the contribution of continent derived aerosol to Japan. Aerosol samples with diameter of 2.5µm were collected at Fukue island, one of Goto islands and at the Cape Hedo is located at the northern end of Okinawa Island. The ¹⁴C contents of EC of PM_{2.5} aerosols collected from October, 2009 and May, 2010 including the Kosa event in Cape Hedo and Fukue were measured. The ¹⁴C content represents in the unit of pMC. Results of EC-¹⁴C in both sites were 25-30pMC in Cape Hedo and 18-44pMC in Fukue, respectively. These results mean that relative apportionments of biomass burning and fossil fuel were 25-30% and 18-44% in Cape Hedo and 25-35% and 65-75% in Fukue, respectively. The observed variations of pMC in Cape Hedo during February and March were relatively smaller than those of Fukue, which was more than 20%. According to back trajectory analysis in this duration, because ca. 70% of air mass in both sites was derived from the continent. The aerosols particulate matter to be transferred to Cape Hedo from continent would be relatively smaller than those to Fukue. Our data of EC-¹⁴C obtained during the Kosa event showed the relatively higher contribution of biomass burning sources in Fukue although these interpretation need to consider variation of the magnitude and concentration of EC in both sites. In further study we need to investigate details of the source of EC during this period.

Keywords: Radiocarbon, PM_{2.5}, aerosol, source apportioning

Study on monitoring of volcanic activity using $^{129}\text{I} / ^{127}\text{I}$ ratios in crater lake and hot spring at Zao volcano

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Volcanic tremors and mountain gradient changes have been detected at Zao volcano in Miyagi and Yamagata since January 2013, volcanic activity began to intensify although Zao volcano will not erupt immediately^[1]. Since the water quality of crater lake are correlating with volcanism changes^{[2][3]}, basic water quality of crater lake and hot spring at Zao volcano have been studied by the group of Tohoku University from September 2013. As a part of this project, we are trying to monitor the volcanic activity using $^{129}\text{I} / ^{127}\text{I}$ ratios (atomic ratio of radioiodine and stable iodine) in crater lake and hot spring of Zao volcano.

Natural ^{129}I (half-life: 15.7 million year) are produced by nuclear spallation reaction of ^{129}Xe with cosmic ray in the atmosphere and spontaneous fission of ^{238}U in the geological layer. In the ocean, steady-state $^{129}\text{I} / ^{127}\text{I}$ ratio of the seawater is estimated to be 1.5×10^{-12} ^[4]. Sunken iodine by the ocean plate having lower $^{129}\text{I} / ^{127}\text{I}$ ratio (older ^{129}I age) compared to the steady-state ratio of seawater, are supplied to the atmosphere mainly via magmatic activity. In general, $^{129}\text{I} / ^{127}\text{I}$ ratio in hot spring water and brine water are used as indicator of origin and behavior of iodine in the water^{[5][6]}. $^{129}\text{I} / ^{127}\text{I}$ ratio of hydrothermal at Zao volcano are considered to become lower by the supply of chronologically-old iodine in terms of global iodine cycle.

In September 2013, water samples of 2 L were collected from the surface of crater lake (Okama, diameter: 350 m, maximum depth: 35 m) located at 1,560 m in elevation and hot spring (Kamoshika Hot Spring) located at 1,230 m in elevation in the eastern side of Zao volcano. Water temperature and pH were measured on site. After water samples were filtered by 0.2 μm filter, $^{129}\text{I} / ^{127}\text{I}$ ratio were measured for the isotopic diluted water samples by adding carrier (^{127}I standard) at MALT, The University of Tokyo. ^{127}I concentrations were measured by ICP-MS, and original $^{129}\text{I} / ^{127}\text{I}$ ratio of water samples were estimated.

Water temperature and pH were 10.2 °C and 3.3 at Okama; 40.0 °C and 3.3 - 4.0 at Kamoshika Hot Spring. $^{129}\text{I} / ^{127}\text{I}$ ratios of Okama and Kamoshika Hot Spring were respectively, estimated to be $(1.5 \pm 0.4) \times 10^{-9}$ and $(0.78 \pm 0.2) \times 10^{-9}$, 500 - 1000 times higher than the steady-state ratio of sea water (1.5×10^{-12})^[4]. Since $^{129}\text{I} / ^{127}\text{I}$ ratio of anthropogenic metric water were over 9.0×10^{-12} ^[7], surface water of Okama and Kamoshika Hot Spring water were very likely to be strong affected by the meteoric water including anthropogenic ^{129}I . For the monitoring of volcanic activity using $^{129}\text{I} / ^{127}\text{I}$ ratio, it is necessary to decide the site as few anthropogenic ^{129}I as possible through the measuring of $^{129}\text{I} / ^{127}\text{I}$ ratio of the Okama bottom water and some hot spring around Zao volcano. Continuous water quality survey of 1 - 2 times for Okama and 1 time per 1 - 2 months for hot springs are planned from June to November of this year.

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Speciation analysis of the Fukushima accident derived I-129 in the soil using sequential extraction method

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In previous study, we investigated the depth profile of the accident derived ¹²⁹I ($T_{1/2} = 1.57 \times 10^7$ y) and downward migration speed in soils of near field of Fukushima Dai-ichi Nuclear Power Plant (FDNPP), including crop fields and man-made fields. ¹²⁹I in soil was measured by AMS and stable iodine (¹²⁷I) was measured by ICP-MS at MALT (Micro Analysis Laboratory, Tandem accelerator), The University of Tokyo. It was found that ¹²⁹I was concentrated near surface but distributed deeper compared with ¹³⁷Cs ($T_{1/2} = 30$ y). From the estimation of relaxation length using depth profiles, the FDNPP derived ¹²⁹I move 0.6 cm/y downward and ¹³⁷Cs 0.3 cm/y for it. It was also found that ¹²⁹I seems to move downward more quickly than ¹³⁷Cs.

To investigate the adsorption mechanism and the elemental process of migration of the accident derived ¹²⁹I in soil, it is important to know what kind of component the ¹²⁹I combines with.

Recent studies on the X-ray absorption fine structure (XAFS), especially near edge structure (XANES), reported that the stable iodine (¹²⁷I) in soil existed as an organic component^[1]. However, it had not yet been proved that it was also the case with the accident derived ¹²⁹I because it had been incorporated in the soil system only recently and the abundance of ¹²⁹I in soil was more than 8 orders of magnitude smaller than sub-ppm level stable iodine (¹²⁷I).

In this study a progressive sequential extraction method including the dialysis was newly developed to obtain only the iodine sticking to the soil organic component. The advantage of sequential extraction over other method is that stable iodine can be quantified by direct analysis of the fraction and ¹²⁹I can be quantified by AMS method of the fraction added with carrier. The fraction of the organic component for ¹²⁷I and ¹²⁹I can be evaluated respectively by comparing with the other fraction and/or with the total concentration obtained by the bulk analysis (e.g. by the pyrohydrolysis).

Repeatability is 20% for the water soluble, oxides and organic fraction, 10% for Exchangeable fraction and 50% Residue (mainly minerals).

The results show that 60% of the total ¹²⁹I are associated with oxides and 30% associated with organic matter in crop field soil. The former, the oxides bond iodine, it takes a form of iodate (IO_3^-) absorbed in amorphous oxides, especially goethite or delta- MnO_2 . They are formation of monodentate mononuclear outer-sphere species and bidentate, binuclear inner-sphere species^[2]. The latter iodine are linked to organic carbon directly by a covalent bond.

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