Toxicology

Metal(loid)s urinary level among workers of gas refinery and petrochemical companies: Health risk assessment of metal(loid)s in drinking water and dust

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ABSTRACT

Background: Asalouyeh (southern Iran) contains many pollution sources like petrochemical and gas refinery companies. Few studies were conducted on the body burden of metal(loid)s in occupationally exposed workers of the companies in this area.

Objectives: The urine concentration of metal(loid)s in workers of gas refinery and petrochemical companies in Asalouyeh (who have been worked as "two weeks work-two weeks rest" schedule) was evaluated during a before-and-after observational study. The risks of metal(loid)s in drinking water and dust particles in the studied area were also assessed.

Methods: Urinary samples (n = 179) were gathered at the first day of two weeks of work (before) and at the end of two weeks of work (after). The concentration of V, Ni, Mn, Cd, and As was measured using a graphite furnace atomic absorption spectrometry. The health hazards of metal(loid)s in the air dust and drinking water of workers were also evaluated.

Results: The median concentration of metal(loid)s for workers of gas refinery and petrochemical companies for before and after two weeks of work was measured, respectively, as: As (11.44 and 9.31 μg/L), Ni (1.06 and 0.51 μg/L), Cd (0.36 and 0.31 μg/L), Mn (0.29 and 0.24 μg/L), and V (0.08 and 0.05 μg/L). After two weeks work, the median of all metal(loid)s in the urine of petrochemical and gas refinery workers was significantly increased. The non-cancer risk due to intake metal(loid)s from drinking water was more than the threshold value and the cancer risk from drinking water and inhaled air dust was less than the threshold.

Conclusion: Our results revealed the effect of gas refinery and petrochemical activities on increasing the metal(loid)s concentration of the worker's body and the necessity to protect this group. Additionally, the metal(loid)s intake from drinking water and inhaled dust posed no cancer risk to the workers.

1. Introduction

Providing a healthy and safe working condition requires special attention in any workplace. Millions of workers worldwide need to ensure occupational and environmental safety during facing different risks in each stage of work. Various surveys around the world indicate the global shortage of occupational health in term of chemical exposure for various industrial workers [1–4].

The gas refinery and petrochemical industry are the world's largest economic levers especially in developing countries with oil and gas

reservoirs [5]. These industries despite the undeniable role in the development of societies are a threat to human health and environment due to the emission of pollutants as well [6]. Kafaei et al. [7] detected some metals in the urine of schoolchildren living around the gas refinery and petrochemical companies. Fustinoni et al. [8] referred to the association between near residence to petrochemical sites and increasing benzene uptake. Different types of cancers, respiratory disorders, and atherosclerosis are the example of reported health risks due to the increasing body burden of contaminants in petrochemical workers [9–11].

Heavy metals and metalloids are one of the integral components of crude oil and gas refinery. Monitoring of water, soil, vegetation, and other environmental matrixes reveal the footprints of harmful elements in the environment around the petrochemical sites [12–14]. Due to toxicity, bioaccumulity, and non-degradability, metal(loid)s are very dangerous elements for exposed groups [15,16].

Having the second largest reservoirs of natural gas in the world, Iran becomes the active country to the high attainment of gas and petrochemical capacities. South Pars field is the largest gas field in Iran that feeds gas refineries and petrochemical complexes that are located in Asalouyeh, in the south of Iran [17,18]. About 60 thousand people are working in the Pars Special Economic Energy Zone [19]. Workers occupied in the gas refinery and petrochemical sites, especially those do not work in the office like operator and sampler person, usually, work for two weeks, and consequently go to rest for two weeks. This group is the most vulnerable group to expose to the emitted pollutants.

Gas and petrochemical activities in Asalouyeh area is suspected to the emission of many pollutants consist of heavy metals and metalloids. Presence of these elements in water and sediments in this area is a piece of evidence for this claim [20,21], but adverse health effects of metal(loid)s emitted from gas and petrochemical activities on workers are still controversial. Human biomonitoring is a good means of evaluating exposure to environmental chemicals that have been used in occupational medicine since the early 1930s [22,23]. Between different matrixes, the urinary concentrations of metals have been used as good biomarkers indicating individual's short-term or long-term internal exposure dose and have been used in many epidemiological studies [22,24,25].

Vanadium (V), nickel (Ni), manganese (Mn), cadmium (Cd), and arsenic (As) are metal(loid)s that have observed before in gas refinery and petrochemical emissions [24,26,27]. The current paper aims to evaluate the hypotheses that gas refinery and petrochemical workers occupied in Asalouyeh area (which involved in the "two weeks work-two weeks rest" schedule) are threatened to increase body burden of metal(loid)s during two weeks work by measuring the urinary concentration of As, Cd, V, Mn, and Ni. The health hazards of metal(loid)s in atmospheric dust and drinking water was also assessed. The study results can be useful to awareness of the impact of short-term exposure to toxic elements originated from gas and petrochemical activities on the safety and health of the workers and can be used to determining the occupational exposure level for these industries workers in the term of metal(loid)s exposure.

2. Materials and method

2.1. Study design

A before-and-after observational study was conducted in the Pars Special Economic Energy Zone located in Asalouyeh (27°28′34″ N, 52°36′27″ E), southern Iran. Fig. 1 shows the location of the studied area. The target community was workers of petrochemical and gas refinery companies who included the regulation of "two weeks work-two weeks rest". The urinary level of participants was considered before and after the two weeks of work. So, the demographic, socio-economic, and medical conditions for before and after exposed (workers in each group) were similar. Workers in both groups (gas refineries and petrochemical

companies) who worked outdoor at least 4 h per day were considered for this research.

In this study, the number of 85 and 94 workers from the gas refinery and petrochemical companies was participated, respectively. More details regarding the sample size are provided in Supplementary data.

All of the participants were informed about the aims of this work and agreed to collaborate. The proposal of this research was approved by the Medical Research Ethics Committee of Bushehr University of Medical Sciences. Volunteer participants gave written consent and at any time, they were free to withdraw their co-operation. Confidentiality of the results was also guaranteed.

2.2. Urine sample collection and analysis

Spot morning urine samples were collected in 100 m L-polystyrene containers which acid washed with HNO_3 (20%) and rinsed twice with MilliQ water. Samples transferred to the laboratory beside ice, their pH were decreased below 2 by adding HNO_3 (65%) and then stored in −20 °C for about one month (to gather all urine samples). For instrument analyzing samples defrosted at 4 °C, homogenized, filtered, and were sent to the laboratory of the School of Pharmacy (Shiraz University of Medical Science, Iran) to measured the metal(loid)s.

The experimental method for urinary metal(loid)s analysis were previously described in details [28]. Briefly, the concentration of Cd, Mn, Ni, and V determined through a graphite furnace atomic absorption spectrometry (PerkinElmer® PinAAcle™ 900 T, Shelton, CT, USA), and urinary concentration of As measured by direct flow injection through a hydride generation system. The high purity chemicals including nitric acid (65%), ammonium dihydrogen phosphate, magnesium nitrate, hydrochloric acid (30%), barium fluoride, palladium nitrate, ultrapure water (with a resistivity of 18.2 MΩ cm), and Triton X100 were purchased from Merck Company. The standard solution of the studied metal(loid)s was also provided from Merck Company at the highest purity to prepare the calibration curve. The quality of the measurement method was controlled by certified reference materials (CRM). The CRM sample for urine (ref. 201,205) was supplied by Seronorm (Billingstad, Norway). The difference between target and the found value for CRM for elements of Mn, Cd, V, Ni, and As was obtained as 2.20%, 1.75%, 2.74%, 5.44%, and 3.50%, respectively. All samples were measured three times to be more precise and the average of measurements was used in the statistical analyses. Blanks were also prepared in the same analytical conditions to determine the background interferences. The limits of detection (LOD) were stated to be 0.03 μg/L for Cd, 0.24 μg/L for Ni, 0.12 μg/L for Mn, 0.11 μg/L for V, and 0.03 μg/L for As.

2.3. Drinking water and dust sample collection and analysis

During the study period, the workers have used 6 types of bottled water for drinking, all of which were tested. Each sample contained 200 mL of drinking water. For each group (the gas refinery and petrochemical companies), six bottled water were sampled. The method of preserving and measuring metal(loid)s in water samples was similar to that in urine ones.

Dust sampling was done passively. Dust collectors were installed approximately 175 cm above the ground on a metal tripod. Each sample collector was included of a circular plastic surface (32 cm in diameter and 12 cm in depth) and fixed by a holder. Five stations were considered for each of the gas refinery and petrochemical companies (where the workers were busy working), and they were subjected to sampling for particle matter for a period of one month (see Fig. 1). The sampling stations were selected according to the following criteria. The stations were not shaded by buildings or trees, were easily accessible, and safe against animals and extreme wind currents. At the end of the sampling, the dust samples were carefully collected with double distilled water in polyethylene containers, labeled, and then shipped to the

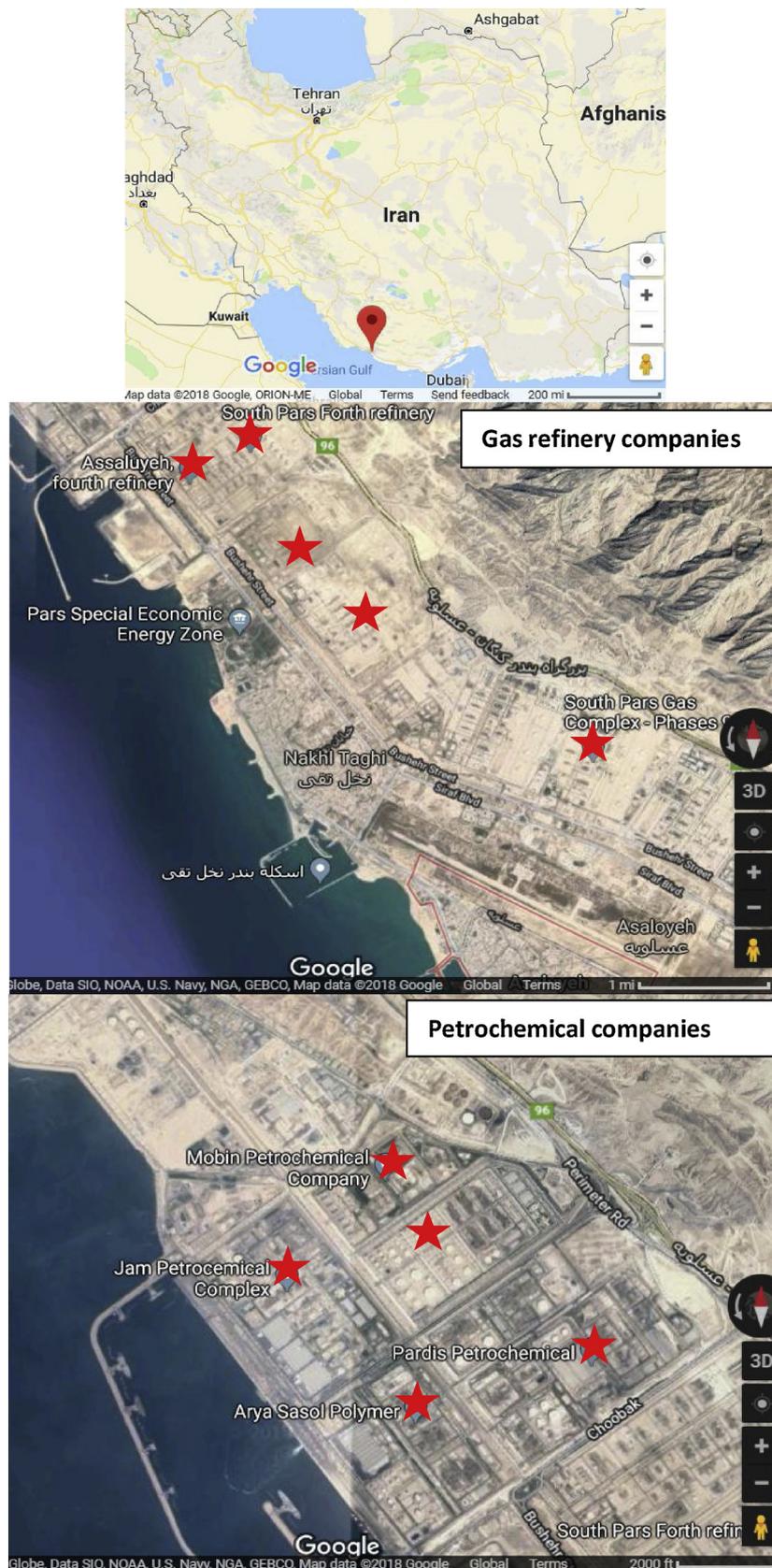**Fig. 1.** Map of the study area, red stars showing the air dust sampling points (Image from Google Earth© software.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1
Urinary metal(loid)s concentration in all participant workers (n = 179).

Element	Sampling group	Median(P25-75)	Min-Max	P-value
Cd	Before	0.36 (0.13-0.46)	0.03-1.00	< **0.001**
	After	0.31 (0.15-0.53)	0.03-1.01	
V	Before	0.08 (0.04-0.08)	0.02-0.20	< **0.001**
	After	0.05 (0.06-0.12)	0.03-3.99	
Ni	Before	1.06 (0.33-0.72)	0.20-1.47	< **0.001**
	After	0.51 (0.74-1.48)	0.48-3.11	
Mn	Before	0.29 (0.13-0.39)	0.06-1.14	**0.002**
	After	0.24 (0.16-0.43)	0.08-1.13	
As	Before	11.44 (5.91-11.82)	1.15-47.72	< **0.001**
	After	9.31 (7.63-14.20)	1.26-52.13	

lab. The total sample was 10 for both industries (gas refinery and petrochemical companies). All samples were dried at 55 °C for 48 h to prevent the evaporation of the elements. The specimens were then passed through a nylon sieve (1 mm holes diameter) to separate refuse and sand particles. To measure the concentration of metal(loid)s, the sample was again screened by a nylon sieve (diameter of the holes was 63 μm) [29,30]. The digestion of the samples was done according to our previous study [31].

The digestion method of dust sample was performed according to our previous study [31]. Briefly, 2 mL of perchloric acid (Merck Co., 90% (w/w), suprapure) and 8 mL of nitric acid (Fluka, 35% (w/w), suprapure) were added to one gram of powdered dust samples. The solution was pre-digested at room temperature (24 ± 2 °C) during 12 h. The pre-digested dust samples were placed at an oven (100 °C) for 4 h and then 140 °C for 4 h to achieve a clear solution. The tubes were cooled at room temperature and then filtered. The volume of the filtrate was elevated using ultrapure demineralized water (Milli-Q System) to 50 mL. The target metal/metalloid was measured in the final solution

2.4. Health risk assessment of metal(loid)s intake from drinking water and dust

Risk assessment was carried out to estimate cancer and non-cancer risks from drinking water. In this study, for drinking water samples the intake from inhalation and dermal routes are negligible, thus, the ingestion path was only evaluated according to the following equation:

$$D_{ing} = \frac{C \times IR_{ing} \times F \times ED}{BW \times AT} \tag{2}$$

where D_{ing} is an exposure dose through water consumption (mg/kg.d), C is the contaminant concentration (mg/L), IR_{ing} is the intake rate of the contaminated water (2 L/d-adult), F is the frequency of exposure (182 day/year), ED is the exposure duration (30 years), BW is the body weight (70 kg), AT is the averaging time (ED × 365 day/year; for non-cancer hazard and 70 × 365 day/year; for cancer hazard).

In the case of air dust samples, the risk assessment was only assessed for the inhalation route [32]. To do this, in the first step, the average daily intake was calculated using the following equation:

$$D_{inh} = \frac{C \times P_{Air} \times IR_{inh} \times F \times ED}{BW \times AT} \tag{3}$$

where D_{inh} is the exposure dose through air dust inhalation (mg/kg.d), C is the contaminant concentration (mg/kg), P_{Air} is the particulate concentration in the air (kg/m^3), IR_{ing} is the intake rate (15.2 m^3/d).

In the second step, for non-cancer risk, the hazard quotient (HQ) was calculated by using the following equation:

$$HQ = \frac{D_{ing,inh}}{RfD} \tag{4}$$

where RfD is the reference dose (mg/kg.d).

In the next step, HI (hazard index) was obtained from the summation of the calculated HQ for each metal(loid)s (HQ$_i$) (Eq. (4)).

$$HI = \sum_{i=1}^{n=5} HQ_i \tag{5}$$

The cancer risk (CR) for each metal(loid)s (Ni, Cd, and As) was obtained with considering the cancer slope factor (Sf, mg/kg.d) and it was calculated using Eq. (6).

$$CR = D_{ing,inh} \times Sf \tag{6}$$

Total CR was calculated from the summation of CR evaluated for each metal(loid)s. All calculations were carried out for gas refinery and petrochemical companies, separately.

The HI and CR values were based on the adjudication the potential of studied metal(loid)s to create the hazard.

All formulas and RfD and Sf values were gathered from the related references [6,33–35].

2.5. Statistical analysis

The statistical analyses were conducted using the IBM SPSS 22 software (SPSS Inc., IBM Company, Chicago, Ill., USA). Based on Shapiro-Wilk's test, the distribution of our data was not normal. The median levels of urinary metal(loid)s between two groups (gas refinery and petrochemical workers) were compared by using Mann-Whitney *U* test Comparing of median differences between before and after time (two weeks work) of urinary metal(loid)s levels in gas refinery and petrochemical workers were tested by using the Wilcoxon signed rank test. A p-value < 0.05 was defined as statistically significant. Minimum (min), maximum (max), median, and 25th and 75th percentiles (Px) was used to describe the metal(loid)s concentration.

3. Result

Table 1 shows a summary of statically analysis for all participant workers. The results of the urine sample analysis for both gas refinery and petrochemical workers are also summarized in Table 2. For both gas refinery and petrochemical workers, the median concentration of all studied metal(loid)s of the after time have higher values than that of before time (p-value < 0.05). Further, for all participants (n = 179, Table 1), the difference between after and before times of the metal (loid)s were considerable (p-value < 0.05). The median of nickel and vanadium for the after measurements increased by at least 60% relative to the before time for both groups. In the comparison between pre-exposure groups of gas and petrochemical industries, all measured metal(loid)s (with an exception of arsenic element) were a little higher in gas workers. These results were also found for post-exposure measurements.

Table 3 shows the median level for elevating metal(loid)s amount after the end of two-week works. The sequence of increasing urinary metal(loid)s levels (by percent) after two weeks work for workers of gas and petrochemical companies were observed as 'Ni > V > As > Mn > Cd' and 'Ni > V > Mn > Cd > As', respectively. A significant increase of metal(loid)s levels during two work weeks was more pronounced for As metalloid between gas and petrochemical workers (p-value < 0.05). The increase of median concentration of arsenic for workers of gas refineries was 40% higher than the petrochemical companies. The highest median growth was detected for metals of Ni and V in the workers' urine of gas (46% and 26%, respectively) and petrochemical (41% and 40%, respectively).

The measuring data of metal(loid)s in the air dust and drinking water samples from the gas refinery and petrochemical sites are presented in Table 4. The median concentration of cadmium was different in the air dust of gas and petrochemical companies. The Cd metal of the gas refinery dust samples was reported as 9.6 fold higher compared to petrochemical complex dust. This increasing trend was also observed for other studied metal(loid)s, however, it was not more pronounced.

From Table 4, in the bottled water samples, the significance value

Table 2

Urinary metal(loid)s concentration (µg/L) in the workers of gas refinery (n = 94) and petrochemical companies (n = 85) group.

Element	Group	Sampling time	Median (P25-75)	Min-Max	P-value	P-value for gas-petrochemical	
						Before	After
Cd	Gas refinery	Before	0.37 (0.13-0.46)	0.03-0.92	< **0.001**	0733	0.735
		After	0.32 (0.15-0.53)	0.03-0.93			
	Petrochemical	Before	0.35 (0.13-0.46)	0.03-1.00	< **0.001**		
		After	0.31 (0.15-0.53)	0.03-1.01			
V	Gas refinery	Before	0.08 (0.04-0.08)	0.02-0.20	**0.002**	0.391	0.400
		After	0.05 (0.05-0.12)	0.03-3.99			
	Petrochemical	Before	0.08 (0.04-0.08)	0.02-0.20	< **0.001**		
		After	0.05 (0.05-0.12)	0.03-3.99			
Ni	Gas refinery	Before	1.09 (0.35-0.72)	0.21-1.47	< **0.001**	0.131	0.151
		After	0.056 (0.91-1.47)	0.48-3.11			
	Petrochemical	Before	1.05 (0.30-0.71)	0.20-1.40	< **0.001**		
		After	0.50 (0.64-1.51)	0.50-2.61			
Mn	Gas refinery	Before	0.33 (0.14-0.38)	0.08-1.12	**0.012**	0.131	0.209
		After	0.24 (0.24-0.41)	0.08-1.12			
	Petrochemical	Before	0.28 (0.12-0.39)	0.06-1.14	**0.047**		
		After	0.23 (0.14-0.43)	0.08-1.13			
As	Gas refinery	Before	12.25 (7.02-11.82)	1.18-28.36	< **0.001**	**0.041**	< **0.001**
		After	9.45 (9.38-17.38)	1.29-35.81			
	Petrochemical	Before	10.06 (5.82-11.64)	1.15-47.72	< **0.001**		
		After	9.21 (6.36-12.72)	1.26-52.13			

was only observed for Mn (p-value < 0.05). The median concentration of Mn in the water of petrochemical companies was measured 4.8 fold higher than the gas refinery. It was also found that the cadmium concentration in water samples of petrochemical companies is approximately 3 times higher than that of gas companies. In the other hand, gas companies had more arsenic content in their waters compared to petrochemical companies.

The non-cancer effects of the studied metal(loid)s from the ingestion of drinking water for the gas refinery workers were slightly greater than those calculated for petrochemical workers. The calculated HI for the workers of gas refinery and petrochemical companies was obtained 4.23 and 4.04, respectively. The cancer effect in drinking water was only calculable for arsenic. The CR measured for gas refinery and petrochemical workers from As due to the drinking water was calculated to be 0.72×10^{-6} and 0.36×10^{-6}, respectively. The CR value from air dust inhalation was calculable for As, Cd, and Ni. The total CR measured for the workers of gas refinery and petrochemical companies was attained to be 6.55×10^{-9} and 3.06×10^{-9}, respectively.

4. Discussion

Totally 179 workers (94 gas refinery workers and 85 petrochemical workers) participated in the study for the sampling campaigns. The urine metal(loid)s concentrations in both groups were similar (for both before and after sampling times), that was consistent to those reported for the studied children living in Asalouyeh zone [28].

By comparison of urinary metal(loid)s content of gas and petrochemical workers, it was found that the exposure to Cd, Ni, V, and Mn is similar in both groups for before and after two work weeks. In contrast, the concentration of arsenic metalloid was significantly different for both studied times in two groups. In previous studies [28,31], it has been confirmed that the gas extracted from the Asalouyeh region naturally contains metal(loid)s, so higher urinary concentrations of

metal(loid)s in the workers of gas companies than those of petrochemical companies can be attributed to this issue.

However, according to Table 3, it can be concluded that exposure to heavy metals of Ni, Cd, Mn, and V in both industries showed the same effect on the workers. The highest percentage of differences was found for Ni and V. These two elements are important metals in gas and petrochemical activities and the findings show the effect of these activities on increasing of metals in the urine of workers [37]. Several studies demonstrated the significant effect of petrochemical activity on increasing of the body burden of trace elements in occupationally exposed workers [38,39]. For the public population, the residency to petrochemical sites, it has been recognized as the most important factor in increasing the urinary level of heavy metals [40]. In studies on the children and adults population [41,42], the urinary level of Cd, As, and V was decreased with increasing distance from the petrochemical industries.

In studies among people living near petrochemical site areas, similar to our results, a higher urinary concentration of As and Ni compared to V and Cd was reported by Chen et al. [43]. Yuan et al. [42] were also measured a higher urinary level of As than V and Cd. But in previous studies [42,43], the reported level of urinary Cd was higher than V metal. The various process involved in petrochemical industries and uptake metals from other sources such as food, air, and water can affect the variation in the distribution of heavy metals in biological matrixes.

The highest concentration of measured metal(loid)s for both groups was seen for arsenic, however, it was lower than the biological exposure limit in urine determined by ACGHI for As (35 µg/L; end of the work-week) [44]. The maximum-minimum concentration of urinary As in workers from 3 petrochemical plants were as ND–874.30 µg/L, 2.20–265.60 µg/L, and 1.39–476.40 µg/L [39], that was notably higher than our results for both groups after two weeks work. Median of urinary arsenic (9.4 µg/L) in the workers of artisanal and small-scale gold mining in Tanzania [45] is more matched to the level reported for

Table 3

Comparing the changes of the before- and after- time concentration of urinary elements (µg/L) between two groups. Data show the 'median(P25-75)'.

Element	Cd	V	Ni	Mn	As
Gas refinery	0.045 (0.018-0.065)	0.021 (0.022-0.057)	0.507 (0.300-0.888)	0.046 (0.084-0.177)	1.201 (0.764-5.385)
Petrochemical	0.042 (0.016-0.061)	0.032 (0.001-0.066)	0.440 (0.266-0.789)	0.045 (0.135-0.202)	0.851 (0.538-1.076)
P-value	0.470	0.167	0.512	0.919	< **0.001**

Table 4

Comparison of metal(loid)s concentration in the drinking water served by workers and air dust during sampling times.

Element	Group	Air dust (µg/g, n = 5 stations)		P-value [a]	Drinking water (mg/L, n = 6)				P-value [a]
		Median (P25-75)	Min- Max		Median (P25-75)	Min- Max	Standard		
							WHO	US EPA	
Cd	Gas refinery	1.44 (0.68-6.86)	0.520-10.700	**0.016**	0.026 (0.007-0.068)	0.00-0.130	0.003	0.005	0.589
	Petrochemical	0.15 (0.12-0.39)	0.100-0.560		0.075 (0.007-0.167)	0.00-0.220			
V	Gas refinery	5.60 (2.20-11.35)	2.100-14.900	0.421	0.080 (0.060-0.098)	0.060-0.110	_[b]	–	0.999
	Petrochemical	2.30 (0.98-8.00)	0.770-9.200		0.083 (0.007-0.121)	0.00-0.140			
Ni	Gas refinery	49.90 (32.68-80.00)	19.360-100.00	0.056	0.040 (0.007-0.061)	0.00-0.080	0.07	0.10	0.310
	Petrochemical	25.30 (1.85-32.25)	0.500-38.500		0.065 (0.017-0.090)	0.011-0.092			
Mn	Gas refinery	89.00 (36.90-110.50)	28.600-110.00	0.151	0.010 (0.003-0.013)	0.00-0.020	0.05	0.05	**0.004**
	Petrochemical	39.01 (16.17-48.43)	12.530-48.650		0.048 (0.022-0.065)	0.012-0.090			
As	Gas refinery	2.50 (1.29-10.05)	1.500-12.100	0.548	0.055(0.009-0.102)	0.009-0.140	0.01	0.01	0.394
	Petrochemical	1.58 (0.75-7.55)	0.570-11.780		0.030(0.007-0.062)	0.00-0.070			

[a] P- values are based on Mann-Whitney *U* test

[b] The US EPA put vanadium on the top in the list of contaminant candidate. The California Department Public of Health (CDPH) established a notification level of 50 µg/L for vanadium in drinking water [36].

exposed workers of both groups. The range of As in our exposed group after two weeks work (gas refinery: 1.29–35.81 µg/L and petrochemical companies: 1.26–52.13 µg/L) was lower than the exposed (11.95–70.08 µg/L) and control groups (5.56–46.52 µg/L) in a semi-conductor manufacturing industry [46]. In addition to ambient air [47], the food consumption is an important way to uptake arsenic, as for petrochemical workers, well correlation was found between food consumption and urinary level of arsenic [39].

Ni was the second major measured element that showed significantly increased (p-value < 0.001) and had a 2-fold difference in urine samples of before and after times. Similar to our finding, the urinary nickel was indicated as a reliable indicator in the biological monitoring of occupationally Ni exposure in workers from galvanizing plants [48]. Urinary Ni concentration in pre- and post-shift samples from battery plant workers on two consecutive days [49] and Ni concentration among workers in a jewelry manufacturing and control group [50] was found very higher than our results.

Urinary cadmium is a preferred marker to reflect body burden of Cd under short- and long-term exposure [51]. However, in our study, the potential of urinary Cd to verify recent exposure successfully evaluated, as its median concentration after two weeks work showed a significant increase in both industries (p-value < 0.001). The median of urinary cadmium in workers of this study was about one-third of those reported in the Buser et al. study [52]. In compare with steel production workers, the range of Cd concentration in the urine of control workers (0.60–6.81 µg/L) was several times higher than us, while the range in production workers (3.08–22.61 µg/L) and quality control ones (3.18–10.32 µg/L) were even more measured [53]. Our measurements were also lower than those reported for jewelry manufacturing workers and the reference group [50].

The median of urinary manganese in all workers of gas refinery and petrochemical was detected to be 0.24 µg/L at the end of two weeks work (after time). It was significantly increased to 0.29 µg/L for before one (p-value < 0.05). Our data was near to those reported for exposed workers from dry cell battery factory (range: 0.2 − 0.7 µg/L) [54] but was lower than those reported for workers of a ferroalloy plant (0.7–7 µg/L) [55] and smelter workers from South Africa [56].

Lowest concentration in measured urinary metal(loid)s was related to vanadium, however, petroleum, coal, and oil industries are the main origins of vanadium released into the environment [36,57]. According to literature, vanadium is a prevalent metal found in the environment around petrochemical sites [47,57] and urinary vanadium is a good bioindicator to reflect the exposure to vanadium in the air [47]. We measured significantly higher the median level of vanadium in the after time compared to before time (p-value < 0.001), but this finding yet

was far away from the biological exposure limit in urine determined by ACGIH at the end of workweek (50 µg/L) [44] and was very lower than the urinary level reported for workers who were occupationally exposed to vanadium from the steel production plant (range: 2.12–95.3 µg/L) and control group workers (range: 0.07–1.4 µg/L) [58]. In workers exposed to vanadium dust, absorption from the respiratory tract and consequently increasing of vanadium concentration in urine has been detected [59].

As discussed earlier, in comparison with workers from other industries all around the world, the urinary metal concentrations in both before- and after- time populations of gas refinery and petrochemical industries were lower than those reported in the literature, but it is not guaranteed the safety of workers to exposure metal(loid)s. As implied from the findings, after two workweeks the difference between detected levels was significant (p-value < 0.001) for most of the studied metal(loid)s. Although the exposure path to metal(loid)s and their uptake level is very different in various industries, due to the lack of published information about exposure to metal(loid)s among gas and petrochemical workers, we obliged to compare our results to other studied industries or public population.

The three main ways of receiving metal(loid)s from the environment to humans include air, water, and food. In this study, the amount of metal(loid)s in the dust and drinking water of workers was determined. Differences between metal(loid)s level were significant in the case of Cd in dust samples and Mn in water samples, while as noted in Table 3, only arsenic metalloid in workers urine samples of the gas refinery and petrochemical sites significantly differed. Type and amount of exposure, intake route, metabolism of metal(loid)s in body, and intake from a major source like food (especially seafood due to adjacent to sea), can be related to the different pattern of distribution and accumulation of the metal(loid)s in the environment and the body of workers.

As for urine obtained, the median of metal(loid)s in dust samples in gas refinery companies was reported greater than that of petrochemical companies. So, we can presume the distribution of measured contaminants in the air can be related to the increase in their levels in the body. The correlation between the urinary levels of trace metals in exposed groups to industries emissions with inhaled air has been reported for various industries [38,49]. In the semiconductor manufacturing industry, a strong relationship between metal concentration in the inhalable air and urine for employees was detected [46]. So, use of the respiratory protection by industrial workers seemed to be necessary, as Yokota et al. [49] were found no correlation between Ni in the inhaled air and urine among battery pant workers, due to use of such equipment. Also, among petrochemical workers, a lower

concentration of toxic metals in the hair of production workers compare to office workers was related to use of personal protective equipment by this group [38]. Like air dust samples, trend of occurrence of metal (loid)s in drinking water samples was not match to urine, but according to Table 4, exceeded level of Cd and As from standards level (WHO and US EPA) in drinking water can be an important source to contribute of these metal(loid)s in the urine sample of workers. The drinking water was reported to be related to increasing of trace elements in the urine of e-waste recycling workers in Ghana [60].

The risk assessment was evaluated to determine the health effect of intake of metal(loid)s from drinking water and dust. Although, the calculated HI showed a higher risk for gas refinery workers rather than petrochemical ones, both of them were reported higher than the threshold number of 1. The two estimated HI was about 4 fold higher than unity. This indicated both groups of workers are at non-cancer risk from drinking water including hyperpigmentation, central nervous system (CNS) effects, and decreased body or organ weights [61]. In the other hand, CR values from drinking water (only measurable for As) in two worker groups, was less than 10^{-6}, the threshold of 1 case in million exposed people. This shows the uptake of the studied metal (loid)s from drinking water is a negligible source of cancer risk [62]. The risk for gas refinery workers was twice as high as that of petrochemical companies.

Risk assessment values from air dust inhalation showed higher CR for the gas refinery workers rather petrochemical workers. However, in both groups, the evaluated CR was less than one per million. The CR calculated in two industries ranged between 0.05×10^{-9} (Cd; for petrochemical companies) and 3.25×10^{-9} (Ni; for gas refinery). It is concluded that intake of the metal(loid)s of drinking water and inhaled air is not a risk factor for cancer.

5. Conclusion

In this before-and-after observational study, the amount of metal (loid)s in the urine of the workers of gas refinery and petrochemical companies was detected. For the petrochemical and gas refinery workers, the before- and after- exposed urinary concentration of all studied metal(loid)s was significantly different. The exposure level of the workers of the gas refinery and petrochemical companies to metal (lois)s was similar and followed the sequence of 'As > Ni > Cd > Mn > V'. Gas refinery and petrochemical plants detected as a potential source of metal(loid)s emission to the environment, so protection of employees and public population near them have to be more considered. The results of monitoring of air dust and drinking water suggested that these sources can be effected on the increasing body burden of the metal(lois)s. The health risk assessment showed that the metal(loid)s intake from drinking water is a potential source for non-cancer hazards. The results also implicitly suggest that the work schedule of 'two weeks work-two weeks rest' for gas refinery and petrochemical companies or other industries with such pollutants can save the workers.

Declaration of interest

None.

Acknowledgment

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jtemb.2019.05.001.

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