

High concentrations of lead and barium in hair of the rural population caused by water pollution in the Thar Jath oilfields in South Sudan



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ARTICLE INFO

Article history:

Available online 23 December 2016

Keywords:

Barium

Drinking water

Environmental pollution

Hair analysis

Lead

Oil exploration

ABSTRACT

In the oil fields of Thar Jath, South Sudan, increasing salinity of drinking water was observed together with human incompatibilities and rise in livestock mortalities. Hair analysis was used to characterize the toxic exposure of the population. Hair samples of volunteers from four communities with different distance from the center of the oil field (Koch 23 km, n = 24; Leer 50 km, n = 26; Nyal 110 km, n = 21; and Rumbek 220 km, n = 25) were analyzed for altogether 39 elements by inductively coupled plasma–mass spectrometry. Very high concentrations and a toxic health endangerment were assessed for lead and barium. The concentration of lead increased steadily with decreasing distance from the oil field from Rumbek (mean 2.8 µg/g) to Koch (mean 18.7 µg/g) and was there in the same range as in highly contaminated mining regions in Kosovo, China or Bolivia. The weighting materials in drilling muds barite (BaSO₄) and galena (PbS) were considered to be the sources of drinking water pollution and high hair values. The high concentrations of lead and barium in hair demonstrate clearly the health risk caused by harmful deposition of toxic industrial waste but cannot be used for diagnosis of a chronic intoxication of the individuals.

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1. Introduction

Since 1974, exploratory drillings for crude oil were performed in the southern areas of Sudan and large deposits were discovered between 1979 and 1982 in the states Upper Nile and Unity of the later South Sudan [1]. However, caused by civil war and political instability, oil production in larger scale started only in 1999 in the Unity oilfield (Fig. 1). The Thar Jath and Mala oil fields (block 5A, Unity state) were discovered in 2001 and production began there in 2006 and 2007 respectively after the Comprehensive Peace Agreement was signed and the political autonomy of South Sudan

was granted. The oil production increased until 2012 when new military conflicts emerged between Sudan and the meanwhile independent South Sudan and the pipeline to Port Sudan at the Red Sea was shut down. Since then, oil is produced only sporadically and to a much lower level. Production facilities are abandoned and dilapidated.

In 2007, complaints of the population of the Thar Jath region became known for the first time about a bitter and salty taste of the drinking water. Diarrhea and gastrointestinal problems had increased reportedly, particularly of children and older persons. Increased mortalities of livestock were also associated with the contaminated water. Drinking water for the rural population of about 180,000 and for livestock in the surrounding villages of the oil fields is mainly supplied by hand pumps from the upper aquifer in 40–80 m depth. Altogether 90 water samples from hand pump operated wells, surface water of wetlands, ponds of oil processing water and drilling mud pits were collected during five field trips in 2008 and 2009 and were tested for pH, electrical conductivity, total

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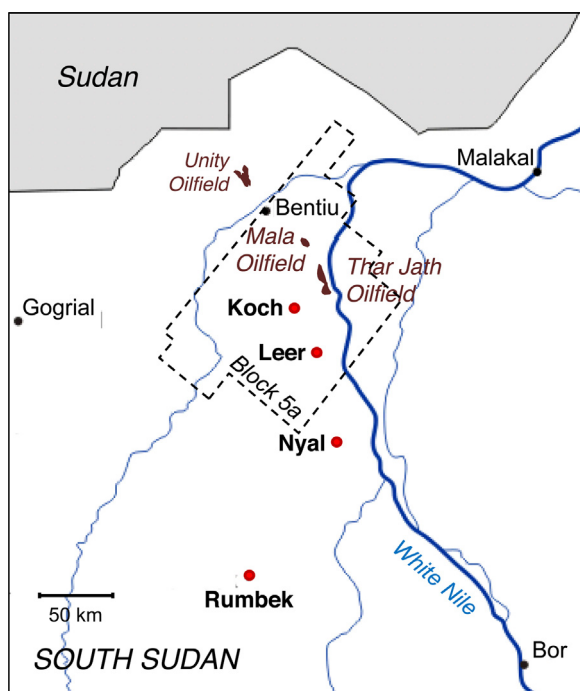


Fig. 1. Map of the oilfields in South Sudan with the locations of hair sampling Koch, Leer, Nyal and Rumbek.

dissolved solids (TDS), usual electrolyte anions and cations as well as heavy metals and polycyclic aromatic hydrocarbons [2,3]. A strongly increased total salt content with TDS up to 6400 mg/L and strongly elevated electrical conductivity up to 8150 $\mu\text{S}/\text{cm}$ were found in 24 from 37 drinking water samples (drinking water standards <1000 mg/L and <2500 $\mu\text{S}/\text{cm}$). This increased salinity was mainly caused by high levels of Cl^- (up to 1600 mg/L), SO_4^{2-} (up to 2980 mg/L) and Na^+ (up to 1400 mg/L). Typical was also an increased content of K^+ (up to 189 mg/L with one extreme sample of 5180 mg/L).

Extremely high concentrations of these ions were measured in the samples from drilling pits, e.g. Cl^- 42,400 mg/L, SO_4^{2-} 2786 mg/L, Na^+ 8630 mg/L, K^+ 24,570 mg/L in a pit north of the village Koch. It was concluded from the direction of groundwater flow, the spatial distribution of salt contamination and the hydro-geological boundary conditions found in low water permeable alluvial deposits that the cause of high conductivities in drinking water wells can only be attributed to selective seepage of salt-containing water from the produced water ponds and drilling mud pits of the Unity, Mala and Thar Jath oilfields operating in the studied area [2].

Lead above the limit level of 0.01 mg/L with a maximum value of 0.59 mg/L was measured in 14 from 37 drinking water samples. The water samples from three abandoned drilling pits contained 0.37, 2.06 and 2.15 mg/L lead. Furthermore, chromium (0.01–0.52 mg/L), barium (0.10–0.30 mg/L) and strontium (0.27–8.0 mg/L) were

found in many of the drinking water samples whereas arsenic, cadmium, copper and mercury were always below the limits of detection (0.001 mg/L, 0.0002 mg/L, 0.005 mg/L and 0.001 mg/L respectively). The concentration of barium was 140 mg/L in a sample from an abandoned drilling pit and 0.61–1.2 mg/L in samples from oil processing water ponds. Aluminum and iron had concentrations above the Sudanese drinking water standards (0.2 and 0.3 mg/L) only in surface water but not in drinking water. Manganese was below the Sudanese drinking water standard (0.5 mg/L) in all samples with exception of one deep drilling water sample (0.91 mg/L), but 5 drinking water samples from the upper aquifer with 0.25–0.43 mg/L were above the German drinking water standard of 0.05 mg/L. Cobalt, thorium and vanadium which had elevated concentrations in hair (see below) were not measured in water.

In order to evaluate the health hazard of the population caused by this contamination of drinking water, hair samples from inhabitants of the locations Koch, Leer, Nyal and Rumbek (geographic map see Fig. 1) were collected in 2015 and investigated by multi-element analysis using inductively coupled plasma–mass spectrometry (ICP–MS). Whereas the distance from the Thar Jath oilfield to Koch (23 km), Leer (50 km) and Nyal (110 km) is relatively close, Rumbek (220 km) is further away from the oil activities and can be regarded as a relatively unpolluted region for comparison.

2. Material and methods

2.1. Participants of the study and living conditions

The participants of the study were inhabitants of the locations Koch (n = 24), Leer (n = 26), Nyal (n = 21) and Rumbek (n = 25) and lived there steadily and for a long time. They were not employed in oil exploration and production. Under the constraints of the situation, they were chosen as most easily available. They were recruited as customers of barber shops, were approached in the immediate surroundings of a health care center of the organization Sign of Hope or after announcement of the study in a church. Age and gender of the participants are given in Table 1. There is a difference in age distribution between the four locations with elder participants in Rumbek and younger participants in Nyal. However, this does not essentially impair the study since the metal concentrations in hair were found not to be statistically biased by age within the locations. Female participants were generally difficult to persuade for the study and only five women took part in Koch.

Most of the participants lived in traditional homesteads made from clay and wooden poles for the walls and thatched grass for roof. Housing conditions were damp during the rainy season (4–5 months per year). Water was supplied by local hand pumps. The usual diet was a combination of local food (sorghum, dried fish, green vegetables, cow milk) and food from the World Food Program. Hygiene was generally poor. The 10–18 year olds washed their hair once a day when taking a bath either in the river/swamp

Table 1

Age and gender of volunteers. m = male, f = female, y = years.

Location	Number	Age, years		Age distribution, numbers				
		Mean	Median	<10 y	10–20 y	21–30 y	31–40 y	>40 y
Koch	19 m + 5 f	21	22	1	10	11	1	1
Leer	26 m	25,8	16,5	0	15	4	3	4
Nyal	21 m	17,3	15	3	15	3	0	0
Rumbek	25 m	41,3	38	0	0	0	16	9
Total	91 m + 5 f	27,1	23,5	4	40	15	23	14

site or at home with water fetched from the borehole. Hair was washed usually with water only, sometimes with bar soap when it was available. Men who had regular access to water washed usually their hair with water only, once or twice a day.

2.2. Hair samples

The hair samples were collected by local barbers who, on this occasion, always shaved the whole head bald. The hair was cut directly above the skin using a new razor blade for every volunteer. Sufficient material was mainly taken from the front of the head and was stored in zip-lock plastic bags and labeled with name, date of birth and place of residence of the volunteer. The length of the curly and wiry hair which was grown after previous shavings was at least 1 cm and was always investigated in full length.

2.3. Multi-element analysis by ICP-MS

Levels of 39 elements were measured in hair based on the testing available from Doctor's Data (St. Charles, IL, USA—www.doctorsdata.com). Doctor's Data is certified by CLIA, the Clinical Laboratory Improvement Amendments program operated by the US Department of Health and Human Services. The methods were described in detail in previous papers [4–6]. Briefly, the hair sample is cut into approx. 0.3 cm pieces, washed four times using a standardized procedure with a 1:200 dilution of Triton X-100, rinsed with acetone, allowed to drain, rinsed three times with deionized water and again two times with acetone and dried at 75 °C. About 200 mg of the washed hair pieces are accurately weighed into 50 mL disposable polypropylene centrifuge tubes and 3 mL concentrated trace-metal-grade nitric acid are added. Then, the hair is digested in a microwave oven (MARS5 and MARS6, CEM Corporation, Matthews, NC, USA) in two stages for each 15 min at 70 °C and 115 °C. After cooling, 500 μ L of an internal standard mixture (^{71}Ga , ^{115}In , and ^{173}Lu) are added and the sample is diluted to 50 mL with 18 M Ω deionized water. All elements were determined on an ICP-MS Elan 9000 and DRCII instrument (Perkin-Elmer, Norwalk, CT) using the ESI fast sample introducer (Elemental Scientific, Omaha NE).

2.4. Statistical analysis

The software IBM SPSS Statistics 22 (Statistical Package for the Social Sciences) and Microsoft Excel 2013 were used for all statistical evaluations in this study.

2.5. Ethical aspects

This study was performed according to the Helsinki ethical principles for medical research involving human subjects of the World Medical Association. An informed consent letter with the objectives and the practical performance of the study was read or if necessary translated to each participant. All participants gave their consent by signature. In case of children or adolescents, the informed consent was additionally signed by a guardian. For publication, the samples were anonymized in a way that an identification of the person is impossible.

3. Results

As a result of the measurements, a database of the concentrations of 39 elements in 96 hair samples was obtained. For a closer toxicological evaluation, only those elements were included for which (a) a connection between concentrations in human hair and pollution of environment was shown in previous studies

described in literature, (b) for which concentrations clearly above the reference ranges of the laboratory were found for at least one of the four locations, and (c) which possess a high chronic toxicity after absorption to blood. From these points of view, the ubiquitous elements Na, K, Mg, Ca, P and S as well as most of the metals including the strongly toxic metals As, Cd, Hg and Tl were excluded although in single cases concentrations above the reference ranges were detected. The ranges, means and medians of the concentrations of the remaining elements Al, Ba, Co, Fe, Mn, Pb, Sr, Th and V are given in Table 2 for the total of all samples and separately for the four locations together with the reporting limits (limits of quantification LOQ) and reference ranges (95th percentile) of the laboratory.

The reference ranges of the laboratory give an orientation about the normal metal burden of the population in developed countries but are not necessarily applicable to the rural and simple conditions of life and hygiene and to the climate in the region under investigation with different possibilities of external incorporation and elimination of the elements in hair. Differences between the four locations with Rumbek as the least affected community should give additional evidence for the connection with the industrial pollution.

Therefore, the concentrations of the 9 metals in Table 2 were statistically compared between Koch, Leer, Nyal and Rumbek by univariate ANOVA (analysis of variance) using the software SPSS. The significance level $\sigma \leq 0.05$ was used as the criterion for a significant difference of the concentrations between the locations. Table 3 shows the σ -values of the pairwise comparison with the significant differences printed in bold. No significant difference was found for Al, Fe, Th and V showing that the high concentrations of these elements obviously are not associated with the industrial activities. For Ba, Co, Mn, Pb and Sr significant differences were obtained mainly between Koch and Rumbek with higher concentrations in Koch. As examples, the box and whiskers plots are shown in Fig. 2 for Al, Ba, Fe, and Pb. Beside the lower mean and median concentrations of Ba and Pb in the samples from Rumbek there is also a much smaller variation of the concentrations in comparison to the other locations. This difference in variation is not observed for Al and Fe.

4. Discussion

4.1. Comparison of the metal concentrations in hair with literature data

High concentrations of toxic metals in hair of a certain population are generally accepted as an indicator of an environmental pollution and of a potential health endangerment [7,8]. Advantages of hair in comparison to blood or urine are the longer time window for long-term monitoring, the non-invasive sampling and the simpler storage and transport of the samples. However, in addition to the exposure by food and environment, metal concentrations in hair depend on many further endogenous and exogenous factors such as age, gender, race, hair color, hair care and hair cosmetics, habits of nutrition, smoking, geographic region, climate, profession and occupational exposure, living conditions and hygiene. It is not generally clear and cannot be distinguished in a single case whether a metal is incorporated in hair from the blood stream or directly from exogenous sources. Therefore, a high concentration of a toxic metal in hair of a patient is not an unambiguous indicator of a chronic intoxication but should give rise to further medical investigations including analysis of blood.

Beside the reference ranges of the laboratory given in Table 2, the concentrations of the present study were also compared with data from the general population in France [9], Italy [10], Russia [11,12], Poland [13], and populations from regions with evidently

Table 2
Concentrations of metals with results above the reference ranges in hair of volunteers of the locations Koch (n = 24), Leer (n = 26), Nyal (n = 21) and Rumbek (n = 25) in South Sudan and reporting limits (LOQ) and reference ranges (95th percentile) of the laboratory.

Element, reporting limit and reference range ($\mu\text{g/g}$)	Location	Concentration in hair ($\mu\text{g/g}$)		
		Range	Mean	Median
Aluminum LOQ 0.1 Ref. range <19	Koch	32–1500	354.71	135.00
	Leer	22–1300	219.73	145.00
	Nyal	40–470	166.48	140.00
	Rumbek	30–410	181.40	180.00
	Total	22–1500	231.84	150.00
Barium LOQ 0.04 Ref. range <3	Koch	4.6–50	16.46	11.00
	Leer	5.8–33	14.26	12.50
	Nyal	5.8–39	18.57	20.00
	Rumbek	2.9–10 (950 ^a)	4.91	4.80
	Total	2.9–50 (950 ^a)	23.16	11.00
Cobalt LOQ 0.002 Ref. range 0.003–0.08	Koch	0.026–0.75	0.24	0.12
	Leer	0.019–0.52	0.19	0.15
	Nyal	0.034–0.44	0.19	0.15
	Rumbek	0.031–0.20	0.10	0.10
	Total	0.019–0.75	0.18	0.14
Iron LOQ 1.0 Ref. range 4–31	Koch	74–1500	335.88	165.00
	Leer	26–1100	264.15	195.00
	Nyal	52–630	221.24	160.00
	Rumbek	48–1000	314.40	280.00
	Total	26–1500	285.78	205
Lead LOQ 0.01 Ref. range <5	Koch	1.9–150	18.71	8.15
	Leer	1.1–61	10.27	6.60
	Nyal	0.94–22	5.49	3.40
	Rumbek	0.85–4.8	2.80	2.80
	Total	1.1–150	9.39	4.20
Manganese LOQ 0.009 Ref. range 0.05–1.3	Koch	4.5–170	23.2	10.4
	Leer	3.2–40	16.6	14.0
	Nyal	2.6–38	19.5	17.0
	Rumbek	2.4–14	6.3	6.0
	Total	2.4–170	16.2	12.0
Strontium LOQ 0.01 Ref. range 0.14–10	Koch	5.1–48	17.77	11.50
	Leer	6.1–32	13.87	13.00
	Nyal	4.6–28	14.02	15.00
	Rumbek	1.2–10	2.89	2.50
	Total	1.2–48	12.02	9.90
Thorium LOQ 0.001 Ref. range <0.005	Koch	0.009–0.83	0.17	0.06
	Leer	0.010–0.64	0.11	0.06
	Nyal	0.023–0.28	0.09	0.07
	Rumbek	0.010–0.25	0.10	0.10
	Total	0.009–0.83	0.12	0.07
Vanadium LOQ 0.008 Ref. range 0.01–0.2	Koch	0.15–4.2	1.11	0.69
	Leer	0.13–2.5	1.22	1.00
	Nyal	0.21–2.8	1.05	0.85
	Rumbek	0.21–2.3	0.80	0.82
	Total	0.13–4.2	1.04	0.85

^a Extreme outlier of barium, omitted in statistical analysis.

Table 3
Significance σ of the difference between the metal concentrations in hair of the volunteers from Koch, Leer, Nyal and Rumbek obtained by ANOVA (analysis of variance). A significant difference can be assumed for $\sigma \leq 0.05$ (bold printed).

Metal	Koch Leer	Koch Nyal	Koch Rumbek	Leer Nyal	Leer Rumbek	Nyal Rumbek
Aluminum	0.300	0.100	0.121	0.908	0.958	0.998
Barium	0.805	0.845	0.000	0.329	0.001	0.000
Cobalt	0.713	0.907	0.012	0.987	0.148	0.092
Iron	0.745	0.426	0.991	0.937	0.891	0.595
Lead	0.299	0.050	0.008	0.770	0.397	0.950
Manganese	0.585	0.910	0.010	0.948	0.204	0.082
Strontium	0.327	0.409	0.000	1.000	0.000	0.000
Thorium	0.386	0.282	0.374	0.992	1.000	0.994
Vanadium	0.965	0.996	0.560	0.905	0.273	0.723

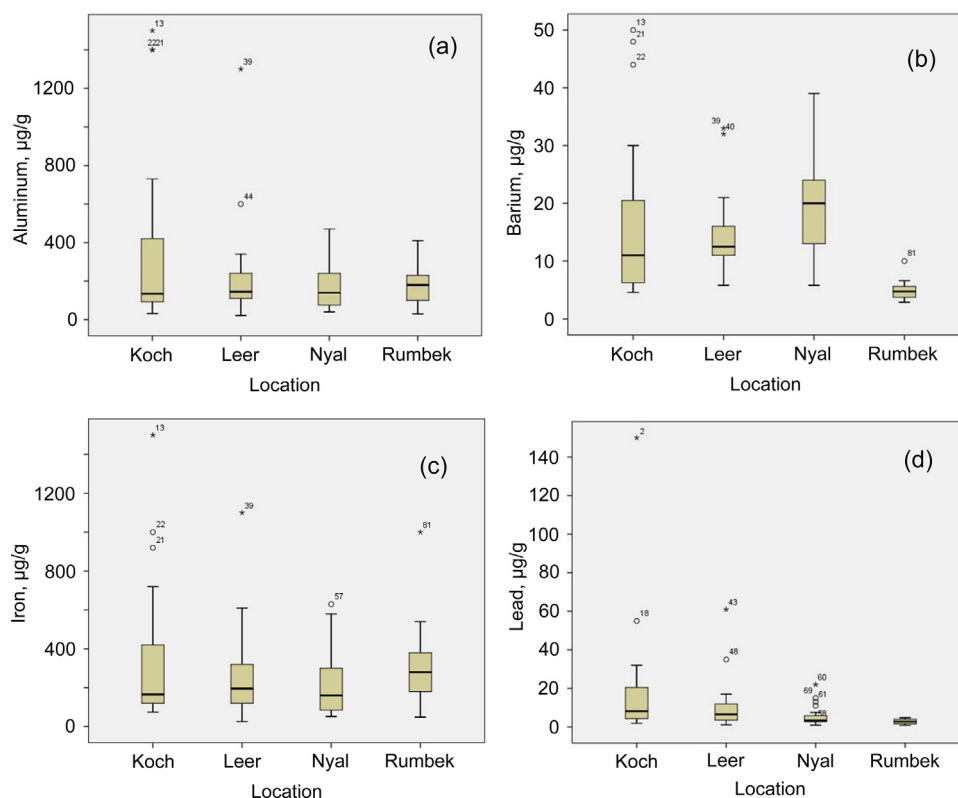


Fig. 2. Box and whiskers plots of the concentrations of (a) aluminum, (b) barium, (c) iron and (d) lead in hair samples from the locations Koch, Leer, Nyal and Rumbek.

high exposure to the metals given in Table 2. The concentrations of the ubiquitously occurring elements Al and Fe (mean 232 and 286 $\mu\text{g/g}$) are extremely high in comparison to this data (mean 6–12 $\mu\text{g/g}$ for Al and 12–23 $\mu\text{g/g}$ for Fe). However, they do neither reflect a toxic endangerment nor a particularly high environmental exposure by these elements but can be explained by a very intense direct incorporation in hair caused by steady and close contact with soil and dust under the simple and rural life conditions of the population. This is also supported by the missing statistically significant difference between the four locations (Tables 2 and 3 and Fig. 2a and c). Similarly high mean values were found in samples from Katanga, Democratic Republic of Congo (Al 308 $\mu\text{g/g}$, Fe 235 $\mu\text{g/g}$) [14], from Nigeria (Al 69.7 $\mu\text{g/g}$, Fe 97 $\mu\text{g/g}$) [15], from China (Al 84 $\mu\text{g/g}$) [16], and from India (Fe 135 $\mu\text{g/g}$) [17]. This confirms the experience of Wilhelm and Idel that Al in hair is of no value in environmental medicine [18].

The reason for the higher concentrations of Th and V (mean 0.12 and 1.04 $\mu\text{g/g}$) in comparison to the reference ranges of the laboratory and to data described for Th, e.g. in the Serbian Niška Banja Town (mean of Th 0.0019 $\mu\text{g/g}$) [19], as well as for V in multi-element studies [10–15,20] and in hair from volunteers with vanadium containing dental crowns (mean 0.27 $\mu\text{g/g}$) [21] is not clear. However, a connection to the oil industries is improbable since there is no significant difference between the four locations.

For the remaining five metals Ba, Co, Mn, Pb and Sr the concentrations in the samples from Koch were significantly higher than in the samples from Rumbek with intermediate values for Leer and Nyal. Since the distance from the oil fields increases in the order of Koch, Leer, Nyal and Rumbek, a connection between the increased concentration in hair of the inhabitants and the industrial activities has to be considered for these elements. Comparison with literature data about hair results from normal

and strongly exposed population and consideration of the chronic toxicity support the assumption of a toxic endangerment with Ba and Pb. These two elements will be discussed more in detail in Section 4.3.

The mean concentration of Co (0.24 $\mu\text{g/g}$ in Koch) is higher than in some studies about normal exposed population, e.g. 0.015 $\mu\text{g/g}$ in Russia [11], and 0.018 $\mu\text{g/g}$ in Mongolia [20], but much lower than in hair from steelworkers in Pakistan (4.7 $\mu\text{g/g}$) [22], or from patients with metallic hip implantation (62 $\mu\text{g/g}$,) [23]. Therefore, a toxic endangerment by Co is rather improbable.

The elevated concentrations of Sr in hair (mean 17.8 $\mu\text{g/g}$ in Koch) in comparison to published values of normal and exposed populations, e.g. mean values 6.6 $\mu\text{g/g}$ in Bangladesh [24], and 6.9 $\mu\text{g/g}$ in Russia [11] can be explained by its frequent occurrence as an impurity in barite as weighting agent [30]. This is supported by the relatively high concentrations in drinking water samples (0.27–8.0 mg/L) and by the difference between the concentrations in hair from the four locations which parallels that of Ba (Table 2). However, strontium displays generally no essential chronic toxicity.

The manganese concentrations for the four locations (mean 6.3–23.2 $\mu\text{g/g}$, Table 2) exceeded the reference range of the laboratory (0.05–1.3 $\mu\text{g/g}$) and the strongly varying literature data for normally exposed populations (mean 0.23–7.6 $\mu\text{g/g}$ [9–13]). Hair concentrations reported for Mn of higher exposed populations near ferroalloy plants (mean 0.12 $\mu\text{g/g}$ [25] and 15.2 $\mu\text{g/g}$ [26]), or with Mn containing tap water (mean 5.1 $\mu\text{g/g}$ [27]) varied also very strongly, probably depending on the analytical hair washing procedure [25]. Although Mn may occur in produced water of oil production (1.3–2.7 mg/L [28]) it was below detection limit (<0.02 mg/L) in the water samples from oil processing ponds of the present study. The concentration in two samples from abundant drilling pits was 0.72 and 0.70 mg/L and between

0.25 and 0.91 $\mu\text{g/g}$ in drinking five water samples from Koch and one from Nyal. Based on this data and on the fact that Mn is not a usual impurity of barite, oil industry as the source of the elevated Mn concentrations in hair appears to be improbable.

4.2. Possible sources of contamination from oil exploration and production

A prerequisite for the connection between the high salinity of the ground water, the high concentration of some metals in hair of the population in the present study and the oil industry is the occurrence of corresponding chemicals in the technical processes. Possible pollution sources of oil exploration and production are drilling muds (drilling fluids) and produced water.

Produced waters are generated during oil exploration, extraction and processing with volumes ranging from one to 50 barrels per barrel of oil and originate either from formation water reservoirs in the oil field or from injection to increase oil recovery by maintaining pressure [29]. They are often saline or hypersaline with high concentrations of chloride, sulfate, sodium, calcium, iron, manganese and boron, naturally occurring radioactive material (NORM), organics (e.g. phenols, *n*-alkanes, and aromatic hydrocarbons), as well as biocides, demulsifiers and corrosion inhibitors added during operation of the well. Depending on the geographic location and age of the producing well they may contain high concentrations of toxic metal ions including lead [30].

Drilling muds are used to aid the drilling of boreholes, in South Sudan between 2000 m and more than 3000 m depth. The most important functions of drilling muds are to transport drill cuttings to the surface, to balance subsurface and formation pressures, to prevent a blowout, to cool and lubricate the drill bit and to support part of the weight of the drill pipe and bit [31]. In order to fulfill these requirements, sophisticated compositions with a large number of additives were developed. Inorganic components of water based drilling muds are weighting agents (usually 15–35% BaSO_4 , barite, percentage increasing with borehole depth), gelling products (e.g. 4% bentonite, a clay-like silicate), salinity chemicals NaCl and/or KCl in order to increase density, alkaline chemicals NaOH, $\text{Ca}(\text{OH})_2$ and Na_2CO_3 to install alkaline conditions (pH 8–12.5), corrosion inhibitors (NH_4HSO_3), or chromium salts for crosslinking xanthan gum. Instead of barite (specific weight 4.2 g/cm^3), in special cases galena (PbS , 7.4 g/cm^3), magnetite (Fe_3O_4 , 5.0 g/cm^3) or manganese tetroxide (Mn_3O_4 , 4.8 g/cm^3) are used as weighting materials. Oil based drilling muds contain basically the same inorganic components.

Environmental impacts of metal ions in both oil and water based drilling mud and cuttings in Southwestern Nigeria were reported [32]. It was shown that barite is not only the source for contamination by Ba but also by other metals which are present as impurities in this mineral [30,33]. The lead content was found to be 0.018–0.137% and 0.068% respectively. However, according to a previous study, the lead content of barite can be up to 4% by weight depending on the geochemical origin [34]. It was assumed that lead is present in barite as PbS and as such has only a very small solubility and bioavailability [33].

Another possible source of lead could be galena (PbS) which can be applied as weighting material for particularly deep wells because of its higher specific weight as compared to barite and as a locally available substitute of barite [35,36]. However, there is no evidence that galena was really used for this purpose in South Sudan. Both barite and galena are generally believed to be nonhazardous because of their very low solubility in water. However, there are chemical and microbiological processes of weathering and mobilization of the metal ions known for both

minerals. BaSO_4 can be transformed to the soluble BaS by sulfate-reducing bacteria under anaerobic conditions [37,38]. On the other hand, weathering of galena under calcareous conditions leads to PbSO_4 and PbCO_3 with a higher bioaccessibility, thus increasing the mobility and toxicity of lead [39]. Sulfur oxidizing bacteria can play a role in this process [40]. Furthermore, it is known that acidic conditions facilitate the mobilization of lead from contaminated soils and sediments [41].

Drilling mud as the metal contamination source in the oilfields of South Sudan is also obvious from the water analyses [3]. For instance, 140 mg/L Ba and 2.15 mg/L Pb were determined in the water sample from an abandoned drilling pit near Koch.

4.3. Interpretation of lead and barium concentrations in hair

Because of this connection to the oil industry, a more profound interpretation is necessary for lead and barium. Lead concentrations in hair were frequently described in context of occupational and environmental exposure. Some examples of normally and highly exposed populations are compared with the results for the four locations in South Sudan in Fig. 3. Despite the many individual and analytical variations, it can be concluded from the literature data as a whole that the means and medians of normally exposed populations are around $1\text{ }\mu\text{g/g}$ and not higher than $2\text{ }\mu\text{g/g}$ with single values rarely above $10\text{ }\mu\text{g/g}$. The means and medians of highly exposed populations are as a rule above $5\text{ }\mu\text{g/g}$ with single values often above $20\text{ }\mu\text{g/g}$ and peak values above $100\text{ }\mu\text{g/g}$. Therefore, the high lead concentrations in hair of the volunteers from Koch and to a lower extent also from Leer and Nyal indicate a serious exposure by this toxic metal. Detection of high lead concentrations in local well water samples suggests that the contaminated water plays an essential role as a source of the lead hair results [2,3].

The portions of incorporation in hair from blood (after drinking contaminated water, eating contaminated food or breathing contaminated air) and of direct deposition from external sources (washing or wetting with contaminated water, from dust or contaminated hands mediated by sweat, absorption from air) vary strongly depending on the local situation and cannot be determined. It was shown, that external incorporation of lead in hair plays an important role, particularly in stronger polluted regions [48]. For this reason, the high concentrations in hair indicate a serious exposure but cannot unambiguously prove a chronic lead intoxication of the tested individuals.

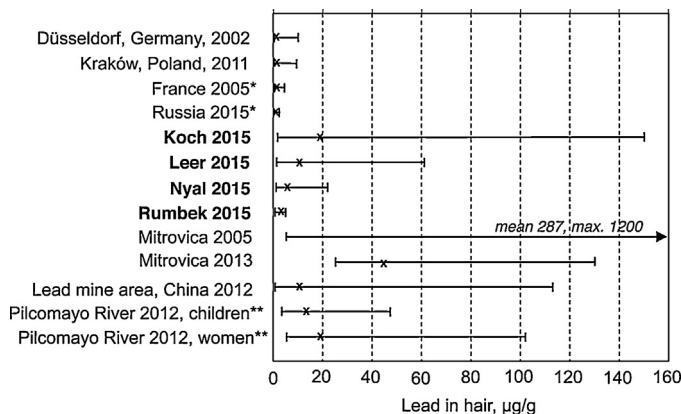


Fig. 3. Comparison of the lead concentrations in hair (ranges and mean) from the four locations in South Sudan (present study) with literature data from normal exposed population in Germany [42], Poland [43], France [9], and Russia [11], as well as highly exposed population in Kosovo [44,45], China [46], and Bolivia [47]. *Median and 5th–95th percentile, **mean and 10th–90th percentile.

The adverse health effects of chronic lead exposure include developmental neurotoxicity, reproductive dysfunction and toxicity to the kidneys, blood and endocrine systems [49]. The neurodevelopment of children can be adversely affected already at low chronic exposure [50].

Barium is essentially known for its acute toxicity and epidemiological data for chronic low-level exposure are still sparse [51]. The reported health effects include cardiovascular and kidney diseases, metabolic, neurological, and mental disorders. Toxic effects are based on the blockade of the potassium channels and hypokalemia [52]. High level environmental contamination by barium seems also to be associated with high incidence clustering of multiple sclerosis and other neurodegenerative diseases [53].

Literature data of barium concentrations in hair are compared with the data from South Sudan in Fig. 4. As a rule, mean values and medians of normally exposed population are below 3 µg/g. The results for Koch, Leer and Nyal are five- to ten-times higher and indicate a high barium exposure and possible health endangerment of the population. For the population in Kandal, a location in the Mekong River basin of Cambodia with 0.87–2.62 mg/L Ba in drinking water, still higher values (0.33–328 µg/g mean 22.8 µg/g) in hair were described [54].

4.4. Limitations of the present study

Limitations of this study are mainly caused by the difficult political situation and the tough living conditions in the investigated area. This concerns the relatively low number of participants, the inhomogeneity of age and gender distribution within and between the four locations, and the lack of detailed information in the individual cases about occupation, alimentary habits and housing conditions and other ecological and hygienic parameters. Another drawback is that the water and hair samples were not collected at the same time thus impeding a closer comparison between both results. Furthermore, it was not possible to collect blood and urine samples for comparison and confirmation of the toxic hazard.

It was an analytical limitation that the curly and relatively short hair of the volunteers did not allow to investigate a uniform hair length. However, despite these limitations, the severe exposure of the population to lead and barium and the connection to the environmental damage by the oil exploration and production are clearly seen from the results.

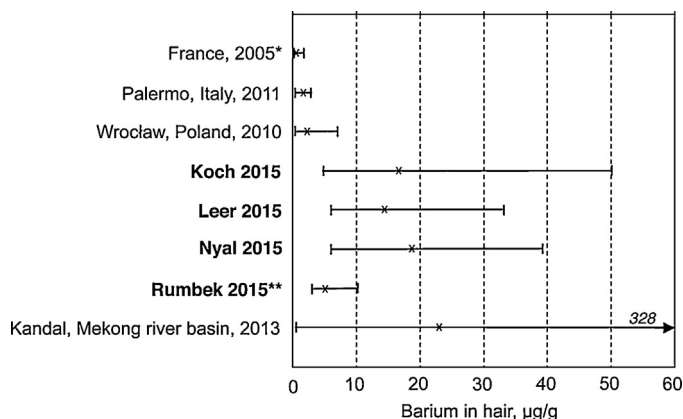


Fig. 4. Comparison of the barium concentrations in hair (ranges and mean) from the four locations in South Sudan (present study) with literature data from normally exposed population in France [9], Italy [10], and Poland [13], and from a highly exposed population in the Mekong River basin of Cambodia [54].

5. Conclusions

According to the author's knowledge, this is the first study using hair analysis for survey of health hazards by toxic metal pollution from oil exploration and production. However, environmental impacts from metals including lead and barium in produced water and drilling waste discharges were previously reported [28,29,33,55,56]. The high concentrations of lead and barium in hair of the volunteers from Koch, Leer and Nyal in comparison to Rumbek and to literature data as well as in context of the presence in water samples, and the use of barite as weighting material in drilling muds prove badly disposed wastes of the oil industries to be the source of the contamination. Other reasons of toxic lead exposure such as leaded gasoline, leaden water tubes or metal mining, processing and recycling could be excluded. The findings indicate a persistent health endangerment of the population and require further blood tests, particularly for lead, and possibly corresponding medical treatment. This interpretation is independent of the incorporation mechanism in hair either systemic from blood stream or directly from surroundings. But, contamination by toxic metals is only one part of the unsustainable situation of the population and adds to saline drinking water [2,3], to the insufficient conditions of alimentation, hygiene and housing and to the insecure situation of the ongoing political unrest.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

- [1] K. Stieglitz, S. Pamperrien, Oil, Power and a Sign of Hope, Rüffer & Rub Sachbuchverlag GmbH, Zürich, Switzerland, 2016.
- [2] H. Rueskamp, J. Ariki, K. Stieglitz, C. Treskatis, Effect of oil exploration and production on the salinity of a marginally permeable aquifer system in the Thar Jath-, Mala- and Unity oilfields, Southern Sudan, Zbl. Geol. Paläont. Teil I (2014) 95–115.
- [3] H. Rueskamp, C. Treskatis, K. Stieglitz, J. Ariki, Einfluss anthropogener Schadstoffe auf die Wasserqualität eines Grundwasserleitersystems im Südsudan, (2014), pp. 888–895 gwf-Wasser Abwasser.
- [4] D.A. Bass, D. Hickock, D. Quig, K. Urek, Trace element analysis in hair: factors determining accuracy, precision, and reliability, Altern. Med. Rev. 6 (2001) 472–481.
- [5] M.E. Druyan, D. Bass, R. Puchyr, K. Urek, D. Quig, E. Harmon, W. Marquardt, Determination of reference ranges for elements in human scalp hair, Biol. Trace Elem. Res. 62 (1998) 183–197.
- [6] R.F. Puchyr, D.A. Bass, R. Gajewski, M. Calvin, W. Marquardt, K. Urek, M.E. Druyan, D. Quig, Preparation of hair for measurement of elements by inductively coupled plasma-mass spectrometry (ICP-MS), Biol. Trace Elem. Res. 62 (1998) 167–182.
- [7] F. Gil, A.F. Hernández, Toxicological importance of human biomonitoring of metallic and metalloids elements in different biological samples, Food Chem. Toxicol. 80 (2015) 287–297.
- [8] H. Drexler, K.-H. Schaller, Haaranalysen in der klinischen Umweltmedizin. Eine kritische Betrachtung, Dtsch. Ärztebl. 99 (2002) A3026–A3029.
- [9] J.P. Goullé, L. Mahieu, J. Castermant, N. Neveu, L. Bonneau, G. Lainé, D. Bouige, C. Lacroix, Metal and metalloids multi-elementary ICP-MS validation in whole blood, plasma, urine and hair. Reference values, Forensic Sci. Int. 153 (2005) 39–44.
- [10] G. Dongarrà, M. Lombardo, E. Tamburo, D. Varrica, F. Cibella, G. Cuttitta, Concentration and reference interval of trace elements in human hair from students living in Palermo, Sicily (Italy), Environ. Toxicol. Pharmacol. 32 (2011) 27–34.
- [11] A.V. Skalny, M.G. Skalnaya, A.A. Tinkov, E.P. Serebryansky, V.A. Demidov, Y.N. Lobanova, A.R. Grabeklis, E.S. Berezkina, I.V. Gryazeva, A.A. Skalny, A.A. Nikonorov, Reference values of hair toxic trace elements content in occupationally non-exposed Russian population, Environ. Toxicol. Pharmacol. 40 (2015) 18–21.
- [12] A.V. Skalny, M.G. Skalnaya, A.A. Tinkov, E.P. Serebryansky, V.A. Demidov, Y.N. Lobanova, A.R. Grabeklis, E.S. Berezkina, I.V. Gryazeva, A.A. Skalny, O.A. Skalnaya, N.G. Zhivaev, A.A. Nikonorov, Hair concentration of essential trace elements in adult non-exposed Russian population, Environ. Monit. Assess. 187 (2015) 677.
- [13] K. Chojnacka, A. Zielinska, H. Górecka, Z. Dobrzanski, H. Henryk Górecki, Reference values for hair minerals of Polish students, Environ. Toxicol. Pharmacol. 29 (2010) 314–319.

- [14] M.M. Elenge, J.C. Aubry, L. Jacob, C. De Brouwer, Heavy metal in hair samples of 109 non-industrial (miners) population in Katanga, *Sante* 21 (2011) 41–46.
- [15] O.I. Alatishe, G.N. Schrauzer, Lead exposure: a contributing cause of the current breast cancer epidemic in Nigerian women, *Biol. Trace Elem. Res.* 136 (2010) 127–139.
- [16] J. Li, D. Cen, D. Huang, X. Li, J. Xu, S. Fu, R. Cai, X. Wu, M. Tang, Y. Sun, J. Zhang, J. Zheng, Detection and analysis of 12 heavy metals in blood and hair sample from a general population of Pearl River Delta area, *Cell Biochem. Biophys.* 70 (2014) 1663–1669.
- [17] R. Chaturvedi, S. Banerjee, P. Chattopadhyay, C.R. Bhattacharjee, P. Raul, K. Borah, High iron accumulation in hair and nail of people living in iron affected areas of Assam, India, *Ecotoxicol. Environ. Saf.* 110 (2014) 216–220.
- [18] M. Wilhelm, H. Idel, Hair analysis in environmental medicine, *Zentralbl. Hyg. Umweltmed.* 198 (1996) 485–501.
- [19] S.K. Sahoo, Z.S. Žunić, R. Kritsanuwat, P. Zagrodzki, P. Bossew, N. Veselinovic, S. Mishra, H. Yonehara, S. Tokonami, Distribution of uranium thorium and some stable trace and toxic elements in human hair and nails in Niška Banja Town, a high natural background radiation area of Serbia (Balkan Region, South-East Europe), *J. Environ. Radioact.* 145 (2015) 66–77.
- [20] F. Komatsu, Y. Kagawa, T. Kawabata, Y. Kaneko, U. Chimedregzen, B. Purvee, J. Otgon, A high accumulation of hair minerals in Mongolian people: 2(nd) report; influence of manganese, iron, lead, cadmium and aluminum to oxidative stress, parkinsonism and arthritis, *Curr. Aging Sci.* 4 (2011) 42–56.
- [21] H. Kodaira, K. Ohno, N. Fukase, M. Kuroda, S. Adachi, M. Kikuchi, Y. Asada, Release and systemic accumulation of heavy metals from preformed crowns used in restoration of primary teeth, *J. Oral Sci.* 55 (2013) 161–165.
- [22] H.I. Afridi, T.G. Kazi, N.G. Kazi, M.K. Jamali, M.B. Arain, Sirajuddin, G.A. Kandhro, A.Q. Shah, J.A. Baig, Evaluation of arsenic, cobalt, copper and manganese in biological samples of steel mill workers by electrothermal atomic absorption spectrometry, *Toxicol. Ind. Health* 25 (2009) 59–69.
- [23] M. Rodríguez de la Flor, D. Hernández-Vaquero, J.M. Fernández-Carreira, Metal presence in hair after metal-on-metal resurfacing arthroplasty, *Orthop. Res.* 31 (2013) 2025–2031.
- [24] M. Kato, M.Y. Kumasaka, S. Ohnuma, A. Furuta, Y. Kato, H.U. Shekhar, M. Kojima, Y. Koike, N. Dinh Thang, N. Ohgami, T.B. Ly, X. Jia, H. Yetti, H. Naito, G. Ichihara, I. Yajima, Comparison of barium and arsenic concentrations in well drinking water and in human body samples and a novel remediation system for these elements in well drinking water, *PLoS One* 8 (2013) e66681.
- [25] R.R. Eastman, T.P. Jursa, C. Benedetti, R.G. Lucchini, D.R. Smith, Hair as a biomarker of environmental manganese exposure, *Environ. Sci. Technol.* 47 (2013) 1629–1637.
- [26] J.A. Menezes-Filho, C.R. Paes, Â.M. de C. Pontes, J.C. Moreira, P.N. Sarcinelli, D. Mergler, High levels of hair manganese in children living in the vicinity of a ferro-manganese alloy production plant, *Neurotoxicology* 30 (2009) 1207–1213.
- [27] M. Bouchard, F. Laforest, L. Vandelay, D. Bellinger, D. Mergler, Hair manganese and hyperactive behaviors: pilot study of school-age children exposed through tap water, *Environ. Health Perspect.* 115 (2007) 122–126.
- [28] K. Azetsu-Scott, P. Yeats, G. Wohlgeschaffen, J. Dalziel, S. Niven, K. Lee, Precipitation of heavy metals in produced water: influence on contaminant transport and toxicity, *Mar. Environ. Res.* 63 (2007) 146–167.
- [29] B. Alley, A. Beebe, J. Rodgers, J.W. Castle, Chemical and physical characterization of produced waters from conventional and unconventional fossil fuel resources, *Chemosphere* 85 (2011) 74–82.
- [30] S.I. Onwukwe, M.S. Nwakaudu, Drilling wastes generation and management approach, *Int. J. Environ. Sci. Dev.* 3 (2012) 252–257.
- [31] R. Caenn, H.C.H. Darley, G. Robert, Composition and Properties of Drilling and Completion Fluids, Gulf Professional Publishing, Oxford, UK, 2011.
- [32] A.M. Gbadebo, A.M. Taiwo, U. Egehele, Environmental impacts of drilling mud and cutting wastes from the Igbokoda onshore oil wells, Southwestern Nigeria, *Indian J. Sci. Technol.* 3 (2010) 504–510.
- [33] J.M. Neff, Estimation of bioavailability of metals from drilling mud barite, *Integr. Environ. Assess. Manag.* 4 (2008) 184–193.
- [34] B. Takano, K. Watanuki, Geochemical implications of the lead content of barite from various origins, *Geochem. J.* 8 (1974) 87–95.
- [35] A.U. Julius, I.A. Offiong, O.E. Idorenyin, The use of galena as weighting material in drilling mud, *J. Sci. Res. Rep.* 7 (2015) 455–465.
- [36] O.Á. Omoniye, S. Mubarak, Potential usage of local weighting materials in drilling fluid a substitute to barite, *Int. J. Innov. Res. Dev.* 3 (2014) 491–501.
- [37] C.E. Bolze, P.G. Malone, M.J. Smith, Microbial mobilization of barite, *Chem. Geol.* 13 (1974) 141–143.
- [38] F. Baldi, M. Pepi, D. Burrini, G. Kniewald, D. Scali, E. Lanciotti, Dissolution of barium from barite in sewage sludges and cultures of desulfurovibrio desulfuricans, *Appl. Environ. Microbiol.* 62 (1996) 2398–2404.
- [39] R.H. Lara, R. Briones, M.G. Monroy, M. Mullet, B. Humbert, M. Dossot, G.M. Naja, R. Cruz, Galena weathering under simulated calcareous soil conditions, *Sci. Total Environ.* 409 (2011) 3971–3979.
- [40] S. Hassan, A. Daryoush, O.M. Sadegh, Galena bio-oxidation by moderate sulphur bacteria, *African, J. Microbiol. Res.* 5 (2011) 4170–4174.
- [41] W. Calmano, J. Hong, U. Förstner, Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential, *Water Sci. Technol.* 28 (1993) 223–235.
- [42] M. Wilhelm, A. Pesch, U. Rostek, J. Begerow, N. Schmitz, H. Idel, U. Ranft, Concentrations of lead in blood, hair and saliva of German children living in three different areas of traffic density, *Sci. Total Environ.* 297 (2002) 109–118.
- [43] H.J. Barton, Advantages of the use of deciduous teeth, hair, and blood analysis for lead and cadmium bio-monitoring in children. A study of 6-year-old children from Krakow (Poland), *Biol. Trace Elem. Res.* 143 (2011) 637–658.
- [44] K.D. Runow, Investigation of the heavy metal load in refugee camps with Mitrovica in Kosovo: results of the hair analyses, Society of Threatened People. Dossier of Evidence. Lead Contaminated Camps of Internally Displaced Roma, Ashkali and Kosovan-Egyptian Families in North Mitrovica, Kosovo, Institute for Functional Medicine, Wolfhagen, 2009 https://assets.gfbv.ch/.dossier_of_evidence_with_hyperlinks_062009.pdf (Assessed 15 June 2016).
- [45] N. Boisa, G. Bird, P.A. Brewer, J.R. Dean, J.A. Entwistle, S.J. Kemp, M.G. Macklin, Potentially harmful elements (PHEs) in scalp hair, soil and metallurgical wastes in Mitrovica, Kosovo: the role of oral bioaccessibility and mineralogy in human PHE exposure, *Environ. Int.* 60 (2013) 56–70.
- [46] Y. Li, X. Zhang, L. Yang, H. Li, Levels of Cd, Pb As, Hg, and Se in hair of residents living in villages around Fenghuang polymetallic mine, southwestern China, *Bull. Environ. Contam. Toxicol.* 89 (2012) 125–128.
- [47] M.J. Stassen, N.L. Preeker, A.M. Ragas, M.W. van de Ven, A.J. Smolders, N. Roeleveld, Metal exposure and reproductive disorders in indigenous communities living along the Pilcomayo River, Bolivia, *Sci. Total Environ.* 427–428 (2012) 26–34.
- [48] J. Štupar, F. Dolinsek, I. Erzen, Hair-Pb longitudinal profiles and blood-Pb in the population of young Slovenian males, *Ecotoxicol. Environ. Saf.* 68 (2006) 134–143.
- [49] M.D. Sanborn, A. Abelsohn, M. Campbell, E. Weir, Identifying and managing adverse environmental health effects: 3. lead exposure, *Can. Med. Assoc. J.* 166 (2002) 1287–1292.
- [50] S.N. Tsekrekos, I. Buka, Lead levels in Canadian children: do we have to review the standard? *Paediatr. Child Health* 10 (2005) 215–220.
- [51] J. Kravchenko, T.H. Darrach, R.K. Miller, H.K. Lyerly, A. Vengosh, A review of the health impacts of barium from natural and anthropogenic exposure, *Environ. Geochem. Health* 36 (2014) 797–814.
- [52] B.S. Bhoelan, C.H. Stevering, A.T. van der Boog, M.A. van der Heyden, Barium toxicity and the role of the potassium inward rectifier current, *Clin. Toxicol. (Phila.)* 52 (2014) 584–593.
- [53] M. Purdey, Chronic barium intoxication disrupts sulphated proteoglycan synthesis: a hypothesis for the origins of multiple sclerosis, *Med. Hypotheses* 62 (2004) 746–754.
- [54] K. Phan, S. Phan, L. Huoy, B. Suy, M.H. Wong, J.H. Hashim, M.S. Yasin, S.M. Aljunid, S. Sthiannopkao, K.W. Kim, Assessing mixed trace elements in groundwater and their health risk of residents living in the Mekong River basin of Cambodia, *Environ. Pollut.* 182 (2013) 111–119.
- [55] A.S. Naidu, A.L. Blanchard, D. Misra, J.H. Trefry, D.H. Dasher, J.J. Kelley, M.I. Venkatesan, Historical changes in trace metals and hydrocarbons in nearshore sediments, Beaufort Sea, prior and subsequent to petroleum-related industrial development: part I. trace metals, *Mar. Pollut. Bull.* 64 (2012) 2177–2189.
- [56] J.H. Trefry, K.H. Dunton, R.P. Trocine, S.V. Schonberg, D. Nathan, N.D. McTigue, E.S. Hersh, T.J. McDonald, Chemical and biological assessment of two offshore drilling sites in the Alaskan Arctic, *Mar. Environ. Res.* 86 (2013) 35–45.