

From geochemical background determination to pollution assessment of heavy metals in sediments and soils

Tran Thi Thu Dung · Valérie Cappuyns ·
Rudy Swennen · Nguyen Ky Phung

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Abstract Establishing geochemical background concentrations to distinguish the natural background from anthropogenic concentrations of heavy metals in sediments and soils is necessary to develop guidelines for environmental legislation. Due to the fact that the background concentrations strongly depend on geological characteristics such as mineral composition, grain size distribution and organic matter content, several normalization methods have been developed. Empirical (geochemical), theoretical (statistical) and integrated methods (combining both empirical and theoretical methods) are the main approaches described in literature for determination of geochemical background concentrations. In this review paper, the different approaches as well as the main normalization methods for heavy metal

concentrations in sediments and soils will be discussed. Both geochemical background concentrations and added risk level (maximum permissible addition) should be taken into account for setting up legal threshold limits. Moreover, different approaches to evaluate the pollution status of heavy metals in sediments and soils, from Sediment/Soil Quality Guidelines to quantitative indices (Geo-accumulation Index- I_{geo} , Enrichment Factor-EF, Pollution Load Index-PLI and Risk assessment Code-RAC) will be presented. Although guidelines to establish whether a sediment or soil is polluted or not are generally only related to total metal concentrations, the available/reactive pool i.e., availability/reactivity of metals should be taken into account for sediment/soil pollution assessment.

T. T. T. Dung · V. Cappuyns · R. Swennen
Geology, Department of Earth and Environmental
Sciences, Katholieke Universiteit Leuven, Leuven,
Belgium

T. T. T. Dung (✉)
Faculty of Environment, University of Science,
Ho Chi Minh City, Vietnam
e-mail: tran_thi_thu_dung@yahoo.com

V. Cappuyns
Center for Economics and Corporate Sustainability,
Hogeschool-Universiteit Brussel, Brussel, Belgium

N. K. Phung
Department of Science and Technology,
Ho Chi Minh City, Vietnam

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1 Introduction

One of the definitions of pollution given in literature is “the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or amenity, or interference with legitimate use of the environment” (Holdgate 1979). It is apparent from this definition that pollution is caused

by anthropogenic activities. Hence, pollution assessment is related to the work of differentiating natural and anthropogenic concentrations in environmental media. Although contamination and pollution are often used in the same context, Chapman (2007) offered a clear definition of these terms: “Contamination is simply the presence of a substance where it should not be or at concentrations above background. Pollution is contamination that results in or can result in adverse biological effects”. It can be seen from this distinction that pollution is a serious case of contamination. Heavy metals are not biodegradable and they occur in “normal” background concentrations in sediments, soils, waters and living organisms. Therefore, it appears difficult to distinguish between natural and anthropogenic concentrations of heavy metals. Related to this, there is also a practical issue with regard to the development of guidelines for environmental legislation because most of the environmental guidelines are based on background values and toxicity levels (Carlson 2007). Consequently, several studies which addressed determination methods as well as terminologies related to background values have been published (e.g., Tack et al. 1997; Matschullat et al. 2000; Reimann and Garrett 2005). Recently, Gałuszka and Migaszewski (2011) addressed the problem of defining and understanding the term “geochemical background”. They also described methods to evaluate the geochemical background as well as methods of evaluation of anthropogenic influence on the environment. Desaulles (2012) attempted to evaluate the potential and limitations of a series of soil contamination assessment methods by using a data set from Swiss Soil Monitoring Network. The present article provides a review of the advantages and drawbacks of the existing approaches in determining the geochemical background concentrations and pollution status assessment of heavy metals, both in soils and sediments. For this purpose, it starts with listing the main methods of data normalization and background determination. To address the pollution assessment, sediment/soil quality guidelines and quantitative indices will be discussed. Examples of studies on the determination of background concentrations and pollution levels of heavy metals in soils and sediments are numerous, and discussing all these studies is not the purpose of the present review article. However, for each method, reference will be made to some (recent) examples from literature.

Prior to discussing the existing approaches in determining the geochemical background concentrations and pollution status assessment of heavy metals in soils and sediments, it is necessary to provide a brief explanation of used terminologies.

The term “heavy metal” refers to metals with a specific density greater than 4 or 5 g/cm³, but this also includes the lanthanides and actinides. However, many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity (Duffus 2002). Although a lot of controversy exists about the use of the term ‘heavy metals’ and some authors refer it as “a meaningless or “a poor scientific term” (Duffus 2002; Chapman 2012), it is widely used to indicate transition metals, that are of environmental concern (Batley 2012). In environmental sciences, “heavy metals” usually refers to trace metals which potentially cause harmful effects, including Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn, while As is considered to be a metalloid (Alexander and Fairbridge 1999; US EPA 2000).

There are also many definitions of geochemical background (or natural background) concentration of an element documented in literature (e.g., Hawkes and Webb 1962; Pfannkuch 1990; Porteous 1996; Tack et al. 1997; Matschullat et al. 2000). Reviewing the terminologies and definitions proposed for geochemical background concentrations is not subjected in this article, but it must be clearly defined in which context the term is used here. The approaches to derive this term differ between exploration geochemistry, where it was originally defined and environmental sciences where it has been applied widely since the last decades of the twentieth century (Reimann and Garrett 2005; Reimann et al. 2005). As a consequence, the term “geochemical background” also has a different meaning in exploration geochemistry compared to environmental sciences. It was pointed by Gałuszka and Migaszewski (2011) that the concept of geochemical background is important in exploration geochemistry for searching new mineral ores whereas in environmental sciences it is used to detect anthropogenic influences on the environment. In the present article, geochemical background concentration is defined as the element concentration reflecting natural processes and thus not influenced by human activities (Matschullat et al. 2000) which is in agreement with the

definition of Gałuszka (2007) for geochemical background from the environmental science point of view. The differentiation between natural and anthropogenic origin of heavy metals is a relative measure (Matschullat et al. 2000), which is also determined by, for example, the composition of the parent material. The geochemical background concentration allows the distinction of polluted areas from unpolluted ones, and is useful for assessing the extent of human activities and the fate (mobilization, migration, and deposition/uptake of substances in the environment) of elements (Gałuszka 2007). Furthermore, it also allows recognizing areas with higher local background because of the occurrence of mineralization.

According to Reimann et al. (2005), Reimann and Garrett (2005) and Gałuszka and Migaszewski (2011) the terms “threshold value” and “baseline” are often used in equivalency to “geochemical background” even though this has been criticized due to the different meaning. “Threshold” indicates the outer limit of background variation (Garrett 1991) while “baseline” refers to the present concentration in order to be able to quantify future concentration changes (Reimann and Garrett 2005).

Soils and sediments are two different materials. Soil is defined as “a natural body consisting of layered soil horizons) that are primarily composed of minerals which differ from their parent materials in their texture, structure, consistency, color, chemical, biological and other characteristics. It is the unconsolidated or loose covering of fine rock particles that covers the surface of the earth” (Birkeland 1999). Sediment is defined as “particles derived from rocks or biological materials that have been transported by a fluid or solid material suspended in or settled from water” (Horowitz 1985).

From an environmental point of view, soil composition is greatly influenced by pedogenic processes and agricultural activities, while alterations in sediment are mainly influenced by weathering, erosion, dredging or re-suspension. On the one hand, soils are usually well aerated. Therefore, the organic matter content is generally <5 %, and the composing minerals mainly consists of oxidized materials such as hydrated oxides of iron and aluminum (Brady and Weil 1999). On the other hand, sediments are often characterized by aerobic as well as anaerobic conditions. In the later case, organic matter tends to accumulate. For instance, wetlands, including estuarine sediments, can contain

an organic matter content in excess of 20 % (Luthy et al. 2003). When sediment contains sulfur, anaerobic conditions can result in the precipitation of minerals such as pyrite or other iron sulfide phases (Morse et al. 1987).

However, soil and sediments are similar to a certain extent. They are both solid environmental materials, mainly derived from weathering processes and the decay of organic materials, and situated at the interface between the geosphere, the atmosphere, the biosphere and the hydrosphere, where they represent a major sink for heavy metals released to the environment as the result of anthropogenic activities (Manceau et al. 2002). Although some methods to determine background values and “mobile/available pools” of heavy metals stated in this article are similar for soils and sediments, data interpretation should be done with great care, taking into account the particular context because heavy metals in a different matrix can react differently (Sahuquillo 2003).

2 Methods for data normalization

Heavy metal concentrations are influenced by sediment/soil characteristics such as grain size distribution, organic matter and/or clay content and major element content (Loring 1990). Therefore, both geochemical background determination and pollution assessment should take into account these effects and compensate or normalize for these differences in composition (Aloupi and Angelidis 2001). There are two main methods for normalization, namely based on granulometry and on geochemical characteristics.

2.1 Granulometric methods

According to Loring and Rantala (1992), grain size distribution is an important factor controlling the distribution of trace elements in sediment/soil. Therefore, normalization for the grain size effects is a common method because the trace element content tends to increase with the increase of the finer fraction (Aloupi and Angelidis 2001). Heavy metals show a strong affinity with the clay fraction and its coating formations (e.g., organic matter, iron and manganese oxides) (Roussiez et al. 2005) and generally the coarser fraction (sand-sized fraction) has lower content of heavy metals (Loring and Rantala 1992).

Because the separation of the clay size fraction ($<2\ \mu\text{m}$) for analysis is laborious, several authors (e.g., Herut and Sandler 2006) suggested to choose the fraction <20 or $<64\ \mu\text{m}$ fraction for use in granulometric normalization.

Besides the method based on heavy metal analysis from the finer fraction, another method using grain size normalization is the method in which the value of a specific heavy metal is calculated by dividing the measured heavy metal concentration to the fine fraction content (Loring and Rantala 1992). It should be noted that normalization based on clay content ($<2\ \mu\text{m}$) and finer-grain content ($<63\ \mu\text{m}$) is not recommended for sediments/soils derived from glacial erosion of igneous and metamorphic rocks (Loring and Rantala 1992; UNEP 1995) because this type of sediments/soils are often heterogeneous in grain size (mixing of rock fragments and minerals of the clay grain size fraction).

However, it has been criticized by Forstner et al. (1989) that normalization using granulometric data is insufficient because samples can be different with respect to their mineralogical characteristics, which is not systematically reflected in differences in grain size distribution. In that case, granulometric distribution cannot explain the variability in trace element concentrations.

2.2 Geochemical methods

Because heavy metals tend to bind to clay minerals, iron and manganese (oxy)hydroxides and organic matter, normalization can be obtained by using one of the factors representatives for these sediment/soil components as a proxy. Geochemical normalization commonly uses a conservative element as a normalizer. Furthermore, the normalizer should be insensitive to inputs from anthropogenic sources and stable to environmental influences such as reduction/oxidation, adsorption/desorption and other diagenetic processes (Schiff and Weisberg 1999).

According to Loring (1990), an element used as normalizer must be a main constituent of the heavy metal carrier and it should reflect the granulometric variations in the samples. Aluminium (Al)-the main constituent of the aluminosilicate fraction, is commonly used as a normalizer (Prohic et al. 1995; Cheevaporn and San Diego-McGlone 1997; Soto-Jiménez and Páez-Osuna 2001; Jokšas et al. 2008; Ho et al. 2010, 2012).

Using Al-normalization is easy, precise and it is feasible to determine Al-concentrations accurately (Herut and Sandler 2006; Ho et al. 2012). Although aluminium is a suitable proxy for grain size in most sediment/soil types, normalization with Al is not valid in sediments/soils with variable feldspar content, neither in metamorphic sediments/soils (Herut and Sandler 2006; UNEP 1995). Certain elements like Hg and Cd can accumulate in organic matter (Loring and Rantala 1992) or in anoxic strata where heavy metals are found to be entrained in secondary sulphidic phases (Baeyens et al. 1991). In those circumstances, Al-normalization is not effective because of a poor or insignificant correlation between heavy metals and Al (Baeyens et al. 1991). Iron (Fe) and organic matter have been used as normalizers if there is no evidence of an anthropogenic source with regard to these components (Aloupi and Angelidis 2001). However, it should be noted that Fe and organic matter content can significantly be affected by early diagenetic processes, or strong redox effects which are frequently observed in estuarine and coastal sediments (Kersten and Förstner 1991). Moreover, changing salinity in an estuarine environment may cause a precipitation of iron and aluminium hydroxides (Görllich et al. 1989) which may interfere with the normalization. Loring (1990) indicated that Li was more effective as a normalizing factor than Al in samples enriched in T-O-T phyllosilicates [two tetrahedral (T) sheets for every octahedral (O) sheet] for sediments derived from the glacial erosion of crystalline rocks.

It should be mentioned that not only the elements above are used for normalization but also other elements have been proposed (e.g., K, Sc, Ga, Zr, Cs, Be, Ti and Si) (Ackermann 1980; Grant and Middleton 1990; Grousset et al. 1995; Herut et al. 1995). However, difficulties in determination of some of these elements prevent them from being used widely as a normalizer.

According to Herut and Sandler (2006), geochemical normalization shows advantages if compared to normalization based on granulometry because it normalizes both for the grain size and the composition variation in samples. The main modes of geochemical normalizations are stated below:

1. By dividing the raw concentration of heavy metals to the concentration of the normalizer. It is applied when the geo-accumulation index (I_{geo}) or the

enrichment factor (EF) is calculated (Prohic et al. 1995, Soto-Jiménez and Páez-Osuna 2001, Jan et al. 2002). These indices are used to determine the pollution status (I_{geo}) or degree of enrichment (EF) in sediments/soils.

2. By calculating the linear regression equation of a heavy metal concentration versus the normalizer concentration or a ratio of heavy metal concentration and normalizer concentration (Prohic et al. 1995, Covelli and Fontolan 1997, Ho et al. 2010).
3. By calculating the regression line between a heavy metal and normalizer through a pivot point (non-polluted sand is commonly used) and selecting the standard sediment/soil composition (Herut and Sandler 2006).
4. Multi-parameter normalization: using the combination of clay fraction and normalizing elements to build up a multi regression equation with high regression coefficient (Muller-Karulis et al. 2003).

The pitfalls of using a common divisor in normalization of geochemical data are described by van der Weijden (2002). According to this author, normalization using a common divisor can introduce spurious correlation between variables. This effect can be more pronounced when the coefficient of variation of the normalizer is large compared to the coefficient of variation of the other variables. Furthermore, it can destroy the correlation existing before the normalization.

3 Methods to determine geochemical background

Once the geochemical background is determined, the pollution status can more accurately be assessed. On the one hand, several authors (e.g., Matschullat et al. 2000; Reimann and Garrett 2005; Desaulles 2012) distinguish two main methods for determination of geochemical background concentrations. These methods are known as statistical (indirect, theoretical) and empirical (direct, geochemical) methods. On the other hand, integrated methods which combine both statistical and empirical methods are mentioned and applied by other authors (Gałuszka 2007; Qi et al. 2010).

3.1 Geochemical methods

Geochemical methods are also called direct methods or empirical methods which relate to the field and

laboratory work. These methods refer to the investigation of samples that are unaffected by industrial activities, also often referred to as preindustrial samples. In these geochemical methods, deep core samples or samples collected at a certain distance from anthropogenic pollution sources are used to establish the background levels of heavy metals in the sediments or soils of a target area. Examples of sampling media that can be used to deduce background values are overbank sediments sampled at depth, cave sediments, bore hole samples, etc.... (De Vos et al. 1996; Boviken et al. 1996; Swennen and Van der Sluys 1998; Cappuyns 2004). The sampling of overbank sediments was applied by Swennen and Van der Sluys (1998) in Belgium and Luxembourg to deduce the background concentrations of heavy metals in sediments. Geochemical characteristics like pH, carbon and sulfur content, isotope and dated data are usually required for data interpretation (Matschullat et al. 2000). By collecting various kinds of samples (e.g., stream water, stream sediments, flood plain sediments, soils and humus), the Forum of European Geological Surveys (FOREGS, now EuroGeoSurveys) provided a geochemical baseline map for Europe (Salminen et al. 1998). Overbank sediment in combination with information on sedimentological history and age of samples allow reconstructing the pollution history of a given area (Cappuyns 2004). In this approach, the mean or median values of heavy metals in sediment layers that are assumed to have a pre-industrial origin are used as geochemical background value.

3.2 Statistical methods

These methods determine and eliminate the outliers—which are related to anthropogenic sources—within the data set consisting of element concentrations in soils or sediments. Outliers are mainly identified based on the calculation of standard deviation, the regression analysis technique (Matschullat et al. 2000) or using the Tukey boxplot method.

According to Reimann et al. (2005) geochemical background concentrations correspond to the values within the range of [mean \pm 2 standard deviation (SDEV)] or [median \pm 2 maximum absolute standard deviation (MAD)]. This concept comes originally from exploratory geochemistry which defined the outliers as the values falling outside the range [mean \pm 2 SDEV] (Hawkes and Webb 1962). From the above mentioned

calculation, the exact value of [mean + 2 SDEV] is referred to the upper limit of geochemical background variation and this was suggested as “threshold level” for clean up goal of environmental legislation (Reimann et al. 2005).

Comparing the performance of different outlier detection methods, Matschullat et al. (2000) and Reimann et al. (2005) concluded that for real geochemical data, the simple rule of [mean \pm 2 SDEV] is less appropriate compared to the [median \pm 2 MAD] and the Tukey boxplot method.

Another method that uses statistical techniques is regression analysis. In this method, a linear regression is performed between the concentrations of an element and one or several conservative factors (fine fraction, Al, Fe, Li...), which are considered as “inert” or not influenced by anthropogenic activities. Data that falls beyond the confidence interval (95 %) are considered as anthropogenic loads while the data that are well-fitted with the linear regression conditions represent the background values (Covelli and Fontolan 1997; Matschullat et al. 2000; Aloupi and Angelidis 2001). It can be deduced from the descriptions above that the geochemical background concentration determined by statistical methods is a range of values and not a single value.

Beside the conventional statistical techniques, other more recently developed geostatistical methods (e.g., principle component analysis (PCA), multivariate analysis) are also widely used in determining geochemical background of heavy metals in soils (e.g., Ungaro et al. 2008; Bing et al. 2011) or sediments (Romano et al. 2012). Saby et al. (2009, 2011) performed a multivariate spatial analysis and used a robust geostatistical method based on the method of moments to differentiate between natural background concentrations of Cd, Co, Cr, Cu, Ni, Pb, Tl, Zn in topsoils in France and pollution due to human activities. The authors concluded that soil texture, variations in parent material geology and weathering, and various anthropogenic sources were the main factors controlling the examined trace element distribution and that robust methods are required to explain their variation at the national-scale.

Although statistical methods are associated with several advantages such as the wide selection of different statistical tests, graphical methods and easily available computer programs for data processing (Gałuszka 2007), these methods were criticized

because the particular characteristics of geochemical data. Generally, geochemical data from a particular site are strongly influenced by spatial and temporal variability and there is also the uncertainty in sampling, sample preparation and analysis which is not considered in statistical methods for background determination (Rencz et al. 2006). In a review on causes of arsenic enrichment, Paikaray (2012) found that there is a wide variation in As concentrations (from 1 to 200 mg/kg) in soils which depends strongly on the type of minerals occurring in the studied area. These effects might result in the determination of a wrong geochemical background. In addition, the requirement of a large number of data to be able to perform significant statistical tests is not always met in real case situations. With regard to the size of the dataset for derivation of geochemical background, Garrett and Grunsky (2011) recommended that a subset of data in a poly-population dataset should have a minimum size of 30. When multivariate procedures are used, the minimum size of the dataset should be 8 or 9 times the number of elements that are analyzed.

3.3 Integrated method

The combination of statistical and geochemical methods is referred to as “integrated method” (Gałuszka 2007; Gałuszka and Migaszewski 2011). In this method, the samples are collected in pristine areas and the analytical results are subjected to statistical calculations. Non-polluted samples from an area located at a certain distance from the source of pollution or deep core samples can serve as samples from which background values can be derived. With this method, data are less affected by differences in site sampling because of the representativeness of the samples for the study area. Furthermore, data processing is less complex due to the fact that a restricted amount of data is obtained with this method (Gałuszka 2007). This integrated method was supported and applied by several authors (e.g., Tume et al. 2006; Gałuszka 2007; Zhao et al. 2007; Pérez-Sirvent et al. 2009; Qi et al. 2010; Bini et al. 2011). Bini et al. (2011) applied an integrated method to evaluate the background level of heavy metals in soils of Northern Italy and they concluded that statistical methods improve the differentiation between soil groups with different weathering stages and pedogenetic processes.

Therefore, the integrated method can also be considered as an effective tool to depict pedogenetic trends in relation to background concentrations of heavy metals. However, identifying a real pristine area, which is a requirement for this integrated method, remains difficult because of the influence of the long-range transport of atmospheric deposition of heavy metals on soils (Pacyna and Pacyna 2001; Peirson and Cawse 1979) and sediments (Injuk et al. 1998).

Advantages and pitfalls of the different methods used to determine the geochemical background are presented in Table 1. The issue of adequate reference materials for the reliable determination of geochemical background has been addressed in detail by Desaulles (2012) and will not be discussed in the present manuscript.

4 Pollution assessment methods

A series of pollution assessment procedures have been developed, taking into account the effects of various types of anthropogenic activities such as agriculture, industry, transportation, etc. Besides methods based

Table 1 Advantages and pitfalls of different methods to determine geochemical background concentrations (modified from Gafuszka 2007)

	Advantages	Pitfalls
Statistical methods	Providing background in a range values Wide selection of different statistical tests and computer programs for data processing	Requirements for data distribution Not considering geochemical context, uncertainty in sampling and chemical analysis
Geochemical methods	Providing background as a single value Not requiring complicated data processing Specific for study area	High cost Heavy laboratory work Requiring knowledge of the area
Integrated methods	Providing background in a range of values Specific to study area	High cost Heavy laboratory work Requiring knowledge of the area

on total concentrations, some methods are based on the available/reactive pool of an element.

4.1 Methods based on total concentration

4.1.1 Sediment/soil quality guidelines

The simplest way to assess the heavy metal pollution in sediments/soils is using Sediment/Soil Quality Guidelines (SQGs). These guidelines consist of a set of values of heavy metal concentrations that need to be assessed. These values can be considered as the threshold concentrations of heavy metals that cause adverse biological effects. Heavy metal pollution can be assessed simply by comparing the measured concentrations and the concentrations given by SQGs. Generally, these values are not only based on background concentrations but they can also be derived from bioassay tests (Burton 2002; CCME 2002; Carlon 2007).

Ideally, different ecological functions of sediment and soil should result in different sediment/soil quality guidelines. For instance, several aquatic organisms ingest aquatic sediments or particulate detritus or live within the sediment (Luthy et al. 2003). Therefore, sediment quality guidelines are based on an aquatic life protecting approach (CCME 2002; Burton 2002) whereas soil quality guidelines are often based on a land-use dependent approach (Carlon 2007). This is clearly shown by the Canadian case where sediment/soil quality guidelines have been developed by the Canadian Council of Ministers of the Environment (CCME). For sediments, two types of guideline values are defined in the Canadian environmental legislation, namely the ISQG (Interim Sediment Quality Guidelines) and PEL (Probable Effect Level). The ISQG is the more conservative level and the PEL represents “the lower limit of the range of chemical concentrations that are usually or always associated with adverse biological effects” (CCME 2002). Canadian soil quality guidelines are defined for four different types of land use, namely agricultural, residential/parkland, commercial and industrial land use (CCME 2007). In Flanders (Belgium), a similar division in land-use classes has been made to define quality guidelines for soil, but considering “natural areas” as an additional type of land-use. Another perspective is the “added risk approach” in which upper limits for heavy metal concentrations are defined in environmental legislation

(Struijs et al. 1997). Desaulles (2012) introduced the word “Reference Regulatory Values (RRVs)” as a terminology referring to “trigger values” for soil pollution. According to Carlon (2007), legal threshold limits should be a sum of the geochemical background and the added risk level (like a Maximum Permissible Addition). This is based on the principle of the adaptation of the local system to the local circumstances. It can be deduced from this assumption that only anthropogenic addition of pollutants is considered for causing the risk to the local ecosystem.

In some EU countries (Belgium-Wallonia, Germany, The Netherlands, and Switzerland), soil screening values are classified into three levels related to three different risk assessment levels, namely negligible risk, intermediate risk and unacceptable risk (Carlon 2007; Desaulles 2012). In Flanders region (Belgium), the risk levels are also determined by the time when soil pollution was caused. In the case of new pollution (soil pollution caused after 1995), soil clean-up standards refer to unacceptable risk (remediation should take place) while in historical pollution (soil pollution caused before 1995), soil clean-up standards refer to an intermediate risk for which further investigation are required (Carlon 2007).

In recent years, several improvements have been made to achieve a better accuracy for these values. For instance, a correction procedure towards sediment/soil properties (clay and/or organic matter content, pH) has been developed to reduce the effect of the variation in geochemical characteristics between samples (CCME 2002, 2007; Carlon 2007). In the Netherlands, soil quality guidelines are corrected based on clay fraction and organic matter (Spijker 2012), whereas in Belgium (Flanders) pH(KCl), organic matter and clay content are taken into account (VLAREBO 2006).

4.1.2 Statistical relationship between geochemical characteristics

This method has been used widely with statistical tools such as linear regression, factor analysis, principle component analysis and multiple linear regression to identify the background value as well as to assess contamination status (e.g., De Saedeleer et al. 2010; Ho et al. 2010). By using relationships of heavy metals to clay and organic matter content in a data set containing 600 arable soil samples, De Temmerman

et al. (2003) identified the contamination of the Northern region of Belgium based on values falling outside the normal range. Isotopic ratios (of Pb, Cd, Cr, Cu and Zn isotopes) are also suggested to be a sensitive tool to distinguish between the geochemical background and anthropogenic fractions of these elements (Church 1993; Church et al. 1999; Wong and Li 2004; Izbicki et al. 2008; Hoefs 2009). However, the existence of ores and biogeochemical processes can affect the results of geochemical and isotopic relationships (Reimann and De Caritat 2005). Although stable isotopes have been considered as a new and sensitive tool compared to conventional techniques to trace anthropogenic heavy metal pollution, there are several limitations regarding this technique (Hoefs 2009). For instance, the Cu isotopic method can be used to trace natural redox processes, but the variations due to the redox processes in a single deposit usually are much larger than the variation between deposits (Hoefs 2009).

Duzgoren-Aydn and Weiss (2008) illustrated the short-coming of using Pb isotopic ratio analyses in distinguishing the sources of Pb contamination by examining three case studies including areas in Pearl River Delta (Southeast China), New York City (USA), and New Jersey (USA). These authors concluded that it is difficult to distinguish between the sources of Pb in areas where Pb isotopic compositions of natural and anthropogenic sources including regional Pb ore deposits are similar or in cases where the sample isotopic ratio is a composite of Pb from different radiogenic sources.

4.1.3 Quantitative indices

Quantitative methods are based on the calculation of environmental quality indices (sediment/soil quality indices). These methods are considered as an effective tool for transforming the raw environmental data into generic information for non specialists. This transformation provides information to decision makers for ranking and prioritizing the contaminated areas for further investigation (Caeiro et al. 2005). The indices discussed below are all used for the evaluation of sediment/soil pollution, except Marine Sediment Pollution Index (MSPI), Sediment Pollution Index (SPI), the Sediment metal Enrichment Index (SEF) and the Neremo soil index.

4.1.3.1 Geo-Accumulation Index (I_{geo}) The Geo-accumulation Index (I_{geo}) proposed by Müller (1969) allows to identify and classify the pollution status of sediments/soils into seven levels from unpolluted to very polluted. I_{geo} is calculated by the formula described in Table 2. I_{geo} is a simple quantitative measure of heavy metal pollution in sediments/soils, but it does not take into account grain-size and natural geochemical variability owing to the use of a single reference background, and it tends to minimize the degree of pollution because of the numerical factor (1.5) artificially introduced (Covelli and Fontolan 1997).

4.1.3.2 Enrichment factors (EFs) The enrichment factor is used to assess heavy metal pollution of sediments/soils. The formula to calculate EF is given in Table 2. Normally, shale, continental crust or upper continental crust, sedimentary rock, etc. are often used as reference material. The use of the crust as the reference material has been argued, because the compositions of sampling sites are specific and different from site to site (Reimann and De Caritat 2005). In order to deal with this argument, Abraham and Parker (2008) suggested the use of local background values (e.g., from a deep sediment layer not affected by pollution) instead of the average crust composition.

This index has been used in many studies (e.g., Covelli and Fontolan 1997; Loska et al. 1997; Rubio et al. 2000; Woitke et al. 2003; Abraham and Parker 2008; Ho et al. 2010), applying different normalizing elements and using background values determined by different methods. Regardless its wide use, this general method is criticized for its arbitrary “cutoff value” and the assumption of the constancy of heavy metal/reference element ratios in nature (Reimann and De Caritat 2005).

4.1.3.3 The Pollution Load Index The Pollution Load Index (PLI) was suggested by Tomlinson et al. (1980) to determine the pollution status of heavy metals in sediment/soil of a specific area. Although this index was originally developed for soils, it has also been applied to sediments. This is an integrated index because it covers all studied heavy metals in one index. The advantage of this index is that it is easily understood by non scientists and that it allows comparing the pollution status of different locations because all studied metals are considered together in one index. This index is

calculated through the Contamination Factor (CF). CF is the quotient of concentration of a heavy metal in a sample and the concentration of the same heavy metal in a background or reference material. The pollution status of a single heavy metal in the sampling site is assessed by comparing the CF of each heavy metal. Calculation of CF and PLI is described in Table 2.

4.1.3.4 Marine Sediment Pollution Index (MSPI) The Marine Sediment Pollution Index (MSPI) was proposed by Shin and Lam (2001) and has been applied by many authors (e.g., Praveena et al. 2007; Caeiro et al. 2009). This index is modified from the Water Quality Index which was developed by the Scottish Development Department (1976). After a detailed study using MSPI to demonstrate the usefulness of this index, Shin and Lam (2001) concluded that MSPI can be used by non specialists to more easily transform scientific data and is easier to understand compared to the Sediment Quality Triad provided by Chapman et al. (1997).

Apart from the above mentioned indices, other indices have been developed and applied elsewhere such as the Sediment Pollution Index (SPI) (Singh et al. 2002), the Sediment metal Enrichment Index (SEF) (Caeiro et al. 2005) and the Neremo index (Hong-gui et al. 2012). Because of the limited usage, these indices are not addressed in detail. Brief descriptions of those indices can be found in Table 2. Each index has its own advantages and disadvantages and no single method for assessment of heavy metal pollution came out as the best method. However sediment/soil quality guidelines are helpful in screening heavy metal pollution. Moreover, the calculation of enrichment factors taking into account site-specific local geochemical background concentrations and normalization are simple and useful for the assessment of the degree of pollution because they compensate for the differences in geo-characteristics between samples.

4.2 Methods based on available/reactive pool

Heavy metals can exist in many forms in sediments and soils. In sediments, heavy metals can be present in many forms such as dissolved form (as a free ion in the porewater, or as a complex linked to organic or inorganic compounds), and in suspended forms (as precipitate or adsorbed to organic matter, clay minerals and oxides of Fe, Mn and Al) (Bordas and Bourg 2001). Total concentration cannot be used to predict

Table 2 Summary of different method for pollution assessment

Method/Name of Index	Description	Advantages/pitfalls	References
Sediment/soil quality guidelines	Comparing the measured concentrations and the concentrations given by SQGs	Simple and easy to apply Clarity for polluters, regulators and non-specialists Reducing the cost in the initial stage of risk assessment Not considering the site specific effect	CCME (2002), Carlton (2007)
Geo—accumulation Index (I_{geo})	$I_{geo} = \log_2 [(metal)_s / 1.5(metal)_b]$ (metal) _s and (metal) _b are the concentrations of heavy metal in sediment/soil sample and the reference material. $I_{geo} < 0$: unpolluted; $0 \leq I_{geo} < 1$: unpolluted to moderately polluted; $1 \leq I_{geo} < 2$: moderately polluted; $2 \leq I_{geo} < 3$: moderately to strongly polluted; $3 \leq I_{geo} < 4$: strongly polluted; $4 \leq I_{geo} < 5$: strongly to very strongly polluted; $I_{geo} \geq 5$: very strongly polluted	Quantitative assessment Single index Simple quantitative, easy to apply Not considering the grain-size and natural geochemical variability Neglecting the changes of heavy metal/reference element ratios based on natural process Neglecting the available/reactive characteristics of heavy metals	Müller (1969), Christophoridis et al. (2009), Loska et al. (1997), Jumbe and Nandini (2009), Sekabira et al. (2010), Adokoh et al. (2011), Bing et al. (2011)
Enrichment factors (EFs)	$EF = [C_{metal}/C_{normalizer}]_{sample} / [C_{metal}/C_{normalizer}]_{reference\ material}$ C_{metal} and $C_{normalizer}$ are the concentrations of heavy metal and normalizer in the sediment/soil samples and the reference material. $EF \leq 1$: no enrichment, $1 < EF \leq 3$: minor enrichment, $3 < EF \leq 5$: moderately enrichment, $5 < EF \leq 10$: moderately severe enrichment, $10 < EF \leq 25$: severe enrichment, $25 < EF \leq 50$: very severe enrichment, $EF > 50$: extremely severe enrichment	Single index Easy to apply Compensating the differences in geo -characteristics between the samples and the reference material Neglecting the changes of heavy metal/reference element ratios based on natural processes Neglecting the available/reactive characteristics of heavy metals	Covelli and Fontolan (1997), Loska et al. (1997), Rubio et al. (2000), Woitke et al. (2003), Abraham and Parker (2008), Ho et al. (2010), Sekabira et al. (2010), Adokoh et al. (2011), Bing et al. (2011)

Table 2 continued

Method/Name of Index	Description	Advantages/pitfalls	References
Pollution Load Index (PLI)	$CF = C_{\text{metal}}/C_0$ $PLI = (CF_1 \times CF_2 \times CF_3 \dots \times CF_n)^{1/n}$ PLI is the Pollution Load Index, C_{metal} the concentration of metal in sediment/soil sample, C_0 concentration of metal in reference material, n number of metals, and CF Contamination Factor. PLI < 0: unpolluted; 0 < PLI ≤ 1: baseline levels of pollutant present; 1 < PLI ≤ 10: polluted; 10 < PLI ≤ 100: highly polluted; PLI > 100: progressive deterioration of environment	Integrated index, combine all heavy metals to one index Allowing comparing the pollution status of various sites Easy to apply Not considering the grain-size and natural geochemical variability Neglecting the changes of heavy metal/reference element ratios based on natural processes No weighting factor for each heavy metal	Tomlinson et al. (1980), Caeiro et al. (2005), Praveena et al. (2007), Jumbe and Nandini (2009), Sekabira et al. (2010), Adokoh et al. (2011)
Marine Sediment Pollution Index (MSPI)	$MSPI = (\sum q_i w_i)^2 / 100$ Where w_i is the weight attributed to the i variable (proportion of eigen values obtained from the results of a principal component analysis, PCA); q_i is the sediment quality rating of the i contaminant, q_i is ranging from 0 (best possible quality) to 100 (worst possible quality). MSPI 0-20: sediment in excellent condition; MSPI 21-40: sediment in good condition; MSPI 41-60: sediment in average condition; MSPI 61-80: sediment in poor condition; MSPI 81-100: sediment in bad condition	Integrated index, combine all heavy metals to one index Allowing comparing the pollution status of various sites Gives different weights to each contaminant Not considering the grain-size and natural geochemical variability Ranking system of q_i is arbitrary	Shin and Lam (2001), Caeiro et al. (2005), Praveena et al. (2007)

Table 2 continued

Method/Name of Index	Description	Advantages/pitfalls	References
Sediment Pollution Index (SPI)	<p>Sediment Pollution Index = $\Sigma(EF_{m*}W_m)/\Sigma W_m$</p> <p>Where: EF = ratio between total content in a given sediment sample and average shale concentration of a metal m; W = toxicity weight of metal m (A weight 1 was assigned to Cr and Zn, the less toxic metals. The weights for Ni and Cu were 2; 5 for Pb and 300 for Cd). SPI has a set of five classes ranging from natural to dangerous levels.</p> <p>$0 \leq SPI < 2$: natural sediments; $2 \leq SPI < 5$: low polluted sediments; $5 \leq SPI < 10$: moderately polluted sediments; $10 \leq SPI < 20$: highly polluted sediments; $SPI > 20$: dangerous sediments</p>	<p>Combined index</p> <p>Account of metal toxicity weights</p> <p>Allowing comparing the pollution status of various sites</p> <p>Easy to apply</p> <p>Not considering the grain-size and natural geochemical variability</p> <p>Neglecting the changes of heavy metal/reference element ratios based on natural processes</p> <p>Only metal toxicity weights for Cd, Cr, Cu, Ni, Pb and Zn are available</p>	Singh et al. (2002)
Sediment metal Enrichment Index (SEF)	<p>Metal enrichment index contamination index (SEF):</p> $SEF = (C_i - C_0)/C_0$ <p>C_i is the total concentration of each metal i measured in the sediment; C_0 the heavy metal background level established for studied area</p>	<p>Single index</p> <p>No threshold for maximum pollution</p> <p>Neglecting the available/reactive characteristics of heavy metals</p>	Cairo et al. (2005)

Table 2 continued

Method/Name of Index	Description	Advantages/pitfalls	References
Nereomo index	$P_i = \frac{\sqrt{(P_{iave})^2 + (P_{imax})^2}}{2}$ <p>Where P_i is the pollution index of the i-functional area; P_{iave}: average value in the single-factor pollution index; P_{imax}: maximum value in the single-factor pollution index</p> $P_{ij} = C_{ij}/S_{ij}$ <p>P_{ij}: single factor pollution index of the heavy metal j in the i-functional area; C_{ij}: heavy metal concentration in soil sample; S_{ij}: background value of heavy metal. Pollution grade can be classified as follow:</p> <p>$P_i \leq 0.7$: clean; $0.7 < P_i \leq 1$: warning limit; $1 < P_i \leq 2$: slight pollution; $2 < P_i \leq 3$: moderate pollution; $P_i > 3$: heavy pollution</p>	<p>Integrated index</p> <p>Ranking system is arbitrary</p> <p>Not including weighing factor for each heavy metal</p> <p>Not considering the grain-size and natural geochemical variability</p>	<p>Hong-gui et al.(2012)</p>
Risk Assessment Code (RAC)	<p>Percentage extracted by CH_3COOH 0.11 M solution is compared to the following scale:</p> <p>RAC < 1: no risk; $1 < \text{RAC} \leq 10$: low risk; $11 < \text{RAC} \leq 30$: medium risk; $31 < \text{RAC} \leq 50$: very high risk</p> <p>Percentage extracted by EDTA or DPTA</p>	<p>Taking into account the available/reactive fraction of heavy metals</p> <p>Difficult to distinguish geochemical background from anthropogenic content</p>	<p>Perin et al. (1985)</p> <p>Passos et al. (2011)</p>
Available fraction	<p>Percentage extracted by EDTA or DPTA</p>	<p>Taking into account the available/reactive fraction of heavy metals</p> <p>Difficult to distinguish geochemical background from anthropogenic content</p> <p>Lacking of uniformity of extracting agent and evaluation scale</p>	<p>Massas et al. (2010)</p> <p>Ramos-Miras et al. (2011)</p>

the response of a receptor organism (van Hullebusch et al. 2005) and the most toxic heavy metal form for an ecosystem is the most labile form (Alloway and Ayres 1997). According to van Hullebusch et al. (2005), the speciation of a heavy metal is important because it determines its mobility which depends on reactivity and solubility of a heavy metal. It can be seen that one of the limitations of the indices presented above (EF, I_{geo} , PLI and MSPI) is that they do not take into account the differences in speciation of heavy metals in sediments/soils. All the quantitative indices such as EF, I_{geo} , PLI and MSPI are calculated based on the total heavy metal concentration and this comes with the assumption that all the species of a particular metal possess an equal impact with regard to the ecosystem. To overcome this limitation, and because the direct determination of heavy metal speciation in soils and sediments is still difficult in routine analysis, methods based on the available/reactive fraction which employ chemical extractions have been developed. The sequential extraction proposed by Tessier et al. (1979) is known as a complete but long procedure to extract different target phases in solid environmental samples. Although this extraction procedure was originally developed for sediments, it has also been applied to soils. Moreover, numerous other sequential extraction schemes have been developed since then, often without any consistency (Rao et al. 2008). The Tessier scheme classifies the heavy metals into five fractions: exchangeable, acid-soluble (carbonate bound), reducible (Fe/Mn-oxide bound), oxidizable (organically bound + sulphide bound), residual (residual/silicate). Heavy metals in the exchangeable and acid soluble fractions are considered readily and potentially bioavailable, while the reducible and oxidisable fractions are relatively stable under normal sediment/soil conditions (Filgueiras et al. 2002).

The common assumption about differentiation between anthropogenic enrichments and geochemical sources of most heavy metals in sediments and soils based on methods to determine the available/reactive fraction is that the heavy metals from anthropogenic enrichment are more reactive and as a result potentially more available to human, organisms and plant than the naturally occurring fractions (Filgueiras et al. 2002; Spijker et al. 2011). Therefore, evaluation of the sediment/soil pollution and risk assessment is ideally based on the exchangeable and acid soluble fractions. However, (sequential) chemical extractions do not

really reflect the true metal speciations because of the non-selectivity of reagents (Hlavay et al. 2004). For instance, by using X-ray absorption spectroscopy and sequential extractions to examine the true metal speciation in anoxic environments, Peltier et al. (2005) concluded that part of Zn sulphide (known as reducible fraction) was extracted in the exchangeable and carbonate step.

Besides sequential extractions, single extractions are also frequently used to evaluate heavy metal availability in soils and sediments. Perin et al. (1985) proposed a classification in which the availability of heavy metals is assessed by the percentage of metals in the exchangeable and carbonate fraction of the sediment. This classification system was called Risk Assessment Code (RAC). The exchangeable and carbonate fraction are determined by a single extraction with a CH_3COOH 0.11 M solution. In the RAC classification, risk is defined in different levels going from zero, to low, medium, high and finally very high risk. This approach gives the indication of a potential risk to the ecosystem because the fraction extracted by the acid acetic solution is considered as the fraction of heavy metals weakly bound in the sediment/soil (Raph et al. 2009). Therefore, they may easily be released and form a potential threat to the environment. According to Spijker et al. (2011), an extraction with HNO_3 0.43 M provides the estimation of anthropogenic enrichment of heavy metals and Spijker (2012) recommended to apply this extraction to get an insight in the ecotoxicological implications of anthropogenic heavy metal enrichments in soils when screening values are exceeded. In a study about background levels of heavy metals in Mediterranean greenhouse soils (Spain), Ramos-Miras et al. (2011) used the ethylene diamine tetraacetic acid (EDTA) extractable fraction as bioavailable index for heavy metals. They also defined the bioavailable background levels for the studied area based on 160 surface soil sample data. The available fraction can be considered as a comparative index for heavy metal mobility and thus also as an indicator for the recent soil pollution history (Massas et al. 2010, Ramos-Miras et al. 2011). However, many different extracting agents are used to determine the “available” fraction, which results in a lack of uniformity in this method. For example, some author use EDTA (Ramos-Miras et al. 2011) while others use diethylene triamine pentaacetic acid (DTPA) as extracting agent (Massas et al. 2010; Roca

et al. 2012). Even for one extracting agent like EDTA, there is still a lack of uniformity because different types of EDTA salts are used in different concentrations and at different solid/liquid ratios (Cappuyns 2012). Through comparison of the effectiveness of two complexing agents (EDTA and DTPA) for agricultural soils, Sahuquillo (2003) indicated that EDTA is more suitable for soil with a low carbonate content while DTPA is considered suitable for calcareous soil. In practice, data interpretation should be performed carefully, taking into account the particular context of a specific heavy metal due to the fact that the effectiveness of the extraction not only depends on the extracting procedure but also on heavy metal speciation and the composition of the soil/sediment sample (e.g., carbonate content, pH, CEC, content of Fe (hydr)oxides, etc.). Despite the fact that these extractions cannot directly be related to the bioavailability of elements as well as the true metal speciation, they can provide input data for use in risk assessment models. Additionally, they also offer possibilities to perform a fast screening of the mobilizable pool of elements in soils and sediments (Cappuyns 2012). Rao et al. (2008) proposed to use regional maps which show the distribution of a certain metal fraction (that is, for example, linked to plant availability or leachability) to identify problem areas for further investigations.

Because of diversity of chemical extraction procedures in determining the available/reactive fraction of heavy metals in sediments and soils, it is necessary to agree on a uniform extraction method so that researchers can compare their data. In the framework of harmonization of leaching procedures for risk assessment of trace elements in soils, ammonium-EDTA 0.05 mol/L and CH₃COOH 0.43 mol/L were selected as extracting agents by the European Standards, Measurements and Testing program (SMT) for assessment of “potential availability” (Ure 1996). A summary of different methods for pollution assessment is given in Table 2.

5 Conclusions

There is clearly a need to assess the degree and extent of heavy metal pollution accurately and several methods are currently applied to determine whether a soil or sediment is polluted or not. The above mentioned methods indicate the necessity of establishing site-

specific geochemical background concentrations for pollution assessment. Establishing the geochemical background plays an important role in unraveling threshold limits for environmental legislation. Threshold limit as a basis for clean-up goal for remediation not only relate to environmental aspects but also financial aspects. Based on the added risk approach, legal threshold limits should be a sum of the geochemical background and the added risk level (like a Maximum Permissible Addition). Since guidelines generally are only related to total metal concentrations instead of the available/reactive pool, availability/reactivity of metals should be taken into account for sediment/soil pollution assessment. Comparing results is not straightforward because evaluation scales are not standardized and because of the diversity of chemical extraction procedures used to determine the available/reactive fraction of heavy metals in sediments and soils.

Also it is clear from this review article that every method for heavy metal pollution assessment has its own advantages and disadvantages. Therefore, no single method for assessment of heavy metal pollution can be recommended, but the selection of a method should be made based on site-specific criteria and the purpose of assessment. The establishment of specific guidelines, indicating which method to use under which circumstances would be a step forward to establish more adequate methods for background determination and pollution assessment.

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