

Indices of soil contamination by heavy metals – methodology of calculation for pollution assessment (minireview)

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Abstract This article provides the assessment of heavy metal soil pollution with using the calculation of various pollution indices and contains also summarization of the sources of heavy metal soil pollution. Twenty described indices of the assessment of soil pollution consist of two groups: single indices and total complex indices of pollution or contamination with relevant classes of pollution. This minireview provides also the classification of pollution indices in terms of the complex assessment of soil quality. In addition, based on the comparison of metal concentrations in soil-selected sites of the world and used indices of pollution or contamination in soils, the concentration of heavy metal in contaminated soils varied widely, and pollution indices confirmed the significant contribution of soil pollution from anthropogenic activities mainly in urban and industrial areas.

Keywords Heavy metals · Soils · Sources of pollution · Single indices · Total complex indices

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Introduction

Currently, soil pollution by heavy metals represents one among the foremost necessary environmental issues. According to numerous scientific environmental studies, heavy metals are regarded as potentially harmful substances released from anthropogenic activity exhibiting the risk to surrounding environment and to human health. The growing contamination by heavy metals in environmental components leads to an increase in global risk to human and ecological health; soil contamination by toxic and dangerous compounds result in the degradation or loss of some soil functions globally. A close interaction to other environmental compartments (water and atmosphere) leads to a negative influence on soils due to anthropogenic activity. The generalized mobilization and dispersion of pollutants from their natural reservoirs to the atmosphere, soil, and water is one of the most significant negative impacts of human activities on terrestrial and aquatic ecosystem (Wang and Qin 2007; Driscoll et al. 2013; Karimi Nezhad et al. 2014; Zhao et al. 2014; Wang et al. 2015a, 2015c; Hou et al. 2017). Heavy metals are accumulated in soils mainly due to dry and wet atmospheric deposition from various sources; the main and most important origin of heavy metals is related to industrial emissions (chemistry, mining, iron and steel industry, metallurgy, building and electronics industry, etc.), fuel combustion, and waste management and transport (automobile traffic, a fuel composition, road types, types of the engine, and drive mode). The growing waste production of various potentially hazardous materials, such as domestic or industrial wastes, incineration wastes, use of fertilizers and agrochemicals, etc., contributes to pollution of urban soils and causes in growing heavy metal amount in soils (Guillén et al. 2011; Pastor and Hernández 2012; Wang et al. 2012; Hu et al. 2013; Cheng et al. 2014; Gonçalves et al. 2014; Teng et al. 2014; Werkenthin et al. 2014; Li et al. 2015a; Soliman et al. 2015; Wu et al. 2015a, 2015b; Gu et al. 2016). The increasing population density and the corresponding increase in the number of vehicles result in significant negative impact on the urban environment (Wong et al. 2006; Lu and Bai 2010; Wei and Yang 2010; Al Obaidy and Al Mashhadi 2013; Werkenthin et al. 2014; Li et al. 2015a, 2015b). A huge proportion of soils in industrialized countries contain higher levels of many dangerous and toxic elements and compounds that are considered hazardous pollutants and their background values are above those in corresponding undisturbed areas (Hijmans et al. 2005; Hu et al. 2013). The soils with unique properties and structure act as a filter and a deposition site for heavy metals and others toxic substances. The input of heavy metals from anthropogenic activities generally includes: As, Cd, Cr (only Cr (VI) is toxic), Cu, Hg, Ni, Pb, and Zn. Unfortunately, heavy metal pollution is practically almost irreversible (Lado et al. 2008; Liang et al. 2011; Wuana and Okieimen 2011; Teng et al. 2014; Wu et al. 2015a, 2015b; Streets et al. 2017). The geology, the geographical characteristics, and local climate are considered the main natural factors of heavy metal dispersion environment. Generally, that increased density of population, intense industrialization, and excessive exploitation of natural resources result in negative impacts on the structures and functions of the whole ecosystem and environment (Zahida et al. 2014). Heavy metals can be transferred into the human body as a consequence of dermal contact, inhalation, and ingestion (Lim et al. 2008; Ji et al. 2008, 2013; Varrica et al. 2014). Much heavy metal accumulates in organisms due to their long biological half-lives of elimination and non-biodegradability. It is widely known that presence toxic heavy metals in soils have adverse effects on human health, especially on children (Ljung et al. 2006a, 2006b; Poggio et al. 2009; Varrica et al. 2014). The objectives of this review were: (1) soil pollution/contamination by heavy metals was analyzed and pollution sources were summarized, (2) 20 different indices of heavy metal pollution were

reviewed, (3) indices were classified into single indices and total complex indices of pollution/contamination, and (4) minireview provides also the classification of pollution indices in terms of the complex assessment of soil quality.

Heavy metals in soils

Inputs of heavy metals into environment include atmospheric deposition from industrial areas, dumping and treatment of wastes, commercial fertilizers, using sewage sludges, and other processes originated from degradation of various materials (He et al. 2005a, 2005b; Skordas and Kelepertsis 2005; Biasioli et al. 2006; Han et al. 2006; Wong et al. 2006; Barkouch et al. 2007; Oliva and Espinosa 2007; Zhang et al. 2016, 2017). The amounts of heavy metals in soils are different and worldwide average concentrations fluctuate, for example, Cu (20 mg kg^{-1}), Cd (0.06 mg kg^{-1}), Cr (20– 200 mg kg⁻¹), Pb (10–150 mg kg⁻¹), Ni (40 mg kg⁻¹), and Zn (10–300 mg kg⁻¹). But the containing of heavy metals in metal-rich soils can attain at 10-1000 times greater concentrations via basic parent materials or pollution (He et al. 2005a, 2005b). The hazardous metals in soils, such as As, Cd, Cr, Cu, Hg, Pb, and Zn are considered the most contamination metals in soils, and their basic properties are non-degradability, persistence, bioaccumulation, and biomagnification in a food chain. The chemical forms and metal speciation are important factors for the fate and transport of heavy metals in soils. The first process with various rates, from minutes to days or years is adsorption and after that heavy metals are redistributed into different chemical forms with various bioavailability, mobility, and toxicity. The final equilibrium state of redistributing heavy metals between the solid and liquid phase in soil is influenced many chemical and biochemical processes (Kabata-Pendias 2011). The processes precipitationdissolution, adsorption-desorption, complexation-dissociation, and oxidation-reduction control the metal mobility and availability whereas only a small portion of metals in soil is bioavailable (Yang et al. 2004; He et al. 2005a, 2005b). The bioavailability of metal and its compounds is also affected by physical factors (pH level, temperature, association of phases, adsorption, composition, and quality of soil solution) and chemical factors (speciation at thermodynamic equilibrium, redox potential, complexation kinetics, cation exchange capacity, ions competition, lipid solubility, and octanol/ water partition coefficients). Biological factors are significant for metal bioavailability, i.e., type and sort of species, trophic interactions, and biochemical/ physiological adaptation (Skordas and Kelepertsis 2005; Barkouch et al. 2007; Oliva and Espinosa 2007; Kabata-Pendias 2011; Zhao et al. 2013, 2014). As a consequence of rapidly growing amounts of heavy metals in soils, their its accumulation, the contaminated soils become unavailable for plant growing crop cultivation, and the quality of soils change in terms of biodiversity, water cycles, a microclimate of an area, which results to facilitating floods and erosion. Thus, pollution of soil can change the whole ecosystems. The transfer of metals from soils via food chain or atmospheric deposition can cause the typical chronic effect, where the most serious toxic effect with delayed toxic response is related to mutagenicity and carcinogenicity. Mutagenesis and carcinogenesis very often occur after chronic exposure by some of the heavy metals. The specific characteristics and physical-chemical properties of each metal affected its toxicological profiles and its toxicological mode of action (WHO/FAO/IAEA 1996; Damek-Poprawa and Sawicka-Kapusta 2003; Türkdoğan et al. 2003; Islam et al. 2007; Kibble and Russell 2010; Kabata-Pendias 2011; Brevik and Burgess 2012; Morgan 2012).

Sources of heavy metals in soils

Metals are naturally occurring elements that are found throughout the earth's crust; however, anthropogenic activities are the main proportion of environmental contamination, human exposure, disturbance in metal geochemical cycles, and metal accumulation over background levels (Table 1). The presence of metals (Cu, Zn, Fe, Mn, Co, Ni, Pb, Cd, Cr, As, Hg) has been often extensively monitored in environment (Rudnick and Gao 2003). The soil contamination can be classified to the three groups: (i) contamination via industrial processes and solid wastes with major effect to contamination of surface soils and disturbances in soil profile, (ii) contamination due to urban and agricultural activities, and (iii) contamination with dominant impact on surface soils and underground soils (Kaasalainen and Yli-Halla 2003; Basta et al. 2005; He et al. 2005a, 2005b; Khan et al. 2008; Arruti et al. 2010; Sträter et al. 2010; Al Obaidy and Al Mashhadi 2013; Gao et al. 2013; Cheng et al. 2014; Wang et al. 2015a, 2015b; Wu et al. 2015a, 2015b; Liao et al. 2016). Summary of major negative impact of heavy metals on soils are listed in Table 2. The input of heavy metals due to human activities has increasing trend. Pollution caused by heavy metals is

Table 1 Background contents of heavy metals in continental crust and surface soils over the world (average, mg kg^{-1})

Elements	Continental crust			Worldwi	de soils			Agricultural soils, Sweden	US soils	Soils, Europe
	Clemente et al. (2003) and Kabata- Pendias (2011)	Rudnik and Gao (2003)	Yaroshevsky (2006)	Kabata- Pendias (2011)	Adriano (2001)	Xie and Lu (2000)	Clemente et al. (2003)	Eriksson (2001) and FOREGS (2005)	Kabata- Pendias (2011)	FOREGS (2005) and Yaroshevsky (2006)
As	1.8	4.8	1.7	6.83	6.1	_	0.62	0.25	7.2	11.6
Cd	0.1	0.09	0.13	0.41	0.35	0.06	1.1	0.17	0.01-41	0.28
Cr	100	92	83	59.5	70	20-200	42	22	54	94.8
Co	10	17.3	18	11.3	_	_	6.9	7.1	9.1	10.4
Cu	55	28	47	38.9	30	20	14	17	25	17.3
Hg	0.07	0.05	0.08	0.07	0.03	0.03	0.1	0.043	0.09	0.061
Pb	15	17	16	27	35	10-150	25	18	19	32
Mo	1.5	1.1	1.1	1.1	_	_	1.8	0.58	0.97	0.94
Ni	20	47	58	29	50	40	18	13	19	37
Zn	70	67	83	70	90	10-300	62	65	60	68.1
V	135	97	90	129	_	-	60	69	80	68
Mn	900	-	1000	488	-	-	418	411	550	524

Table 2	Summary of heavy	negative metal	effects on soils
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Agricultural effect
Reduction of soil fertility
Reduction of nitrogen fixation
Increased erosion factor
Increasing soil loss
Increase nutrient deficiency
Reduction of crop yields
Imbalance in the soil biota (flora, fauna, microorganism)
Decrease of soil biodiversity
Industrial effect
Transfer of dangerous chemicals
Ecological imbalance
Release of pollutant gases
Increased salinity
Urban effect
Clogging of the drains soil deposits
Flooding areas
Health problems
Contamination of drinking water sources
Problems of waste management

especially problematic in areas where synergy with other types of polluting agents exists. In the case of industrial areas, the large inputs of acidifying compounds are often typical and creates specific conditions for increased mobilization, bioavailability, and thereby toxicity of the metals stored in soils (Clemente et al. 2003; Cappuyns et al. 2004; De Vries et al. 2005; European Communities 2006). The studies of urban soils in many cities around the world confirmed significantly higher concentration of cadmium, copper, lead, zinc, mercury, and other metals (Chen et al. 2005; Biasioli et al. 2006, 2007; Lee et al. 2006; Wong et al. 2006; Morton-Bermea et al. 2009; Ajmone-Marsan and Biasioli 2010; Morton-Bermea et al. 2010; Awadh et al. 2015; Karim et al. 2015; Chen et al. 2015, 2016; Wu et al. 2015a; Liu et al. 2016; Streets et al. 2017; Xia et al. 2017). In urban localities, metals can input into soil via emissions from industry and traffic, combustion of fossil fuels, and municipal wastes. Lead and copper mainly come from traffic and combustion, and Cu originates from brake consumption. Incinerators and material degradation (pipes, cables) are other sources of urban contamination of soils. Soils receive also Cu, Pb, Cd, and Hg mainly from atmospheric deposition, irrigation water, applications of agrochemicals, fertilizers, and sewage sludge (Wong et al. 2006; Biasioli et al. 2007; Díaz Rizo et al. 2013; Gonçalves Jr. et al. 2014; Sager et al. 2015). In Europe, mandatory reductions on the annual emissions of cadmium, lead, and mercury to avoid significant adverse effects on ecosystems have been introduced in the Heavy Metals Protocol (UN/ECE 1998). This will have an increasing importance because, according to the most recent report of the Coordination Centre for Effects, the distribution and magnitude of the deposition of these elements puts large areas of European ecosystems at risk both in 2000 and 2020 (Posch et al. 2005).

Industrial contributions

Generally, heavy metal sources in the environment include geogenic, industrial, agricultural, wastes, and atmospheric sources. The weathering and volcanic eruptions contribute to heavy metal pollution. Industrial sources include mining and smelting operations, metal mine tailings, disposal of high metal wastes in improperly protected landfills, industrial production, metal processing in refineries, coal burning in power plants and local coal burning, petroleum combustion, plastics, textiles and microelectronics, and also domestic and agricultural use of metals and metal-containing compounds, land application of fertilizer, animal manures, biosolids (sewage sludge), compost, and pesticides. The contamination of environment can also result from corrosion of metals, atmospheric deposition, soil erosion of metal ions, and leaching of the heavy metals under an acid condition, resuspension of sediment, and metal evaporation from water resources to soil and ground water. Metal emissions from large metal refineries, steel industry, and coal mine spoils, metalliferous mine spoils and smelters, mainly Pb and Zn ore mining, and smelting have enormous effects on accumulation of metals in soils, and high metal emissions are also from power stations and incinerators. The ashes and particulate matter originating from the burning of fossil fuel have high content Cd, Zn, As, Se, Cu, Mn, and V (Anikwe and Nwobodo 2002; Basta et al. 2005; De Vries et al. 2005; European Communities 2006; Ajmone-Marsan and Biasioli 2010; Lin et al. 2013; Guan et al. 2014; Karimi Nezhad et al. 2014; Kelepertzis 2014; Li et al. 2014; Wu et al. 2015a; Liao et al. 2016; Mukhopadhyay et al.

Table 3 Comparison of heavy metals content in soil aroundindustrial zones as coefficients of metal concentration (Caroli2000; Davydova and Tagasov 2004)

Industries	>100 km	100–50 km	50–10 km
Warmthenergetics	Ni, V	Sb, Se, Hg	Cr, Pb, Zn
Electrotechnics	Pb, Cd	Ni, V, Cr	Mo, Zn, Sn
Machinery	-	Ni, Cr, Pb	Cr, Mn, Sb
Motor vehicles	Pb	Ni, V, Cr	Zn, Co, Hg
Black metallurgy	_	Fe, Mn, Sb	Ni, Cr, V

2016; Obiora et al. 2016). Industrial wastewaters often contain higher concentration of heavy metals such as Cd, Ni, Pb, Zn, Co, Cr, Cu, and Mn. Contaminated soils may contain heavy metal concentrations of 100 to 1000 times higher than their background (Jiang et al. 2004, 2014; Pastor and Hernández 2012; Díaz Rizo et al. 2013; Wu et al. 2015a; Cantinho et al. 2016; Xiao et al. 2017; Zhang et al. 2017). The type and content of heavy metals in soils due to dry and wet deposits are influenced by the origin of sources and distance of sources and also depend upon the specific conditions of sites because all solid particles from atmospheric deposition are eventually stored on land or water. For example, the contents of nickel and copper in soil are exponentially growing with a decreasing distance from the pollution source, see Table 3 (Caroli 2000; Davydova and Tagasov 2004). The various emission sources of heavy metals contributing to soil pollution and based on data from literature are summarized and listed in Table 4 (Chen et al. 2005, 2015; McLaren et al. 2005; Biasioli et al. 2006, 2007; Lee et al. 2006; Morton-Bermea et al. 2009; Ajmone-Marsan and Biasioli 2010; Simasuwannarong et al. 2012; Kuusisto-Hjort and Hjort 2013; Li et al. 2014; Resongles et al. 2014; Shen et al. 2017).

Agricultural contribution

Metal application of Cu, Zn, Fe, Mn, and B as important and essential elements for plant growth is now a common practice for remedy of metal deficiencies in soils (Kelepertzis 2014; Su et al. 2014; Tóth et al. 2016). Many chemicals used in agricultural applications contain Cu, Zn, Fe, Mn, and As. Applications of P fertilizers lead to increase concentration of Cd, As, Pb, and Hg. Heavy metal concentration in rock phosphate and P fertilizers were found to be 500 mg kg⁻¹ of Cd, **Table 4** Emission sources of heavy metals contributing to soilpollution due anthropogenic activities (Chen et al. 2005; McLarenet al. 2005; Biasioli et al. 2006, 2007; Lee et al. 2006; Morton-Bermea et al. 2009; Ajmone-Marsan and Biasioli 2010)

Industries	Heavy metals
Metalliferous mining	As, Cd, Cu, Ni, Pb, Zn
Smelters	As, Cd, Pb
Metallurgy, rolling, electronic industry	Ni, Cd, Pb, Hg, Se
Dyes and paints industry	Pb, Cr, As, Se, Mo, Cd, Co, Ba, Zn
Metal corrosion of materials	Cu, Pb, Cr, Ni, Co, Cr, Pb
Plastics industry	Cd, Zn, Pb, Sn
Chemical industry	Pb, Ni, Nb, Hg, Pt, Ru
Combustion of fossil fuels	Cd, Zn, As, Se, Cu, Mn, V
Wood industry	Cu, As, Cr
Tire wear, lubricant oils	Zn, Cd

273 mg kg^{-1} of As, 17.2 mg kg^{-1} of Pb, and 0.42 mg kg^{-1} of Hg (Roberts 2014). The use of biosolids (livestock manures, composts, and municipal sewage sludge) to soil results to accumulation of metals in soils (As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, etc.) (Basta et al. 2005). Use of biosolid sand/or municipal compost leads to the higher content of metals (Cu, Zn, Pb, Cd, Fe, and Mn) in the soils. The metals such as Pb, Ni, Cd, Cr, Cu, and Zn can be released from biosolids under specific conditions and can contaminate soil profile and then water source and groundwater (McLaren et al. 2005; Yaroshevsky 2006, Gonçalves et al. 2014; Teh et al. 2016). Repeated applications of biosolids result to enrichment of metal in soil; the levels of Cu is 463 mg kg⁻¹, Zn 725 mg kg⁻¹, Ni 29 mg kg⁻¹, Pb 106 mg kg⁻¹, Cd 7 mg kg⁻¹, and Cr 40 mg kg⁻¹, respectively (McBride and Cherney 2004; McBride 2013). The upward trends of agro-livestock activities were reported for Zn, As, and Cu due to its growing application as additives to animal diet, and they are excreted by animals and lead to appreciable higher metal concentration in soils. The repeated use of the metalcontaining chemicals (Cu, Zn, Pb, and As) as fungicides and pesticides for the treatment or prevention of apple, citrus, grape, cherry, and peach diseases resulted to the accumulation of these metals in soils. For instance, soils from 30-year-old citrus groves have 200-300 mg kg⁻¹ extractable Cu (state Mehlich III solution), that is 10–15 times upper levels than other soils (Chaney et al. 2001; McBride and Cherney 2004; Fan et al. 2011; McBride 2013).

Indicators of soil contamination and assessment methods of heavy metal soil pollution

The key to an effective assessment of soil contamination with heavy metals is the use of suitable indicators and indices of pollution/contamination that can be regarded as a tool and guide for a comprehensive geochemical assessment of the soil environment state. The comprehensive way to assess the soil quality through the use of indices is also demonstrated by the ability to estimate environmental risk and soil degradation due to longterm accumulation of heavy metals. Moreover, the indices help to determine whether the accumulation of heavy metals was due to natural processes or is the result of anthropogenic activities, and therefore, the indices of pollution can contribute also to human activity monitoring (Ministry of Environment 1994; Birke and Rauch 2000; Reimann and de Caritat 2000; Sutherland 2000; Linde et al. 2001; Pagotto et al. 2001; Manta et al. 2002; Tijhuis et al. 2002; Skordas and Kelepertsis 2005; Ljung et al. 2006a, 2006b; Yang et al. 2006; Oliva and Espinosa 2007; Morton-Bermea et al. 2009; Silva et al. 2009; Ajmone-Marsan and Biasioli 2010; Lu and Bai 2010; Guillén et al. 2011; Serbaji et al. 2012; Likuku et al. 2013; Brady et al. 2014; Rahmanipour et al. 2014; Karim et al. 2015; Omran 2016; Pan et al. 2016; Paz-Ferreiro and Fu 2016; Zhang et al. 2016). The most commonly used assessment methods of metal pollution/contamination in soils are based on various indicators and indices. An indicator of soil contamination by heavy metals depends on various characteristics such as chemical properties (total/recoverable content, available/extractable amount, and fractionation/speciation), biochemical properties (enzyme activity, FDA hydrolysis), and microbial properties (microbial biomass, microbial quotient, specific respiration, microbial metabolic quotient, and microbial community structure).

Chemical indicators

Total concentration of metals and metalloids is still the most useful common chemical indicators of soils pollution. However, the total concentration cannot exactly indicate the mobility and the actual bioavailability of the metals in soils because less than 5% of the total content is just mobile or bioavailable (He et al. 2005a, 2005b; Ma et al. 2016). The most frequently used method for the estimation of the mobility of metals is sequential extraction, which is closely related to bioavailability (Gleyzes et al. 2002; Nieto et al. 2007; Rao et al. 2008; Long et al. 2009; Yu et al. 2010; Ivezić et al. 2013; Rowe 2014). The BCR-701 method/procedure, developed by the Community Bureau of Reference (Ivezić et al. 2013; Sahito et al. 2015; Wan et al. 2017), is widely used as well. The selective extraction methods are generally applied procedures used for the evaluation of the environmental impact of heavy metals (Rao et al. 2008). The extractable metals have been suggested to represent their bioavailability or toxicity. A number of extraction procedures were proposed for estimation of their mobility in soil and are based on heavy metals water solubility or chemical association with soil constituents (Table 5) (Rao et al. 2008; Kabata-Pendias 2011; Esmaeilzadeh et al. 2016; Rosado et al. 2016; Wan et al. 2017). The advantage of sequential extraction is the improved phase specificity. Extractants can be classified based on their reaction mode: (1) acids such as HCl, HNO₃, (2) chelating agents like EDTA and DTPA, (3) buffered salt solutions such as NH₄OAc, and (4) unbuffered salt solutions such as

Table 5 Extractable heavy metal content as indicators forassessing soil contamination (Rao et al. 2008; Kabata-Pendias2011; Esmaeilzadeh et al. 2016; Rosado et al. 2016; Wan et al.2017)

Fractions	Extraction methods
Water soluble	Centrifugation, displacement, dialysis, filtration, ultrafiltration
Exchangeable	KCl, CaCl ₂ , MgCl ₂ , KNO ₃ , Ca(NO ₃) ₂ , NH ₄ NO ₃ , BaCl ₂ , NH ₄ Cl, Mg(NO ₃) ₂ , AlCl ₃ , NaNO ₃
Potentially exchangeable	Pb(NO ₃) ₂ , NH ₄ OAc, NH ₄ NO ₃
Organically bound	Na ₄ P ₂ O ₇ , K ₄ P ₂ O ₇ , NaOCl, EDTA/H ₂ O ₂ /HNO ₃ /NaOAc
Carbonate-bound	HOAc, NaOAc, HOAc, EDTA
Oxide-bound	Hydroxylamine hydrochloride, dithionite/citrate/bicarbonate
Residual	HNO ₃ , HCl + HNO ₃
Mineral lattice	HNO ₃ /HF/HClO ₄

Table 6 Pollution indices — single indices and total complex indices (include integrated indices and indices of ecological risk)

Single indices of pollution

Index	Formula	References
Geoaccumulation index (I_{geo})	$I_{\text{geo}} = \log_2\left(\frac{c_n}{1.5 B_n}\right)$	Muller (1969)), Loska et al. (2003)), Ji et al. (2008)), and Lu and Bai (2010)
Enrichment factor (EF)	$\begin{split} \mathrm{EF} &= \frac{\frac{c_{\mathrm{n}} (\mathrm{sample})}{c_{\mathrm{Ref}} (\mathrm{sample})}}{\frac{B_{\mathrm{n}} (\mathrm{background})}{B_{\mathrm{Ref}} (\mathrm{background})}} \\ \% \mathrm{EF} &= \left(\left(\frac{c-c_{\mathrm{min}}}{c_{\mathrm{max}}-c_{\mathrm{min}}} \right) \cdot 100 \right) \end{split}$	Reimann and de Caritat (2000)) and Sutherland (2000)
Percentage enrichment factor (%EF)	$\% EF = \left(\frac{c - c_{\min}}{c - c_{\min}}\right) \cdot 100$	Loska et al. (2003)
Single pollution index (PI)	$PI = \frac{c_n}{B_n}$	Hakanson (1980)), Muller (1981)), Qu et al. (2004)), Cheng et al. (2007)), Abrahim and Parker (2008)), Cheng and Hu (2012)), Wu et al. (2015a, 2015b))
Treshold pollution index (PI _T)	$\mathrm{PI}_{\mathrm{T}} = \frac{c_i}{c_{\mathrm{TL}}}$	Qingjie et al. (2008)), Xu et al. (2008)), and Lu et al. (2009))
Contamination factor (CF)	$CF = \frac{c_M}{c_{np}}$	Hakanson (1980)) and Loska et al. (2004))
Total complex indices		
Sum of pollution index (PI_{sum})	$\mathrm{PI}_{\mathrm{sum}} = \sum_{i=1}^{m} \mathrm{PI}_{i}$	Gong et al. (2008))
Average of pollution index (PI_{Avg})	$\mathrm{PI}_{\mathrm{Avg}} = \frac{1}{m} \sum_{i=1}^{m} \mathrm{PI}_{i}$	Bhattacharya et al. (2006)), Gong et al. (2008)), and Inengite et al. (2015))
Weighted average of pollution index (PI_{wAvg})	$\mathrm{PI}_{\mathrm{wAvg}} = \sum_{i=1}^{m} \mathrm{w}_i \mathrm{PI}_i$	Hakanson (1980)), Muller (1981)), Cheng et al. (2007)), Qingjie et al. (2008)), Xu et al. (2008)), and Cheng and Hu (2012))
New pollution index (PIN)	$PIN = \sum_{i=1}^{m} W_i^2 PI_i$	Caeiro et al. (2005)) and Doležalová Weissmannová et al. (2015))
Integrated pollution index (IPI)	$IPI = mean(PI_i)$	Caeiro et al. (2005)) and Gong et al. (2008)
Integrated threshold pollution index (IPI_T)	$\operatorname{IPT} = \frac{1}{n} \left(\frac{1}{n} + \frac{1}{n} + \dots + \frac{1}{n} \right)$	Lu et al. (2009)), Adamu and Nganje (2010)), Oje et al. (2010)), and Doležalová Weissmannová et al. (2015))
Pollution load index (PLI)	$PLI = \sqrt[n]{CF_1.CF_2 . CF_3 CF_n}$	Liu et al. (2005))
Degree of contamination (C_{deg})	$C_{\text{deg}} = \sum_{i=1}^{n} C_f$	Hakanson (1980)) and Caeiro et al. (2005))
Modified contamination factor (mC_{deg})	$mC_{\text{deg}} = \frac{1}{n} \sum_{i=1}^{n} \text{CF}_i$	Abrahim and Parker (2008))
Nemerow pollution index $(PI_{Nemerow})$	$\mathrm{PI}_{Nemerow} = \sqrt{\left(\frac{1}{n}\sum_{i=1}^{n}\mathrm{PI}_{i}\right)} \frac{{}^{2}+\mathrm{P}_{i}^{2}}{2}$	Cheng et al. (2007)), Jiang et al. (2011)), and Inengite et al. (2015))
Indices of ecological risk		
Pollution coefficient of a single heavy metal $(C_{\rm f}^{\rm i})$	$C_f^i = C_s^i / C_n^i$	Hakanson (1980)), Biasioli et al. (2006, 2007)), Lim et al. (2008)), Xu et al. (2008)), Ajmone-Marsan and Biasioli (2010)), and Rahman et al. (2014))
Single index of ecological risk factor (E_r^i)	$E_r^i = T_r^i \cdot C_f^i$	Hakanson (1980)) and Gong et al. (2008))
Risk index (PERI)	$PERI = \sum_{i=1}^{n} E_r^i$	Kowalska et al. (2016))
Mean ERM quotient (MERMQ)	$MERMQ = \frac{\sum_{i=1}^{n} C_i / \text{ERM}_i}{n}$	McCready et al. (2006)), Christophoridis et al. (2009)), and Violintzis et al. (2009))
Contamination severity index (CSI)	$\text{CSI} = \sum_{i=1}^{n} W_{\text{ia}} \left[\left(\frac{C_i}{\text{ERL}_i} \right)^{\frac{1}{2}} + \left(\frac{C_i}{\text{ERL}_i} \right)^2 \right]$	Long et al. (2000, 2006)) and Gao and Chen (2012))

Explanation: c_m heavy metal content in soil; B_m , concentration of heavy metal (*n*) geochemical background, constant factor 1.5, compensating the B_n due to lithogenic effects (fluctuations of heavy metals content as a result of natural processes); c_n (sample), metal concentration in soil analyzed sample; c_{Ref} (sample), concentration of the reference metal in soil analyzed sample; B_n (background), metal concentration in the reference environment; B_{Ref} (background), reference metal concentration in the reference environment; c_max , maximum concentration; c_i , metal concentration; c_{TL} , tolerance levels of metal concentration; c_M , mean metal concentration; c_{pp} , preindustrial concentration of metal; PI_i , single pollution index of heavy metal *i*; *m*, number of determined heavy metals; w_i , weight of PI_i ; W_i , class of heavy metals; TL_1 , TL_2 , TL_n , tolerable levels of heavy metals; *n*, number of heavy metal; $CF_T - CF_n$, contamination factor CF; P_{imax} , maximum of single pollution indices PI of all heavy metals; C_s^i -, concentration of heavy metal; C_n^i -, background level heavy metal in soil; C_f^i , pollution coefficient of single element (heavy metals); T_r^i , -, toxic response factor of individual metal; E_n^i , single index of ecological risk factor; C_i , concentration of heavy metal; ERM_i , effects range median; ERL_i , effects range-low; W_{ia} , weight of heavy metals (resulted from PCA/FA)

CaCl₂ and NH₄NO₃ (Kabata-Pendias 2011). Fractionation of metals in soil can improve understanding of their association with soil constituents and their mobility characteristics in case of change of soil and environmental conditions. In this approach, the bioavailable fractions are fractionated into water soluble and exchangeable. Organically bound, carbonate-bound, oxide-bound fractions can be potentially bioavailable. The residual fractions are in the resistant minerals and these nonextractable fractions are not available to organisms. The ratio of the individual fractions largely determines the availability and mobility of metals in soil and also varies significantly in soils. Single-step chemical extraction is the most useful method for the determination of the amount of available metals in soil, including watersoluble and exchangeable metals such as available to plants and its amount closely correlated with plant uptake. This phenomenon of available metals can be used as indicators of metal availability in soil (Jing et al. 2008; Ivezić et al. 2013; Sungur et al. 2015; Fernández-Ondoño et al. 2017).

Pollution indices

The often used indices can be divided into two groups: single indices and total complex indices including integrated indices and indices of ecological risk. The calculation formulae for pollution indices are summarized in Tables 6 and 7; Table 8 includes the classes of pollution.

Single indices of pollution

The single indices as indicators of soil pollution comprise numerous indices, such as Geoaccumulation Index (I_{geo}) , Enrichment Factor (EF), Pollution Index (PI), Threshold Pollution Index (PI_T), and Contamination Factor (CF). These indices are calculated from the contents of each individual metal in soils, and these indices can be used for the classification of soils into several classes according to the degree of pollution (see Tables 6 and 7) (Muller 1969, Muller 1981; Hakanson 1980; Qu et al. 2004; Cheng et al. 2007, 2014; Abrahim and Parker 2008; Qingjie et al. 2008; Xu et al. 2008; Lu et al. 2009; Cheng and Hu 2012; Ye et al. 2012; Zahra et al. 2014; Awadh et al. 2015; Chai et al. 2015; Chen et al. 2015; Wu et al. 2015a; Ke et al. 2017; Peña-Icart et al. 2017).

 I_{geo} is commonly used for the assessment of soil pollution by heavy metals. This index formulates as the ratio of the concentrations of heavy metals in soils to background metal levels in soils or in corresponding soils. The constant 1.5 is used to state of natural fluctuations of metals in the environment and detection of small anthropogenic impacts (Muller 1969; Loska et al. 2003; Ji et al. 2008; Lu and Bai 2010). The index of geoaccumulation consists of seven grades.

The EF is given by standardization of a tested metal against a reference metal with low occurrence variability, and EF has five classes (Sutherland 2000). The most

Table 7 Classes of single indices: I_{geo} , EF, PI, PI_T, and CF

Single indices	Value	Soil quality
Igeo	$I_{\rm geo} \le 0$	Uncontaminated
	$0 \le I_{\rm geo} < 1$	Uncontaminated to moderately contaminated
	$1 \leq I_{\text{geo}} < 2$	Moderately contaminated
	$2 \le I_{\text{geo}} < 3$	Moderately to strongly contaminated
	$3 \le I_{\text{geo}} < 4$	Strongly contaminated
	$4 \leq I_{\rm geo} < 5$	Strongly to extremely contaminated
	$I_{\rm geo} > 5$	Extremely high contaminated
EF	EF < 2	Deficiency to minimal mineral enrichment
	EF = 2 - 5	Moderate enrichment
	EF = 5–20	Significant enrichment
	EF = 20–40	Very high enrichment
	EF > 40	Extremely high enrichment
PI	PI < 1	Unpolluted, low level of pollution
	$1 \leq PI \leq 3$	Moderate polluted
	$3 \leq \mathrm{PI}$	Strong polluted
PI_T	$PI_T < 1$	Unpolluted
	$1 \leq PI_T \leq 2$	Low polluted
	$2 \leq PI_T \leq 3$	Moderate polluted
	$3 \leq \text{PI}_T \leq 5$	Strong polluted
	$5 \leq \mathrm{PI}_\mathrm{T}$	Very strong polluted
CF	CF < 1	Low contamination factor
	$1 \leq \mathrm{CF} \leq 3$	Moderate contamination factor
	$3 \leq \mathrm{CF} \leq 6$	Considerable contamination factor
	$6 \leq CF$	Very high contamination factor

Explanation: Geoaccumulation index (I_{geo}) , enrichment factor (EF), single pollution index (PI), treshold pollution index (PI_T), and contamination factor (CF)

referenced metals are Sc, Mn, Ti, Al, Fe, and Ca (Reimann and de Caritat 2000). The normally used reference metals are Mn, Al, and Fe. Soil contamination can also be expressed as the percentage enrichment factor (%EF) (Loska et al. 2003).

Single PI uses often various reference values of metals in soils, such as preindustrial level, average crust level, background level, baseline values, values of national criteria, or threshold pollution values. For example, PI_T is formulated on the basis of average ratio of metal concentration (c_i) and tolerance levels of metals (c_{TL} given by national guidelines or criteria of metal and exceeding concentrations are considered hazardous for human health.

The CF is defined as ratio of mean metal concentration in the soil from at least five samples (c_M) and metal concentration in unpolluted soil (c_n) . The concentration of elements in the Earth's crust is commonly used as the preindustrial concentrations and is considered as a reference value for evaluation of soil contamination by heavy metals (Hakanson 1980; Loska et al. 2004).

Total complex indices

Total complex indices of pollution are calculated as multielement indices based on single pollution indices (Qingjie et al. 2008). Each type of total complex indices of pollution can be composed of the mentioned single indices separately. Integrated indices of pollution contain following indices and are summarized in Tables 6 and 8 where the calculation method and classes of pollution/contamination are described: Sum of Pollution Index (PI_{sum}), Average Pollution Index (PIAvg), Integrated Pollution Index (IPI), Integrated Threshold Pollution Index (IPI_T), Pollution Load Index (PLI), New Pollution Index (PIN), Nemerow Pollution Index (PI_{Nemerow}), Degree of Contamination (C_{deg}) , Modified Contamination Factor (mC_{deg}) , and indices of ecological risk are Potential Ecological Risk Index (PERI), Mean ERM Quotient (MERMQ), and Contamination Severity Index (CSI) (Hakanson 1980; Muller 1981; Cheng et al. 2007; Xu et al. 2008; Cheng and Hu 2012; Zhu et al. 2012; Likuku et al. 2013; Rahmanipour et al. 2014; Wang et al. 2014; Al-Anbari et al. 2015; Soliman et al. 2015).

 PI_{sum} is stated as the sum of all heavy metals in contaminated soil and this index was very often was used to the assessment of soil and sediment quality (Gong et al. 2008).

 PI_{Avg} is expressed on the basis of single PI and number metals. If this index exceeds 1.0, the soils are heavily contaminated and have low quality (Bhattacharya et al. 2006; Gong et al. 2008; Inengite et al. 2015).

IPI is expressed as the mean value of the PI by Lu et al. (2009), Oje et al. (2010), and Doležalová Weissmannová et al. (2015).

 IPI_T express multielement contamination and can be used for the assessment of soil pollution with regard to the common effect of metals in soil. If the value of this index is above 1.0, the average concentration of metal is Table 8Classes of total complex indices—integrated indices of pollution (IPI, PLI, PI_{Nemerow}, C_{deg} , mC_{deg}) and classes of indices ofecological risk (E_r , PERI, MERMQ, SCI)

Total complex indices

Value	Soil quality	Ecological risk
Integrated indices of pollution	n	
IPI		
IPI < 1	Low contaminated/polluted	
$1 \leq IPI \leq 2$	Moderate contaminated/polluted	
IPI < 2	Strongly contaminated/polluted	
PLI		
PLI > 1	Polluted	
PLI = 1	Baseline levels of pollution	
PLI < 1	Not polluted	
PIN		
0–7	Clean (class 1)	
7–95.1	Trace contaminated (class 2)	
95.1–518.1	Lightly contaminated (class 3)	
518.1–25,486	Contaminated (class 4)	
2548.6-∞	Highly contaminated (class 5)	
PI _{Nemerow}		
$\mathrm{PI}_{\mathrm{Nemerow}} \leq 0.7$	Clean	
$0.7 \leq PI_{Nemerow} \leq 1$	Warning limit	
$1 \leq PI_{Nemerow} \leq 2$	Slight pollution	
$2 \leq PI_{Nemerow} \leq 3$	Moderate pollution	
$3 \leq PI_{Nemerow}$	Heavy pollution	
C_{deg}		
$C_{\rm deg} < 8$	Low degree of contamination	
$8 \le C_{\text{deg}} \le 16$	Moderate degree of contamination	
$16 \le C_{\text{deg}} \le 32$	Considerable degree of contamination	
$32 \le C_{\text{deg}}$	Very high degree of contamination	
mC_{deg}		
$mC_{\rm deg} \le 1.5$	Very low contamination	
$1.5 \le mC_{\text{deg}} \le 2$	Low contamination	
$2 \le mC_{\text{deg}} \le 4$	Moderate contamination	
$4 \le mC_{\text{deg}} \le 8$	High contamination	
$8 \le mC_{\text{deg}} \le 16$	Very high contamination	
$16 \le mC_{\text{deg}} \le 32$	Extremely high contamination	
$32 \le mC_{\text{deg}}$	Ultra high contamination	
Indices of ecological risk		
E_r		
$E_r < 40$		Low ecological risk
$40 < E_r \le 80$		Moderate ecological risk
$80 < E_r \le 160$		Considerable ecological risk
$160 < E_r \le 320$		High ecological risk
$E_r > 320$		Serious ecological risk
PERI		
PERI < 150		Low ecological risk
150 < PERI < 300		Moderate ecological risk

Table 8 (continued)

Total complex indices

Value	Soil quality	Ecological risk
300 < PERI < 600		High potential ecological risk
$PERI \ge 600$		Significantly high ecological risk
MERMQ		
$MERMQ \le 0.1$		Low priority (probability existing toxicity 9%)
$0.1 < MERMQ \le 0.5$		Medium-low priority (probability existing toxicity 21%)
$0.5 < MERMQ \le 1.5$		High-medium priority (probability existing toxicity 49%)
MERMQ > 5		High priority (probability existing toxicity 76%)
SCI		
$SCI \le 0.5$		Uncontaminated
$0.5 < SCI \le 1$		Very low severity of contamination
$1 < SCI \le 1.5$		Low severity of contamination
$1.5 < SCI \le 2$		Low to moderate severity of contamination
$2 < SCI \le 2.5$		Moderate severity of contamination
$2.5 < SCI \le 3$		Moderate to high severity of contamination
$3 < SCI \le 4$		Migh severity of contamination
$4 < SCI \le 5$		Very high severity of contamination
SCI > 5		Ultra high severity of contamination

Explanation: Integrated Pollution Index (IPI), Pollution Load Index (PLI), New Pollution Index (PIN), Nemerow Pollution Index ($PI_{Nemerow}$), Degree of Contamination (C_{deg}), Modified Contamination Factor (mC_{deg}), Single Index of Ecological Risk (E_r), Potential Ecological Risk Index (PERI), Mean ERM Quotient (MERMQ), Contamination Severity Index (CSI)

above permissible levels (Adamu and Nganje 2010; Doležalová Weissmannová et al. 2015).

The pollution level of soil by heavy metals can be described also through PLI. The value of PLI being close to 1 indicates heavy metal pollution similar to the background level, while values above 1 indicate soil pollution (Liu et al. 2005). The PLI provides simple but comparative means for assessing site quality.

PIN (Caeiro et al. 2005) is used for the calculation of the single PI of heavy metal and class of heavy metals (W_i) considering the degree of contamination, and it varies from 1 to 5. Each index threshold was calculated using the W_i and C_i values for the corresponding class—classes 1–5.

 $PI_{Nemerow}$ evaluates the soil pollution and also assesses the soil quality with using five classes (Cheng et al. 2007; Jiang et al. 2011, 2014; Inengite et al. 2015).

 C_{deg} assesses soil contamination, and values of this index determine four classes of contamination (Hakanson 1980; Caeiro et al. 2005).

 mC_{deg} allows the assessment of the overall soil contamination by heavy metals (Abrahim and

Parker 2008) and classification of soil into four classes.

Potential Ecological Risk Index (PERI, or RI) is calculated on the basis of 3 indices: single index of ecological risk factor (E_r^i) , the pollution coefficient of a single element (C_f^i) , and toxic response factor of individual metals (T_r^i) . The toxic response factors are for Pb (5), Cd (30), Cr (2), Cu (5), Zn (1), Ni

Table 9 The values of ERL and ERM (mg kg⁻¹) (Long et al. 2000, 2006; Christophoridis et al. 2009; Violintzis et al. 2009; Gao and Chen 2012)

Heavy metals	ERL	ERM
As	8.2	70
Hg	0.15	0.17
Cu	34	270
Zn	150	410
Cr	81	370
Ni	20.9	51.6
Pb	46.7	218
Cd	1.2	9.6

Type of soils	Heavy metals	Indices	ses									References
		Id	$I_{\rm geo}$	EF	CF	PI _{sum}	$\mathrm{PI}_{\mathrm{Avg}}$	PI _{Nemerow}	PLI	Cdeg	PERI	
Urban	As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn											Luo et al. (2012)
	Cr, Ni, Cu, Pb, Zn, As, Hg and Cd	+	+									Wei and Yang (2010)
	Cd, Cu, Pb and Zn		+									Liu et al. (2016)
	Zn, Pb, Cu, Mn, Cr, Cd, Ni, Sn, Ag	+	+	+		+		+			+	Kowalska et al. (2016)
	As, Cd, Cr. Hg, Pb,	+									+	Hong-gui et al. (2012)
	Pb, Cd, Cu, Zn, Cr	+	+	+					+		+	Sayadi et al. (2015)
	Cu, Zn, Pb		+	+	+					+		Abrahim and Parker (2008)
	Cu, Pb, and Zn	+	+	+	+	+	+	+			+	Gong et al. (2008)
Industrial	Cd, Cu, Mn, Ni, Pb Zn		+		+							Pam et al. (2013)
	Cu, Ni, V, Co, Cd, Zn, Mo, and Pb		+									Karbassi et al. (2015)
	Cd, Cu, Pb, Zn	+	+	+					+			Mohamed et al. (2014)
	Pb, Cu, Cd, Cr, and Zn	+						+			+	Ogunkunle and Fatoba (2013)
	Cd, Pb, Cu, Cr, and Zn	+						+			+	Jiang et al. (2014)
	Cu, Cd, Fe, Zn, Pb		+	+								Elias and Gbadegesin (2011)
	As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Zn		+	+	+							Loska et al. (2004)
	Cr, Cd, Pb, Zn, Cu, and Ni	+	+								+	Qing et al. (2015)
	As, Cd, Cr, Cu, Ni, Pb, Zn, and Hg		+					+			+	Guan et al. (2014)
	Ni, Cu, Fe, Cr, and Cd	+	+	+	+				+			Ololade (2014)
	Cu, Cr, Ni, Cd, Pb	+										Ripin et al. (2014)
	Fe, Ni, Cd, Cr, Zn, Cu, and Pb	+	+	+	+	+	+	+		+	+	Inengite et al. (2015)
	Cd, Cr, Cu, Zn, Pb, and Ni		+	+							+	Wang et al. (2015a, 2015b, 2015c)
	Pb, Cd, Cr, As, and Hg	+						+				Shu and Zhai (2014)
	Co, Cr, Fe, Hg, Mn, Ni, and Pb	+		+				+			+	Hu et al. (2013)
	Zn, Pb, Cu, Mn, Cr, Cd, Ni, Sn, Ag	+	+	+		+		+			+	Doležalová Weissmannová et al. (2015) and Kowalska et al. (2016)
Park	Cd, Pb, Cr, Ni, Cu, Zn, Fe, Mn			+								Gu et al. (2016)
	Cu, Ni, Pb, and Zn	+		+								Chen et al. (2005)
Sediments	Cd, Cr, Cu, Hg, Ni, Pb, and Zn		+	+							+	Zhang et al. (2008, 2016, 2017)
	Fe, Cu, Zn, Cr, Ni, Pb, Cd, and V								+	+	+	Pejman et al. (2015)

(5), and Mn (1), and preindustrial levels of metals are 0.25, 1.0, 15, 50, 70, 90, and 175 (Hakanson 1980; Biasioli et al. 2006, 2007; Xu et al. 2008; Ajmone-Marsan and Biasioli 2010; Rahman et al. 2014). These indices include also toxic effects to environment, and evaluate pollution using comparable and equivalent methods. The average earth's crustal abundance is used as background concentrations of metals (see Table 1). PERI index covers a various environmental effects, such as toxicology, environmental chemistry, and ecology, and can evaluate ecological risks caused by heavy metals (Lim et al. 2008; Ke et al. 2017).

MERMQ is suitable tool for assessing the harmful impact on soils and was the first applied for evaluation of sediment quality with respect to the evidence of negative effects (Christophoridis et al. 2009; Violintzis et al. 2009). Chemical concentrations of metals corresponding to the 10th and 50th percentiles of adverse biological effects were called the effects range-low (ERL) and effects range-median (ERM), see Table 9. There are three ranges in chemical concentrations, where adverse effects rarely (< ERL), occasionally $(\geq \text{ERL and} < \text{ERM})$, and frequently occur $(\geq \text{ERM})$ (McCready et al. 2006; Christophoridis et al. 2009). The value of ERM is used for the calculation of MERMQ. This index can be applied to identification and prioritization of areas with potential hazards with respect to quality of soils.

The CSI can be calculated using the values of ERL and ERM along with multicomponent statistical methods, such as principal component analysis (PCA) and factor analysis (FA) that identify specific factor weight of each metal (W_{ia}) (Long et al. 2000, 2006; Gao and Chen 2012; Zhu et al. 2012). The value of W_{ia} originates from PCA/FA (Pejman et al. 2015). This method can identify the sources and origin of heavy metals in every locality, and the weighted values are the factors of anthropogenic pollution contribution.

Comparison of contamination in various world countries

The heavy metal contents in soils correlate to the intensity of anthropogenic and natural processes. The concentrations of heavy metals in soils are used for the calculation of pollution indices of pollution. The most

 Table 10 (continued)

Type of soils	Type of soils Heavy metals	Indices	SS									References	on M
		ΡΙ	$I_{\rm geo}$	EF	CF	PIsum	$\mathrm{PI}_{\mathrm{Avg}}$	PI Igeo EF CF PIsum PIAvg PINemerow PLI Cdeg PERI	PLI	C_{deg}	PERI		onit A
	As, Cd, Co, Cr, Cu, Mn, Ni, and Zn	+	+	+	+				+			Varol (2011)	ssess
	Cd, Pb, Zn, As, Cu, Cr, and Hg	+						+	+			Caeiro et al. (2005)	(20
Explanations: I Nemerow Polli	Explanations: PI, Pollution Index; I _{geo} , Geoaccumulation Index; EF, Enrichment Factor; CF, Contamination Factor; PI _{sum} , Sum of Pollution Index; PI _{Avg} , Average Pollution Index; PI _{Nemerow} Nemerow Pollution Index: PI.1. Pollution Load Index: C _{1.2} . Decree of Contamination: PFR1. Potential Ecological Risk Index	Index;	EF, Em	ichmen	tt Facto ninatio	r; CF, Coi n: PERL	ntaminati	on Factor; PI _{su} Ecological Ri	m, Sum sk Inder	of Polluti K	on Index;	PIAvg, Average Pollution Index; PI _{Nemerow}	017) 18

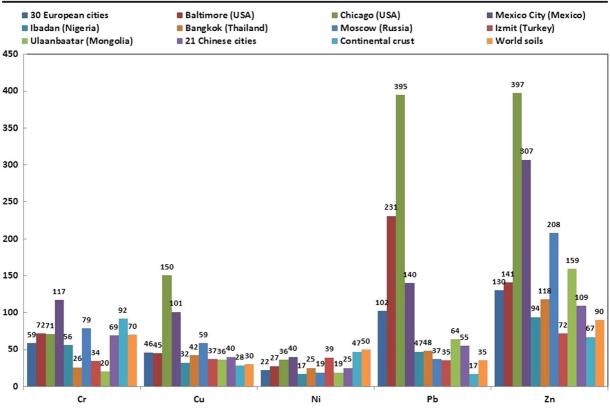
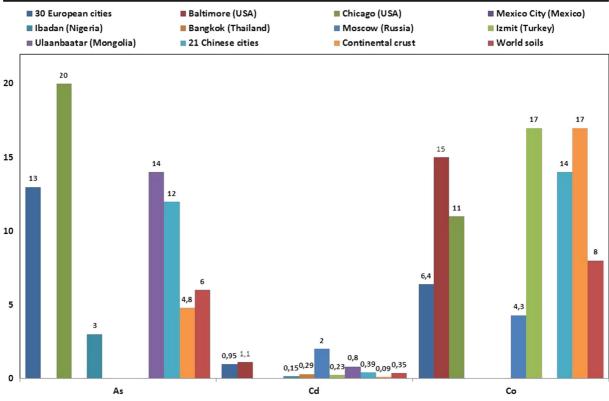
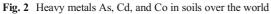


Fig. 1 Heavy metals Cr, Cu, Ni, Pb, and Zn in soils over the world

important indices for assessment of soil pollution/ contamination by heavy metals and its classification of pollution/contamination are listed in Tables 6, 7, and 8. Assessment of anthropogenic impact on soil can be expressed using specified indices. The most important indices of the degree of heavy metal pollution in the soils are the I_{geo} and EF, as well as the Single PI, PI_{sum} , PINemerow, and PERI. The selected heavy metals and used indices of pollution varied greatly in soils over the world and many various indices of pollution (Table 10) verified and confirmed major contributions from anthropogenic activities. The concentrations of heavy metals in soils have been determined in soils many world areas, and their contents depend on the various intensity of anthropogenic inputs, and also development and expansion of industry and urbanization. The concentrations of heavy metals in soils have increasing trend and generally, the highest amounts are in older and more heavily industrialized localities. The concentration of metals As, Cd, Cu, Cr, Ni, and Pb are the highest in old and mega-urbanized cities with huge industrialization like Chicago (As 20, Co 11, Cr 71, Cu 150, Pb 395, and Zn 397 mg kg^{-1}) or Moscow (Cd 2, Co 4.3, Cu 59, Ni 19, Pb 37, and Zn 208 mg kg^{-1}) and are also higher than in case of some cities in Europe with median of heavy metals As 13, Cd 0.95, Co 6.4, Cr 59, Cu 46, Pb 102, and Zn 130 mg kg⁻¹ (Figs. 1 and 2) (Sanders 2003; Markiewicz-Patkowska et al. 2005; Lee et al. 2007; Pouyat et al. 2007; Gong et al. 2008; Birch et al. 2011; Hong-gui et al. 2012; Ogunkunle and Fatoba 2013; Jiang et al. 2014; Mohamed et al. 2014; Ripin et al. 2014; Qing et al. 2015; Sayadi et al. 2015). Luo et al. (2012) reports heavy metals levels in soils from 21 cities in China and median of heavy metals were As 12, Cd 0.39, Co 14, Cr 69, Cu 40, Hg 0.31, Ni 25, Pb 55, and Zn 109 mg kg^{-1} , while the concentrations fall within the range As 6.86-32.8, Cd 0.13-6.90, Co 3.55-58.9, Cr 17.8-197, Cu 16.2-1226, Hg 0.12-0.77, Ni 4.08–910, Pb 26.7–110, and Zn 69.1–301 mg kg⁻¹. Metal concentrations are generally high in old industrial cities with characteristic inputs from emissions of traffic, power plants, and various industries. The metal pollution of soils reflects disparities in the historical development of areas or cities, land use, specific industrial





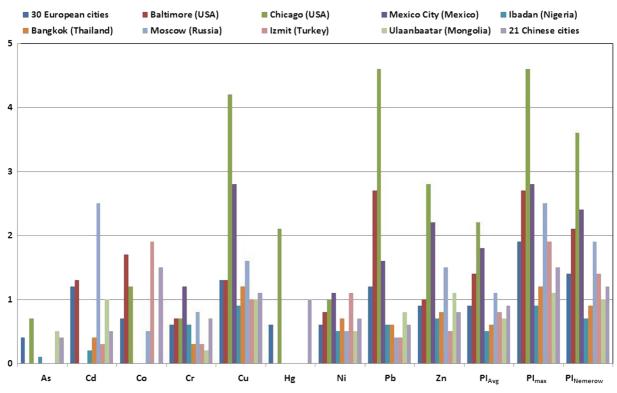


Fig. 3 Pollution indices (PI, PIAvg, PIMax, PINemerow) of heavy metals in soils of selected world cities

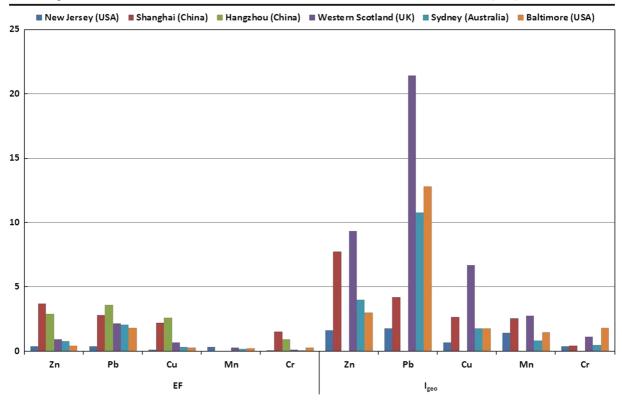


Fig. 4 EF and I_{geo} in urban soils of selected cities in the world

activities, growing trend of population density, local climate conditions, and also the differences in socioeconomic development in these countries.

According to the PI_{Nemerow} index, most soils are polluted from slightly polluted with warning limit to heavy polluted. The levels of warning limit soils pollution were identified in Ibadan (Nigeria), Bangkok (Thailand), and Ulaanbaatar (Mongolia) with PI_{Nemerow} 0.7, 0.9, and 1. The ranges of PI_{Nemerow} (1-2) were obtained in European cities (1.4), Izmit 1.4 (Turkey), and Moscow (Russia) with a value of 1.9. PI_{Nemerow} values of 2.1 and 2.4 were obtained for Baltimore (USA) and Mexico City (Mexico); it means that these soils are moderately polluted by heavy metals. Heavy polluted soils were detected in Chicago (USA) with a PI_{Nemerow} value of 3.6. In Chicago, Pb, Cu, Hg, and Zn were identified as the most contributed metals. The analyzed values of used pollution indices confirmed the possibility of dividing heavy metals into two groups, the so-called urban metals (Pb, Cu, Zn, Hg, and Cd) and non-urban metals (Ni and Cr). According to the pollution indices in Fig. 3, where PI, PI_{Avg} , PI_{max} , and $PI_{Nemerow}$ of metals in soils of selected world cities are depicted, most soils in European and American cities were moderately or heavily polluted in the case of Pb, Cd, Cu, and Zn more extensively than cities in Africa and Asia (Sanders 2003; Markiewicz-Patkowska et al. 2005; Pouyat et al. 2007; Birch et al. 2011). The index of EF and I_{geo} has been used to determine the degree of contamination for soils in various localities and verified different degrees of heavy metal contamination in soil (Sanders 2003; Markiewicz-Patkowska et al. 2005; Pouyat et al. 2007; Birch et al. 2011). The indices EF and I_{geo} are presented in Fig. 4. The value of EF confirmed slightly moderate to moderate enrichment of soils by Pb and Zn. Levels of I_{geo} varied from uncontaminated to moderately contaminated in the case of Mn; values of Cr varied from 0.84 (Sydney, Australia) to 2.75 (Western Scotland, UK). The obtained value of "urban metals" verified contamination grades from moderate contamination of 1.76 (New Jersey, USA) to extremely high contamination of 21.44 (Western Scotland, UK) in the case of Pb. The range of I_{geo} was from 0.66 (New Jersey, USA) to 6.71 (Western Scotland, UK), and the same trend was observed for Zn (1.62 New Jersey, USA) to 9.33 (Western Scotland, UK). $I_{\rm geo}$ value reflects the background levels of area and reflects the antropogenic contribution of heavy metals as it was confirmed by analysis of data from scientific literature.

Conclusion

The heavy metal concentrations and indices of pollution/ contamination varied greatly in soils over the world, and many various indices of pollution confirmed and verified major contributions from anthropogenic activities. Indices of soil pollution/contamination were divided into two groups: individual indices and total complex indices. It is evident that the metal pollution of soils reflects many factors (historical development, land use, industrialization processes, growing trend of population density, climate conditions, biogeography, etc.). This review provides analyses of soil pollution/contamination by heavy metals and summarizes the pollution sources; 20 different indices of heavy metal pollution were reviewed and classified into single indices and total complex indices of pollution/ contamination. This review also contains classification of indices of pollution in the context of complex assessment of soil quality. The soil is one of the most important components of ecosystems in relation to human health; therefore, it is essential that the soil quality has been included in environmental quality management on a worldwide. The assessment of soil pollution and evaluation of soil quality have to be still monitored over the world.

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