FNCA 2021 Study Panel
Tokyo

Monitoring of environmental changes due to nuclear techniques:

Development from radiometric analysis to mass spectrometric techniques

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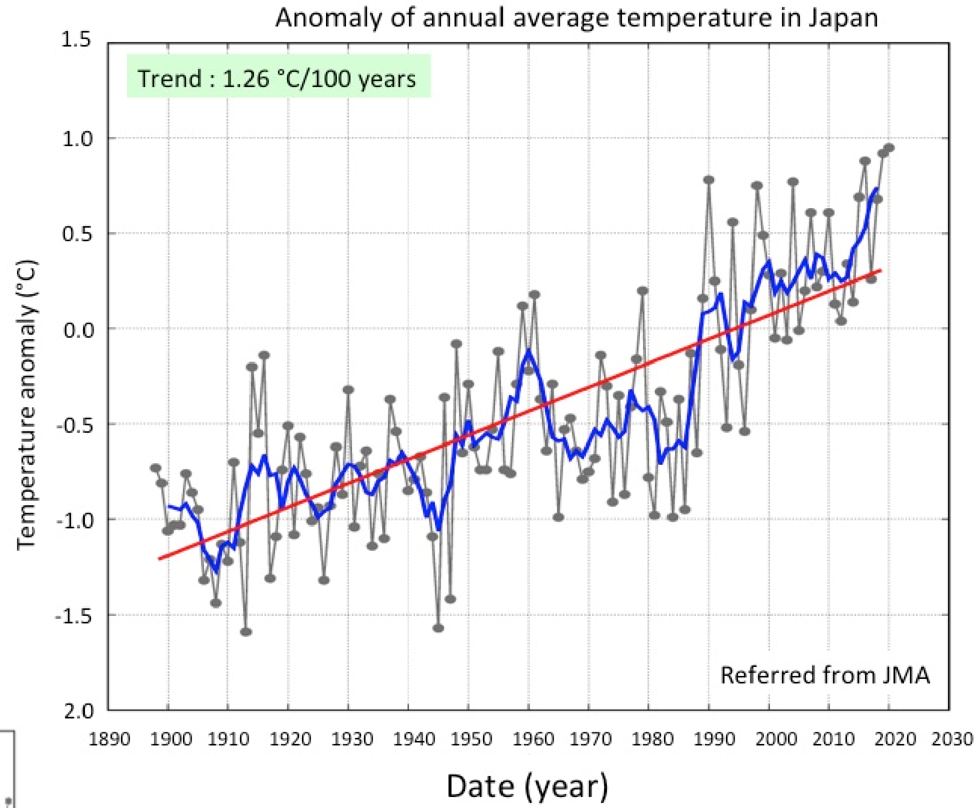
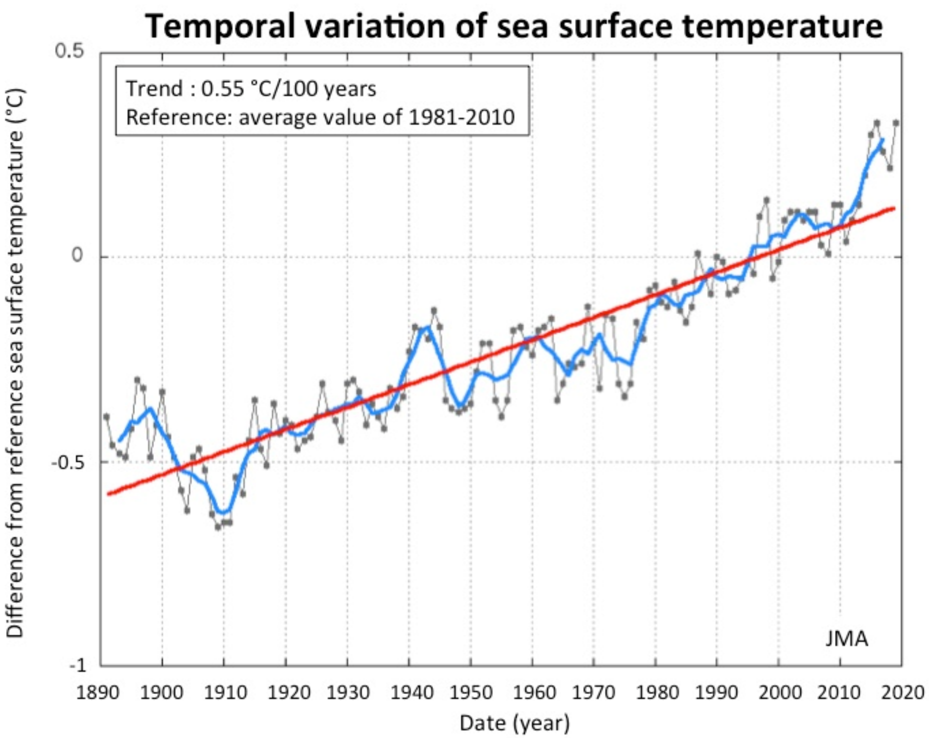
Climate change and environmental impacts

- Current major concern of public is climate change and related environmental effects.
- Biosphere sensitively responds to climate change. Severe weather, typically super typhoon, hazards land and human society due to floods, landslide and others. Especially agriculture and fishing are seriously affected by climate change. Sustainability of human society is closely dependent on stable climate because of predictability of future environment.

Present status of climate:

Evidence of global warming



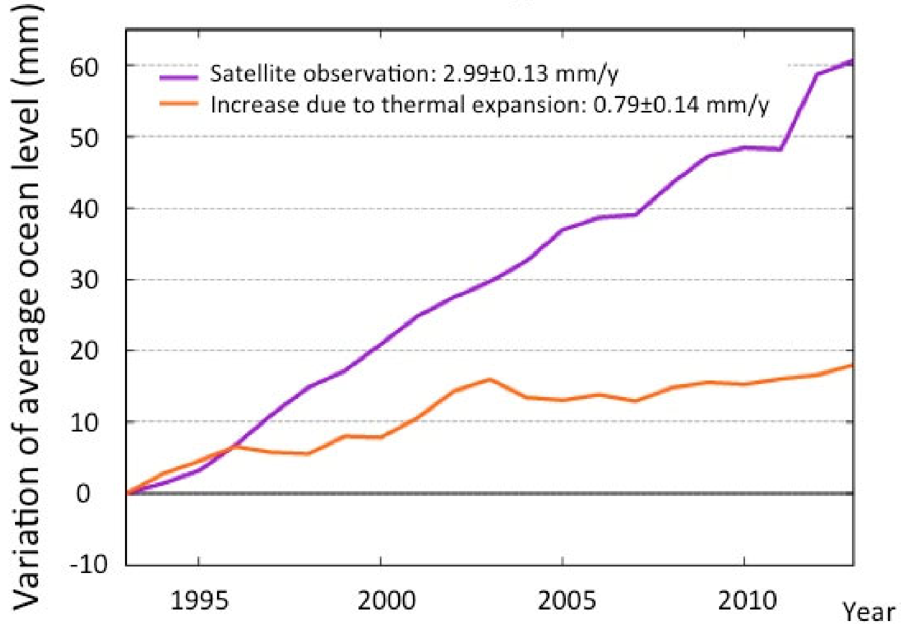


The most important point is increase of sea surface temperature due to response to surface air temperature.

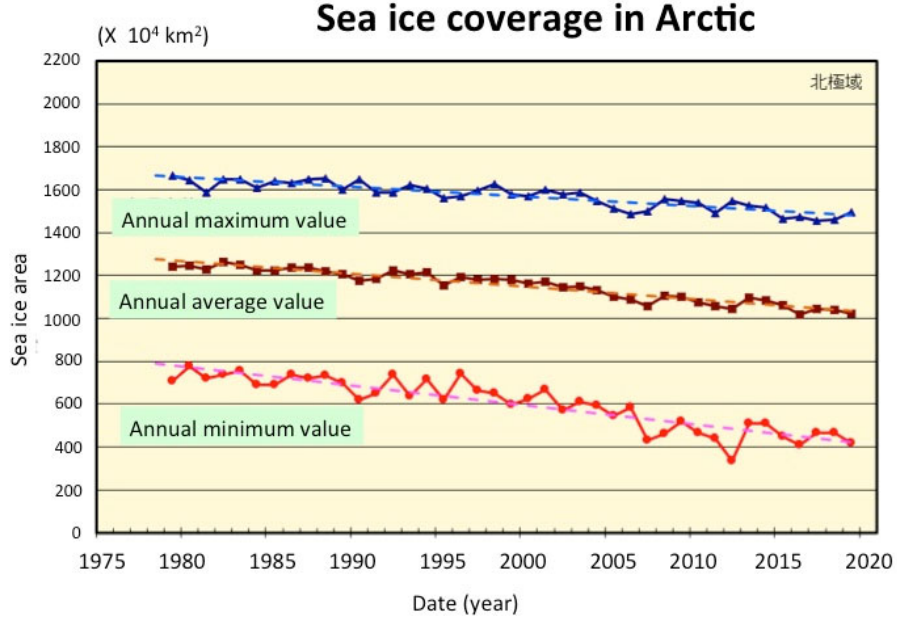
Environmental response to global warming

Examples: 1. rising of ocean level
2. decrease of sea ice coverage

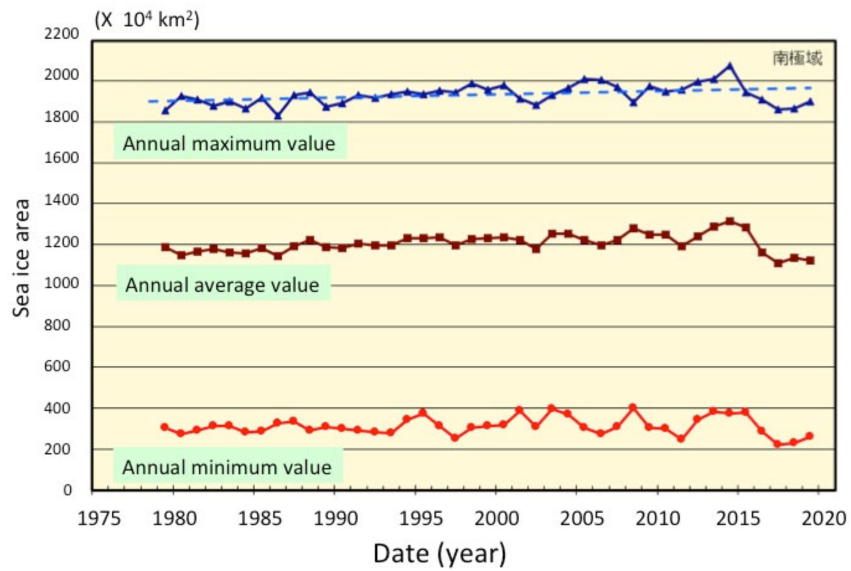
Increase of average ocean level



Sea ice coverage in Arctic



Sea ice coverage in Antarctica



Impacts of on-going climate change

The highest temperature (18.3 °C) was recorded in Esperanza, Antarctica on 6 Feb. 2020.

Global warming

increasing occurrence of extreme meteorological events

drought desertification

wildfires (ex. California (July- Nov. 200M$ lost), US; Australia (Jan. 50M$ lost))

Heavy rain floods (ex. China (June-Oct. 320M$ lost; Japan, Kyushu(July 85M$ lost);

landslide India (June-Oct. 100M$ lost))

loss of ice in polar regions rising of sea surface height

Examples are severe disasters happened in 2020.

Ecological effects

Effects of biological diversity ex. decrease of coral

Decrease of water resource, decrease of agricultural production

Human effects

Increase of heatstroke

Occurrence of pandemic of infection

Japan was the greatest economical lost in the world in 2018 due to global warming.

Assessment and prediction of future earth environment

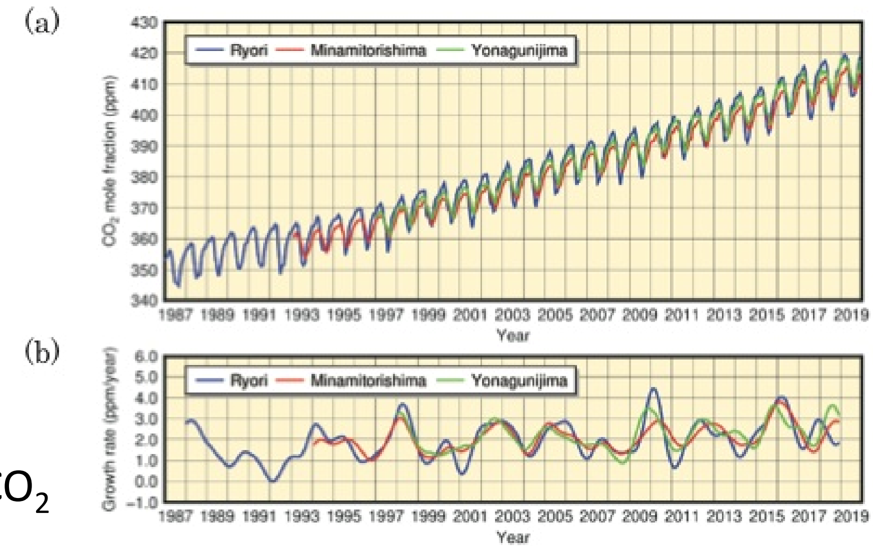
- Long-term monitoring of green-house gases and environmental tracers

CO_2 observation in air started in the late 1950s

Green-house gases: CO_2, CH_4, N_2O, others

Environmental tracers: radioisotopes, others : next slide

- Construction of climate change history accompanied with social effects.



Monthly mean concentrations of atmospheric CO_2 and its growth rates in Japan.

From JMA

Isotopic tracers of environment

- Tracers related to meteorological parameters (temperature and humidity)

  $\delta^{18}O$ in tree-ring : a proxy of relative humidity and precipitation

- Tracers of sources identification

  Anthropogenic radionuclides (fission products, Pu isotopes, ^{129}I, ^{14}C and others), stable isotopes (^{13}C, ^{18}O, ^{15}N and others)

- Tracers to give time scale (chronology)

  Radiocarbon (^{14}C), ^{210}Pb, and others

- Tracers of geophysical and geochemical processes

  Transport of aerosols in atmosphere: anthropogenic radionuclides
  Ocean circulation: ^{14}C, ^{3}H, ^{137}Cs, ^{236}U…
  Solar activity: ^{14}C, ^{7}Be, ^{10}Be, …
  Biogeochemical processes: Pu isotopes, …
  Changes of land environment (erosion): ^{137}Cs, Pu isotopes, …

Plutonium is strongly associated with biogenic organic matter.
Cesium strongly attaches to clay minerals.

Anthropogenic activities has perturbed isotope world

1. Atomic activities (Nuclear-weapons testing, nuclear reactor accidents, atmospheric and ocean releases of nuclear wastes, …)

new comers: ^{137}Cs, ^{90}Sr, ^{129}I, Pu isotopes, …

perturbed natural isotope ratios: ^{3}H, ^{14}C,…

2. Non-atomic activities (consumption of fossil fuels, …)

Supply of dead carbon

Development of isotope analysis

- Radioactivity monitoring has been developed new techniques.
- Radiometric analysis: alpha, beta, and gamma spectrometry from alpha, beta and gamma counting.
- Low background measurements (underground facility)
- Development of mass spectrometry: Thermal ionization mass spectrometry, ICP-MS, AMS

As a typical example of tracers, plutonium isotopes in environment are introduced in this presentation.

Kinds of Mass Spectrometry

- Inductively coupled plasma mass spectrometry (ICP-MS)
- Accelerator mass spectrometry (AMS)

  ICP-MS and AMS are current powerful tools and installed in many research institute of the world

- Thermal ionization mass spectrometry (TIMS)

  TIMS: high sensitive, but less accessible

- Resonance ionization mass spectrometry (RIMS)

  RIMS instrument is not commercial available.

- Secondary ion mass spectrometry (SIMS)
- Glow discharge mass spectrometry (GDMS)

  SIMS and GDMS: low sensitivity (used surface analysis of high level samples)

ICP-MS

Target radionuclides: uranium, thorium and plutonium isotopes,
^{79}Se, ^{90}Sr, ^{99}Tc, ^{129}I, ^{135}Cs, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{231}Pa, ^{237}Np, ^{241}Am, ^{243}Am, ^{244}Cm

Detection limits: 10^{-15} g – 10^{-8} g, depending interferences and the sensitivity of the instrument.

Typical examples:

^{99}Tc ($T_{1/2}$: 2.11 $\times 10^{5}$y, beta emitter) DL: 10^{-12} g (about 1 mBq) comparable with beta counting

benefit: short time measurement, while beta counting is time consuming

Plutonium isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu): absolute DL: 5×10^{-18} g (Aridus/SF-ICP-MS)

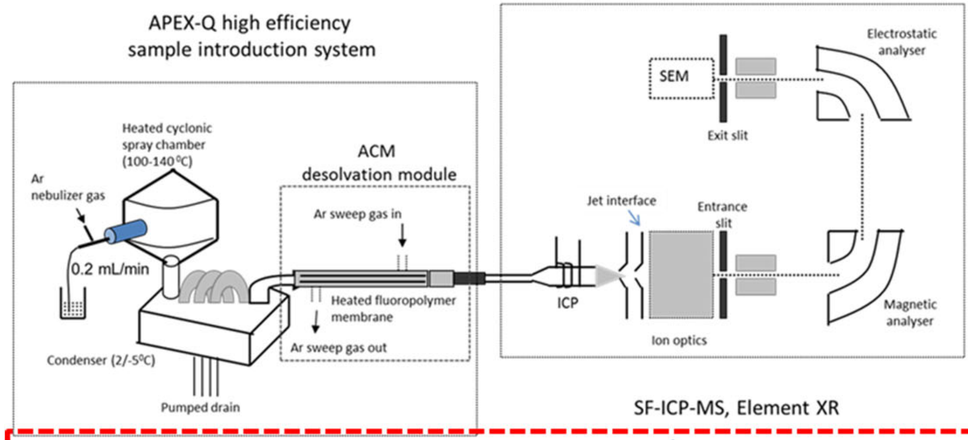
The most advantage of ICP-MS is its ability to measure ^{239}Pu and ^{240}Pu individually, while alpha spectrometry can be only provided information of sum of ^{239}Pu and ^{240}Pu due to very close alpha energies.

^{135}Cs ($T_{1/2}$: 2.3 $\times 10^{6}$y, beta emitter) DL: 10 pg/L (Agilent 8800ICP-QQQ) Ba-free solution
(^{135}Cs: 0.41 µBq/L, ^{137}Cs: 32 mBq/L)
theoretical $^{135}Cs/^{133}Cs$ abundant sensitivity: 10^{-14}

Zheng et al., 2014

Sector Field-Induced Coupled Plasma -Mass Spectrometry (SF-ICP-MS)

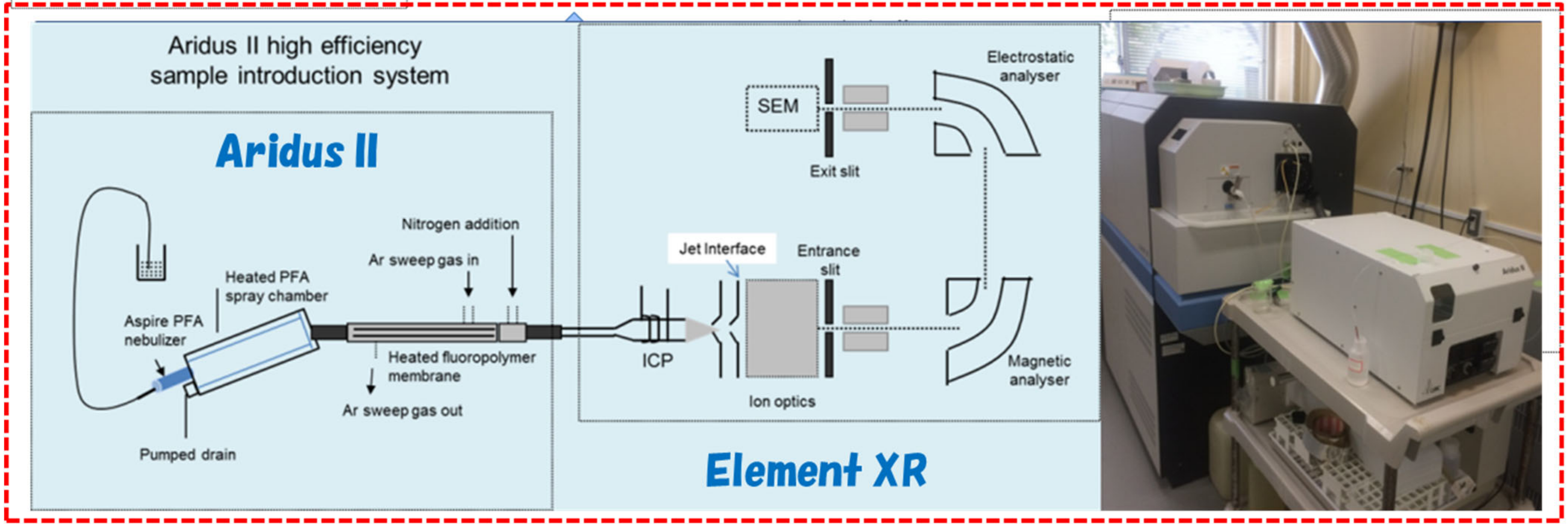
Plutonium isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) analysis



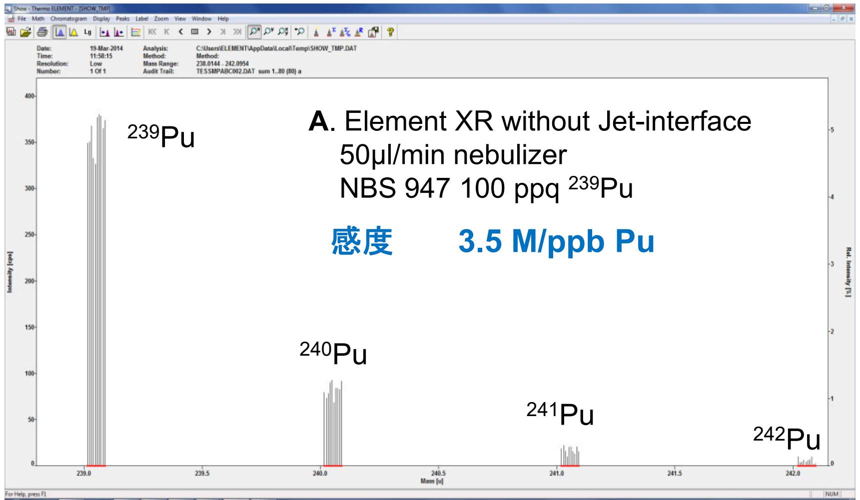
Element XR with Jet-interface

Two high efficiency sample introduction systems APEX-Q and Aridus II were combined to the new SF-ICP-MS to further enhance the sensitivity

Provided by Dr. Zheng



Machine performance of SF-ICP-MS (Element XR)

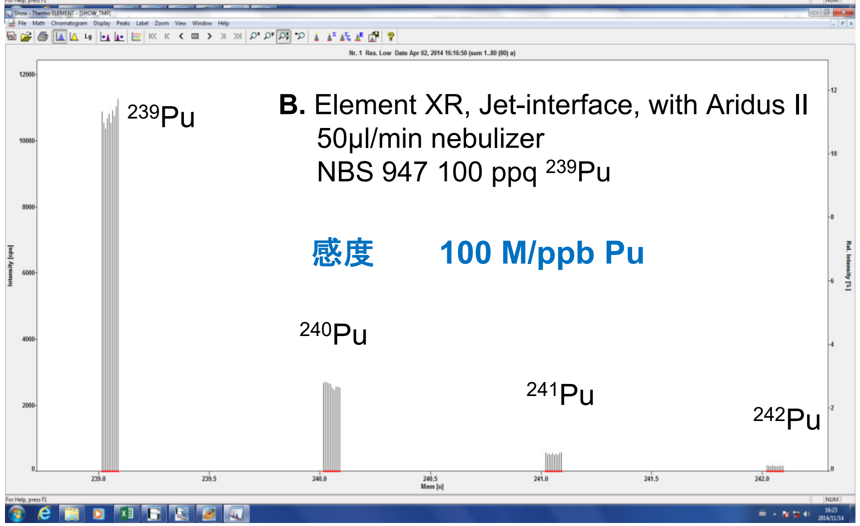


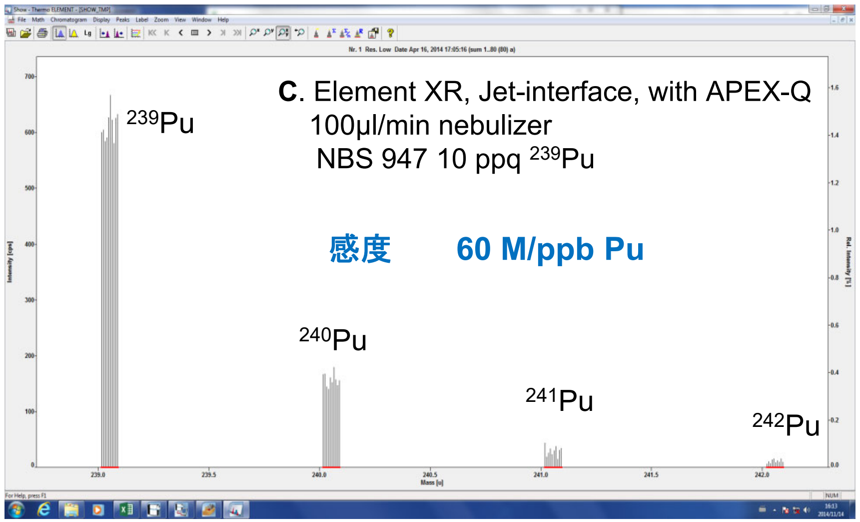
Extremely low detection limit is achieved for Pu isotope analysis (DL: 0.043 fg/mL)

{ ^{239}Pu (0.1 µBq/mL, ^{240}Pu(0.35 µBq/mL), ^{241}Pu(170 µBq/mL)}

Effective sensibility: 0.005 fg (one run)

This sensitivity is the same level as that of AMS technique.





Zheng, JNRS, 2015

AMS

(Ultra-sensitive mass spectrometric technique for long-lived radionuclides)

Target radionuclides: Radiocarbon, ^{129}I,
^{10}Be, ^{26}Al, ^{36}Cl, ^{129}I, ^{41}Ca, ^{59}Ni, ^{135}Cs, ^{182}Hf, and actinides (^{236}U, ^{239}Pu, ^{240}Pu)

Typical examples:

^{14}C ($T_{1/2}$: 5.7 $\times 10^3$y, beta emitter); AMS is the most powerful technique of ^{14}C measurements for radiocarbon dating.

^{129}I ($T_{1/2}$: 1.57 $\times 10^7$y, beta emitter with low energy); AMS is the only technique enabling to measure ^{129}I in pre-nuclear era samples with $^{129}I/^{127}I$ ratio (< 10^{-10}).

^{236}U (neutron activation product of ^{235}U, $T_{1/2}$: 2.34 $\times 10^7$y, alpha emitter having similar energy with ^{235}U); detection limit for $^{236}U/^{238}U$: 10^{-15}

^{239}Pu, ^{240}Pu; detection limit for ^{239}Pu and ^{240}Pu: 0.5 – 2 μBq
AMS is one of the most sensitive method for Pu isotopes.

The largest benefit of AMS is downsizing of sample and short-time measurement due to high sensitivity.

Plutonium in environment

- The first global-scale contamination of plutonium was occurred by the Nagasaki nuclear explosion in 1945. Nagasaki plutonium was detected in ice core in the Arctic Canada.
- Major source of plutonium in the environment is global fallout due to the 1961—62 large scale nuclear testing. Estimated total release of bomb-derived $^{239,240}Pu$ is 15 PBq.
- Significant amounts of plutonium dispersed in globe due to the stratospheric fallout, whereas bomb-derived plutonium contaminated locally.
- Plutonium deposition due to the stratospheric fallout showed a typical geographical distribution with mid-latitude maximum in northern hemisphere.
- Plutonium is chemically reactive element with some valences Pu(III, IV, V, VI); plutonium form stable complexes with organic ligands. Environmental behaviors of Pu differ from those of ^{137}Cs and ^{90}Sr.

Plutonium isotope ratios in environmental samples

Sources	$^{238}Pu/^{239,240}Pu$	$^{241}Pu/^{239,240}Pu$	$^{240}Pu/^{239}Pu$
	Activity ratio		atomic ratio
Nuclear Fuel Reprocessing plants	0.25	25	
Nuclear Test (1961-62)	0.026	15	0.18
Bikini ash	0.001	26	0.32
Weapon grade Pu	0.014	3	0.051
Fallout from the 21st Chinese test	0.03	11	
Fallout from the 26th Chinese test	0.02	5.5	
Chernobyl (IAEA, 1986)	0.5	85	
Chernobyl fallout (South Sweden)	0.57	85	
Bikini soil	0.004		0.34
Nagasaki soil			0.042
Irish Sea sediment			0.19-0.22
Japanese soil			0.17
Fukushima core	2.39		0.32
Fukushima black substance	1.64-2.64	108	0.32-0.33

half-life

^{238}Pu:87.7 y

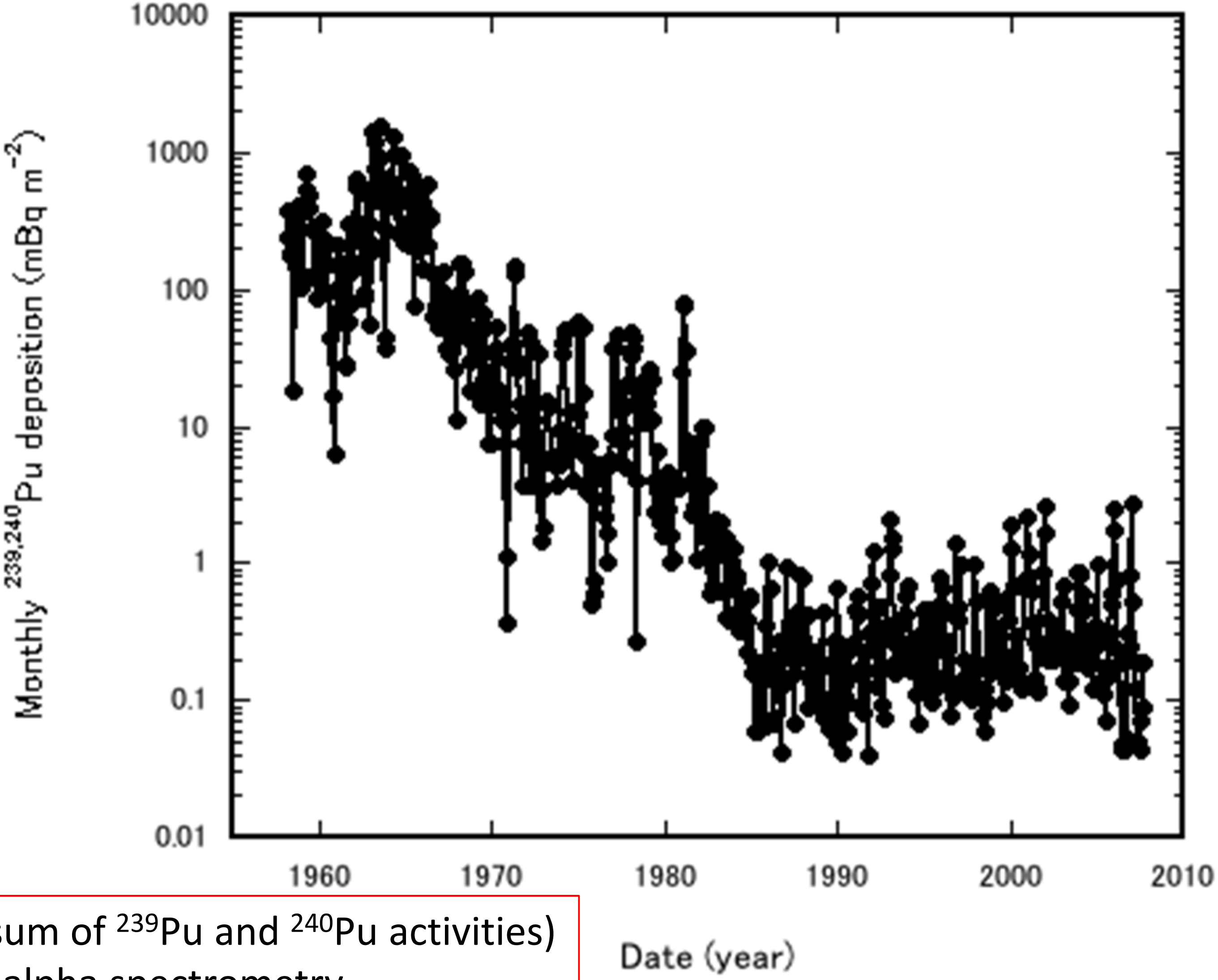
^{239}Pu:2.413x10^4 y

^{240}Pu:6,571 y

^{241}Pu:14.4 y

Plutonium isotopes are a useful tracer to have better understanding on sources and environmental changes.

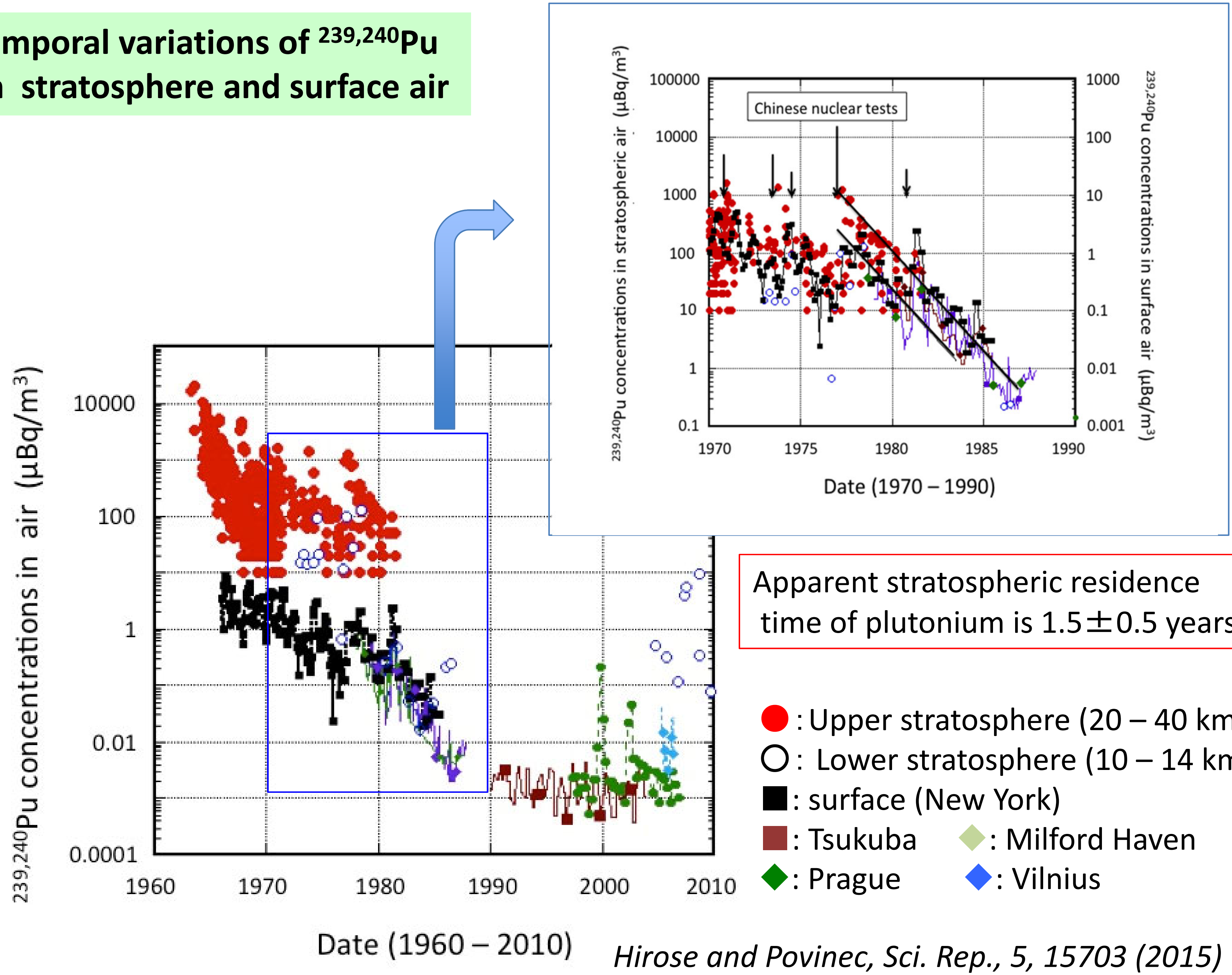
Temporal variation of monthly ^{239,240}Pu deposition observed at Koenji (Tokyo) and Tsukuba



^{239,240}Pu activities (sum of ^{239}Pu and ^{240}Pu activities) were measured by alpha spectrometry

Hirose et al., Appl. Radiat. Isot., 66, 1975 (2008)

Temporal variations of $^{239,240}Pu$ in stratosphere and surface air

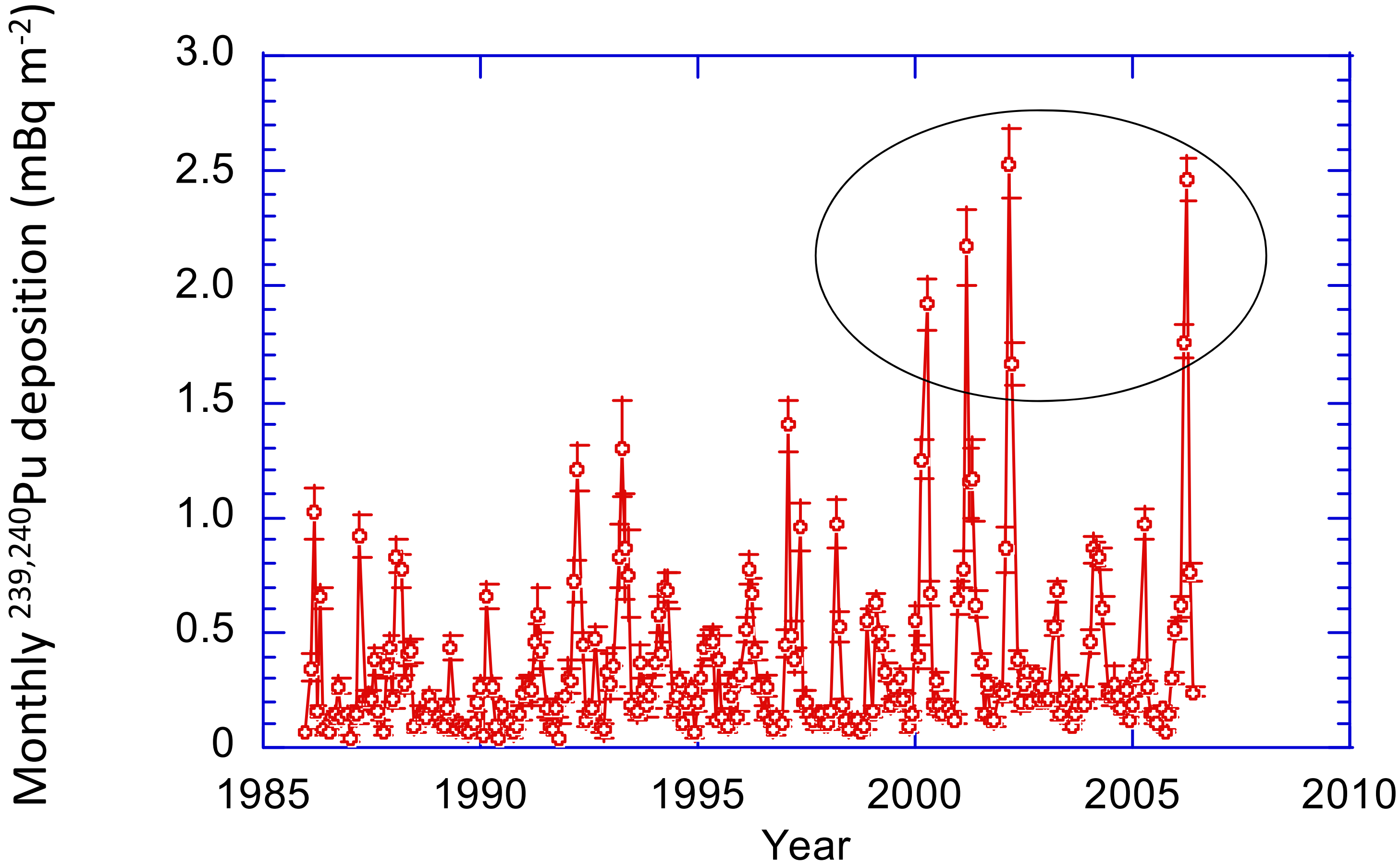


Apparent stratospheric residence time of plutonium is 1.5±0.5 years.

- ●: Upper stratosphere (20 – 40 km)
- ○: Lower stratosphere (10 – 14 km)
- ■: surface (New York)
- ■: Tsukuba
- ◆: Milford Haven
- ◆: Prague
- ◆: Vilnius

Hirose and Povinec, Sci. Rep., 5, 15703 (2015)

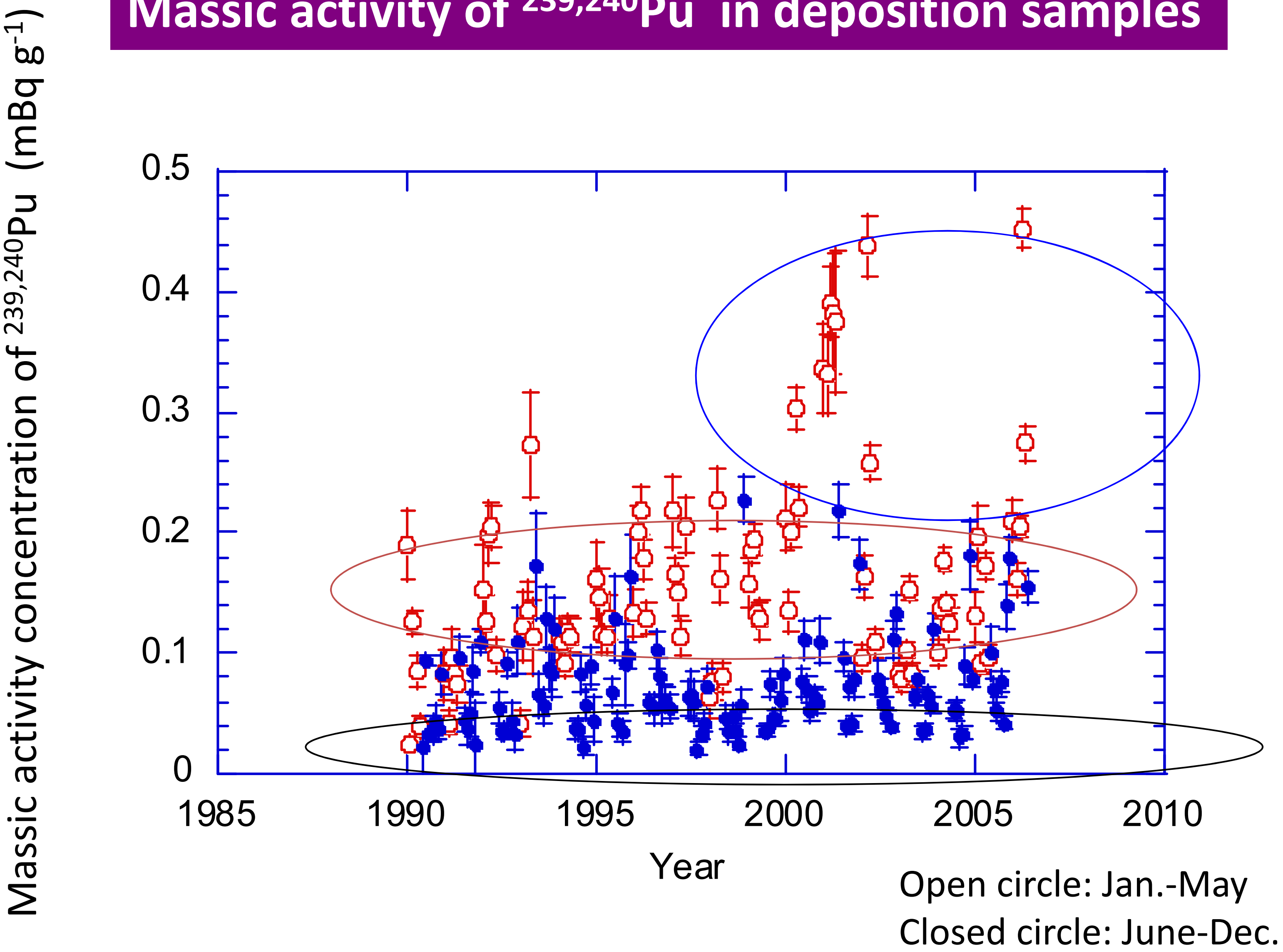
Temporal variation of monthly $^{239,240}Pu$ deposition at Tsukuba



Marked seasonal change of $^{239,240}Pu$ deposition with spring maximum was observed.

Hirose et al., 2003

Massic activity of $^{239,240}Pu$ in deposition samples

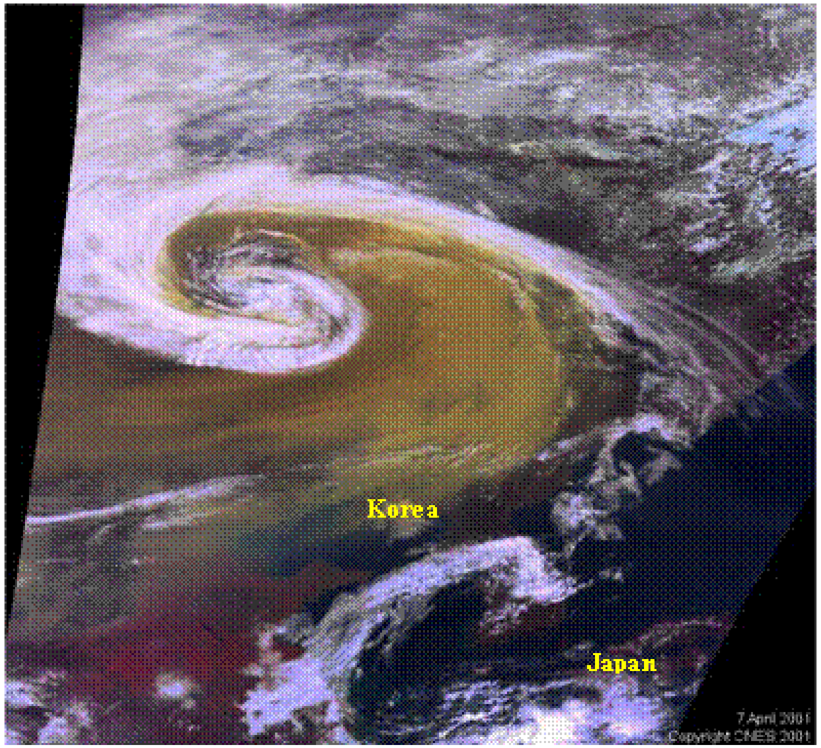


Higher massic activities of $^{239,240}Pu$ occurred in Kosa-season (spring).
Especially high massic activities of $^{239,240}Pu$ were observed in the early 2000s.

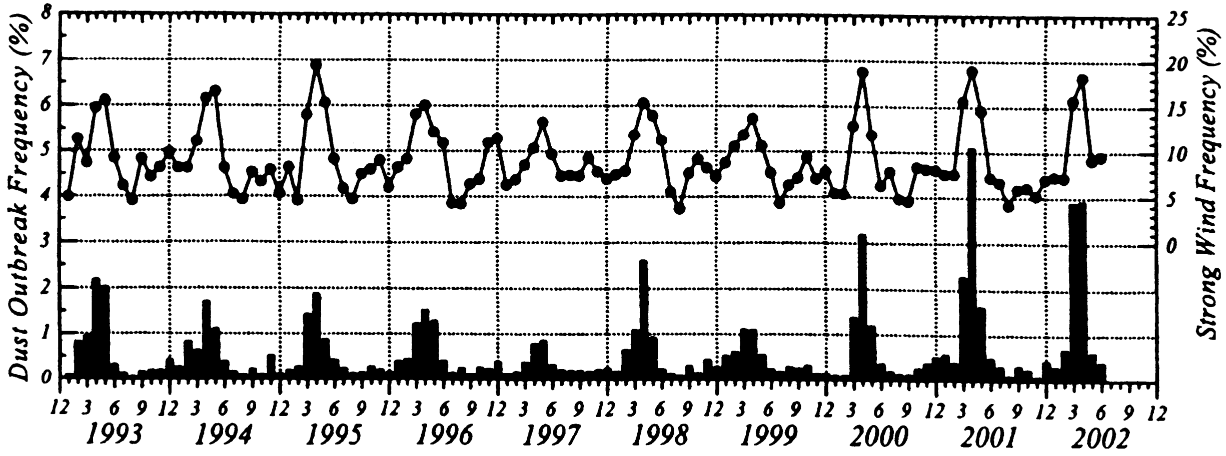
Outbreak of dust storm in Chinese deserts

Dust storm in Chinese deserts occurred in spring.

Long-range transport of Kosa (Chinese dust)

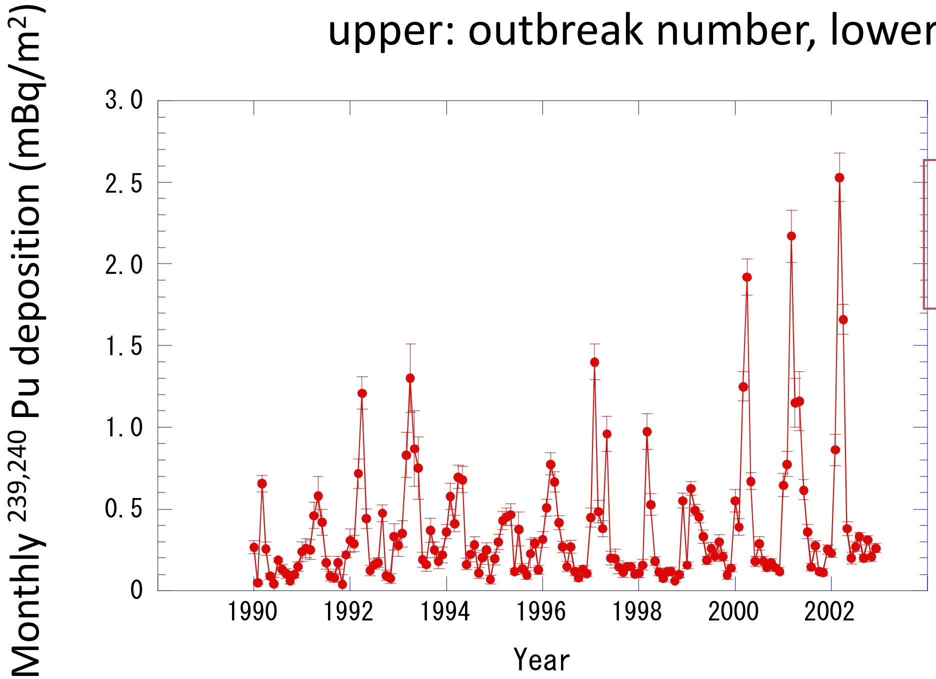


Frequency of dust storm in Chinese deserts and arid regions



Monthly outbreak frequency of dust storm
upper: outbreak number, lower: frequency of strong wind

Kurosaki and Mikami (2003)



Temporal change of monthly $^{239,240}Pu$ deposition

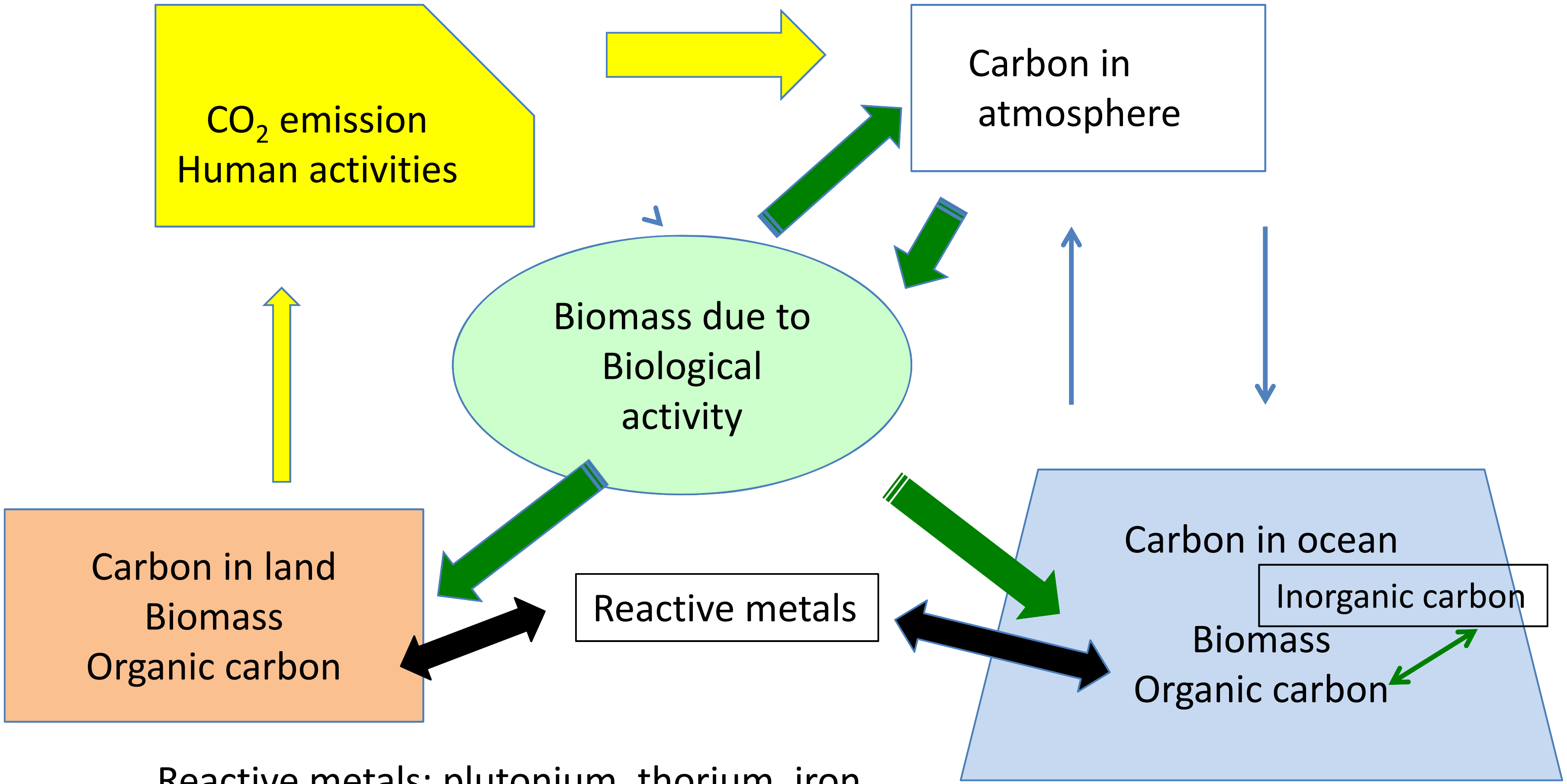
Seasonal changes may reflect natural processes.

Hirose et al. J. Environ Monitor(2003)

Plutonium isotopes as biogeochemical processes

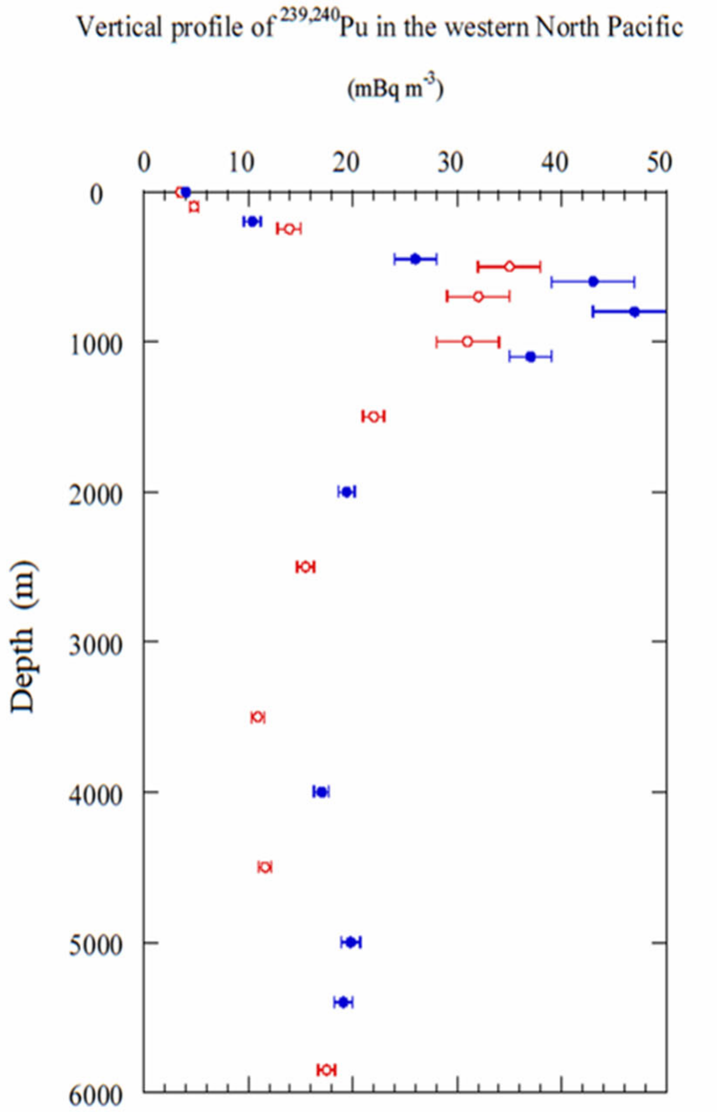
What is biogeochemical process?

Biological activities are an important factor to control earth system.
Biogeochemical processes are closely related to Carbon Cycling on earth

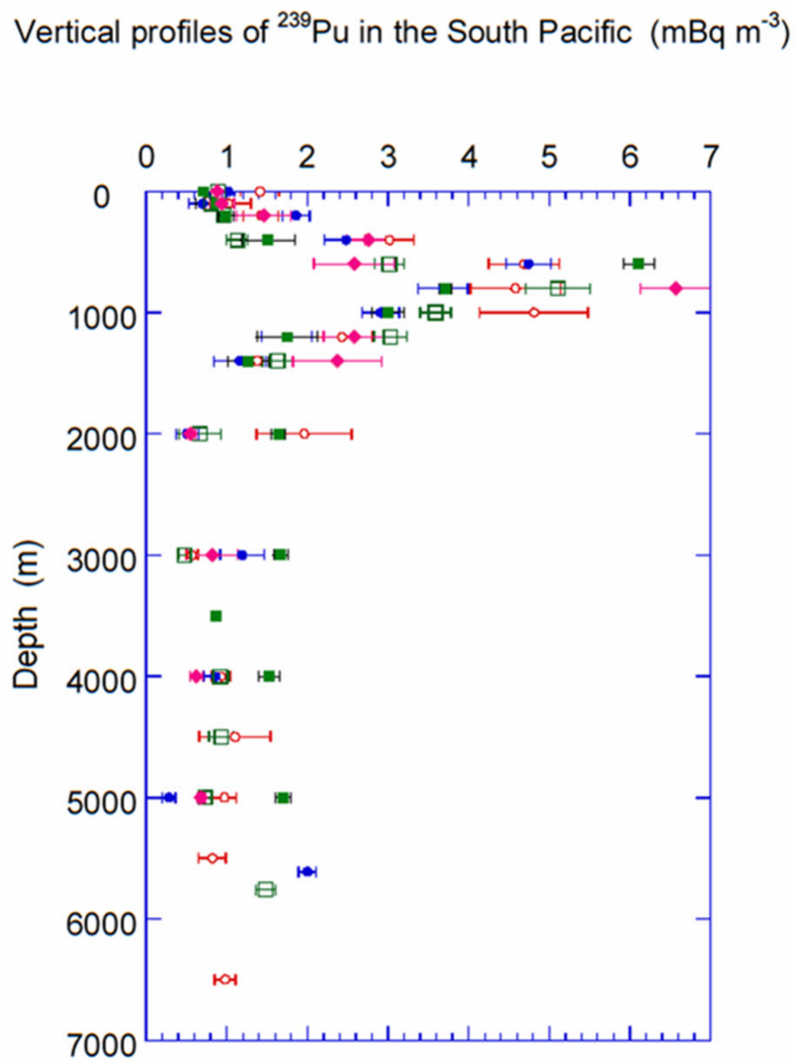


Reactive metals: plutonium, thorium, iron,…

North Pacific



South Pacific

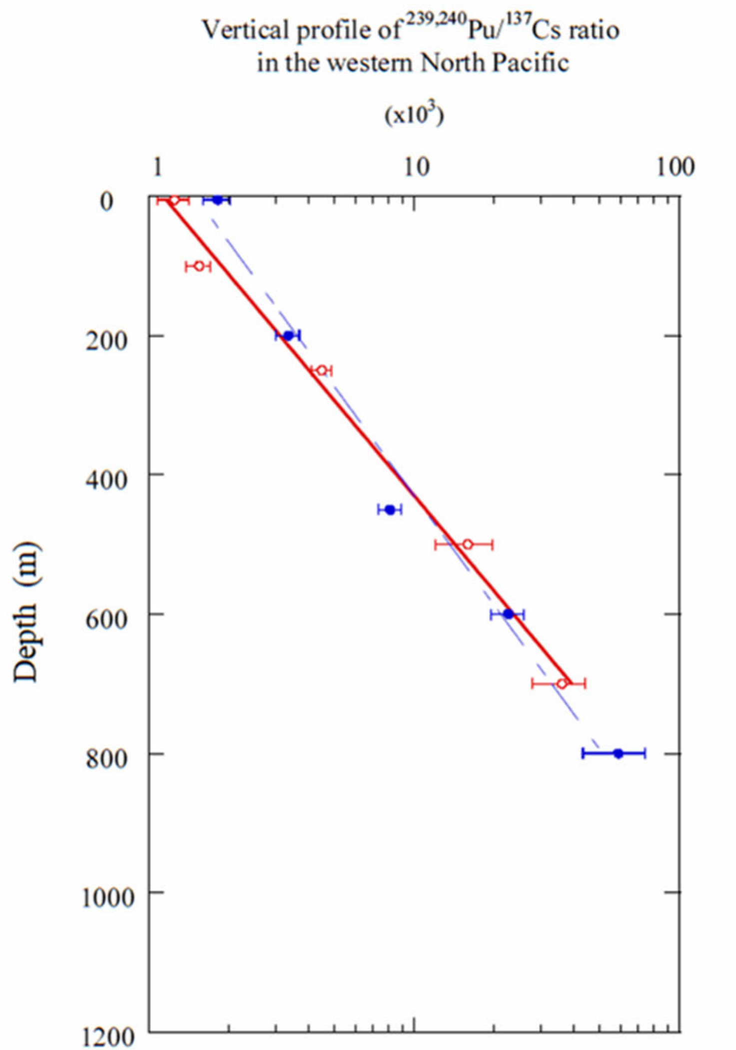


Vertical distributions of plutonium in the ocean are controlled by biogeochemical processes: Biological uptake, sinking of biogenic particles, decomposition biogenic particle in deeper layer.

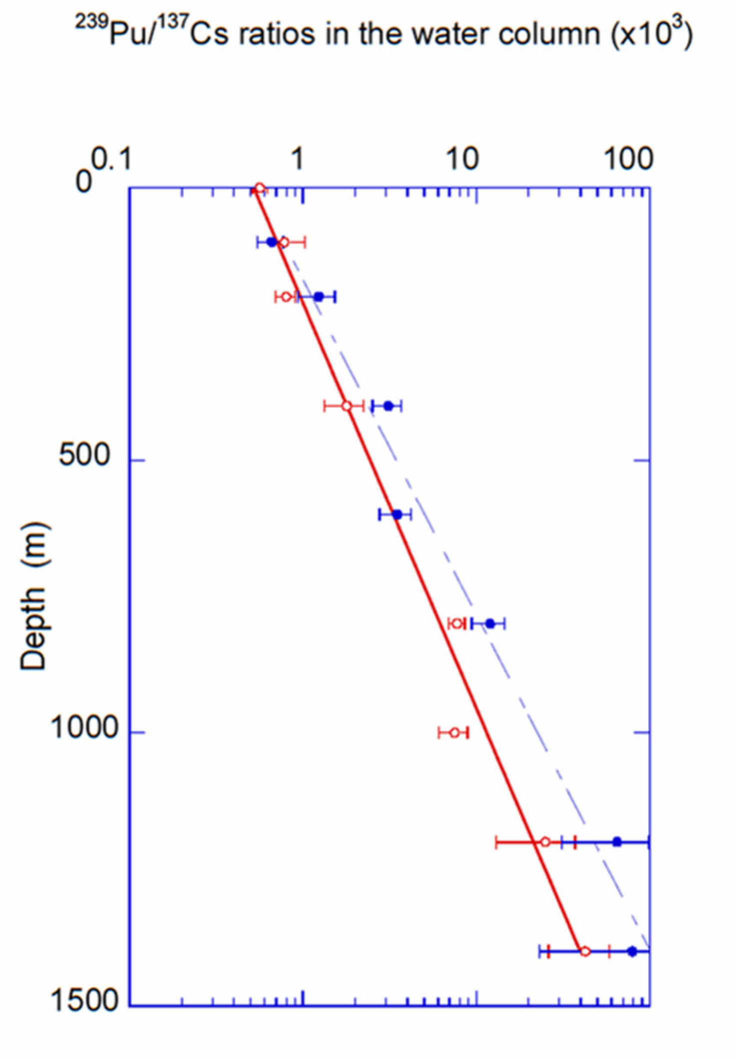
Vertical profiles of Pu/^{137}Cs ratios

Hirose, Aoyama, Povinec., JER, 2009

North Pacific



South Pacific



^{239,240}Pu/^{137}Cs ratio is an indicator of biogeochemical process:
Vertical transport of particles and regeneration due to biological decomposition of particles.

^{239,240}Pu/^{137}Cs ratios exponentially increase with depth in the ocean.

Summary

- We require long-term monitoring of anthropogenic radionuclides to assess their radiological effects released from nuclear facilities (nuclear reactors and others) including accidental releases.

1. Radioactivity monitoring has provided huge amounts of time series data in atmosphere, land and ocean at global scale.
2. The time series data reflect environmental change due to human activities such as climate change, as do natural variations.
3. Anthropogenic radionuclides are effective tools as tracers of environmental change.
4. New techniques of radionuclides with high sensitivity and high selectivity open new world for use of radionuclides as environmental tracers.

Final Remark

Climate change is a threat to sustainability of human society.
The monitoring of anthropogenic radionuclides has to effectively use for assessment of environmental effects due to climate changes.

Thank you for your attention!

Acknowledgement:
I would appreciate providing an opportunity to participate FNCA2021 for Mr. Sano Commissioner of JAEC and Prof. Nakanishi.
I also thank Dr. Zheng and many colleagues to provide information on new techniques.