Mapping of Heavy Metals Accumulated Implants Using a Submili-PIXE Camera

V. 3. Mapping of Heavy Metals Accumulated Implants Using a Submili-PIXE Camera

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Introduction

Heavy metal contamination in the subsurface environment is a major problem for human health and environmental quality. A number of technologies for remediation of soils contaminated by heavy metals have been developed. Most of these technologies, however, are expensive, and they occasionally produce secondary waste[1)]. Recently, environmentally friendly, low-input approaches such as phytoremediation have been proposed to cleanup soils contaminated with heavy metals and metalloids[2)]. Phytoremediation is a technology for cleaning environments using the metabolism of plants, and interaction between plants and microorganisms in the rhizosphere. To develop practical applications of this technology, it is necessary to explicate effective accumulation mechanisms for heavy metals. In general, contaminated soil and plant samples are chemically analyzed using atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS), after oxidizing pre-treatment. However, these methods are laborious and provide only average metal concentrations in each plant organ. For this reason, Particle-induced X-ray Emission (PIXE) analysis is an attractive analytical tool. PIXE analysis has high sensitivity and multi-elemental capability[3,4)], does not require sample pretreatment, and can be performed quickly and simply.

The purpose of this work is to investigate the localization and speciation of heavy metals in plants using a submilli-PIXE camera and to establish fundamental information about the mechanism of heavy metal accumulation in plants.

Materials and methods

Plant and soil samples were obtained on 23 April 2003, from a shooting range in Japan. Whole bodies of *Polygonum cuspidatum* were sampled. The ground part of this plant was about 10cm tall. The following pretreatment was conducted for the plant and soil samples: firstly, the plant samples were rinsed with tap water, then deionized water, prior to PIXE analysis. In contrast, the subterranean stems were oven-dried at 105 ℃ and decomposed with concentrated HNO_3 to measure their heavy metal content.

The soil sample was air-dried and sieved using a 2 mm mesh sieve. For PIXE analysis, the soil sample was oven-dried at 105, ground and stuck on to a tape. In addition, the sample was chemically analyzed. The total contents of heavy metals were determined by dissolution with a mixture of concentrated H_2SO_4, HNO_3 and $HClO_4$ (1:5:20). Different chemical and physical forms were analyzed by a sequential extraction procedure (following the Community Bureau of Reference (BCR)[5], which is the Standard Measurement and Testing Program of the European Community (STM) [6], which identified the following forms: Fraction 1: water soluble, exchangeable and carbonate bound; Fraction 2: Fe-Mn oxide bound; Fraction 3: organic matter and sulfide bound.

Heavy metals in the plant and soil extracts were analyzed by ICP-MS. The soil components and distribution of elements in the leaf and subterranean stem were analyzed by submill- PIXE camera of Tohoku University[7].

This PIXE analysis system provides spatial distribution images of elements in a region several cm^2 with a resolution of < 0.5 mm. 3 MeV proton beam (10 nA beam current, <0.5 mm beam diameter) from a 4.5-MV single-ended Dynamitron accelerator was extracted to open air through a thin polyimid (Kapton) film of 12.5 μm. In usual manner, beam was scanned mm^2 on a surface of samples. Plant samples were fixed to the target frame and set up just after the beam exit window. The distance from the beam exit window and a sample is around 5mm. Fig. 1 shows experimental set-up. The X-ray energy and the beam position were simultaneously measured in order to obtain spatial distribution of elements. The X- rays from a target passed through the exit window and a 110-μm Mylar absorber and were measured with a Si (Li) detector (10-mm diam. x4-mm thick crystal with 25-μm Be window) which viewed a target at a distance of 45 mm with an angle of 135 degree with respect to the beam axis. The absorber in front of the detector removed recoil protons and low-energy X-ray components. This resulted in a decrease of the dead time of the signal processing and pile-up. The list mode data acquisition system can sort the data for a

selected element/ energy region and generate an elemental image even while the data are accumulated.

Results and Discussion

Table 1 shows the different forms of Cu and Pb metals in the soil samples. The total concentrations of Cu and Pb were 7000 and 5000 mg/kg, respectively, which are two-orders of magnitude greater than in common soils (Cu 30mg/kg, Pb 35mg/kg)[8]. The metals have mobility in the soil, since the proportion of water-soluble fraction is large (Fraction 1, Table 1). Plants readily absorb these metals, although the spread of contamination is a problem. In common soils, K, Ca, Ti, Mn and Fe occur in relatively high concentrations, but Cu, Pb and Zn occur at lower levels. The characteristic X-ray spectrum of each element in the soil samples is shown in Fig. 2. K, Ca, Ti, Mn, Fe, Cu, Zn and Pb are detected in the soil by PIXE analysis (Fig. 2), which proves the effectiveness of PIXE analysis for rapid determination of heavy metal contamination in soils.

Fig. 3 shows the characteristic X-ray spectrum of each element in the leaf sample of *P. cuspidatum*. Some toxic heavy metals, i.e. Cu, Pb and Zn were detected. Also, essential plant elements K, Ca and Fe, were detected. The elemental distribution images of K, Ca, Cu and Pb are shown in Fig. 4. Potassium is uniformly distributed, whereas Cu and Pb occur mainly in the vein. Calcium mostly occurs in the vein, but also at a low level in the lamina.

The average concentrations of Cu, Pb in the subterranean stem are 200 and 400mg/kg, respectively, which are very low compared with typical values in soil. The characteristic X-ray spectrum for subterranean stems is shown in Fig. 5 and elemental distribution images are shown in Fig. 6, with similar patterns for Cu and Pb that accumulated in the epidermis of subterranean stems. However, the distribution patterns are not strongly developed inside the plant. These results lead to the speculation that *P. cuspidatum* acquires tolerance for heavy metals by accumulating them on the epidermis. In Figs. 4 and 6, K and Ca are distributed over the entire plant. In contrast, Cu and Pb are translocated from the subterranean stem to leaves, but into the vein rather than tissue, as they are unnecessary and possibly toxic. The fixing of Cu and Pb into the vein is a feature revealed by PIXE mapping.

Plants grown in contaminated soil are harvested and disposed when phytoremediation is adapted, so it is desirable to accumulate most of the heavy metal component in the ground part of plants. Cu and Pb mostly accumulated in roots and are not translocated to the ground part[9,10]. Therefore, phytoremediation is regarded as being a difficult technique to put into

practical use for remediation of Cu and Pb. However, *P. cuspidatum* analyzed in this study has a tolerance to heavy metals and tends to accumulate Cu and Pb in the ground part, so it can be potentially utilized to cleanup soil that is contaminated by heavy metals.

Conclusion

In this study, PIXE was used to analyze *P. cuspidatum* that inhabited soil contaminated by heavy metals (mainly Cu and Pb). The submilli-scale distribution of Cu, Pb and other elements in leaves and subterranean stems was investigated. The images lead to the clarification of an accumulation mechanism, such as the route of absorption and correlation of each element. PIXE analysis can be used to investigate components in soils, and very useful for phytoremediation research.

References

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Table 1. Total and different chemical and physical forms of heavy metals in soils.

Element	Total (mg/kg)	Fraction 1 (%)	Fraction 2 (%)	Fraction 3 (%)
Cu	7000	63	32	3
Pb	5000	87	11	1

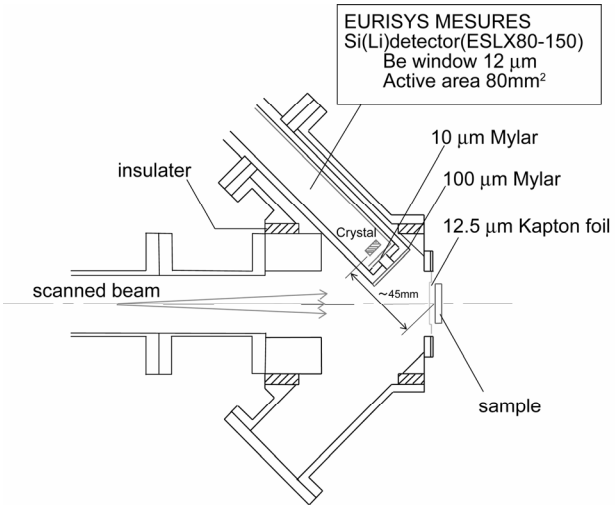

Fig. 1 Layout of the submilli-PIXE analysis system at the Dynamitron laboratory in Tohoku University.

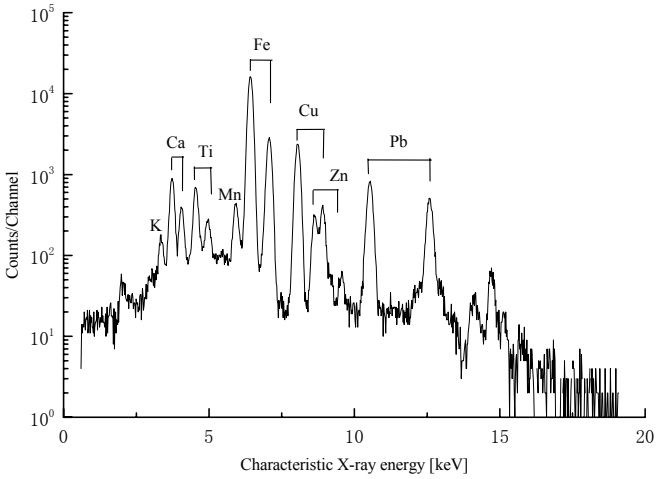

Fig. 2 X-ray spectrum of heavy metal contaminated soil analyzed by PIXE.

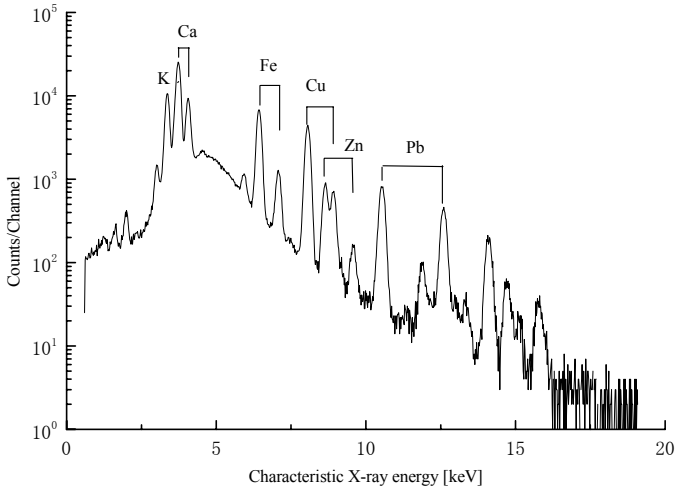

Fig. 3 X-ray spectrum of leaf of *P. cuspidatum* analyzed by PIXE

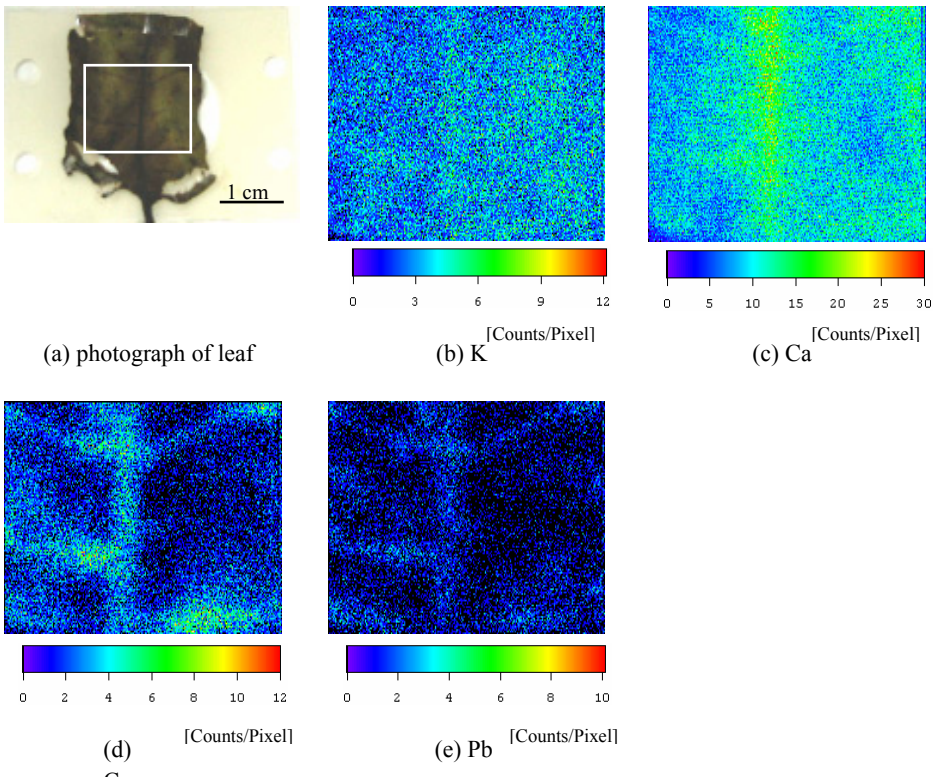

Fig. 4 Photograph of leaf (a), the corresponding to PIXE dot-maps of K, Ca, Cu and Pb (b, c, d and e, respectively).

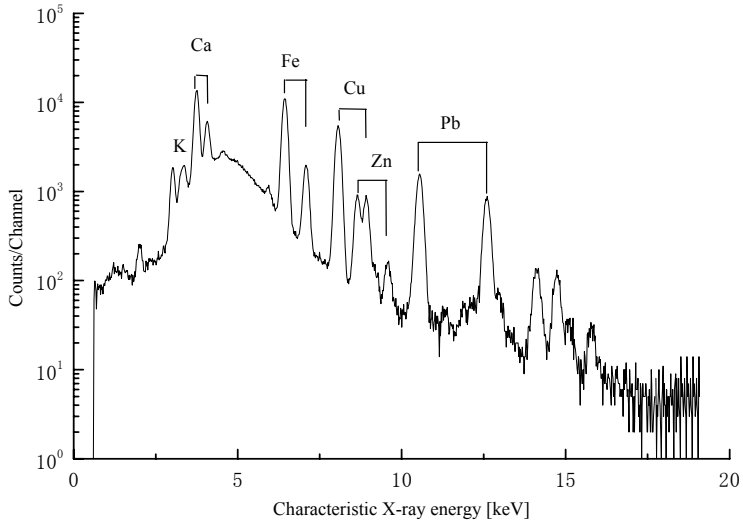

Fig. 5 X-ray spectrum of subterranean stems of *P. cuspidatum* analyzed by PIXE.

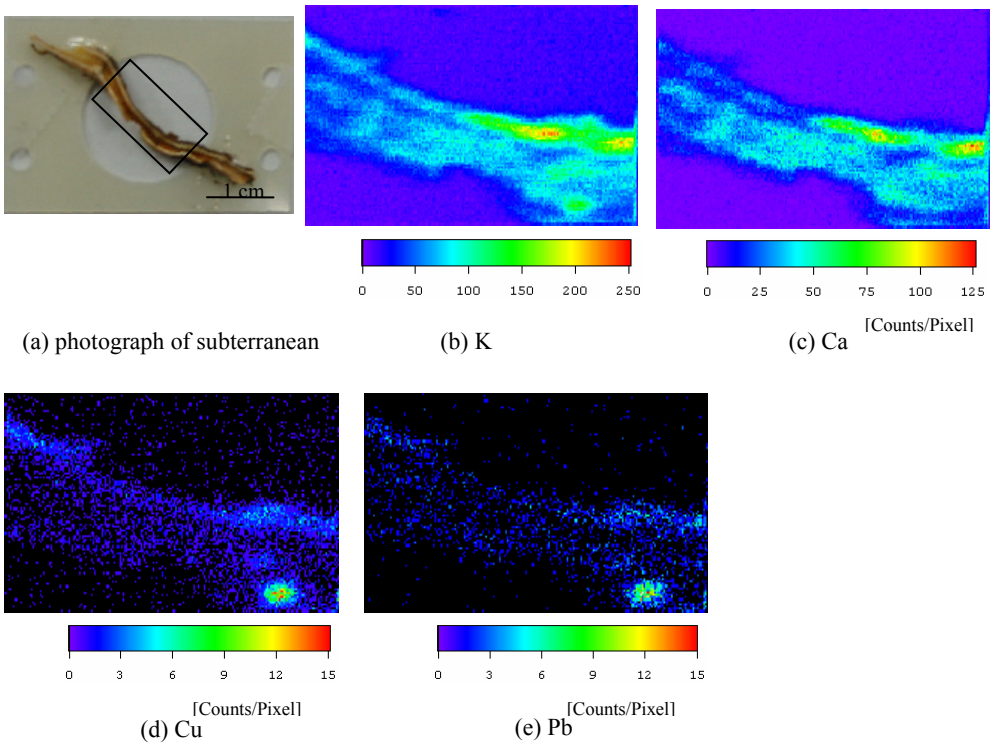

Fig. 6. Photograph of subterranean stems cut perpendicularly (a), the corresponding to PIXE dot-maps of K, Ca, Cu and Pb (b, c, d and e, respectively).