



Portable laser induced breakdown spectrometry to characterize the environmental impact of potentially hazardous elements of suspended particulate matter transported during a storm event in an urban river catchment



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ABSTRACT

The main objective of this work is to provide researchers with a fast methodology of analysis capable to assess water quality in an urban river catchment during extreme rainfall events without previous elemental quantification. The analytical methodology combines measurement with portable laser-induced breakdown spectroscopy (LIBS) and direct chemometric treatment of the LIBS spectra. With this aim, suspended particulate matter (SPM) samples were collected during five storm events, every 2 h with an automatic water sampler in three control points (gauging stations) of an urban river (Deba River, Basque Country, Spain). SPM samples were analyzed in situ by a handheld laser induced breakdown spectrometry (HH-LIBS), and the complete LIBS spectra were statistically analyzed by Principal Component Analysis (PCA) after outlier identification by k-nearest neighbors (kNN). The PCA results showed differentiation between monitored localizations and the period when the storm event occurred. It was also possible to identify important discriminant variables, some of them corresponding to hazardous elements such as Pb, Cr, Ni, and Cu. Basing on the correlation between variables, it was possible to identify their sources (urban/municipal contamination, anthropogenic activities, etc.). Moreover, thanks to this methodology, it was possible to predict the mobilization of hazardous elements at the end of a storm event and determine the environmental risk assessment in an urban river.

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1. Introduction

Hazardous elements (HEs) present in water systems can come from different pathways, such as natural inputs (rocks, minerals, etc.) and/or anthropogenic sources (transformation products, industrial activities, mining activities, untreated effluents from municipal waste waters, intensive agriculture, etc.).

Although HEs are frequently incorporated in riverine waters in the lattice of freshly formed inorganic compounds such as Al, Fe and Mn (oxy)hydroxides, or absorbed onto organic matter [1–3], it has been observed an increase of various heavy metals as insoluble compounds in SPMs and a decrease of their dissolved forms [4,5].

SPM is composed of colloids and particles with different sizes including heterogeneous aggregates of mineral, organic, and biological phases [6]. Its composition is influenced by river-derived material, geologic nature of the catchment area by weathering of rocks, anthropogenic inputs, etc. HEs in water tend to accumulate in SPM because of its direct interface with water. The high available surface area of SPM is adequate for the adsorption of components such as oxyhydroxides, aluminosilicates, etc. Environmental factors such as pH, dissolved oxygen, electrical conductivity of the water, together with the type of metal transported and the composition of the SPM (humic organic ligands or colloids, etc.) play also an important role on the adsorption process of metals onto SPM. Hydrological conditions during storm events are also important.

The transport of SPMs occurs predominantly during discharge events [7,8]. During a rainfall/storm, flood/discharge event or snow melt in contaminated water systems (river, estuary or lakes) the fate and behaviour of pollutants such as nanoparticles, nanominerals and

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HEs adsorbed or deposited into SPMs is a phenomenon with effects on the environment, biota and also on human health. Despite metals such as Pb, Zn, and Cu adsorbed to SPMs are often present in relatively bio-available reducible forms [1] the adsorption process of HEs onto SPM is not risky in itself. The deposition of HEs adsorbed onto SPM in specific areas of a riverine system is the primary process for the accumulation of heavy metals from the overlying water to the sediment. Sediments may act as a temporary or long-term sink for the pollutants they are associated with [9]. The chemical redistribution processes between bed and suspended sediments is hardly dependent on environmental (nature and amounts of releases in the riverine system), chemical-physical and hydrological conditions [10].

Almost all the analytical procedures used for the determination of HEs in SPM include an acid extraction together with elemental analysis of the extracts by inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) or atomic absorption technique (AAS), between others [11–13]. The extraction step usually required before the use of these analytical techniques impedes the possibility to analyze some other analytes and/or parameters in the samples due to its destructive character. The aggressive chemicals used in extraction steps are considered HE by themselves.

Direct analysis or in situ analysis by Laser-induced breakdown spectroscopy (LIBS) analysis is a good alternative to these traditional techniques [14]. LIBS is a fast (order of seconds) spectroscopic technique for multi-elemental compositional analysis for all kind of solid samples such as sediments. LIBS doesn't require consumables or sample preparation before the analysis, thus, SPM samples can be analyzed successively without being destroyed. LIBS meets the principles of the Green Chemistry [15]. Moreover, the sample spectra obtained from LIBS are complex and contain a lot of information, but unfortunately extracting useful information like underlying patterns is difficult and a challenge. The LIBS spectra obtained from the analysis of soils and sediments contain important and useful information about elements considered as pollutants such as heavy metals, but usually this information is mixed with the signals of the major constituents of the samples. The difficulties related to the applicability of LIBS for the analysis of trace elements in environmental samples has been illustrated in different works [16,17].

In this study an analytical methodology based on the combined use of portable LIBS and chemometrics on LIBS spectra is used. The main advantage and innovation of our method is that it can assess the water quality in situ without previous elemental quantification. The objective of this combination is to investigate the environmental influences that flood events charged with SPM could have in urban/industrial river catchments. The methodology proposed could be carried out in situ and just when the rainfall or the storm takes place, respecting besides the principles of environmentally friendly chemistry, Green Chemistry. The combination proposed has been used in the Deba River (north of Spain) with satisfactory results.

2. Methods and materials

2.1. Study area and sample collection

LIBS and chemometrics were used to study the Deba River Catchment (533,8 km² of area), one of the most polluted rivers in the province of Gipuzkoa (Basque Country, north of Spain) [18]. The Deba River is 58 km long with several small tributaries (Arantzazu, Urkulu, Aixola, Sallobente, etc.), but the Ego and the Oñati rivers, are the most important ones. The mean water discharge of the basin is around 10,89 m³/s, which means an annual discharge of 457 hm³. Highest discharges are recorded principally in winter, between December and February.

Due to its industrial history, the population around Deba River is around 135.000 inhabitants. The three most important urban areas are Eibar, Arrasate and Ermua, where the 50% of all the inhabitants live.

The main industrial activities currently in force in the area are metallurgy, galvanism and automotive plants, and they are focused near the main channel of the river. Despite the waste water treatment plants built to prevent the contamination of the river water, a great quantity of water is still discharged directly to the river, without any previous treatment [19,20].

For the SPM collection three gauging stations, Altzola (AL), Oñati (OÑ) and San Prudencio (SP) were chosen. AL (near to the river mouth) is located in the municipality of Elgoibar and drains a total catchment area of 464.25 km². SP (near the confluence of the main channel with the Oñati River) located in the main channel the Deba River, drains a sub-catchment of 121.78 km². The last, OÑ is situated in the Oñati tributary river, in the municipality of Oñati, near SP, and its area is about 105.78 km² (see Fig. S1).

Table 1 shows the 27 water samples collected for the SPM capture during five flood events/campaigns. Two campaigns correspond to 2014 (the first flood event of May was identified as A and the one of November as C), one to January of 2015 (D campaign), and the last two were collected in February of 2016 (E and F).

For the sampling of water samples an automatic water sampler (SIGMA 900), consisted of a sample container holding up to 24 bottles and an outlet pipe made of polyethylene, was installed at each gauging station. Bottles were previously washed in 10% (v/v) nitric acid for 24 h and then rinsed with Milli-Q water prior to sampling. To ensure monitoring of events the autosampler was programmed to start pumping when turbidity in the stream reached 100 NTU. Water samples (800 mL) were pumped by an air pump vacuum system and the frequency of the sampling was every 2 h during the event. For the capture of SPM, the water samples were filtrated through 0.45 µm filters.

2.2. Handheld LIBS spectrometer

A handheld EasyLIBS IVEA system (model Easy 2C) was employed for the measurements on the filters with SPM. For the analysis, filters containing enough sediment quantity (a thickness of at least 2 mm) were selected. The portable EasyLIBS IVEA system employs a pulsed Nd:YAG laser, with the possibility to dual pulse mode, and emits at the fundamental wavelength of 1064 nm. The laser energy per pulse on the sample is higher than 25 mJ with a repetition rate of 1 Hz and

Table 1
Identification of the SPM samples analyzed.

Sample	Gauging station	Campaign	Campaign code	Sample code
11	Oñati	2016/02/15	E	11ONE
12	Oñati	2016/02/15	E	12ONE
13	Oñati	2016/02/15	E	13ONE
14	Oñati	2016/02/15	E	14ONE
15	Oñati	2016/02/15	E	15ONE
16	Oñati	2016/02/15	E	16ONE
17	Oñati	2016/02/15	E	17ONE
18	Oñati	2016/02/15	E	18ONE
3	San Prudencio	2016/02/15	E	3SPE
6	San Prudencio	2016/02/15	E	6SPE
7	San Prudencio	2016/02/15	E	7SPE
8	San Prudencio	2016/02/15	E	8SPE
2	Altzola	2014/05/30	A	2ALA
4	Altzola	2014/05/30	A	4ALA
6	Altzola	2014/05/30	A	6ALA
2	Altzola	2014/11/17	C	2ALC
4	Altzola	2014/11/17	C	4ALC
7	Altzola	2014/11/17	C	7ALC
12	Altzola	2014/11/17	C	12ALC
18	Altzola	2014/11/17	C	18ALC
3	Altzola	2015/01/29	D	3ALD
9	Altzola	2015/01/29	D	9ALD
19	Altzola	2015/01/29	D	19ALD
4	Altzola	2016/02/27	F	4ALF
8	Altzola	2016/02/27	F	8ALF
14	Altzola	2016/02/27	F	14ALF

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