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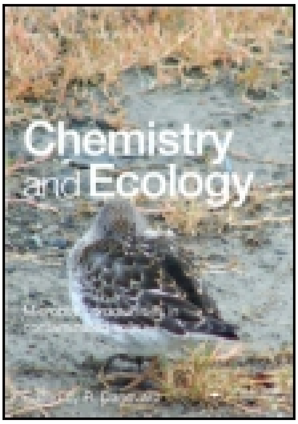

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High geochemical background of potentially harmful elements in soils and sediments: implications for the remediation of contaminated sites

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REVIEW ARTICLE

High geochemical background of potentially harmful elements in soils and sediments: implications for the remediation of contaminated sites

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Geochemical background concentrations of potentially harmful elements and species (PHES) may have a high spatial variability and their natural levels can be higher than those caused by anthropogenic sources of pollution. Therefore, the use of a threshold value for assessing contamination can be inadequate and local variability should be considered. In Europe, soil quality standards are widely variable. In Italy concentration levels exceeding threshold values (TVs) are allowed only if the natural concentrations for a given area are higher than those specified by law. For sediments, in Italian law TVs have not been yet established but TVs with local validity are used for contamination assessment in areas with different geochemistry. A short outline of the worldwide regulatory frameworks is presented with the intent of singling out suitable approaches and priority actions needed to tackle the weak points in law, following the indications of the scientific community and stressing the importance of assessing the real hazard using tools for the evaluation of site-specific mobility and toxicity of PHES. Cases of areas with high PHES background concentration are presented as evidence of this widespread phenomenon and of the need to find effective approaches and solutions.

Keywords: background concentrations; potentially harmful elements; site remediation; soil screening values; geochemical hazard

1. Introduction

The rocks, soils, sediments and waters forming the earth's surface play critical roles as sources, sinks and reactive media for trace elements. Almost all elements present in the environment are biogeochemically cycled and the primary control on their distribution is exerted by the nature of the underlying rocks. Soils originate from the alteration, disaggregation and transformation of parent rock, whose characteristics determine their primary mineralogical composition and the derived geochemical inhomogeneity leads to areas with enhanced or depressed element levels that may cause biological effects due to either toxicity or deficiency [1–3]. As an example, potentially harmful inorganic elements such as As, Cd, Hg and Pb are known to have adverse physiological

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effects at low levels, and elements and species such as Se, I and NO_x can be essential or harmful depending on their concentration, speciation and bioavailability [4].

As a consequence, the natural levels of potentially harmful elements and species (PHES) in different areas can be highly variable and may be as high or higher than those caused by anthropogenic sources of pollution, and thus determine a natural potential ('geochemical hazard') to create risk.

Therefore, the use of a single value based on regulatory thresholds for assessing contamination in soils and sediments may be inadequate and local variability should be considered for properly evaluating the contamination.

The problem of polluted soils and sediments is of outstanding relevance all over the world, given the number and extension of contaminated sites already listed, not considering those yet to be identified and studied, particularly in developing countries. In many areas, soil is being irreversibly lost and degraded as a result of past and current human activities, and soil contamination poses great concern with regard to health risks, from both direct contact and secondary contamination of water supplies.

In the past, distinctions have been made between contamination (concentration above background value) and pollution (concentration above background value with adverse effects on soil uses and functions or on other parts of the environment). Contamination and pollution are nowadays used more or less as synonyms [5].

The term 'geochemical background' comes from exploration geochemistry and was introduced to differentiate between normal element concentrations and 'anomalies' (a deviation from the geochemical patterns that are normal for a given area or geochemical landscape) [6]. Many authors have discussed the use of this term ([3,7,8] and references therein) and we can summarise, defining the 'geochemical background' as the natural abundance of an element in a particular material (e.g. soil, sediment, rock) with reference to a particular area. It is usually expressed as a single value showing the limit (threshold) between anomalous and background concentrations, even if a more correct definition would be given by a range of values [3]. By contrast, the term 'geochemical baseline' is assumed to represent the natural background in areas with heavy anthropogenic impact where the ubiquitous substances, distributed as a consequence of diffuse entry into the soil, cannot be distinguished from the geogenic basic content [8]. Both terms represent important concepts in environmental legislation that prescribe limits for the assessment of contamination and are required to document the present state of an area to provide a datum against which any change can be measured [9].

Various strategies and methods are applied in different countries in considering the eventuality of high natural concentrations of potentially toxic elements.

U.S. legislation has a site-specific approach that also takes into consideration high background concentrations and the real threat has to be assessed by means of a risk analysis based on the real parameters that characterise the site [10,11].

As regards Europe, the Soil Thematic Strategy (STS) adopted by EU Commission with the objective to protecting soils, by definition and for practical reasons, associates natural average background values with negligible risk levels, because reaching soil-quality objectives lower than the naturally occurring concentrations can be extremely expensive and usually is not achievable [5].

In Italy, concentration levels exceeding regulatory limits are allowed only if the background values for a given area are higher than those specified by law.

Besides the issue of estimating background concentrations, another aspect has to be taken into account during the assessment of contamination, i.e. that the 'simple' total concentration of a potentially harmful element is not directly related to risk, where levels depend also on the chemical form and could only be determined after careful study of how the element is bound and under what circumstances it may be bioavailable and able to damage the ecosystem [12–14]. Therefore, to

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determine the need for a response, the site investigation should also include collecting data on the speciation/fractionation of the chemicals of potential concern, because contaminant mobility and bioavailability are important elements in the risk assessment. In fact, it is well known that various ‘forms’ of metals are more or less toxic and can behave as quite disparate compounds in terms of exposure and risk, and so an in-depth evaluation of chemical speciation and bioavailability has to be conducted as part of a more detailed site-specific risk assessment.

Another important worldwide concern in the remediation of polluted sites is represented by sediments because they are major sinks for contaminants and reflect the former large-scale pollution of surface waters and relative catchments (heavy metals, mineral oils, polyaromatic hydrocarbons, polychlorinated biphenyls, etc.). The issue of sediment dredging and dumping, as a consequence of remedial actions, is a huge burden for a community, given that the disposal of large volumes of dredged sediments results in elevated costs and management difficulties, and this is further complicated by the fact that the environmental objectives related to sediment remediation are often not exactly formulated.

Cases of areas characterised by high PHES background concentration worldwide and in Italy are well-known and represent evidence of the widespread presence of the phenomenon and of the need to find effective solutions.

2. International regulatory framework: brief overview

National regulatory frameworks regarding contaminated site remediation are different across various countries and methods adopted by national authorities to derive screening values are very variable. The differences in some cases derive from environmental or sociocultural factors; in other cases, they may reflect different national strategies in environmental policies, and sometimes a substantial disagreement within the scientific community [15].

2.1. *USA*

In the USA, the Environmental Protection Agency (EPA) has provided ‘The Soil Screening Guidance’, a tool developed to help standardise and accelerate the evaluation and clean-up of contaminated soils [10,16].

The methodology provided by US authorities is a step-by-step procedure to calculate risk-based, site-specific soil screening levels (SSLs) that are used to identify areas needing further investigation. Screening levels identify the lower bound of the spectrum levels below which the EPA believes there is no threat to human health or to ecological receptors. If soil screening values are not exceeded, no further action is warranted, otherwise further study or investigation, but not necessarily clean-up, are performed because SSLs alone do not trigger the need for remediation or define ‘unacceptable’ levels of contaminants in soil.

The presence of high background concentrations of hazardous substances found at a site is a factor considered in risk assessment and risk management [11]. Two types of background are considered: naturally occurring and anthropogenic. Natural background is usually limited to metals; whereas, anthropogenic background can include both organic and inorganic contaminants. A comparison of available data on local background concentrations with generic SSLs may indicate whether background concentrations at the site are elevated. The US EPA considers that, in some cases, the same hazardous substances (elements/species/compounds, pollutants/contaminants) associated with a release can also be background components. These constituents should be included in the risk assessment, particularly when their concentrations exceed risk-based concentrations. Background information is important to risk managers because generally, clean-up to concentrations below natural or anthropogenic background levels is not feasible [10,11] and background concentrations exceeding generic SSLs do not necessarily indicate that a health threat exists and further investigation may be necessary.

The ‘Soil Screening Guidance’ provides also generic SSLs for the most common contaminants. Generic SSLs are based on a number of default assumptions chosen to be protective of human health for most site conditions and can be used in place of site-specific SSLs; however, in general, they are expected to be more stringent than site-specific levels. The site manager should weigh the cost of collecting the data necessary to develop site-specific SSLs with the eventuality of having higher costs related to lower SSLs [11].

The US EPA uses the Hazard Ranking System (HRS) to evaluate the potential relative risks to public health and the environment, based on information obtained from the site inspection: with this aim, a site-specific baseline risk assessment is generally conducted to characterise current and potential threats to human health and the environment that may be posed by hazardous substances.

In light of more recent guidance for risk-based screening and risk characterisation, this policy recommends a baseline risk assessment approach that retains constituents that exceed risk-based screening concentrations. Specifically, chemicals of potential concern (COPCs) with high background concentrations should be discussed in the risk characterisation, and if data are available, the contribution of the background to site concentrations should be distinguished. COPCs that have both release-related and background-related sources should be included in the risk assessment.

Where the contribution of background concentrations is relevant and the risk-based clean-up goal for a COPC is below background concentrations, the clean-up level may be established based on background.

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2.2. *Europe*

Recently, the European Commission has conducted an extensive review, with the aim of harmonising soil screening values (SVs) used to regulate land contamination, and the main conclusion has been that they vary widely in several aspects. The following account is mostly derived from Carlon [15].

Soil SVs are generic quality standards used to define land contamination and are expressed as concentration limits for contaminants in soil, above which certain actions are prescribed or imposed [15].

Derivation methods for SVs have scientific and political bases; they also differ from country to country and consequently, the numerical values of SVs vary. They are usually in the form of concentration thresholds ($\mathrm{mg{\cdot}kg^{-1}}$ soil dry weight) of contaminants in soil, above which certain actions are recommended or enforced.

The large variability in SVs adopted by the European Commission can be associated with multiple reasons. National regulatory frameworks are different and methods adopted by national authorities to derive SVs are very variable, in summary, the principal factors are related to:

(1) Derivation methods. In most countries, SVs are based on the application of exposure modelling and risk characterisation, in other countries they are based on a review of SVs adopted by others and derivation procedures are currently undergoing further implementation or revision in most EU countries.
(2) The aim: from setting long-term quality objectives, to triggering further investigations, to enforcing remedial actions. In some countries, reference to generic SVs is mandatory and the derivation of alternative values based on site-specific risk assessment is possible only under certain circumstances. In other countries, SVs are provided as generic indication of the contamination in the soil in a first level of investigation, and are followed by a site-specific risk assessment.

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(3) Different levels of risk considered, for example, negligible risk or potentially unacceptable risk levels. In general terms, the derivation of negligible risk levels aims at excluding any type of adverse effect, even in the most sensitive land use. The level of risk to consider in the derivation of a specific SV is usually related to the intended application within the legal framework. Natural average background values are usually considered to be associated with a negligible risk level, because soil-quality objectives lower than the average background levels would not be realistic.

(4) Soil conditions. In general, SVs are derived for standard soil conditions and applied to a wide range of soil types. Because the mobility and bioavailability of soil contaminants can be strongly related to specific soil characteristics, like pH, clay and organic matter content, in a few countries SVs are provided as functions of these parameters. In the Flemish region (Belgium) and the Netherlands, soil SVs are corrected for the clay and organic matter content. In the UK, different soil SVs are published for pH and organic matter content. In Lithuania, different background values are provided for sandy-loamy and loamy-clayey soils. In Poland, where the main concern is groundwater contamination, different values are provided for depth classes and hydraulic conductivity. In some countries (e.g. Sweden), limits are given for soil properties (e.g. pH and organic matter) for which the generic guidelines are applicable.

Table 1 clearly demonstrates the variability in SVs and shows that the highest and lowest values often differ by a factor of one or two orders of magnitude (for Sn the difference between the highest and lowest value is a factor of 900). It is notable that for Italy the SVs for potentially unacceptable risk (residential soil-use) are lower for many metals and metalloids relative to other countries. The same arises considering SVs for organic contaminants and for other land uses. The variability in the number of soil SVs provided by different countries across Europe is remarkable. Four countries provide less than 20 SVs (United Kingdom, Austria, Belgium – Walloon, Germany), six countries provide between 40 and 60 soil SVs (Czech Republic, Belgium – Flanders, Finland, Poland, Spain, Sweden), four countries provide between 60 and 80 soil SVs (Netherlands, Slovakia, Denmark, Lithuania), and Italy provides up to 100 soil SVs [15].

Table 1. Screening values for potentially unacceptable risk (residential soil-use) for metals and metalloids (mg·kg^{-1} dry weight).

	AT	BE(F)	BE(B)	BE(W)	CZ	FI	IT	LT	NL	PL	SK	UK	DK	KPc	KPs
As	50	110	110	300	70	50	20	10	55	22.5	50	20	20	1.8	4.7
Ba					1000			600	625	285	2000			400	362
Be					20		2	10	30		30			3	1.9
Cd	10	6	6	30	20	10	2	3	12	5.5	20	2	5	0.1	1.1
Co					300	100	20	30	240	45	300			10	6.9
Cr	250		300	520	500	200	150	100	380	170	800	130	1000	100	42
Cu	600	400	400	290	600	150	120	100	190	100	500		1000	55	14
Hg	10	15	15	56	10	2	1	1.5	10	4	10	8	3	0.07	0.1
Pb	500	700	700	700	300	200	100	100	530	150	600	450	400	14	25
Mo					100			5	200	25	200			1.5	1.8
Ni	140	470	470	300	250	100	120	75	210	75	500		30	20	18
Sb	5				40	10	10	10	15					0.2	0.62
Se							3	5	100		20	35		0.05	0.7
Sn					300		1	10	900	40	300			2.5	–
Te									600					0.005	–
Tl	10						1		15					0.5	0.6
V					450	150	90	150	250		500			135	60
Zn		1000	1000	710	2500	250	150	300	720	325	3000		1000	70	62

Notes: AT, Austria; BE(F), Belgium – Flanders; BE(B), Belgium – Bruxelles; BE(W), Belgium – Walloon; CZ, Czech Republic; DK, Denmark; FI, Finland; IT, Italy; LT, Lithuania; NL, Netherlands; PL, Poland; SK, Slovakia; UK, United Kingdom. KPc, crustal average content; KPs, worldwide mean values for soils [21]. Table modified from Carlon [15].

The evaluation of these data raises a great issue and requires effort toward integration, harmonisation and, in some instances, simplification. In addition, greater attention has to be paid to site-specific risk assessment and natural background levels: comparison of site and background concentrations may help risk managers in making decisions concerning appropriate remedial actions.

For sediment quality assessment, in Europe, the application of guidelines based on reference conditions has been widely applied. These reference conditions can be defined either as 'background concentrations' or as an array of chemical and biological parameters measured at references sites. The reference condition approach is, or has been, used by Flanders in Belgium, France, Germany and Italy. However, several of these countries have begun to develop effects-based sediment quality guidelines (SQGs), which are or will be used instead of, or in combination with, the reference condition approach [17].

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2.2.1. *Italy*

Until a few years ago, in Italy, the definition of a contaminated site referred to the mere exceeding of concentration thresholds in soil and/or groundwater. Usually, remedial actions were accomplished when just one of the considered contaminants exceeded its limit in soils and/or groundwater, and the SVs were usually intended as both intervention and remediation target values.

The current law (Ministry of Environment, D.Lgs 152/06) considers a more detailed study of the site when measured concentrations exceed limit values, as well as a risk analysis assessment, so the 'remediation target values' should be determined through a site-specific risk analysis.

In practice, the risk analysis is often disregarded, given the uncertainty of results. A difficulty about the reliability of the models applied to derive the risk assessment is related to the inefficacity of accuratley reproducing the processes occurring as a chemical species travels from source to receptor (structural uncertainty), another weakness is due to parametric uncertainty, associated with the difficulty in estimating model input parameters (chemical–physical parameters of contaminant, transport parameters, soil characteristics, etc.). As a consequence, the assumption necessary to make the models applicable to real cases leads to the choice of parameters that may differ of several orders of magnitude. The result is a 'conditional' risk estimate that can also be potentially subject to manipulation. Moreover, the multimedia complex exposure pathways, the limited site-specific data and the impossibility of confirming the model forecasts through direct measurements can further limit the usefulness and, ultimately, the credibility of the evaluation process [18]. According to Italian regulations, if the naturally occurring element concentrations for a given area are higher than the thresholds specified by the law, background values will be defined as 'remediation target values', but the way of assessing background values and the values themselves are not sufficiently acknowledged and accepted by government agencies.

Soil and groundwater 'concentration limits' have been derived on the basis of health protection criteria and according to the land use (residential/public park and commercial/industrial), the 'worst case' method has been chosen: the 'target', i.e. humans, is assumed to be exposed to the specific substance, through all exposure routes (inhalation, ingestion, skin contact) for the longest possible exposure time.

For groundwater, SVs refer to the restrictive use of potable water, making no difference among type of aquifers and/or their use.

Italian soil and groundwater SVs so defined are consequently very conservative. Achievement of these values as a remediation target can be a heavy burden for landowners and public administrations in charge of acting toward remediation of the site; and even more if natural background levels are not considered. In short, the current Italian regulatory system lacks flexibility and does not take sufficient account of regional and local specificities [15]. The constraints imposed by

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restrictive SVs, the limited awareness of natural background concentrations, the number of elements and substances to analyse (regardless of site and peculiarity) play an important role in the delays in remediation that currently affect Italian land management policy.

The situation is even more complex when sediments are considered (both for dredging and dumping), given that, in Italy, legal thresholds have not yet been established and only limit values with local validity (e.g. Venice) are currently available, though in practice they are often extended to geochemically completely different areas.

Usually, sediment classification refers to generic ‘basic chemical levels’ that represent an average national situation, not considering sediments from areas with natural anomalies. A specific study of the local SVs, based on geochemical and ecotoxicological characteristics, would be appropriate [19] but often resources for this are inadequate.

Under current legislation, different classes of sediments are defined according to their contaminant concentrations and each class is assigned to different purposes, therefore without a site-specific consideration of natural background levels, sediments with natural concentrations that exceed regulatory limits would not be available for, e.g. disposal, crop growing, construction or habitat restoration and can become a further drawback for site remediation.

3. Examples of geochemical anomalies

Many studies and site characterisation plans have pointed out the widespread presence of elevated natural background levels with respect to regulatory threshold limits and SVs. In the following, a few of the numerous ascertained cases are reported, emphasising the role of the assessment of background values as a starting point for land remediation. Clearly, no mention will be made of striking cases such as naturally occurring arsenic in Bangladesh, West Bengal and India where millions of people are affected by this problem, because these situations are beyond the scope of this review.

Reimann and Garrett [3] reported some cases of anomalies detected at a subcontinental scale, analysing the data provided by the geochemical atlas of soils in northern Europe [20]. For example, the case of vanadium is reported, for which high natural concentrations are evident in various regions: in Norway, where the high V contents can be attributed to the occurrence of greenstones, rocks naturally rich in Fe-Mg alumino-silicate minerals that contain transition metals; in the northern part of Russia, due to the occurrence of black shales; and in south Finland and Sweden, where high V levels are related to clay-rich soils. It is notable that the natural V levels of Scandinavia by far exceed the concentrations found in Germany, where by contrast they are attributed to a possible contamination. Garrett [1] proposes quite different backgrounds (upper limits) for three regions: 170 $\text{mg}\cdot\text{kg}^{-1}$ for Norway and Sweden; 125 $\text{mg}\cdot\text{kg}^{-1}$ for Finland and Russia; and 55 $\text{mg}\cdot\text{kg}^{-1}$ for the Baltic States, Belarus, Poland and north Germany, and this gives an idea of how natural variability can be elevated. Reimann and Garrett [3] report another evident case of a geochemical anomaly regarding the arsenic in Austria, where levels are 6–20 times the world values [21,22] and far above most soil SVs. For the same Austrian region (Saualpe, Carinthia), Göd and Zemann [23] report As concentrations reaching as hight as 1.4 wt% due to an unusual kind of mineralisation in brecciated marbles, consisting predominantly of native arsenic and realgar.

Sierra et al. [24], recently reported high concentration for As and Pb in Almeria (southeast Spain), where both elements show values exceeding the SSLs established for the area (24 and 400 $\text{mg}\cdot\text{kg}^{-1}$ for arsenic and Pb, respectively). The high values are attributed to the hydrothermal and volcanic episodes which the region underwent from the Miocene to the Holocene and the authors propose baseline values of 50 and 400 $\text{mg}\cdot\text{kg}^{-1}$, respectively for As and Pb.

Very high natural As concentrations have been reported for the Kutahya region of western Anatolia in Turkey [25] where an unusual occurrence of As- and B-rich minerals are found due to the geological history of the area, characterised by diffuse evaporitic rocks and hydrothermal processes. As contents vary from hundreds to thousand mg·kg^{-1} in different rock types of the area and may reach 0.95 mg·L^{-1} in thermal waters.

In Hungary, besides the case of Pannonian basin (spanning Hungary, Romania, Serbia and Croatia) where groundwater in Quaternary and Neogene sediments is known to contain elevated levels of naturally occurring As [26], the mountain region (northeastern Hungary) represents another 'anomalous' area with high background levels. The Mátra Mountains comprise andesitic volcanic rocks of predominantly Miocene age involved in two types of mineralisations events, in particular, one low-temperature hydrothermal mineralisation characterised by barite and elements like As, Sb and Hg exploited with mineral ores. The background levels have been estimated by Ódor et al. [27], who also calculated that the 'threshold of anomaly' for some elements in the area reachs up to 25 mg·kg^{-1} for As, 60 mg·kg^{-1} for Pb and 140 mg·kg^{-1} for Zn, but maximum levels one or two orders of magnitude higher than these values have been found in the area.

High natural As levels are often also generated by pyroclastic acid rocks from the numerous volcanoes aligned along the Andine Cordillera and recently a noticeable case has come up in the Jujuy Province in northern Argentina [28]. Very high concentrations of As up to ~13 mg·L^{-1} and 890 mg·kg^{-1} have been found in river water and soils respectively, at the foot of the Tuzgle volcano, which is supposed to be the main source of As diffusion in that area.

Shifting the focus to Italy, several geological features can be found among those able to generate high natural levels of PHES, varying from the occurrence of distinctive volcanic settings to peculiar mineralisations due to different types of geological events.

The Late Quaternary sediments of the Po coastal plain are characterised by high Cr and Ni contents, exceeding national regulatory limits. These high natural concentrations are attributed to erosion by the Po river and its tributaries of the widespread Cr- and Ni-rich ultramaphic rocks outcropping in several areas of the western Alps and the northern Apennines, and represent background levels that do not reflect any anthropogenic influence [29].

The sediments of Liguria are characterised by high natural levels of Cr, Ni and other heavy metals due to the presence of ophiolitic rocks (Voltri Group, Bracco-Graveglia Unit) diffusely outcropping in the region. With the exception of Cu, which also has an anthropogenic origin, V, As, Cr, Ni, Co have background values that often exceed the regulatory limits for both residential and industrial use [30]. This means that reference background levels have to be taken into account for the remedial planning of several contaminated sites in the area, including costal zones.

In Piemonte, former mining sites for the exploitation of gold are present along the Anzasca valley. The mere fact that mining sites have been exploited in the zone indicates the presence of a geochemical enrichment in some elements and this phenomenon occurs also in many other similar area in Italy and worldwide. As (derived from arsenopyrite, naturally occurring in gold veins) shows concentrations higher than regulatory limits not only near mining sites, but also in the majority of rocks outcropping in the valley. The regional environmental agency of Piemonte has conducted analyses of samples from former mining sites and 97% of them exceed the national soil limits for residential and industrial use [31].

In the province of Trento, during a survey near the site of a factory (Sloi) formerly producing lead tetraethile and now listed as contaminated site of national relevance, high Pb levels were found in areas where there was no evidence that the factory had an influence. Further investigations have shown that Pb, As, Zn and Sn have significantly elevated natural concentrations due to the presence of a diffuse mineralisation of the area [32].

Finally, it is important to mention problems that have arisen quite recently as a consequence of lowering the limit for As in drinking water (from 50 to 10 μg·L^{-1}) and the scarce awareness of the worldwide existence of areas with high natural concentrations level of this element. As an example, cases from Switzerland and Italy are reported, giving evidence of the same problem originating from different geological situations. Switzerland has three main areas with elevated

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natural As concentrations: (1) northeastern Switzerland, where a number of As-containing thermal and mineral springs are located; (2) the Jura, with its Fe-containing limestones and clays; and (3) the Alps, where As-bearing ore deposits and crystalline rock formations can be found. In addition, there are also other isolated thermal and mineral springs. In the Alps between Switzerland and Italy, weathering and erosion of rocks containing As releases this element into soils, sediments and natural waters. The Swiss limit for drinking water of 50 $\mu g{\cdot}L^{-1}$ is not exceeded; however in Cantons Ticino, Grisons and Valais, As concentrations in drinking water are above the Italian level of 10 $\mu g{\cdot}L^{-1}$ recommended by World Health Organization (WHO) [33,34].

High As concentrations in groundwater from geothermal sources have been found in northern Greece where drinking water with As concentrations up to 120 $\mu g\,L^{-1}$ is being consumed and concentrations up to ∼1800 $\mu g{\cdot}L^{-1}$ are measured [35,36]. High As levles of geothermal origin up to 6900 $\mu g{\cdot}L^{-1}$ have been detected in the Campanian Volcanic Province of Italy [37]. Concentrations up to 150 $\mu g{\cdot}L^{-1}$ have been detected in the southern part of the Great Hungarian Plain [26,38]. Gurzau and Gurzau [39] also reported As concentrations up to 176 $\mu g{\cdot}L^{-1}$ in the associated aquifers of neighbouring Romania [40].

In the volcanic areas of central (and some parts of southern) Italy high As concentrations have been related to the deep-rising fluids of the active geothermal systems [41]. The available hydrochemical data frequently show As, F and other minor and trace constituents above the regulatory limits in the groundwater of the Vulsini, Cimino-Vico-Sabatini, Alban Hills, Phlegrean Field and Isle of Ischia systems. Some springs and wells of these volcanic aquifers that are used as public water supplies are characterised by fresh water with As and F levels up to 70 $\mu g{\cdot}L^{-1}$ and 4 $mg{\cdot}L^{-1}$, respectively. Thermal waters in a few volcanic aquifers can reach As concentrations up to 7000 $\mu g{\cdot}L^{-1}$ [41–45].

4. Conclusions

Given that element content in soils is variable depending on the soil parent material and land use, and not only as a consequence of anthropogenic inputs, to assess soil contamination it is essential that background levels of the relevant elements in soil are known. Providing a geological context for geochemical hazards due to the natural presence of potentially toxic elements, can give information essential to environmental management, planning and health protection. A comparison of site and background PHES concentrations may help managers make decisions concerning appropriate risk management and remedial actions.

The mapping and characterisation of contaminated soil sites and the resulting clean-up are time-consuming and expensive, requiring a long time to regenerate contaminated lands and considerable investment for remedial measures. Specific and additional investigations aimed at gaining knowledge of the natural background while planning remedial actions may increase the time and cost of the intervention. To overcome this practical limit, basic regional knowledge has to be increased by creating accessible and manageable base inventories, by sharing and publishing the existing data and by producing data from areas not yet investigated. In addition, lower costs can be achieved by using site-specific limit values rather than ‘generic’ thresholds, given that the latter are always more stringent, being based on default assumptions chosen to be protective of human health and applicable for most site conditions.

Moreover, risk levels depend on the chemical form and concentration of elements and could only be assessed after careful study of how an element is bound and under what circumstances it may be bioavailable and able to damage the ecosystem. Screening methodologies will play a key role in the characterisation of contaminated sites for minimising ‘classical’ laboratory analyses. Efforts should be concentrated on standardising fast procedures that enable a guided real-time survey.

The occurrence of high concentrations of PHES, even if natural, does not mean that the risk related to particular condition (several examples are well known worldwide) has to be disregarded and where a potential and serious risk to the population is established, restrictions on land uses at least are still needed.

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