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Elemental Profiling and Identification of Eco-Toxic Elements in Agricultural Soil by Laser-Induced Breakdown Spectroscopy

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Abstract Laser induced breakdown spectroscopy (LIBS) was used to determine the elemental content and to detect probable eco-toxic elements in agricultural soil in Gazipur, Bangladesh (latitude: 24.0958 ° N, longitude: 90.4125 ° E). Soil samples were collected from three experimental plots of Bangladesh Rice Research Institute (BRRI), Gazipur and from a fallow land in the same area where no crop has been produced for a long time. This land is believed to be contaminated by the affluent discharged from nearby industries. Rice and husk samples were also collected from one of the experimental plots. Several elements such as **Ni, Cu, Zn, Fe, Ca, Al, Si, Sn, Na, K, Ti, Mn, Li, Mo, Co** were identified in the soil samples of the three experimental plots. Rice and husk samples also have the same elements including Sr, P, C and Mg. The LIBS study of the soil of the fallow land confirms the presence of the toxic element Cd along with all the elements found in the soil samples of the experimental plots. The sample from the fallow land from Gazipur was also analyzed for Cd by atomic absorption spectroscopy (AAS). The presence of 6.5 ppm of Cd in this fallow land above the tolerance limit (3 ppm) is supposedly the main reason for barrenness of the fallow land in the present case.

Keywords: *LIBS, cadmium, eco-toxic, barrenness, AAS*

1. Introduction

LIBS has been established as a fast spectroscopic technique for multi-elemental detection of elements in many diverse situations [1,2,3]. In this technique a high power laser pulse is used for the generation of weakly ionized plasma from the samples. The spectral emission lines from the excited atoms/ions of the plasma are then spectroscopically analyzed for both qualitative and quantitative detection of multiple elements in the sample. The technique is extremely versatile and powerful, and is capable of analyzing solid, liquid and gaseous samples. For example, LIBS has been used for the detection of trace elements of soils [4,5], geological analysis [6], aerosol analysis[7,8], analyses of industrial waste water [9,10] etc, to name a few.

In this paper, we used LIBS technique for the analysis of agricultural soil in Gazipur in Bangladesh (latitude: 24.0958 °N, longitude: 90.4125 °E) with a view to detect potentially harmful elements and to determine whether they (the toxic elements) get into our food chain through rice and husk.

2. Experimental Details

In the present LIBS experiment intense, transient plasma was produced by focusing the fundamental beam at 1064nm from a Q-switched Nd: YAG laser (Spectra-Physics LAB-170-10) on the sample by a convex lens of 100mm focal length. The laser pulse had a temporal width of 8nsec and repetition rate of 10Hz. The beam has a Gaussian profile in the far-field and has a beam divergence of less than 0.5m rad. The experiments were performed in air. The laser pulse energy used was 40mJ. The spot size at the sample position was about 200μm. The light emitted from the plasma was focused by a fused quartz lens (f=50mm) and collected by a 3m long multimode silica optical fiber and was then transmitted through the fiber to the entrance slit of a 750mm focal length computerized Czerny-Turner spectrograph (Acton Model SP-2758). The spectrograph was equipped with three ruled gratings: 2400, 600 and 300 grooves/mm blazed at 240, 500 and 300nm, respectively, which were interchangeable under computer control. The schematic diagram of the experimental set up and more details are available elsewhere [11].

The spectrum was detected by an intensified and gated CCD camera (Unigen II coated Princeton PI-MAX camera with 1024X1024 pixels). The ICCD camera was electrically triggered by the Nd: YAG laser pulse after a software-controlled, adjustable time delay. In this way, the intense background initially created by the high-temperature plasma was largely eliminated, and the atomic/ionic emission lines of the elements were more clearly observed. In the present experiments, a delay time t_d of 1.5 μs and a gate width t_w of 50 μs were selected for the optimum signal. Usually, spectra from a number of laser shots (about 40–80) were acquired and averaged to increase the signal-to-noise ratio. Samples were manually moved between exposures to prevent crater formation and to avoid other deleterious effects. The spectrum, captured by the ICCD camera, was transferred to the personal computer by USB cable. All the functions of the ICCD camera and the Acton spectrograph were fully controlled by the WinSpec/32 software provided by the manufacturer [12].

2.1. Sample Processing

Soil samples from three experimental plots of Bangladesh Rice Research Institute (BRRI), Gazipur, were collected with crop yield records. Varieties of fertilizers were used in different plots. The fertilizers that were applied to the fields were NPK (Nitrogen, Phosphorous Potassium), NPKSZn (Nitrogen, Phosphorous, Potassium, Sulphur, zinc) and NPKSZnCu (Nitrogen, Phosphorous, Potassium, Sulphur, Zinc, and Copper). Again samples were collected from a fallow land (of Gazipur), where no crop is produced for a long time. This land is believed to be contaminated by the affluent discharged from nearby industries (textile and paint industry). Rice and husk samples were also collected from the land where NPK fertilizer was applied.

The collected samples were powdered by hand mortar and pestle. Then the powder of each sample was passed separately through a 75 micron sieving machine which makes the sample most homogeneous to carry out LIBS experiment. Small pellets were made by using a hand press with sufficient pressure (80 bars).

3. Results and Discussions

For every sample spectra were acquired in the UV to IR region (190 to 900nm) using two gratings. A 600 grooves/mm grating blazed at 500nm was used to take spectra in the range of 360-880nm. Another grating of 2400g/mm blazed at 240nm was used for 190-360nm spectral range.

Some representative LIBS spectra for the soil sample NPK are shown in the Figure 1(a) and Figure 2(a) where different emission lines are labeled with the charge state of the elements. The standard database of atomic emission lines of the US National Institute of Standard and Technology [13] was used for the identification of the elements from the observed spectrum [14]. Table 1 summarizes the elements detected in different soil samples including rice and husk samples from the experimental plot NPK.

Table 1. Elements found in different soil samples including rice and husk. A tick indicates the presence of the element in the sample whereas a cross indicates the absence of the element in the sample

Elements	NPK	NPKSZn	NPKSZnCu	Fallow land (Gazipur)	Rice	Husk
Fe	√	√	√	√	√	√
Cu	√	√	√	√	√	√
Na	√	√	√	√	√	√
Ca	√	√	√	√	√	√
Ti	√	√	√	√	√	√
Si	√	√	√	√	√	√
Co	√	√	√	√	√	√
Ni	√	√	√	√	√	√
Al	√	√	√	√	√	√
Zn	√	√	√	√	√	√
Li	√	√	√	√	√	√
K	√	√	√	√	√	√
Cd	×	×	×	√	×	×
Sn	√	√	√	√	√	√
Mn	√	√	√	√	√	√
Sr	×	×	×	×	√	√
Mo	√	√	√	√	√	√
P	×	×	×	×	√	√
C	×	×	×	×	√	√
Mg	×	×	×	×	√	√

The LIBS spectrum for the soil samples of the fallow land in Gazipur are shown in Figure 1(b) and Figure 2(b) and the different emission lines are labeled with the charge state of the elements. In the LIBS spectra of the fallow land, we identified five (three of them shown in Figure 1(b) and Figure 2(b)) unambiguous lines of Cd which conclusively proves the existence of Cd in the soil sample of the fallow land. No other heavy/toxic metal could be detected in this soil sample.

The concentration of Cd in the fallow land was determined by AAS. In this technique, for digestion, powdered soil samples approximately 0.5gm was taken in digestion vessel. Then 10ml concentrated HNO_3 (65% annular grade) was added and the sample was micro-wave digested for 30 minutes at 115 ℃. After digestion, the sample was transferred in a 25ml volumetric flask and made up to mark with de-ionized water and then filtered. Dilution of the sample was done by de-ionized water. Cadmium (228.8nm) specific hollow cathode lamp was used for this purpose.

The concentration of Cd in the soil sample of the fallow land was determined to be 6.5 ppm by the ASS technique.

From the consolidated Table 1, it is found that the elements **Ni, Cu, Zn, Fe, Ca, Al, Si, Sn, Na, K, Ti, Mn, Li, Mo, Co** are present in all the soil samples of the experimental plots (NPK, NPKSZn, NPKSZn). Michael

E. Essington et al. [15] found the elements Al, Ca, Fe, and Mg, Ti, Ba, Na, Cu, and Mn by LIBS but they could not detect the emission lines of Cr, Ni, and Zn, P and K in soil samples. We have found Ni, Zn and K because of the greater sensitivity of our intensified and gated CCD detector.

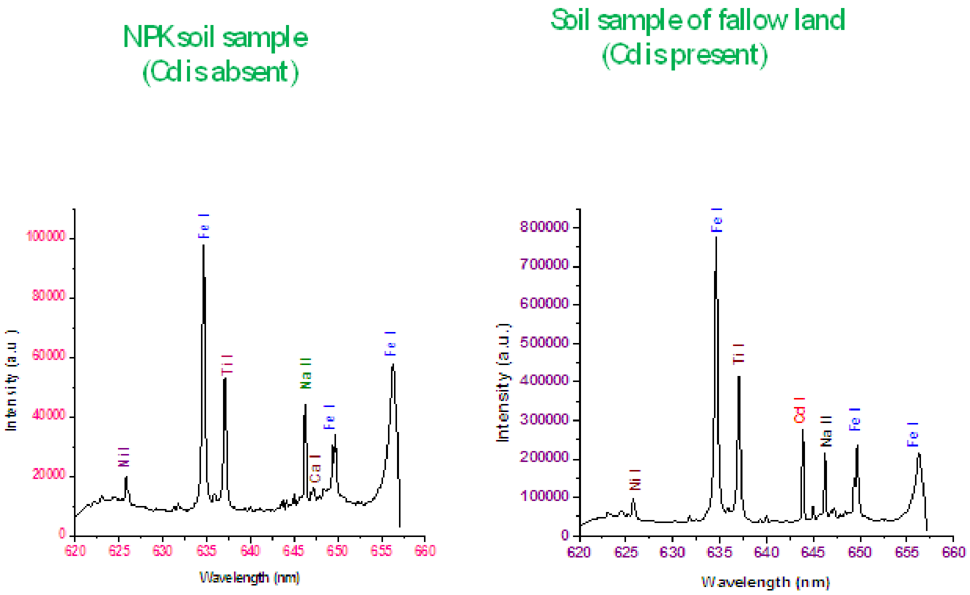

Figure 1(a) Figure 1(b)

Figure 1. The LIBS spectra of NPK soil sample (a) and of fallow land soil sample (b) in the spectral range of 620 nm to 657 nm

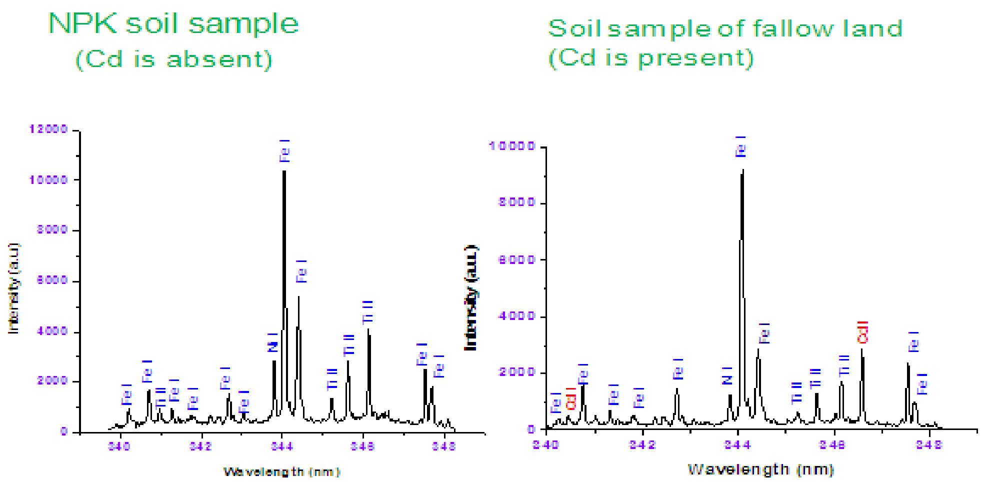

Figure 2(a) Figure 2(b)

Figure 2. The LIBS spectra of NPK soil sample (a) and of fallow land soil sample (b) in the spectral range of 340 nm to 348nm

Rice and husk samples also showed the presence of the same elements as those found in experimental soil samples in addition to Sr, P, C and Mg (Table 1). The elements except carbon enter into our food chain through rice from the soil. Carbon from atmosphere gets into our food system through photosynthesis in the leaves of the paddy plants. The concentrations of P, Sr and Mg in soil samples are perhaps below the detection limit of the present LIBS set up while the concentrations of these elements in rice and husk are high enough (due to their selective absorption by the paddy plants from the soil) to be detected by the present LIBS set up. The soil sample of the fallow land has the same elements which were found in the soil samples of the experimental plots in addition to the toxic element Cd. None of the experimental plots with significant crop yield contains toxic elements like Cd, Cr, Hg, Pb nor does the rice and husk samples. So there is no alarm for these toxic elements to get into the food chain of the people/domestic animals that uses the rice/husk from Gazipur.

This experiment has detected the presence of micronutrients (such as Ni, Cu, Zn, Fe, Mn, Na) as well as some macro-nutrients (such as Ca, K, Si) in all the experimental plots irrespective of the fertilizers given to the different plots. The addition of different fertilizers has increased the amount of these micro-macro nutrients in the soils. However no quantitative determination of these nutrients was attempted in the present study. These elements are essential for plants [16]. The study of the soil samples of the fallow land reveals the presence of toxic element **Cd** at a concentration of 6.5 ppm (which is above the tolerance limit) along with all the elements found in the soil samples of the experimental plots. The maximum tolerance limit of Cd for soil is 3 ppm [17,18].

4. Conclusion

The present LIBS technique has been applied to get an elemental profile of the soil samples of agricultural lands. Cadmium coming from the affluent discharged from nearby industries is responsible for turning the previously fertile agricultural land into a fallow land. The elemental contents of rice and husk indicate that most of the elements present in the soil get into our food chain through the rice we consume. Since no toxic elements were identified in rice and husk, there is no risk of any toxic element getting into our food chain.

Cd was found only in the fallow land. No Cd was found in any experimental plots with satisfactory crop yields. Cd has deleterious effect on plant whose presence in the soil inhibits significant plant growth in the soil. This is consistent with the known adverse effects of Cd on plant growth in general [19]. The presence of Cd in the fallow land is responsible for this land to be barren. Any chemical treatment of this fallow land which can remove the Cd, can make the fallow land productive again, since other toxic elements like Cr, Hg, Pb were not found in the fallow land.

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