

# ON-SITE ANALYSES AS A DECISION SUPPORT TOOL FOR DREDGING AND SUSTAINABLE SEDIMENT MANAGEMENT

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## ABSTRACT

On-site chemical characterisation technologies are of key importance for sustainable management of sediments in a perspective of circular economy, either in a marine (harbours) or inland (waterways) context.

They allow the collection of data on mineral chemistry of sediments, in view of the evaluation of their suitability for a reuse scenario, as well as on their contents in contaminants, in order to provide a first evaluation of their acceptability.

On-site characterisation technologies can be profitably used at several stages:

- during detailed sediment mapping prior to dredging. On-site analyses of each sample provide a better data quality than composite analyses and allow refining the dredging strategies,
- during dredging operations allows a better management of each load, according to contamination and reuse suitability,
- for selective storage and processing of sediments stocks on land,
- during the application of reused sediments.

Portable X-ray fluorescence (pXRF) allows routine measurements for many major elements and inorganic contaminants. Some contaminants cannot be routinely analysed but may be detected when present at elevated levels. Light or volatile organic contaminants can be routinely detected with portable gas chromatography and GC/MS. .

The detection of heavier organic contaminants, the measurement of light elements, and the identification of mineral phases still require emerging technologies (pFTIR, pXRD, LIBS, and portable microRaman spectroscopy).

Data obtained with on-site technologies cannot be used for compliance, but they are invaluable for decision support. They provide immediate results – usually within minutes – and allow dynamic or adaptive sampling strategies. A laboratory confirmation scheme is still required for validation, but sample selection for laboratory analyses is improved if on-site measurements are available.

*Keywords: portable XRF, contaminated sediments, waterways, harbour, dredging*

## INTRODUCTION

The management of sediments in a sustainable perspective of circular economy, requires real time decisions during operations, either about their suitability for reuse scenarios (mineral chemistry) or about their level and type of contamination. Delays for laboratory analyses are usually too high. This is necessary for both marine (harbours) or inland (waterways) sediments.

On-site chemical characterisation technologies allow the collection of data on sediments, in view of the evaluation of their suitability for a reuse scenario, as well as on their contents in contaminants, in order to provide a first evaluation of their potential risks and their acceptability.

However, management decisions need sometimes a rapid evaluation of critical properties in order to fit operational constraints, such as dredging

operations, dredged loads management or sediment batches application during works.

## SCOPE

Data obtained with on-site technologies cannot be used for compliance, but they are invaluable for decision support. They provide immediate results – usually within minutes – and allow dynamic or adaptive sampling strategies. A laboratory confirmation scheme is still required for validation, but sample selection for laboratory analyses is improved if on-site measurements are available.

### Prior to dredging operations

Data collection can be carried out during detailed sediment mapping prior to dredging. This is usually performed with laboratory analyses on composite samples, in order to evaluate precisely the level of risk associated with the whole lot of dredged sediments, similarly with the management of waste flows. On-site analyses of each subsample provide a much more precise map of the contamination, a denser data set, and therefore a better data quality than composite analyses (Fig. 1). This allows refining the dredging strategies, optimising environmental dredging and delineating contaminated sediment zones for selective dredging.

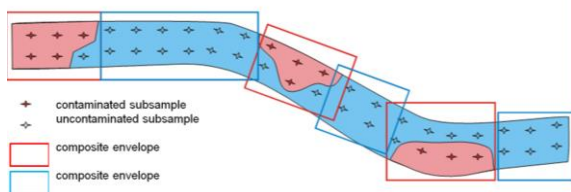


Fig. 1 Detailed analysis program on a canal, with individual subsamples (on-site) and composites (lab), for selective dredging.

### During dredging operations

Sediment characterisation during dredging operations allows a better management of each load, according to contamination and reuse suitability. If the dredging operation is based on a preliminary contamination map, on-site analyses should confirm the expected level of contamination of each sediment load.

### Dredged loads management operations

On-site analyses allow selective storage and processing of sediments stocks on land. If the dredging operation is a batch one, measurements on loads may help to redirect each load towards selective disposal or treatment options (hazardous, non hazardous or inert, depending upon the type and concentration of contaminants). If it is a selective dredging operation, on-site analyses are used to verify that the nature and level of contamination dredged material is the same as expected from the initial characterisation map.

### Reuse operations after disposal

Inert or non-hazardous sediments stored at a disposal site may be available for reuse in civil works or other applications, after a dehydration time or after specific treatment operations to reduce contamination.

On-site analyses allow a verification of the contaminants level, and of other physicochemical properties of interest for the reuse application needs. They contribute to reduce any risks involved in reuse. They contribute to public and authorities acceptance through public monitoring data.

### Long term monitoring

A monitoring program can be led on the civil works in which sediments were incorporated. This is intended at providing public information on the behaviour of sediments, and on contaminants emissions from the works.

Such programs contribute to public acceptance of sediments as building materials if the monitoring data are published.

On-site analyses allow more closely spaced, and more frequent analyses than sampling and laboratory analyses. They allow a quicker feedback and are better understood by communities. Laboratory confirmation is required for anomalies.

## TECHNOLOGIES

Many laboratory analysis methods were made available to field investigation in the last decades, both for inorganics (pXRF [1]-[2]) and organics (GC and others).

Emerging technologies provide promising perspectives for the detection of heavier organic contaminants, the speciation of some inorganic contaminants, the measurement of light elements, inaccessible to pXRF, and the identification of mineral phases. These include portable Fourier transform infrared spectroscopy (pFTIR), portable X-ray diffraction (pXRD), laser-induced breakdown spectroscopy (LIBS) and portable microRaman spectroscopy.

### pXRF

Among currently available technologies for sediments, portable X-ray fluorescence (pXRF) is one of the best known, and its operation is straightforward (Fig. 2). It allows routine measurements for most of the major elements (Ca, Fe, K, Ti, Mn, and with less precision, Si, Al, P, S and Cl) and for many inorganic contaminants (or "heavy metals": Pb, Zn, Cu, As, Sb, Cr, V, etc, Fig. 3). Its analytical range (Table 1) is less sensitive than the range of many recent laboratory techniques, but nevertheless sufficient for the discrimination of contaminated sediments.

Table 1 Analytical ranges for selected elements in sediments, by pXRF

Element	LD	Element	LD
SiO <sub>2</sub>	1 %	Pb	5 ppm
Fe <sub>2</sub> O <sub>3</sub>	500 ppm	Zn	10 ppm
TiO <sub>2</sub>	100 ppm	Cu	10 ppm
K <sub>2</sub> O	500 ppm	Ni	20 ppm
CaO	500 ppm	Cr	20 ppm
MnO	100 ppm	Cd	10 ppm
S	1000 ppm	As	10 ppm
		Hg	20 ppm

Note: all elements in ppm (mg/kg) on the instrument. Conversion to oxide % for major elements. LD: lower analytical limit

Some contaminants (Hg, Cd, Ag) cannot be routinely analysed at low concentrations but may be detected when present at elevated levels.



Fig. 2 pXRF analysis onboard a sampling boat.

Though adversely affected by moisture, pXRF can be used for screening or decision help purposes after a rapid dehydration procedure [3].

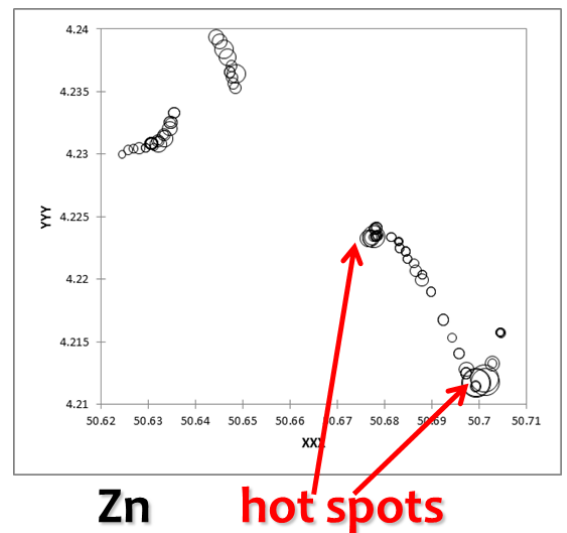
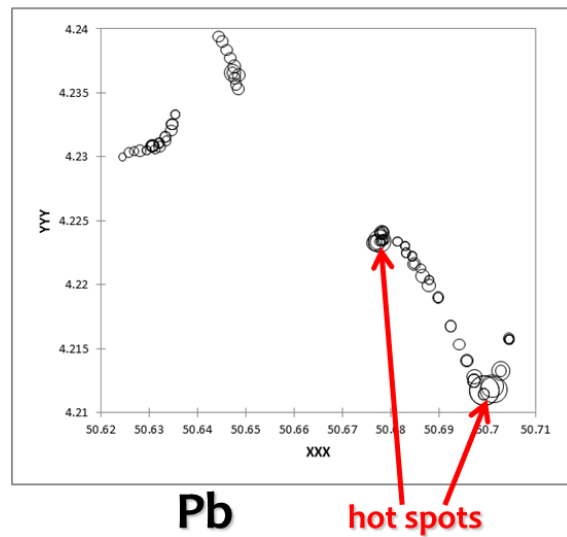


Fig. 3 Mapping pollution hotspots on a canal with pXRF.

### LIBS

Laser-induced breakdown spectroscopy (LIBS) is a fast developing technique, but still far from the routine status of pXRF. It provides semi-quantitative measurements for some major elements (Ca, Fe, Mg, Si, Na, C, N, O), trace elements (Li, Be, B) and inorganic contaminants (Pb, Zn, Cu, Ni, Cr, V). While published results did not show the same level of robustness as pXRF for the same elements, its real benefit is the possible measurement of light elements, inaccessible to pXRF [4,5].

## pXRD

Portable X-ray diffraction (pXRD) was first developed for the mining industry. Instruments are heavier and bulkier than most pXRFs.

pXRD allows the identification of mineral phases, similarly to laboratory XRD, but with compromises due to instrument size and tube characteristics.

Its application to sediments is not yet documented, though possible (quartz, carbonates, oxides, sulphides). Mineral phase identification can be used as a guide for civil engineering or cement material applications.

## Gas chromatography

Portable gas chromatography and GC/MS provide routinely field data on light or volatile organic contaminants. It is traditionally used for soil analyses at contaminated sites.

Though these contaminants are easier to manage than inorganics or heavier organics, they may play a part in hazardousness classification, and in requirements for treatment at the disposal site, such as bioremediation.

Their on-site measurement is therefore desirable at all the sediment management stages.

## pFTIR and $\mu$ Raman

Portable Fourier transform infrared spectroscopy (pFTIR) and portable microRaman spectroscopy ( $\mu$ Raman) are emerging technologies and their application database is still thin, despite the fact that both are based on well-known laboratory technologies. Their focus is not on elements but on atomic bonds. They are currently investigated for the detection of heavier organic contaminants, the speciation of inorganic contaminants, and the identification of mineral phases.

pFTIR is easier in first approach, but it suffers from intense absorption from water and from dark organic matter - both ubiquitous in sediments.

$\mu$ Raman is more complex and subject to many interferences, including the nature of incident light and the fine-tuning of the distance to the sample.

As both methods are highly matrix-sensitive, and no protocol is currently available for the analysis of any contaminant, the current approach is to determine baseline spectra, on samples without organic contaminants, spiked spectra (with known amounts of the expected contaminants added to an uncontaminated sample, and compare them with spectra of possibly contaminated sediments.

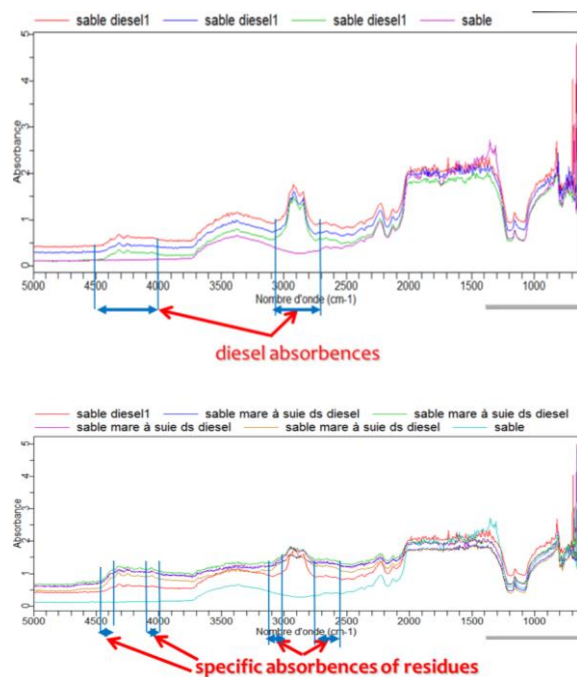


Fig. 3 pFTIR analysis of diesel- and PAH residues-spiked silica sand.

## DECISION SUPPORT INTERPRETATION OF ON-SITE ANALYSES

Using field data for real-time decision making without waiting for laboratory results is possible if the differences between them are known and estimated prior to operations, and if the uncertainty is quantified. Examples are given for pXRF (Fig. 4) but the principle can be extended to any on-site method.

In the second case (phosphate), probable concentrations may be calculated with reasonable accuracy from field data using a simple  $y=ax+b$  correction. The uncertainty on the corrected data is based on the dispersion of data around the black axis.

Another application is the evaluation of actual concentrations from measurements performed on wet sediments. A quasi-linear relationship between wet and dry measurements (Fig. 5) allows an acceptable prediction of concentrations on wet material without drying.

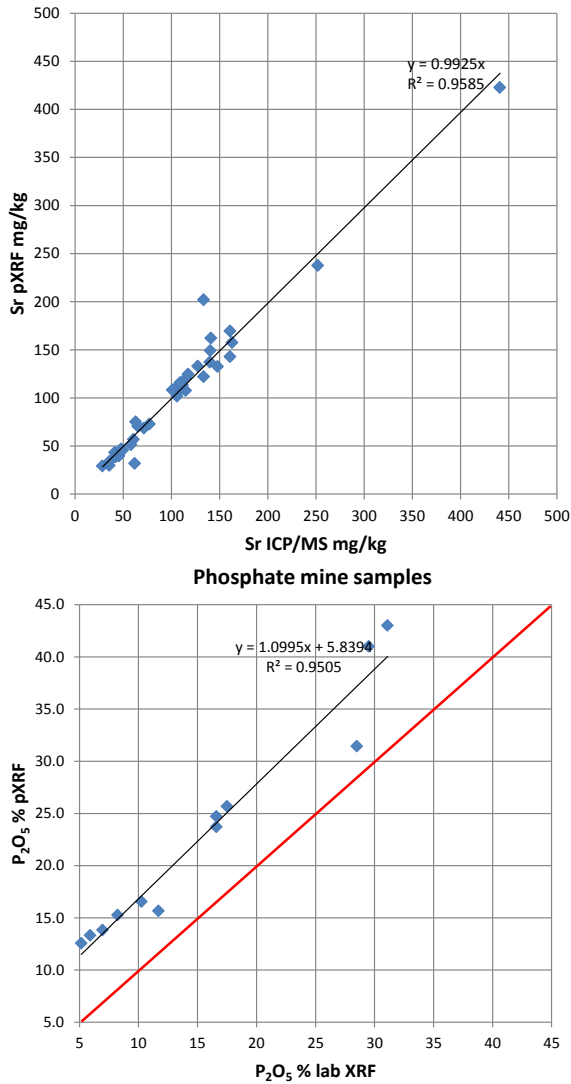


Fig. 4 Bias and shift between on-site and laboratory analyses for an accurately analysed (Sr) and a biased (P) element. [4]

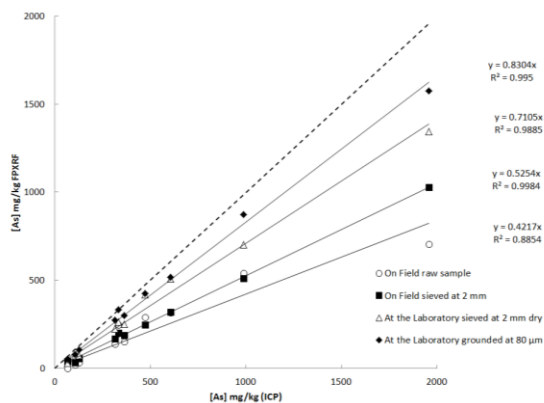


Fig. 5 Bias and shift between on-site and laboratory analyses for an accurately analysed (Sr) and a biased (P) element. [4]

The key factor for decision making (accuracy) may be substituted by precision if there is a linear relationship between on-site and laboratory data, especially if the intrinsic uncertainty of on-site data is known. This condition is met for pXRF and allows the quantification of the level of confidence of decisions based on it (Fig. 6).

Application of on-site methods to compliance control should therefore take into account any correction factor calculated from a consistent set of data, made of on-site and lab analyses on a set of local samples analysed before the operations, and on the uncertainty segments for each of them (Fig. 5).

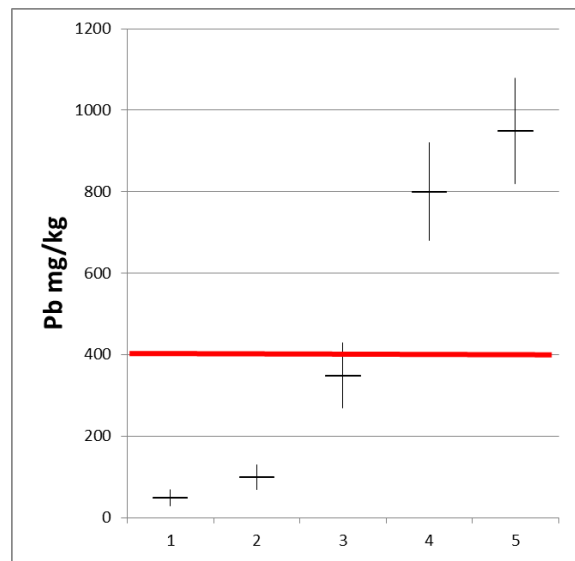


Fig. 6 Confidence of a decision made on corrected on-site analyses (Pb) in relation with a regulatory threshold (in red).

## CONCLUSIONS

On-site analytical techniques bring an invaluable help to sediment management projects, to sediment reuse and therefore are a key factor for the implementation of circular economy strategies. They promote shifting dredged sediments from a very bulky waste status towards that of a mineral resource, available as a substitute to mineral extraction.

On-site techniques allow real-time decisions during dredging, disposal and reuse operations, with time- and cost-effectiveness as a direct benefit.

They cannot replace laboratory analyses for risk analyses and regulatory compliance, or for reuse application development, but they can provide a reliable estimate of compliance if the result is higher or lower enough to avoid uncertainty overlap. It is also highly recommended to incorporate a laboratory analysis program on selected samples in any on-site

analysis program, in order to ensure reliability in sediment management decisions based on analyses.

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#### REFERENCES

- [1] Stallard, M.O, Apitz, S.E., & Dooley, C.A. (1995) X-ray fluorescence spectrometry for field analysis of metals in marine sediments. *Marine Pollution Bulletin*, 31 (4-12), 297-305.
- [2] Kirtay, V.J., Kellum, J.H., & Apitz, S.E. (1998) Field-portable X-ray Fluorescence Spectrometry for metals in marine sediments. *Water Science and Technology* 37, 6–7, 141–148
- [3] Lemiere, B., Laperche, V., Haouche, L. & Auger, P. (2014) Portable XRF and wet materials: application to dredged contaminated sediments from waterways. *Geochemistry: Exploration, Environment, Analysis* 14, 257-264.
- [4] Lemiere, B (2015) Field Analytical Techniques for Geochemical Surveys. 27th International Appl. Geochem. Sympos., Tucson, Az, USA ([https://www.appliedgeochemists.org/images/stories/IAGS\\_2015/Abstracts/27th\\_IAGS\\_Lemiere\\_Keynote\\_Field\\_Analytical\\_Techniques.pdf](https://www.appliedgeochemists.org/images/stories/IAGS_2015/Abstracts/27th_IAGS_Lemiere_Keynote_Field_Analytical_Techniques.pdf)).
- [5] Harmon, R.S., Russo, R.E., & Hark, R.R. (2013) Applications of laser-induced breakdown spectroscopy for geochemical and environmental analysis: A comprehensive review. *Spectrochimica Acta Part B* 87, 11–26.