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SHORT COMMUNICATION

A Quick Analysis of Various Elements (Heavy) in Sand Collected from the Topical River (Ganga and Yamuna) Using LIBS Coupled with Multivariate Technique

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Abstract The present study investigates the presence of heavy/toxic elements in the sand collected at different depths (5 cm, 10 cm, and 15 cm) from the Ganga, Yamuna basin, and the Sangam using the LIBS technique. The presence of several heavy/toxic elements is detected along with some other minerals in all samples. Sedimentation velocity is an important factor for the variation of concentration of Cr and other elements at different depths. The variation in the concentration of Cr is explained based on the settling velocity of the particle in the fluid. The multivariate analysis of the LIBS data has been applied to discriminate the sands collected from different locations and at different depths.

Keywords Ganga · Yamuna · LIBS · PCA

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The Ganga and Yamuna have glorious significance in Indian mythology and are also the lifeline of the major population. The river provides life resources to the environment and ecology [1].

River pollution is mainly caused by anthropogenic activities like the burn-up of fossil fuels and the release of industrial waste from various industries and the expulsion of sewage. It causes serious environmental and ecological problems creating harsh warnings to human beings. The Central Pollution Control Board survey reports that Delhi contributes mostly 23 percent of the total wastewater generated by continental cities around it in the Yamuna river. This causes river water pollution in most metropolitan cities [2].

Heavy elements are one of the major concerns among pollutants because heavy metals are not readily degradable. These elements may accumulate in the animal and human bodies to a very high toxic amount leading to undesirable effects beyond a certain limit [3].

The contamination of the heavy elements in the sand might be because of erosion, and weathering [4]. Sedimentation may be the key factor for heavy metal contamination and the presence of heavy metals, as the precipitation of metal carbonates, metal oxides, and metal sulfides, settle down and form the part of sediments. Sedimentation occurs when eroded material that is being transported by water, settles out of the water column onto the surface, as the water flow slows. The variation in sediment load is due to geology, geomorphology, and organic elements[4].

Laser-induced Breakdown Spectroscopy (LIBS) is multifaceted technology for qualitative and quantitative analysis of the various contaminants ranging from soil samples, sediments, and other geological materials [5]. LIBS has been employed to analyze the sand collected from Ganga, Yamuna, and Sangam regions to detect heavy metal contamination in it. Since LIBS has large spectral data, chemometric analysis (Principal Component Analysis, PCA) has been applied to discriminate the sample based on the content of pollutants in it. To the best of our knowledge depth-wise and region-wise elemental investigation of the sand has been performed for the first time.

The sand samples are collected from Ganga and Yamuna basin and the confluence area (known as Sangam) of Ganga and Yamuna. The samples are dried at a temperature of 100 °C for five hours and converted into powder using Mortar and Pestel and sieved with a 120 µm sieve, after that it was pelletized using a hydraulic press machine at a Pressure of 1200 Pa.

Sands from the Ganga at different depths (5, 10, and 15 cm) are named G5, G10, G15, and the Yamuna at depths (5, 10, and 15 cm) are named Y5, Y10, and Y15 whereas sands from Sangam at depths (5, 10, and 15 cm) are named S5, S10, and S15.

LIBS spectra of all samples have been recorded using the experimental setup as explained by Kumar et al. [6].

It is clear from Fig. 1I, that spectral lines of elements like Fe, Si, Mg, Ca, and Al is present and the spectral signatures are nearly the same in all three samples (G5, G10, and G15) but with non-identical spectral intensities. The spectral signatures of toxic/heavy metals like Cr, Hg, Ba, Sr, and Ni are also observed in all three samples. The identification of the elements has been confirmed by atomic spectroscopic data from the NIST database.

A similar spectral signature of elements as observed in the Ganga basin is also observed in all three sand samples of the Yamuna basin (Fig. 1II and Sangam (Fig. 1III. But the spectral intensities are different in the LIBS spectra of

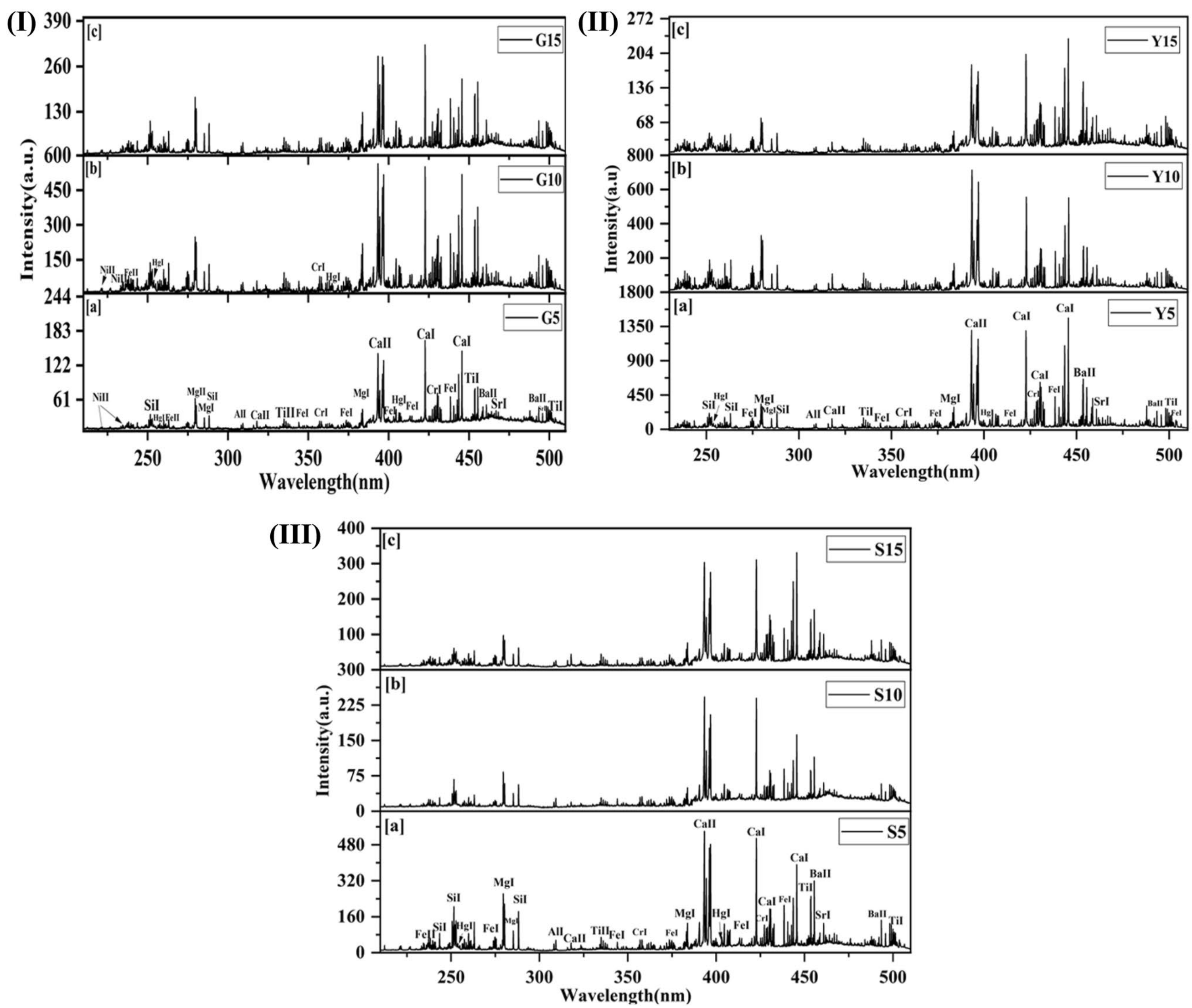

Fig. 1 LIB spectra of **I** Ganga **II** Yamuna and **III** Sangam at depths [a] 5 [b] 10 and [c] 15 cm

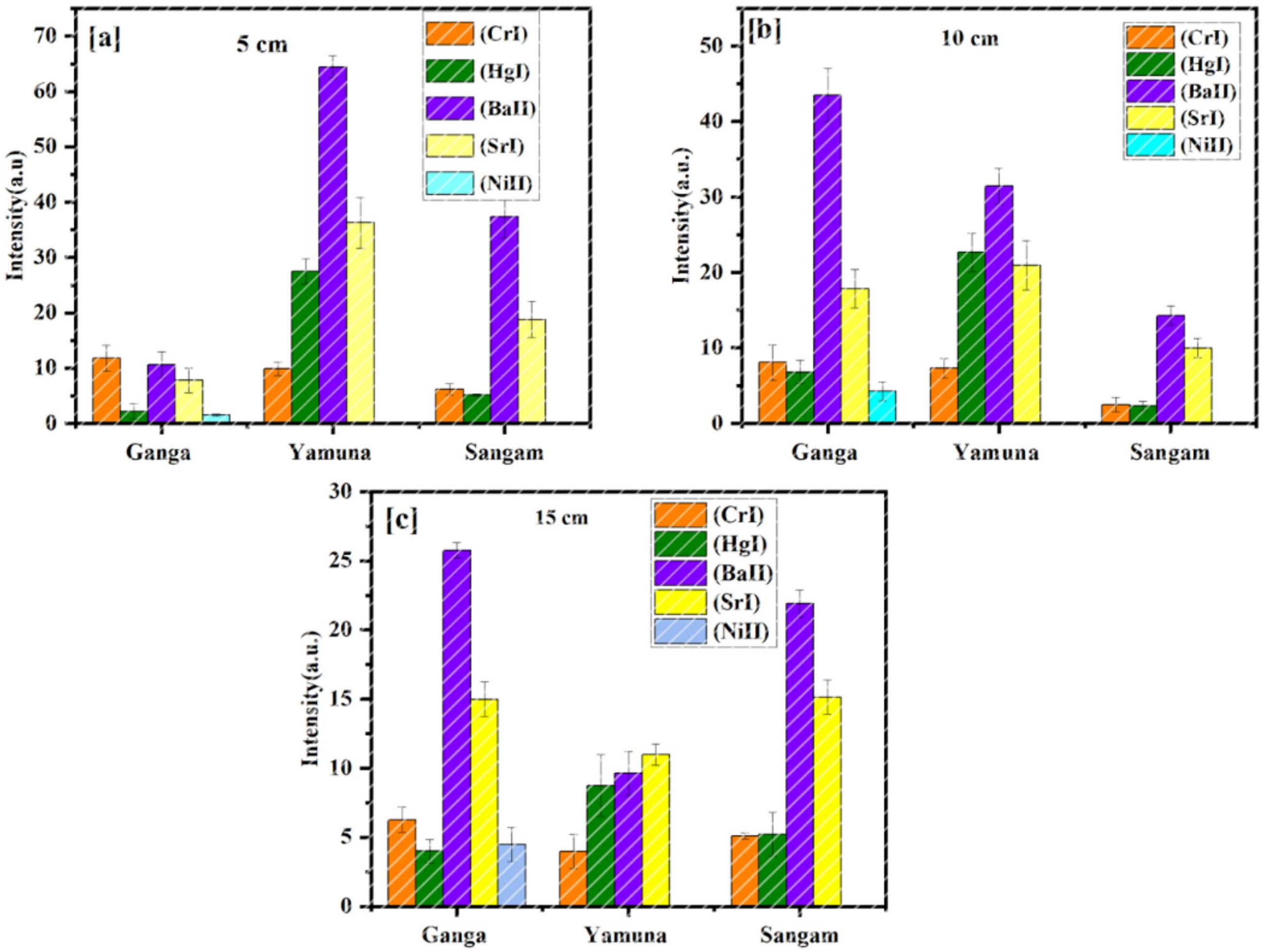

Fig. 2 Region-wise variation of the integrated intensity of heavy/toxic metals in sands at depths at **a** 5 cm **b** 10 cm **c** 15 cm

all sand samples. By comparing the LIBS spectra of all samples, it is clear that the spectral signature of Ni is observed only in Ganga sand.

Figure 2a, b, c, shows the variation of integrated intensities at depth of 5 cm in which the trends are obtained as Y5 > S5 > G5 (Ba), Y5 > S5 > G5 (Sr), Y5 > S5 > G5 (Hg), and G5 > Y5 > S5 (Cr), at 10 cm depth, which follows the trend as G10 > Y10 > S10 (Ba), Y10 > G10 > S10 (Sr), Y10 > G10 > S10 (Hg) and G10 > Y10 > S10 (Cr) and at 15 cm depth which shows the trends G15 > S15 > Y15 (Ba), G15≈S15 > Y15 (Sr), G15 > S15 > Y15 (Cr) and Y15 > S15 > G15 (Hg).

The intensity of the spectral line of an element is directly proportional to the concentration in the samples [7]. The concentration of Cr is large in the Ganga basin which can be explained as follows:

1. The variation in the concentration at the various depth in the Ganga and Yamuna basins may be explained using the settling velocity of the particle as given below [8]

   $$\text{Vs} = g\left(\rho_p - \sigma_f\right) D_p^2/18\mu$$

   where Vs = settling velocity of the particle, g = gravitational constant, ρ_p = Particle density (5.22 g/cm^3 for Cr_2O_3 [9]), σ_f = Fluid density, D_p = Particle diameter(> 30 μm [10]), μ = fluid viscosity.

The fluid viscosity of the Yamuna river sand is higher than the Ganga river [3]; hence the settling velocity is less for a particle in Yamuna river sand as compared to the Ganga river sand. That may be a factor that, Chromium is found maximum (according to relative intensity) in Ganga river in comparison to Yamuna river (Fig. 2).

2. A large number of industrial waste having Cr salt from the different industries such as leather tanning, electroplating, and battery industries situated in Kanpur city is

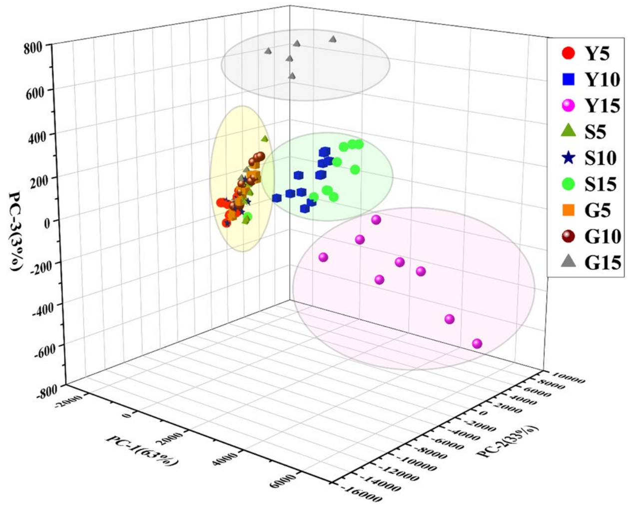

Fig. 3 3D-Score plot of LIBS data of Ganga, Yamuna, and Sangam sands

coming directly into the Ganga river [6]. Therefore the concentration of Cr is large in the Ganga basin.

Principal Components Analysis (PCA) has been employed to discriminate the sand samples based on their LIBS spectral data. In the score plot (Fig. 3), each data points represent one spectrum of the sand sample. Data points are clustered according to their similarities in LIBS spectral data. Data corresponding to Y15 and G15 are forming two groups on the positive side of the PC1 axis whereas data points of S15 are clustered in between data points of G15 and Y15. The loading plots of PC1, PC2, and PC3 are given in Supplementary Figure S1.

This study reveals that heavy elements such as Cr, Hg, Ba, and Sr along with other elements like Fe, Al, and Ca are present in the sands at different depths of Ganga, Yamuna basin, and Sangam. The concentration of Cr at 5 cm depth is higher than 10 and 15 cm depths in Ganga, whereas Hg, Sr, and Ba have higher concentrations at 10 cm comparable to 5 and 15 cm. The variation in the concentration of Cr in the Ganga and Yamuna basins is explained using the settling velocity of the particle in the fluid. PCA successfully discriminates samples according to the region and depthwise. Our results reflect that sands collected from Sangam at different depths have mixed spectral features as observed in sands from both Ganga and Yamuna.

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Declarations

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