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Environmental nickel exposure from oil refinery emissions: a case study in Ecuador

Raúl Harari[1], **Florencia Harari**[1] **and Francesco Forastiere**[2]

[1]*Corporación para el Desarrollo de la Producción y el Medio Ambiente Laboral – IFA, Quito, Ecuador*
[2]*Dipartimento di Epidemiologia del Servizio Sanitario Regionale del Lazio, Rome, Italy*

Abstract
Introduction. Nickel is a strong skin and respiratory sensitizer and a recognized carcinogen. Oil refineries are important sources of atmospheric emissions of toxic pollutants, including nickel. Populations residing close to oil refineries are at potential risk.
The aim of this study was to evaluate the exposure to nickel in a population living close to the largest oil refinery in Ecuador, located in the city of Esmeraldas.
Methodology. We recruited 47 workers from the oil refinery as well as 195 students from 4 different schools close to the plant and 94 students from another school 25 km far from the industry. Urinary nickel concentrations were used to assess the exposure to nickel.
Results. Students from the school next to the oil refinery showed the highest urinary nickel concentrations while workers from the refinery showed the lowest concentrations. Median nickel concentrations were > 2µg/L in all study groups.
Conclusions. The populations living close to the oil refineries are potentially exposed to nickel from atmospheric emissions. Further studies investigating nickel-related health effects in the population residing close to the refinery of Esmeralda are needed.

Key words
- nickel
- Ecuador
- heavy metals
- oil refineries

INTRODUCTION

The metal nickel (atomic number 28, atomic weight 58.71) is a potent skin and respiratory sensitizer and a recognized human carcinogen [1]. Exposure to nickel is associated with a higher risk for lung and nasal cavity cancer as well as contact dermatitis and asthma [1-4]. Skin contact is a major exposure route for nickel absorption [5, 6]. Environmental exposure to nickel occurs primarily from air pollution from oil combustion and nickel factories, and to a less extent from food and drinking water, being inhalation and ingestion two other important exposure routes [7-10].

About 0.2% of all workforces is estimated to be exposed to considerable levels of nickel at the workplace but a broader fraction of the general population could be exposed to nickel from industrial emissions [7-14]. Oil refineries are important sources of atmospheric emissions. Oil refining involves the emission of gases and dust containing hydrocarbons, sulfur, nitrogen oxide, carbon monoxide as well as nickel and other metals, according to production and environmental conditions [15]. Therefore, populations living in areas close to oil refineries might be potentially exposed to nickel.

The present study aimed at evaluating the exposure to nickel in a population living close to an oil refinery in the Ecuadorian Coast and potentially exposed to its atmospheric emissions.

MATERIALS AND METHODS

Study population

The study was performed in the city of Esmeraldas, in Ecuador, where the largest oil refinery is located. The city of Esmeraldas is located in the northwest of the country and has approximately 150 000 inhabitants, most of them of Afro-Ecuadorian origin [16]. The city is influenced by emissions from the oil refinery when the wind blows from the southwest, being this about to 52% of the time. This is due to thermic inversion processes where the wind blows toward the sea during the day and blows back to the ground during the night.

The study population consisted of 6 study groups: students from five different schools (schools n. 1 to 5) located in the surrounding areas of the refinery at different distances and workers recruited from the oil refinery (Group n. 6) (*Figure 1*). We aimed at recruiting 50 workers from the refinery, 50 students from each of the four closest surrounding schools and 100 students from the fifth school located at 25 km from the oil refinery (control area). All the subjects, students from 1st and 2nd grades (aged 6-8 years, schools 2-5), teenagers

Address for correspondence: Raúl Harari, Corporación para el Desarrollo de la Producción y el Medio Ambiente Laboral – IFA, Domingo de Brieva N38-107 y Villalengua, PO Box 17-08-8386, Quito, Ecuador. E-mail: ifa@ifa.org.ec.

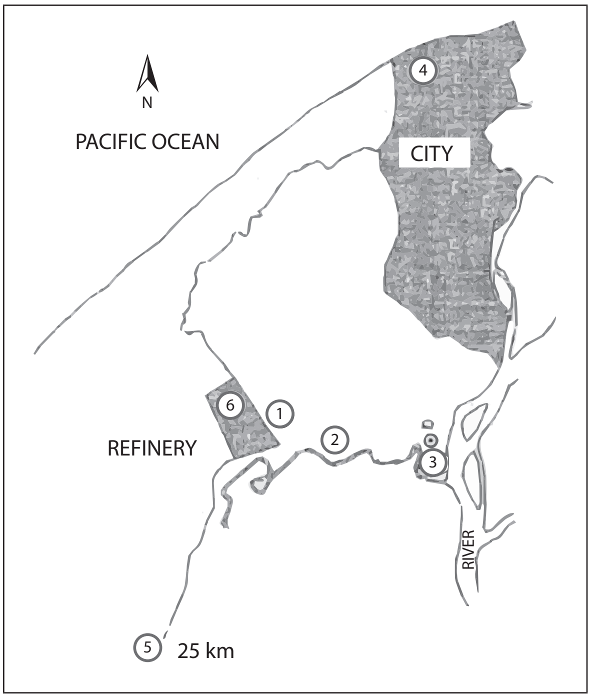

Figure 1
Map of the 6 study sites in the city of Esmeraldas, Ecuador.

from a boarding school (school 1) and workers from the refinery (study group 6), were randomly selected within the specific study population and both male and women were included. Exceptions were made for workers from the oil refinery (as only male are employed there) and from the boarding school as it was a masculine school. A questionnaire was filled in by the parents or closest caregiver to each student (as well as from workers) to obtain information regarding individual characteristics and health status. An informed consent was obtained from the parents after explanation of the study.

Assessment of environmental nickel concentrations

For assessment of environmental nickel exposure, we collected dust and waste water samples from the oil refinery. Direct dust samples were collected from the chimneys of the oil refinery. Details regarding sample collection of direct dust samples have been described elsewhere [17, 18]. Waste water samples were collected from the sedimentation pool and the dam of the ventilation pool at the oil refinery.

Nickel measurement in dust samples was framed on knowledge of production conditions (number of barrels of refined oil and American Petroleum Institute, API, degree), climate (temperature, humidity and wind direction and speed), geography (coastal location of the study area), and topography (slopes of ground), using a mobile Mass Spectrophotometer type CIMS-500 (mass range = 1-500 atomic mass units (AMU)), applying a chemical ionization mode to give a relatively low ionization potential. This method also calculated the particle size in the dust samples. The sampling tube was Teflon®, inner diameter 4 mm, with a flow of about 4 liters per minute.

Dust samples were collected using a sampling system where dust is stored in two filters of 142 mm every day (during 8 consecutive hours). The filtered gas is cooled in an air cooling and then dried in a silica gel column. The water contained in the resulting gas is condensed and the weight increases in the silica gel. The dry gas volume is recorded by a calibrated gasometer. In the gasometer, gas temperature and the sampled pressure is recorded for a later use as a correction factor. The amount of dust is calculated despite the increased weight and the sampling volume [19].

Subsequently, based on measurements made at approximately every 20 minutes, a trend analysis was performed, giving an average value. The components identified outside the existing spectrum are calculated and presented in concentrations at the exact time as the respective spectra were analyzed because the concentrations of the run are stable, set at an accuracy of + 20%. The dust is partially determined in mg/m^3, normalized, but also in relation to the size distribution, content of metal in the dust, breathable content of metal stuff in their respective size fractions, and finally presented in g/h.

The results are shown and calculated at normal pressure (101.325 kPa), temperature 273 °K but also at 11% O_2. In the samples, the calculated values were also computed at 10% CO_2 and 10% O_2. Analyses were performed considering a mass spectrum of 1-300. These spectra were made in three different runs: 1) ionization with krypton gas (Kr^+) having an ionization potential of 14.1 eV; 2) ionization with xenon gas (Xe^+) having an ionization potential of 12.3 eV; and 3) with gas ionization in mercury vapor (Hg^+), having an ionization potential of 10 eV [20].

Measurement of nickel in waste water samples was done using the Microtox® Test.

Assessment of urinary nickel concentrations

We assessed the exposure to nickel by measuring the nickel concentrations in urine, as urinary nickel concentrations are a well-known exposure marker for nickel [5, 7, 21, 22]. Individuals were asked to collect one spot-urine sample, following careful instructions, into plastic tubes and a drop of hydrochloric acid was added to prevent contamination during the collection period. Urine samples were frozen and kept at -20 °C until they were sent for analyses to the Laboratory of the Luigi Devoto Clinic at the University of Milano, Italy.

The quality control of the analytical method was based on a linearity range of 0.3-50 µg/L and at an accuracy in set < 6% and between sets < 10%. The limit of detection was 0.3 µg/L. Values above 2 µg/L were considered as high and above 10 µg/L, as very high. Specific gravity in urine was measured to correct the nickel concentrations for the mean urinary dilution of the study population (0.017).

Statistical analyses

Statistical analyses were performed using Stata (StataCorp. 2013. Stata Statistical Software: Release 13. College Station, TX: StataCorp LP). A *p*-value < 0.05 was considered statistically significant. Median and ranges are presented for continuous variables and number and percentage for categorical variables. Kruskal-Wallis rank test and Mann-Whitney U test were used for comparison among groups. Box plots were used to present the distribution of the urinary nickel concentrations among the different study groups.

RESULTS

The environmental parameters of the study area were: average temperature between 15° and 35 °C, 50-80% humidity, and wind direction towards southeast and southwest to north. The scattering occurred shoreward in the day and returned at night from the sea towards the close coast.

Nickel concentrations in dust samples at the different emission points in the oil refinery are presented in *Table 1*. Dust emissions from chimneys 3, 4 and 5 at the oil refinery showed the highest nickel concentrations. Fifty one percent of particles had a size below 10 μ (21.5% below 2 μ; 20.4% between 2 and 5 μ; and 9.0% between 5 and 10 μ), representing the breathing fraction and being those particles following the same path as gases, while 21.5% were between 10 and 15 μ, and 27.7% above 15 μ.

Nickel concentrations in the waste water samples showed levels of 0.02 to 0.08 mg/L. However, nickel concentrations in the refinery sludge (from flotation) were 66 mg/kg and from the sludge sedimentation pool were 240 mg/kg.

Characteristics of the study individuals recruited from each study site are presented in *Table 2*. The highest urinary nickel concentrations were found among children of the school located beside the oil refinery and differed statistically from all other study groups ($p < 0.001$ for all). The second highest urinary nickel concentrations were found in the school 3, which were statistically different from the school beside the oil refinery (school 1) and from the workers of the oil refinery ($p = 0.009$). The lowest nickel concentrations were found in the group of workers of the oil refinery (*Table 2* and *Figure 2*). Nickel concentrations did not differ statistically between males and females.

DISCUSSION

This study shows that emissions from oil refinery chimneys might contain elevated nickel concentrations

Table 1
Nickel concentrations in dust samples at the different emission points in the oil refinery

N.	Emission point	Nickel concentrations (g/h)[a]
1	Chimney	28
2	Stack	50
3	Chimney	357
4	Chimney	177
5	Chimney	273
6	Stack	1.1

[a]Average nickel concentrations in air samples (g/h) collected during 8 consecutive hours.

Table 2
Characteristics of the study participants by study group

Study groups	n. (%) or median (range)
School 1	
N	48
Male n. (%)	48 (100%)
Age (years)	14 (12-32)
Urinary nickel (μg/L)a	11 (1.7-28)
School 2	
N	50
Male n. (%)	20 (58%)
Age (years)	6 (6-7)
Urinary nickel (μg/L)a	2.7 (0.59-19)
School 3	
N	49
Male n. (%)	32 (65%)
Age (years)	6 (6-6)
Urinary nickel (μg/L)a	3.2 (< LOD-18)
School 4	
N	48
Male n. (%)	14 (29%)
Age (years)	6 (6-12)
Urinary nickel (μg/L)[a]	2.6 (0.41-21)
School 5 (control)	
N	94
Male n. (%)	54 (57%)
Age (years)	6 (4-8)
Urinary nickel (μg/L)a	2.7 (< LOD-10)
Workers from the oil refinery	
N	47
Male n. (%)	47 (100%)
Age (years)	37 (28-62)
Urinary nickel (μg/L)a	2.2 (< LOD-9.6)

[a] Urinary nickel concentrations were adjusted for the mean urinary specific gravity (1017).

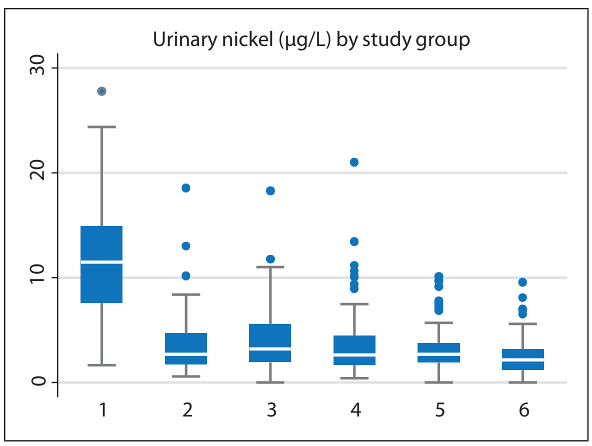

Figure 2
Distribution of urinary nickel concentrations in the different study groups. Box layers describe the 75th, 50th and 25th percentiles.

and that individuals studying at schools close to oil refineries might be exposed to nickel. Varying nickel concentrations were found in urine but individuals studying at the school beside the refinery showed the highest nickel concentrations. On the contrary, workers from the oil refinery working at the bottom of the chimneys showed the lowest urinary concentrations.

Workers from the oil refinery had the lowest nickel concentrations in urine. This might be due to the use of personal protection and because they usually work at the bottom of the chimneys and, thus, are not directly exposed to the dust from the chimneys emissions that go out of the refinery. On the contrary, students from the school beside the oil refinery showed the highest nickel concentrations in urine. Students attending this school usually spend some time outdoors and are, therefore, potentially exposed to the emissions from the oil refinery. The presence of nickel in urine from students from the control area might indicate that some emissions from the oil refinery could still reach this area or that they are exposed to nickel through other potential sources that were not investigated in this study.

The median nickel concentrations in urine in our study were above 2 µg/L in all study groups. The median urinary concentrations of nickel in the workers from the refinery were 2.2 µg/L; similar to those found in welders welding on stainless steel in a Norwegian study [23]. Nickel concentrations in urine in the school beside the oil refinery were, however, 3-to-4-fold higher than those in the workers (median 11 µg/L, range 1.7-28) and 10-fold higher than those found in smokers [24]. High nickel concentrations in environmental samples have been also found close to oil refineries in other countries. In our study, nickel concentrations in sludge ranged 66-250 mg/kg, at least 2-fold higher than those found in the Numaligarh Refinery in India [25].

Nickel is known to be a strong skin sensitizer as well as a recognized carcinogen [1]. Exposure to nickel from occupational and non-occupational sources has been associated with lung and nasal cavity cancer, as well as allergic diseases such as dermatitis and asthma [5]. Inhalation is one of the main exposure routes for nickel [5, 6]. In our study, more than half of the dust particles had a size below 10 µ. This means that, after breathing these particles, they will eventually end up in the lung alveoli and cannot be expectorated. Particles above 10 µ are so-called total powder and will only remain in the upper part of the airways [26], representing a potential risk of nickel-related diseases.

CONCLUSION

The present study shows the presence of elevated nickel concentrations in urine from students at a school beside an oil refinery. These results are of public health relevance and reinforce the need for more rigorous monitoring in populations residing close to oil refineries. Further studies investigating nickel-related health effects in this population are needed.

Author's contributions statement

RH and FF designed the study, RH performed the sample collection, FH performed statistical analyses, RH, FH and FF drafted the manuscript and accepted its final version.

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Conflict of interest statement

No competing financial interests exist.

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