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Profile of selenium in soil and crops in seleniferous area of Punjab, India by neutron activation analysis

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Abstract In the Nawanshahr–Hoshiarpur region of Punjab, India, more than 1000 hectares of agricultural land is significantly affected by high levels of selenium (Se). Studies were carried out to examine Se levels in soil and crops such as wheat grains, wheat husk, rice, maize and mustard using neutron activation analysis. The Se concentrations in soil and crop products were found to be ranging from 2.7 to 6.5 mg kg^{-1} and 13 to 670 mg kg^{-1}, respectively, indicating significantly high selenium in these crop products. Two reference materials were analysed for Se contents by INAA as controls.

Keywords Selenium · Soil · Crops · INAA

Introduction

Selenium (Se) occupies the 70th position in order of abundance among naturally occurring elements. It combines with both metals and non-metals, directly and hydrochemically and can form both organic and inorganic compounds. The prominent regions known for high levels of environmental selenium include China's Great Plains [1, 2], Canada [3], Mexican belt [4], certain pockets in Latin American countries, New Zealand and Australia [5]. The region that has been extensively examined for selenium is Kesterson Reservoir in California, USA where Se concentrations were between 40 and 70 mg kg^{-1} in top soil [6].

Pockets of seleniferous soils have also been identified in India especially in the Northeastern parts of Punjab [7] and Haryana [8]. In the Nawanshahr–Hoshiarpur region in Punjab, Se in the soil ranged from 0.25 to 4.55 mg kg^{-1} with a mean value of 3.63 mg kg^{-1} [9–11]. In this region, the irrigation water source being exclusively ground water, Se concentration is as high as 479 μg L^{-1} with a mean value of 170 μg L^{-1} [11]. Limited observations on human population in selenium contaminated areas have also reported selenium toxicity due to consumption of grains and vegetables harvested from selenium-rich agricultural soils [7, 12]. The average selenium intake of both men and women and corresponding Se in human nails (4.4 mg kg^{-1}), hair (2.5 mg kg^{-1}) and urine (0.26 μg mL^{-1}), were significantly higher than that in the non-endemic area (0.1, 0.05 and 0.01, respectively) and exceeded the maximum tolerable limit in more than 60% of the men [12]. The tolerable upper level (TUL) Se-intake for adults is 400 μg day^{-1} [13] against the daily requirement of 40 μg [14].

Instrumental neutron activation analysis (INAA) [14–17] has been extensively used to determine the levels of total selenium in environmental and biological samples [14–17] and also has been used for Se quantification in samples from this seleniferous region. In the present study, samples of soil and crop products like wheat grains, wheat husk, rice, maize and mustard from two locations of Punjab, India were analysed by INAA for their selenium contents. Two reference materials namely CRM DOLT-1 of National Research

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Council of Canada (NRCC) and SL-1 of International Atomic Energy Agency (IAEA) were analysed to evaluate accuracy of INAA method.

Experimental

Plants and rhizospheric soil samples were collected from the severely (village Jainpur) and moderately (village Barwa) affected pockets of the seleniferous belt. Plant parts namely leaves, stems and grains were washed with tap water and dried at 40 °C before maceration using mortar and pestle. Precautions were taken during sample preparation by cleaning of the grinding apparatus with ethanol after maceration of every sample. Samples were air dried followed by oven at 40 °C for 48 h before irradiation. Elemental standard of selenium was prepared using ICP liquid standard (Spex) containing known concentrations of Se (5–20 μg) fused in pure amorphous silica powder. Control samples of DOLT-1 and SL-1 were also used. Samples and reference materials weighing about 100 mg were packed in thin aluminum foils.

The samples, the reference materials, Se standards and blank silica were introduced into Harwell cans. Samples were irradiated in self-server position of CIRUS reactor, BARC for 7 h duration with the reactor operating at a nominal power of 20 MW. The samples were allowed to cool for about 10 days before radioactive assay and were counted for 1–10 h depending on selenium concentration levels. The gamma-ray spectrometric measurements were carried out using a Compton suppressed spectrometer consisting of HPGe-BGO detector systems coupled to PC based 8k MCA card (PHAST-BARC). A typical gamma ray spectrum generated using data obtained from HPGe-BGO with Compton suppressed detection system for mustard is presented in Fig. 1. The figure indicates gamma rays (136, 264.7 and 279 keV) of ^{75}Se. The peak areas were determined using peak-fit software PHAST. The resolution of detector was 2.0 keV at 1332 keV of ^{60}Co.

Results and discussion

The selenium concentrations determined in two reference materials, IAEA SL-1 and NRCC CRM DOLT-1 are 2.82 ± 0.08 and 7.43 ± 0.18 mg kg^{-1}, respectively as against the reported values of 2.9 and 7.34 ± 0.42 mg kg^{-1}, respectively. The percent deviations from certified/information values are within ±3%. The selenium concentrations obtained in soil and crop products from two locations (villages) are given in Table 1. The uncertainties quoted in Table 1 are the standard deviations at ±1 s confidence limits obtained from four independent sample analyses and the % relative standard deviations are in the range of 1.5–5%.

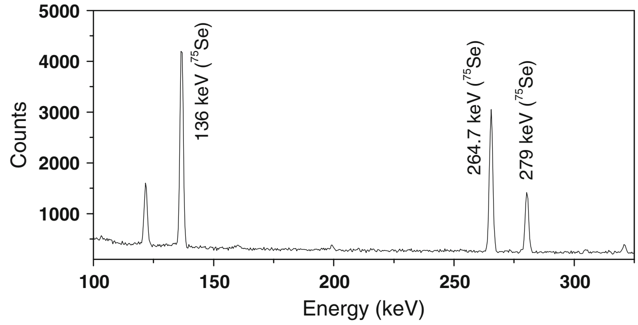

Fig. 1 Partial gamma ray spectrum of neutron activated mustard grains acquired using HPGe-BGO Compton suppressed detection system, after irradiation in Cirus reactor for 7 h and cooling period of 9 days

The selenium levels observed in the crop products (15–670 mg kg^{-1}) in this region are significantly higher than the global data on Se in food crops. The selenium levels in the wheat grain (115.1 ± 2.4 mg kg^{-1}) and husks (115.2 ± 1.8 mg kg^{-1}) were nearly same whereas in the case of mustard, the Se uptake in the seeds (670 ± 18 mg kg^{-1}) was twice that of mustard pods (278 ± 5 mg kg^{-1}). The high level of Se in mustard is presumably due to its similar chemistry with sulphur (S), which is expected to be high in mustard. Selenium levels in rice indicated a different pattern with concentration in the husk (21.7 ± 1.1 mg kg^{-1}), which is greater than the level observed in grains (16.21 ± 0.5 mg kg^{-1}). Relatively low uptake of selenium by rice crop was assumed to be due to volatilization of selenium during the water logging process, reducing the availability of selenium to plants.

Observations on the crop products from moderately affected area indicated a similar trend of higher levels in grains/seeds of both mustard (594 ± 14 mg kg^{-1}) and wheat (41.1 ± 1.0 mg kg^{-1}). The reduced uptake by the

Table 1 Selenium content in crop produce and soil collected from two villages in the seleniferous region

Crop product	Selenium levels (mg kg^{-1})	
	Village Jainpur	Village Barwa
Wheat grain	115.1 ± 2.4	41.1 ± 1.0
Husk	115.2 ± 1.8	14.9 ± 0.5
Maize	13.0 ± 0.5	ND
Mustard	670 ± 18	594 ± 14
Mustard pods	278 ± 5	263.8 ± 8.9
Rice	16.2 ± 0.5	ND
Rice husk	21.7 ± 1.1	ND
Soil	6.5 ± 0.3	2.7 ± 0.1

ND not determined

wheat was attributed to changes in agronomic practices and depth of water source. The soil samples examined from the Se-impacted pockets of agricultural lands from the two villages were found to be alkaline and contain 6.5 and 2.7 mg kg^{-1} of selenium, respectively (Table 1). The range observed in the present study is above the estimated threshold level [18] of 4 mg kg^{-1}. However, the Se levels seem to be varying within the region with Se rich and Se adequate regions observable within small tract in seleniferous belts [19].

In reference to selenium levels in foods observed in other parts of the world, wheat grain produced in North and South Dakota in the USA was reported to contain more than 2000 µg kg^{-1} Grain Se concentrations were proposed to be in the ranges of <25, 25–40, 40–1000 and >1000 µg kg^{-1} represent deficient, marginal, moderate to high and excessive concentrations in China [14, 20], respectively. The recommended dietary allowances (RDA) for selenium for adults, both male and female, are 55 µg day^{-1} with TUL of 400 µg day^{-1} [13, 21]. If the RDA values are to be considered, the concentrations obtained in grains are exceeding the recommended values [22]. In addition, based on the data reviewed of various crop produce from European countries [17], the observations obtained in the present study clearly indicated a substantially high uptake of selenium in the crop produce from the seleniferous soil of the region under study.

Plant foods are the major dietary sources of selenium in most of the countries throughout the world. The selenium content of the soil where plants are grown or animals are raised might influence the content of selenium in food. Mustard, mushrooms, alliums (onion and garlic), broccoli and Brazilian nuts have the ability to accumulate selenium from soil to significantly high levels [19, 23]. Selenium levels ranging from 0.3 to 0.5 mg kg^{-1} was reported in different varieties of onions grown in Japan [15]. The typical levels of selenium in vegetables and fruits in Portugal, New Zealand, Finland and Mainland China range from 1 to 25 µg kg^{-1} [14, 16, 17].

Presently, no data are available on the selenium levels in crop produce and food grains from Indian sub-continent as estimated by nuclear analytical and other techniques. Majority of the reports indicate quantification of selenium using invasive techniques. The selenium estimations carried out using differential pulse cathode stripping voltametry indicated an average intake by adult population in Mumbai region, India to be 61.9 µg day^{-1}. The average intake is within the global standards and relative above the values observed in the European countries [24]. Singular report on dietary intake of selenium in human population of seleniferous region of Punjab [12], examined using hydride-generated atomic absorption spectrometry, indicated that selenium intake in the seleniferous area was more than nine times of that in the non-endemic area with an average intake of 632 µg day^{-1} in the case of males and 435 µg day^{-1} in the case of females. Despite its biological importance, data on selenium in foods are still limited and the present work indicates a strong need for further studies. Studies are in progress to estimate and correlate the Se levels with the field practices and also to investigate the fate of Se in various environmental vis-à-vis crops to establish their biological implications.

Conclusions

Selenium in wheat grains, wheat husk, maize, mustard, mustard pods, rice, rice husk and soil collected from selenium-affected areas in the Nawanshahr–Hoshiarpur regions has been detected by INAA. The levels in crop products (13–670 mg kg^{-1}) are higher than the recommended values, indicating that Se in soil is entering the life cycle.

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