Energy-dispersive X-ray fluorescence study of elemental uptake in cauliflower

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Abstract. A ^{109}Cd radioisotope-induced energy-dispersive X-ray fluorescence (EDXRF) study has been performed on samples of cauliflower consisting of the flower, the leaves and the associated root soil. The cauliflowers were collected from farms near the main dumping site of municipal solid waste in the city of Kolkata, India and also from uncontaminated farms about 50 km away from the city. A unified calibration approach was undertaken for the elemental analysis of the samples of widely varying matrices. The present study suggests that the elemental concentrations in the root soils and leaves of the samples vary from farm to farm, whereby the concentrations of Cu, Zn and Pb in root soils of MSW-contaminated farms are higher by almost an order of magnitude compared to uncontaminated farms. But, the most notable feature of this study is the strikingly similar elemental concentrations in the edible flower part of all samples irrespective of the type of soil.

Keywords. Energy-dispersive X-ray fluorescence; elemental analysis; cauliflower; environment.

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1. Introduction

An area on the eastern fringes of the city of Kolkata, West Bengal, India, known as Dhapa, has been earmarked since the middle of the 19th century for dumping municipal solid waste (MSW) generated in the city and its suburbs. Dumping of MSW is still continuing in certain parts of Dhapa and the rest of the vast stretch of land is used by the farmers to grow vegetables. This region has small vegetable growing farms, the total area of which is about 2000 acres. The top soil of these vegetable cultivating farms evolved from dumped MSW which was found to contain higher concentrations of essential elements as well as heavy metals [1]. Thus the Dhapa top soil and vegetables grown there are also expected to contain elements in higher concentrations than those in uncontaminated soil.

Cauliflower, one of the most widely cultivated and consumed vegetable among the local population during the winter was selected as a sample of study. Using a unified calibration

approach in the EDXRF analysis technique, investigation has been made to characterize the elemental distribution in root soil, leaves and flower of each sample collected from Dhapa and from two village farms, about 50 km away from Kolkata.

2. Experimental procedure

2.1 *Sample collection and preparation*

During the harvesting season, cauliflowers from two farms of Dhapa, approximately 300 m apart, were collected. These farms are about 1 km away from the present dumping site of the MSW. The cauliflower plants including their respective root zone soils (root soils) are further referred to as Dp1 from the first farm (1) and Dp2 from the other farm (2). Fully-grown cauliflowers along with the root soils were also collected from two villages about 50 km away from Kolkata during the same period of the year. The soil of those villages may be considered as 'uncontaminated' when compared with that of Dhapa. These samples collected from villages are labelled as Cs1 and Cs2.

The root-soil samples were first air dried, large impurities like pebbles, stones, twigs, plastics were removed, and then the samples were dried in an oven at 105°C. Two parts of each dried soil sample was then mixed with one part of cellulose to make pellets in a hydraulic press. Following similar technique, a pellet was also prepared with the National Institute of Standard and Technology (NIST) Reference Material (NIST-SRM 2586) comprising 'Soil containing lead from paint'.

Edible flower part and leaves of the cauliflower samples were dissected, washed in triple distilled water, dried and kept frozen at −20°C for 24 h. After lyophilization, the samples were kept in a desiccator for 24 h. Pure sample pellets were made from the dry samples of the edible part and the leaves without mixing any binder. Similarly, a pure pellet of NIST-SRM1570a comprising 'Spinach leaves' was also made.

2.2 *Experimental set-up*

The experimental set-up consisted of a ^{109}Cd source (4 mm Ø) of effective activity 325 MBq and a Si(Li) detector (active crystal area $= 12$ mm^2 and resolution of 159 eV at 5.9 keV). The mechanical arrangement showing relative positions of the source, sample and the detectors along with the graded collimators is shown in figure 1. Graded collimators made of Bi, Cu and Al were placed at both the entrance and the exit ports of the sample holder. From a transmission measurement [2] it was observed that the effective angles of incidence and emergence were $45.7° \pm 2°$ and $44.8° \pm 2°$, respectively. The source–sample holder assembly was fitted inside a perspex chamber with silica gel to keep the environment clean and dry. Data acquisition was done on an EG&G ORTEC MCA card.

3. Analysis

The entire analysis of the EDXRF spectra was done using the quantitative X-ray analysis system (QXAS) [3]. The full fundamental parameters (FFP) program in the QXAS

Figure 1. Schematic diagram of source–target–detector arrangement of the [109]Cd-Si(Li) EDXRF experimental set-up along with the graded collimators.

software was used for the quantitative analysis [4–6]. Dark matrix which was mainly composed of the low-Z elements (H, C, O etc.) of the sample was calculated by the FFP code as a weighted combination of two elements Z and $Z+2$. For this purpose, the code requires the input of geometrical constants for fluorescent and scattered X-rays.

To get geometrical constants for fluorescence lines, standard foils were placed at the sample position under the same experimental conditions. In order to obtain the geometrical constants for scattered peaks, several standards comprising of compounds or mixtures (of known stoichiometry) of low-Z elements were prepared and irradiated in identical experimental conditions. The average geometrical scatter constants $G_{coh} = 102.0$ and $G_{inc} = 92.9$ along with the average geometrical fluorescence constant $G_{F} = 7.64$ had been used for the quantitative analysis using QXAS.

The pellets made from the NIST standards (SRM 2586: soil and 1570a: spinach) were quantitatively analysed with the QXAS program. Their results are found to be within 10% of the cited values by NIST. After establishing the validity of the method with the NIST-SRMs, the samples of cauliflower root soils, edible flower parts and leaves were quantified following the same procedure.

4. Results and discussions

The EDXRF quantified elemental distributions in the root soil of samples of Dp1,2 and of Cs1,2 show that concentrations of trace metals Cr, Mn, Ni and Sr are higher in the

dumping site samples while Cu, Zn and Pb are higher by almost an order of magnitude compared to the countryside samples (see figure 2).

Most ions, along with the available toxic ones are expected to get accumulated in the leaves. Leaf samples of the cauliflowers from the dumping site Dp1 showed higher concentrations of Fe, Cu and Pb, although the concentrations of these elements in both Dp1 and Dp2 soil samples were high. Pb was below the detection limit for other samples.

It is quite remarkable that the edible part of cauliflower of the two samples from Dhapa (Dp1,2) as well as the two control samples from countryside (Cs1,2) did not show much difference in elemental compositions. A slightly higher (almost 1.5 times) concentration of Ca and Fe was seen in Dp2 compared to the other three samples. Cu concentration was approximately twice higher in sample Dp1 than in Cs1,2. Pb was found to be below the detection limits in all the edible parts in spite of its significant presence in the dumping site soils.

5. Summary

In the present investigation, radioisotope-induced EDXRF method has been employed to obtain the absolute quantification of elements in flower, leaves and root soil of the
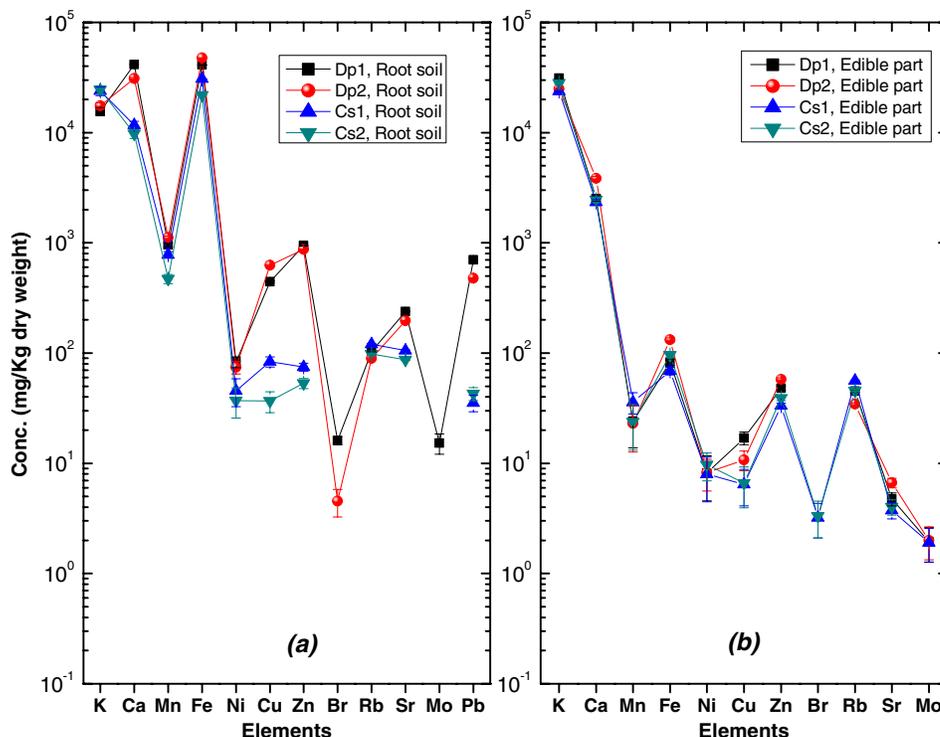
Figure 2. Comparative plot of concentrations (mg/kg dry weight) of elements in (**a**) cauliflower root soils and (**b**) cauliflower edible parts of MSW dumping site samples Dp1, Dp2 and country side samples Cs1, Cs2, respectively.

cauliflowers grown on a municipal waste dumping site and uncontaminated village soil. A unified calibration approach has been adopted in the characterization of dark matrices of the three different sample matrices, i.e. the soil, the leaf and the flower. The observations of the present experiment suggest that there is significant difference in the cauliflower root soil samples of the two sites and enhanced presence of toxic elements in the contaminated soil. The leaves which uptake salts directly through the root from the soil also show enhanced presence of heavy elements like Cu, Zn and toxic element like Pb. But the elemental distributions in the edible flower components of the cauliflowers grown on contaminated and uncontaminated sites are very much similar. These similar elemental concentrations in the edible parts show that there is a well-controlled regulatory mechanism for accumulation of elements in the flower or fruit.

Acknowledgements

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