

Instrumental neutron activation analysis of environmental samples from a region with prevalence of population disabilities in the North Gondar, Ethiopia

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Abstract Instrumental neutron activation analysis (INAA) of soil, coal, water, and crops from the village of Awdarda in the North Gondar, Ethiopia, where the residents suffer from various disabilities, was performed in an attempt to elucidate the existing health problems. More than forty elements were determined in the samples analyzed. Comparison of our results with literature values indicates highly elevated contents of terrigenous elements in Awdarda cereals, possibly due to contamination by excavation and indoor combustion of local coal-bearing sediments. Impact is discussed of the elevated aluminium and the rare earth elements levels in crops on the health problems.

Keywords INAA · North Gondar, Ethiopia · Environmental pollution · Health problems · Rare earth elements

Introduction

Abnormalities or adverse effects on human health may be the consequences of the deficiency or excess of various substances (stressors) in the environment. The stressors

include also the major, minor and mostly trace elements, both essential and toxic ones [1–3]. Humans can be exposed to the stressors via various routes, such as inhalation or digestion from drinking water and the food chain. On the global scale, these topics are dealt with in environmental health, the field of science that studies how the environment influences human health and disease, and environmental risk assessment [4, 5]. “Environment” in this context, means things in the natural environment like air, water and soil, and also all the physical, chemical, biological and social features of the surroundings. Here we report a case study from a small village of Awdarda in the Chilga District, the North Gondar administrative zone, Ethiopia, located at N 12°33.1', E 37°6.4', elevation 1950 m, with population of about 7500. In the North Gondar region, there is prevalence of various disabilities, mainly disabilities of lower and upper limbs, blindness, hearing loss, and mental retardation [6], which are also frequent in Awdarda. In the surroundings of the village there is no industry, but the area is rich in surface layers of coal. Coal mining has not started yet in the region, but the residents use coal combustion as the means of energy source for heating and for cooking, as well. They commonly burn coal in open stoves, directly exposing themselves to the emissions. The elemental composition of coal depends on its rank and geological origin [7]. Depending on the occurrence of elements, different health and environmental impacts will ensue. The organically bonded trace elements tend to be vaporized upon combustion, with subsequent adsorption on the fine fly ash particles. The inorganically bonded elements are generally less volatile, and tend to be retained in the bottom ash and/or in the coarser fly ash particles. On the other hand, the major environmental concern of the elements in lignite combustion is that the elements concentrate on particulates of various

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sizes and may reach toxic levels for organisms, especially if bioaccumulation and biomagnification processes take place [8]. For the above reasons, the element and radionuclide contents in coal, coal ash and emissions have frequently been studied [9–11], just to give a few recent examples. It has been deemed useful to perform elemental characterization of coal, soil, fresh water and locally produced and consumed crops from the vicinity of Awdarda to get an insight into the existing health problems. INAA has been chosen for this purpose, because of its multielemental character, low detection limits for many elements, and its inherent accuracy.

Experimental

Sampling, sample and standard preparation

About 1-kg soil sample was collected in a farming field within Awdarda (small farming fields are scattered within the village) using a hand auger with stainless steel bucket with cutting heads from depth up to 20 cm. After quartering to get mass of approximately 250 g, the soil was sieved with a nylon 1 mm mesh and eventually dried, pulverized and homogenized by milling in an agate planetary ball mill Pulverizette 5 (Fritsch, Germany), and stored in plastic vial prior to analysis.

Two coal samples (denoted “brown” and “black”, each about 1 kg) were collected from near-to-surface deposits in the vicinity of Awdarda and the adjacent soil was scraped off. Then, the coal samples were disintegrated in a jaw crusher and dried in an oven at 50 °C till constant mass (for 3 days) followed by pulverization and homogenization as in the case of the soil sample.

Fresh water was collected from a stream into a 0.5 L PET bottle, acidified by 1 mL of concentrated nitric acid (reagent grade). The solid particulates were removed by means of filtration with a membrane filter Pragopor 3 (pore size $1.5 \pm 0.4 \mu\text{m}$). The liquid fraction was evaporated to dryness on a hotplate in glass and Teflon beakers (last portions). From the dry residue aliquots were taken for analysis.

The crops analyzed were obtained from the farmers of the village. They included various cereals—finger millet (*Eleusine coracana*), sorghum (*Sorghum bicolor*), barley (*Hordeum vulgare*), and pulses—chickpea (*Cicer arietinum*). These samples were dried in an oven at 50 °C for 8 h. Finger millet was analyzed without any size diminution. The other samples were pulverized in a mill with a stainless steel blade. Barley was additionally homogenized in an agate ball mill.

The aliquots for analysis with mass 100–150 mg were sealed into pre-cleaned polyethylene (PE) disk shaped capsules made by sealing PE foils of 0.2 mm thickness

with 25 and 20 mm diameter for irradiation with thermal and epithermal neutrons, respectively. For quality control purposes, NIST standard reference materials (SRM) 1633b Constituent Elements in Coal Fly Ash, 2711 Montana Soil, and 1547 Peach Leaves were prepared for irradiation as the other samples.

For relative standardization, synthetic multi-element standards (MES) were used as calibrators, which were prepared according to the procedure described earlier [12–14].

Irradiation and counting

Three modes of INAA routinely employed at the Nuclear Physics Institute (NPI) based on irradiation in the experimental reactor LVR-15 of the Research Centre Rez [12–14] were used with minor modifications. Short-time irradiation for 1 min with the whole reactor neutron spectrum (S-INAA) was carried out in an irradiation channel located at the outskirts of the active core behind a beryllium reflector, in which fluence rates of thermal, epithermal and fast neutrons were 3.2×10^{13} , 1.1×10^{13} , and $1.1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, respectively. Short-time irradiation for 45 s with epithermal and fast neutrons (S-ENAA) was carried out in the same channel. Thermal neutrons were shielded off by placing the samples into a disk shaped Cd box with 1-mm thick walls. Both short-time irradiation modes were carried out using a pneumatic facility with transport time of 3.5 s. The samples, MES calibrators, blank PE capsules and quality control samples were irradiated individually together with neutron flux monitors (5-mg disks of 0.1% Au–Al foil, IRMM, Belgium, Nuclear reference material IRMM-530a, 0.1 mm thickness) to check the neutron fluence rate stability in time. Long-time irradiation for 2 h with the whole reactor neutron spectrum (L-INAA) was performed in a channel located in the Be reflector, in which fluence rates of thermal, epithermal and fast neutrons were 3.6×10^{13} , 8.4×10^{12} , and $8.6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, respectively. In this case, the samples, MES calibrators, blank PE capsules and quality control samples were stacked together to form a column that was inserted into an aluminium irradiation can. Iron monitors (50-mg disks) were inserted between each set of 5 samples and/or calibrators to determine the axial neutron flux gradient. Gamma-ray spectrometry measurements were performed using various (three coaxial and two planar) HPGe detectors according to the INAA modes applied. All HPGe detectors were interfaced to a Canberra Genie 2000 computer controlled gamma-spectrometry analyzer through a chain of associated linear electronics, which included a Canberra 599 Loss Free Counting module to correct the variable count-rate and dead time. Canberra Genie 2000 software was used for evaluation of gamma-ray spectra. Nuclear parameters of radionuclides measured have

already been given earlier [15], whereas counting conditions and correction factors for evaluation of contributions of interfering nuclear reactions with fast neutrons have been described elsewhere [16]. The irradiated blank PE capsules were used for determination of elemental impurities in the packing material to allow for appropriate corrections. Typically, even a moderate blank signal was significant and was subtracted for the evaluation of contents of Na, Br, Cr, La, and Ce. Irradiations and measurements were carried out within the CANAM research infrastructure (MŠMT project No. LM2011019).

Results and discussion

Quality control

INAA results for quality control samples of various matrices, namely NIST SRMs 1633b Constituent Elements in Coal Fly Ash [17], 2711 Montana Soil [18], and 1547 Peach Leaves [19] are listed in Table 1. Fairly good agreement was obtained between our results and NIST certified values within uncertainty margins, where available, or our results are close to NIST noncertified values. A significantly higher value of Na in NIST SRM 1547 has

been found in our and other laboratories than the NIST certified value. The increase was explained by probable corrosion of the glass bottle, in which the material was distributed by NIST, over the time [20]. Other slight differences between our and NIST values have no systematic nature and thus the accuracy of our results have been proved.

Soil and coal samples

The elemental composition of soil and coal samples from Awdarda is compared with worldwide median values (WMV) in Table 2. For the comparison WMV for 70 elements evaluated by Bowen [21] were chosen, because no such extensive review is available from other authors and Bowen's value do not significantly differ from newer data provided, e.g., by Kabata-Pendias [22]. The comparison is presented in the form of a ratio R of a measured value and corresponding WMV. Thus, $R < 1$ and $R > 1$ indicate element depletion and enrichment, respectively, compared with WMV. The question is, however, how low or high the R value should be to make a significant difference, which could be considered deleterious for the environment and the population living in a studied region. The worldwide ranges are quite broad, sometimes spanning

Table 1 INAA results for quality control materials (mass fractions in mg kg^{-1} unless otherwise stated)

Element (unit)	NIST SRM 1633b [17]		NIST SRM 2711 [18]		NIST SRM 1547 [19]	
	This work ^a	NIST value ^b	This work ^a	NIST value ^b	This work ^a	NIST value ^b
Na (wt%)	0.183 ± 0.006	0.201 ± 0.003	1.08 ± 0.03	1.14 ± 0.03	0.0032 ± 0.0001	0.0024 ± 0.0002
Mg (wt%)	0.513 ± 0.20	0.482 ± 0.008	1.08 ± 0.14	1.05 ± 0.03	0.432 ± 0.018	0.432 ± 0.008
Al (wt%)	15.0 ± 0.6	15.05 ± 0.27	6.42 ± 0.22	6.53 ± 0.09	0.0264 ± 0.0010	0.0249 ± 0.0008
Si (wt%)	24.0 ± 1.2	23.02 ± 0.08	30.4 ± 1.4	30.44 ± 0.19	Not determined	–
Cl	<40	–	110 ± 50	–	337 ± 14	360 ± 19
K (wt%)	1.82 ± 0.08	1.95 ± 0.03	2.27 ± 0.10	2.45 ± 0.08	2.42 ± 0.10	2.43 ± 0.03
Ca (wt%)	1.53 ± 0.12	1.51 ± 0.06	2.89 ± 0.16	2.88 ± 0.08	1.52 ± 0.06	1.56 ± 0.02
Sc	39.5 ± 1.2	(41)	9.5 ± 0.3	(9)	0.041 ± 0.002	(0.040)
Ti (wt%)	0.79 ± 0.04	0.791 ± 0.014	0.31 ± 0.03	0.306 ± 0.023	0.0028 ± 0.0010	–
V	294 ± 10	295.7 ± 3.6	82 ± 4	81.6 ± 2.9	0.36 ± 0.08	0.37 ± 0.03
Cr	192 ± 6	198.2 ± 4.7	44.2 ± 1.6	(47)	0.96 ± 0.10	(1)
Mn	136 ± 8	131.8 ± 1.7	660 ± 30	638 ± 28	100 ± 4	98 ± 3
Fe (wt%)	7.32 ± 0.24	7.78 ± 0.23	2.75 ± 0.08	2.89 ± 0.06	0.021 ± 0.001	(0.0220)
Co	46.3 ± 1.4	(50)	9.3 ± 0.3	(10)	0.067 ± 0.006	(0.070)
Ni	110 ± 30	120.6 ± 1.8	23 ± 12	20.6 ± 1.1	<1.2	0.69 ± 0.09
Cu	<140	112.8 ± 2.6	<120	114 ± 2	4.2 ± 0.3	3.7 ± 0.4
Zn	197 ± 6	(210)	332 ± 10	350.4 ± 4.8	17.2 ± 1.0	17.9 ± 0.4
Ga	52 ± 8	–	15 ± 8	(15)	<0.4	–
As	144 ± 5	136.2 ± 2.6	111 ± 4	105 ± 8	0.086 ± 0.014	0.060 ± 0.018
Se	8.9 ± 0.5	10.26 ± 0.17	1.24 ± 0.22	1.52 ± 0.14	0.123 ± 0.004	0.120 ± 0.009
Br	2.7 ± 0.3	(2.9)	4.8 ± 0.4	(5)	10.1 ± 0.3	(11)

Table 1 continued

Element (unit)	NIST SRM 1633b [17]		NIST SRM 2711 [18]		NIST SRM 1547 [19]	
	This work ^a	NIST value ^b	This work ^a	NIST value ^b	This work ^a	NIST value ^b
Rb	133 ± 6	(140)	112 ± 4	(110)	17.6 ± 1.0	(19)
Sr	880 ± 60	1041 ± 14	244 ± 16	245.3 ± 0.7	54 ± 3	53 ± 4
Ag	<0.6	–	4.3 ± 0.6	4.63 ± 0.39	<30	–
Cd	<5	0.784 ± 0.006	34 ± 3	41.70 ± 0.25	<0.6	(0.03)
Sb	4.3 ± 0.2	(6)	17.3 ± 0.6	19.4 ± 1.8	0.019 ± 0.005	(0.02)
I	<1.1	–	2.9 ± 0.6	(3)	0.285 ± 0.08	(0.3)
Cs	9.4 ± 0.3	(11)	5.96 ± 0.20	(6.1)	0.068 ± 0.005	–
Ba	770 ± 80	709 ± 27	680 ± 40	726 ± 38	111 ± 8	124 ± 4
La	83.5 ± 1.6	(94)	35.3 ± 1.2	(40)	9.8 ± 0.3	(9)
Ce	183 ± 6	(190)	71.2 ± 2.2	(69)	9.4 ± 0.6	(10)
Nd	81 ± 4	(85)	25.4 ± 2.4	(31)	6.3 ± 0.6	(7)
Sm	17.5 ± 0.8	(20)	5.63 ± 0.24	(5.9)	1.13 ± 0.04	(1)
Eu	3.79 ± 0.12	(4.1)	1.03 ± 0.04	(1.1)	0.19 ± 0.01	(0.17)
Tb	2.54 ± 0.10	(2.6)	0.78 ± 0.03	–	0.11 ± 0.06	(0.1)
Dy	19.1 ± 1.0	(17)	6.1 ± 0.6	(5.6)	0.62 ± 0.04	–
Ho	3.60 ± 0.20	(3.5)	1.40 ± 0.16	(1)	0.09 ± 0.01	–
Tm	1.50 ± 0.08	(2.1)	0.66 ± 0.04	–	0.025 ± 0.004	–
Yb	7.1 ± 0.3	(7.6)	2.96 ± 0.02	(2.7)	0.14 ± 0.02	(0.2)
Lu	1.20 ± 0.10	(1.2)	0.57 ± 0.06	–	0.017 ± 0.004	–
Hf	6.70 ± 0.24	(6.8)	7.9 ± 0.3	(7.3)	0.079 ± 0.006	–
Ta	1.69 ± 0.08	(1.8)	1.24 ± 0.06	–	0.005 ± 0.002	–
W	4.8 ± 0.3	(5.6)	3.0 ± 0.3	(3)	<0.04	–
Th	23.7 ± 0.8	25.7 ± 1.3	13.0 ± 0.4	(14)	0.053 ± 0.004	(0.05)
U	9.3 ± 0.4	8.79 ± 0.36	3.15 ± 0.14	(2.6)	0.030 ± 0.010	(0.015)

^a Arithmetic mean ($n = 2-4$) ± expanded uncertainty (coverage factor $k = 2$)

^b Certified values are given with uncertainties, noncertified values are given in parenthesis

Table 2 Comparison of elemental composition (mass fractions in mg kg⁻¹ unless otherwise stated) of soil and coal from the village of Awdarda with worldwide median values (WMV)

Element	Soil ^a	WMV soil ^b [21]	Ratio soil ^c	Black coal ^a	Brown coal ^a	WMV coal ^b [21]	Ratio coal ^c	
							Black	Brown
Na	1160 ± 18	5000 (150–25,000)	0.23	633 ± 10	277 ± 5	400 (100–6000)	1.58	0.69
Mg (wt%)	0.76 ± 0.06	0.500 (0.04–9.0)	1.52	0.37 ± 0.05	0.52 ± 0.06	0.2 (0.01–0.35)	1.85	2.60
Al (wt%)	8.51 ± 0.14	7.1 (1.0–30.0)	1.20	8.37 ± 0.14	8.21 ± 0.14	1.0 (0.3–3.0)	8.37	8.21
Si (wt%)	28.1 ± 0.6	33.0 (25.0–41.0)	0.85	30.4 ± 0.7	29.4 ± 0.7	3.0 (0.5–11.0)	10.1	9.80
Cl	<22	100 (8–1800)	–	14 ± 5	<17	500 (10–8000)	0.03	–
K (wt%)	0.353 ± 0.010	1.40 (0.008–3.7)	0.25	0.185 ± 0.008	0.168 ± 0.006	0.3 (0.005–0.65)	0.62	0.56
Ca (wt%)	0.90 ± 0.03	1.50 (0.07–50.0)	0.60	0.67 ± 0.03	0.67 ± 0.03	0.15 (0.05–3.7)	4.47	4.47
Sc	24.8 ± 0.4	7 (0.5–55)	3.54	21.0 ± 0.3	18.0 ± 0.3	5 (0.5–30)	4.20	3.60
Ti (wt%)	1.096 ± 0.023	0.50 (0.015–2.50)	2.19	0.795 ± 0.016	0.544 ± 0.013	0.05 (0.02–0.18)	15.9	10.9
V	229 ± 4	90 (3–500)	2.54	275 ± 5	150 ± 3	20 (2–130)	13.8	7.50
Cr	206 ± 3	70 (5–1500)	2.94	87.4 ± 1.5	71.1 ± 1.3	10 (2–400)	8.74	7.11
Mn	1237 ± 24	1000 (20–10,000)	1.24	54.1 ± 1.5	41.0 ± 1.2	50 (3–900)	1.08	0.82
Fe (wt%)	7.58 ± 0.12	4.0 (0.2–55.0)	1.90	2.30 ± 0.04	2.82 ± 0.04	0.8 (0.05–4.3)	2.88	3.53
Co	54.4 ± 0.8	8 (0.05–65)	6.80	8.34 ± 0.13	14.30 ± 0.22	4 (1–90)	2.09	3.58
Ni	78 ± 11	50 (2–750)	1.56	27 ± 9	53 ± 8	10 (1–80)	2.70	5.30

Table 2 continued

Element	Soil ^a	WMV soil ^b [21]	Ratio soil ^c	Black coal ^a	Brown coal ^a	WMV coal ^b [21]	Ratio coal ^c	
							Black	Brown
Cu	<110	30 (2–250)	–	<90	<90	15 (3–180)	–	–
Zn	91.3 ± 1.6	90 (1–900)	1.01	488 ± 8	184 ± 3	50 (8–500)	9.76	3.68
Ga	22.2 ± 2.4	20 (2–100)	1.11	33.8 ± 2.4	29.8 ± 2.3	5 (0.3–30)	6.76	5.96
As	9.03 ± 0.17	6 (0.1–40)	1.51	2.03 ± 0.08	5.62 ± 0.12	5 (0.3–93)	0.41	1.12
Se	<0.9	0.4 (0.01–12)	–	1.37 ± 0.16	0.82 ± 0.14	3 (0.04–10)	0.46	0.27
Br	1.76 ± 0.22	10 (1–110)	0.18	<0.4	0.87 ± 0.15	5 (1–50)	–	0.17
Rb	46.6 ± 1.8	150 (20–1000)	0.31	21.5 ± 1.3	21.7 ± 1.1	20 (1–150)	1.08	1.09
Sr	<50	250 (4–2000)	0.20	<50	48 ± 7	150 (20–1000)	0.33	0.32
Ag	<0.6	0.05 (0.01–8)	–	<0.5	<0.5	0.05 (0.01–3.7)	–	–
Cd	<4	0.35 (0.01–2)	–	<6	<4	0.2 (<0.01–22)	–	–
Sb	0.55 ± 0.04	1 (0.2–10)	0.55	0.61 ± 0.04	0.47 ± 0.03	1 (0.1–9)	0.61	0.47
I	7.6 ± 0.4	5 (0.1–25)	1.52	<0.8	<0.8	1 (0.1–14)	–	–
Cs	3.17 ± 0.06	4 (0.3–20)	0.79	1.41 ± 0.03	1.14 ± 0.05	0.3 (0.03–9)	4.70	3.80
Ba	321 ± 19	500 (100–3000)	0.64	218 ± 18	138 ± 17	200 (1–3000)	1.09	0.69
La	39.7 ± 0.6	40 (2–180)	0.99	124.9 ± 2.0	50.0 ± 0.8	5 (0.3–40)	25.0	10.0
Ce	99.3 ± 1.5	50 (3–170)	1.99	247 ± 4	131.7 ± 2.0	12 (11–30)	20.6	11.0
Pr	10.7 ± 1.5	7 (3–12)	1.53	29.5 ± 2.0	12.1 ± 1.3	1.8	16.4	6.72
Nd	37.1 ± 1.2	35 (4–63)	1.06	103 ± 3	52.2 ± 1.5	9 (4–36)	11.4	5.80
Sm	8.91 ± 0.18	4.5 (0.6–23)	1.98	23.9 ± 0.5	13.6 ± 0.3	1.2 (0.2–6)	19.9	11.3
Eu	2.10 ± 0.03	1 (0.1–3.2)	2.10	4.08 ± 0.07	1.90 ± 0.3	0.5 (0.1–0.9)	8.16	3.80
Tb	1.31 ± 0.03	0.7 (0.1–1.6)	1.87	3.85 ± 0.06	2.28 ± 0.04	0.22 (0.1–2)	17.5	10.4
Dy	9.3 ± 0.3	5 (2–12)	1.86	28.7 ± 0.5	16.7 ± 0.3	2.5 (0.2–5)	11.5	6.68
Ho	1.87 ± 0.06	0.6 (0.4–2)	3.12	5.28 ± 0.12	3.15 ± 0.08	0.19 (0.1–0.4)	27.8	16.6
Tm	0.93 ± 0.03	0.6 (0.3–1.2)	1.55	3.63 ± 0.06	2.05 ± 0.04	0.06	60.5	34.2
Yb	4.11 ± 0.10	3 (0.04–12)	1.37	14.5 ± 0.3	7.48 ± 0.14	0.37 (0.1–1.5)	39.2	20.2
Lu	0.635 ± 0.021	0.4 (0.1–0.7)	1.59	2.39 ± 0.04	1.14 ± 0.02	0.07 (0.01–0.4)	34.1	16.3
Hf	7.63 ± 0.13	6 (0.5–34)	1.27	23.1 ± 0.4	12.99 ± 0.22	0.9 (0.1–4)	25.7	14.4
Ta	1.65 ± 0.04	2 (0.4–6)	0.83	8.04 ± 0.13	4.96 ± 0.08	0.2 (0.06–8)	40.2	24.8
W	1.32 ± 0.09	1.5 (0.5–83)	0.88	2.77 ± 0.12	2.04 ± 0.09	0.5 (0.1–4)	5.54	4.08
Th	9.09 ± 0.14	9 (1–35)	1.01	16.6 ± 0.3	10.51 ± 0.17	2 (0.1–10)	8.30	5.26
U	1.96 ± 0.04	2 (0.7–9)	0.98	7.47 ± 0.15	3.43 ± 0.07	1 (0.005–200)	7.47	3.43

^a Measured value ± combined uncertainty (coverage factor $k = 1$)

^b Median (range)

^c Measured value/WMV

over two orders of magnitude, even for major constituents (elements with mass fractions >1 wt%), especially for soil, obviously due to different soil types, different bedrock composition, weathering conditions, etc. The large scatter is more frequent for minor constituents and trace elements. Therefore, for the purpose of this work, the R values <0.1 and >10 are considered significantly different from WMV, thus being of environmental concern. The R values were not calculated for elements with contents below the limit of detection (LOD).

The elemental composition of soil collected at Awdarda does not deviate markedly from the soil WMV. However, a

more detailed inspection of data for the rare earth elements (REE) has been performed regarding their high levels found in the Awdarda coal (see the following paragraph). It has been found that the REE levels in Awdarda soil are similar or slightly higher than those found in soil from an area in the Czech Republic contaminated by REE from emissions of a phosphate fertilizer plant [14], and possibly exceeding existing regulatory limits, e.g., a Dutch maximum permissible concentration for Ce in soil is 53 mg kg⁻¹ [23]. The main purpose of soil analysis was to estimate the transfer of the contained elements into locally grown and consumed cereals and pulses.

In both Awdarda coal samples, the mass fractions of several elements, such as Al, Si, Ti, V, and namely most REE, are much higher than the WMV for coal. The relatively high contents of major elements in both coal samples, particularly Al and Si (about 8 and 30 wt%, respectively), corresponding to about 80 wt% of the sum of oxides of all major elements, indicate that classification of the samples denoted as brown or black coal among coal may be not quite proper due to very high mineral fraction represented probably mainly by clay minerals. For proper identification of the type of carbonaceous sediments, organic petrology of both samples was studied by optical microscopy. Both samples are quite similar and have been classified as carbonaceous sediments dominated by clay minerals with admixture of carbonates, silica, quartz, pyrite, and other accessory minerals. The organic fraction is about 35 vol%, and based on vitrinite reflectance it corresponds to sub-bituminous coal or transition between brown and black coal. Detailed maceral composition indicates origin of the sediments in a wet, possibly quiet lacustrine environment (I. Sýkorová unpublished data). This characterization agrees with published description of coal-bearing sediments situated at the Chilga Basin. The Chilga coal-bearing sediments represent intervolcanic sediments between two lava flows, deposited on the Eocene–Oligocene (~30 Ma) basaltic substratum and overlain by the upper basalt at ~8 Ma. Centimeter to meter-thick coal beds are interbedded in the carbonaceous sediments (shales, mudstones and claystones) deposited from a standing water environment, possibly from lakes in a floodplain. Mineral fractions (ash contents) of Chilga coals are mostly below 50 wt% [24]. The studied Awdarda “coal” samples were probably collected from the carbonaceous coal-bearing sediments, not directly from a coal seam. For simplicity reasons, however, designation of the samples as coal will continue in the further text. The elemental

composition of Chilga coals and other Ethiopian coal deposits was not known prior to this study. Only results of proximate analysis (moisture, volatile matter, ash content, fixed carbon, calorific value), sulfur content, and vitrinite reflectance have been published for the Ethiopian coals [24].

As for the high levels of REE found in the studied coals, it is known that REE occur in coal ash at concentrations comparable to or even higher than those in conventional economic deposits, such as monazite- or bastnaesite-type ore [25, 26]. A detailed geological survey is needed to find out whether the REE production from coal ash of the North Gondar region would be economically feasible. Exploration of Ethiopian coal resources started several years ago to find an alternative to current main sources of energy—wood, oil and hydroelectric power [24]. Presently, the coal is burnt in households for cooking and heating, so that the population concerned may be exposed to dust and aerosols rich with REE. Discussion of possible health effects of the elevated levels of REE and other elements in Awdarda coal and soil is presented later in this section in the context of data obtained for crops consumed in Awdarda.

Water

It follows from the data presented in Table 3 that there are no significant differences of element concentrations in Awdarda fresh water from WMV, except for somewhat higher concentration of vanadium in the studied region, which is still within the range of values used to establish WMV. The low chlorine value determined suggests that most of the element was lost on repeated evaporation of HNO₃ acidified sample.

None of the measured values exceeds the WHO Guidelines values for drinking-water quality [27]. There is no recommendation concerning vanadium in the

Table 3 Comparison of element concentrations in fresh water in $\mu\text{g L}^{-1}$ with worldwide median values (WMV) and WHO Guidelines values

Element	This work ^a	WMV ^b	WHO ^c	Ratio ^d
Na	13,740 ± 240	6000 (700–25,000)	–	2.29
Mg	18,300 ± 400	4000 (400–6000)	–	4.58
Al	353 ± 12	300 (8–3500)	900	1.18
Si	23,500 ± 600	7000 (500–12,000)	–	3.36
Cl	46 ± 5	7000 (1000–35,000)	5000	0.01
K	710 ± 160	2200 (500–10,000)	–	0.32
Ca	52,000 ± 1200	15,000 (2000–120,000)	–	3.47
Sc	0.087 ± 0.002	0.01 (0.004–0.04)	–	8.70
Ti	<40	5 (3–18)	–	–
V	6.48 ± 0.17	0.5 (0.01–20)	–	13.0
Cr	0.66 ± 0.03	1 (0.1–6)	50	0.66
Mn	15.6 ± 0.6	8 (0.02–130)	400	1.95
Fe	313 ± 8	500 (10–1400)	2000	0.63

Table 3 continued

Element	This work ^a	WMV ^b	WHO ^c	Ratio ^d
Co	0.475 ± 0.012	0.2 (0.04–8)	–	2.38
Ni	0.84 ± 0.13	0.5 (0.02–27)	70	1.68
Cu	<25	3 (0.2–30)	2000	–
Zn	12.4 ± 0.3	15 (0.2–100)	–	0.83
Ga	<13	0.09	–	–
As	<0.16	0.5 (0.2–230)	10	–
Se	0.81 ± 0.03	0.2 (0.02–1000)	40	4.05
Br	38.8 ± 11	14 (0.05–55)	–	2.77
Rb	0.84 ± 0.06	1 (0.6–9)	–	0.84
Sr	201 ± 5	70 (3–1000)	–	2.87
Ag	<0.017	0.3 (0.01–3.5)	–	–
Cd	<1	0.1 (0.01–3)	3	–
Sb	0.660 ± 0.019	0.2 (0.01–5)	20	3.30
I	0.22 ± 0.04	2 (0.5–7)	–	0.11
Cs	0.0551 ± 0.0017	0.02 (0.005–1)	–	2.75
Ba	26.2 ± 1.2	10 (<3–150)	700	2.62
La	0.215 ± 0.007	0.1 (<0.05–0.8)	–	2.15
Ce	0.544 ± 0.015	0.2 (0.1–0.2)	–	2.72
Nd	0.253 ± 0.023	0.15 (<0.06–0.25)	–	1.69
Sm	0.0602 ± 0.0013	0.06? (0.01–0.12)	–	1.00
Eu	0.0154 ± 0.0005	0.006 (0.002–0.009)	–	2.57
Tb	0.0094 ± 0.0008	0.003 (0.001–0.005)	–	3.13
Dy	<0.08	–	–	–
Ho	<0.07	–	–	–
Tm	<0.005	–	–	–
Yb	0.029 ± 0.003	0.01 (0.005–0.2)	–	2.90
Lu	0.0042 ± 0.0010	0.003 (0.002–0.005)	–	1.40
Hf	0.0244 ± 0.0010	0.01 (0.005–0.13)	–	2.44
Ta	0.0040 ± 0.0008	<0.002	–	–
W	<0.3	0.03 (<0.02–0.1)	–	–
Th	0.0211 ± 0.0008	0.03 (0.007–0.1)	–	0.70
U	0.252 ± 0.006	0.4 (0.002–5)	30	0.63

^a Measured value ± combined uncertainty (coverage factor $k = 1$)

^b Median (range) by [21]

^c WHO Guidelines values [27]

^d Measured value/WMV

Guidelines. According to the Toxicological profile for vanadium, issued by the Agency for Toxic Substances and Disease Registry of the U.S. Department of Health and Human Services [28], common vanadium concentrations (mean, median, or typical values since 1960s) in drinking water range from 1 to 4.3 $\mu\text{g L}^{-1}$ in the USA. An intermediate-duration oral minimal risk level of 0.01 $\text{mg V kg}^{-1} \text{d}^{-1}$ has also been established. In conclusion, elemental composition of Awdarda fresh water does not indicate any health risk associated with its use for drinking and cooking.

Crops

The elemental compositions of crops studied in this work are given in Table 4. Knowledge of element contents in these agricultural products, which form a significant part of human diet in Awdarda, is important for two reasons. First is to find out whether crops do not contain elevated levels of toxic trace elements, second is that there are commonly lacking mineral elements, namely Mg, Ca, Fe, Cu, Zn, Se and I in human diets, which may cause mineral malnutrition [29]. Table 4 shows that, in most cases, the highest

Table 4 Comparison of element contents for crops (mass fractions in $\mu\text{g kg}^{-1}$ unless otherwise stated, dry matter basis, value \pm combined uncertainty, coverage factor $k = 1$) with literature values

Element	Chickpea	Finger millet	Sorghum	Barley	Literature values ^a
Na (mg kg^{-1})	18.9 \pm 0.3	26.4 \pm 0.4	20.5 \pm 0.3	35.4 \pm 0.6	–
Mg (mg kg^{-1})	1430 \pm 30	1590 \pm 40	1600 \pm 30	1070 \pm 30	–
Al (mg kg^{-1})	29.1 \pm 1.2	811 \pm 13	78.8 \pm 1.8	561 \pm 9	31
Si (mg kg^{-1})	<500	900 \pm 300	1280 \pm 240	3180 \pm 170	–
Cl (mg kg^{-1})	790 \pm 13	583 \pm 10	552 \pm 9	572 \pm 9	–
K (mg kg^{-1})	8560 \pm 170	5200 \pm 160	5040 \pm 110	5060 \pm 130	–
Ca (mg kg^{-1})	2250 \pm 50	4220 \pm 80	210 \pm 10	473 \pm 15	–
Sc	6.9 \pm 0.2	291 \pm 8	171 \pm 5	169 \pm 5	(14)
Ti (mg kg^{-1})	<7	92 \pm 8	9 \pm 3	73 \pm 3	0.9
V	85 \pm 18	2240 \pm 600	213 \pm 20	1670 \pm 40	7–10
Cr	<50	1950 \pm 70	1640 \pm 60	1860 \pm 60	4–20
Mn (mg kg^{-1})	26.3 \pm 0.5	273 \pm 4	11.75 \pm 0.23	20.5 \pm 0.4	16–103
Fe (mg kg^{-1})	63.6 \pm 2.1	930 \pm 30	553 \pm 15	553 \pm 15	17–50 (145–182)
Co	105 \pm 3	516 \pm 14	614 \pm 16	314 \pm 9	1.1–380
Ni (mg kg^{-1})	1.6 \pm 0.3	2.1 \pm 0.6	<1.5	<1.2	0.15–1.28
Cu (mg kg^{-1})	7.5 \pm 1.1	12 \pm 2	2.9 \pm 0.9	5.6 \pm 1.2	1.3–10
Zn (mg kg^{-1})	28.0 \pm 0.7	19.4 \pm 0.5	17.1 \pm 0.5	23.9 \pm 0.6	23–37
Ga (mg kg^{-1})	<0.15	0.42 \pm 0.06	<0.3	<0.17	–
As	<18	99 \pm 4	80 \pm 5	56 \pm 3	3–10
Se	54 \pm 13	<60	<70	<60	1–1040
Br (mg kg^{-1})	8.11 \pm 0.13	19.5 \pm 0.3	8.31 \pm 0.14	10.36 \pm 0.17	2.1–6.4
Rb (mg kg^{-1})	4.75 \pm 0.15	2.95 \pm 0.13	2.87 \pm 0.12	2.27 \pm 0.11	4
Sr (mg kg^{-1})	8.9 \pm 0.4	14.2 \pm 0.7	<3	<3	0.48–2.3
Ag	<15	<40	<40	25 \pm 8	<0.5–2.7
Cd	<400	<500	<400	<400	20–70
Sb	<3	<9	<9	<7	0.5
I	<60	<140	<80	86 \pm 23	5–38
Cs	6.2 \pm 1.5	39 \pm 4	28 \pm 4	20 \pm 3	–
Ba (mg kg^{-1})	4.8 \pm 0.6	27.5 \pm 1.5	3.0 \pm 0.9	2.7 \pm 0.8	3.2
La	<2	483 \pm 9	285 \pm 6	337 \pm 6	1.7–16.8 (85–285)
Ce	40 \pm 19	980 \pm 30	970 \pm 30	609 \pm 20	3.4–26.9 (96–461)
Nd	<300	490 \pm 50	<300	<300	0.9–6.8 (<20)
Sm	3.3 \pm 0.8	117 \pm 2	65.0 \pm 1.4	52.1 \pm 0.9	0.2–1.1 (5.0–20.1)
Eu	0.60 \pm 0.18	25.2 \pm 1.1	16.6 \pm 1.0	15.4 \pm 0.8	<0.1–0.3 (1.0–3.4)
Tb	<1.6	17.9 \pm 1.4	8.6 \pm 1.2	9.5 \pm 0.9	<0.1–0.1 (<1)
Dy	<23	66 \pm 20	<20	45 \pm 10	0.1–0.7
Ho	<13	22 \pm 5	<17	<13	<0.1–0.1 (3.0)
Tm	<14	<15	<18	<17	<0.1–1.8 (<4)
Yb	<20	47 \pm 7	<30	<30	<0.1–1.5 (6.9)
Lu	<3	9.0 \pm 1.4	5.3 \pm 1.3	5.9 \pm 1.7	<0.1–1.5 (1.1)
Hf	<3	92 \pm 4	47 \pm 3	46 \pm 3	0.6 (7–36)
Ta	<1.2	23.9 \pm 2.0	10.7 \pm 1.7	9.1 \pm 1.3	1.1–5 (0.9–3.9)
W	<20	<22	<30	<21	6
Th	4.7 \pm 1.4	95 \pm 3	62 \pm 3	47.3 \pm 1.7	(10.2–43.1)
U	<9	<15	<11	<10	(<15)

^a Mean values or range in cereal grains: for most elements in wheat, except for Ta (wheat and barley), Br and I (barley), and Ni, Rb, and Ag (not specified cereals) by Kabata-Pendias [22]; in parenthesis contents of REE and terrigenous elements Sc, Fe, Hf and Ta in wheat chaff from an area polluted by emissions from a phosphate fertilizer plant [14]

contents of mineral elements, both macro- and trace or microelements, were found in finger millet, which is widely grown as a cereal in the arid areas of Africa and Asia. Finger millet, in Ethiopia called *dagusa*, probably originated in the highlands of Uganda and Ethiopia and has been grown there for thousands of years. As a staple food, finger millet is valuable for its high content of minerals and the amino acid methionine, which is often lacking in the diet of poor people [30]. It is difficult to judge whether the element contents found in the crops analyzed are excessive or scarce, because there is a paucity of data from other regions. For a general comparison, ranges or mean values of element contents compiled in literature for cereals (barley and wheat) from various parts are presented in Table 4. This comparison shows that highly elevated contents of terrigenous elements, namely Al, Ti, V, Cr, Fe, Co, Hf, Th and REE (incl. Sc), were found in all Awdarda cereals, but not in the legume (chickpea). This seems to suggest that the high levels of the above elements are due to external contamination. In analyses of the cereals, whole grains including their casings (chaff) were used for sample preparation without any effort to remove the possible surface contamination. In the case of chickpea, seeds separated from possibly contaminated pods were used. For wheat from a REE contaminated area, substantially higher levels of REE and Th were found in chaff compared to whole grains washed with distilled water [14]. The wheat chaff data reported by Kučera et al. [14] is also presented in Table 4 for comparison. It is evident that Awdarda cereals must be much more contaminated, possibly due to the excavation of the REE rich coal-bearing sediments and their local combustion.

Finger millet was analyzed in the “as received” state thanks to the small size of the seeds. The other crops with larger seeds were pulverized prior to analysis to obtain representative sample. The milling process, however, potentially contaminated the material with elements

abundant in the steel blade. A comparison of results for milled and whole sorghum samples from different locality (data not presented in this study) indicated the milled sample was to some extent contaminated with Cr. Unfortunately, it is not easy to estimate a degree of contamination for individual crops with different hardness, a parameter with high impact on the amount of blade abrasion. In the subsequent discussion of possible health effect the emphasis is given on finger millet to eliminate possible effect of sample contamination.

Possible health effects of pollution in the Awdarda environment

The high levels of REE and some other, mostly terrigenous elements in coal and cereals from the village of Awdarda should draw the attention as one of possible reasons for the health problems in the local population. Since coal is burnt in households for cooking and heating in open stoves, the population may be exposed to dust and aerosols rich in those elements. The cereals analyzed represent a substantial part of diet of Awdarda population, except for barley used mostly only for the production of local beer.

Information on toxicology of the critical elements is presented in Table 5. It has mostly been adopted from documents available at the Toxic Substances Portal of the Agency for Toxic Substances and Disease Registry (ATSDR) of the U.S. Department of Health and Human Services [28]. No information has been provided by ATSDR for REE and some other elements (Ti, Fe, Hf), but for REE the information is provided in a document of the U.S. Environmental Protection Agency [31] and other literature [32–36].

It is evident that the adverse health effects summarized in Table 5 for selected elements found at elevated levels in Awdarda cereals generally do not include the disabilities occurring in the North Gondar region, i.e., disabilities of

Table 5 Toxicological facts for elements found at elevated levels in Awdarda cereals

Element	Health effect (noncarcinogenic)	Carcinogenicity ^a	Regulations, guidelines ^b
Al	Excessive inhalation of Al can cause lung problems and affect functions of nervous system. Excessive Al storage in people with kidney disease may develop bone or brain diseases. Development of Alzheimer’s disease is uncertain	Not evaluated by DHHS and EPA	RfD not derived; intermediate- and chronic-duration oral MRL both 1 mg kg ⁻¹ d ⁻¹
V	Excessive inhalation of V can cause lung damage. Some V compounds can cause nausea, mild diarrhea, and stomach cramps. In animal tests, ingestion of V compounds caused decrease in the number of red blood cells, increased blood pressure, and mild neurological effects	Not classified as carcinogenic by DHHS and EPA; according to IARC possibly carcinogenic	RfD not derived; intermediate-duration oral MRL 0.01 mg kg ⁻¹ d ⁻¹

Table 5 continued

Element	Health effect (noncarcinogenic)	Carcinogenicity ^a	Regulations, guidelines ^b
Cr	Excessive inhalation of Cr(VI) can cause nose irritation and breathing problems such as asthma. In animal tests, ingestion of Cr(VI) caused irritation and ulcers in stomach and small intestine, anemia, and damage to male reproductive system. Cr(III) is much less toxic. Allergic skin reactions can occur to both Cr(VI) and Cr(III)	Cr(VI) classified as carcinogenic by DHHS, IARC, and EPA	Cr(VI): chronic oral RfD $0.003 \text{ mg kg}^{-1} \text{ d}^{-1}$ Cr(III): chronic oral RfD $1.5 \text{ mg kg}^{-1} \text{ d}^{-1}$
Co	Exposure to high Co levels can result in lung and heart effects and dermatitis. In animal tests, liver and kidney negative effects have also been observed	Not classified as carcinogenic by DHHS and EPA; according to IARC possibly carcinogenic	RfD not derived; intermediate-duration oral MRL $0.01 \text{ mg kg}^{-1} \text{ d}^{-1}$
As	The observed health effects apply to inorganic As, organic As is less toxic. Ingesting very high levels of As can be lethal. Excessive inhalation can irritate throat and lungs. Lower As levels can cause nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, “pins and needles” sensation in hands and feet. Long-term low level intake can cause skin darkening and formation of warts. Skin contact may cause redness and swelling. Long-term exposure in children may decrease their IQ. Exposure during pregnancy can injure both mother and child. As also transfers into breast milk	As (inorganic) classified as carcinogenic by DHHS, IARC, and EPA	Chronic oral RfD $0.0003 \text{ mg kg}^{-1} \text{ d}^{-1}$ (inorganic As)
REE	Pulmonary diseases such as pneumoconiosis from occupational exposure to REE have been documented. Adverse effects include cell growth inhibition and differentiation, cytogenetic effects and tissue/organ-specific bioaccumulation and toxicity (lung, blood, liver, brain, bones), and prooxidant processes. Deviations from normal values were observed in some blood biochemical indices in population from REE-high regions indicating possible negative effects to liver, kidney, and immunity	Assigned a weight-of-evidence description of “inadequate information to assess carcinogenic potential” by EPA	See [31] for a list of available provisional subchronical RfD for individual REE in various chemical forms; total REE (incl. Sc and Y) doses $>0.1 \text{ mg kg}^{-1} \text{ d}^{-1}$ can damage human health [33]
Th	Health effects from exposure to Th may be partly due to its radioactivity. Long-term low level intake by inhalation may damage lungs. Deposition of Th in body cells may change the genetic material, but it is not known to cause infertility and birth defects	Carcinogenic risk in miners not significant, but appreciable with medical use of Th (IARC)	system of radiation exposure limits not specific to Th, but including other radioactive elements

Excerpts from toxicological profiles and fact sheets (ToxFAQs™) released by the Agency for Toxic Substances and Disease Registry (ATSDR) of the U.S. Department of Health and Human Services (DHSS) and available through the ATSDR Toxic Substances Portal [28], except for REE information summarized from the document EPA/600/R-12/572 of the U.S. Environmental Protection Agency [31] and literature [32–36]

^a Classification according to DHSS, EPA, and the International Agency for Research on Cancer (IARC) [28]

^b RfD (Reference Dose) is a value derived by EPA as an estimate of daily human exposure likely to be without an appreciable risk of deleterious noncancer effects during a lifetime; MRL (Minimal Risk Level) is a value derived by ATSDR as an estimate of daily human exposure likely to be without an appreciable risk of adverse noncancer health effects over a specified route and duration of exposure

lower and upper limbs, blindness, hearing loss, and mental retardation. To judge whether consumption of the contaminated cereals could be associated with a serious health risk, amounts of cereals necessary to reach the regulation intake doses for the critical elements presented in Table 5

were calculated. Finger millet was chosen for this calculation, because it well represents staple food consumed in Awdarda. Its analysis in the as received state without milling eliminated possible contamination from the steel blade. Finger millet was preferred also because of the most

complete list of elements determined above LOD (namely REE, cf. Table 4). Assuming a body weight of 50 kg, reaching the regulation intake doses would require daily consumption of the analyzed finger millet (whole grains including the externally contaminated chaff) in following approximate amounts (in kg): Al 0.06, V 0.22, Cr(III) 385, Cr(VI) 0.77, Co 0.97, As 0.15, and total REE 1.95. According to the results, it seems that the most serious risk is presented by Al, followed by As and V. We are not able to assess intake of these most critical elements by inhalation, either from dust or the indoor coal combustion.

The finding that the high levels of Al in Awdarda cereals may pose a serious health risk has been surprising due to its ubiquity in the environment. Detailed inspection of the ATSDR Toxicological Profile for Aluminium [28] has drawn our attention to reported neurological and musculoskeletal effects of Al. Dialysis encephalopathy syndrome (dialysis dementia), a degenerative neurological disease characterized by the gradual loss of motor, speech, and cognitive functions, has been well known in patients with reduced renal function who accumulated Al in the brain as a result of long-term intravenous hemodialysis therapy. Excessive exposure to Al may have also been associated with unusually high prevalence of two neurodegenerative diseases—amyotrophic lateral sclerosis and Parkinsonism dementia—in Guam, Southwest New Guinea, and the Kii Peninsula of Honshu Island, Japan. This may have been related to the natural abundance of highly bioavailable Al compounds coupled with long-term dietary deficiencies of Ca and Mg. On the other hand, it has not been proven that Al is a causative agent of Alzheimer's disease, although it may play a role in its development. Skeletal changes (e.g., osteomalacia) due to long-term use of Al-containing antacids have been reported.

An interesting reference for the Awdarda study may be the occurrence of the endemic arsenosis caused by indoor combustion of high-As coal (10^2 – 10^4 mg kg⁻¹) and related contamination of crops and food known from Guizhou Province, China [37]. However, As content in the Awdarda coal is much lower, and the reason for high As levels in Awdarda cereals is actually unclear. Moreover, the long-term low level intake of As is commonly associated with typical unmistakable dermal effects, which accompanied also the coal-burning arsenosis. We have no information on dermal effects attributable to arsenosis from Awdarda. Chronic As exposure may also be associated with intellectual deficits in children [28], but probably not to the point of mental retardation encountered in the North Gondar population.

Thorough reinspection of the ATSDR Toxicological Profile for Vanadium [28] led us to conviction that the health problems in Awdarda cannot be attributed to excessive exposure of Awdarda population to V.

Suspected fluorine poisoning

The fact that the health problems in the North Gondar include locomotor disabilities and mental retardation, and a suspicion that at least some of these problems may be associated with indoor combustion of coal (carbonaceous claystone), led us to considering, besides the possible harmful effects of high levels of Al, also an analogy with the coal-burning endemic fluorosis known from China. Indoor burning of coal mixed with fluorine-rich clay causes contamination of stored cereals and vegetables, similarly to the above discussed case of As contamination. The excess fluorine intake leads to dental fluorosis and the more serious skeletal fluorosis (osteofluorosis) with associated deformities and disabilities [38]. It may also increase probability of developing low IQ in children [39]. To check a possibility of a high fluorine content in the studied Awdarda coals and soil, an attempt was made to quickly assay fluorine via ²⁰F (half-life 11 s, analytical line 1633.6 keV) using the above described S-INAA procedure with a modified irradiation–decay–counting time regime (10–18–20 s) as described by Havránek et al. [40]. A high background from mainly ²⁸Al did not allow detection of ²⁰F in most analyzed samples (soil and both coals in triplicates) except for one aliquot of the Awdarda brown coal, where F was determined just above the LOD of about 2000 mg kg⁻¹. Average fluorine contents in coal range from 80 to 150 mg kg⁻¹ [41]. Additional analyses are required to verify such an extreme fluorine level, and precisely and accurately determine F contents also in other Awdarda samples including the REE contaminated cereals. Preparation for analyses using two independent, more sensitive techniques available at NPI, instrumental photon activation analysis [41] and PIGE [40], is underway.

More information about the possible reasons of the health problems in the North Gondar, and specifically in the Awdarda population, could be derived from air pollution monitoring to assess the effect of the main suspected influencing factor, i.e., in-house burning of local coals. Unfortunately, no aerosol sampling device was available for this study. To be able to use suitable air pollution biomonitors, such as lichens, mosses, etc., a survey will be done whether some of the biomonitors are available in the examined and background (unpolluted) regions for a continuation of this study.

Conclusions

The elemental composition of several compartments of the environment in the village of Awdarda in the North Gondar, Ethiopia, and staple foods from this region was determined using INAA to find out whether the element

contents can be associated with the existing health problems in the local population. The results clearly indicate strong contamination of Awdarda cereals by terrigenous elements, possibly from excavation and indoor combustion of local coal-bearing sediments. A straightforward indication has not been obtained that the elemental composition of the compartments of the environment studied is associated with severe health problems of a part of the North Gondar population. However, high excess of aluminium found in the studied Awdarda cereals, due to its known association with neurological and musculoskeletal effects, would deserve more attention including clinical and biochemical investigations in the disabled population. Also the preliminary indication of extremely high fluorine levels in the Awdarda coal-bearing sediments requires further research. The originally planned small scale environmental risk assessment study has also two important byproducts. The first is finding high contents of REE and several other elements in the local coal-bearing sediments, which might be utilized for production of these valuable elements in the future. The second is obtaining the elemental composition of crops grown in the studied region, which is largely missing in the literature worldwide.

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