



# Health risk assessment related to an effect of sample size fractions: methodological remarks

Alicja Kicińska<sup>1</sup>

Published online: 25 November 2017

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## Abstract

Contents of As, Cd, Co, Cr, Cu, Ni, Pb and Zn were determined in the material collected in sandboxes of seven spa resorts located in S Poland (CCE) and their results used to establish a health risk of children. After sieving out grains  $> 2$  mm, the bulk samples were quantitatively separated into four grain fractions: 2000–1000, 1000–200, 200–63 and  $< 63$   $\mu\text{m}$ . In each of them were determined: the mineral composition, the total contents of the elements, and the distribution of the elements among the fractions distribution factor. In the bulk material  $< 2$  mm, the totals of the elements are 5–64 times lower than in the finest fractions ( $< 63$   $\mu\text{m}$ ). Considering that the finest fractions are enriched in clay minerals such as clinochlore, illite and kaolinite, which can adsorb and desorb metals, this material is most dangerous for children, staying both permanently and temporarily in the spas. The total health risks  $HI$  resulting from non-carcinogenic elements present in the fractions  $< 63$   $\mu\text{m}$  are 1.26 and 0.94, for the children-residents 3 and 6 years old, respectively. The figures are disturbing as one of them exceeds and the other is close to a permissible limit of 1. The highest contribution (93.4%) into the total  $HI$  is caused by inadvertent swallowing the soil “dirt”: the ingestion path  $HQ_{ing}$  for the 3 years old residents is 1.17, and for the 6-year olds 0.88. With respect to the elements, the highest is the risk resulting from Pb:  $HQ_{in}$  values of the residents are  $4.71\text{E}-01$  and  $3.54\text{E}-01$  for the 3-year olds and the 6-year olds. Slightly lower are the  $HQ_{ing}$  values calculated for both age groups: in the case of Cr— $3.12\text{E}-01$  and  $2.34\text{E}-01$  and As— $2.92\text{E}-01$  and  $2.19\text{E}-01$ . The dermal path ( $HQ_{dermal}$ ) contributes to the total  $HI$  much less as it equals 6.5%, while the contribution of the inhalation path ( $HQ_{inhal}$ ) is considerably the lowest and equals only 0.1%. The  $Risk$  indexes determined in the case of cancerogenic components for both age groups of the spa residents are lower than the permissible limit  $10\text{E}-5$  and equal  $6.48\text{E}-06$  and  $9.72\text{E}-06$ , respectively. Considering the children that only visit the spas, all the calculated indexes, i.e.,  $HI$  and  $Risk$ , are significantly lower than those determined for the children-residents.

**Keywords** Grain fraction · Analytical methods · Metal variability · Risk assessment

## 1 Introduction

Significant factors in environmental investigations pertaining to the health risk include methods of collecting samples, their kind, number, and representativeness of the environment component considered. The issues of the chemical nature, such as the methodology and correctness

of analyses, as well as the precision and accuracy of determinations seem currently to be easily verified due to using standardized procedures and reference standards. Therefore, the magnitude of possible errors in the environmental studies depends mainly on the selection of a strategy and a procedure of sampling, the process of sampling itself, and the field determinations (Migaszewski and Galuszka 2016). They are followed by data processing, the selection of a statistical method, then the interpretation and evaluation of the results, and eventually provide final pieces of information on the state of the environment and rectifying (if necessary) steps. The reliability and precision of determinations are highly important when they refer to toxic substances present in the environment (Hlavay et al.

✉ Alicja Kicińska  
kicinska@geol.agh.edu.pl

<sup>1</sup> Department of Environment Protection, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Mickiewicza 30 Av, 30-059 Kraków, Poland

1992; Gong et al. 2014; Kłojzy-Karczmarczyk 2014; Al-Hwaiti and Al-Khashman 2015; Stala-Szlugaj 2016). Deleterious elements include heavy metals, particularly Cd, Pb, Tl and As (in fact, arsenic is a metalloid, but for the brevity it will be further referred to as a metal). These elements may not only affect a proper functioning of organisms, but irreversibly disturb their growth (Kabata-Pendias and Pendias 1999; Al-Hwaiti et al. 2014; Islam et al. 2016; Taiwo et al. 2017).

A health risk caused by toxic substances is assessed using environmental samples collected in the places where children come into contact with them most often or most probably. Such sites include mainly playing grounds, sport fields, sandboxes, urban parks, gardens of nurseries and school recreational grounds (Jartun et al. 2003; Yamamoto et al. 2006; De Miguel et al. 2007; Guney et al. 2010; Wei and Yang 2010; Diatta and Grzebisz 2011; Figueiredo et al. 2011; Ak et al. 2012; Du et al. 2013; Niec et al. 2013; Kicińska 2016a; Wang et al. 2016). The collection of samples to be used for establishing a degree of ground or soil contamination and the calculating a health risk caused by metals the samples contain are controlled by various standards being in force in different countries (US EPA 1996; Ministry 2003; Minister 2016). Usually the material finer than 2 mm is the subject of analyses (Jartun et al. 2003; Bai et al. 2009; Marjanović et al. 2009; Guney et al. 2010; Wei and Yang 2010; Figueiredo et al. 2011; Al-Hwaiti et al. 2015; Dziubanek et al. 2015; Kicińska 2016b; Stajic et al. 2016), but some authors suggest analyzing other grain fractions. For instance, in the samples rich in the organic matter Boone et al. (1999) recommended a fraction with grains < 0.5 mm. A finer fraction of < 0.1 mm was separated by De Miguel et al. (2007) when investigating the health risk of children in the playgrounds of Madrid. In turn, Diatta and Grzebisz (2011) concentrated on the grain fraction < 1 mm when analysing the quantity of metals the visitors of the urban parks of Poznań (Poland) are exposed to. The grain fractions obtained using the set of sieves 2, 0.250 and 0.125 mm were separated when studying (Valskys et al. 2016) the material of the playing grounds of Vilnius (Lithuania).

The dependency between the content of elements and the grain size of the analytical sample was dealt with, among others, by Ljung et al. (2006), Yamamoto et al. (2006), Ajmone-Marsan et al. (2008), Gong et al. (2014) and Kosa and Kicińska (2016). The latter authors underlined a high concentration of As, Cd, Pb and Cr in the finest grain fractions. Simultaneously, Yamamoto et al. (2006) established that these are soil and ground particles with the size  $39 \pm 26 \mu\text{m}$  that adhere best to children hands, and the total mass of such a stack “dirt” may reach even 162.5 mg per hand. A recommendation of the United State Environmental Protection Agency (US EPA) pertaining to

the evaluation of the health risk suggest accepting a soil mass of 200 mg per day in the case of children from 1 to 6 years old, and lower this dose at least at a half in the case of adults (US EPA 1986).

Considering the said above, the investigations centered on the impact of a sampled material grain size when evaluating the health risk of children that use playing grounds of the spas recommended for youngsters in Poland (Central-Eastern Europe—CEE). In seven such spa resorts the surface (0–20 cm u.g.l.) sand material of the sandboxes was collected in 2016 and the following determinations were made:

- (1) separating four grain fractions and establishing their contributions to bulk samples,
- (2) establishing the mineral composition and the morphology of particles in each grain fraction,
- (3) determining the quantity of selected elements in the bulk sandy material < 2 mm and the four grain fractions separated. The elements included are those related to road traffic (Cu, Zn, Ni, Cr, Co and Pb) and to the low emission (mainly As and Cd), considering them as major anthropogenic pollutants of the spa localities.
- (4) calculating from the results of the steps 1–3 the health risk indexes *HI* caused by non-carcinogenic substances and the indexes *Risk* caused by carcinogenic substances containing the elements specified in (3). Children are endangered by contaminants entering their organisms along three possible paths, i.e., ingesting, inhaling and skin contacting. The calculations were directed into finding any relation between sample grain sizes and the total contents of the elements considered. The most crucial aim, important for further investigations, was establishing the sample grain fraction whose analyses provide the most sound basis in the calculations of the health risk for children.

## 2 Materials and methods

### 2.1 Site selection and sampling

The investigations were carried out in seven spas of Poland (CEE): Krynica, Muszyna, Piwniczna, Rabka, Swoszowice, Szczawnica and Wysowa. Six of them are located within the Carpathians, and Swoszowice at the very margin of the hills, in the Malopolska Voivodeship administrative area (Fig. 1). The spa status was granted them in 1967, and mineral waters as their main medicinal resource. The problems of the upper and lower respiratory tracts are treated in all the spas except for Swoszowice.

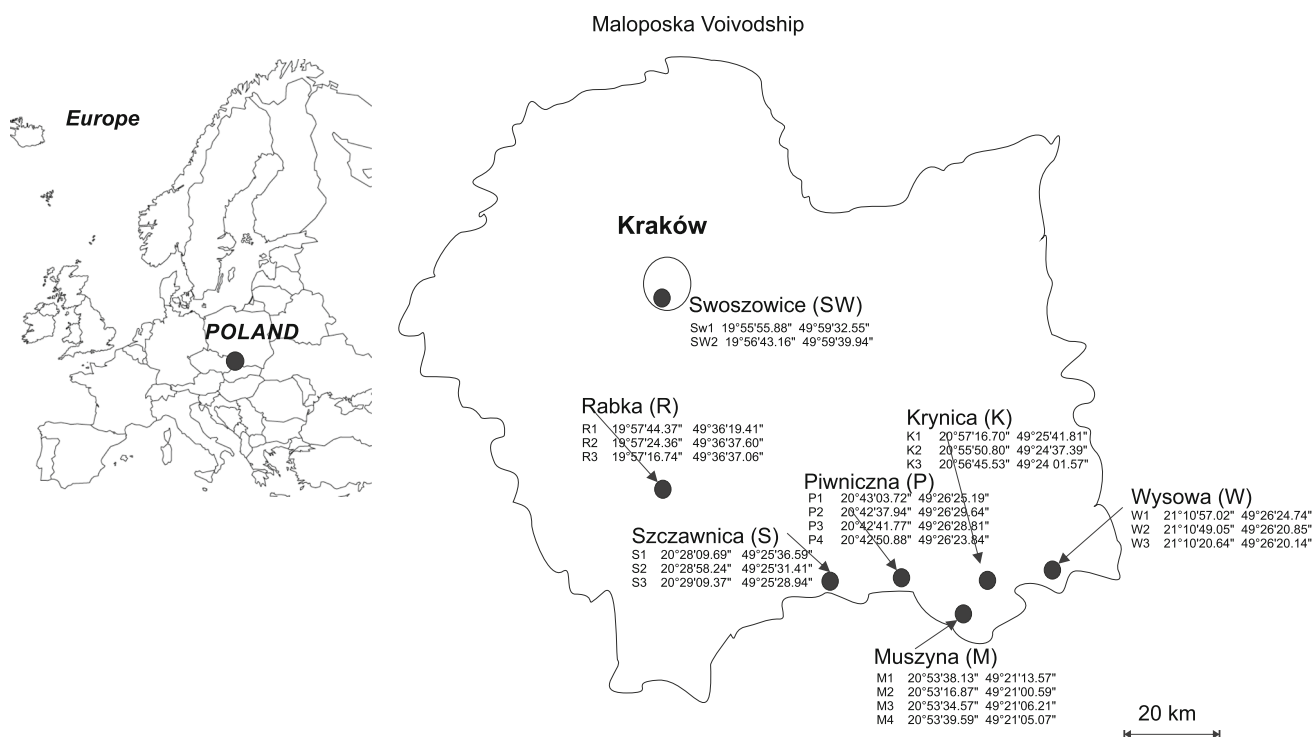


Fig. 1 Sampling sites

In each of the spas there are two to four playing grounds that contain sandboxes. The sandy material was collected in four sites within every sandbox and represented so-called general surface samples. The total of samples was 88 and a mass of each around 2 kg.

The material collected on-site was placed into plastic bags, then dried and prepared to chemical analyses, which were conducted at the Laboratory of Trace Analyses, the Chair of Environment Protection in Cracow. The fraction above 2 mm was removed in the first stage and the remainders (weight  $1 \pm 0.01$  kg) of each sample were dry-sieved into three grain fractions: 2000–1000 (symbol  $F_{2000-1000}$ ), 1000–200 (symbol  $F_{1000-200}$ ) and 200–63 (symbol  $F_{200-63}$ )  $\mu\text{m}$ ; the fourth, finest fraction  $< 63$   $\mu\text{m}$  (symbol  $F_{<63}$ ) was wet-sieved. The subject of further analyses were the bulk samples  $< 2$  mm and the four grain fractions separated from each of them.

The determinations of the quasi-totals of elements were made by dissolving the samples in *aqua regia* ( $\text{HCl} + \text{HNO}_3$ , at the ratio 3:1) in a microwave oven SCP SCIENCE, DigiPREP HT type, at 130 °C and 90, 100 and 110 psi (“quasi” as *aqua regia* does not completely decompose silicate-rich samples). The mass of the analytical samples was 0.5 g.

The phase composition of crystalline components was carried out applying the powder Debye-Sherrer method using a Rigaku MiniFlex 600 XRD diffractometer. The measurement parameters were as follows:  $\text{CuK}_\alpha$  radiation,

reflection graphitic monochromator, lamp voltage 40 kV, lamp current 20 mA, recording range  $2-72^\circ 2\theta$ ; step  $0.05^\circ 2\theta$ , impulse count rate 1sek/step. The interplanar distances obtained from the X-rays patterns were used for identifying crystalline phases based on the data of the ICDD (International Centre for Diffraction Data) catalogue and the XRAYAN software.

Optical microscopy (a Nikon Eclipse 50i-POL unit) and scanning electron microscopy SEM-EDS (a FEI Quanta model 200 FEG unit) were used for observing the morphology of the grains in all the fractions and conducting spot analyses. The observations were extended by chemical analyses of microareas applying an EDS detector (SEM-EDS method) conducted in the high vacuum mode. The resolution power of the microscope was increased by covering the samples with carbon prior to analysing. The accelerating voltage was 20 kV. The mineral composition was assessed macroscopically except for the finest ( $F_{<63}$ ) fraction.

The chemical composition was determined using the method of induced coupled plasma mass emission spectroscopy (ICP-MS) at the certified hydrogeochemical laboratory (certificate of the Polish Accreditation Commission no. AB1050) of the AGH University of Science and Technology in Krakow. The Certipur Certified Reference Material (HC69208280) was used as a standard. The precision of the determining Fe, Ca, Al, K, Mg, Si, Mn, Na,

Zn, Ba, Pb, As, Ti, Cd, Ni, Tl, Cr and Co was 10%, while the accuracies (AO) ranged between 95 and 105%.

The following equations were used when calculating the limits of detection LOD and quantification LOQ presented in Table 2:

$$\text{LOD} = X_b + 3SD_b, \quad (1)$$

$$\text{LOQ} = X_b + 10SD_b, \quad (2)$$

where  $X_b$ , mean concentration of the blank (zero concentration) sample,  $SD_b$ , the standard deviation of the blank sample.

The health risk  $HI$  was calculated according to the US Environmental Protection Agency (US EPA 1996, 1997) procedure, accepting three pathways:  $HQ_{ing}$ —direct ingestion of substrate particles (US EPA 1986, Kicińska et al. 2017),  $HQ_{inh}$ —inhalation of re-suspended particles via mouth and nose, and  $HQ_{dermal}$ —dermal absorption of metals from the particles adhered to an exposed skin (De Miguel et al. 2007). The health risk values:  $HQ_{ing}$ ,  $HQ_{inh}$  and  $HQ_{dermal}$  were calculated for each element as the ratio of the contact doses ( $D_{ing}$ ,  $D_{inh}$ , and  $D_{dermal}$ , respectively) to the corresponding reference doses ( $RfD_{ing}$ ,  $RfD_{inh}$ , and  $RfD_{dermal}$ , respectively) following the US EPA (2005).

The doses  $D_{ing}$ ,  $D_{inh}$  and  $D_{dermal}$  were calculated using the following equations (US EPA 1986):

$$D_{ingestion} = C \cdot \frac{IngR \cdot EF \cdot ED}{BW \cdot AT} \cdot CF1, \quad (3)$$

$$D_{inhalation} = C \cdot \frac{InhR \cdot EF \cdot ED}{PEF \cdot BW \cdot AT}, \quad (4)$$

$$D_{dermal} = C \cdot \frac{SA \cdot SL \cdot ABS \cdot EF \cdot ED}{BW \cdot AT} \cdot CF1, \quad (5)$$

where  $C$ , mean concentration of the metal in a sample (mg/kg),  $IngR$ , conservative estimates of dust ingestion rates; for children 100 (mg per hour) (US EPA 2011),  $InhR$ , inhalation rate; in this study 1.2 (m<sup>3</sup>/hour) (US EPA 2011),  $EF$ , exposure frequency; for residents accepted as 646 (hours/year) after De Miguel et al. (2007), for visitors as 84 (hours/year),  $ED$ , exposure duration; for younger children 3 (years) and for older ones 6 (years),  $BW$ , body mass; for children 3 years old 15 (kg), for those 6 years old 20 (kg) (US EPA 2011),  $AT$ , averaging time. In the case of non-carcinogens: for 3 years old children its value is 1095 (days) and for 6 years old children 2190 (days), while in the case of carcinogens the value is 25,550 (days),  $SA$ , exposed skin area, 2800 (cm<sup>2</sup>) after De Miguel et al. (2007),  $SL$ , skin adherence factor, 0.07 (mg/cm<sup>2</sup> per hour) after De Miguel et al. (2007),  $ABS$ , dermal absorption factor, 0.001 (for all the elements except As, for which  $ABS$  is 0.03) after De Miguel et al. (2007),  $PEF$ , particle emission factor, 6.8E+08 (m<sup>3</sup>/kg) after De Miguel et al. (2007),  $CF1$ , unit conversion factor of 10<sup>-6</sup>.

The  $HI$  index was calculated as a sum of  $HQ_{ing}$ ,  $HQ_{inh}$ , and  $HQ_{dermal}$  values. At  $HI \leq 1$  the adverse health effects are of a low probability to occur, at  $HI > 1$  they are probable, while the  $HI > 10$  values are a sign of a high exposure and a highly possible chronic health risk caused by a toxic factor(s).

To establish a level of the cancer *Risk* for carcinogens, the  $HQ$  doses were multiplied by the respective slope factors (US EPA 2005, for Pb WHO 1993).

The distribution of the elements considered within the grain fractions has been expressed calculating the distribution factor ( $DF_x$ ). It is one of the important indexes which was used in this study to evaluate in which fraction the metals (As including) are preferentially accumulated by referring the fraction to bulk quantities (Eq. 6):

$$DF_x = \frac{X_{fraction}}{X_{bulk}}, \quad (6)$$

where  $X_{fraction}$  and  $X_{bulk}$  are concentration of element (mg/kg) in the given fraction and bulk sample, respectively. If  $DF_x > 1$  for the specific fraction, the element (here: metal) is enriched. Statistical calculations and data presentations were conducted with the Statistica ver. 10 and Excel applications. The differences between means were detected by the Turkey's HSD test at a significance level of 0.05.

### 3 Results and discussion

#### 3.1 Grain and mineral composition of the sand samples

The sieve analyses conducted on the set of 88 samples provide the results sufficient to compare the distribution of grain fractions in the sands of the spa sandboxes (Table 1). The arithmetical means indicate that the grains between 1000 and 200  $\mu\text{m}$  ( $F_{1000-200}$ ) are the prevailing material and make up 78.2 wt% on the average. The grains with sizes from 200 to 63  $\mu\text{m}$  ( $F_{200-63}$ ) are approximately 5 times less frequent and make up 18.72 wt%. The contents of the coarsest ( $F_{2000-1000}$ ) and finest ( $F_{<63}$ ) grain fractions are insignificant, close in both cases to 1.5 wt%.

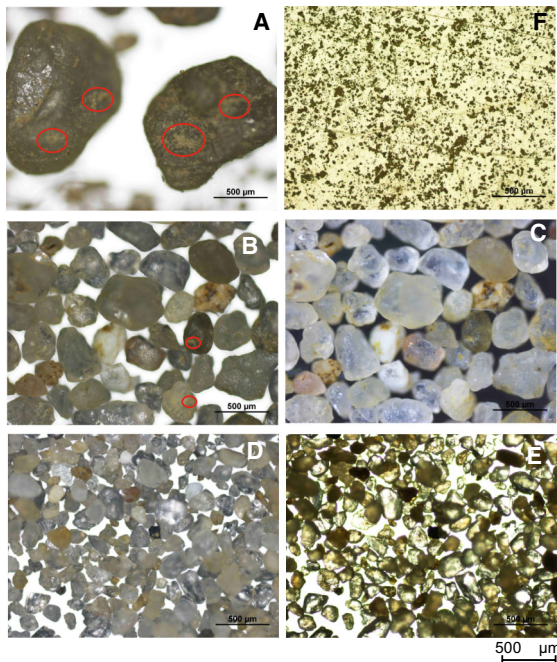
Each of the fractions, if observed under the optical microscope, is composed mostly (around 90–80%) of oval, well rounded quartz grains. They are highly transparent (Fig. 2c, e), some of them possess a delicate milky brown coloration. Minor particles are represented by black, opaque grains, possibly amphiboles and pyroxenes, and greenish grains that may be olivines. The list is supplemented by fine plates of both micas, i.e., muscovite and biotite. Some grains of the two coarsest fractions ( $F_{2000-1000}$  and  $F_{1000-200}$ ) have rough, uneven surfaces and their small hollows and fractures are filled with an adhering



**Table 1** Share of sand fractions

Site	n	Grain size ( $\mu\text{m}$ )			
		2000–1000	1000–200	200–63	<63
		Share of fraction (%)			
Szczawnica	12	0.76–1.80	71.48–79.56	15.01–23.33	1.50–2.84
Rabka	12	0.07–1.34	79.28–91.79	6.53–15.74	0.32–1.38
Krynica	12	1.89–2.46	64.79–75.04	17.55–24.73	0.78–1.67
Muszyna	16	0.29–1.26	63.94–79.33	15.74–26.01	1.04–2.43
Piwniczna	16	0.49–2.33	70.01–79.37	15.26–27.39	1.72–3.65
Wysowa	12	0.42–6.01	73.29–73.30	16.84–23.86	0.90–2.12
Swoszowice	8	0.50–0.52	83.65–85.18	13.40–13.66	0.65–0.88
<i>For all destination</i>					
min.–max.	88	0.07–6.01	63.94–91.79	6.53–27.39	0.32–3.65
Average		1.49	78.20	18.72	1.59

*n* number of samples, *min.* minimum, *max.* maximum, *average* arithmetic average



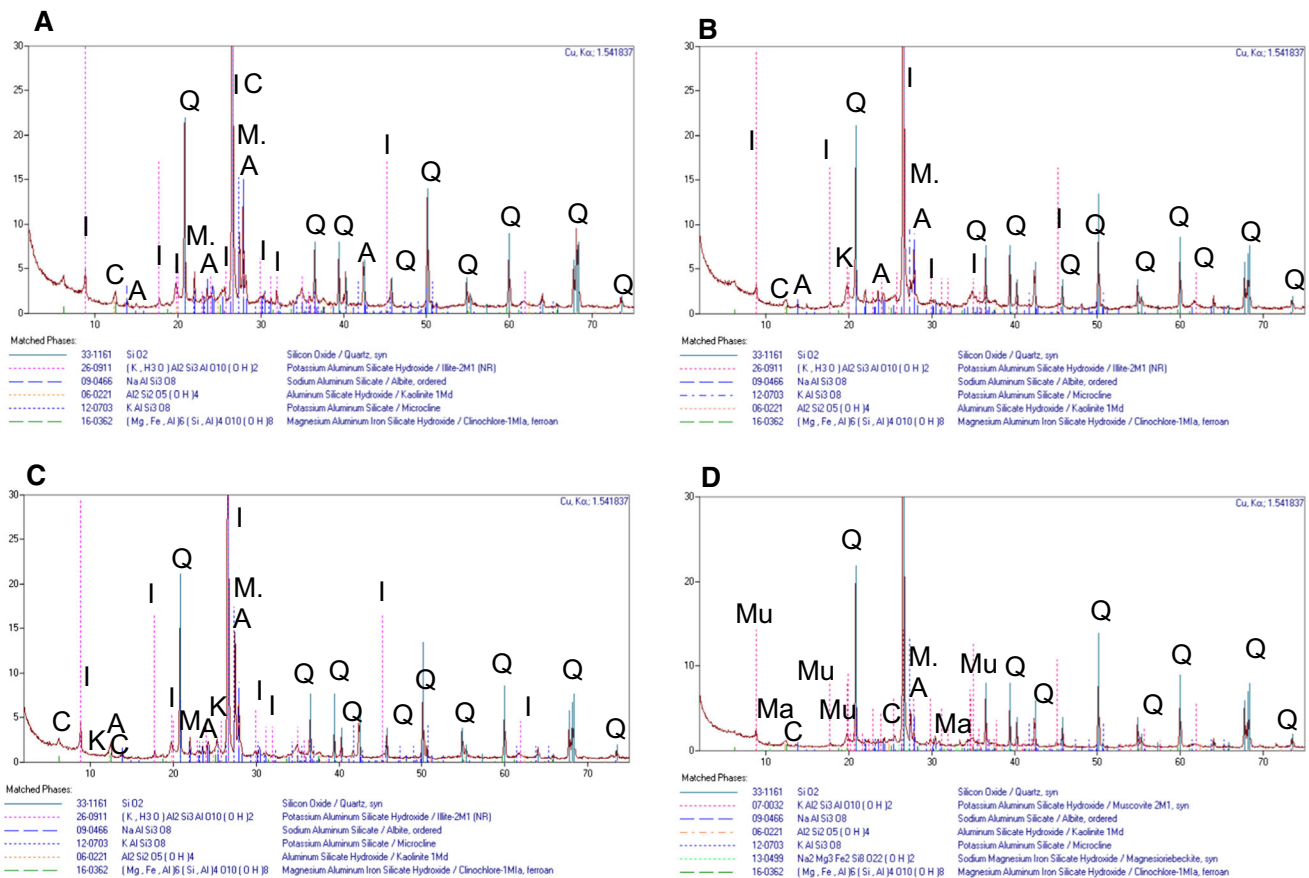
**Fig. 2** Macro and transmitted plane-polarized light microscope images of the sample P3 from Piwniczna: sand fractions 2000–1000, **b**, **c** 1000–200, **d**, **e** 200–63, and **f** < 63  $\mu\text{m}$  red circle accumulation of  $F < 63$

material (Fig. 2a, b, d). In the fraction  $F_{2000-1000}$  also occur grains whose surfaces are completely covered by a fine-grained, usually darker material. The finest grain fraction  $F_{<63}$  is composed of compact, mostly pelitic aggregates, whose identification has not been possible using optical microscopy (Fig. 2f). Therefore, more sophisticated methods had to be applied, namely X-ray diffraction XRD and scanning electron microscopy SEM–EDS.

X-ray diffraction patterns reveal that the fraction  $F < 63$  is composed mainly of quartz ( $\text{SiO}_2$ ), a mineral resistant to

atmospheric and chemical factors (Fig. 3). It is accompanied by feldspars: Na-rich albite ( $\text{Na}[\text{AlSi}_3\text{O}_8]$ ) of the plagioclase group, and K-feldspar microcline  $\text{K}[\text{AlSi}_3\text{O}_8]$ . Feldspars as a whole group are less resistant to weathering than quartz and within the group their potassium varieties are more resistant than plagioclases. Kaolinite  $\text{Al}_4[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$ , belonging to the group of clay minerals and identified in some samples, may be a product of plagioclase weathering. In most of the samples tested identified amphibole—magnesioriebeckite  $\text{Na}_2\text{Mg}_3\text{Fe}_2^{3+}[(\text{OH}, \text{F})|\text{Si}_4\text{O}_{11}]_2$ , belonging to the group of glaucophosphates (alkaline amphiboles). Muscovite  $\text{KAl}_2[(\text{OH})_2|\text{AlSi}_3\text{O}_{10}]$ , a dioctahedral mica, is a common, however minor or trace component of sands. This mineral is to a certain degree resistant to physical and chemical changes, but advanced weathering of sediments may transform it to hydromuscovite, while a further degradation to illite ( $\text{K}, \text{H}_3\text{O})\text{Al}_2[(\text{OH})_2|\text{AlSi}_3\text{O}_{10}]$ . Illite, one of the clay minerals, may also be formed by structural changes of other clay minerals. Two clay minerals, illite and clinochlore ( $\text{Mg}, \text{Al})_3[(\text{OH})_2|\text{AlSi}_3\text{O}_{10}] \cdot \text{Mg}_3(\text{OH})_6$ , have been XRD-identified in traces. One of the properties of clay minerals is their adsorption of cations (Sotch 1974) due to not compensated charge of the layer units that is related to isomorphic substitutions within the tetra- and octahedral layers. Adsorption depends on (after Sotch 1974) the cation type, concentration of a solution, pH, the presence of other cations, mineral structure, time of the exchange, temperature and the size of the mineral. Clay minerals are thus mineral substances with the highest sorption capacity of cations (Kabata-Pendias and Pendias 1999, Wardas-Lasoń 2014).

Morphological observations using the SEM–EDS method were supported by spot analyses in microareas of particles of the fraction  $F_{<63}$  (Figs. 4 and 5). The grains are



**Fig. 3** XRD patterns of sand samples collected in: **a** Krynica (sample no. K1), **b** Szczawnica (sample no. SZ2), **c** Piwniczna (sample no. P2), **d** Swoszowice (sample no. SW2). *Q* quartz, *I* illite, *A* albite, *M*. microcline, *K* kaolinite, *C* clinochlore, *Mu* muscovite, *Ma* magnesianriebeckite

mostly irregular and jagged, with sizes from 1 to 5  $\mu\text{m}$  (Fig. 4a, b), some are sharp-edged and elongated, often coated with much finer material (Fig. 4a). Other grains represent larger aggregates (see central part of Fig. 4b, the size of the aggregate is  $20 \times 30 \mu\text{m}$ ), cemented with an amorphous material, being probably a Ca and Mg carbonate. The analyses of the sample collected in Krynica indicate a dominance of Fe, Si, Pb, Al and Sn oxides (Fig. 4a). The spectrum recorded in Fig. 4b (point 1) identifies dioxides of Si (quartz), Ti (rutile) and oxides and oxy/hydroxides of Fe and Al. A larger, oval grain (Fig. 4c, top right corner) is probably ilmenite ( $\text{FeTiO}_3$ ). The spectrum in the point 2 (Fig. 4c) suggests the presence of zircon  $\text{Zr}[\text{SiO}_4]$ , a mineral resistant to chemical factors. Other minerals of the fraction  $< 63 \mu\text{m}$  include clinochlore (point 3, Fig. 4c), rutile  $\text{TiO}_2$  (point 4, Fig. 4c), and beside clinochlore, other clay minerals (magnetite or hematite) is shown in Fig. 4d (point 1), while probable zircon in point 2. Figure 5 presents the morphology and chemistry of grains identified in the samples  $F_{<63}$  collected in Swoszowice. The grains marked 1(A) and 2(A) in Fig. 5 have been identified as chlorites (clinochlore, baileychlore?), Fe oxy/hydroxides, and—

tentatively—as fayalite  $\text{Fe}_2^{2+}[\text{SiO}_4]$ . The grains 3(A) and 1(B) in Fig. 5 contain rare earth elements (REE) and may represent monacite ( $\text{Ce,La,Th,Nd,Y,Pr}\text{PO}_4$ ). Among the grains in samples from Szczawnica (Fig. 5c, d), an unidentified large, oval grain (diameter around  $50 \mu\text{m}$ ) has the uneven surface covered with a finer material (Fig. 5c, central part). The spot analyses in points 1(C) and 2(C) indicate that the coating particles are clay minerals (illite, clinochlore?). Another grain in Fig. 5d (point 1(D)) may be a phyllosilicate (but its Ba content is strikingly high) of 12.74 wt%.

## 3.2 Metal contents of the sand samples

### 3.2.1 Bulk sand samples

In the bulk samples. i.e., those without the material  $> 2 \text{ mm}$ , the average contents of the metals considered range as follows: As 0.20–3.60, Cd 0.01–0.18, Co 0.21–1.59, Cr 2.40–6.02, Cu 0.56–2.24, Ni 1.46–5.37, Pb 0.68–5.50 and Zn 7.59–37.92 mg/kg (Table 2). Detailed characteristics on the metal quantities and forms of metal occurrences were described separately (Kicińska et al.

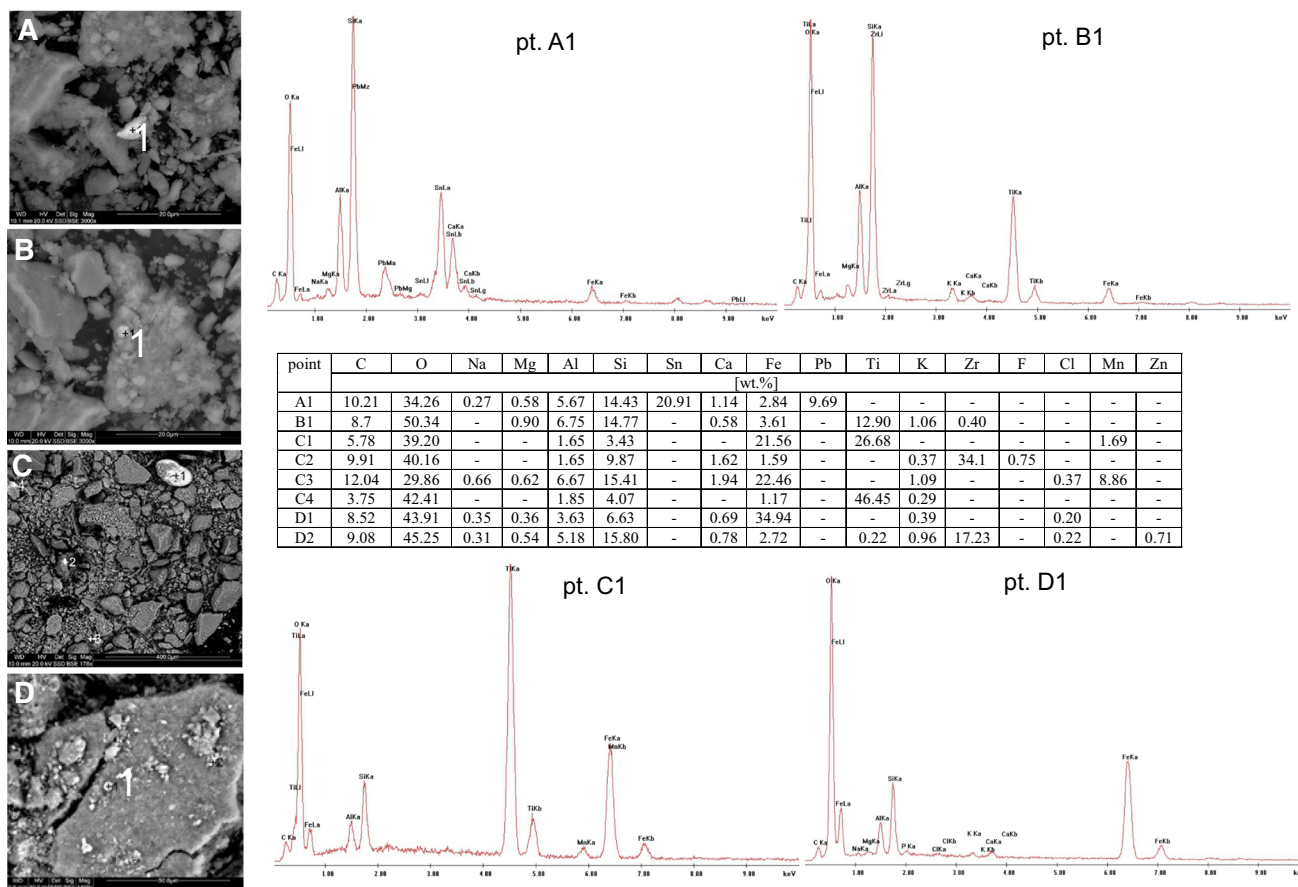


Fig. 4 SEM images and EDS spectra of sand samples F < 63 μm collected in Krynica (a, b), Piwniczna (c, d), “-” not identified

2017). The quantities of Cd, Co, Cu, Pb, Ni and Zn determined here are significantly lower than those found in analogous samples in Silesia, an industrial region of Poland (Kicińska 2016a, b). Arsenic makes in the spa material a difference: it occurs in significantly higher quantities than in Silesia. The results of the analyses are lower than the legal upper limits in force in 2016, i.e., the year of sampling in the case of As, Cd, Co, Cu, Ni, Pb and Zn (Minister 2002, Ministerie 2000; Alexander 2006) except for Cr. The chromium contents exceed in 36% of the spa samples a limit of 5 mg Cr<sup>6+</sup>/kg stipulated in the Norwegian standards (Alexander 2006). This value refers to the chromium in the hexavalent form that is soluble and then becomes toxic, but in the well rain-washed sandboxes the Cr<sup>6+</sup> quantities are insignificant and do not represent a real threat.

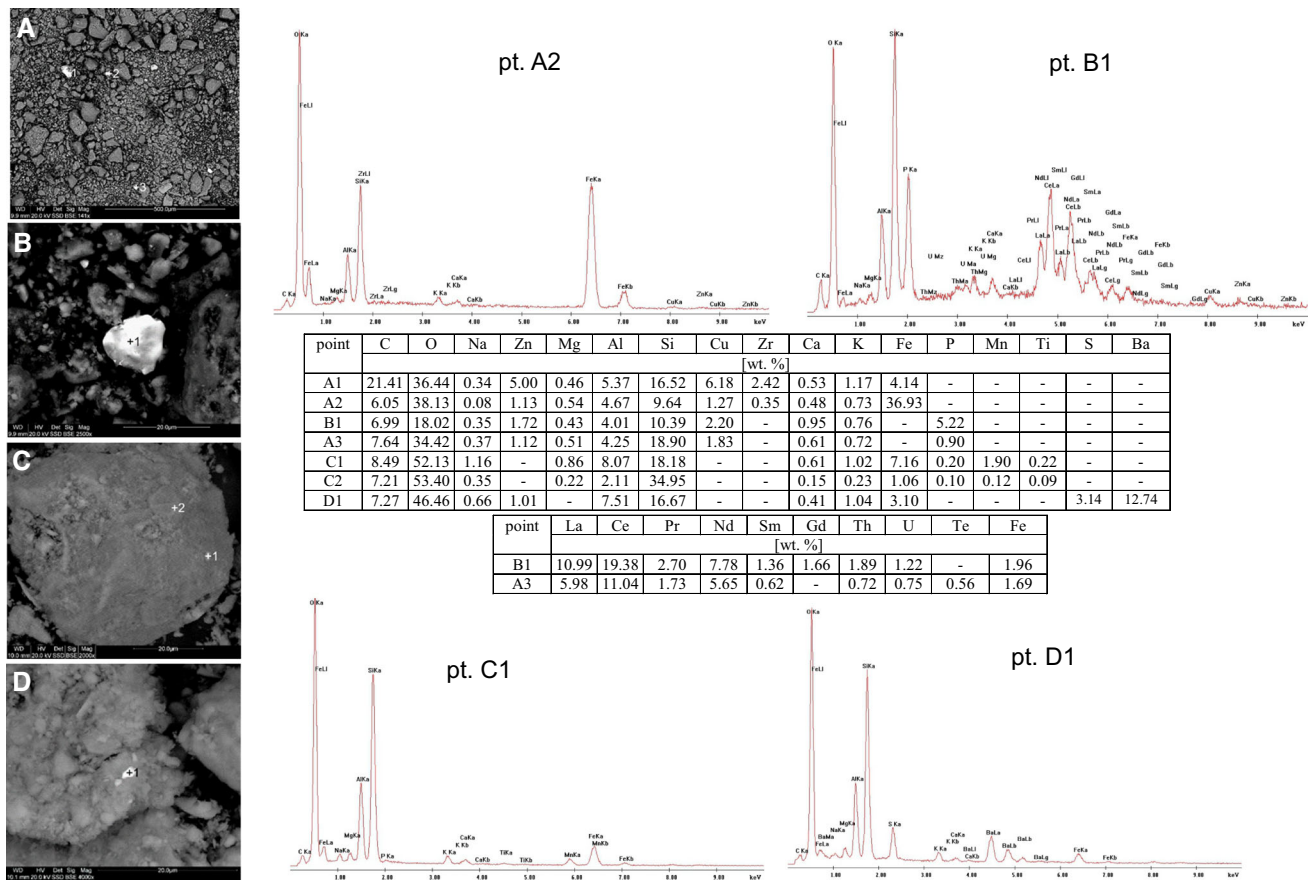
### 3.2.2 Fractions F<63 of the sands

Considering all the F<63 samples, the metal quantities range as follows: As 2.92–9.51 mg/kg, Cd 0.19–3.55 mg/kg, Co 5.12–20.85, Cr 39.46–119.84, Cu 45.97–188.89 and Ni 31.18–85.22 mg/kg (Table 2). The highest values were

determined in the case of Pb and Zn, 39–342 and 126–1198 mg/kg, respectively.

The results were compared with the upper limits in force in the Polish legal regulations referring to the Polish land classification (Minister 2002, Ministerie 2000; Alexander 2006). If the areas of seven spas investigated here were included into the **group A** (i.e., protected areas), the contents of three elements in all the samples (100%) exceed the permissible limits (Minister 2002): Cu—of 30 mg/kg, Pb—of 50 mg/kg and Zn—of 100 mg/kg. In 86% and 91% of the samples the results exceed the upper legal limits of Cr—50 mg/kg and Ni—35 mg/kg, respectively. In the case of Cd, 18% of the samples exceed the upper limit of 1 mg/kg, and in the case of Co only 9% of the samples exceeds the limit of 20 mg/kg. In the case of As, none of the samples exceeds the limit of 20 mg/kg. If the spa areas belonged to the **group B** (i.e., areas other than the protected and industrial ones), more samples would have higher limits. In the case of As, Cd, Cr and Ni, the upper element contents 20, 4, 150 and 100 mg/kg (Minister 2002), respectively, are not exceeded in all the samples (100%). In the case of Co and Cu only 9% of the samples do not meet legal requirements of 20 and 150 mg/kg,





**Fig. 5** SEM images and EDS spectra of sand samples  $F < 63 \mu\text{m}$  collected in Swoszowice (**a**, **b**) and in Szczawnica (**c**, **d**) “–” not identified

respectively, whereas in the case of Zn 23% of the samples exceed a limit of 300 mg/kg. The highest number of samples, 46%, exceed the upper limit of Pb—100 mg/kg.

In the Dutch regulations (Ministerie 2000), the standards for Cd and Co are much more restrictive and for Cr, Pb and Zn slightly less restrictive than in Poland, while for As, Cu and Ni are almost the same, if considering the areas belonging to the Polish group A. Comparing the spa contents of the finest fraction (Table 2) none of the samples exceeds the Dutch limit of As, 14% exceeds this limit of Cr, 32% of Cd, 64% of Pb, 86% of Ni, 91% of Co, 95% of Zn and 100% of Cu.

Assessing the spa samples according to the Norwegian standards (Alexander 2006), none of the samples exceeds their upper limits of As, Cd and Ni, while all the samples contain more Cr than the upper limit of 5 mg/kg. In the case of Pb, almost half of the samples (46%) contains more than its limit of 100 mg/kg. For the three remaining elements, i.e., Co, Cu and Zn, there are no standards in Norway.

Analysing the distribution of the elements within the spas, the highest quantities of Cd, Cr, Cu, Ni, Pb and Zn are

in Swoszowice, located adjacent to the Cracow agglomeration of almost 1 million inhabitants (Fig. 1). The lowest quantities of Cd, Cu, Pb and Zn occur in samples from Muszyna, a spa without any industry, while the lowest quantities of As, Co and Ni in Rabka. The samples lowest in Cu were collected in Krynica, but on the other hand this spa has the highest sample content of As.

Correlation coefficients ( $r^2$ , for  $p = 0.05$ ) of the metals contained in the finest fraction  $F_{<63}$  are highly correlated ( $0.5 \leq r^2 < 0.7$ ) in the case of three pairs: Co/Cr, Cu/Ni and Pb/Zn (Table 3). A very strong correlation ( $0.7 \leq r^2 < 0.9$ ) show Cr/Cu, Co/Ni and Cd/Zn, while almost fully correlated ( $0.9 \leq r^2 < 1$ ) is the pair Cr/Ni. Very close to these figures are the data of Ajmone-Marsan et al. (2008) for 500 soil samples from five European towns. The Pearson correlation coefficients for Ni/Cr concentrations was 0.92, and for Zn/Pb the  $r^2$  value was 0.66. The calculations of the Polish spa values and the comparison of the results above indicate that the road traffic contaminations resulting from the fuel combustion and common wearing away of vehicle parts are main



**Table 2** Average content (Av.) and standard deviation (SD) of elements (metals and a metalloid) in sand fractions < 2000 and < 63 μm collected from sandboxes in health-resorts

Parameters	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	
									[mg/kg]
CRM	reference values	98 ± 5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5	9.9 ± 0.5
	measured values (AO%)	92.88 (94.8)	9.53 (96.3)	9.82 (99.2)	10.16 (102.7)	9.64 (97.2)	10.16 (103.7)	10.07 (101.7)	102.6 (103.6)
	LOD	0.0358	0.0013	0.0008	0.0039	0.0015	0.0064	0.0323	0.0473
	LOQ	0.1552	0.0055	0.0036	0.0139	0.0064	0.0216	0.1198	0.2053
Site	fraction								
	n								
	[μm]								
Szczawnica	<2000	1.50 ± 0.44	0.04 ± 0.01	0.74 ± 0.07	4.19 ± 0.15	1.67 ± 0.14	3.09 ± 0.38	1.52 ± 0.77	12.04 ± 3.90
	<63	7.03 ± 1.31	0.52 ± 0.09	12.83 ± 1.41	76.81 ± 17.04	95.28 ± 5.61	52.46 ± 10.94	78.46 ± 14.01	224.6 ± 34.34
Rabka	<2000	2.15 ± 0.94	0.09 ± 0.04	0.52 ± 0.32	3.41 ± 1.02	1.34 ± 0.30	2.56 ± 1.11	1.63 ± 0.18	12.01 ± 1.94
	<63	5.29 ± 1.48	1.49 ± 0.51	9.02 ± 3.20	57.79 ± 1.80	85.81 ± 27.66	36.47 ± 2.21	150.47 ± 59.29	316.0 ± 48.47
Krynica	<2000	1.48 ± 0.13	0.11 ± 0.06	0.94 ± 0.45	4.21 ± 0.92	1.58 ± 0.43	3.56 ± 1.52	2.78 ± 1.53	14.72 ± 3.95
	<63	8.25 ± 1.63	0.64 ± 0.17	12.80 ± 1.74	46.64 ± 3.18	74.62 ± 10.17	37.48 ± 3.30	178.03 ± 56.49	376.5 ± 159.59
Muszyzna	<2000	1.24 ± 0.13	0.02 ± 0.01	1.00 ± 0.09	5.08 ± 0.40	1.59 ± 0.16	3.89 ± 0.33	1.29 ± 0.24	8.63 ± 1.05
	<63	5.73 ± 2.04	0.33 ± 0.12	12.34 ± 2.35	59.43 ± 22.40	71.82 ± 21.32	44.27 ± 12.62	71.86 ± 11.71	162.7 ± 15.88
Piwniczna	<2000	0.36 ± 0.16	0.02 ± 0.01	1.16 ± 0.37	5.11 ± 0.32	2.21 ± 0.03	4.47 ± 0.91	1.52 ± 0.84	9.85 ± 0.34
	<63	7.82 ± 0.92	0.62 ± 0.22	17.53 ± 2.67	96.72 ± 12.63	127.10 ± 40.46	70.64 ± 7.34	160.78 ± 104.46	193.4 ± 11.86
Wysowa	<2000	0.91 ± 0.14	0.04 ± 0.03	1.16 ± 0.43	5.14 ± 0.88	1.72 ± 0.27	4.19 ± 0.89	1.60 ± 0.75	10.65 ± 2.93
	<63	7.72 ± 1.61	0.48 ± 0.15	17.88 ± 2.21	89.02 ± 12.51	80.98 ± 21.77	69.44 ± 6.48	91.52 ± 55.14	191.9 ± 46.72
Swoszowice	<2000	2.56 ± 1.04	0.12 ± 0.01	0.59 ± 0.02	3.27 ± 0.02	0.65 ± 0.09	2.33 ± 0.04	4.01 ± 1.49	26.56 ± 11.36
	<63	7.25 ± 0.58	2.60 ± 0.95	14.72 ± 2.62	102.11 ± 17.74	164.24 ± 22.80	70.66 ± 14.56	234.82 ± 107.47	759.0 ± 438.86
<b>for all destination</b>									
min. <sup>1</sup>	88	0.20	0.01	0.21	2.40	0.56	1.46	0.68	7.59
max.		3.60	0.18	1.59	6.02	2.24	5.37	5.50	37.92
Av.		1.46	0.06	0.87	4.34	1.54	3.44	2.05	13.50
SD		0.89	0.05	0.39	0.98	0.50	1.16	1.33	7.51
V		0.61	0.83	0.44	0.23	0.32	0.34	0.65	0.56
min.	88	2.92	0.19	5.12	39.46	45.97	31.18	39.11	126.31
max.		9.51	3.55	20.85	119.84	188.89	85.22	342.30	1197.89
Av.		6.98	0.84	13.93	74.53	97.01	54.02	131.62	284.98
SD		1.81	0.76	3.78	24.19	37.77	16.94	84.46	222.39
V		0.26	0.90	0.27	0.32	0.39	0.31	0.64	0.78
Upper limit		<sup>2</sup> A	20 (0%)	20 (9%)	50 (86%)	30 (100%)	35 (91%)	50 (100%)	100 (100%)
(% of samples F<63		<sup>2</sup> B	20 (0%)	20 (9%)	150 (9%)	150 (9%)	100 (0%)	100 (46%)	300 (23%)
above limit)		<sup>3</sup> DT	29 (0%)	9 (91%)	100 (14%)	36 (100%)	35 (86%)	85 (64%)	140 (95%)
		<sup>4</sup> NC	20 (0%)	-	5 (100%)	-	135 (0%)	100 (46%)	-

LOD limit of detection, LOQ limits of quantification, AO analysis trueness (%)

<sup>1</sup>Data from Kicińska et al. (2017), n number of samples, min. minimum, max. maximum, Av. arithmetic average, SD standard deviation, V coefficient of variation, calculated as the ratio SD to Av

<sup>2</sup>According to Minister (2002) for < 2 mm fraction, A protecting areas, B other than protecting and industry areas, CRM certified research material

<sup>3</sup>DT—Dutch Target and Intervention values for earth/sediment ([www.esdat.net/2000](http://www.esdat.net/2000))

<sup>4</sup>NC—Norway quality criteria for soil day-care centres, playgrounds and schools (Alexander 2006)

<sup>5</sup>For Cr<sup>6+</sup>

**Table 3** Correlation coefficients ( $r_{xy}$ ) calculated for the total content of metals in sand fraction < 63 $\mu$ m

Element	Cd	Co	Cr	Cu	Ni	Pb	Zn
As	– 0.06	0.29	0.44*	0.37	0.45*	0.46*	0.19
Cd	–	– 0.03	0.28	0.46*	0.21	0.47*	<b>0.85***</b>
Co		–	<b>0.61**</b>	0.33	<b>0.80***</b>	0.14	0.03
Cr			–	<b>0.75***</b>	<b>0.95***</b>	0.34	0.24
Cu				–	<b>0.66***</b>	<b>0.74***</b>	0.49*
Ni					–	0.28	0.21
Pb						–	<b>0.64**</b>
Zn							–

Bold: high correlation ( $0.5 \leq r < 0.7$ ); Bold italic: very high correlation ( $0.7 \leq r < 0.9$ ); Bold with underline: almost full correlation ( $0.9 \leq r < 1$ )

Statistically significant at: \*  $p < 0.05$ ; \*\*  $p < 0.01$ ; \*\*\*  $p < 0.001$

sources of the metals mentioned that form the correlated pairs.

The quantities of metals, As including, in the fractions  $F_{<63}$  are very close to the data of De Miguel et al. (2007) for the parks in Madrid but only in the case of As, whose soil and airborne dust contents of the urban parks ranged 3.7–16 mg/kg (6.9 mg/kg on the average) in 2003. In the case of Cd, Cu, Pb and Zn, the spa sample contents are 3–4 times lower than the figures for Madrid (op. cit.). A reason of such a difference may be caused by various fractions of the material studied: the Spanish data were obtained for the grain fractions < 100  $\mu$ m.

### 3.3 Distribution of metals throughout the grain fractions

The comparisons of the metal quantities in the bulk samples ( $F_{<2000}$ ) to those in the finest grain fractions  $F_{<63}$  reveal significant differences (Fig. 6). The mean element contents of the bulk material for all the samples are: As 1.46, Cd 0.06, Co 0.87, Cr 4.34, Cu 1.54, Ni 3.44, Pb 2.05 and Zn 13.50 mg/kg, whereas the respective values for the finest fractions are: As 6.98, Cd 0.84, Co 13.93, Cr 74.53, Cu 97.01, Ni 54.02, Pb 131.62 and Zn 284.98 mg/kg. The Student's  $t$  test (assuming  $p = 0.05$ ) applied for both sets reveals significant differences of the quasi-total contents of all the elements between  $F_{<2000}$  and  $F_{<63}$  (Fig. 7).

The samples of finest material contain significantly higher quantities of metals than the bulk samples. The most differ the values of Cu and Pb whose quantities are 63 times higher. The ranking list is followed by Zn with the 21-time difference; Cr, Ni and Co—the differences are around 16 times; Cd 13 times, while As—the lowest one barely reaching 5 times. Guney et al. (2010) also report significant differences in the quantity of elements in the material collected in the parks of Istanbul. The samples richest in the clay fraction (they contribute 22–26% to the bulk samples with grains < 2 mm) revealed the highest Cr

contents (up to 186 mg/kg), Cu (up to 230 mg/kg) and Zn (up to 182 mg/kg), while the averages of the bulk samples 45.8, 59.8 and 53.0 mg/kg, respectively.

In the case of the remaining grain fractions from the Polish spas ( $F_{2000-1000}$ ,  $F_{1000-200}$ ,  $F_{200-63}$ ), their differences related to the bulk samples were higher but weaker expressed than those in the finest fraction  $F_{<63}$ . The quantities of the elements have been recalculated into their contributions (Table 4) and ranked in the decreasing order:

- for As and Cd :  $F_{<63} \gg F_{2000-1000} > F_{1000-200} > F_{200-63}$ ,
- for Co, Cu and Ni :  $F_{<63} \gg F_{2000-1000} \cong F_{200-63} > F_{1000-200}$ ,
- for Cr, Pb and Zn :  $F_{<63} \gg F_{200-63} \cong F_{2000-1000} > F_{1000-200}$ .

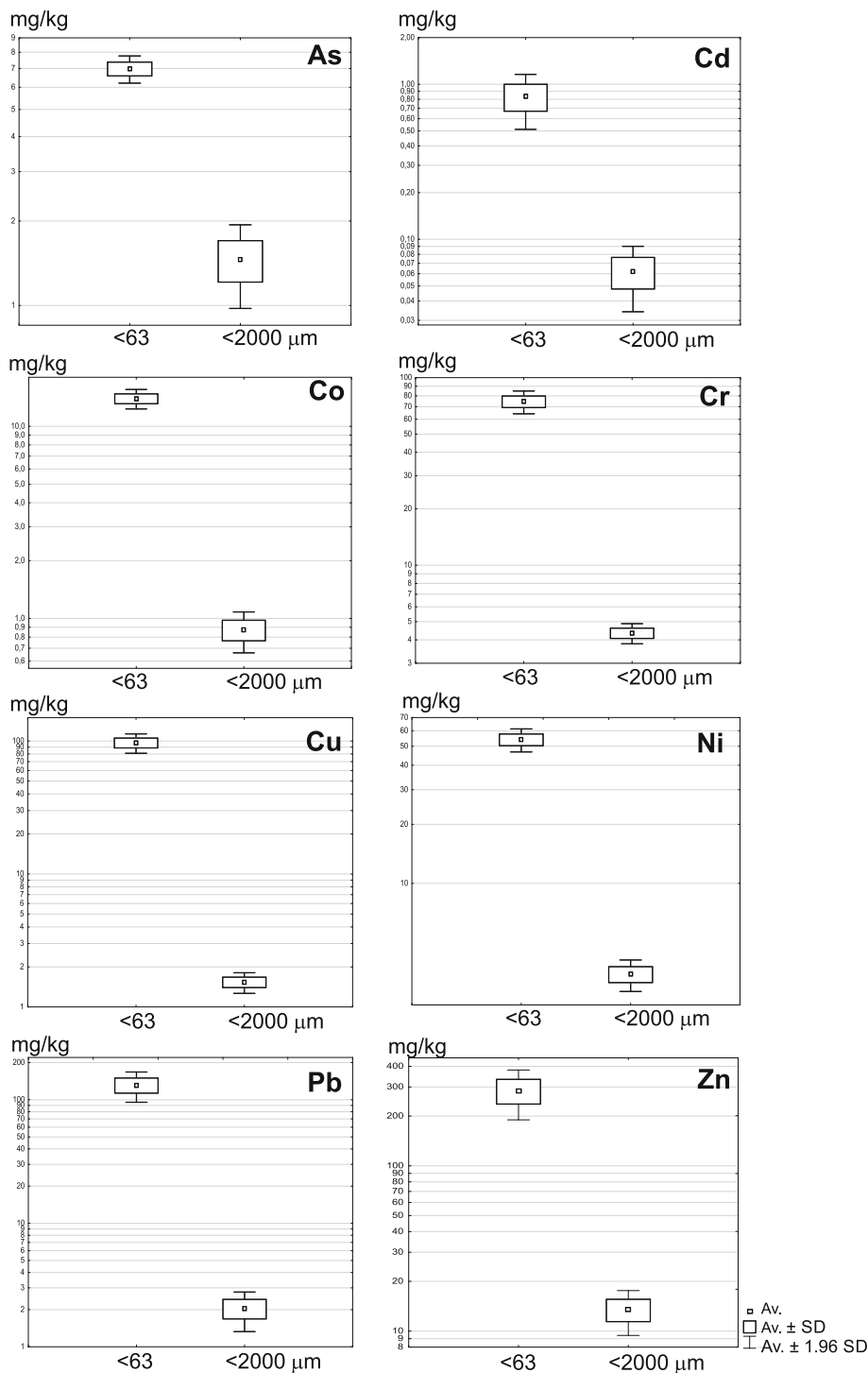
In the fraction  $F_{<63}$ , considerably higher metal contributions range from 57.3% for As to even 96.4% for Pb. Considering only these two elements (As and Pb), the remaining ranges are: from 1.5% Pb to 8.9% As in the fraction  $F_{200-63}$ , from 0.9% Pb to 12.5% As in the fraction  $F_{1000-200}$ , and from 1.3% Pb to 21.3% As in the fraction  $F_{2000-1000}$ .

The diagram of the metal contributions in the most polluted samples (Piwniczna P2, Wysowa W3, Fig. 8a, b) and of the mean metal contributions in all the grain fractions of all the samples (Fig. 8c) univocally indicates that most of the elements are accumulated in the finest fraction ( $F_{<63}$ ): they concentrate 89% As, 93–95% Cd, Co, Cr, Ni and Zn, and 98.4% Cu and Pb contained in the bulk samples (< 2 mm).

This tendency is even better expressed after calculating the distribution factor ( $DF$ ) as the quotient “fraction content to bulk content” (Eq. 6). The highest are the  $DF$  values of the fraction  $F_{<63}$  and equal to (in the decreasing rank of elements): Pb 11.71, Cu 11.19, Cr 8.41, Co 8.08, Ni 8.06, Zn 7.18, Cd 4.64 and As 4.09 (Table 5). The metal enrichment of the finest fractions is significant, above four



**Fig. 7** Scatters of elements content in sand samples in fractions  $F < 2000$  and  $F < 63 \mu\text{m}$  *Av* average, *SD* standard deviation



times, and the accumulation sequence of the  $F_{<63}$  is as follows:

$$Pb = Cu > Cr \cong Co = Ni \cong Zn \gg Cd = As$$

Considering the remaining fractions and elements, it is only a single fraction  $F_{2000-1000}$  with the *DF* index 1.52 for As that is a single enriched element.

### 3.4 Health risk for children

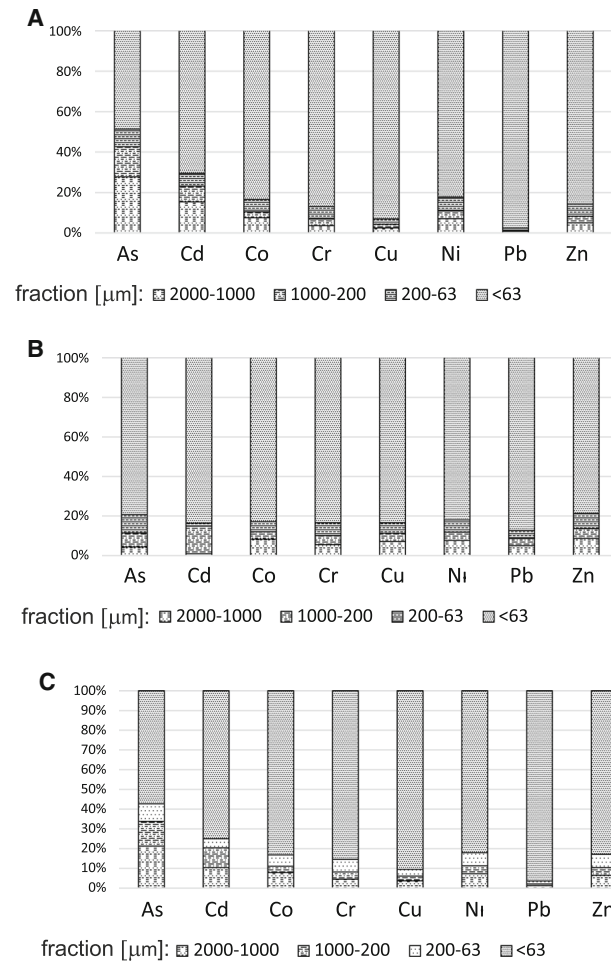
In the calculations of the health risk indexes, the finest fractions  $F_{<63}$  that concentrate the highest quantities of elements and represent the most serious health threat. The time that children spent in the spa resorts playing in the open (*EF*) is also an important factor to be considered. Two



**Table 4** Contributions of elements to separated sand fraction for all spa-resort

Fraction (μm)	Parameter	As (%)	Cd	Co	Cr	Cu	Ni	Pb	Zn
2000–1000	min.–max.	4–28	1–15	7–8	4–6	3–7	7–8	1–5	5–9
	Av.	21.3	10.4	7.9	4.5	3.7	7.3	1.3	6.5
1000–200	min.–max.	7–15	8–14	3–4	3–5	2–4	3–4	1–4	3–5
	Av.	12.5	10.0	3.2	3.8	2.4	3.9	0.9	3.9
200–63	min.–max.	8–9	2–6	5–6	7–8	3–5	6–7	1–4	6–8
	Av.	8.9	4.6	5.7	6.4	3.4	6.6	1.5	6.7
< 63	min.–max.	<b>49–79</b>	<b>70–84</b>	<b>83–84</b>	<b>83–87</b>	<b>83–93</b>	<b>80–84</b>	<b>87–98</b>	<b>79–86</b>
	Av.	<b>57.3</b>	<b>75.0</b>	<b>83.2</b>	<b>85.4</b>	<b>90.5</b>	<b>82.1</b>	<b>96.4</b>	<b>82.9</b>

Bolded share > 50%



**Fig. 8** Content of elements in separated sand fractions. **a** Piwniczna (P2), **b** Wysowa (W3) and **c** all samples ( $n = 88$ ) averaged

groups of children have been distinguished, i.e., residents (permanent stay), for which the  $EF = 688$  h per year [365–21(holidays) = 344 days × 2 h spent daily in the open], and visitors, for which the  $EF = 84$  h per year (21 days × 4 h spent daily in the open). Then, the values of the  $D_{ing}$ ,  $D_{inh}$  and  $D_{dermal}$  calculated from the Eqs. (3–5)

**Table 5** Distribution factor ( $DF$ ) of elements in separated sand fractions for all sampling sites

Fraction (μm)	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
2000–1000	<b>1.52</b>	0.03	0.77	0.44	0.46	0.72	0.16	0.56
1000–200	0.89	0.62	0.31	0.37	0.30	0.39	0.11	0.34
200–63	0.64	0.29	0.55	0.63	0.42	0.65	0.18	0.58
< 63	<b>4.09</b>	<b>4.64</b>	<b>8.08</b>	<b>8.41</b>	<b>11.19</b>	<b>8.06</b>	<b>11.71</b>	<b>7.18</b>

Bolded  $DF > 1$ —the metal/metalloid enriched in this fraction

were divided by the respective values of the RfD (US EPA 1986), and the  $HQ_{ing}$ ,  $HQ_{inh}$  oraz  $HQ_{dermal}$  established for the children-residents permanently staying in the spa resorts (Table 6) and the children-visitors (Table 7).

For the children 3 and 6 years old being **spa residents**, the total health indexes  $HI$  resulting from the exposure to the non-carcinogenic substances are  $1.26E+00$  and  $9.41E-01$ , respectively. The  $HI$  value exceeds the unity for the 3-year olds, which means that there is a probability of appearing negative health effects. These children are endangered mainly by three metals: Pb ( $HQ_i = 4.79E-01$ ), Cr ( $HQ_i = 3.43E-01$ ) and As ( $HQ_i = 3.34E-01$ ), whereas the  $HQ_i$  values of the remaining elements are considerably lower and decrease in the sequence: Ni > Cu > Cd > Zn > Co. In the case of the 6-year olds, the total indexes of the of health exposure to the non-carcinogenic substances  $HI$  are below the unity ( $9.41E-01$ ), although quite close to it. The differences between the two age groups are caused by the higher body mass of the elder children. The sequence of the endangering elements is the same as before: Pb > Cr > As > Ni > Cu > Cd > Zn > Co (Table 6).

The *Risk* index shows the health impacts of carcinogenic substances. For the 3-year olds it is  $6.48E-06$ , while for the 6-year olds slightly is higher— $9.72E-06$ . The highest negative health contribution for both age groups (99.51%) is caused by the As-cancer. In comparison with arsenic, the

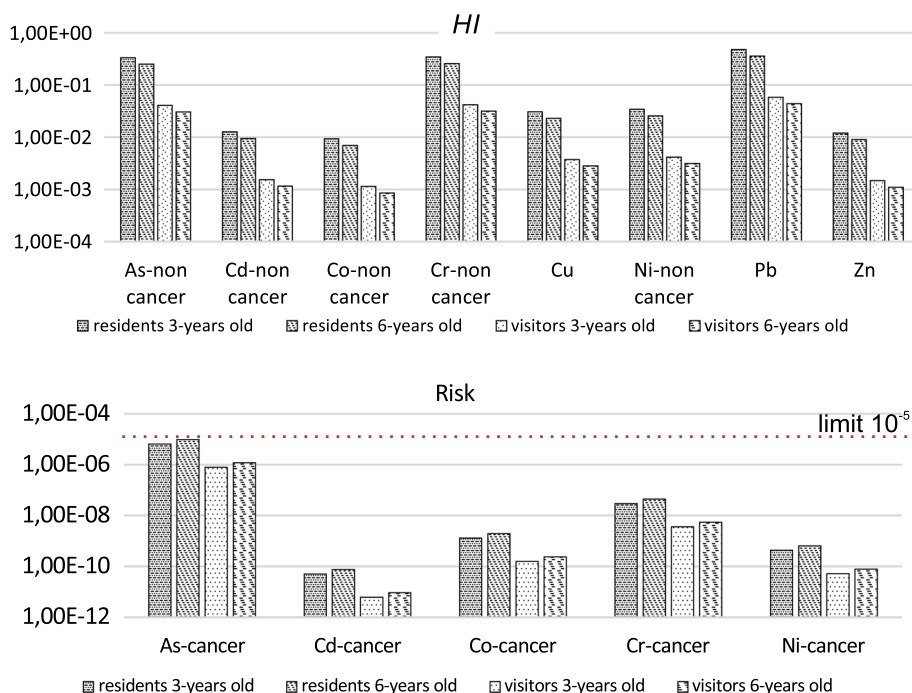
**Table 6** Hazard quotient ( $HQ_i$ ) and  $Risk$  calculated for 3 and 6 years old spa residents

Element	3 years old children						6 years old children					
	inhal		dermal		ing		inhal		dermal		ing	
	RfD (mg/kg day <sup>-1</sup> )	$HQ_i$	$HQ_{dermal}$	$HQ_{inh}$	$HQ_{ing}$	$\sum HQ_i$	$Risk$	$HQ_{dermal}$	$HQ_{inh}$	$HQ_{ing}$	$\sum HQ_i$	$Risk$
As-non cancer	3.00E-04	3.00E-04	1.23E-04	5.16E-06	2.92E-01	3.34E-01	6.45E-06	4.19E-02	3.87E-06	2.19E-01	2.51E-01	9.67E-06
As-cancer	1.50E+00	1.50E+01	3.66E+00	9.95E-10	5.64E-06	8.09E-07	5.03E-11	8.09E-07	1.49E-09	8.46E-06	9.47E-03	9.67E-06
Cd-non cancer	1.00E-03	1.00E-03	1.00E-05	1.86E-07	1.06E-02	1.26E-02	5.03E-11	2.07E-03	1.40E-07	7.92E-03	9.47E-03	7.54E-11
Cd-cancer	2.00E-02	5.71E-06	1.60E-02	5.41E-04	8.75E-03	9.31E-03	5.03E-11	2.14E-05	4.06E-04	6.56E-03	6.99E-03	7.54E-11
Co-non cancer	3.00E-03	2.86E-05	6.00E-05	5.78E-04	3.12E-01	3.43E-01	1.30E-09	3.06E-02	1.95E-09	2.34E-01	2.58E-01	1.95E-09
Co-cancer	4.00E-02	4.00E-02	1.20E-02	5.38E-07	3.05E-02	3.07E-02	2.97E-08	1.99E-04	4.46E-08	2.29E-02	2.30E-02	4.46E-08
Cu	2.00E-02	2.00E-02	5.40E-03	5.99E-07	3.39E-02	3.42E-02	4.31E-10	2.46E-04	4.49E-07	2.55E-02	2.56E-02	6.47E-10
Ni-non cancer	3.50E-03	3.50E-03	5.25E-04	8.34E-06	4.73E-01	4.79E-01	4.31E-10	6.17E-03	6.25E-06	3.54E-01	3.59E-01	6.47E-10
Ni-cancer	3.00E-01	3.00E-01	6.00E-02	2.11E-07	1.19E-02	1.21E-02	4.31E-10	1.17E-04	1.58E-03	8.95E-03	9.04E-03	6.47E-10
Pb	3.00E-01	3.00E-01	6.00E-02	1.13E-03	1.17E+00	1.26E+00	6.48E-06	8.14E-02	8.50E-04	8.80E-01	9.41E-01	9.72E-06
Zn	3.00E-01	3.00E-01	6.00E-02	1.13E-03	1.17E+00	1.26E+00	6.48E-06	8.14E-02	8.50E-04	8.80E-01	9.41E-01	9.72E-06
$\sum$												

**Table 7** Hazard quotient ( $HQ_i$ ) and *Risk* calculated for 3 and 6 years old spa visitors

Element	3 years old children				6 years old children				
	ing	inhal	dermal	$RFD (mg/kg day^{-1})$	$HQ_{ing}$	$HQ_{inh}$	$HQ_{dermal}$	$\sum HQ_i$	<i>Risk</i>
As-non cancer	3.00E-04	3.00E-04	1.23E-04	3.57E-02	6.30E-07	6.30E-07	5.12E-03	4.08E-02	7.87E-07
As-cancer	1.50E+00	1.50E+01	3.66E+00	6.88E-07	1.21E-10	1.21E-10	9.88E-08	1.54E-03	6.14E-12
Cd-non cancer	1.00E-03	1.00E-03	1.00E-05	1.29E-03	2.27E-08	2.27E-08	2.53E-04	1.14E-03	1.58E-10
Cd-cancer	6.30E+00	6.30E+00	6.30E+00	6.61E-05	6.61E-05	6.61E-05	2.62E-06	4.19E-02	3.63E-09
Co-non cancer	2.00E-02	5.71E-06	1.60E-02	1.07E-03	1.58E-10	1.58E-10	3.74E-03	3.75E-03	5.27E-11
Co-cancer	3.00E-03	2.86E-05	6.00E-05	3.81E-02	7.06E-05	7.06E-05	3.01E-05	4.17E-03	7.91E-07
Cr-non cancer	4.00E-02	4.00E-02	1.20E-02	3.72E-03	6.57E-08	6.57E-08	2.43E-05	5.85E-02	1.07E-05
Cr-cancer	2.00E-02	2.00E-02	5.40E-03	4.14E-03	7.31E-08	7.31E-08	3.01E-05	1.47E-03	1.07E-05
Ni-non cancer	3.50E-03	3.50E-03	5.25E-04	5.77E-02	1.02E-06	1.02E-06	7.54E-04	1.53E-01	7.91E-07
Ni-cancer	3.00E-01	3.00E-01	6.00E-02	1.46E-03	2.57E-08	2.57E-08	1.43E-05	1.47E-03	1.07E-05
Pb	3.00E-01	3.00E-01	6.00E-02	1.43E-01	1.38E-04	1.38E-04	9.93E-03	1.53E-01	7.91E-07
Zn									
$\sum$									

**Fig. 9** *HI* and *Risk* values calculated for 3 and 6 years old children for cancer and non-cancer elements—sand fraction  $F < 63 \mu\text{m}$



contributions of other three cancer-metals are almost insignificant: Cr—0.46%, Co—0.02% and Ni—< 0.01%). The impact of As caused by swallowing “dirt” (ingestion path) is the highest: above 87% As enter the organisms in this way; along the dermal paths enters 12.5%, whereas along the inhalation path only 0.01% As.

For the second group distinguished, i.e., short-term **visitors**, the total indexes *HI* of the health exposure to the non-carcinogenic substances are  $1.53\text{E}-01$  and  $1.15\text{E}-01$  for the children 3 and 6 years old, respectively. The *HI* values below the unity indicate that the health risk resulting from the elements considered in the environment does not exist. The partial  $HQ_i$  indexes for both age groups are given in Table 7: their values decrease in the order:  $\text{Pb} > \text{Cr} > \text{As} > \text{Ni} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Co}$ .

The *Risk* indexes for visitors 3 and 6 years old are  $7.91\text{E}-07$  and  $1.19\text{E}-06$ , respectively. These are values lower than those for residents. The upper permissible limit  $10\text{E}-05$  has not been exceeded, which is a satisfactory find of the study (Fig. 9).

For both distinguished groups of children, residents and visitors of the spas, several significant dependencies results been established.

In the case of the carcinogenic substances, they are as follows:

- (1) There is no health risk caused by the presence of the carcinogenic forms of As, Cd, Co, Cr, Cu, Ni, Pb and Zn for children 3 and 6 years old playing in the spa sandboxes. For both groups the total indexes *Risk* do not exceed the value  $10\text{E}-05$ .

- (2) The by far highest contribution to the total *Risk* results from the As-cancer, which makes up 99.5% of the *Risk* value. The As-cancer enters children organisms mostly via the ingestion path (87.4%), considerably less via the dermal path (12.5%), and negligibly via the inhalation one (around 0.01%).
- (3) In the case of the remaining metals, their total indexes *Risk* are lower than 0.5%, and they enter young organisms mainly via the inhalation path.

In the case of the non-carcinogenic forms, they are as follows

- (1) The health risk index *HI* with the value above the unity ( $1.26\text{E}+00$ ) for children 3 and less years old is alarming. The *HI* is below the limit of 1 ( $9.41\text{E}-01$ ) for the 6-year olds.
- (2) The highest health threat in the case of non-carcinogenic substances is caused by Pb (38%), Cr (27%) and As (27%). The partial indexes  $HQ_i$  calculated for Ni, Cu, Cd, Zn and Co are considerably lower than those for Pb: their total contribution to the total *HI* is only 8% (Fig. 9).
- (3) The highest health threat results from the elements entering along the ingestion path ( $HQ_{ing}$ ), which contributes from 87.5% (for the As-non cancer) to over 99.3% (for Ni-non cancer) to the total metal indexes *HI* of the both age groups of children. The other two access paths are of much lower threats: the dermal path contributes from 0.2% (for the Co-non cancer) to 16.4% (for the Cd-non cancer). The



contribution in the case of the inhaling path is low: from  $< 0.002\%$  (for As, Cd, Cu, Ni, Pb, Zn) to almost  $6\%$  (Co).

### 3.5 Discussion

The considerations on the values of the indexes *HI* and *Risk* focused on the bulk grain fractions and the finest fractions. The former (bulk) contain the material  $< 2$  mm and give the chemical basis of the study, while the latter contain the material  $< 63 \mu\text{m}$  which sticks best to the hands of children and its probability to be swallowed is much higher than that of coarser grain fractions (Ljung et al. 2006, Acosta et al. 2009). The finest fractions also become easily airborne and inhaled by children when playing: Ajmone-Marsan et al. (2008) identified the fractions  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  separated from soils as a potential source of PTE (potentially toxic elements): Cr, Ni, Cu, Pb and Zn.

Considering the deliberate ingestion of soil (so-called *pica behaviour*), a daily soil intake is considerably higher and may reach even 10 g (Ljung et al. 2006). After substituting this value into the equations for *HI* and *Risk*, the values of both the indexes are also much higher. For both age groups the values of the *HI* non-cancer are higher than the unity. For the 3 and 6 years old spa resident these values are  $1.10\text{E}+02$  and  $8.26\text{E}+01$ , respectively, while for the spa visitors  $1.43\text{E}+01$  and  $1.07\text{E}+01$ , respectively. The *Risk* values in two age groups (3 and 6-years old) are  $5.30\text{E}-04$  and  $7.95\text{E}-04$  for residents while  $6.89\text{E}-05$  and  $1.03\text{E}-04$  for visitors, and exceed a permissible limit of  $10\text{E}-05$ . Therefore, the children with the *pica* behaviour are at health risk considering the elements considered in the paper.

The indexes *HI* and *Risk* calculated on the basis of the quasi-total contents of the metals determined in the bulk samples ( $F_{<2000}$ ) and in the fractions  $F_{<63}$  are presented in Table 8. Their comparison indicate the following.

- The indexes *HI* and *Risk* calculated for bulk samples ( $F_{<2000}$ ) are considerably lower than those for the finest fractions ( $F_{<63}$ ).
- In the case of the non-cancer metals, the highest *HI* values (the figures are quotients expressing  $F_{<63}$  to  $F_{<2000}$  ratios; their pairs refer to children-residents and children-visitors, respectively) are for Pb (64 and 68, respectively) and Cu (67 and 63); around 3–3.5 times lower for Zn (23 and 21), Cr (18 and 17), Ni and Co (17 and 16), Cd (15 and 14); whereas for As they are the same (5 and 5). The differences of the indexes *HI* in the case of 3- and 6-year olds are insignificant.
- In the case of the cancer-metals, the *Risk* values (the figures are quotients expressing  $F_{<63}$ : $F_{<2000}$  ratios; their pairs refer to children-residents and children-visitors,

respectively) are exactly the same as those cited above for the non-cancer metals: Cr (18 and 17, respectively), Ni and Co (17 and 16), Cd (15 and 14) and As (5 and 5).

- Higher differences (for Cu and Pb equal to 4, for the remaining metals equal to around 1) occur in the case of children-residents. This is a result of their longer time of staying in the spas (factor *EF*) accepted in calculations.
- For children-visitors the differences of the indexes *HI* and *Risk* of specific grain fractions are the same as the differences of the quasi-totals of the metals in the fractions (Fig. 9). It is a mathematical result of the equations used.

Comparing the health risk assessments to those presented by other authors is difficult because of the differences in the material used in the determinations (bulk samples, fraction diameters) and various methods of sample decomposition (Table 9). These two methodical steps are major reasons of obtaining differing conclusions. However, there are some similarities of the results presented here to those obtained for the urban parks of Madrid (De Miguel et al. 2007) and Nanjing Wang et al. (2016). They refer mainly to the threats caused by the presence of As, Cr and Zn. Since Wang et al. (op.cit.) also analysed grain fractions  $< 63 \mu\text{m}$ , their results for As, Cd, Cu, Co, Ni and Pb very close to ours.

Lower health risk was found in the urban parks of Istanbul (Guney et al. 2010) in the case of As, Cu and Zn. It should be mentioned, however, those authors (Guney et al. 2010) analysed coarser material, i.e.,  $< 2$  mm, and in the samples with higher metal quantities also fractions  $< 0.25$  mm. Considering Cd, Cr, Cu and Zn in the parks of Cracow (Jasiewicz et al. 2009), their threat is more serious than in the spas considered.

## 4 Conclusions

The results obtained in our study on park sandboxes of seven Polish spas indicate that analysing materials of various grain sizes (i.e., various fractions) may lead to highly differing conclusions and assessments children's health. Already the stage of taking samples and preparing them to chemical determinations may involve some simplifications, and the analytical data differ, not saying about the calculated indexes that describe the state of the environment and the human health.

The elements considered: As, Cd, Co, Cr, Cu, Ni, Pb and Zn accumulate mainly in the finest of the fractions analysed (i.e.,  $F_{<63}$ ). Although the quantity of the finest fractions in the bulk material  $< 2$  mm is low (for  $n = 88$  samples the

**Table 8** Comparison of *HI* and *Risk* values calculated for the  $F_{<63}$  and for the  $F_{<2000}$  fractions

Elements	HI (non-cancer)				Risk (cancer)				TC (average) (mg/kg)
	Residents		Visitors		Residents		Visitors		
	3 years old	6 years old	3 years old	6 years old	3 years old	6 years old	3 years old	6 years old	
$F_{<63}$									
$F_{<2000}^*$									
As	<u>3.34E-01</u>	<u>2.51E-01</u>	<u>4.08E-02</u>	<u>3.06E-02</u>	<u>6.45E-06</u>	<u>9.67E-06</u>	<u>7.87E-07</u>	<u>1.18E-06</u>	<u>6.98</u>
	6.57E-02	4.92E-02	8.54E-03	6.40E-03	1.27E-06	1.90E-06	1.65E-07	2.47E-07	1.46
Cd	<u>1.26E-02</u>	<u>9.47E-03</u>	<u>1.54E-03</u>	<u>1.16E-03</u>	<u>5.03E-11</u>	<u>7.54E-11</u>	<u>6.14E-12</u>	<u>9.21E-12</u>	<u>0.84</u>
	8.47E-04	6.35E-04	1.10E-04	8.26E-05	3.37E-12	5.06E-12	4.39E-13	6.58E-13	0.06
Co	<u>9.31E-03</u>	<u>6.99E-03</u>	<u>1.14E-03</u>	<u>8.53E-04</u>	<u>1.30E-09</u>	<u>1.95E-09</u>	<u>1.58E-10</u>	<u>2.38E-10</u>	<u>13.93</u>
	5.46E-04	4.10E-04	7.10E-05	5.33E-05	7.61E-11	1.14E-10	9.89E-12	1.48E-11	0.87
Cr	<u>3.43E-01</u>	<u>2.58E-01</u>	<u>4.19E-02</u>	<u>3.14E-02</u>	<u>2.97E-08</u>	<u>4.46E-08</u>	<u>3.63E-09</u>	<u>5.45E-09</u>	<u>74.53</u>
	1.88E-02	1.41E-02	2.44E-03	1.83E-03	1.63E-09	2.44E-09	2.12E-10	3.17E-10	4.34
Cu	<u>3.07E-02</u>	<u>2.30E-02</u>	<u>3.75E-03</u>	<u>2.81E-03</u>					<u>97.01</u>
	4.57E-04	3.43E-04	5.95E-05	4.46E-05					1.54
Ni	<u>3.42E-02</u>	<u>2.56E-02</u>	<u>4.17E-03</u>	<u>3.13E-03</u>	<u>4.31E-10</u>	<u>6.47E-10</u>	<u>5.27E-11</u>	<u>7.90E-11</u>	<u>54.02</u>
	2.04E-03	1.53E-03	2.66E-04	1.99E-04	2.58E-11	3.87E-11	3.35E-12	5.03E-12	3.44
Pb	<u>4.79E-01</u>	<u>3.59E-01</u>	<u>5.85E-02</u>	<u>4.38E-02</u>					<u>131.62</u>
	7.00E-03	5.25E-03	9.10E-04	6.83E-04					2.05
Zn	<u>1.21E-02</u>	<u>9.04E-03</u>	<u>1.47E-03</u>	<u>1.10E-03</u>					<u>284.98</u>
	5.36E-04	4.02E-04	6.97E-05	5.23E-05					13.50
V									
As	5	5	5	5	5	5	5	5	5
Cd	15	15	14	14	15	15	14	14	14
Co	17	17	16	16	17	17	16	16	16
Cr	18	18	17	17	18	18	17	17	17
Cu	67	67	63	63					63
Ni	17	17	16	16	17	17	16	16	16
Pb	68	68	64	64					64
Zn	23	23	21	21					21

\* For  $F_{<2000}$  data from Kicińska et al. (2017), *V* variability coefficient, *HI* and *Risk* values calculated by dividing adequate  $F_{<63}$  and  $F_{<2000}$  values

range is 0.32–3.65 wt% with the average 1.59 wt%), the contribution of metals associated with the minerals present in the  $F_{<63}$  ranges from the lowest 57% of As to the highest 96% of Pb. The metals are fixed mainly by oxy/hydroxides of Fe and Mn, and clay minerals (clinochlore, illite, kaolinite).

Despite that the fractions dominating in the sandy samples has the grain size 1000–200  $\mu\text{m}$ , their metal contributions to the quasi-total (the totals decomposed in *aqua regia*) contents ranged from the lowest 1% Pb to the highest 13% As.

Assessing the state of the environment, none of bulk sandbox samples contains the metals considered above the permitted limits. However, if the finest fractions are considered, their metal contents exceed the limits legally required for soils of the protected areas in 86% of the sand

separates in the case of Cr and Ni, and in all (100%) the separates in the case of Cu, Pb and Zn.

The grain fractions  $< 63$  contain significantly more metals than the bulk samples: from the lowest 5 times for As to the highest 64 times for Pb. As a result, these differences directly and decisively affect the calculated values of the indexes *HI* and *Risk* for children 3 and 6 years old.

The highest values of the health risk index *HI* calculated from the quasi-total metal contents in the fractions  $F_{<63}$  have been determined for the children 3 and 6 years old permanently staying in the spas in the case of Pb (4.79E-01 and 3.59E-01, respectively), Cr (3.43E-01 and 2.58E-01, respectively) and As (3.34E-01 and 2.51E-01, respectively). In the calculations made for the bulk samples  $F_{<2000}$  the indexes *HI* are considerably lower for both age groups. For the spa children-residents of both age groups they are, respectively: 7.00E-03 and 5.25E-03

**Table 9** Comparative HI and Risk values

Site/type of sample	Methods of extraction	Fraction (µm)	BW (kg)	HI										Risk									
				As	Cd	Cr	Cu	Co	Ni	Pb	Zn	As	Cd	Cr	Ni	Co							
Madrid (Spain) <sup>1</sup> / sandy substrate	HCl + HNO <sub>3</sub> + H <sub>2</sub> O (ICP-MS)	< 100	15	1.09E-01	1.09E-03	2.72E-02	1.41E-03	-	9.61E-04	3.11E-04	7.10E-02	7.10E-04	4.19E-06	2.62E-11	1.73E-08	1.37E-09	-						
Istanbul (Turkey) <sup>2</sup> / sandy clayey loam	HNO <sub>3</sub> + HF (ICP-MS)	< 2000 or < 250	18.6	1.4E-02	-	< 0.001	-	-	-	-	< 0.001	4.25E-07	-	-	-	-	-						
Sandy loam																							
Sandy clayey				2.1E-02	-	< 0.001	-	-	-	-	3.0E-03	6.86E-07	-	-	-	-	-						
				4.2E-02	-	< 0.001	-	-	-	-	1.2E-02	1.35E-06	-	-	-	-	-						
Nanjing (China) <sup>3</sup> / urban park dust	HNO <sub>3</sub> + HClO <sub>4</sub> (ICP-MS)	< 63	-	1.84E-01	1.31E-02	7.59E-02	1.05E-02	1.88E-02	1.08E-03	1.54E-01	7.19E-03	9.21E-06	6.12E-06	2.84E-07	4.87E-09	5.69E-09	-						
Health resorts (Poland) <sup>4,5</sup> / sand	HNO <sub>3</sub> + HClO <sub>4</sub> + HCl (ICP-MS)	< 2000 <sup>4</sup>	15	6.57E-02	8.47E-04	1.88E-02	4.57E-04	5.46E-04	2.04E-04	7.00E-03	5.36E-04	1.27E-06	3.37E-12	1.63E-09	2.58E-11	7.61E-11	-						
Krakow (Poland) <sup>6</sup> / sand	HNO <sub>3</sub> + HClO <sub>4</sub> + HCl (ICP-EAS)	< 63 <sup>5</sup>	15	3.34E-01	1.26E-02	3.43E-01	3.07E-02	9.31E-03	3.42E-03	4.79E-01	1.21E-02	6.45E-06	5.03E-11	2.97E-08	4.31E-10	1.30E-09	-						
			15	D absorbed dose [(mg/kg BW *day) <sup>-1</sup> ]																			
				-	2.0E-03	2.0E-03	1.00E-02	-	3.0E-03	1.2E-01	5.3E-01	-	-	-	-	-	-						

<sup>1</sup>De Miguel et al. (2007)

<sup>2</sup>Guney et al. (2010)

<sup>3</sup>Wang et al. (2016)

<sup>4</sup>Kicińska et al. (2017)

<sup>5</sup>this study, data for residents

<sup>6</sup>Jasiewicz et al. (2009), “-” no information, BW body weight

for Pb,  $1.88\text{E}-02$  and  $1.41\text{E}-02$  for Cr and  $6.57\text{E}-02$  and  $4.92\text{E}-02$  for As. The metals considered in the case of non-cancer elements penetrate children's organisms mainly via the digestive path (average 93.4% for all the elements), occasionally via the dermal path (average 6.5%), and almost negligibly via the inhaling path (average 0.1%).

The highest index *Risk* caused by carcinogenic substances has been determined in the finest grain fractions ( $< 63 \mu\text{m}$ ) for the spa residents: it is  $9.67\text{E}-06$  for the 6 year olds, and  $6.45\text{E}-06$  for the 3 years old. When the *Risk* calculations were made for the bulk samples, the indexes were significantly lower ( $1.90\text{E}-06$  and  $1.27\text{E}-06$ , respectively both age groups).

The difference of the indexes *HI* and *Risk* for the bulk samples and their finest fractions corresponds to the differences in the metal quantities in both sample types. These differences are also confirmed by the distribution index *DF*. In the case of the finest fraction  $F_{<63}$ , its value is the highest and equals 11.71 for Pb, while for the remaining metals the values are significantly lower but exceed  $> 4$ , which proves a high enrichment of the fine fraction in the metals concerned.

The index *HI* exceeding the unity for the 3-year olds spa residents indicates that negative health effects are probable to appear for children of this age group.

The essential conclusion of the current investigations is that the degree of the human (not only children's) health risk should be assessed carrying out the chemical determinations on the fine fractions ( $< 63 \mu\text{m}$ ), in which clay minerals and Fe and Mn oxy/hydroxides are accumulated and represent mineral substances with strong sorption/desorption capacities of such metals as Pb, Cu, Zn, Cd, also Cr and Ni. These are just the grain fractions sticking most to the hands of children and may be accidentally swallowed when a child concentrates on playing, e.g. in sandboxes. Coarser grain fractions ( $> 200 \mu\text{m}$ ) contain insignificant portion of metals if compared with the fractions  $< 63 \mu\text{m}$ , moreover coarser fractions are organoleptically sensed: they usually grit in one's teeth and are at least partly removed with saliva. It is thus the finest fraction— $< 63 \mu\text{m}$ , which should be investigated in the health risk assessments.

**Acknowledgements** This research was financial support by AGH-UST Grant KOŚ No. 11.11.140.017.

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