

Approach of an economic geologist for solving land contamination issues

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Ministry of Environment of Japan made the Soil Contamination Countermeasures Law (referred to hereafter as the Law) on 29 May 2002, in order to prevent health damage which toxic substances in soils could cause by oral ingestion. The pollutants in many cases are toxic metals as Pb, As, Cr(VI) and Hg. The administration of the Law obliges landowners, managers and occupiers of sites of business establishments handling these toxic metals to examine soil contamination by field survey and chemical analysis to determine toxic metal concentrations and their leachabilities when they close their facilities.

Because As, Se, Cd, Hg, and Pb are very important metals for economic geologists, we have a lot of knowledge and techniques on geochemistry and mineralogy of these metals. Therefore, we can contribute to develop techniques surveying toxic metals in contaminated lands, as well as controlling their leachabilities.

The followings are important subjects economic geologists have advantages to develop;

- 1) Mapping natural levels of toxic heavy metal concentrations in soils
- 2) Developing analytical methods for identifying contaminations by anthropogenic or natural processes.
- 3) Developing on-site chemical analytical techniques for surveying contaminated sites.

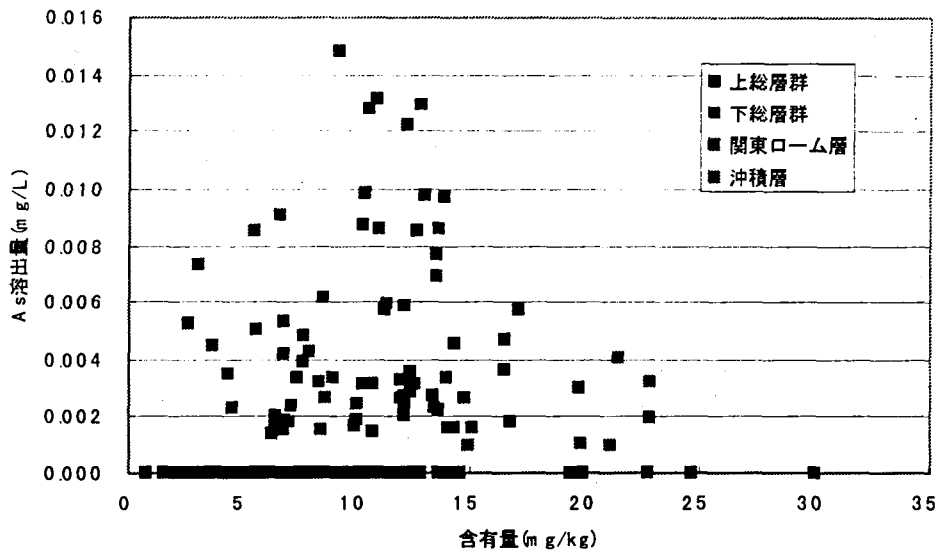
(1) Mapping natural levels of toxic heavy metal concentrations in soils

In order to carry out the Law, we must judge whether soils have high toxic metal concentrations or high leachabilities caused by anthropogenic or natural processes. If high toxic metal concentrations or high leachabilities are caused by natural processes, the administration of the Law should not oblige landowners, managers and occupiers of contaminated sites to remedy them.

Therefore, it is essential to determine natural levels of Pb, As, Cr(VI) and Cd concentrations and their leachabilities of soils and sediments which have a wide range of chemical and mineralogical composition.

We obtained Pb, As, Cr(VI) and Cd concentrations and leachabilities of soils and sediments, using XRF and conventional wet chemical analytical methods. We also obtained mineralogical data of

these sediments and soils, using XRD, TG-DTA and analytical TEM. These data were superimposed on 1:50,000 geological and published as the “Regional geochemistry of soil and sediment of Anesaki (1:50,000)”.



Arsenic leachabilities and contents of Japanese soils and sediments from Anesaki area

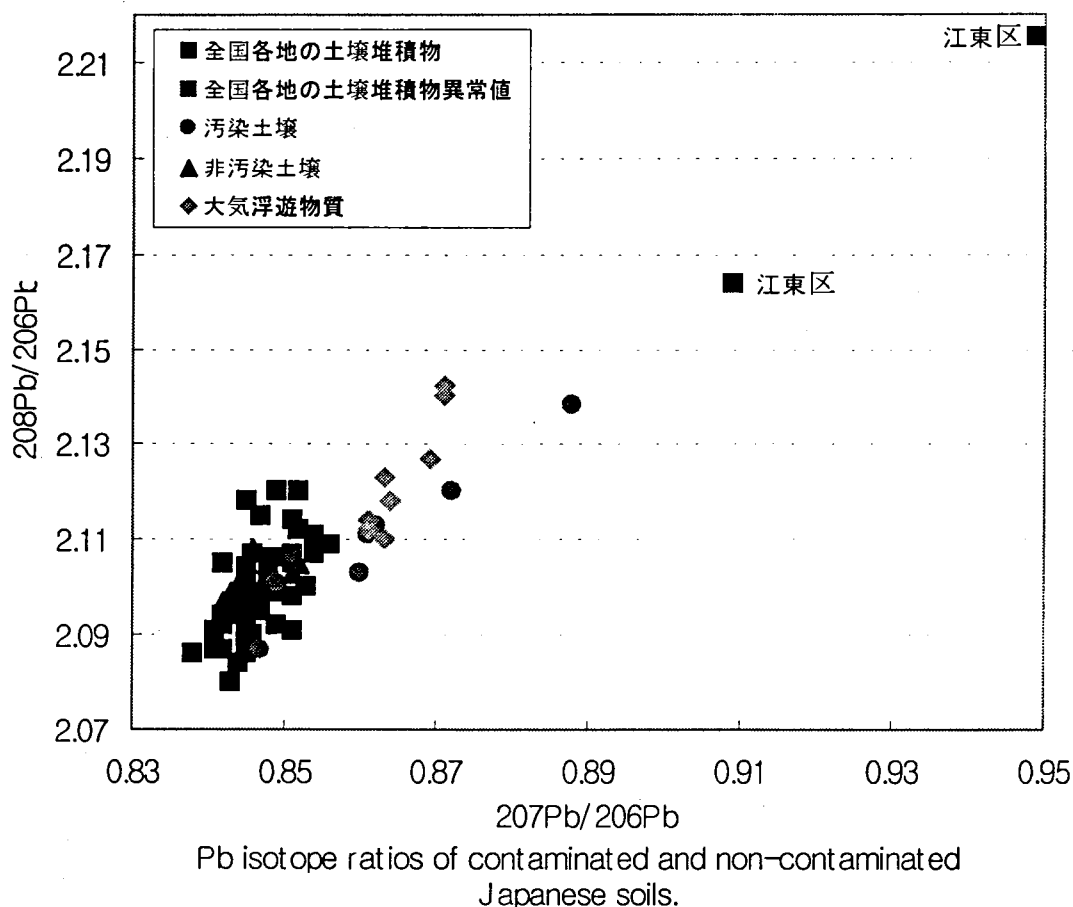
(2) Developing analytical methods for identifying contaminations by anthropogenic or natural processes

It is also very important to develop analytical methods to judge whether soils have high toxic metal concentrations or high leachabilities caused by anthropogenic or natural processes. Among toxic metals, Se, Sb, Cd, Hg and Pb have isotopes, therefore these metal contaminations can be traced using their isotopes. $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, obtained using a conventional ICP-Mass, are very useful to identify their origin. Lead isotope ratios of con-contaminated soils are significantly different from contaminated soils from industrial sites. The range of Pb isotope ratios of air dusts fall midway between con-contaminated soils and contaminated soils.

Because determination of isotope ratios of Se, Sb, Cd and Hg require a multicollector inductively coupled plasma mass spectrometer (MC-ICP-Mass), there are not so many data on these isotope ratios. We started Hg isotope analysis of sulfide ores of middle Miocene Kuroko deposits to evaluate variations of Hg isotope ratios for the natural process, using a MC-ICP-MS (Thermo Finnigan Neptune). The analytical procedure is as follow;

- 1) 1.5g of each sample was weighted out into a clean labeled 20ml glass tube.
- 2) With adding 0.6 ml of conc. HNO₃ and 1.8ml of conc. HCl to the sample. The sample was heated for about 2 hours.
- 3) DI H₂O was added to each sample to reach the final volume of 10ml.
- 4) Each sample was centrifuged for 15min (2500rpm).
- 5) Hg concentration of each sample was determined using Flow Injection Mercury System.
- 6) Each sample was mixed with SnCl₂ and then with argon (carrier gas). After gas liquid separation, the argon delivered Hg to the torch directly. All other metals were removed to drain.

Because there is no available standard material for Hg isotope analysis, we used S-HG02027 (Inorganic Ventures, Inc) for the standard. We analyzed Hg isotope ratios of dacite lava and sulfide samples from the Suiyo seafloor hydrothermal system. We also analyzed Hg isotope ratios sulfide and sedimentary rock samples from Middle Miocene fossil seafloor hydrothermal systems (Kuroko deposits) for comparison.

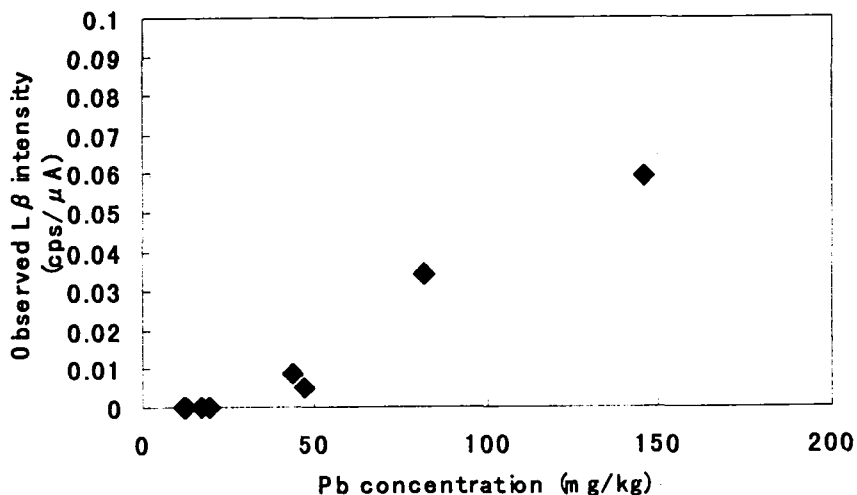


(3) Developing on-site chemical analytical techniques for surveying contaminated sites

Off-site chemical analysis of arsenic and lead in soil samples is expensive and too time consuming for determining detailed distribution of contaminated soils. To meet the demand of on site screening and fast chemical analysis of arsenic and lead in contaminated sites, we developed an analytical method for portable energy dispersive X-ray fluorescence spectrometry (EDXRF).

Quantitative arsenic and lead analysis by the EDXRF method requires calibration of arsenic $K\alpha$ and lead $L\beta$ intensities using standard soils with known arsenic and lead concentrations. Because spectral resolutions of solid-state X-ray detectors of EDXRF are not enough for separating arsenic $K\alpha$ peak from lead $L\alpha$ peak, these two peaks overlap around 10.5keV. Therefore we must subtract lead $L\alpha$ peak intensity from total intensities around 10.5keV, for evaluating arsenic $K\alpha$ peak intensity. The lead $L\alpha$ peak intensity can be estimated from lead $L\beta$ peak intensity, assuming that the peak intensity ratio of lead $L\alpha$ to lead $L\beta$ is constant.

Sample matrix effect arise from variations in concentrations of interfering elements as major heavy metal as iron. Because soils contain up to 30% iron, their arsenic $K\alpha$ and lead $L\beta$ peak intensities are affected its matrix factor. The Fe $K\alpha$ sum peak, appearing at lead $L\beta$ position, also affects for evaluating lead concentration. These matrix factor and Fe $K\alpha$ sum peak restrict the detection limits of arsenic and lead in soil samples. In order to minimize the effect of the matrix factor and sum peak caused by iron, we need to set a Cr thin foil as a secondary filter between soil sample and solid –state X-ray detector. Combination of Ni filter between a 50W Rh X-ray tube and sample, together with the Cr secondary filter, enables us to detect up to 15mg/kg arsenic and lead in soil samples.



Effects of a Cr secondary filter on PbLβ intensities for soil standards