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On-Site Analyses as a Decision Support Tool for Dredging and Sustainable Sediment Management

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Abstract: Beneficial use of dredged sediments, either in harbours or waterways, is based on their potential as alternative resources. Such sediments can be considered as bulk materials for industrial needs, which is predicated on their current waste status or meeting end-of-waste constraints. They also can be an integral part of beneficial use projects using sediments as a bulk component, including civil engineering and landscaping. This is particularly important for beneficial use projects focusing on climate change effects mitigation, such as flood protection works, coastline defence or littoral urban areas redevelopment. When dredged sediment is used as a bulk material, its acceptability is based on an assumed homogeneity of its properties. On-site analyses allow pre-dredging detailed mapping at a denser scale than laboratory ones; monitoring dredgings during operations and during processing; and continuous control of their properties at the implementation site. This is currently possible only for a selection of inorganic analytes. When dredgings are part of a larger beneficial use project, on-site analyses facilitate first the baseline survey and the sediment source characterisation. Continuous monitoring of the sediment load allows a fast detection of contamination hot spots and their adequate management. Site survey via on-site instruments allow end users and communities to check themselves the contamination level, hence acceptability is better. On-site dredged sediment analyses monitor both building properties and environmental compliance; soil and sediment analyses at receiving sites; surface and groundwater, either for impact assessment or for monitoring works. On-site instruments provide immediate results and allow dynamic or adaptive sampling strategies, as well as allowing operational decisions in real time. Confirmation by laboratory analyses is required for validation, but on-site sample screening for laboratory analyses improves their efficiency. The present paper was developed on the basis of an earlier presentation, which it developed and updated extensively.

Keywords: contaminated sediments; waterways; harbour; dredging; beneficial use; field analysis; portable XRF

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1. Introduction

1.1. Dredged Sediments Beneficial Use and Circular Economy

The sustainable management of dredged sediments in a circular economy perspective is not yet routine practice, due to limitations in operating costs, environmental uncertainties (in both the short and long term), and societal issues (acceptability, community leaders' responsibility). More than 90% of sediments dredged are still therefore relocated at sea. Selective storage and processing of sediment stocks on land is currently the preferred strategy, as it allows for delays between dredging and use, and uses these delays to perform further testing and improvement operations (dehydration, desalination, bioremediation . . .) as well as constituting large stocks of homogeneous material.

When beneficial use is considered, sediments may be directly shipped to the planned site location (example: dike or shoreline nourishment), or to a temporary location. This may be a selective storage facility or a treatment facility. Sediments that are too contaminated for beneficial use or do not have the required properties for it, and cannot be modified by an economically acceptable treatment, are sent to a final disposal site [1,2].

Despite limitations due to waste status, sediment beneficial use is an increasing alternative to minerals extraction for civil engineering, especially for beneficial use projects focusing on climate change effects mitigation, such as flood protection works, coastline defence or littoral urban areas redevelopment. Pilot projects provide opportunities to test circular economy options at a full scale and under community monitoring.

1.2. On-Site Analysis Methods for Sediments

On-site analysis techniques are far from new [3–5] but their application to sediments was first limited to exploration geochemistry and stream sediments [6,7], or to marine sediments [8,9]. Their ability to provide almost real-time results was quickly recognized. Due to their lower cost and ease of application, on-site analyses can be performed on a much larger number of samples than laboratory samples for a given budget.

While on-site analyses has continuously improved to get closer to laboratory results, it is apparent that absolute accuracy is not necessary for routine control of variations in a batch process, and for decision making purposes, as long as a robust relationship can be established between on-site measurements and accurate laboratory analyses. This relationship is usually linear, expressed by $Y = aX + b$, Y being the accurate concentration, X the on-site measurement, a being the bias and less frequently b being a systematic shift (Examples are given in Section 4.3). Thus on-site measurement results cannot be used for compliance reporting if the results are close to regulatory thresholds.

1.3. Dredged Sediments Beneficial Use and Near Real-Time Analyses On-Site

Beneficial use of dredged sediments requires both precise analyses at the design stage and large numbers of analyses, for both site and batch characterisation, during the operations. Both mineral chemistry and contamination data are needed on sediments for their suitability for beneficial use scenarios, and for control of operations. On-site analysis technologies were tested for contamination assessment as soon as they were available [8,9], and lighter matrix elements came at a later date with improved instruments. During operations, on-site analyses are needed for real time management decisions, as laboratory delays may be too large for a rapid evaluation of critical properties in the context of operational constraints [10]. This is applicable to dredging operations, individual sediment load management, treatment [11] or sediment batch applications during works. This is necessary for both marine (harbours) or inland (waterways) sediments.

On-site analyses provide a first evaluation of potential risks and suitability for use on much denser data sets and site grids, even if selected laboratory results may be necessary for full confirmation. Sample selection for laboratory analyses is improved if on-site measurements are available. On-site analyses allow dynamic or adaptive sampling strategies [12,13]. This is applicable to site investigations before application (baseline surveys) as well as to site verification after sediment application. It also al-lows for greater input from project stakeholders and communities during project monitoring.

However, on-site analyses are not yet in widespread use in full scale sediment management operations, and no references to such applications were found from an extensive literature survey. This paper aims to evaluate how far on-site analyses techniques can support the beneficial use of dredged sediments.

1.4. Scope of Near Real-Time Analyses On-Site

Many analytes may need to be determined to assess the suitability of sediments for beneficial use projects. This includes traditional environmental contaminants: potentially toxic metals and metalloids, organic contaminants, emerging contaminants, biologic contaminants, and unwanted solids: suspended particles, microplastics, etc. However, it is also desirable to determine matrix constituents, for suitability for beneficial use: physical characteristics of sediments (grain size, porosity, permeability, mechanical strength); matrix chemistry and mineralogy of sediments, including organic matter and salinity. Not all these parameters can be measured on site with the current state of technology, although the range of available parameters increases every day. For organic contaminants, operational techniques are available only for those of low molecular mass (gas chromatography) and development is still ongoing for the higher mass ones, such as PAHs and PCBs.

On-site control is effective only if most critical parameters can be measured on site with enough reliability for decision making. This requires an orientation survey to be conducted with both on-site and laboratory analyses prior to the implementation of on-site systematic surveys.

Beneficial use industrial or pilot projects comprise different phases, from preparation studies to ensure control, through operational monitoring. Before the project, a baseline characterisation of sediments to be dredged prior to their extraction is performed, both for feasibility and permitting purposes. Composite samples are usually analysed in the laboratory, to precisely evaluate the level of risk overall. On-site analyses of each subsample would provide a much more precise map of the contamination, and therefore a better data quality set than composite analyses. This allows for refining the dredging strategies, optimising environmental dredging and delineating contaminated sediment zones for selective dredging. This also includes target site investigations, baseline surveys, impact assessment and risk studies and economic viability. These investigations would also benefit from denser data grids and dynamic recognition of contamination spots.

During dredging operations, systematic monitoring of each load can be performed, according to contamination and reuse suitability, to allow a better management for selective storage and processing of sediment stocks on land, and then during the application of dredged sediments. If the dredging operation is based on a preliminary contamination assessment, on-site analyses should confirm the expected level of contamination of each sediment load. The environmental impact of dredging operations is also better monitored by on-site, real time analyses, especially for water (turbidity, contaminants), rather than by retrospective laboratory analyses on discrete samples. A verification of the characteristics of sediments that are shipped for further beneficial use after temporary storage, such as concrete, cement, or civil works, can thus be performed. Inert or non-hazardous sediments stored at a disposal site may be available for beneficial use, after a dehydration time or after specific treatment operations to reduce contamination, and then verified.

After works completion, a monitoring program can be completed on the relocation area, or the civil works in which sediments were incorporated. This is aimed at providing public information on the behaviour of sediments, and on contaminant 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 for quicker feedback and are better understood by communities and authorities.

1.5. Limitations of Near Real-Time Analyses On-Site

On-site analyses cannot reach the accuracy or precision of high quality laboratory results, and therefore cannot be used for compliance reporting if results are close to regulatory thresholds. However, the former deliver results within minutes (with a simple sample preparation) or within a few hours (with a careful preparation), while the latter come within several days at best, or more usually several weeks, which is not compatible with operational decision making on sediment batches. On-site analyses are sensitive to variations and can be used to improve the representativeness of regulatory samples. Laboratory confirmation is, however, required for a subset of on-site analyses, usually 5 to 10% of the total of samples.

Another limitation is that on-site analyses provide only total element contents, but not the bioavailable fraction or porewater. This is of prime importance for the risk analysis, itself part of the permitting process, so requires laboratory analyses. On-site analyses are not to be used at this stage of the project, unless maybe as an aid for sampling point selection. Once the potentially critical elements are identified, on-site analyses can be used for operations monitoring and batch verification, when rapid results are required. When the undesirable element is weakly leachable, this may lead to on-site measurements being too conservative.

Some of the analytes that have to be considered for decision-making cannot be analysed by on site techniques. This potential limitation can be addressed by an orientation survey, conducted prior to the on-site analytical campaign, in which potentially contaminated samples are submitted to laboratory analysis for all analytes of concern. The analytes that cannot be measured on site may be ignored during on site testing if they are found to be either significantly below thresholds or correlated with analytes that can be measured on site. The latter case is frequent, as many contaminants coexist spatially or temporally due to common contamination sources [14]. The abovementioned conformational analysis on a subset of samples allows for further verification. This provides additional safety for decision making based on on-site measurements.

2. Materials and Methods

2.1. Sampling Technologies

2.1.1. Underwater Sediment Sampling

Shallow underwater sediment sampling is done from a sampling vessel, using a hand corer. Deeper underwater sampling is undertaken using either a grab or an Ekman-type dredge sampler, or a weight operated coring device. In most cases, the sediments are homogenised manually in a bucket before being analysed. Samples collected for on-site analysis cannot be sieved, and any fragments have to be removed manually. In order to allow on-site analyses without moisture problems [4,15,16], sediment is then part dehydrated and pelletised using a hand press (“cartridge gun-type”) before pXRF analyses [17]. This can be performed even on board the vessel. Moisture reduction can be further controlled by using a mechanical press.

For each sample, a pellet is made using the hand press to maximise water removal and ensure the cohesion of the sediment sample. The process is described in [17]. Each pellet may be used for measurement by pXRF, LIBS, pFTIR or µRaman (Section 2.2).

2.1.2. Soil and Sediment above Water

Soil sample preparation tools comprise home gardening hand-trowels and -rakes made of unpainted stainless steel for small shallow samples (<20 cm depth). Larger garden tools are used for deeper horizons or larger samples. Hand operated augers are used between 20 cm and the bedrock.

Stainless steel wire sieves of various mesh sizes are used for dry sieving on-site, but the usual range covers 250 µm to 2 mm. Dry sieving can be performed if the soil is sufficiently dry. In all cases, gravel, debris and vegetation need to be removed manually.

When sediment is sampled above the water level (river bank, beach, low tide, on land disposal sites), the same tools are used. Hand trowels fitted to telescopic poles can be used in more hazardous site conditions (unconsolidated lagoons, or from barges, see Figure 1a,b).


(**a**) (**b**) (**c**)

Figure 1. Sampling and analysis during sediment loading and unloading: (**a**) Sampling a barge load with a small trowel mounted on a telescopic handle; (**b**) Sampling from an unconsolidated lagoon; (**c**) checking lots before sending to a processing test.

When the sample is too wet for direct analysis, the above described sample dehydration method can be applied.

2.1.3. Water

Water samplers used for on-site measurements comprise:

- spot samplers, carried and operated by monitoring staff for spot site visits and single sampling operations. Most types of lightweight sampling equipment can be used (bucket, bottle, bailer, battery-operated pump, etc.).
- permanent samplers, installed on-site for periodic sampling operations. They may be operated by monitoring staff during site visits or be programmed for unsupervised sampling operations.

Water autosamplers are used for the collection of samples at regular time or volume flow in-tervals. Automatic samplers used for periodic sampling during works can be also used for monitoring, when they are fitted with water quality sensors (pH, EC, DO …). In this case, they may be programmed for collecting spot samples when a specific water qual-ity condition is met: for instance, pH < 4 or EC > 1 mS/cm.

2.2. On-Site Analytical Technologies

A comprehensive summary of on-site analytical techniques [5] was provided for geo-materials in mineral exploration. Most are applicable to sediments and water at dredging sites.

Many laboratory analysis methods were made available for field investigation of solid samples in the last decades, both for inorganic [8,9] and organic substances, mainly gas chromatography. This evolution was the result of electronic miniaturisation and lower energy requirements, as well as the availability of rugged sensors that could operate outside the laboratory.

More challenging were 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. The emerging technologies include portable Fourier transform infrared spectroscopy (pFTIR), portable X-ray diffraction (pXRD), laser-induced breakdown spectroscopy (LIBS) and portable microRaman spectroscopy.

A non-exhaustive list of the most widely used and emerging methods is present-ed below for solid and water analyses. First the methods used in the case studies presented in this paper (the pXRF and the multiparametric water probe) then the other methods.

2.2.1. On-Site Analytical Technologies Used in the Different Case Studies

pXRF

Among currently available technologies for sediments, portable X-ray fluorescence (pXRF) is one of the best known, and its operation is straightforward [18–20]. It allows routine measurements for most of the major elements (Ca, Fe, K, Ti, Mn, and, often with lesser accuracy or higher deviation, Si, Al, P, S and Cl) and for many trace elements (often contaminants: Pb, Zn, Cu, As, Sb, Cr, V, etc). 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 dry sediments, by pXRF.

Element	LD	Element	LD
SiO_2	1%	Pb	5 ppm
Fe_2O_3	500 ppm	Zn	5 ppm
TiO_2	100 ppm	Cu	10 ppm
K_2O	500 ppm	Ni	20 ppm
CaO	500 ppm	Cr	20 ppm
MnO	100 ppm	Cd	5 ppm
S	1000 ppm	As	5 ppm
		Hg	20 ppm

Note: all elements in ppm (mg/kg) on the instrument. Conversion to oxide % for major elements. LD: lower analytical limit, usually reported for high specification devices (detection limit or LOD according to IUPAC).

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

pXRF sensitivity is sufficient for the discrimination of contaminated sediments,

- sampling is done by traditional methods, usually GPS-located auger coring,
- the sample is partly dehydrated using a hand press [10],
- pXRF analysis is performed immediately on the sample pellet, and direct readings are corrected for moisture. Two measurements are usually made on each pellet in two different places on the same face of the pellet.

Multiparametric Water Probe

Multiparametric probes are field instruments comprising a pressure/depth profiler and several physicochemical sensors for water monitoring (temperature, EC (electric conductivity/salinity/TDS), pH, ORP (redox potential), dissolved oxygen), housed in sturdy 2-inch to 4-inch cylinders that can be manoeuvred with a steel wire and/or connector cable. They allow the continuous recording of these parameters during operation. In a well, an open water basin or at sea, they record these variations along with depth. In an open basin, river, or canal, they record these variations along the geographic position by coupling with GPS records. The precision of the instrument is slightly lower than laboratory instruments. Two probes were used in the case studies: the YSI 6920 V2 (Figure 2) which provided the best performance, and the Aquaread, selected for its ability to operate in small-diameter wells (2″).

2.2.2. Other On-Site Analytical Technologies

These technologies were not used in practice at the described case studies, due to development limitations or because their targeted analytes were not critical for them. They are nevertheless described here as they are relevant for beneficial use projects with sediments, to provide the reader with the same level of information.

LIBS

Laser-induced breakdown spectroscopy (LIBS) was offered more recently in field portable or handheld instruments [21–23]. Despite rapid progress, it is 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). Calibration is more challenging than with pXRF for the same elements. Its main benefit for sediments is the possible measurement of light elements, inaccessible to pXRF.

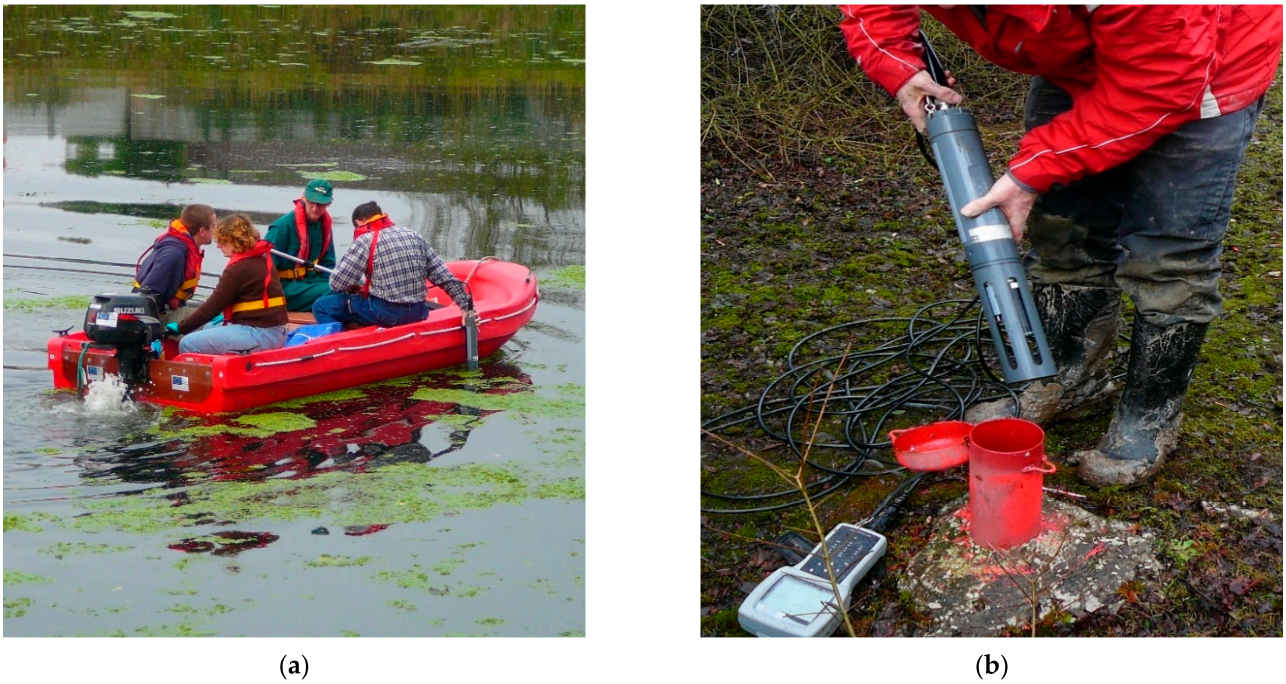

(a) (b)

Figure 2. Multiparametric water probe operation during canal and observation well monitoring surveys (**a**) from a boat and (**b**) in an observation well.

pXRD

Portable X-ray diffraction (pXRD) instruments can be considered as field portable, but not handheld, as the optical constraints are stricter than for pXRFs. They were mainly developed for the mining industry [24].

They allow the identification of mineral phases, similarly to laboratory XRD, but with lower analytical performance (resolution and range) due to size and tube characteristics.

No reference was found for sediment applications, though constitutive minerals (quartz, carbonates, oxides, sulphides) can be identified. This suggests that pXRD could be used as a field guide for civil engineering or cement material applications.

Gas Chromatography

Portable gas chromatography and GC-MS routinely provide field data on light or volatile organic contaminants. It is traditionally used for gas analyses (ambient air and soil gas). It is also possible to take samples of soil, sediment, or water in a vial fitted with a septum. It is then possible, after an equilibrium time at room temperature, to take an air sample in the vial and to analyse the molecules in equilibrium with the solid or liquid phase of the vial. The same procedure can be done after heating the vial to 60 °C to increase the analyte gas flux.

Though these contaminants are easier to extract than inorganics or heavier organics, they may play a part in hazard 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 µRaman

Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy (µRaman) are not aimed at providing elemental analyses, but rather information on molecular information and chemical bonds. They therefore offer information on organic compounds in favourable cases, mainly the heavier ones (such as PAHs) or the polar ones (such as phenols). They also offer possibilities for mineral identification [25,26], especially if complemented by pXRF or LIBS.

They are still emerging technologies in their field portable form, despite the fact that both are based on well-known laboratory technologies.

At first, pFTIR seems easier to use, but this technique is extremely sensitive to sample moisture and darkness. It is unable to give any proper analysis if the sample is wet and/or rich in organic matter—both characteristics which are ubiquitous in sediments.

µRaman (portable micro-Raman spectroscopy) is less sensitive to moisture or colour, but it is more complex and subject to many environmental interferences, including the nature of incident light and the fine-tuning of the distance to the sample. This makes µRaman challenging in field conditions. The two methods may be considered as complementary, but both are highly matrix-sensitive.

Direct quantification of the analyte using specific spectrum regions is difficult and most often impossible, as the spectra are generally very noisy and have many overlapping absorption bands, depending on the sample matrix and on other compounds. Currently, the best way to exploit these data is by using chemometrics [27–30]. Mathematical tools, especially multivariate statistics are used to obtain the maximum information from chemical data. Its development has been greatly accelerated by that of near-infrared spectrometry in analytical chemistry laboratories.

An alternative approach is to obtain matrix-specific baseline spectra on samples known to be without organic contaminants, then spiked spectra (with known amounts of the expected contaminants added to uncontaminated samples), and compare them with spectra of possibly contaminated sediments.

Spectral Gamma

Handheld gamma spectrometers are used for the recognition of gamma emission anomalies in sediments and soils, and their attribution to a gamma emitter (K, Th or U). They can be used for monitoring radionuclide contamination on-site [31–33]. In case of high contamination, the signal may be correlated with pXRF measurements.

Turbidimetry

One of the easiest, and most frequently requested monitoring parameters is turbidity, based on light transmission. It can be used as a proxy for suspended material content. It therefore provides a direct observation of the impact of dredging and relocation operations, and the time needed for settling. Turbidity is water cloudiness caused by suspended and dissolved particles. As water turbidity is mainly caused by the presence of Suspended Particular Material (SPM), turbidity has often been used to estimate SPM concentration. Turbidity is a function not only of SPM but also of the size, shape, and composition/colour of the particles. These variables may introduce bias to SPM estimation. Handheld turbidimeters operate either electrochemical or optical turbidity cells, the latter being by far more stable and easier to operate. The same cells can be incorporated in multiparametric probes.

Trace Element Water Analysis

Though on-site analysis of trace elements in water requires technical compromises, compared with laboratory analyses, and cannot yet offer the same sensitivity and accuracy, attempts to “move the lab to the field” were made, mainly to allow dynamic sampling or to shorten delays [5]. Electrochemical techniques are routinely used: Anodic Stripping Voltammetry (ASV), polarography and Ion Specific Electrodes (ISE). They require skilled personnel. More recently, pXRF was combined with adsorption filters to offer a more robust alternative [34]. Development is ongoing.

3. Results

3.1. Case Study 1: Rotterdam

3.1.1. Pilot Site for Beneficial Use

The Port of Rotterdam site pilot aims to demonstrate and to evaluate innovative sediment beneficial use solutions for flood and erosion protection. The pilot consists of the relocation of upstream sediment within the system to 'reset' a natural system for bank nourishment in the estuary. Between 2019 and early 2020, 5×10^6 m^3 (2×10^6 tons) of sediments were dredged and relocated (Figure 3 and [35]).

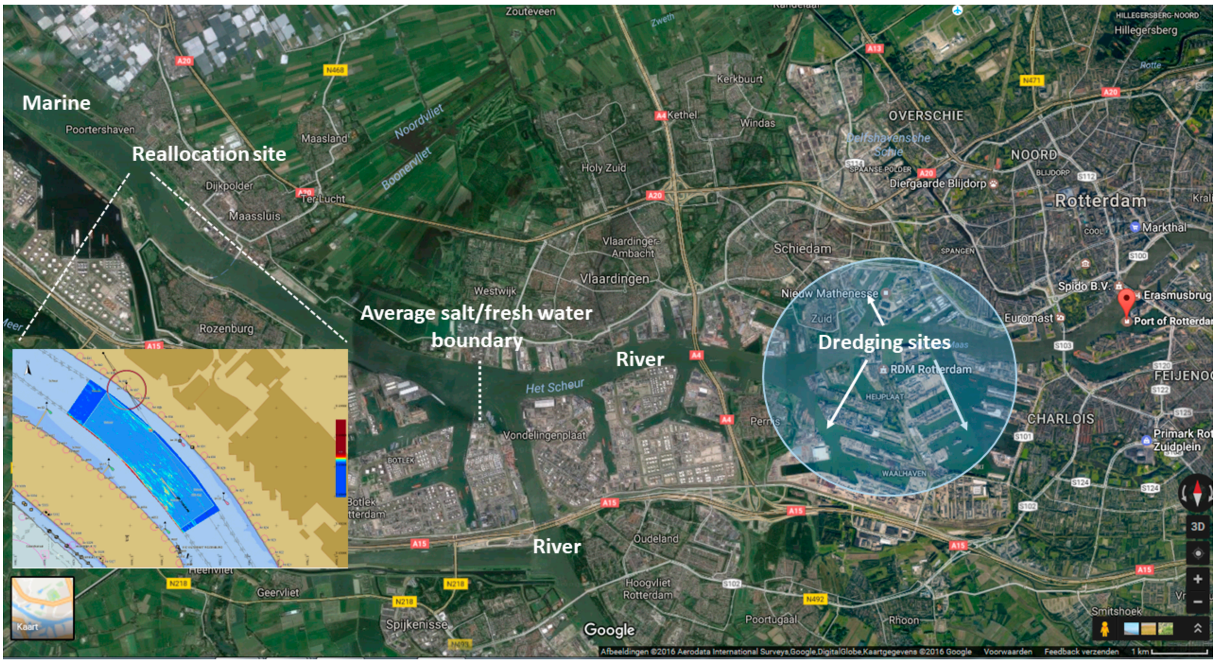


Figure 3. Rotterdam pilot location.

Relocation is done underwater. Full water monitoring was not considered as the pilot is carried out in an open system. The on-site baseline survey was therefore limited to real-time measurements during a bottom sediment sampling cruise, on 6 February 2019 (T0). Then three operational campaigns (T1, T2, and T3) were led on 2 July 2019, 4 September 2019 and 18 February 2020. At most, according to the campaigns, 20 points were sampled along the estuary (Figure 4).

3.1.2. On-Site Monitoring (Baseline and Pilot Work)

Sediment was sampled underwater from a sampling vessel, using either an Ekman-type sampler, or a weight operated coring device. It was noticed during surveys that several buckets could be collected from one grab or core operation, but sediment was not further homogenised on board. The fraction of the sample collected for pXRF analysis was collected from any bucket, which might result in minor heterogeneity problems when compared with laboratory analyses.

Sediment dehydration and pelletisation using a hand press before pXRF analyses (Section 2.1) proved to be efficient despite the sandy characteristics of most samples. No element anomalies were recorded beyond expected geochemical background [36,37]. Timebound variations are limited and may reflect sampling heterogeneity. Contami-nant ranges decrease from upstream to downstream, but are never very high (Table 2 and [38]).

Figure 4. Location of sediment sampling points along the estuary during the survey (4 campaigns).

Table 2. Rotterdam site, Statistic parameters (mg/kg) for Pb, As, Zn, and Cu analysed by pXRF on the boat.

Statistic	Pb	As	Zn	Cu
Minimum	12	4	22	13
Maximum	195	66	643	128
Median	19	7	66	23
Mean	33	10	112	30
SD [1]	41	14	138	26

[1] SD: Standard-deviation. Full data will be published as SURICATES project deliverables in 2022 [35].

Major and trace element analyses were performed in quasi-real time on board the sampling ships, using a handy dehydration press and freshly dredged samples. It was possible to obtain a first measurement of the main contaminants (Pb, Zn, Cu, Cr, As) within minutes, between sampling stops. This would have allowed refinement of the sampling plan if anomalies had been encountered at sampled sites.

3.1.3. Benefits of On-Site Monitoring Techniques

On-site analyses allowed performance of a fast scan of the background level for key contaminants throughout the project area and their evolution during pilot works. Results show that upstream sediments are consistently less polluted than downstream sediments, and that the general level of contamination is low when compared to historic studies [1]. It is therefore possible to use the upstream sediments and relocate them to a new place for bank nourishment in the estuary.

The on-site analyses did not show any anomaly, and dredging and relocation operations were safely completed. However, the monitoring operation was performed on a spot basis rather than continuously.

Water monitoring tasks (especially turbidity) were performed by the operator and are not described here.

3.2. Case Study 2: Bowling (Scotland, UK)

3.2.1. Pilot Site in a Canalside Regeneration Area

The Bowling site is an area between the Clyde Estuary and the Forth-Clyde Canal, 30 km west of Glasgow (Scotland, UK). It is part of a regional regeneration initiative which elsewhere includes revitalising a former oil terminal and riverside industrial area on the north bank of the Clyde, downstream from the former coal, metallurgical, and shipbuilding sites in the Glasgow area, by creating employment, housing, and recreational areas (Figures 5 and 6). An earlier intrusive site investigation of the case study area had indicated the presence of some contaminated made ground at shallow depths (0.2–3.0 m). In 32 analysed soils the pertaining ICRCL trigger levels at the time for domestic gardens had been found to be most commonly exceeded for As ($n = 28$), Cu ($n = 11$), Pb ($n = 9$), and Ni ($n = 9$). Our initial laboratory assessment of 4 local sediment samples indicated that average concentrations of Zn (829 $\mathrm{mg \cdot kg^{-1}}$) or Cu (131 $\mathrm{mg \cdot kg^{-1}}$), rather than Ni (36 $\mathrm{mg \cdot kg^{-1}}$), might exceed limits for those potentially phytotoxic elements provided in analogous standards for topsoil products [39] so would require monitoring during beneficial reuse. Pb levels averaged 241 $\mathrm{mg \cdot kg^{-1}}$ in our sediments.

Figure 5. Bowling pilot site: Site before rehabilitation. Figure from Scottish Canals.

Figure 6. Bowling pilot site: Possible site re-development project. Figure from Scottish Canals. R: proposed new residential area, C: new cycle path on former railway track, G: new green land.

Sediments could potentially be used to cover and enhance the area between the Clyde and the canal (for green space, or flood prevention) alongside a long-distance cycle track developed on a former railway line (the "Bowline") and to reinforce the coastline along the Clyde with blocks (erosion protection) next to the historic canal entrance.

3.2.2. On-Site Baseline Monitoring

The objective was to measure the initial condition of key receptor media prior to the pilot test where sediments will be applied [40]. Surface groundwater, soils and sediments on the Clyde waterfront were considered. Only the surface horizon of the site soils were analysed.

Sampling and measurements were done on the beach, the Clyde and canal sides of the former railway line. pXRF measurements were performed on surface soils following an irregular grid pattern with points spaced approximately at 50–75 m intervals (Figure 7). They constitute 5 sampling lines roughly parallel to the Clyde waterfront: one in the forested area north of the old railway line, one on the old railway (future cycle track route) in the soils formed on the old ballast, two in the forested soils south of the old railway line on the Clyde side, and one line along the Clyde tidal beach.

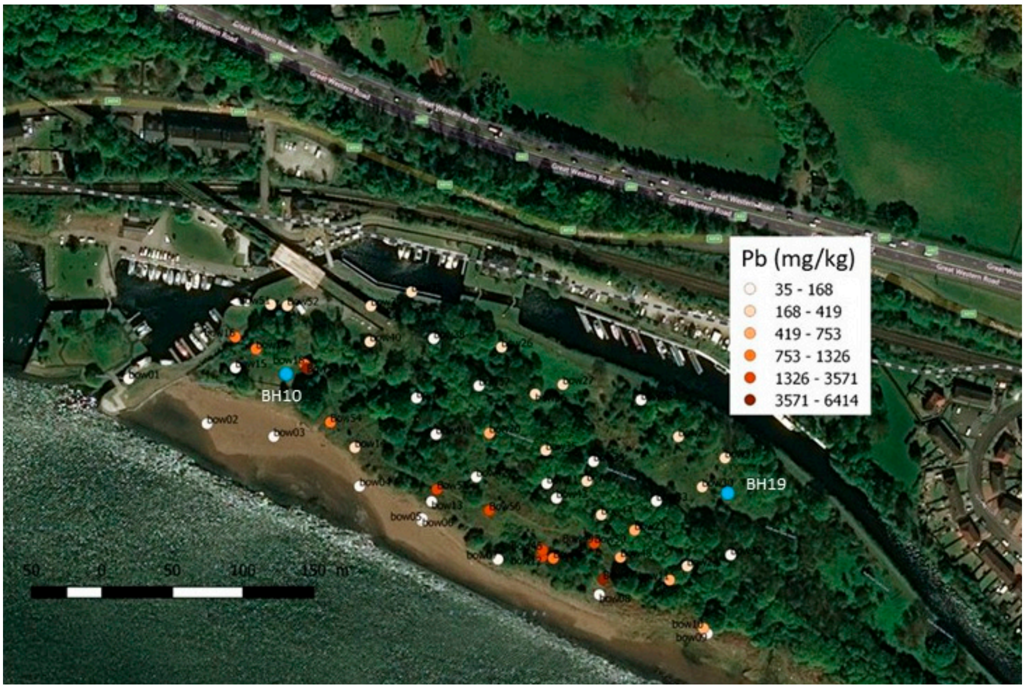


Figure 7. Bowling pilot site: Pb measurements by pXRF in soil and location of the well BH10 and BH19.

Five soil samples from the 56 analysed by pXRF were selected for laboratory analysis [40]. They were dried at 105 °C to determine their water content. The soil samples were then analysed by ICP-AES at the BRGM laboratory. The good correlation between field and laboratory results allows for validation of the results obtained in the field ($[\mathrm{Pb}]_{\mathrm{pXRF}} = 0.9336 \times [\mathrm{Pb}]_{\mathrm{ICP}}$ with $r^2 = 0.\ 9989$).

According to the map (Figure 7), the most impacted samples are in an area between the beach and the wooded area, which is separated by the eroded river bank. Lead levels are between 35 and 6414 mg/kg, Zn levels are between 23 and 3818 mg/kg, As levels are between <6 and 340 mg/kg and the levels measured for Cu are between <14 and 1403 mg/kg. Zn, As and Cu have spatial distributions similar to Pb (Figures S1–S3 in Supplementary File). This corresponds to the presence of made ground including coal ash and clinker.

If the average levels of the three zones are compared, it is clear that the area between the beach and the old railway line is the most impacted, compared to the beach and to the area between the old railway and the canal. This is clearly visible for all elements in Figure 8.

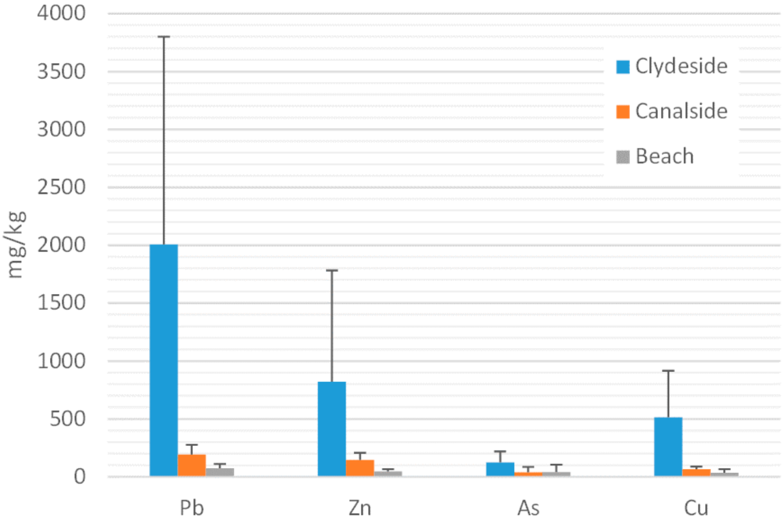
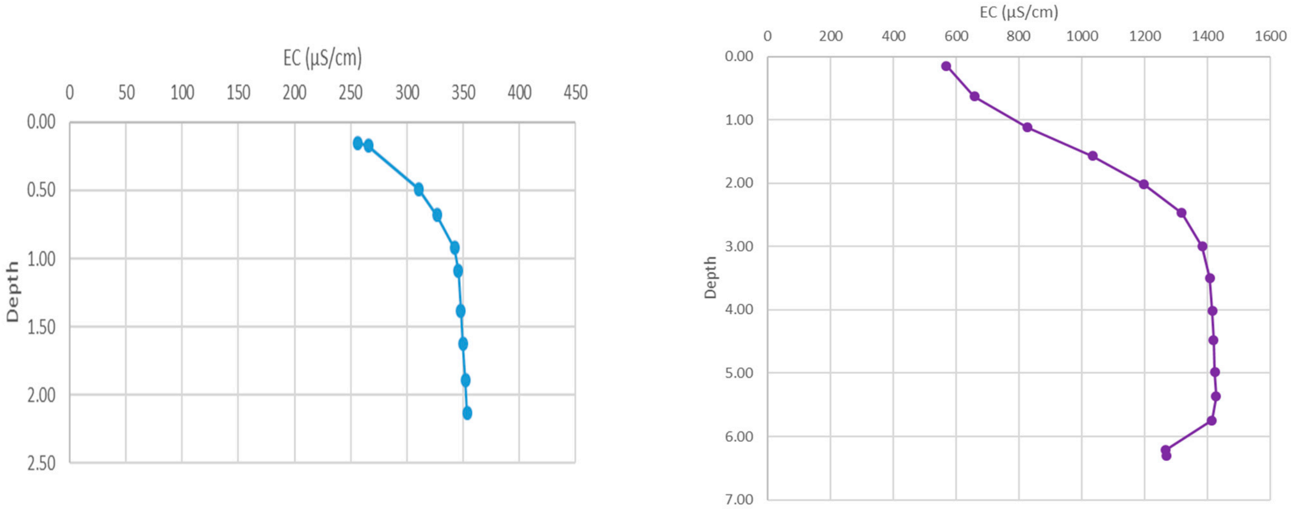


Figure 8. Comparison of mean content in Pb, Zn, As and Cu in the 3 zones.

Physicochemical parameters of shallow groundwater were monitored with the Aquaread multiparametric probe. It includes water temperature sensors, pH, EC, ORP, DO, and depth, as well as a time stamp. The hydrostatic level was measured with a dipper. Well location and presumed flow direction was based on previous site investigation work at Bowling in 1999. Many wells were found to be dry or clogged. Measurements on 9 open wells allowed the distinction between shallow aquifer, rainwater infiltration, and marine water intrusions (EC similar to water in the estuary). Conductivity measurements (Figure 9) allow a simple separation between meteoric recharge (low EC and pH), groundwater (moderate values), and seawater or brackish water (high EC). Variations in water level indicated tidal influence in some boreholes.



(**a**) (**b**)

Figure 9. Electrical conductivity profile of wells by multiparametric probe (µS/cm): (**a**) BH10 well; (**b**) BH 19 well.

3.2.3. Benefits of On-Site Monitoring Techniques

On-site techniques were used for a rapid evaluation of the inorganic contamination of both sediments to be dredged, and of receptor sites (soils and beach sediments). Laboratory analyses showed good consistency between results, but with some biases which did not affect sample ranking or site mapping [40]. Full data will be published as SURICATES project deliverables in 2022 [35]. The on-site techniques can therefore be used for sample screening, for increasing sampling density, and for checking the extent of anomalies as soon as they are found. They also provide almost instant results, which is a desirable characteristic for operations monitoring.

A good example is provided here, where denser pXRF measurements allow construction of a distribution map of soil contamination, with more detail than discrete laboratory analyses would allow. This map can be used to suggest site management options.

The sediments proposed for pilot use are less contaminated than soils from the zone between the Clyde and the old railway line, but more so than soils from the canal side or beach zones. Thus, on-site analyses could be used during any future pilot application to verify their contamination level, and make a decision where to use them on the site or not to use them.

Baseline water quality monitoring was applied at available wells, using multiparametric probes (pH, EC, ORP, DO, turbidity, Figure 2b). These devices are particularly useful for their continuous recording capabilities, either with depth (groundwater or open channels, recording salinity or oxygen profiles), or along spatial profiles (channels, basins), or with time (especially turbidity and EC during dredging operations). These measurements can also be used for sample screening before laboratory analysis.

3.3. Case Study 3: Walloon Waterways Sediment Characterisation Surveys, Belgium

3.3.1. Pilot Test Site to Improve Sediment Management at Temporary Disposal Sites

The pilot test area belongs to one of the most important axes of Belgium waterways, the Brussels–Charleroi Canal which connects Walloon and Northern French regions with the port of Antwerp in the north (Flanders) and the Netherlands, via the Brussels–Scheldt Maritime Canal.

Prior to maintenance dredging operations, the waterways operator (SPW, Service Public de Wallonie Mobilité & infrastructures) performed detailed sampling of canal sediments to evaluate precisely the physicochemical and environmental characteristics of the sediments to be dredged (Table 3), to ensure their proper management in temporary disposal sites (Centres de Regroupement) and later, their beneficial use. This led to splitting sediment loads into category A (low contamination, with possible valorisation as secondary materials in civil or fluvial works and brownfield remediation) and category B (contaminated, mainly oriented to disposal sites, due to the lack of economically viable clean-up options). Historically, sediment characterisation was designed from the perspective of risk analysis and disposal safety, using composite samples made of 5 to 20 core samples, collected from a boat. This practice has led to mixing of contaminated and uncontaminated samples in canal sections where pollution point sources were scattered in otherwise uncontaminated zones. This could lead to classifying the whole canal section as category B while up to 90% of the sediments would qualify as category A if each subsample could have been analysed. The pilot test was aimed at demonstrating the feasibility of high density analysis as a support to a more efficient management.

3.3.2. Orientation Survey

The orientation laboratory data described in Section 1.5 are given in Table 3 for 10 samples. A full regional data set will be available on the project site [41].

According to the results of the orientation survey, most inorganic contaminants are expected to be present but not at a critical level. Non-volatile organic contaminants (PAHs and PCBs) may occur at a critical level and this would be potentially an issue for on-site decision making until reliable on-site analysis of these compounds is possible. However, most PAH and PCB occurrences are spatially associated with Pb, Zn, or Cu anomalies in the studied region.

Table 3. Laboratory analyses on selected sediments from the survey area.

Inorganic Element or Substance	Minimum mg/kg	Maximum mg/kg	Guide Value mg/kg
As	6.1	22.8	50
Cd	0.6	3.9	6
Co	42	90	200
Cu	39	87	150
Cr	6.6	14.7	25
Hg	0.19	0.52	1.5
Ni	18	33	75
Pb	49	149	250
Zn	261	658	1200
F^-	46	121	250
CN^-		<4	5
Organic Substance or Group	**Minimum mg/kg**	**Maximum mg/kg**	**Guide Value mg/kg**
Aliphatic hydrocarbons C10–C40	6.08	24.02	1500
Halogenated solvents, most abundant substance		<0.95	1
PAH, sum of 16′ Borneff compounds	2.77	10.16	9
Total organochlorine pesticides		<0.06	0.25
PCB *	0.075	0.333	0.25

Note: all concentrations are reported on dry matter. * PCB sum according to Ballschmieter's classification.

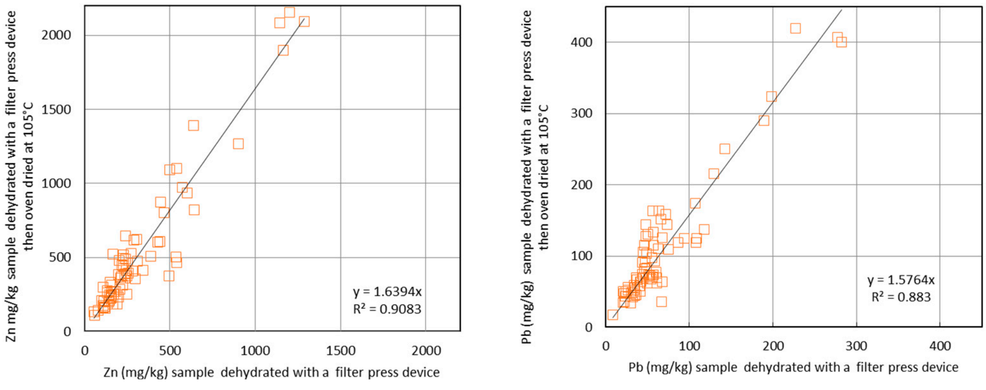
3.3.3. On-Site Monitoring (Pre-Dredging Mapping)

A high precision sampling map can be obtained by analysing each core, but this is not achievable with laboratory analyses, for cost reasons. On-site analysis on the sampling boat was carried out as a test to demonstrate the feasibility of a high density, low cost measurement scheme. The resulting contamination map would allow a better delimitation of contaminated zones and a reduction of the sediment volume classified as category B through mixing.

The technique described in Section 2.1, based on a hand press, requires less than 15 min and can be performed on board between sampling points, without slowing down the coring operations. The reduced water contents significantly increases the reproducibility, sensitivity, and accuracy of pXRF measurements.

During a routine sampling cruise by the SPW team, 83 subsamples were dehydrated and analysed by pXRF by two operators while the team collected the subsamples and prepared the 10 composite samples. Raw results were therefore available before moving the ship and could have been used for selecting another sampling point, in case anomalous concentrations were found, in order to delimit better the contamination hotspots and allow for future selective dredging. This sampling strategy is also called ASAP (Adaptive Sampling and Analyses Program [42] or Dynamic Sampling Plans [12]) and is known to provide large cost and time savings in projects [13].

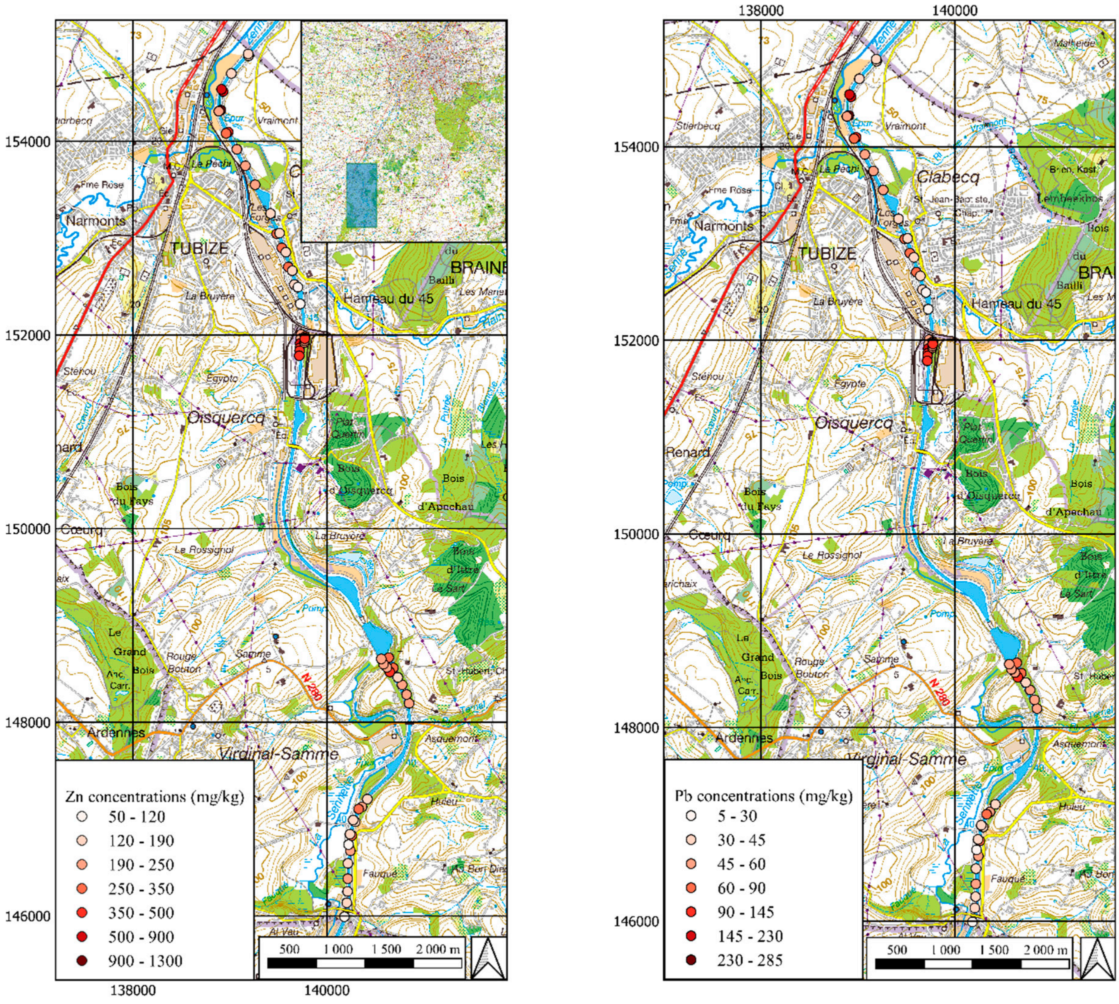
Back in the laboratory, the field pressed samples were oven dried at 105 °C overnight, and were analysed by pXRF again (Figure 10). The higher concentrations measured on the dried sample reflect the effect of moisture on field measurements. However, an acceptable linear relationship is observed. This demonstrates that samples were properly ranked, and that field results may be compared with an action level, provided an acceptable safety margin is maintained [20]. This can be used to help sediment batch management before and during dredging operations.



(**a**) (**b**)

Figure 10. pXRF analyses on pressed and part dehydrated samples compared to analyses on samples oven dried at 105 °C; (**a**) Zn and (**b**) Pb.

The field results were mapped (Figure 11), allowing the location of any hot spots or contamination areas at a finer scale, than using the traditional composite sampling scheme.



(**a**) (**b**)

Figure 11. Mapping Pb (**a**) and Zn (**b**) pollution hotspots on a canal with pXRF. Projection Belgian Lambert 72.

3.3.4. Benefits of On-Site Monitoring Techniques

On-site analyses can be used to outline further detail on a particular area, if this was not carried out during the first sampling leg. The detection of the exact location of particular hot spots through on-site subsampling would allow a more selective extraction of these more contaminated sediments, but also significant reduction of the dispersal of the contaminant to the material still to be dredged. The knowledge of the precise location of the hot spots along with the levels of any remaining contaminants (see Table 3) would clearly help to more accurately classify and ship extracted sediments directly into the right storage category. This refined classification reduced the volume of sediments to be classified as category B when compared to the procedure based on composite samples and batch mixing.

4. Discussion

4.1. When Can On-Site Techniques Be Used?

The abovementioned case studies provide various situations in which on-site measurement and analysis techniques can be used to optimise sediment management, to facilitate its beneficial use and promote circular economy options. These can be classified according to the operational phase:

- Before dredging and sediment relocation,
- During operations, either dredging or application,
- After application, to monitor their use at the target site.

Samples can be collected directly from a bucket during loading and unloading operations (Figure 1), from the dredging site to the disposal site or the processing facility, as well as from the temporary disposal site to the final beneficial use site by waterway. Processing operational efficiency is greatly improved if incoming sediment loads are classified before unloading [11].

The potential beneficial uses of sediments that were considered here include secondary mineral resources (clay, concrete or cement production, or soil substitute, for instance), as well as bulk sediments for civil engineering (flood protection dykes, noise walls, landscaping mounds).

During detailed mapping, dredging, and unloading operations, the need for rapid analyses is critical [43]. Dredgers, loading vessels and trucks cannot remain on hold until laboratory results are available. Delays for pXRF results, for instance, are adequate for this type of operation.

On-site analyses are not only more rapid, but also much cheaper than laboratory analyses, as they require only investment and have very low operational costs. However, this should not lead to a substitution for economic reasons, as their scope and reliability are not the same. Analyses performed for permitting purposes have indeed to be made by an accredited laboratory, as they need to be defendable against regulatory thresholds. On-site analyses are to be used for fast monitoring [44] or for high density sampling, with a subset of samples analysed in the laboratory.

4.2. Current Limitations of On-Site Techniques

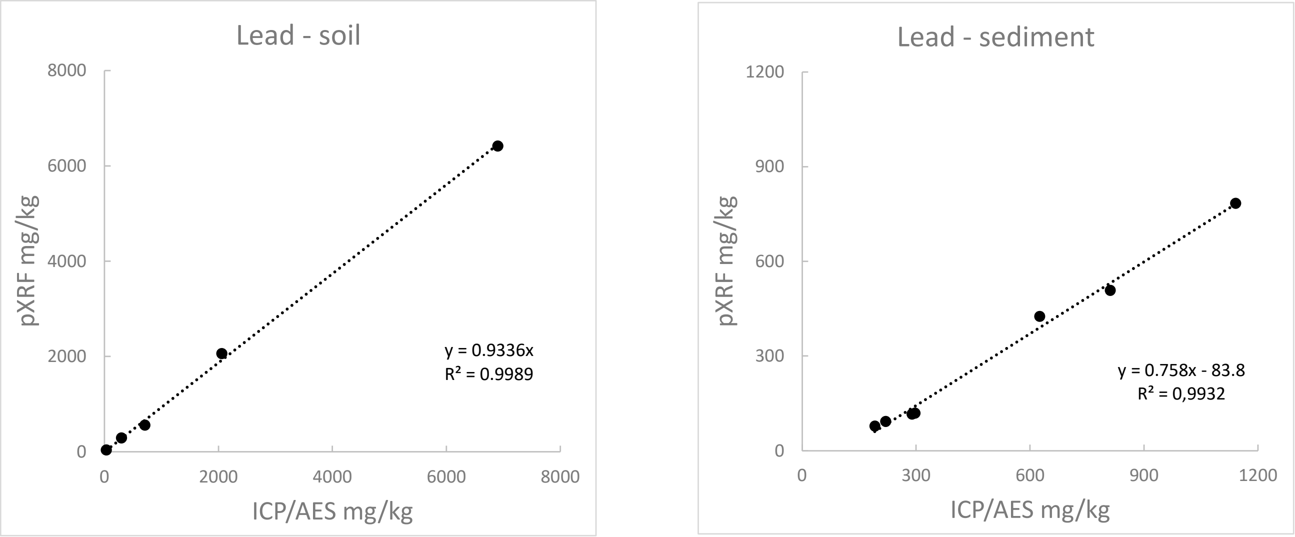
The current development stage of on-site techniques for the detection and analysis of heavier organic substances, such as PAHs, PCBs, or PFAS, is not advanced enough for decision making at sites where they are present at critical levels. Lighter organic substances, including VOCs, can be monitored using gas chromatography. This is not described here as it was not implemented at the case study sites.

A few inorganic contaminants of concern are still difficult to monitor on site. Fluorine requires LIBS to be analysed on site. Cd is detectable by the most recent pXRF spectrometers at low concentrations, and this needs to be tested further. However, most Cd contaminations are accompanied by high Zn concentrations, and abnormally high Zn should prompt a laboratory verification of Cd. Hg is detectable by pXRF at high concentrations, but pXRF is not yet able to provide reliable analyses just above the regulatory thresholds.

These are indeed limitations for the use of on-site analyses, and the orientation survey must indicate which contaminants may occur at critical levels, and if there are potential correlations with contaminants that can be monitored with a reliable on-site technique, such as pXRF. Though there is no geochemical correlation between organic and inorganic contaminants, historic or spatial correlations are often observed. This results from historic associations of industries, such as coking plants with iron metallurgy. The findings of this paper are only applicable to sites where such correlations exist, or to sites with lower concentrations of regulated organic contaminants.

4.3. Reliability of On-Site Results

Faster on-site analysis techniques have higher uncertainty levels than laboratory analyses [5], but in most cases, results are reliably correlated. Using them for real-time decisions before laboratory results are available is possible if the potential bias is estimated prior to operations, and if the uncertainty is quantified. Examples are given below for pXRF (Figure 12) but this can be applied to any on-site method.



(**a**) (**b**)

Figure 12. Bias and shift between on-site and laboratory analyses for an accurately analysed (**a**) and a biased (**b**) element on different matrixes.

The bias on Figure 12a is acceptable for decision making from raw measurements, while in the second case (Figure 12b), probable concentrations need to be calculated from the raw measurements. Reasonably accurate corrected data can be obtained using a simple $Y = aX + b$ correction. Most of the uncertainty in corrected data then reflects the minor dispersion of data around the regression line. The bias can be very significant if the sample is raw and wet compared to dried and ground samples (Figure 13) but despite this bias, the data are usable if there is a linear relationship between pXRF and laboratory results.

A specific application of this approach is the evaluation of real concentrations from measurements performed on wet sediments. A quasi-linear relationship is observed between wet and dry measurements [17]. This allows an acceptable prediction of concentrations from wet material without drying.

Absolute accuracy is expected for decision making, especially if regulatory thresholds are applicable, but it may be substituted by precision if a good linear relationship can be demonstrated between on-site and laboratory data. The estimation of uncertainty allows the quantification of the level of confidence of decisions based on on-site analyses (Figure 14).

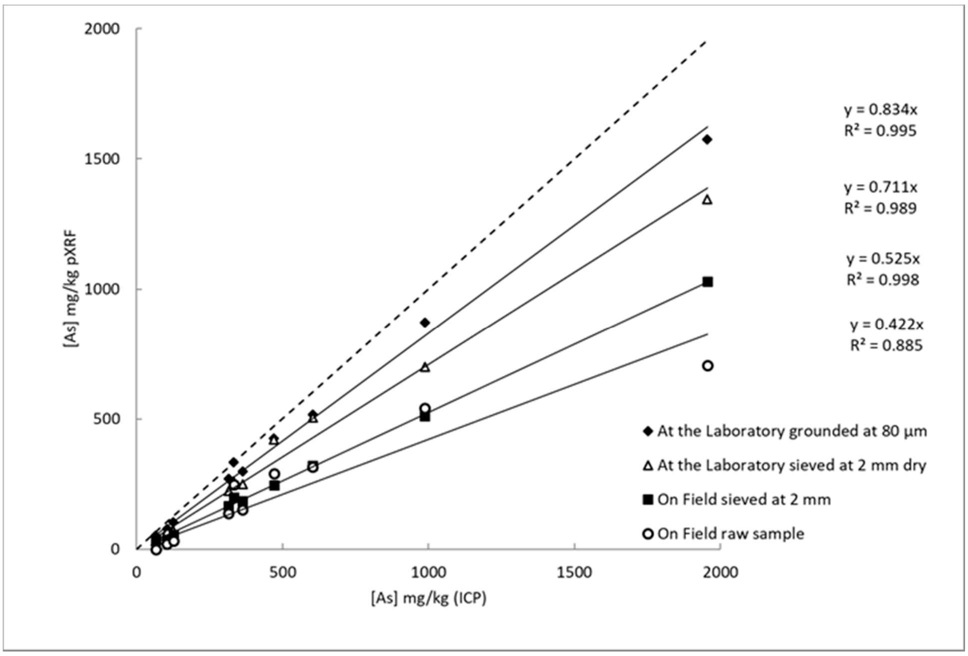


Figure 13. Bias and shift between on-site and laboratory analyses for sieved and raw samples. Modified from [18].

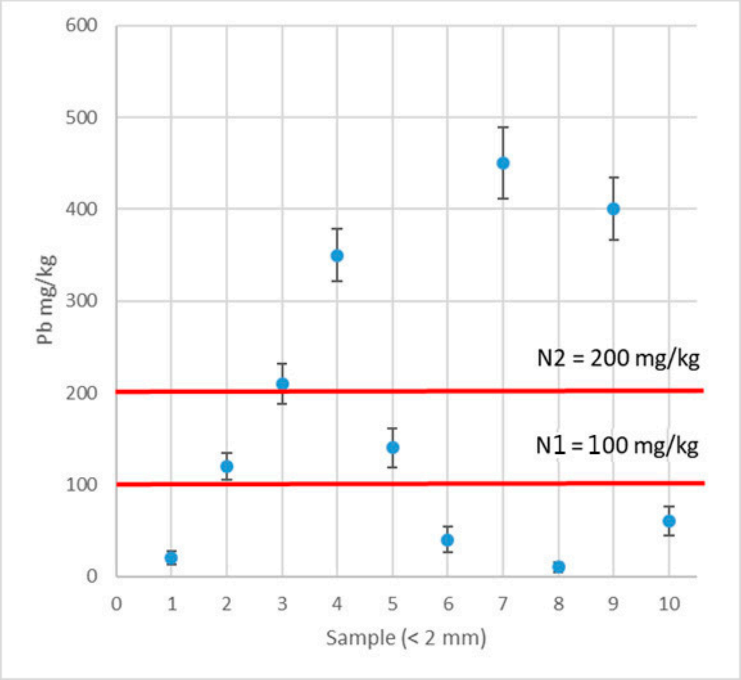


Figure 14. Confidence of a decision made on corrected multi-locational on-site analyses (Pb) in relation with a French regulatory threshold [45].

Another strength of on-site analyses is that they are sensitive to even small variations in continuous processes. Systematic measurements allow the identification of anomalies in sediment batches. As they can be performed more frequently than laboratory analyses, they offer a better monitoring efficiency and an improved detection of contaminated batches.

Decisions based around on-site results can be acceptably safe, because the on-site techniques allow the user to:

- select more representative samples for laboratory analysis, chosen from a larger number of field samples, on the basis of their on-site analyses,
- increase the sampling density to improve the detection of anomalies and the delineation of polluted areas,
- manage more efficiently the sediment loads during dredging operations.

4.4. Before Dredging and Management Operations

On-site analysis allowed the performance of a fast, higher density scan of the background level of key contaminants throughout the project area and to identify preferential locations for pilot work monitoring before redevelopment of the site.

At most of the investigated sites, the inorganic contaminant levels range from moderate to insignificant (natural baseline levels). Multielement pXRF analyses also provide information on the sediment matrix (K, Ca, Fe, Ti, Si, Al) that can be used for guiding sediment beneficial use (civil engineering, concrete, cement).

Though there are potentially applicable technologies (infrared or Raman spectroscopies) for the on-site measurement of organic contaminants, we were not able to obtain satisfactory results in simulations in the laboratory. For this reason, they have not yet been used at pilot sites. Organic contaminant levels (TPH, PAH, PCB) were established by laboratory analyses.

Water quality probe measurements allow for a quick on-site investigation of shallow water composition and dynamics, to be used as a complement to traditional pump sampling and analyses. It may be improved by the addition of dedicated sensors, provided that the well diameter is sufficiently large to accommodate a larger probe. 2″ probes can be used in most wells, but cannot receive all sensors; 3″ or 4″ probes may take more sensors, but will not be accepted by all wells.

4.5. During Dredging and Management Operations

In all cases, operational and regulatory decisions are based in part on sample analysis results, mostly from accredited or certified laboratories. The results require several days to several weeks to become available, and in many cases, the waiting time is not compatible with the operations workflow. Traditionally, proven "business as usual" options will be preferred to minimise risk, as waiting for results would entail higher operating costs.

Soil contamination level and water quality measurements can be used during and after pilot works to communicate with stakeholders and local communities. On-site analyses may be performed in their presence to increase the level of confidence in beneficial use options.

5. Conclusions

Dredged sediments should be shifted from the status of a high-volume waste stream towards that of a mineral resource, substituting for primary mineral extraction. On-site analytical techniques contribute to alleviating the current limitations to beneficial use in sediment management projects, and are a key factor for the implementation of circular economy strategies. This is achieved:

- by reducing cost risks and environmental uncertainties through continuous measurements of sediment quality,
- by reducing environmental risks over the long term, through high density site monitoring,
- by addressing acceptability and community responsibility issues through easier access to community monitoring, with immediate feedback.

From the operational point of view, quasi-real time analyses performed on site:

- facilitate beneficial use projects by allowing rapid on-site decisions,
- provide immediate data if mineral processing is required,
- and generally, offer a significant advantage for daily operational decision making compared to more precise but lengthy and expensive laboratory work. The compromises

on precision are safely manageable in most cases, provided that regular laboratory controls are performed.

These benefits are particularly critical for beneficial use projects focusing on climate change effects mitigation (flood protection works, coastline defence, littoral urban areas redevelopment, etc.) as these should provide a high level of sustainability, of carbon balance efficiency, and of social acceptance.

On-site analyses cannot replace laboratory analyses for regulatory or process compliance, but they can provide a reliable estimate of compliance if the result is sufficiently higher or lower than the threshold to avoid the range of analytical uncertainty. It is thus necessary to incorporate a laboratory analysis program on selected samples, to ensure reliability in management decision making.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/land11020274/s1, Figure S1: Bowling pilot site: Zn measurements by pXRF in soil. Figure S2: Bowling pilot site: Cu measurements by pXRF in soil. Figure S3: Bowling pilot site: As measurements by pXRF in soil.

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