Appropriate sampling strategy and analytical methodology to address contamination by industry. Part 2: Geochemistry and speciation analysis

Review Article

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Abstract: The degree of contamination in soils, sediments and dusts can be assessed based on knowledge of a variety of factors, such as industrialization, type of contaminants, deposition conditions, contamination-control techniques, along with the characteristics of the recipient environmental compartments, which include pathways for contamination transport, depth of infiltration, and degree of groundwater contamination. The impact of contaminants also depends on the quantity, mobility and speciation of contaminants/wastes as well as on the sensitivity of the recipient compartments. With sufficient knowledge of these factors, a number of conclusions can be drawn concerning the status of contamination in industrialized areas. This literature review aims to scrutinize some of the methods used to analyse the occurrence, speciation, mobility, bioavailability and likely the toxic effects of contaminants in the environment.

Keywords: single extractions • sequential extraction • pH_{stat} • leaching • mobility • speciation • industrial contaminants
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1. Introduction

The intensive industrial production and transformation of ores and metals, and particularly, the transportation and storage of contaminants/wastes in the environment in the last hundred years have produced large quantities of waste. Erosion and weathering of contaminated soils and wastes results in the release of heavy metals and metalloids into nearby rivers and sediments [1]. To

investigate the pollution levels and the mobility of the heavy metals and metalloids classical and/or innovative techniques can be used [2]. To measure contamination levels and assess heavy metal mobility is a challenging task because many factors affect the occurrence and the mobility of heavy metals, such as pH, solubility, cation exchange capacity, presence of clays, acid/base neutralizing capacity of soils/sediments, and so on. The selection of an appropriate conceptual sampling model requires that the entire surface under investigation is characterized accurately and any 'hot spots' are properly represented in the sampling inventory [3].

The development of a conceptual model and the selection of appropriate sampling media for characterization of con-

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taminants were addressed in the first part of this article [4]. Once the sampling types are selected and collected, the measurement protocols are applied. An analytical protocol is a specific procedure to make observations, determine the characteristics, and conclusions for each sample or for a group of samples [5]. Analytical chemistry has become the science that does not just provide the results, but the best strategy to measure chemical properties of various sampling media. Selection of appropriate sampling types, sample collection, sample pre-treatment and chemistry analysis are the main subsequent steps that will infer the contamination in a specific site [6]. The aim of this literature review is to summarize and address the advantages and pitfalls of: the key steps in sample pre-treatment; the general characterization of the sample; the selected methods that are used to assess mobility and speciation of contaminants in past or present industrial sites. To address the speciation, the example of chromium (Cr) is used due to the different toxicities related to the different chromium species Cr(III) versus Cr(VI).

2. Analytical protocols

Environmental samples collected in one contaminated site have the main contaminant(s) in common, but are heterogeneous with respect to the amount of the contaminant(s) they contain. This can be explained with the heterogeneity and the physico-chemical composition of the sample. The influences of sampling and sample pre-treatment on the final results are of major concern in environmental chemistry, therefore they shall be described in detail [4, 7–9]. An important step after sampling is the pre-treatment and selection of the most appropriate analytical protocols to be applied in order to characterize the contaminant chemical reactivity, speciation, retention, leaching, (bio)availability and mobility. Choosing the most appropriate analytical technique requires an understanding on how the contaminants are binding and the conditions under which they will be released into the environment [8]. Some of the commonly used techniques used generally in environmental studies to characterize heavy metal concentrations and mobility will be scrutinized.

2.1. Sample pre-treatment

Sediments often play an important role in maintaining the water quality by removing contaminants from the water column. However, subsequent contaminant remobilization from the sediment can result in elevated dissolved concentrations long after the initial source has been removed. The manner in which contamination is treated ultimately

depends on the particle reactivity [10].

The quantity of the samples to be collected in the field will depend mainly on the type of analytical protocols to be applied. Even after taking into account that some sample loss might occur due to sample pre-treatment, generally for total concentration analysis only a few grams of soils/sediments/dusts are required. If additional analytical protocols are to be applied on the samples such as sequential extraction, pH_{stat} , X-Ray Diffraction (XRD) more sample will be required. It is important to know that not all the samples will be analyzed with all the techniques available due to the large costs and time this will require. Generally for soils and sediments where different techniques will be performed a quantity of 1–2 kg of sample is recommended to be collected. After transportation to the laboratory, the pre-treatment of the samples consists in room temperature drying or oven drying for three days at 40 °C, if the latter does not affect the reactivity of the samples. There are some concerns regarding how the sample pre-treatment affects the speciation and the mobility of the heavy metals and/or major elements [11–15] as well as organic carbon distribution in various soil fractions [16].

Disaggregation by rolling, homogenization, sieving and coning preceded the quartering [9]. The fraction below 2 mm is manually crushed in a porcelain mortar. According to Wagner et al. [17], the ‘disaggregation’ of the samples by rolling’ in a porcelain mortar and ‘coning and quartering’ ensure a more representative homogeneous powder sample than samples crushed mechanically, or split by a ‘spine riffler’. The fine powder obtained from mechanical crushing is transferred into glass flasks prior to analysis, whereby the rest of the sample below 2 mm is put in plastic bags and kept at room temperature and dry conditions for any further analysis (extractions, pH_{stat} , mineralogical determinations, etc. ...). Figure 1 indicates the subsequent steps from sample collection until sample treatment.

2.2. Sample characterization

2.2.1. Solid matrix (Soil/sediment, dust samples)

Guidelines for soil description from FAO [18] can be used as an excellent manual for the characterization of properties for solid matrix samples (soils/sediments and dusts). Although this guideline is not directly intended for characterization of contaminated/polluted sites the initial assessment can be approached in the same way. The color of solid matrix samples (soils, sediments and dusts), pH, cation exchange capacity (CEC), grain size, organic carbon (OC) are only some of the key parameters for solid matrix samples that can be determined in order to give a clear overview on the conditions controlling the mobility

Figure 1. Schematic view of the sample treatment, geochemical and speciation protocols that can be applied on various samples.

*Speciation using the methods reported for liquid media.

of contaminants [2].

Soil color reflects the composition as well as the past and present oxidation-reduction conditions of the soil. It is generally determined by coatings of very fine particles of humified organic matter (dark), iron oxides (yellow, brown, orange and red), manganese oxides (black) and others, or it may be due to the color of the parent rock. The color of the soil matrix of each horizon should be recorded in the moist condition (or both dry and moist conditions where possible) using the notations for hue, value and chroma as given in the Munsell soil color charts [19]. Hue is the dominant spectral color (red, yellow, green, blue or violet), value is the lightness or darkness of color ranging from 1 (dark) to 8 (light), and chroma is the purity or strength of

color ranging from 1 (pale) to 8 (bright). Where there is no dominant soil matrix color, the horizon is described as mottled and two or more colors are given. In addition to the color notations, the standard Munsell color names or codes may also be reported [18, 19].

pH (short for potentiometric hydrogen ion concentration) is the measure for acidity or basicity of a solution. When the pH is measured in the field, the method used should be indicated on the field data sheet. The field soil pH should not be a substitute for a laboratory determination and should be correlated with laboratory determinations where possible [18]. In the field, pH is either estimated using indicator papers, indicator liquids (e.g. Hellige), or measured with a portable pH meter in a soil suspen-

sion (1 part soil and 2.5 parts 1M KCl or 0.1M CaCl₂ solution). After shaking the solution and waiting for 15 minutes, the pH value can be read [18]. Soil pH in the laboratory should always be measured after instrument calibration with known standard buffers, as a check on the functioning of the measurement system and in order to provide reliable results from different operators. The calibration should be performed using two buffers whose values bracket the expected value of the samples being measured. It is essential that the difference between the two calibration buffers should be no more than 2–3 pH units apart (generally buffers at pH 4 and 7 are used). pH in laboratory is measured in a suspension of 10 g soil/sediment in 25 ml deionized water or 1M KCl or 0.1M CaCl₂, after magnetic stirring for 30 minutes and five minutes sediment settling for stable reading values. An overview of various techniques used for pH measurement is summarized in Buck et al., [20] FAO [18]. pH is one of the main controlling parameters of the mobility of heavy metals (in general mobility of heavy metals increases when the pH decreases, while for Cr this depends highly on its speciation).

Effective cation exchange capacity (ECEC/CEC) in the Glossary of Soil Science Terms [21] is defined as the sum of exchangeable cations that a soil, soil constituent (i.e. clay) or other material can adsorb at a specific pH. The main sources of cation exchange in soils are clay minerals, organic matter and amorphous minerals. CEC is highly dependent upon soil texture and organic matter content. In general, the more clay and organic matter in the soil, the higher the CEC. Clay content is important because these small particles have a high ratio of surface area to volume. Different types of clays also vary in CEC. Smectites have the highest CEC (80–100 meq 100 g⁻¹), followed by illites (15–40 meq 100 g⁻¹) and kaolinites (3–15 meq 100 g⁻¹). There are two standardized methods used to determine the CEC: 1. “silver thiourea method” and 2. ammonium acetate method also known as one-step centrifugal extraction [22]. These methods consist in replacing the normal mixture of cations on the exchange sites with a single cation such as ammonium (NH₄⁺), to replace that exchangeable NH₄⁺ with another cation, and then to measure the amount of NH₄⁺ exchanged (which was how much the soil had held). More commonly, the soil testing labs estimate CEC by summing the calcium, magnesium and potassium measured in the soil testing procedure with an estimate of exchangeable hydrogen obtained from the buffer pH. Generally, CEC values arrived at by this summation method will be slightly lower than those obtained by direct measures.

Particle (grain) size is a measurement of the size distribution (i.e. fractionation) of individual particles in the

solid samples [23]. Soil particles smaller than 2000 µm are generally divided into three major groups: sands, silts (loam) and clays. The textural class of the different sampling media (soil and sediments) depends on the percentage of each group. Systematic grain size analysis can be carried out on specific bulk samples in order to obtain information on grain size distribution. There are six different methods (1. sieving, 2. microscopic examination, 3. sedimentation, 4. gravitational settling examination, 5. cascade impaction, 6. laser scattering diffraction) under the OECD-110 or OPTTS 830.7520 guidelines for the determination of the grain size. The purpose of including all these guidelines under one single document is to minimize the variations among the testing procedures that must be performed to meet the requirements of the European Chemical Agency (ECHA) or US Environmental Protection Agency (USEPA) for pure substances. However, for heterogeneous matrixes, such as contaminated soils/sediments/dusts the task of conducting grain size analysis becomes very challenging [9]. The general principles of conducting grain size analysis on soil/sediment are summarized in Gee and Bauder [23]. Apart from quantifying the grain size classes, the determination of clay mineralogy can also be considered important as it allows assessment of some characteristics such as the existence of charged sites, which might be considered crucial in natural attenuation [24]. The clay minerals are product of weathering and have marked effects on both chemical and physical properties of the soils. The importance of clays in the soil chemical properties relates to their comparatively large surface area and permanent charge in the surface [25]. Clay mineralogy can be determined from suspension in demineralized water following sample preparation techniques and interpretation of the mixed clay layers based on Moore and Reynolds [26].

Soil organic matter (SOM), or organic carbon (OC) is a mixture of plant and animal residues in different stages of decomposition, substances synthesized microbiologically or chemically from breakdown products, and the bodies of living and dead microorganisms and their decomposing remains [27]. SOM normally ranges from 0.5–5% in mineral soils and up to 100% in organic soils (Histosols). Even in very low concentrations, the activity of OM is so high that it has a pronounced effect on soil chemical reactions [28]. The Walkley-Black method is the generally accepted method for organic carbon determination [29].

2.2.2. Water samples / eluates

After collection in the field, water samples should be kept refrigerated and transported to the laboratory. Upon arrival, the samples should be filtered and the measurements to be conducted as soon as possible within 24 h, in or-

der to minimize the sample changes. At the end of the various extraction techniques the samples are filtered and the final eluate is stored in the fridge until measurement. The storage period should be as short as possible in order to avoid any precipitation and changes in chemistry or reactivity.

pH, redox potential and electrical conductivity in water samples or eluates should be measured after calibrating the respective apparatuses versus known standards. For additional water sample characterization sulfate and chlorides concentrations in the eluates from the extractions and the water samples can also be measured.

2.3. Total concentrations

The term total concentration is used for the maximum concentration obtained after the hot plate digestion of one or multiple strong acids on solid samples. Due to the total dissolution, the results give no indication of the species in which heavy metals occur in the soil system.

The measurement of the total concentration of metals in soils/sediments is useful for assessing the degree of contamination and for measuring any change in elemental concentrations over time with respect to leaching to groundwater, surface runoff, erosion, etc. The complete dissolution of the solid phase components requires a rigorous digestion of the powdered sample fraction using a hot mixture of several acids [10, 30], which should finally result in a minimum insoluble residue material. With respect to the total concentrations in several studies, Farmer et al. [31], Marguí et al. [32] showed that the finer the powder fraction, the higher is the concentration of the heavy metals released in solution. In a study carried out on chromite ore processing residue wastes [31] the concentration of total Cr as well as mobile Cr (Cr(VI)) in solutions doubled, if the powdered material is $<0.63 \mu\text{m}$.

Total concentrations of major elements such as Fe, Ca, Mg, Al, can be measured by means of Atomic Absorption Spectrometry (AAS) while the trace elements such as Cr, Ni, Co, Zn, Cu, can be measured by means of Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), or Optical Emission Spectrometry (ICP-OES) Atomic Emission Spectroscopy (ICP-AES) Speciated Isotope Dilution Mass Spectrometry (SID-MS), Reversed Phase Liquid Chromatography (HPLC). The selection of the measuring technique will depend highly on the detection limit of the expected concentrations of respective elements. Hill et al. [6] made an extensive summary of all the available detection techniques and possibilities for various sampling types and element speciation.

To evaluate the accuracy of sampling, sample treatment and analysis, is advisable to analyze in duplicate 10% of

samples and to add blank samples to the series. The results from duplicates will indicate whether the analyzed samples are representative especially for the heterogeneity, while the results from the blank samples will indicate whether the generated data are reliable.

2.4. Extractions

Using total concentrations to measure element mobility is inappropriate because this approach includes the assumption that all phases have equal control on element mobility. It is known that contaminants can cycle across the sediment (and less soil)–water interface many times. In general a contaminant is not fixed permanently into a soil/sediment particle, and many physical and chemical variables such as weathering, percolation, solubility, speciation, etc, can influence the contaminant mobility as shown by Linge [33]. Measurement of total concentrations is useful for a certain sampling media, but the mobility of heavy metals depends strongly on speciation, binding capacity as well as on the dominant conditions in the site [32, 34]. Due to these factors, there is an increasing interest in the assessment of the bioavailable metal fraction, the element mobility and the speciation of the trace elements that are mobilized from wastes [35]. However, the determination of speciation is difficult and often impossible. The mobility of a contaminant (especially Cr), can be assessed by the determination of the fraction which becomes available under conditions such as acidification, alkalization, low content of organic carbon. Such determinations might be carried out by simulating similar conditions that could occur in nature with so-called single extractions or by sequential extractions. Such schemes were designed in the 1980s (see for example [36, 37], in order to assess the different conditions for simulating the retention or the release of metals from soils and sediment samples. The idea of a single extraction is that different sampling media are extracted with a reagent that elutes a specific fraction (exchangeable, metal complex release, water soluble) while in a sequential extraction the same sample is successively extracted with several reagents in order to recognize the fraction (i.e. exchangeable, acid extractable, reducible, oxidable and residual) with which the heavy metals associate.

2.4.1. Single extractions

Single extractions are inexpensive, simple, effective and fast. They require minimal technical expertise and give an idea on the overall heavy metal availability from the contaminated media [38]. They are more reliable than total concentrations with respect to the mobility of the pollutants. This type of extraction is devoid of sample losses

due to washing, since there are no subsequent steps as in sequential extraction. The drawbacks of single extractions relate to the operationally defined parameters (i.e. time, ratio, pH of the extracting agent). More quantity of sample is needed if different types of extractions are carried out and inaccuracies may be introduced by sample heterogeneity (Table 1). It is not always possible to compare the results with certified reference materials due to the large variability of the reagents used in the extractions [34, 39]. The numerous single extraction methods that have been reported fall into three categories: dilute solutions of strong acids; solutions of weak acids; solutions of strong complexing and reducing agents [34]. In Table 2 some widely used single extractions are shown with the respective references and their operational parameters.

Quantifying the soluble and insoluble fractions of Cr from the different sampling media is pertinent to the environmental hazards associated especially with: 1. airborne related dust; 2. colloid and solute movement in the groundwater or absorption by plants and microorganisms as stressed by James et al. [40]. Therefore the quantification of the soluble, exchangeable and crystalline forms of Cr(VI) (expressed as the total amount of Cr(VI) in a sampling media), has direct implications for the assessment of Cr hazards in the environment [40]. This information also helps to minimize expenditure on environmental remediation that would be unnecessary if all Cr were present as Cr(VI) [41]. Strong alkaline reagents are recommended for solids in order to minimize undesired Cr(III)-Cr(VI) redox reactions during extraction [42]. The carbonate/hydroxide extraction method has been used by James et al. [40], Szulczewski et al. [43], Vitale et al. [41] and Farmer et al. [31], which consider this method as the most effective for the measurement of "total" Cr(VI) in soils. However the main remark made by Szulczewski et al. [43] is that "not only do such treatment perturb the chemical and the physical properties of the soil-water system, moreover there is no way to verify that all the Cr(VI) has been extracted". It is important to note that, especially with regard to the carbonate/hydroxide extraction, some dark colors (i.e. varying from light brown to dark brown related to high amounts of organic matter which are mobilized) interfere during the colorimetric measurements (for Cr(VI)), artificially increasing the value of the measured Cr(VI) [42].

2.4.2. Cascade Leaching Test (CLT)

Under natural conditions, waste materials are frequently in contact with water (e. g. rain or groundwater). In order to simulate such conditions successive leaching with water is carried out under laboratory conditions. Such a method provides information on the behavior of solid matrix waste

in contact with water. To observe the leaching of the heavy metals under long water exposures, the water leaching procedure is repeated three (DIN 38414-S4 [44]) or five times (NEN 7349, [45]; the so called Cascade Leaching Test, CLT). In Tack et al. [48], such extraction is carried out at a constant pH of 4 to simulate acid rain conditions, while in the NEN 7349 [45] protocol the pH at the end of the CLT is similar to the natural pH of the sample due to the impact of the buffering capacity (BC) of the sample. A summary of the leaching parameters is given in Table 3.

These leaching tests allow the determination of the leached amounts of a component, both per fraction, and as the cumulative leached amount. The sum of elements released in three or five extractions fraction removed from this leaching procedure was termed "soluble", while the amount retained in the sediments was termed "insoluble". Since no reference material exists for these leaching procedures, 10% of the extractions can be carried out in duplicate in order to evaluate the reproducibility of the results. The residue remaining after a specific leaching test can be analyzed by XRD or Scanning Electron Microscopy (SEM), in order to observe the particle changes due to the leaching procedure.

2.4.3. Sequential extractions

The use of such extraction is based on the premise that chemical reagents can remove elements or dissolve specific solid phase fractions. In essence sequential extractions use multiple extraction steps with chemical reagents of various strengths, solid/solution ratios, reaction times, temperature, pH controlling conditions, which are summarized as "operationally defined" parameters [49] in Table 1.

The measurement of operationally defined metal fractions will allow some forecasting of metal release from soils or sediments under certain conditions. It is therefore a valuable tool in the further management of contaminated soils and sediments. Several hybridizations and modifications have been made to the original 5-step sequential extraction procedure of Tessier et al. [36]. On behalf of the European Commission Bureau of Reference (BCR) team, Quevauviller et al. [50] introduced the simplified BCR procedure. This scheme (Table 4) yields information on three metal fractions: 1. the exchangeable fraction (associated with carbonates); 2. the reducible fraction associated with easily and moderately reducible iron and manganese oxides; 3. oxidizable fraction associated with organic matter and sulfide phases; and the residual fraction remaining undissolved after the three steps.

Sequential extraction, when applied in comparative sense, can provide valuable information that highlights the differences in element mobility or reactivity in a particular environmental context. Such information is valuable for

Table 1. Advantages and drawbacks of the single and sequential extractions.

Single Extractions		Sequential Extractions	
Advantages	Drawbacks	Advantages	Drawbacks
<i>More reliable than total concentrations:</i> → Gives idea of the general availability	<i>Operationally defined:</i> → Shaking time, ratio, pH. ...	<i>Valuable information:</i> → Elemental fractioning	<i>Operationally defined:</i> → Shaking time, ratio, pH....
<i>Simple:</i> → Only one extraction step	<i>More sample needed:</i> → Separate extractions	<i>Small quantity of sample:</i> → Same sample	<i>Long:</i> → Due to consecutive extractions
<i>Fast:</i> → Due the simultaneous different extractions	<i>Errors:</i> → Due to sample heterogeneity		<i>Errors:</i> → Due to sample heterogeneity
<i>No risk of sample losses:</i> → Absence of consecutive phase separations and washing steps	<i>Certified references:</i> → Not always available		<i>Risk of sample losses:</i> → During the extractions and washing
<i>Not all the work is lost:</i> → If something goes wrong during one extraction			<i>Hybridization of schemes:</i> → Based on the aim of the study
			<i>Certified references:</i> → Not always available
			<i>Problems:</i> → Readsorption and redistribution might occur

Table 2. Summary of single extractions used to infer the release of metals from soils and sediments under different conditions. S/L - Solid Liquid ratio; CRM - Certified Reference Materials; N. R. - Not Reported.

Single Extractions	Labile fraction	Concentration	pH	S/L ratio	Shaking		CRM	Reference
					time (h)	intensity (rpm)		
CaCl ₂	supposed to reflect soil solution	0.01 M	5	1/10	3	30	CRM 483	Quevauviller et al., [50]
EDTA	complexant, supposed to release metal complexes	0.05 M	7	1/10	1	30	CRM 483	Quevauviller et al., [50]; Pueyo et al., [35].
CH ₃ COOH (acetic acid)	indicates the effect of acidification	0.43M	4.8	0.025	16	30	CRM 483	Quevauviller et al., [50]; Pueyo et al., [35].
Water	indicates the water soluble Cr(VI)	-	5.7	0.05	1	N.R.		Vitale et al., [41]
K ₂ HPO ₄ (Phosphate buffer)	soluble + exchangeable Cr(VI)	5mM	7	0.05	1	N.R.		Vitale et al., [41]
HCl	equal to the 3-step BCR	0.5M		0.05	1	N.R.		Sutherland [34]
Na ₂ CO ₃ /NaOH (Carbonate/Hydroxide)	Total Cr(VI)	0.28M/0.5M	11.8	0.05	1	N.R.		James et al., [40]; Vitale et al., [41]
NaOH sonication (Hydroxide solution)	Total Cr(VI)	0.1M	13	0.05	1	N.R.		James et al., [40]; Vitale et al., [41]
NaOH 95°C (Hydroxide solution)	Total Cr(VI)	0.1M	13	0.05	1	N.R.		James et al., [40]; Vitale et al., [41]

predicting the heavy metal mobility, bioavailability and leaching fractions from the different sampling media [51]. However, there has been criticism regarding the application of sequential extraction procedures [49, 52–54]. According to these authors the methods are not entirely specific for the geochemical fraction of the soil and the eluates may also remove metals from other fractions. Major problems may be associated with readsorption phenomena which leads to artificially low concentrations of the heavy metal being released in a specific extraction step, the duration of the experiment, pH of the leached solution, temperature, particle sizes analyzed, the large number of reagents used as well as the loss of material during ex-

periment manipulations since the sample is filtered after each extraction step. Poor recoveries are obtained if the BCR three-step sequential extraction is applied to 100 mg specimens rather than to 1 g. pH stability during step 2 and its influence on recoveries is also reported [55]. McLean and Bledsoe [10] stated that no extraction procedure can be universally applicable to all the metals and soils. The most suitable extracting agent for defining the mobile fraction of metals in soils under specific site conditions is the one that simulates most accurately the solution chemistry of the soil. A summary of the advantages and drawbacks of the single and sequential extractions is given in Table 1. Despite its drawbacks, the sequential

Table 3. Overview of the parameters to perform the Cascade Leaching Test (CLT) according to NEN 7349 [46], NEN 7341 [47], DIN 38414-S4 [44] and modified NEN7349 [46].

CLT Parameters	NEN 7349	NEN 7341 Tack et al., [48]	DIN 38414-S4	Modified NEN 7349
particle size (mm)	powder	powder	<10	<2
S/L ratio	1/20, 40, 60, 80 100	1/100	1/10	1/20, 40, 60, 80, 100
Liquid	water *	HNO ₃ 1M	demineralized water	water *
pH	initial pH 4	constant pH 4	N.R.	initial pH 4
Shaking frequency (min ⁻¹)	4	N.R.	N.R.	4
Shaking device	mechanical shaker	magnetic stirrer	N.R.	horizontal shaker (45°)
Duration one step (h)	23	4	24	12
Subsequent steps	5	1	3	5
Filtration (μm)	0.45	0.45	0.45	0.45
S/L - Solid Liquid ratio; * water is acidified to pH 4 with a diluted solution of HNO ₃ ; N.R. - Not Reported				

Table 4. Sequential extraction protocols based on Tessier et al., [36] and the Quevauviller et al., [50] schemes.

Scheme	Step	Chemical agents and conditions	Fraction extracted
Tessier et al., [36]	Step 1	8 ml MgCl ₂ (1M; pH 7); 1h agitation	Exchangeable
	Step 2	8 ml CH ₃ COOH acetic acid (1M) to pH 5; 5 hour agitation	Bound to carbonates
	Step 3	20 ml NH ₂ OH.HCl (0,1M) in HNO ₃ (0,01M) pH 2; at 96 ± 3°C with occasional agitation until complete dissolution occurs	Bound to Fe-Mn Oxides
	Step 4	3ml HNO ₃ (0,02M) and 5 ml of H ₂ O ₂ (30%); the mixture is heated for 3 hours up to 85 ± 2°C by occasional agitation; add 3 ml of H ₂ O ₂ (30%); the mixture is heated for 3h with intermediate agitation; after cooling 5ml of 3,2M NH ₄ OAc was added and the sample was diluted up to 20 ml and agitated continuously for 30 min.	Bound to Organic Matter
	Step 5	2 ml HClO ₄ , 10ml HF _{conc} mixture; heat gently until half dry subsequently add 1 ml HClO ₄ conc, 10ml HFconc mixture; heated until completely dry; finally add 1ml HClO ₄ and evaporate until the white fumes disappear; finally redissolve with 25ml HCl (12M) and dilute up to 25ml	Residual
Quevauviller et al., [50]	Step 1	40 ml CH ₃ COONH ₄ (0,11M; pH 7); 16h agitation, 22±5°C	Acid Extractable
	Step 2	40 ml NH ₂ OH.HCl in 0,05M HNO ₃ ; 16h agitation; 22±5°C	Reducible
	Step 3	10 ml H ₂ O ₂ (pH 2-3) heat (85°C); 1h at 20°C; heat at 85°C 1h; add 10 ml H ₂ O ₂ ; heat (85°C), 1h; 50 ml 1M NH ₄ OAc (pH 2) and shake for 16h	Oxidable
	Step 4	add 10 ml aqua regia and evaporate until half dry and let the sample cool down; then add 20ml 2,5M HCl redissolve until solution is clear transfer the samples in the volumetric flasks and dilute to 50 ml	Residue

extraction method can provide a valuable tool to distinguish among trace element fractions of different solubility related to mineralogical phases [56].

Most parts of these extraction procedures rely on solution measurements and must be interpreted with caution. However a few studies have used X-ray diffraction (XRD),

Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM-EDX), XANES (X-Ray Adsorption Near Edge Structure) to analyze the residue solid phase after extraction with a reagent (see [57–59]). Such techniques allow the solid-phase products to be described after each step.

2.4.4. pH_{stat} batch tests

One of the controlling parameters of heavy metal mobility is pH. pH_{stat} leaching experiments are batch leaching tests in which automatic titrators are used to keep pre-defined pH values static over time. Such experiments can be useful to assess the long-term effects of pH variation with regard to the leaching characteristics of the heavy metals [60]. Different acid or alkaline solutions can be used during the leaching experiment in order to study the potential release of the heavy metals under these conditions. These tests estimate the mobility of contaminants by simulating changes that might occur in the natural environment (due to acid rain for example) in time with respect to pH [61]. Moreover, the amount of acid or base added to the suspension to keep the pH value at the pre-defined set-point gives a quantitative estimation of the Acid Neutralizing Capacity (ANC) or Basic Neutralizing Capacity (BNC) of the sample [61–63]. The parameters and the discussion addressing the Cr speciation and mobility are addressed elsewhere [64].

2.4.5. Column test

The principle of the column test consists in simulating the leaching of contaminants from granular materials (soils/sediments) using solutions at various concentrations. Column leaching tests are percolation tests in which a solution (leachate) passes through a column that contains soil/sediment material without agitation [45]. Column tests can be performed with undisturbed soil/sediment material (the original structure is preserved) or on disturbed samples (the structure is not preserved, rather, the sample is packed into the column). The retention time of the solution varies depending on the strength of its interactions with the granular material in the column, the ratio/composition of solvent(s) used, and the flow rate of the mobile phase.

2.5. Speciation

Speciation is a term widely used in chemistry that requires a good definition in order to describe its context. “Chemical species” is the specific form of an element defined as isotopic composition, electronic or oxidation state, and/or complex or molecular structure (i.e. Cr(III) as Cr_2O_3 while Cr(VI) as CrO_4^{2-}) [51, 65]. “Speciation” of an element is defined as the distribution of an element amongst defined species in a system, while the term “speciation analysis” is used to identify and/or measure the quantities of one or more individual species in a sample. Therefore, speciation is a key factor in distinguishing between different signatures (i.e. background and anthropogenic). Moreover, by quantifying the different chemical species, accurate pre-

diction for to heavy metal mobilization, bioavailability, as well as leaching rates of the toxic forms from the wastes can be made [51, 65, 66]. Speciation determines the mobility, bioavailability and the toxicity of a metal and that metal speciation depends highly on the site-specific seasonal and spatial variation existing in a particular water, sediment or soil system [67].

It is often impossible to determine the different chemical species in a system, due to the complexity of such analysis; in this instance fractionation, defined as the process of classification of an analyte according to physical and chemical properties may be a useful approach [51].

Kotas J., Stasicka Z., [68] made a summary of all the techniques available for the Cr speciation in solid matrix samples, while Hill et al. [6] indicated a list of main elements and the relative techniques that can be used to measure them in various sample media. Below will be illustrated the various species of chromium and some techniques for illustration. Cr(VI) species can be quantitatively assessed by colorimetry in the liquid samples (i.e. water, eluates, extractions) and by mineralogy (Figure 1) in the solid matrix samples (i.e. soils, sediments, dusts).

2.5.1. Colorimetry

The quantification of the Cr(VI) in solution is carried out by applying the colorimetric diphenylcarbazide (DCB) method [69]. Diphenylcarbazide at $pH\ 2\pm0.5$ gives a red violet colour in the presence of Cr(VI). Five minutes after the reaction takes place, the absorbance of the sample is measured with an UV-VIS Spectrophotometer 635, at 540 nm employing calibration standards (prepared from 10 mg/L $K_2Cr_2O_7$) in the range 0.05–2.0 mg/L. To minimize changes in chromium speciation, analyses should be carried out within 24 hours. In the eluates it was assumed that all Cr leached was composed of $Cr(III)_{sol.} + Cr(VI)_{sol.}$. If no red-violet colour was formed in the leachates during colorimetry reaction but Cr could be measured by AAS this was assumed to correspond to total soluble Cr (i.e. Cr(III)). If more Cr was detected by AAS than by colorimetry, the surplus was assumed to correspond to soluble Cr(III). To summarize, Cr(III) is calculated as follows:

$$Cr(III)_{sol.} = Cr_{tot.sol.} - Cr(VI)_{sol.}$$

The dissolution of organic matter might overestimate the soluble Cr(VI) in solution. Similar discrepancies have been reported in sites highly contaminated sites by COPR in New Jersey [70], Glasgow [31, 71, 72] and Pettine and Capri [42]. According to the latter authors the dissolution of humic matter (HM), especially in alkaline environments (digestion [41], see Table 2) might be the cause of the overestimation. Therefore, interpretation of the results must be carried out with caution especially when the OC

content is very high. In the case of solid matrix samples, additional mineralogical analysis must be carried out.

2.5.2. Mineralogy

Qualitative analysis (identification) of mineral phases by X Ray Diffraction (XRD) is usually a straightforward procedure based on searching and matching XRD reference patterns with those of unknown materials. Even when the most sophisticated search matches are employed, additional geochemical information is useful in the mineralogical identification. Moreover, Scanning Electron Microscope (SEM) and Energy Dispersive X-ray analysis (EDX) can provide morphological and compositional information that is phase specific and hence supplement data obtained by XRD. Quantitative analysis by XRD is difficult to achieve, especially when the samples contain complex mixtures of phases, as is often the case with highly contaminated sites or from waste materials [73]. Thus the complexity of many such mixtures and the resulting XRD patterns means that quantitative methods based on the measurement of single/several resolved peaks are often not feasible, but the trend (when possible) can be ameliorated by sample pre-treatment. However, a combination of geochemistry, XRD, SEM and EDX often gives consistent data on the composition of different sampling media.

XRD

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. XRD can be carried out for mineralogical characterization of soils, sediments, wastes, dust, and insoluble residue after 4-acid digestion as well as for the residues from different extractions. The samples for XRD analysis can be oven dried, ground in a mortar and then analyzed without any additional treatment. In the case of residues from digestions or extraction, when the quantities are rather small, the grains can be placed on a glass slide and fixed with silica gel, while in the case of soils/sediments, concentrated fractions of the sample should be prepared when possible. Operational conditions are highly dependent on the element to be measured (scanning angle) and the accuracy required (step size & counting). Phase identification of the crystalline phases is made with reference to patterns from Mineral Powder Diffraction Files (1986) of the International Center for the Diffraction Data. Moreover, it is important to stress that XRD allows the identification of crystalline phases that

make up more than 1–2% of the sample [74]. Consequently minor constituents and amorphous phases can hardly be detected by this method. Therefore if soil or sediment samples are analyzed, interference by the soil matrix that accounts for most of the sample (i.e. quartz, calcite) hampers the identification of waste materials from various industrial process. In Figure 2, examples of pure crystalline XRD patterns of Cr_2O_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ are given [75]. Examples of XRD chromium contaminated samples are reported in different publications from [64, 76].

Figure 2. XRD patterns of the pure crystalline phases A. chromite Cr_2O_3 (trivalent Cr); B. potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ (hexavalent Cr) from Shtiza (2007).

SEM-EDX

The Scanning Electron Microscope (SEM) permits the observation and characterization of heterogeneous organic and inorganic materials on a nanometer (nm) and micrometer (μm) scale [77]. This technique consists in collecting images due to scanning with a high energy beam of electrons. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, texture, composition and other properties such as the electrical conductivity.

To reduce their charging during scanning, the samples should be sputter-coated with a conductive layer of Carbon (C) or Gold (Au). After observation of morphological

characteristics by SEM, the elemental composition of specific phases can be determined by Energy Dispersive X-ray (EDX). Apart from the relative contents of the different components, nor SEM nor EDX gives no information on element speciation.

2.5.3. XANES

Synchrotron-based technique of X-ray absorption spectroscopy is a non-destructive method which enables the determination of valence and speciation of elements present in solid or liquid samples at different concentrations. Detailed X-ray adsorption near edge structure (XANES) studies on transition metal complexes have demonstrated the sensitivity of X-ray adsorption versus edge and (pre)edge features for different species (Cr, V, Ti etc. ...) as indicated by Farges et al. [78]; Szulczewski et al. [43]; Zachara et al. [79]. The presence of the (pre)edge features in the XANES scans indicates that a certain species (e.g. Cr(VI)) is present in the analyzed sample, while the edge indicates that the element (e.g. chromium) is present. Thus, by using the XANES technique is possible to have fast information on the presence and the quantities of a certain element in the analyzed samples.

Data from modern techniques such as XAS (X-ray Absorption Spectroscopy) that give information on the molecular scale of a soil/sediment should be used in conjunction with leaching techniques, but they are expensive and can only be conducted in specialized institutes such as the European Synchrotron Radiation Facility.

2.5.4. Geochemical modeling

Several equilibrium thermodynamic computer programs are available for modeling soil solution and solid phase chemistry by providing information on the thermodynamic possibility of certain reactions. As summarized by McLean and Bledsoe [10] these models are used to: 1. calculate the distribution of the free metal ions and metal ligand complexes in a soil solution; 2. predict the fate of the metals added to soil by providing a list of the precipitation and absorption reactions likely to control the solution concentration of metals; 3. provide a method to evaluate the impact of changing one or more soil solution parameters (i.e. the pH, redox, inorganic and organic ligand concentration, or metal concentration) on the adsorption or precipitation behavior of the metal(s) of interest. In addition to the calculation of the equilibrium speciation of the chemical elements in the soil solution and precipitation/dissolution reactions, models such as Geochem [80], MINTEQA 2 [81, 82], PHREEQ C [83], ORCHESTRA [84], Visual MINTEQ 2.4 [85], can provide information on cation exchange reactions and metal ion adsorption. However it must be stressed that these models are equilibrium models

and as such do not take account of the reaction kinetics. The limitations of these models are also related to the thermodynamic database available for the calculations.

2.6. Reproducibility of the data and reference materials

Reproducibility of the results is a key issue in environmental studies, especially if it is desired to compare results for soils from different areas, which might have been sampled, treated and analyzed by different people and with different methods [86]. Fortunati and Pasturenzi [7] stated that the error arising from sampling on location is typically larger than that linked to the preparation, manipulation and analysis of the sample. Wagner et al. [87] stated that it is difficult to guarantee that later investigation will meet exactly the same conditions as in previous studies, due to spatial and temporal variability of samples in the field. OECD principles of GLP (Good Laboratory Practice) and compliance monitoring can be found in the documents prepared by OECD¹. In chemical laboratories there are in place standard quality assurance (QA) and quality control (QC) procedures which represent the administrative and technical steps undertaken to ensure that reliable data are produced with specified precision and accuracy [88]. Apart from several replicates from the same sampling media, there is a considerable interest in the use of certified reference materials (CRMs) for environmental analysis. A CRM is a reference material with one or more properties which are certified by a technically valid procedure, and which is accompanied by a traceable certificate or other documentation issued by a certifying body [30]. The utility of using CRMs lies in the fact that comparison of results obtained by different analytical methods can be achieved by comparing the values with known materials. The increased requirement for assessment of the bioavailable metal fraction as well as of the mobility of heavy metals which could contaminate soils, sediments and groundwater explains the development in the last decades of a large number of analytical approaches (i.e. single or cascade leaching tests, sequential extractions, pH_{stat} batch tests, etc), in order to develop realistic risk assessment models Fairbrother et al. [88]. The large number of methods proposed by Tessier et al. [36], Kerstner and Förstner [37], James et al. [40], La Force and Fendorf [57], Sutherland [34], van Herreweghe et al. [64] and Dold [59] resulted in diversity in the procedures applied, which make the comparison of results extremely difficult. The final

¹ <http://www.oecd.org>

Figure 3. Flowchart of the main steps necessary to perform an environmental investigation of a contaminated site from the industrial activity.

outcome in earlier publications is difficult to assess, due to the lack of certified reference materials for data comparison and the adaptations made during the respective studies. For this reason, the former European Commission Bureau of Reference (BCR), now known as Standard, Measurements and the Testing Program of the European Commission, in an attempt to standardize the procedures and compare the results, has introduced several extraction procedures associated with certified reference materials (CRMs) [51]. Reference materials exist for EDTA, calcium chloride, acetic acid (CRM 483 and 484) and sequential extraction (CRM 601 and BCR 701) methods. The use of the BCR during the tests will provide more reliable data that can be compared with data published in literature or data generated by other laboratories.

Recently a speciated Standard Reference Material (SRM-2701) has been prepared by NIST (US National Institute of Standards and Technology) and assigned certified values for Hexavalent Chromium in Contaminated Soil High Level, while the Low Level SRM-2700 is in preparation Nagourney et al. [89]. The source material for the new SRM was collected from a waste site in Hudson County, N.J. After milling, blending, and sterilizing, sci-

entists analyzed the samples for hexavalent chromium using several EPA-approved methods designed to minimize and compensate for the chameleon-like chemical properties of chromium. The contaminated soil SRM-2701 has certified values for hexavalent chromium, total chromium, iron and manganese as well as reference values for other elements of environmental interest including aluminum, calcium, magnesium, nickel, silicon, sulfur, titanium and vanadium. Therefore it is vital that a sufficiently detailed description of the analytical procedure is provided and strictly followed, if harmonized results are to be obtained.

3. Discussion

The sources of heavy metals in the environment are mainly geogenic and anthropogenic in origin. Heavy metals from solid wastes generated through the mining and processing of mineral ores, as well as from waste generated from daily life, account for a considerable amount of the total released through anthropogenic activities. Improper disposal of waste(s) can cause wind and water erosion, which can ultimately result in the transportation of contaminants.

Depending on the mobility of contaminants, leakage from waste piles could then pollute nearby groundwater systems and surface streams. These processes, as well as additional questions related to the specific impacts of metals on the environment and on human health, reflect the need to establish ready and accessible metal-specific tools and data sets in order to make informed, science-based decisions. Since the methods and models used to evaluate hazards, set priorities, establish environmental criteria, and assess risks, are currently developed and used in different jurisdictions, such as the European Union, the United States, Canada and so on, this makes the final outcome of these investigations very difficult to compare [1, 2]. Over the last few decades, a large number of techniques, such as, total trace element characterization, single extractions, sequential extractions, pH- dependent leaching tests, column tests, etc., have been used to characterize different sampling media, such as soils, sediments, dust particles and, wastes. These techniques were developed to characterize the mobility of contaminants and their impact on the environment, taking into account that the leaching behaviors of specific constituents are a function of key controlling factors which are common to many materials such as pH, organic matter, dissolved organic matter (DOM), redox and salt load [90, 91]. In environmental studies, the release and readsorption of trace elements is important for establishing the mobile fraction as well as speciation under various chemical conditions. While the release of trace elements is important from the ecotoxicity point of view, their retention is relevant in order to design specific physico-chemical treatments that can bind them to the immobile fraction of the soil/sediment particle [91]. Contaminant remobilization occurs when altered ambient conditions induce changes in retention capacity of the soils/sediments particles. Choosing the most appropriate analytical methodology requires an understanding of how the contaminant binds to the soils/sediment and the conditions under which the contaminant will be released. As indicated in the previous sections, the results obtained upon application of operationally-defined speciation protocols largely depend on conditions (reagents and their concentrations, treatment times, temperature, etc.), making comparison between partitioning patterns obtained using different schemes is difficult. The accuracy of sequential extraction methods is much more difficult to estimate than that of a total metal determination due to the many extraction steps involved. Moreover, mimicking field conditions in the laboratory is a difficult task since the methods are operationally defined, whereas the testing techniques are developed to quantify and understand the contaminant mobility under specific leaching or testing conditions and to predict changes over time by using chemical

models [63, 64]. The large variety of environmental problems, a direct legacy of industrial expansion, has to deal also with the large number of techniques used to achieve the most relevant information with respect to risks related to deposition of wastes and different discharge pathways. The total concentration digestion yields data on the total amount of major and trace elements without providing any information on the binding processes or availability of the investigated elements, while the single or sequential extraction will depend highly greatly on the information that needs to be collected. Single extractions are generally considered to be fast methods that provide insights into the sediment/soil leaching behavior for short periods of time. Generally, sequential extractions leaching techniques that last for days are criticized for being time consuming, readsorption process between subsequent steps, and require qualified personnel [49, 55, 56], however they do provide comprehensive information on the origin, occurrence, biological and physico-chemical availability, mobilization and transport of trace elements [91]. They have also shown to be convenient for determining the trace element association with the main accumulative phases in soils and sediments, since the selected extractants are environmentally meaningful, and also for distinguishing between geogene and anthropogene trace element origins [36, 91]. Despite the aforementioned drawbacks, these methods have been extensively used in recent years, especially since the introduction of certified reference materials with certified amounts of extractable trace elements, the use of which can reduce uncertainty and increase the validity and harmonization of the applied techniques. Since the majority of environmental studies have been conducted on soils and sediments, and, very few studies have been conducted on dust particles, fly ash, or solid waste incineration, the use of , these certified reference materials should be expanded in order to broaden the scope of these types of studies and the overall application on these leaching techniques. A three-tiered approach consisting of: 1. historical and reconnaissance study; 2. main sampling campaign and analysis; and 3. results and reports, is proposed to address the possible pollution/contamination caused by industrial activities (Figure 3). This protocol can be used when the deposition, discharge and transportation of pollutants has occurred for some time, and can recommends various steps be followed in order to confine the aerial extension of contamination and quantify the contamination/ pollution levels (Figure 3). Moreover, special attention should be given to the deduction of local background concentrations, chemical speciations, predictions for changes in both the short and long term, and any implications for natural attenuation processes [65, 76]. Not all the collected samples

should be analyzed in detail from the beginning. After general sample characterization in the field and laboratory, geochemical analyses can provide an overview with respect to the distribution of the contaminants based on total concentrations. Specific extractions, mineralogical determinations, and additional treatments can be carried out on particular samples only. This is the case for spectroscopic techniques such as XANES and XAS, which are less accessible, more expensive, and sometimes may not be sensitive enough for background samples [33]. Because uncertainty resulting from sampling and sample pretreatment can have a major impact on the final results even when the most sophisticated techniques are applied [6, 9], accurate and well described sampling, sample pretreatment and application of standard analytical protocols are crucial in obtaining reliable results [17, 86, 87]. Uncertainty associated with the analytical results is an issue of major interest for the whole analytical community. A major effort has been made to improve the detection limits of many analytical techniques in order to decrease uncertainty. Since heterogeneity and sampling techniques have such an important impact on the final results, fast, cost effective, and reliable screening methods that detect multiple contaminants especially in mixed polluted sites should be developed [90]. On-site measurements cannot by any means substitute for laboratory measurements, but can give a good preliminary estimate of general concentrations.

4. Conclusions

In conclusion, it can be stated that after an accurate sampling campaign [4] appropriate sample pre-treatment and the selection of relevant techniques to obtain information on the speciation, mobilization, bioavailability of the contaminants in the environment are required. In order to obtain relevant and reliable results there is a need to use recognized methods and techniques always keeping in mind that project costs must stay within the budget. The key steps to be remembered and applied during sample pre-treatment and selection of relevant techniques and tools identified by this literature review are the following:

1. Strict adherence to the standard operational procedures (SOP) for sample pre-treatment in order to prepare a representative and homogeneous sample for analysis, since this phase has been identified as very crucial for generation of reliable results;
2. Accurate selection of the methods to be used in order to address the main issues based on the scope of the project;
3. Use of recognized certified/standard reference materials in order to generate reliable data;
4. Preparation of a preliminary report specifying the samples that will need additional analysis and the rationale;
5. Documentation of any deviation from the SOP and the rationale for the deviation;
6. Preparation of the final draft of the report, including assessment as to whether the initial scope of the project has been fulfilled.

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