Cent. Eur. J. Geosci. • 1(2) • 2009 • 193-206
DOI: 10.2478/v10085-009-0018-3

VERSITA

Central European Journal of **Geosciences**

Appropriate sampling strategy and analytical methodology to address contamination by industry: Part 1. Conceptual model of a sampling design and sampling types

Review Article

Aurela Shtiza[1,2*], Artan Tashko[3]

1 *Katholieke Universiteit Leuven, Faculty of Sciences, Geo-Institute, Celestijnenlaan 200E, B-3001 Heverlee, Belgium*

2 *Arcadis-EURAS, European Risk Assessment Center, Kortrijsesteenweg 302, 9000 Gent, Belgium*[†]

3 *Polytechnic University Tirana, Faculty of Geology and Mining, Geochemistry Department, Rr. Elbasanit, Tirana, Albania*

Received 25 February 2009; accepted 24 April 2009

Abstract: This paper presents the results of a literature review on the conceptual model of a sampling design and the different types of samples that can be used to characterize the nature and the extent of contamination at a specific site. The main findings stress the importance of sampling for obtaining relevant sample types and subsequent-qualitative results. The proposed sampling design can be used for environmental studies where, the efficient use of time, money, and human resources are very critical. A good quality sampling design should meet the needs of the study with a minimum expenditure of resources.

Keywords: conceptual model • sampling design • sampling types • contamination • risk assessment • cost-benefit analysis

1. Introduction

The aim of industrial development, especially during the 19–20th century, was to produce sufficient goods to supply the increasing demand without paying much attention to the long-term effects of the wastes released, into the atmospheric, aquatic and terrestrial environments. The inability to landfill (mineral) wastes has been one of the most significant factors related to factory closures, inevitably leaving some legacy of toxic wastes [1]. The pattern of contamination is characterized not only by local highly-concentrated sites such as toxic waste dumps and mine tailings, but also by lower-concentrations of contaminants dispersed over the landscape, including sediments in rivers, lakes and estuaries as well as soil in pastures and forests [2]. Therefore today, contamination is perceived as a widespread problem of varying intensity and significance. It is widely recognized that radical risk control, such as cleaning up all sites to background concentrations or to levels suitable for the most sensitive land use, is neither technically nor economically feasible. Although the need for policies to protect soil and groundwater is recognized, strategies for managing con-

*E-mail: aurela_shtiza@yahoo.com
†Current address

taminated land have moved towards a fitness for use approach [3]. According to Hursthouse [4], the risk posed by higher concentrations of trace elements in soils, sediments or other particulate sample media depends strongly on the ability of the contaminants to migrate into the environment through different possible pathways (i.e. environmental compartments, due to favorable pH-Eh conditions, low acid neutralizing capacity or base neutralizing capacity, low organic carbon, clay composition, etc. ...).
To study the industrial impact on the environment, exploration geochemistry serves as an instrument, providing the fundamentals, which consist of: 1. a conceptual model for an appropriate sampling design; 2. sampling types; 3. sample analysis; and 4. interpretation of results [5, 6]. The aim of the present literature review is to summarize the appropriate sampling design by means of a conceptual model and some sampling types that can be used to assess the contamination in a present or former industrial site.

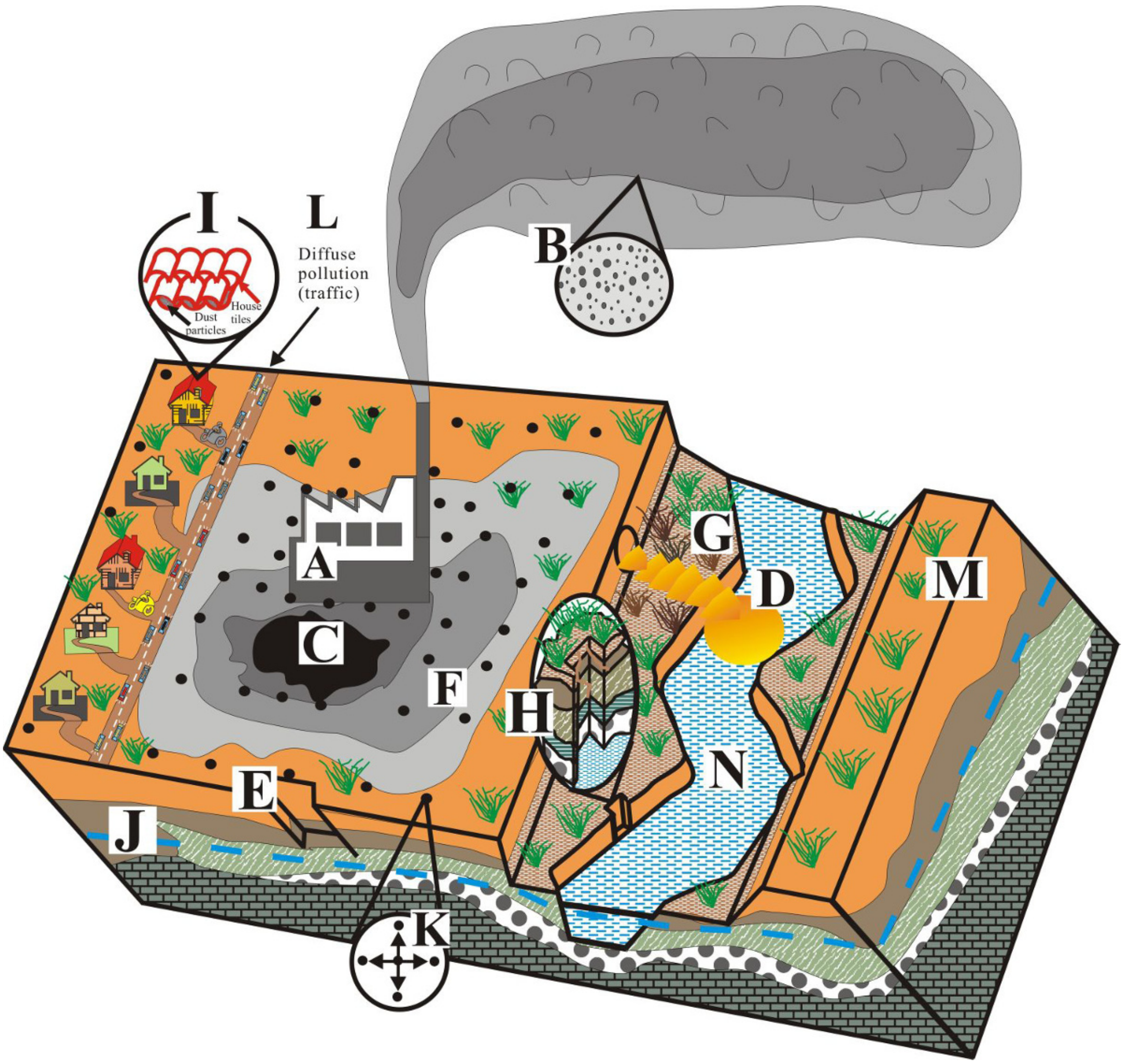

Figure 1. Block diagram showing an industrial plant (A), stalk emissions composed of fine and coarse dust particles (B), solid wastes (C) released and dumped in the immediate vicinity of the industrial site and waste waters (D) discharged into the river system. Additionally the different sampling media soils (E: profile, F: top soils, in regular grid); active stream sediments (G); overbank (H); dust (I), vegetation (M) and surface water (N) and groundwater (J) are also indicated. (K) illustrates the sampling of composite samples for top soils, while (L) illustrates the diffuse pollution caused by car traffic along roads.

2. Sampling design

Three types of wastes are generally released from industrial activity: gasses, waste waters and solid waste. In Figure 1, a conceptual model illustrates an industrial installation and the different waste release pathways. These releases can occur together, or they can occur as standalone depending on the employed industrial process. The scope of a sampling design can vary widely, but generally for an industrial contaminated site it can be summarized as follows: a) characterize the nature and extent of the contamination in a specific site; b) identify the location of 'hot spots' and/or delineate the plume; c) assess the mobility of contaminants; d) monitor trends in environmental conditions or indicators of health; e) support the decision whether contamination levels exceed a threshold of unaccepted risk [6]. A complete sampling design should indicate the total number of samples needed to be collected in a certain area under specific conditions (i.e. distance from a contamination source, geographical location, season, time, and so on) to characterize the spread of the contamination.

A well-planned sampling design is intended to ensure that the collected samples are adequately representative for the scope of the study. Throughout the sampling design process, the efficient use of time, money, and human resources are critical considerations to be applied. A good sampling design should meet the needs of the study with the minimum expenditure of resources [6, 7]. An important notion for sampling design is the conceptual model, since this will help to develop an accurate model to assess the potential hazard(s). The conceptual model describes the expected source of the contaminant in the area of concern, the aerial and vertical distribution of contaminants, identifies the relevant sampling media and the relevant fate and exposure pathway(s) to be considered.

2.1. Types of sampling design

To improve the quality of the information obtained from environmental samples, several types of sampling design can be applied [6]. This section will describe each sampling design and provide useful information on the applicability as well as advantages and pitfalls.

2.1.1. Systematic and grid sampling

A present- or past-contaminated industrial site can be subdivided into regular latitude and longitude sampling intervals over an area (grid sampling) or regular time/depth intervals (systematic). The systematic sampling can refer to the sampling of water samples at regular intervals, or to estimate the spatial trends over time (depth). Initially, the first sampling spot is related to an identification spot and thereafter the remaining sampling sites are specified so they are located according to a regular pattern [8]. The samples can be collected in one, two, or three dimensions if the population has a spatial component. Grid design can vary in shape, orientation and selection criteria for the initial grid node.

The regular grids generally refer to soil/sediment surfaces with a certain shape such as square, rectangular, triangle or radial grids (star pattern). This design provides a uniform coverage of a site or location. In the case where a plume or a waste discharge has to be delineated, the selection of a rectangular or triangular grid can be the most appropriate, so the samples to be collected are already pre-designed thus a uniform coverage of the site or location is ensured. This type of design can be implemented with little or no prior information on the site itself, but information on the total area to be covered and the number of samples are essential before the sampling is initiated. The grid sampling can be of great value, especially in geostatistical studies.

2.1.2. Composite sampling

This type of sampling indicates the physical combination and mixing of selected sampling units in the field in an effort to form a single homogeneous sample [9]. This sampling methodology can be very cost effective since it will reduce the number of analyses to be performed. However it is important to keep in mind that the sample collection will require more time than a grid sampling since the mixing process requires that at least the visual characteristics (such as grain size, color, iron content, organic content and so on) of the samples are similar, so their geochemical signatures will be alike. The composite sampling can also be combined with the grid sampling and in the pre-defined sampling spots, composite samples can be collected.

2.1.3. Simple random sampling

This type of sampling design is selected when: 1. information on the contaminated site is absent so the study is in a reconnaissance phase; 2. no major patterns of contamination or "hot spots" are expected. The main advantage of this sampling design is that it provides unbiased estimates of the mean, proportions and variability; it is easy to implement; and data analysis is very straightforward [6]. This sampling can be used interchangeably for contaminated sites or for the observation of general trends in exploration geochemistry.

2.1.4. Stratified sampling

This type of sampling is selected when patterns or information such as contaminant spreading, geological substrate, prevailing wind direction, soil/sediment are known from pre-existing information or expert judgment. The advantage of this sampling design is that it yields more information and it is easier to group the data on certain common patterns based on pre-existing information, it also allows a reliable estimate for population subgroups to be made. This type of sampling can be generally used for surface or deep profile pattern characterization when the grouping of the different populations facilitates the sample collection and the later interpretation[1] [6]. The prerequisite for this sampling type is that prior knowledge of the population is required in order to effectively define the sampling strategy.

2.1.5. Judgmental sampling

Expert judgmental sampling is generally used for areas or sites that have been already investigated in detail. A further investigation will aim to address particular features or investigate in detail some of the previous results. In this case, the judgment of an expert on where to sample, what to sample and how to sample is crucial [6]. This type of selective sampling can be applied for example to investigate the relation between two (or more) types of samples e.g. soil-sediments; dust precipitation-vegetation; sediment-contaminant availability due to the contact with water; and so on, as shown in the study of Niskavaara et al [10].

3. Investigating local background samples

Forster et al. [11] identified the sampling of a contaminated site as the key element of the overall quality in the evaluation of potentially contaminated sites. The collection of historical information about the site and the potential for the presence of contaminants before the sampling is carried out helps in defining accurately the main objectives of the investigation. A further step consists in a preliminary sampling in order to make an estimation of the contamination levels and design the main sampling campaign. The results from this reconnaissance study will allow the design of a conceptual model and the planning of the detailed investigation [6, 12].

[1] *Shtiza et al., 2005*

3.1. Local background concepts

Before introducing the background sampling strategy, a review of the different concepts with regard to the way local background concentrations are defined is necessary in order to avoid possible confusion with respect to natural concentrations and pollution. The concepts of background, threshold and anomaly will be addressed, in order to grasp the evolution, similarities and differences with respect to their use in exploration geochemistry and environmental geochemistry.

The term *"geochemical background"* was introduced initially by exploration geochemists. *Background* is the normal abundance of an element in earth material and should be considered as a range rather than an absolute value [13]. These authors introduced another concept to discriminate between normal and anomalous element concentrations. By definition a *geochemical anomaly* is a deviation from the norm (the geochemical patterns which are normal for a given area or the geochemical landscape). Moreover, to distinguish between background and anomaly, the term "threshold" was introduced. The *threshold* is the upper limit of normal background fluctuation according to Hawkes and Webb [13], while according to Garrett [14] threshold is the outer limit of background variation. In the dictionary of "Environmental Science and Technology", Porteous [15] defines the background concentration as: "If the environment in a particular area is polluted by some substance from a particular source, then the *local background* level is the concentration, which would exist without the local source being present". In the case of pollutants which are entirely anthropogenic, according to Hursthouse [4], *baseline levels* are those at which the measurement cannot detect the presence of the contaminant. A critical comparative study with respect to the methods for determining background and threshold values was made by Reimann et al. [16]. In exploration geochemistry, the samples which display higher concentrations (known as outliers), may indicate the mineralization sources, while in environmental geochemistry, such outliers are most likely related to the activity of a contamination source. Therefore, the identification of these sources is of paramount interest in order to estimate their impact on the surroundings. Thus, in environmental studies local background is defined as "the elemental concentration(s)" before industrialization [16]. However, pre-industrial background data are not available for every location where industrial activity has occurred. Consequently it is often difficult to correctly assess the real effect of the industrial activity. Moreover, without a full understanding of the local interaction of the contaminants and their ecological impacts, the derivation of the absolute concentrations is meaningless [17]. The strategy for deducing local background sam-

pling is discussed in detail below.
In the literature, examples where background concentrations are referred to as "action level" or "soil clean-up" criteria are found for USA [17], Belgium, The Netherlands, Denmark, Finland, Canada and Norway [3]. Due to the high economic implications, the regulatory regimes are moving towards a risk-based assessment process for contaminated sites [18]. This is a crucial point for the "speciation community" as it will drive the development of appropriate testing systems and stimulate the collection of data linked to the environmental impact. By applying speciation criteria to the investigation, the risk-based approach will allow the development of a more effective remediation strategy. Based on the cost-benefit analysis, sampling types and density versus cost in a specific site, this will provide a more realistic evaluation of the volumes of material to remediate [4].

3.2. Strategy of defining local background concentrations

One of the main aims of this review is to separate the signature between the natural (geogene) and contaminated (anthropogene) areas. To achieve this delineation, the deduction of local background concentrations is compulsory. In order to determine local background concentrations for major and trace elements in different sampling media, sampling locations minimally influenced by man have to be sampled. A summary of the local background sampling strategy applied in some investigations carried out in Albania [19–22] and also inferred from literature follows:

1. To identify local background areas, the study area has to be screened carefully. This screening is based on a desk study during which the geological setting, organic matter, clay content (mineralogy), climate, relief, hydrogeology, vegetation, prevailing wind direction, are considered. Thereafter the field inspection will confirm the strategy designed for the local background sampling. This allows identifying the possible locations where local background values might occur. Specific soils are always developed on specific geological formations, meaning that high concentrations of heavy metals in residual soils and related terrestrial sediments might reflect a weathering signature of parent material with soil (sediment) composition [5]. This is especially relevant for example in soils/sediments developed above ultramafic substrate as is the case for Albania [19, 23], New Caledonia [24] and USA [25]. The residual soils display very high concentrations of Mg, Fe, Cr and Ni far above the eco-toxicological levels proposed by Brooks et al. [26]. Therefore if no consideration is made with regard to the geological substrate, soils/sediments with a high content of specific heavy metals might wrongly be classified as contaminated. This might result in severe financial and social implications. Moreover, if different geological substrates occur within a study area, then background levels must be determined for the different geological substrates separately, as well as for the different sampling media [19, 24, 27], since enrichment and dilution factors have to be taken into account.

2. To establish "local background values/concentrations" for a certain sample type in a study area, an adequate number of samples have to be collected over a sufficiently large area to be able to deduce the geogene (natural) signature for this sample medium. Therefore local background concentrations reflect a range rather than a single value [5, 17].

3. In order to define local background values, the collection of various types of samples in the direction of downwind transportation must be avoided. This is due to the fact that contaminated particles are transported by wind over large distances as shown in Nriagu et al. [28]; Kim et al. [29], Gosar and Sajn [30] and Sajn [31], Pacyna et al. [32] and Wilson et al. [33]. To infer whether deposition of contaminated dust particles has affected the surface samples, surface soil/sediments as well as entire profiles, might be considered for further investigation. If similar concentrations of major and trace elements occur at the surface and in entire profiles, then these samples are suitable for the deduction of local background values indicating that no element translocation has taken place within the selected profile and interference by dust can be discarded.

4. The distance between so-called "background area" and a contamination/pollution source area needs to be sufficiently large to provide samples where the influence of pollution is considered to be non-existent. It is furthermore recommended to avoid inhabited areas or areas with a high population density to minimize possible anthropogenic influences (as described in Horckmans et al., [27]).

5. It is well known that roads are sources of diffuse pollution with traffic contributing gases such as N_xO, SO_x, CO and CO_2 [34]. It is also recommended to avoid roads where raw material or final products of industrial activities may have been transported

since contamination is likely to occur [28]. However it is known that the majority of the habitations are mainly constructed near the main roads, due to the facilities they constitute. Thus a buffering zone between the local background samples and the roads must be respected as well as the rationale behind it. Depending on the surface of a study area in general a distance >100 m from roads might be sufficient for representative local background samples [27].

6. The collection of local background samples under vegetation is strongly advised by Horckmans et al. [27], since the occurrence of an adult population of trees normally ensures that the soils have not been disturbed by human activities, at least for the life time of the tree. The presence of forests, which normally act as long-term stable ecosystems, strongly depends on the specifics of the site (climate, relief, clay content, pH etc. ...). Plants developed upon ultramafic formations are known to be adapted to high concentrations of Cr, Ni and Mg as shown in Shallari et al. [35]. In contaminated sites the deposition of dust particles rich in heavy metals upon leaves and incorporation within the leaf structure results in higher concentrations in plant leaves as shown by Sheppard [36]. Therefore addition of leaves in autumn/winter to the soils may result in a supplement of heavy metals especially in the top soils.

In conclusion, local background values (LBV) reflect the natural distribution of an element in a certain area. LBV can be influenced by the geological substrate, human activities, transportation of dust by the wind according to prevailing directions, presence of additional anthropogenic sources (urbanization, roads etc. ...). Moreover LBV do not reflect an absolute value but rather a range of values and should be differentiated according to the sampling medium (residual soils, river sediments, overbank sediments, dusts, and so on). Thus identification of LBV is a function of the objective, conditions and the scale (local or sub continental) of the study area. Despite these efforts, it must be acknowledged that some or even all sampling media are possibly influenced to some minor extent by past or present contamination related to local point (industry) or diffuse sources such as traffic, urbanization, agricultural activities, etc. ...

4. Sampling types

The overall surface area to be investigated, its geographical position, and absence or presence of different geological formations mainly influence the sampling strategy. However, restrictions in the sampling strategy might be the costs involved, time for the investigation and area to be investigated [7]. Due to the different discharges generated from industrialized factories (Figure 1), the air, biota, aquatic and terrestrial (i.e. soils and sediments) compartments are the most vulnerable in an ecosystem. Mobility is defined as the ease with which an element can move within a specific environment [5] and it depends primarily on factors such as: speciation of a trace element, pH, Eh, CEC, acid/base neutralizing capacity (ANC/BNC), clay content, etc. These factors are responsible for the mobilization of the metals from the solid into the aquatic phase and hence transport within the immediate vicinity, having an impact on the rate of dispersion, dilution, uptake and transfer into living organisms [4]. In Figure 1, the main pollution sources, discharges and migration pathways into the different compartments of the environment are illustrated. The advantage of sampling different media (i.e. soils, active stream sediments or overbank sediments, water, dust, vegetation) is that covers the different mobilization pathways by which the contaminants may be transported within an industrial area. The environmental impact of heavy metals in soils, sediments and other sampling media depends on the chemical speciation of the heavy metals and the matrix response to biological and physico-chemical conditions.

4.1. Soil samples

Soil has been defined as the product of weathering which generally remains in situ above the weathered parent rock. Soil is subject to anthropogenic processes and to the input and/or disturbances from contaminants [4]. The presence of so-called "hot spots" might be recognized in soils by the lack of vegetation due to the disposal of waste materials. In Nortcliff [12], a "hot spot" is defined as an area of extremely high contamination (pollution) within a site that is generally contaminated. Moreover due to several migration pathways (i.e. waters, dusts, etc. ...) the contaminants might be transported into other compartments of the environment. The migration of contaminants and soil processes tends to occur over a larger time scale if compared to sediments [4].

Theocharopoulos et al. [37] compared the European Soil Sampling Guidelines (ESSG) in different countries in order to estimate the differences and similarities and to evaluate how methodologies might affect data quality. The investigation showed that the strategies used in the study of soil pollution, diverge according to differentiated legislation frameworks, sampling strategies (depth, distance, different horizons), sample treatment (homogenization, sieving, oven-drying), methodology applied (analytical protocols), etc. In several countries soil sampling protocols were standardized (e.g. ISO-DIS 10381-5, [38]) and defined by national scientific societies or standardization institutes. The sampling pattern is usually a grid but it may be carried out randomly, or sometimes it is not even mentioned. With respect to the sampling density no real standard exists. Moreover the term "top-soil samples" in different European countries differs according to whether the humus layer has to be sampled separately, as well as its thickness variations. Such differences between the strategies and methodologies make a direct comparison of the results extremely difficult [39].

Soil surveys, as illustrated in Figure 1F, are normally conducted based on a systematic grid system and according to Levinson [7], the space between samples is determined by the costs involved, the intensity of the industrial activity, the area to be investigated, or the type of contaminants to be investigated. By sampling on a regular grid, the area under investigation is equally covered giving an accurate overview of the distribution of the pollutants [40]. The soil samples collected should be representative of the sampled location, but heterogeneities related to the geological and pedogenical formations are always present. In order to minimize such heterogeneities, composite or bulk samples (which represent a wider area, small-scale clusters) can be collected. By doing so, an improvement in the analytical precision is realized [40]. To improve representativity, Adriano [41] and van Herreweghe et al. [9], used a composite sample that was collected according to a star-like pattern at each soil sampling point (Figure 1K). This means that one sub-sample is collected at the predefined spot, while four additional sub samples were collected in four directions perpendicular to each other at a distance of one meter.

The sampling showed that it is important to define the problem accurately and report the type and depth of the sampled soil. Thereafter the combination of different approaches with respect to the different sampling media (Figure 1), strategies and geochemical treatments are selected based on the primary scope of the study. The main reason for collecting soil samples at different depths or in profiles (Figure 1E) is to detect the variation due to pedogenic processes and thus to test the hypothesis of pollution as illustrated and discussed by Baize and Sterckeman [42]; Wagner et al. [40]. An additional reason to collect samples at depth is to investigate whether any possible infiltration of the contaminants has taken place.

4.2. Active stream sediments

While soils act as a sink and/or as a filter that protects the groundwater from the infiltration of pollutants, surface waters and eroded sediments can play a role in the mobilization and transportation of pollutants. Many river basins in the world are seriously affected by heavy metals released into the environment from mining and industrial activities as shown by Wolfenden and Lewin [43]; Swennen et al. [44]; Hursthouse et al. [45]; Hudson-Edwards et al. [46]; and Pirrie et al. [47]. Polluted particles are transported and deposited into the floodplains and wetlands, which act as a temporary sink for heavy metal deposition and storage in river basins [48]. The release of these substances may affect micro-organisms, plants and animals which rely on rivers for habitat and food [46, 49, 50]. Recent studies have demonstrated that contaminants may remain in these deposits for years, centuries or even millennia before they are remobilized by physical, chemical or biological processes (see [48]). During the last decades, the interest in the distribution of heavy metals in the alluvial deposits has increased considerably [19, 43, 48, 51, 52]. Moreover there is growing evidence to suggest that significant amounts of heavy metals are now being mobilized from the floodplain sediments as result of anthropogenic disturbances, including hydrological changes associated with global warming [48, 53]. Thus studies on alluvial (active stream or overbank) sediments have shown that the contaminant history can be accurately determined by investigating the fluvial (river) systems [46].

Active stream sediments (Figure 1G), composed mainly of silts and clay fractions, are the basis of most drainage basin surveys. Although originally developed for mineral exploration, actual river sediment reconnaissance surveys have subsequently been found to be of great value for highlighting geochemical anomalies, as well as for showing the regional patterns of nearby soils [54]. Spread of contaminants can occur along rivers which drain industrial areas as shown by Wolfenden and Lewin [43], Hudson-Edwards et al. [46], Hursthouse et al. [45, 55], Pirrie et al. [47] and Sullivan and Taylor [56]. Moreover sediments become enriched with many heavy metals due to continuous deposition of suspended particles from the overlying water [57], or by dust particles [29]. Often in mining and industrial areas, the active stream sediments reflect the actual pollution occurring in the drainage area [43, 48, 50]. Although sediments are not considered to be soils, they consist of a solid matrix and show similarities with soils in terms of heavy metal interaction. Sediments reflect more dynamic processes of transport, deposition and interaction with fluids, due to the saturated conditions in which they mainly occur. Moreover, when compared to soils, sediments contain minerals and organic matter while the gaseous phase is minimal [4].

4.3. Overbank sediments

Overbank deposits are formed when the water discharge exceeds the capacity of a river channel, depositing part of the sediment load on the flood plains (Figure 1H). Consequently a succession of layers is deposited over time, as long as no erosion occurs. Furthermore, overbank sediments are considered to give a very good indication of the geochemical signature of catchment areas and the evolution in time as shown in Ottesen et al. [58], De Vos et al. [59], Macklin et al. [60], Macklin and Dowsett [61], Swennen et al. [44, 51] and Swennen and Van der Sluys [62]. The general philosophy behind sampling overbank sediments is that sediments from the deeper part of the profile can yield information on the geochemistry of the catchment area before human or industrial disturbance took place, while sediments from the near-surface reflect the recent influence of the anthropogenic input [60]. Detailed sampling of the sediments can be set up to test the assumption that at least pre-industrial (or pristine) samples could be taken from the lower part of most overbank profiles and that geochemical variations may distinguish between geogene (natural) and anthropogene (industrial) signatures.

If the succession of an overbank sediment profile is homogeneous, sampling can be carried out in regular intervals depending on the thickness of the overall profile, but if any textural, colour or additional distinctive features are observed, additional sub-samples can be collected. Detailed description of the samples should be made in the field notebook, with respect to the kind of vegetation present, the existence of organic and/or iron rich layers, distinct colors and textural patterns.

4.4. Pond sediments

Varve (pond) sediments are reported to occur at the bottom of lakes. Because the deposition of the sediments in lakes occurs slowly and in relatively quiet conditions, affected mainly by seasonal variations, very fine laminated layers can form within lacustrine environments [63]. Discharges to the aquatic environment directly from the industrial point source will be subject to some degree of mixing and dilution prior to deposition in the sediment body. This will tend to disperse the contaminants and result in well-defined contaminated layers within the sediment column. Such well-sorted sediments can act as archives of contaminant inputs to the system [4].

The pond sediments collected at the site of Porto-Romano [20], although not sampled in a lake, display similar features to sediments deposited at the bottom of lakes. These sediments possess varve characteristics, composed of clay, silts and sand with yellow-reddish coloured laminations, 0.5-3 cm thick, especially nearby the former chemical plant. Figure 2 illustrate the features observed and the very fine laminates, about 30 in total, collected in Porto-Romano (Albania). This type of sampling can be used to investigate the infiltration of the contaminants at depth and the sedimentation conditions that form these very fine-laminated layers.

4.5. Waters

While soils and sediments are accumulating contaminants, water is a migration pathway for contaminants from surface into the groundwater [4]. Since some organic and inorganic pollutants tend to disperse in water, the study of aqueous media is important for evaluating the transportation pathway and horizontal and vertical migration distance from the contamination source or in groundwater (Figure 1N, J). Polyethylene bottles (125 ml) are common for water sample collection. The bottles generally are completely filled with water in order to minimize potential redox reactions taking place by contact with air. Moreover if the acidification and filtration are carried out in the field they must be reported. A study carried out by Sirinawin and Westelund [64] emphasized the fact that chromium species are stable in sea water samples for at least one month if stored in polyethylene bottles and in natural pH conditions. Moreover these authors recommend freezing the samples when no measurements can be carried out within a month.

4.6. Dust samples

According to Nriagu and Pacyna [65] and Han and Naeher [66] anthropogenic airborne particles come from a variety of sources, which include, but are not restricted to traffic, industry, commerce, domestic heating and additional domestic uses. Airborne contamination is more serious in the developing countries, especially in those currently facing rapid industrialization and changes in land use, like former Eastern European countries [34]. According to Nriagu et al. [28] and Nriagu and Pacyna [65] at any particular time and location, the amount of inorganic contaminants in the atmosphere depends on: 1. the intensity of the production processes and/or proximity to the source; 2. the amount of contaminants released; 3. the degree of mixing with other particles present in the atmosphere which is determined by meteorological factors; 4. the age (deposition time) and 5. the transportation rate and mechanism of the suspended particulate matter. The large number of variables often leads to large variations in the geographical distribution of pollutants in the atmosphere [28, 36]. Moreover air quality both indoors and outdoors influences

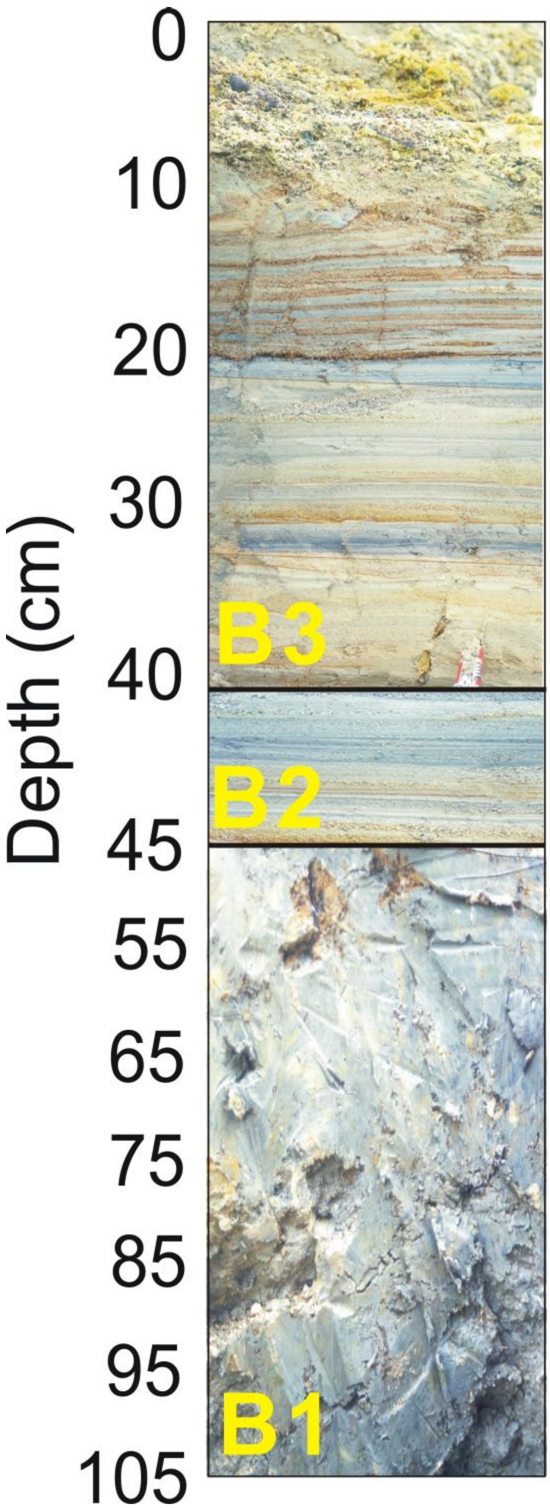

Figure 2. Illustrates the so-called pond profile sediments collected in Porto-Romano (Albania) where the release of chromite ore processing residue has created this varve- like layering within the pond profile.

the respiratory and cardiovascular diseases as stated by Han and Naeher [66]. The dust particles are recognized as an important contributor in heavy metal contamination in top-soils, sediments and plants occurring particularly near industrial sites [19, 21, 27, 29, 35, 67]. However information on the wind rose (directional dependence of the wind frequency) might be relevant to assess the aerial dust dispersion.

Attic dust is a unique archive for inferring the chemical composition of solid particles present in the air from the time when a roof was last refurbished until the sampling time [30, 31, 68, 69]. Assuming that the dust (Figure 1I) samples represent "undisturbed" sedimentation in time and that chemical element contents in attic dust are proportional to their content in air, it is possible to estimate the quality of air through time. Moreover the spatial distribution of the contaminants in relation to the various pollution sources can be assessed by the study of the dust emissions and deposition. Cizdziel et al. [70]; Cizdziel and Hoodge [71] and Ilacqua et al. [72] used attic dust as an indicator of historical air quality concerning pollution by^{137}Cs, ^{239}Pu, pesticides and lead. They demonstrated that plutonium contamination was associated with nuclear detonations in the period 1950-1960, while the amounts of lead accumulated in attic dust, could be related to the combustion of lead-rich gasoline. Gosar and Sajn [30] and Sajn [31] used attic dust to study the spatial distribution of mercury and other elements in Slovenia.

The weight of the dust samples generally is much smaller compared to soils or sediments. The dust samples can be collected with a tooth brush which must be washed after each sample collection in order avoid contamination. The dust samples can be stored in plastic bags, labelled, sealed and transported to the laboratory for analysis.

4.7. Plants

The sampling of vegetation (Figure 1M) is an additional element that can be considered in a sampling strategy [35]. This sampling medium provides information on the ability of vegetation to uptake heavy metals into the upper parts, identify the precipitation of dust particles and the accumulation in leaves and upper stalks.

4.8. Other sampling types

Moss, lichens, humus and spruce needles are considered to be very important contamination indicators in environmental monitoring of airborne anthropogenic heavy metal deposition [10]. However if the results from these sampling media are combined with additional sampling media, like surface waters, sediments and so on, the spreading of contaminants can be better assessed, as shown by Niskavaara et al., [10].

4.9. Sampling techniques

The samples in soils and sediments can be generally collected with a colorless auger, The samples can be stored in plastic bags, sealed, labeled, and a detailed description is mandatory based on the field observations. The reason for a detailed description is to facilitate the later interpretation. The GIS coordinates can also reported where available for the easy location of specific spots. Photographs can also be taken from the different sampling locations, or used to identify special patterns during the fieldwork, in order to document and trace back easily the features observed during sampling. Detailed records are necessary for more specific analysis which can to be performed on particular samples.

5. Discussion

In order to perform a risk analysis to investigate a present- or past-contamination source area, different steps that will justify the scope of the study have to be undertaken. These steps and their order are visualized in the following scheme (Figure 3). After a reconnaissance literature study the needs for further investigations in a present- or past-industrial site are better addressed. Therefore the sampling strategy can be drawn in general lines. By investigating different environmental compartments, a better view and understanding on the fate of contaminants is obtained. Due to the large costs involved in sampling and analytical effort however, the investigations are often carried out seperately for soils, sediments, waters, vegetation or as paired environmental compartments such as suspended solids-sediments [73], dust-soils [74], dust-sediments [29], overbank sediments-active stream sediments [10, 19] and water-sediments [75, 76]. If the area under investigation has been already investigated this can serve as the starting point for the decision making and the sampling types to be investigated, otherwise a reconnaissance study and some general sample characterization might help to better define the entire sampling strategy and reduce the costs for sampling compartments of no interest for the investigation. The need for a specific sampling strategy requires technically qualified people, and standard procedures in order to reduce the inconsistencies in sampling procedures and therefore not compromise the final outcome of the investigation. Since the requirements for a good conceptual model and sampling strategy are resource intensive and multidisciplinary, team work is essential.

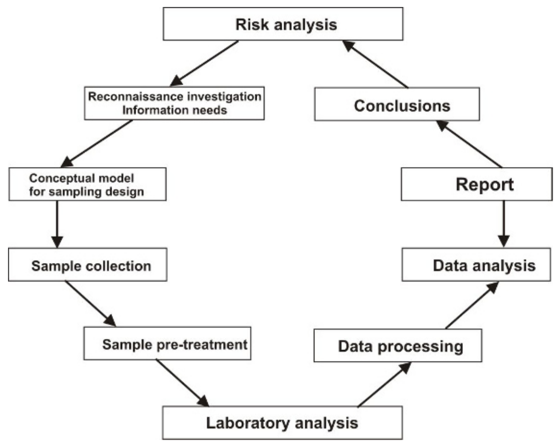

Figure 3. Illustration of the steps to be undertaken in order to perform risk analysis for a present or past contaminated site.

Generally, environmental studies are carried out on a local-, regional- or continental-scale. The main aim of different scale investigations is to obtain information on spatial or temporal trends and patterns [6]. The local-scale industrial sites can be one single pollution source (few square km) or megasites with multiple pollution sources (extended in area up to several km^2). Regional geochemical investigations can compose the area of a country to investigate the spreading of contaminants or to observe the general dominant pattern after a period of monitoring [62]. Continental- or sub-continental investigations involve the investigation of one or several parameters and observe the general trends of soils, sediments and their background values (example: the Foregs, atlas[2]). To characterize point or diffused contaminant sources the approach can be from continental- (background) → regional- → local-scale based on the Technical Guidance Document (TGD) [77].

6. Conclusions

Not all the proposed sampling types apply to all environmental studies. A desk study and thereafter a reconnaissance study will determine the contamination source(s) and the best conceptual model that will fit to a relevant sampling design and the appropriate sampling types. The adaptation approach in a case-by-case base can be implemented. By applying an appropriate sampling design and sample collection the final aim will be to cover the in-

[2] *www.gsf.fi/publ/foregsatlas/ForegsData.php, EuroGeoSurveys Geochemical Baseline Database, December 2008*

vestigated area with a given level of confidence and detect hot spots of a given size. The key steps to be remembered and applied during a sampling campaign identified by this literature review are the following:

1) Historical research consisting of industrial process description, waste type(s), deposition conditions for the waste, life time of the industrial activity, annual discharge rate, exposure pathways;

2) Define the scope of the study, and determine the available budget, personnel and schedule deadlines;

3) Conceptual sampling design considering the boundaries of the study area, sampling media of concern; physical/chemical properties of contaminant;

4) The sampling campaign, which will consist of the selection and application of a specific or a combined sampling design in order to obtain the maximum information with the minimum costs;

5) The main constraints are the appropriate sampling design, the presence of qualified personnel and the budget involved.

Acknowledgements

This literature review was carried out in the framework of a PhD at the Katholieke Universiteit of Leuven that provided partial financial support (East European Initiatives Project 3E000659).

References

[1] Darrie G., Commercial extraction technology and process waste disposal in the manufacture of chromium chemicals from ore, Environ. Geochem. Hlth., 2001, 23, 187-193

[2] Stigliani W.M., Doelman P., Salomons W., Schulin R., Smid G., Van der Zee S., Chemical time bombs: Predicting the unpredictable, Environment, 1991, 33, 4-30

[3] Ferguson C.C., Assessing risks from contaminated sites: Policy and Practice in 16 European countries, Land Contamination and Reclamation, 1999, 7, 33-54

[4] Hursthouse A.S., The relevance of speciation in the remediation of the soils and sediments contaminated by metallic elements – an overview and examples from Central Scotland, J. Environ. Monitor., 2001, 3, 49-60

[5] Levinson A.A., The secondary environment. In: Levinson A.A. (Ed.) Introduction to Geochemical Exploration. Applied Publishing Ltd., 1974, 71-173

[6] USEPA Guidance on choosing a sampling design for environmental data collection. EPA QA/G-5S., 2002, 1-178

[7] Ramsey M.H., Sampling and sampling preparation. In: Gill R. (Ed.) Modern analytical geochemistry. Essex, England: Addison Wesley Longman Limited, 1997, 12-28

[8] Cressie N.A., Statistics for spatial data. John Wiley & Sons, New York, 1993

[9] van Herreweghe S., Swennen R, Cappuyns V., Vandecasteele C., Chemical associations of heavy metals and metalloids in contaminated soils near former ore treatment plants: a differentiated approach with emphasis on pHstat-leaching, J. Geochem. Explor., 2002, 76, 113-138

[10] Niskavaara H., Reimann C., Chekushin V., Distribution and pathways of heavy metals and sulphur in the vicinity of the copper-nickel smelters in nikel and Zapoljarnij, Kola peninsula, Russia, as revealed by different sampling media, Appl. Geochem., 1996, 11, 25-34

[11] Forster V., Heasman L., Kibblewhite M., Quality assurance in the analysis of soil from land contamination. Contaminated soil 98. London: Thomas Telford Publishing, London, 1998, 901-902

[12] Nortcliff S., Sampling and pre-treatment-some observations from the United Kingdom, Sci. Total Environ., 2001, 264, 163-168

[13] Hawkes H.E., Webb J.S., Geochemistry in Mineral Exploration. New York, Harper, 1962

[14] Garrett R.G., The management, analysis and display of the exploration geochemical data. Exploration geochemistry workshop. Ottawa: geological Survey of Canada. Open File 2390, 2001

[15] Porteous A., Dictionary of Environmental Science and Technology. 2^{nd} edition. New York. John Whiley & Sons, 1996, 25-635

[16] Reimann C., Filzmoser R., Garrett R.G., Background and threshold: critical comparison of methods of determination, Sci. Total Environ., 2005, 346, 1-16

[17] Reimann C., Garrett R.G., Geochemical background-concept and reality, Sci. Total Environ., 2005, 350, 12-27

[18] Ferguson C., Darmendrail D., Freier K., Jensen B.K., Jensen J., Kasamas H. et al., The risk assessment of for contaminated sites in Europe, Volume 1, LQM. Press, Nottingham, 1998

[19] Shtiza A., Swennen R., Tashko A., Chromium and nickel distribution in soil, active river, overbank sed-

iments and dust around the Burrel chromium smelter (Albania), J. Geochem. Explor., 2005, 78, 92-108

[20] Shtiza A., Swennen R., Tashko A., Chromium speciation and existing natural attenuation conditions in lagoonal and pond sediments in the former chemical plant of Porto-Romano (Albania), Environ. Geol., 2008, 53, 1107-1128

[21] Shtiza A., Tashko A., Swennen R., Van den Brande A., Impact of metallurgy on the geochemical signature of dusts, soils and sediments in the vicinity of Elbasan complex (Albania), Central European Journal of Geosciences, 2009, 1, 63-83

[22] Mazreku A., Tashko, A., Civici N., Ndikimi mjedisor i zones industriale ne tokat dhe ajrin e qytetit te Elbasanit. Buletini i Shkencave Gjeologjike (in Albanian with English abstract), (in press)

[23] Tashko A., Data on the chemical composition of ultrabasic rocks in Albania, Permbledhje Studimesh, 1973, 2, 107-119 (in Albanian)

[24] Becquer T., Quantin C., Sciot M., Boudot J.P., Chromium availability in ultramafic soils from New Caledonia, Sci. Total Environ., 2003, 301, 251–261

[25] Oze C., Fendorf S., Bird D.K., Coleman R., Chromium geochemistry in serpentinized ultramafic rocks and serpentine soils from the Franciscan complex of California, Am. J. Sci., 2004, 304, 67-101

[26] Brooks R.R., Dunn C.E., Hall G.E.M. (Eds), Biological Systems in Mineral Exploration and Processing. New York: Elis Horwood, 1995

[27] Horckmans L., Swennen R., Deckers J., Maquil R., Local background concentrations of trace elements in soils: a case study in the Grand Duchy of Luxembourg, Catena, 2005, 59, 279-304

[28] Nriagu J.O., Pacyna J.M., Milford J.B., Davidson C.I., Distribution and characteristic features of chromium in the atmosphere, In: Nriagu J.O., Nieboer E. (Eds.), Chromium in the natural and human environment, John Wiley & Sons, New York, 1988, 125-172

[29] Kim K.W., Myung J.H., Ahn J.S., Chon H.T., Heavy metal contamination in dusts and actual river sediments in the Taejon area, Korea, J. Geochem. Explor., 1998, 64, 409-419

[30] Gosar M., Sajn R., Mercury in soil and attic dust as a reflection of Idrija mining and mineralization (Slovenia), Geologija, 2001, 44, 137-159

[31] Sajn R., Using attic dust and soil for the separation of anthropogenic and geogenic elemental distributions in an old metallurgic area (Celje, Slovenia), Geochemistry: Exploration, Environment, Analysis, 2005, 5, 59-67

[32] Pacyna E.G., Pacyna J.M., Steenhuisen F., Wilson S., Global anthropogenic mercury emission inventory for 2000, Atmos. Environ., 2006, 40, 4048-4063

[33] Wilson S.J., Steenhuisen F., Pacyna J.M., Pacyna E.G., Mapping the spatial distribution of global anthropogenic mercury atmospheric emission inventories, Atmos. Environ., 2006, 40, 4621-4632

[34] Fenger J., Air pollution in the last 50 years – From local to global, Atmos. Environ., 2009, 43, 13-22

[35] Shallari S., Schwartz C., Hasko A., Morel J.L., Heavy metals in soils and plants of serpentine and industrial sites of Albania. Sci. Total Environ., 1998, 209, 133-142

[36] Sheppard S.C., A model to predict concentration enrichment of contaminants on soil adhering to plants and skin, Environ. Geochem. Hlth., 1995, 17, 13-20

[37] Theocharopoulos S., Wagner G., Sprengart J., Mohr M-E., Desaules A., Muntau H. et al., European soil sampling guidelines for soil pollution studies, Sci. Total Environ., 2001, 264, 51-62

[38] ISO-DIS 10381-5, Soil quality sampling standard (part 5), Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination, 2005

[39] Wagner G., Lischer P., Theocharopoulos S., Muntau H., Desaules A., Quevauviller Ph., Quantitative evaluation of the CEEM soil sampling intercomparison, Sci. Total Environ., 2001, 264, 73-101

[40] Wagner G., Desaules A., Muntau H., Theocharopoulos S., Quevauviller Ph., Harmonization and quality assurance in pre-analytical steps of soil contamination studies – conclusions and recommendations of the CEEM Soil project, Sci. Total Environ., 2001, 264, 103-117

[41] Adriano D.C., Trace elements in the terrestrial environment, Springer-Verlag, New-York, 1986

[42] Baize D., Sterckman Th., The necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements, Sci. Total Environ., 2001, 264, 127-139

[43] Wolfenden P.J., Lewin J., Distribution of metal pollutants in floodplain sediments, Catena, 1977, 4, 309-317

[44] Swennen R., Van Keer I., De Vos W., Heavy metal contamination in overbank sediments of the Geul river (east Belgium): its relation to former Pb-Zn mining activities, Environ. Geol., 1994, 24, 12-21

[45] Hursthouse A.S., Matthews J., Figures J., Iqbal-Zahid P., Davies I.M., Vaughan D.H., Chromium behavior in intertidal sediments and pore waters, R. Clyde, UK., Environ. Geochem. Hlth., 2001, 23, 253-259

[46] Hudson-Edwards K.A., Macklin M.G., Miller J.R., Lechler P.L., Sources, distribution and storage of heavy metals in the Rio Pilomayo, Bolivia, Journal

of Geochemical Exploration, 2001, 72, 229-250
[47] Pirrie D., Power M.R., Rollinson G., Camm S.G., Hughes S.H., Butcher A.R., Hughes P., The spatial distribution and source of arsenic, copper, tin and zinc within the surface sediments of the Fal Estuary, Cornwall, UK., Sedimentology, 2003, 50, 579-595
[48] Macklin M.G., Metal pollution of soils and sediments: a geographical perspective, In: Newson M.D. (Ed.), Managing the human impact on the natural environment: Patterns and processes. Belhaven Press, London, 1992, 172-195
[49] Calmano W., Ahlf W., Förstner U., Exchange of the heavy metals between sediment components and water, In. Broekaert J.A.C., Güçer S., Adams F. (Eds.), Metal Speciation in the Environment, NATO ASI Series, Springer-Verlag, Ecological Sciences, 1990, 23, 503-522
[50] Japenga J., Zschuppe K.H., De Groot A.J., Salomons W., Heavy metals and organic micropollutants in floodplains of the river Waal, a distributary of the river Rhine, 1958-1981, Neth. J. Agr. Sci., 1990, 38, 381-397
[51] Swennen R., Van der Sluys J., Hindel R., Brusselmans A., chemical characterization of overbank sediments: a way to assess background reference data and environmental pollution in highly industrialized areas (such as Belgium and Luxembourg), Zbl. Geol. Paläont., 1996, 9, 925-942
[52] Zarcinas B.A., Rogers S.L., Copper lead and zinc mobility and bioavailability in a river sediment contaminated with paint stripping residue, Environ. Geochem. Hlth., 2002, 24, 191-203
[53] Leenaers H., The dispersial of metal mining wastes in the catchments of the river Geul (Belgium-The Netherlands). Geografisch Instituut, Rijkskuniversiteit Utrecht, Netherlands Geographical Studies, 1989, 102, 43-167
[54] Alloway B.J., Introduction, In: Alloway B.J. (Ed.), Heavy metals in soils, Blackie Academic Professional, 1995, 1-10
[55] Hursthouse A.S., Matthews J., Figures J., Iqbal-Zahid P., Davies I.M., Vaughan D.H., Chromium in intertidal sediments of Clyde, UK: Potential for remobilization and bioaccumulation, Environ. Geochem. Hlth., 2003, 25, 171-203
[56] Sullivan P., Taylor K.G., Sediment and porewater geochemistry in a metal contaminated estuary, Dulas bay, Anglesey, Environ. Geochem. Hlth., 2003, 25, 115-122
[57] Coleman R.N., Chromium toxicity: effects on microorganisms with special reference to the soil matrix, In: Nriagu J.O., Niober E. (Eds.), Chromium in the natural and human environments. John Wiley & Sons., 1988, 335-350
[58] Ottesen R.T., Bogen J., Bölviken B., Volden T., Overbank sediment: A representative sample medium for regional geochemical mapping, J. Geochem. Explor., 1989, 32, 257-277
[59] De Vos W., Ebbing J., Hindel R., Schalich J., Swennen R., Van Keer I., Geochemical Mapping based on overbank sediments in the heavily industrialized border area of Belgium, Germany and The Netherlands, J. Geochem. Explor., 1994, 56, 91-104
[60] Macklin M.G., Ridgway J., Passmore D.G., Rumsby B.T., The use of overbank sediment for geochemical mapping and contamination assessment: results from selected English and Welsh floodplains, App. Geochem., 1994, 9, 689-700
[61] Macklin M.G., Dowsett R.B., The chemical and physical speciation of trace metals in fine grained overbank flood sediments in the Tyne basin, north-east England, Catena, 1989, 16, 135-151
[62] Swennen R., Van der Sluys J., Anthropogenic impact on sediment composition and geochemistry in vertical overbank profiles of river alluvium from Belgium and Luxembourg, J. Geochem. Explor., 2002, 75, 93-105
[63] Graney J.R., Eriksen. T.M., Metals in pond sediments as archives of anthropogenic activities: a study in response to health concerns, Appl. Geochem., 2004, 19, 1177-1188
[64] Sirinawin W., Westelund S., Analysis and storage of samples for chromium determination in seawater, Anal. Chim. Acta, 1997, 356, 35-40
[65] Nriagu J.O., Pacyna J.M., Quantitative assessment of worldwide contamination of air, water and soils by trace metals, Nature, 1988, 333, 134-139
[66] Han X., Naeher L.P., A review of traffic related air pollution exposure assessment studies in the developing world. Environ. Int., 2006, 32, 106-120
[67] Steinnes E., Allen R.O., Petersen H.M., Rambek J.P., Varsog P., Evidence of large scale heavy-metal contamination of natural surface soils in Norway from long-range atmospheric transport, Sci. Total Environ., 1997, 205, 255-266
[68] Davies D.J.A., Watt J.M., Thornton I., Lead levels in Birmingham dusts and soils, Sci. Total Environ., 1987, 67, 177-185
[69] Tashko A., Elezi M., Shtiza A., Attic dust as time record of air pollution in the industrial zone of Elbasani, Buletini i Shkencave Gjeologjike, 2005, 1, 59-68 (in Albanian: Pluhurat e cative si regjistrues kohor të ndotjes së ajrit në zonën industriale të Elbasanit. English abstract)
[70] Cizdziel J.V., Hodge V.F., Faller S.H., Plutonium

anomalies in attic dust and soils at locations surrounding the Nevada test site, Chemosphere, 1998, 37, 1157-1168

[71] Cizdziel J.V., Hodge V.F., Attics as archives for house infiltrating pollutants: trace elements and pesticides in attic dust and soil from southern Nevada and Utah, Microchem. J., 2000, 64, 85-92

[72] Ilacqua V., Freeman N. C.J., Fagliano J., Lioy P.J., The historical record of air pollution as defined by attic dust, Atmos. Environ., 2003, 37, 2379-2389

[73] Veselý J., Vladimír Majer V., Jan Kucera J., HavranekV., Solid–water partitioning of elements in Czech freshwaters, Appl. Geochem., 2001, 16, 437-450

[74] Petrosyan V., Orlova A., Dunlap C.E., Babayan E., Farfel M., von Braun M., Lead in residential soil and dust in a mining and smelting district in northern Armenia: a pilot study, Environm. Res., 2004, 94, 297-308

[75] Roychoudhury A. N., Starke M. F., Partitioning and mobility of trace metals in the Blesbokspruit: Impact assessment of dewatering of mine waters in the East Rand, South Africa, Appl. Geochem., 2006, 21, 1044-1063

[76] Marcussen H., Dalsgaard A., Holm P. E., Content, distribution and fate of 33 elements in sediments of rivers receiving wastewater in Hanoi, Vietnam, Environ. Pollut., 2008, 155, 41-51

[77] TGD (2008), Development of a Technical Guidance document for preparing the chemical safety assessment (REACH implementation project 3.2-2), Service contract number CCR.IHCP.C432365.XO (version: May 2008)