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ARTICLE

Urinary and hair concentrations of trace metals in pregnant women from Northeastern British Columbia, Canada: a pilot study

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Abstract

Background Northeastern British Columbia (Canada) is an area of intense natural gas exploitation by hydraulic fracturing. Hydraulic fracturing can release contaminants, including trace metals, many of which are known developmental toxicants. To date, there is limited data on human exposure to contaminants in this region.
Objective We aimed to examine trace metals in urine and hair samples from 29 Indigenous and non-Indigenous pregnant women from two communities (Chetwynd and Dawson Creek) in Northeastern British Columbia.
Methods We recruited 29 pregnant women who provided spot urine samples over five consecutive days and one hair sample. We measured 19 trace metals in pooled urine samples from each participant and in the first 2 cm of hair closest to the scalp. We compared urinary and hair concentrations to those measured in women from the general population using data from the Canadian Health Measure Survey (CHMS), or reference values found in the literature for trace metals not measured in the CHMS.
Results Median urinary (0.49 µg/L) and hair (0.16 µg/g) concentrations of manganese were higher in our participants than in the CHMS (<0.05 µg/L in urine) or reference population (0.067 µg/g in hair). In hair, median values for barium (4.48 µg/g), aluminum (4.37 µg/g) and strontium (4.47 µg/g) were respectively 16, 3, and 6 times higher compared with median values in a reference population. Concentrations of barium and strontium in hair were higher in self-identified Indigenous participants (5.9 and 5.46 µg/g, respectively) compared to non-Indigenous participants (3.88 and 2.60 µg/g) (*p*-values = 0.02 and 0.03).
Conclusion Our results suggest higher gestational exposure to certain trace metals in our study population compared to reference populations.

Keywords Trace metals · Biomonitoring · Hydraulic fracturing · Gestational exposure

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Introduction

The Peace River Valley, located in Northeastern British Columbia (Canada), is an area of intensive natural gas exploitation. This region sits on an important source of natural gas, the Montney Formation. More than 30,000 wells of unconventional natural gas development using hydraulic fracturing have been drilled so far in Northeastern British Columbia [1]. Information on impacts of hydraulic fracturing activity is limited, but recent literature highlighted the risk of environmental contamination. Some chemicals used or associated with hydraulic fracturing may contaminate the soil by accidental spills, leaks, or during disposal of hydraulic fracturing fluids [2]. It is also known that hydraulic fracturing operations can release volatile organic compounds such as benzene [3–6]. Moreover, higher concentrations of trace metals like arsenic, barium and strontium were detected in private drinking water wells in areas of active natural gas extraction in Texas [7].

Hydraulic fracturing requires the use of very large amounts of water mixed with different chemicals [8]. Some of the fluid injected into the well during the hydraulic fracturing process returns quickly to the surface (i.e., flowback water). Another portion of the fluid returns to the surface during the production phase of the well (i.e., produced water) [9]. Depending on the geological formation, flowback and produced waters can contain various contaminants, such as trace metals and radioactive elements. A study that investigated the presence of trace elements in rock samples from the Montney formation found relatively high concentrations of barium, aluminum, strontium and manganese [10, 11]. Furthermore, recent studies that characterized the content of flowback and produced waters from hydraulic fracturing activities commonly found relatively high concentrations of trace metals such as aluminum, manganese, barium and strontium [9, 12]. In the Peace River Valley, concentrations of barium in groundwater near Fort St-John and Tumbler Ridge have increased since the natural gas boom in 2007. For example, in three water monitoring stations, barium concentrations in groundwater samples were between 0.05 and 0.3 mg/L prior to 2007, and between 0.3 and 1.0 mg/L after 2007, which may be related to hydraulic fracturing causing the release of barium from deeper groundwater and/or rock formation to shallower groundwater [13]. Drinking water within the city limits of Dawson Creek and Chetwynd comes from surface water sources. In a review about the risks to water resources posed by hydraulic fracturing, Vengosh et al [6]. identified accidental spills and inadequate disposal of hydraulic fracturing wastewaters as potential sources of contamination of surface water and shallow groundwater.

The consumption of water contaminated with metals is a potential source of exposure for the population, including vulnerable groups such as pregnant women and children. In utero exposure to trace metals can occur via their passage through the placental barrier [14–16], and exposure to certain trace metals such as lead, mercury, cadmium and manganese has been associated with adverse health outcomes like reduced birth weight, congenital malformations, miscarriage and impaired neurodevelopment [17–19]. Recent epidemiologic studies provide preliminary evidence that living in close proximity of natural gas may be associated with negative birth outcomes such as higher prevalence of birth defects, low birth weights and fetal death [20–24].

Because concerns have been raised by communities about the potential impacts of hydraulic fracturing activity on the release of contaminants in the Peace River Valley, we conducted a pilot study to assess exposure to various contaminants in pregnant women from two communities in this region (Chetwynd and Dawson Creek). As part of this pilot study, we previously reported higher concentrations of a benzene metabolite in the urine of these participants, particularly in self-identified Indigenous women [25]. In the present analysis, we measured several trace metals in hair and urine samples from the same 29 pregnant women. Based on the flowback water composition, the geological characteristics from the Montney formation and the increasing barium concentrations in groundwater from the Peace River region [3], we assessed whether women might be exposed to higher concentrations of barium, aluminum, strontium and manganese when compared with the general population, and depending on the community of recruitment and Indigenous status.

Materials and methods

Study area and recruitment

The pilot study took place in Dawson Creek and Chetwynd, two communities located in Northeastern British Columbia and surrounded by active natural gas wells and/or natural gas plant. While Dawson Creek is surrounded by more active wells, Chetwynd is located near a major natural gas plant. More details about the study area can be found in our previous article [25]. Thirty pregnant women were recruited in two medical clinics offering prenatal care and located in Chetwynd and Dawson Creek from September to November 2016. Eligible participants (>18 years old, English speaking) were informed about the research project by their physician or nurse practitioner during a prenatal visit. If interested, pregnant women were met privately by a member of the research team, given information about the research project and invited to ask questions. Women who decided to participate signed a written consent form and subsequently filled out a short questionnaire on their life habits, sociodemographic and physiological characteristics (e.g., weight, height, gestational week), diet, occupation, smoking habits and drinking water source. In this pilot study, a total of 30 pregnant women were recruited, and 29 participants completed the sampling process. One participant who miscarried during the period of sampling did not complete the urine sampling procedure. The median sampling time was 9:00 PM, and most samples were collected between 2:00 PM and 11:00 PM. This study was evaluated and approved by the Northern Health Research Review Committee and by the Université de Montréal Institutional Review Board (#16–090-CERES-P). Because we expected to recruit Indigenous women, we also obtained informed consent from the West Moberly First Nations, Saulteau First Nations and Treaty 8 Tribal Association prior to recruitment.

Urine sampling

At home, participants collected five 12 mL urine samples over 5 consecutive days (one urine sample per day) to account for day-to-day variations in exposure. Samples were kept in the participant's freezer until they were retrieved directly at the participant's residence and kept at −20 °C until transportation on dry ice to the laboratory (Université de Montréal) for subsequent chemical analyses. For each participant, 2 mL of each urine sample were pooled into a single 10 mL sample for trace metal analyses.

Hair sampling

One hair sample (from scalp to end) was collected from each participant at the time of recruitment using metal-free ceramic blade scissors. The portion of the hair closest to the scalp was identified, and samples were kept in plastic bags at room temperature until transportation for trace metal analyses at the laboratory (Université de Montréal). The first 2 cm closest to scalp were used for analyses. Because hair typically grows 1 cm every month, measured concentrations are considered to reflect internal exposure over the 2 months prior to hair collection.

Chemical determination of trace metals in urine and hair samples

Nineteen elements (aluminum, arsenic, barium, beryllium, cadmium, chrome, cobalt, copper, gallium, iron, lead, lithium, manganese, nickel, selenium, strontium, uranium, vanadium, zinc) were measured in urine and hair samples using inductively coupled mass spectrometry (ICP-MS) 7700× (Agilent, Mississauga, Canada) in a trace-metal clean room (ISO 3 standards 146442–1). Silver was only measured in hair samples because of interference with biological components in urine. Urine samples were diluted five times with nitric acid at 2% and heated 15 min at 45 °C to dissolve the sediments prior to ICP-MS analysis. Hair samples were first washed as follows: 3 times with a Triton X-100 solution diluted 1/200 in MilliQ water, with sonication 5 min at each washing; rinse with acetone, sonication 3 min at each rinsing; washing 3 times with MilliQ water, sonication 3 min between each washing, rinse with acetone, sonication 3 min at each rinsing; drying of samples with a Thermo Scientific Integrated SpeedVac system. Each hair sample (50 mg) was then weighed and placed in PFA digestion tubes; 1 mL of HNO_3 at 70% and 0.1 mL of internal standard mix (rhodium and indium) at 100 ppb was added to each tube. Tubes were left 15 min at room temperature to dissolve hair and placed in a block heater at 90 °C until complete dissolution; 1.5 mL of H_2O_2 was added, left a few minutes at room temperature, then placed in the block heater at 90 °C for 3 h. The hair solution was then transferred to polypropylene tubes of 15 mL and adjusted to a volume of 3 ml with MilliQ water. Hair samples were diluted 1/5 with HNO_3 at 2% prior to ICP-MS analysis.

For the quantification of trace metals in urine and hair, the ICP-MS was operated in the following conditions: RF Power at 1550 W, nebulizer gas flow at 0.65 L of Ar/minute, dilution gas flow at 0.41 L Ar/minute, collision gas flow in Helium mode at 5 mL He/minute for urine analysis and 4.3 to 5 mL He/minute for hair analysis. The elements indium and rhodium were used as internal standards. Limits of detection varied between 0.01 and 1.8 ppb in urine and between 0.001 and 0.869 μg/g of hair, depending on the element. Average recovery from 10 replicate analyses of blank urine samples spiked at two levels (250 and 1000 ng) was >90%; repeatability coefficient of variation was less than 5%. Average recovery of two replicate analyses of QC ClinChek urine control, Level I (QC1) (Ref: 8847–8849; lot: 122) and Level II (QC2) (Ref: 8847–8849; lot: 122) was >96% for all metals. Average recovery from 10 replicate analyses of blank hair samples spiked at two levels (1500 and 3000 ng) was >90% for all metals; repeatability coefficient of variation was less than 10%. Average recovery of 20 replicate analyses of QC hair sample QM-H-Q1309 from the Institut national de santé publique du Québec (INSPQ) was >92% (except for silver and arsenic with average values around 85%).

Reference populations

Descriptive statistics on urinary concentrations of arsenic, cadmium, cobalt, copper, lead, manganese, nickel, selenium, vanadium, zinc and uranium were first compared to available biological reference concentrations from women from the general Canadian population who participated in the 2nd cycle of the Canadian Health Measure Survey (CHMS) [26]. Other published comparison values of metals concentrations in urine and hair of the Canadian population are limited. Urinary concentrations for trace metals not measured in the CHMS were compared to published reference values from a group of 100 healthy non-occupationally-exposed adults (46 men, 54 women) not suffering from any disease, who were recruited during their routine medical examination at the Groupe Hospitalier du Havre in France [27, 28]. Trace metals in hair samples were compared to the reference values reported by Goullé et al [27]. because hair concentrations were not measured in the CHMS.

Statistical analyses

Statistical analyses comparing urine and hair concentrations of aluminum, barium, manganese and strontium are presented because of their naturally occurring presence in the Montney formation and their hypothesized release by hydraulic fracturing activity. Specifically, urine and hair concentrations of these trace metals were compared between participants who reported smoking or being exposed to second-hand smoke, and non-smoking participants using the non-parametric Mann–Whitney *U* test. Hair concentrations of trace metals measured in participants were compared between regions of recruitment (Chetwynd and Dawson Creek), between self-identified Indigenous and non-Indigenous women, and between drinking water sources using the non-parametric Mann–Whitney *U* test. These statistical analyses were performed on trace metals' concentrations in hair as they represent longer term exposure (compared to urine samples). Moreover, hair has been extensively and successfully used in other biomonitoring studies [29–33]. Correlations between concentrations of trace metals were tested using Spearman's rank correlation test. Analyses comparing hair concentrations between regions of recruitment and ethnicity were also carried out for the other trace metals. Results are presented in Supplementary Information. All statistical analyses were performed using IBM SPSS Statistics for Windows, Version 22.0 (IBM Corp., Armonk, New York, USA).

Results

Fifty percent of the participants were recruited at the Chetwynd medical clinic, and 50% at the Dawson Creek clinic. Forty-three percent of participants self-identified as Indigenous. Specifically, nine and four Indigenous participants were recruited in Chetwynd and Dawson Creek, respectively (Table 1). During their pregnancy, two participants reported smoking and four reported being exposed to second-hand smoke at home. The main drinking water source was tap water for the majority of participants (70%). The proportion of participants using bottled water as their major drinking water source was higher in Chetwynd (33%) compared to Dawson Creek (20%) (Table 1).

Table 1 Characteristics of the pregnant women recruited in Dawson Creek and Chetwynd, Northeastern British Columbia ($n = 30$)

Characteristics	Full population ($n = 30$) Median (range)	Chetwynd ($n = 15$) Median (range)	Dawson Creek ($n = 15$) Median (range)
Pregnant women's age (years)	31 (21–41)	32 (21–41)	31 (21–36)
Gestational age (weeks) at recruitment	18.5 (6.0–39.0)	16.0 (6.0–35.0)	20.0 (8.0–39.0)
	n (%)	*n* (%)	*n* (%)
Self-identified as Indigenous			
Yes	13 (43)	9 (60)	4 (27)
No	17 (57)	6 (40)	11 (73)
Highest education degree obtained			
High school unfinished	2 (7)	1(6)	1 (6)
High school diploma	8 (27)	5 (34)	3 (20)
Certificate, diploma or associate degree	10 (33)	6 (40)	4 (27)
University degree (Bachelor, Master, Doctorate)	10 (33)	3 (20)	7 (47)
Participants working in industrial field[a]			
Yes	6 (20)	4 (27)	2 (13)
No	24 (80)	11 (73)	13 (87)
Smoker at time of recruitment			
Yes	2 (7)	2 (13)	0 (0)
No	28 (93)	13 (87)	15 (100)
Exposed to second-hand smoke during pregnancy			
Yes	4 (13)	3 (20)	1 (7)
No	26 (87)	12 (80)	14 (93)
Main drinking water source			
Tap water	21 (70)	10 (67)	11 (73)
Bottled water	8 (27)	5 (33)	3 (20)
Other	1 (3)	0 (0)	1 (7)

[a] industrial field includes mining, natural gas, construction, forestry, hydroelectricity, pipeline maintenance

Concentrations of trace metals in urine samples

All trace metals were detected in all participants, except for chromium (two samples below the limit of detection) and

Table 2 Distribution of trace metal concentrations measured in urine and hair samples from pregnant women in Dawson Creek and Chetwynd, Northeastern British Columbia ($n = 29$) and concentrations measured in reference populations

Trace elements	Concentrations in urine (μg/L)						Concentrations in hair (μg/g of hair)					
	GM	10th %tile	50th %tile	95th %tile	50th %tile in ref pop	95th %tile in ref pop	GM	10th %tile	50th %tile	95th %tile	50th %tile in ref pop	95th %tile in ref pop
Aluminum[b]	15.29	5.15	7.60	355.00	1.90	11.20	4.88	2.72	4.30	11.31	1.63	5.30
Arsenic[a]	7.40	2.48	5.25	109.23	7.40	73.00	0.011	0.006	0.012	0.037	0.05	0.08
Barium[b]	1.80	0.56	1.52	10.50	0.89	3.85	4.69	2.02	4.48	23.12	0.28	1.58
Beryllium[b]	0.01	0.006	0.008	0.07	0.01	0.04	<LOD	<LOD	<LOD	<LOD	0.0007	0.01
Cadmium[a]	0.12	0.06	0.13	0.61	0.27	3.20	0.005	0.003	0.005	0.014	0.01	0.17
Chromium[b]	0.13	0.02	0.13	0.69	–	–	0.027	0.015	0.026	0.107	0.20	0.52
Cobalt[a]	0.63	0.34	0.63	1.23	0.33	1.20	0.033	0.009	0.039	0.416	0.02	0.14
Copper[a]	6.97	3.62	6.75	49.67	12.00	27.00	19.34	9.74	14.99	58.10	20.30	61.30
Gallium[b]	0.08	0.04	0.10	0.32	0.07	0.28	0.20	0.08	0.19	0.97	0.01	0.07
Iron	6.71	2.90	6.20	21.27	–	–	6.50	4.46	5.64	13.21	–	–
Lead[a]	0.16	0.04	0.16	5.88	0.39	1.70	0.18	0.12	0.18	0.54	0.41	4.57
Lithium[b]	31.92	19.23	29.02	72.38	12.00	219.00	<LOD	<LOD	<LOD	<LOD	0.02	0.04
Manganese[a]	0.63	0.26	0.49	4.40	<LOD	0.34	0.17	0.06	0.16	1.31	0.07	0.57
Nickel[a]	0.96	0.42	1.04	2.12	1.30	5.30	0.15	0.06	0.17	0.46	0.23	0.90
Selenium[a]	58.19	31.80	57.55	172.96	53.00	140.00	0.53	0.38	0.64	0.75	0.54	1.37
Silver	–	–	–	–			0.21	0.06	0.20	1.09	0.08	1.31
Strontium[b]	144.28	65.51	148.40	435.60	90.00	413.00	4.58	2.03	4.47	28.64	0.89	4.63
Uranium[a]	0.003	0.0007	0.003	0.0069	<LOD	0.002	0.019	0.007	0.019	0.052	0.009	0.03
Vanadium[a]	0.17	0.11	0.17	0.32	<LOD	<LOD	0.03	0.01	0.03	0.08	0.02	0.05
Zinc[a]	239.43	69.31	268.05	611.73	280.00	870.00	160.52	127.84	173.71	303.52	162.00	209.00

GM = geometric mean

%tile = percentile

Ref pop = reference population

[a] urinary concentrations compared to CHMS

[b] urinary concentrations compared to Goullé et al. [27]

vanadium (one sample below the limit of detection) (Table 2). Urinary concentrations of arsenic, cadmium, cobalt, copper, lead, nickel, selenium, zinc and uranium were similar to or lower than those measured in women enrolled in the CHMS. In the CHMS participants, the median urinary manganese level was below the limit of detection (<0.05 μg/L); our median level was at least 10 times higher (Table 2). The 95th percentile of urinary manganese concentrations in the CHMS was exceeded by 23 (79%) of the study participants. In the CHMS participants, the median urinary vanadium level and 95th percentile were below the limit of detection (<0.1 μg/L); our 95th percentile was at least 3 times higher (Table 2). Urinary barium, strontium, aluminum, lithium and beryllium were not measured in the CHMS. Urinary concentrations in participants were therefore compared to those reported by Goullé et al. [27]. Beryllium and gallium urinary concentrations measured in our study were similar to those reported by Goullé et al. [27]. Median concentrations in our study were higher than those observed by Goullé et al. [27] for barium (1.7 times), aluminum (4.0 times), and strontium (1.6 times) (Table 2). 95th percentiles reported by Goullé et al. [27] were exceeded by 4 (14%) participants for barium, 9 (31%) participants for aluminum, and 1 (3%) participant for strontium. Participants who reported smoking or being exposed to second-hand smoke during their pregnancy did not have higher urinary concentrations of barium, strontium, manganese or aluminum (results not shown). Urinary concentrations of barium were positively correlated with strontium (Spearman $\rho = 0.78$, $p\text{-value} < 0.0001$). Besides this correlation between barium and strontium, there was no correlation between trace metals urinary concentrations.

Concentrations of trace metals in hair samples

CHMS does not include the measurement of trace metals in hair. Therefore, ranges reported by Goullé et al. [27] were used as a comparison (Table 2). Lithium and beryllium were not detected in any hair sample (Table 2). Arsenic, cadmium, cobalt, copper, lead, nickel, zinc, selenium, silver, uranium and vanadium concentrations in participants' hair were similar or lower than the ranges reported by Goullé et al. [27]. Median concentrations in our study were higher than median concentrations observed by Goullé et al. [27] for gallium (19 times), barium (16 times), aluminum (2.6 times) and strontium (5 times) (Table 2). 95th percentiles reported by Goullé et al. [27] were exceeded by 29 (100%) participants for gallium, 29 (100%) participants for barium, 12 (41%) participants for strontium, and 12 (41%) participants for aluminum. Participants who reported smoking or being exposed to second-hand smoke during their pregnancy did not have higher hair concentrations of barium, strontium, manganese or aluminum (results not shown). Concentrations of these trace metals in urine and hair samples were not correlated (Spearman $\rho = -0.21$ to -0.08). However, concentrations of barium in hair samples were positively correlated with strontium concentrations in hair (Spearman $\rho = 0.92$, $p\text{-value} < 0.0001$) and manganese concentrations in hair (Spearman $\rho = 0.46$, $p\text{-value} = 0.01$).

Concentrations of trace metals between regions of recruitment

The median hair barium concentrations in participants from Chetwynd and Dawson Creek were 5.03 and 3.88 µg/g of hair, but this difference was not statistically significant (p-value = 0.22) (Fig. 1a). Participants from Chetwynd had a median hair aluminum level (7.6 µg/g of hair) that was 2.2 times higher than that of participants from Dawson Creek (3.4 µg/g of hair) (p-value = 0.005) (Fig. 1b). The median strontium and manganese concentrations in participants from Chetwynd (5.38 and 0.19 µg/g of hair, respectively) and Dawson Creek (2.79 and 0.12 µg/g of hair, respectively) were not statistically significant between regions of recruitment (p-values = 0.16 and 0.51) (Fig. 1c, d). Hair concentrations of the other trace metals were not statistically different between the regions of recruitment (Table S1).

Concentrations of trace metals between Indigenous and non-Indigenous participants

The median hair barium level in Indigenous women (5.93 µg/g of hair) was 1.5 times higher than in non-Indigenous women (3.88 µg/g of hair) (p-value = 0.02) (Fig. 2a). The median hair aluminum concentrations in Indigenous women (3.44 µg/g of hair) and non-Indigenous women (4.75 µg/g of hair) were not statistically significant (p-value = 0.74) (Fig. 2b). The median hair strontium level in Indigenous women (5.46 µg/g of hair) was approximately 2 times higher than in non-Indigenous women (2.60 µg/g of hair) (p-value = 0.03) (Fig. 2c). Finally, the median hair manganese level in Indigenous women (0.23 µg/g of hair) was not statistically different from the median level in non-Indigenous women (0.13 µg/g of hair) (p-value = 0.43) (Fig. 2d). Hair concentrations of the other trace metals were not statistically different between Indigenous and non-Indigenous participants, except for gallium (Table S1). Median hair gallium level in Indigenous women (0.25 µg/g of hair) was significantly higher than in non-Indigenous women (0.16 µg/g of hair) (p-value = 0.02).

Concentrations of trace metals between drinking water sources

In this pilot study, 70% of the participants used tap water as their major drinking water source, while 30% of them used either bottled water or filtrated water. Although the median hair concentrations of barium, strontium and manganese seem to be slightly higher in participants using tap water as their major drinking water source, these differences were not statistically significant (Figure S1).

Discussion

Comparison with reference ranges of exposure and other populations

In this pilot study, we analyzed a suite of trace metals in urine and hair samples from 29 pregnant women living in Northeastern British Columbia and compared concentrations to those available for women from the general Canadian population (CHMS) or, when measurements were not available in the CHMS, to those from non-occupationally exposed volunteers from France [27]. Concentrations of some trace metals from our study were higher than those from reference populations, including elements that have been associated with hydraulic fracturing related activities (aluminum, manganese, barium, strontium). Hair concentrations of barium, aluminum, strontium and manganese were also compared between regions of recruitment (Chetwynd vs. Dawson Creek), and between self-identified Indigenous and non-Indigenous participants. We demonstrated in a previous study that concentrations of two urinary benzene metabolites, potentially associated with natural gas exploitation, were higher in participants from Chetwynd and in self-identified Indigenous participants [25].

Overall, the median urinary level of manganese was higher in our pilot study (0.49 µg/L) than that reported in the CHMS (<LOD [0.2 µg/L]). Furthermore, median urinary concentrations of barium, aluminum and strontium were higher in pregnant women from Northeastern British

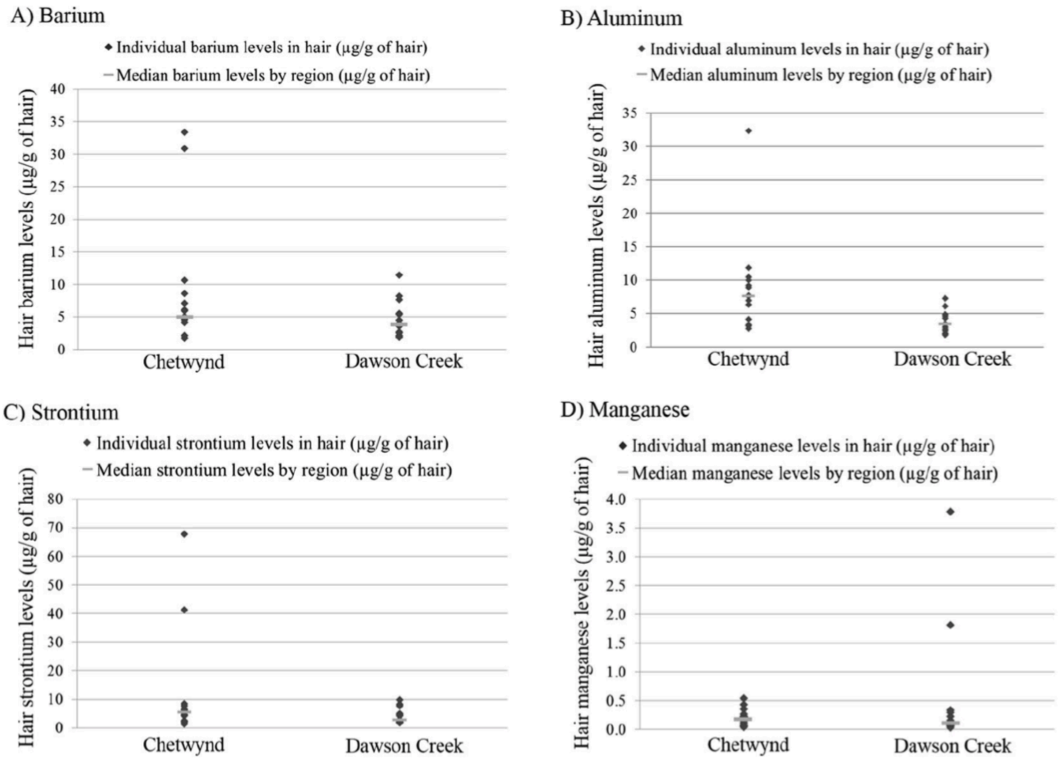

Fig. 1 Individual levels of (**a**) barium, (**b**) aluminum, (**c**) strontium and (**d**) manganese in hair samples (µg/g of hair) in our pilot study, by region. The 2 first cm of hair from the scalp were used for analyses. The grey line represents the median level of trace metals in each group

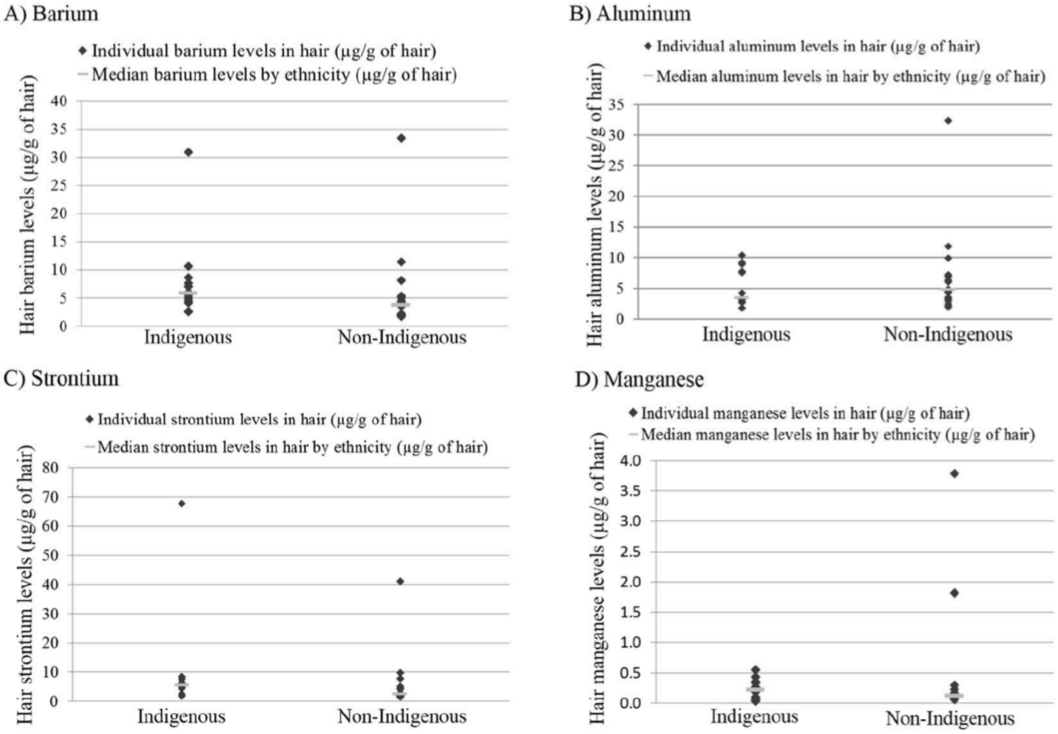

Fig. 2 Individual levels of (**a**) barium, (**b**) aluminum, (**c**) strontium, and (**d**) manganese in hair samples (µg/g of hair) in our pilot study, according to Indigenous status. The 2 first cm of hair from the scalp were used for analyses. The grey line represents the median level of trace elements in each group

Columbia who participated in this pilot study compared to median concentrations described by Goullé et al. [27] (Table 2).

Differences in trace metal concentrations between study participants, and with reference populations were more important when looking at hair concentrations than urine concentrations (Table 2). Concentrations of barium, aluminum, strontium and manganese in hair were not correlated with measured concentrations in urine samples. While trace metals concentrations in hair represent long term exposures, urine concentrations are related to recent exposures, which may explain the lack of correlation. This lack of correlation for trace metal (including manganese) concentrations between different biological matrices was previously observed [34]. Median hair concentrations of barium, aluminum, strontium and manganese were higher in participating pregnant women compared to median concentrations reported by Goullé et al. [27] (Table 2). In addition, concentrations of some trace metals, namely barium and aluminum, seem to be higher in participants from Chetwynd when compared to concentrations of these trace metals measured in participants recruited in Dawson Creek (Table 2). Moreover, median hair concentrations of barium, gallium (which has high chemical affinity with aluminum in rocks and is a common constituent of aluminum bearing minerals [10, 35]) and strontium were significantly higher in participants who self-identified as Indigenous than in non-Indigenous participants (Table S1 and Fig. 2). A study conducted by Pragst et al. [36] measured various trace metals in hair samples of volunteers from communities living in the vicinity of oilfields in South Sudan. Compared to our pilot study, they reported higher median concentrations of barium, aluminum, strontium and manganese (11.0, 150.0, 9.9, and 12.0 μg/g of hair, respectively). Interestingly, Pragst et al. [36] noted increasing concentrations of trace metals in communities closer to the oilfields. A study conducted in Alberta measured trace metals in hair samples from children living in three Indigenous communities near the tar sands. Mean hair concentrations of barium (1.4 μg/g of hair in Fort McKay, 2.9 μg/g of hair in Garden River and 1.5 μg/g of hair in Fort Chipewyan) and strontium (3.62 μg/g of hair in Fort McKay, 1.81 μg/g of hair in Garden River and 1.62 μg/g of hair in Fort Chipewyan) measured in this study [37] were similar to those we reported. In a study that reported associations between exposure to manganese and lower IQ in children from southern Quebec, the median hair manganese level was 0.7 μg/g of hair, and concentrations ranged from 0.2 to 4.7 μg/g of hair (5th to 95th percentiles), which is higher than what we reported in our pilot study [38]. The results of the present analysis are aligned with our previous study, where concentrations of two urinary benzene metabolites were higher in participants self-identified as Indigenous compared to non-Indigenous participants [25]. First Nations already face important health inequities, and environmental exposure to contaminants may exacerbate these disparities [39].

Sources and pathways of exposure to trace metals

Exposure to the trace metals examined in our study (e.g., barium, aluminum, strontium, manganese) can occur through multiple pathways and sources. Barium is a metal naturally present in the environment and can be found in moderate concentrations in drinking water in some areas [40]. Barium is also used in medicine as a radiographic contrast agent [41]. The use of barium in various industrial activities such as petroleum industry and steel industry can contribute to the exposure from anthropogenic sources [42]. Aluminum is also found ubiquitously, and exposure can be from occupational (e.g., welding, aluminum products production) [43] and environmental sources such as drinking water [44]. Humans can also be exposed to aluminum through diet, especially by the consumption of aluminum-containing food additives or the use of cookware containing aluminum [45, 46]. Strontium can be found at various concentrations in drinking water and in food such as grains [47, 48]. Diet is the main source of manganese, an essential element. High concentrations of manganese can also be found in water, in areas where the bedrock naturally contains high manganese concentrations [49], or in regions with important industrial activities [50]. Therefore, biomarker concentrations in our study could be the result of many region-specific exposures, including industry-related releases in the air and drinking water sources.

A growing number of studies have highlighted the potential of hydraulic fracturing activities to negatively impact air and water quality [5, 51–53]. More precisely, Alawattegama et al. [54] reported well-water contamination with metals such as strontium and manganese in Pennsylvania. Although they could not identify the source of contamination, Fontenot et al. [7] found elevated concentrations of barium and strontium in drinking water wells near natural gas extraction sites. Loss of well integrity, inadequate casing, connectivity between deep natural gas source and shallow aquifers, and the challenging treatment and disposal of flowback water are all potential contamination pathways [55–58]. The Montney formation is characterized by the natural presence of barium, aluminum, strontium and manganese [10, 11], which are also common constituents of the flowback water [9, 12]. Preliminary data on surface water quality in this region are provided as Supplementary Information to this paper, and show sporadic higher concentrations of some metals in surface water samples (Figure S2). At this moment, it is not possible to determine the sources of exposure explaining the higher concentrations of barium, aluminum, strontium and manganese in study participants compared to reference populations. However, drinking water should be investigated as a potential exposure pathway to these trace metals.

Limitations

Our pilot study has a number of limitations, including the lack of exposure data in the general Canadian population for various trace metals (including barium, aluminum and strontium). Comparisons with a reference population from France with potentially different baseline exposures are not optimal, and should more hair and urine concentrations become available for Canada, further comparisons should be carried out. Moreover, the data on surface water quality in the Peace River Valley is sparse and highly variable. Indeed, there is no systematic water monitoring program in the region. Also, the small number of participants and the absence of environmental monitoring (e.g., concentrations in tap water) prevented us from drawing conclusions on the possible sources and pathways of exposure to these compounds, and the potential need for an exposure mitigation strategy.

Conclusion

Results from our pilot study suggest that pregnant women from Northeastern British Columbia may be particularly exposed to certain trace metals like barium, aluminum, strontium and manganese. Whether these exposures are related to hydraulic fracturing and oil and gas related activities is still unknown. Given the inherent limitations of our pilot study, further exposure assessment in regions of intensive natural gas exploitation is warranted. In the future, we will carry out a multi-faceted study to assess exposure to contaminants including trace metals with more precision. Results from future projects evaluating the levels of exposure to these contaminants in biological and environmental samples would provide much needed data to better understand and evaluate the potential health risks of environmental contaminants in this region.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Adams C, Janicki E, Balogun A. (2016): Summary of shale gas activity in Northeast British Columbia 2013; in Oil and Gas Reports 2016, British Columbia Ministry of Natural Gas Development, pages 1–39.
2. Werner AK, Vink S, Watt K, Jagals P. Environmental health impacts of unconventional natural gas development: a review of the current strength of evidence. Sci Total Environ. 2015;505:1127–41.
3. Crowe E, Patton S, Thomas D, Thorpe B. When the wind blows: tracking toxic chemicals in gas fields and impacted communities. (Maddy Cobbing ed.) Battleboro, VT; 2016.
4. Gilman JB, Lerner B, Kuster W, De Gouw J. Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado. Environ Sci Technol. 2013;47:1297–305.
5. Macey GP, Breech R, Chernaik M, Cox C, Larson D, Thomas D, et al. Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. Environ Health. 2014;13:82.
6. Vengosh A, Jackson RB, Warner N, Darrah TH, Kondash A. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. Environ Sci Technol. 2014;48:8334–48.
7. Fontenot BE, Hunt LR, Hildenbrand ZL, Carlton Jr DD, Oka H, Walton JL, et al. An evaluation of water quality in private drinking water wells near natural gas extraction sites in the Barnett Shale Formation. Environ Sci Technol. 2013;47:10032–40.
8. Johnson EG, Johnson LA. Hydraulic fracture water usage in northeast British Columbia: locations, volumes and trends. Geosci Rep. Victoria, BC, Canada, 2012. pp 41–63.
9. Pichtel J. Oil and gas production wastewater: soil contamination and pollution prevention. Appl Environ Soil Sci. 2016;2016.
10. Egbobawaye EI. Whole-rock geochemistry and mineralogy of Triassic Montney Formation, Northeastern British Columbia, Western Canada Sedimentary Basin. Int J Geosci. 2016;7:91.
11. Playter T, Corlett H, Konhauser K, Robbins L, Rohais S, Crombez V, et al. Clinoform identification and correlation in fine-grained sediments: a case study using the Triassic Montney Formation. Sedimentology. 2017;65:263–302.
12. Lester Y, Ferrer I, Thurman EM, Sitterley KA, Korak JA, Aiken G, et al. Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment. Sci Total Environ. 2015;512-513:637–44.
13. GWSolutions. Peace river regional district water quality database and analysis. Coming Clean, Nanaimo, BC; 2016.
14. Caserta D, Mantovani A, Ciardo F, Fazi A, Baldi M, Sessa M, et al. Heavy metals in human amniotic fluid: a pilot study. Prenatal Diagn. 2011;31:792–6.
15. Hall G, Carr M, Cummings E, Lee M. Aluminum, barium, silicon, and strontium in amniotic fluid by emission spectrometry. Clin Chem. 1983;29:1318.

16. Kosanovic M, Jokanovic M, Jevremovic M, Dobric S, Bokonjic D. Maternal and fetal cadmium and selenium status in normotensive and hypertensive pregnancy. Biol Trace Elem Res. 2002;89:97–103.
17. Caserta D, Graziano A, Monte GL, Bordi G, Moscarini M. Heavy metals and placental fetal-maternal barrier: a mini-review on the major concerns. Eur Rev Med Pharmacol Sci. 2013;17:2198–206.
18. Lin C-C, Chen Y-C, Su F-C, Lin C-M, Liao H-F, Hwang Y-H, et al. In utero exposure to environmental lead and manganese and neurodevelopment at 2 years of age. Environ Res. 2013;123:52–7.
19. Takser L, Mergler D, Hellier G, Sahuquillo J, Huel G. Manganese, monoamine metabolite levels at birth, and child psychomotor development. Neurotoxicology. 2003;24:667–74.
20. Casey JA, Savitz DA, Rasmussen SG, Ogburn EL, Pollak J, Mercer DG, et al. Unconventional natural gas development and birth outcomes in Pennsylvania, USA. Epidemiology. 2016;27:163–72.
21. Currie J, Greenstone M, Meckel K. Hydraulic fracturing and infant health: New evidence from Pennsylvania. Sci Adv. 2017;3:e1603021.
22. Hill EL. Unconventional natural gas development and infant health: evidence from Pennsylvania. Charles H Dyson School of Applied Economics and Management. Working Paper. 2012. p. 2013.
23. McKenzie LM, Guo R, Witter RZ, Savitz DA, Newman LS, Adgate JL. Birth outcomes and maternal residential proximity to natural gas development in rural Colorado. Environ Health Perspect. 2014;122:412.
24. Whitworth KW, Marshall AK, Symanski E. Maternal residential proximity to unconventional gas development and perinatal outcomes among a diverse urban population in Texas. PLOS ONE. 2017;12:e0180966.
25. Caron-Beaudoin É, Valter N, Chevrier J, Ayotte P, Frohlich K, Verner M-A. Gestational exposure to volatile organic compounds (VOCs) in Northeastern British Columbia, Canada: A pilot study. Environ Int. 2018;110:131–8.
26. Health Canada. Second report on human biomonitoring of environmental chemicals in Canada: results of the Canadian Health Measures Survey Cycle 2 (2009–2011). Ottawa, Canada, 2012.
27. Goullé J-P, Mahieu L, Castermant J, Neveu N, Bonneau L, Lainé G, et al. Metal and metalloid multi-elementary ICP-MS validation in whole blood, plasma, urine and hair: reference values. Forensic Sci Int. 2005;153:39–44.
28. Goullé J-P, Mahieu L, Neveu N, Bouige D, Castermant J, Laine G, et al., (editors) Dosage multiélémentaire des métaux et métalloïdes dans les milieux biologiques par ICP-MS: valeurs usuelles chez 100 témoins. Annales de Toxicologie Analytique; 2004: EDP Sciences.
29. Wilhelm M, Hafner D, Lombeck I, Ohnosorge FK. Monitoring of cadmium, copper, lead and zinc status in young children using toenails: comparison with scalp hair. Sci Total Environ. 1991;103:199–207.
30. Rodushkin I, Axelsson MD. Application of double focusing sector field ICP-MS for multielemental characterization of human hair and nails. Part II. A study of the inhabitants of northern Sweden. Sci Total Environ. 2000;262:21–36.
31. Rodushkin I, Axelsson MD. Application of double focusing sector field ICP-MS for multielemental characterization of human hair and nails. Part I. Analytical methodology. Sci Total Environ. 2000;250:83–100.
32. Wang T, Fu J, Wang Y, Liao C, Tao Y, Jiang G. Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. Environ Pollut. 2009;157:2445–51.
33. Pereira R, Ribeiro R, Gonçalves F. Scalp hair analysis as a tool in assessing human exposure to heavy metals (S. Domingos mine, Portugal). Sci Total Environ. 2004;327:81–92.
34. Gil F, Hernández AF, Márquez C, Femia P, Olmedo P, López-Guarnido O, et al. Biomonitorization of cadmium, chromium, manganese, nickel and lead in whole blood, urine, axillary hair and saliva in an occupationally exposed population. Sci Total Environ. 2011;409:1172–80.
35. Schroll E. Gallium: element and geochemistry. Geochemistry. Dordrecht: Springer Netherlands; 1998. p. 257–9.
36. Pragst F, Stieglitz K, Runge H, Runow K-D, Quig D, Osborne R, et al. High concentrations of lead and barium in hair of the rural population caused by water pollution in the Thar Jath oilfields in South Sudan. Forensic Sci Int. 2017;274:99–106.
37. Moon J, Smith TJ, Tamaro S, Enarson D, Fadl S, Davison AJ, et al. Trace metals in scalp hair of children and adults in three Alberta indian villages. Sci Total Environ. 1986;54:107–25.
38. Bouchard MF, Sauvé S, Barbeau B, Legrand M, Brodeur M-È, Bouffard T, et al. Intellectual impairment in school-age children exposed to manganese from drinking water. Environ Health Perspect. 2011;119:138.
39. Hoover E, Cook K, Plain R, Sanchez K, Waghiyi V, Miller P, et al. Indigenous peoples of North America: environmental exposures and reproductive justice. Environ Health Perspect. 2012;120:1645.
40. Brenniman GR, Kojola WH, Levy PS, Carnow BW, Namekata T. High barium levels in public drinking water and its association with elevated blood pressure. Archiv Environ Health. 1981;36:28–32.
41. Gollub MJ, Bains MS. Barium sulfate: a new (old) contrast agent for diagnosis of postoperative esophageal leaks. Radiology. 1997;202:360–2.
42. Kravchenko J, Darrah TH, Miller RK, Lyerly HK, Vengosh A. A review of the health impacts of barium from natural and anthropogenic exposure. Environ Geochem Health. 2014;36:797–814.
43. Riihimäki V, Aitio A. Occupational exposure to aluminum and its biomonitoring in perspective. Crit Rev Toxicol. 2012;42:827–53.
44. McLachlan D, Bergeron C, Smith J, Boomer D, Rifat S. Risk for neuropathologically confirmed Alzheimer's disease and residual aluminum in municipal drinking water employing weighted residential histories. Neurology. 1996;46:401–5.
45. Yokel RA, Hicks CL, Florence RL. Aluminum bioavailability from basic sodium aluminum phosphate, an approved food additive emulsifying agent, incorporated in cheese. Food Chem Toxicol. 2008;46:2261–6.
46. Fimreite N, Hansen O, Pettersen H. Aluminum concentrations in selected foods prepared in aluminum cookware, and its implications for human health. Bull Environ Contam Toxicol. 1997;58:1–7.
47. Runia LT. Strontium and calcium distribution in plants: effect on palaeodietary studies. J Archaeol Sci. 1987;14:599–608.
48. Curzon M. The relation between caries prevalence and strontium concentrations in drinking water, plaque, and surface enamel. J Dent Res. 1985;64:1386–8.
49. Bouchard M, Laforest F, Vandelac L, Bellinger D, Mergler D. Hair manganese and hyperactive behaviors: pilot study of school-age children exposed through tap water. Environ Health Perspect. 2006;115:122–7.
50. Takser L, Lafond J, Bouchard M, St-Amour G, Mergler D. Manganese levels during pregnancy and at birth: relation to environmental factors and smoking in a Southwest Quebec population. Environ Res. 2004;95:119–25.
51. Colborn T, Schultz K, Herrick L, Kwiatkowski C. An Exploratory Study of Air Quality Near Natural Gas Operations. Human Ecol Risk Assess. 2014;20:86–105.

52. Rahm D. Regulating hydraulic fracturing in shale gas plays: the case of Texas. Energy Policy. 2011;39:2974–81.
53. Vinciguerra T, Yao S, Dadzie J, Chittams A, Deskins T, Ehrman S, et al. Regional air quality impacts of hydraulic fracturing and shale natural gas activity: Evidence from ambient VOC observations. Atmos Environ. 2015;110:144–50.
54. Alawattegama SK, Kondratyuk T, Krynock R, Bricker M, Rutter JK, Bain DJ, et al. Well water contamination in a rural community in southwestern Pennsylvania near unconventional shale gas extraction. J Environ Sci Health Part A. 2015;50:516–28.
55. Ingraffea AR, Wells MT, Santoro RL, Shonkoff SB. Assessment and risk analysis of casing and cement impairment in oil and gas wells in Pennsylvania, 2000–2012. Proc Natl Acad Sci. 2014;111:10955–60.
56. Harrison SS. Evaluating system for ground-water contamination hazards due to gas-well drilling on the glaciated Appalachian plateau. Groundwater. 1983;21:689–700.
57. Darrah TH, Vengosh A, Jackson RB, Warner NR, Poreda RJ. Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. Proc Natl Acad Sci. 2014;111:14076–81.
58. Jackson RB, Vengosh A, Darrah TH, Warner NR, Down A, Poreda RJ, et al. Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. Proc Natl Acad Sci. 2013;110:11250–5.