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Assessment of occupational exposure and contamination by means of airborne particulate matter and biomonitors using k_0 instrumental neutron activation analysis

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In order to assess the elemental concentration level in a galvanizing industry and alert for the need to assess the outcome of a long-term exposure, scalp hair and toenail samples were used as bioindicators and the industry environment was evaluated through airborne particulate matter. The elemental concentration results have pointed out a high exposure to pollutant at workplaces and a high elemental concentration in biomonitors suggesting endogenous contamination. The majority of the elements determined in airborne particulate matter were also determined in hair and toenail samples. The results evidence the efficiency of these matrixes as biomonitors and the importance to carry out the airborne particulate matter sampling in parallel to these biomonitors mainly in occupational epidemiological studies.

Introduction

An occupational disease diagnosis is complex not only because of the difficulty to identify and characterise the exposure, but also because the physicians do not usually have access to the quantity of raw material managed by the worker and the period of exposure to the substances. Besides this, the onset of occupational diseases is similar to other chronic diseases. Many processes take time to produce their effects, and because of that, contamination is difficult to be identified. The effects may appear in a long term. There is no specialized and complete literature about occupational aetiology and neither an evaluation of the onset of the disease linked to a long-term exposure to low levels of toxic agents.[1–3] In general, contamination by metals is a health hazard among workers at different plants, however, there are no records of the levels of metal concentration in the environmental air in industry, neither any records of the levels of contamination of factory workers or even the environment impact.

Belo Horizonte, capital of the Brazilian State of Minas Gerais, and the surrounding region represents an important industrial centre. Among several industries, galvanization is responsible for the majority of patients who look for medical assistance because of metal contamination. Due to this reason, the galvanizing industry was chosen to be studied. Galvanization[4,5] is an electroplating process for depositing a coating in a desirable form by means of electrolysis, involving the following steps: polishing with abrasives, washing the items with acids and sodium hydroxide, and electrodeposition of chromium, copper, gold, nickel, silver or zinc. The factories are mentioned as those with "hard chromium" when the main industrial process is to plate chromium, usually over very big items as car parts, for instance. "Decorative chromium" means that various kinds of electrodeposition are applied involving chromium, zinc, nickel, brass, gold, silver and copper plating. In general the plating is over small items like taps, trays, decorative items.

To develop this project, galvanization factories working with the same procedures and diversified metals, as "decorative chromium" were selected and chosen at random. They are called home factory because they are usually in a small warehouse, operated by 3 to 10 workers. It is a kind of industrial process that does not demand a complex structure to be installed, involving low maintenance costs and locally available inexpensive labour force. Because of the poor working conditions it is common to disregard air pollution, exhaust rate, individual safety, adequate equipment such as goggles, gloves and masks. Besides the cultural behavior and the warm climate, other factors contribute to increase the risks of contamination, such as the kind of job, working hours in this function, the galvanization process itself and the location of the facilities within the factory.

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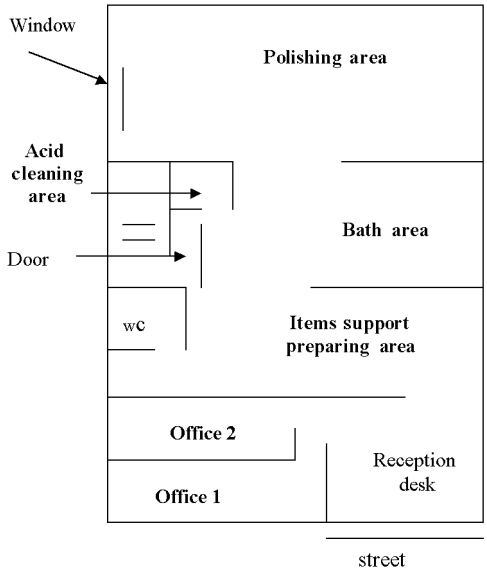

Fig. 1. Distribution of the activities in the galvanizing factory

In order to assess the level of contamination, scalp hair and toenail clippings biomonitors were donated both by workers, the Workers' Group, and by individuals not exposed to the galvanizing environment, the Comparative Group. These bioindicators[6–9] assess the health risk through the evaluation of the level of incorporation or exposure. The level of exposure was evaluated collecting airborne particulate matter in filters.[10,11]

This paper, related to galvanizing, is one step of a survey of people who have been exposed to metals at workplace. This project has been conducted together with the physicians of the Secretaria Municipal de Saúde (Municipal Department of Health) and it was inserted in a Worker Health Awareness Program. This work is related to an IAEA Co-ordinated Research Project "Assessment of levels and health-effects of airborne particulate matter in mining, metal refining and metal working industries using nuclear and related analytical techniques" whose goal was to make a survey of the exposures to metals related to occupational diseases.[12,13]

Experimental

Galvanizing studied

The galvanizing factory[13] was chosen at random downtown. The main galvanization process plates chromium, nickel and copper. Eventually it plates silver and gold. The areas for polishing, baths, items support preparation, acid cleaning, reception desk and offices are located on the ground floor. There is physical communication between the polishing and the bath areas, from the bath area to the items support preparation area and from this to the reception desk and the offices. The acid cleaning is inside the bath area. On the first floor, there is another acid cleaning area, one small kitchen, one small storeroom and the workers' private area. The distribution of the activities is shown in Fig. 1.

In this galvanizer there are two Item Cleaners, that wash the material with water, dry it with sawdust and also execute other tasks such as to organising the clients' orders and cleaning the areas; three platers that are responsible for the items chemical cleaning and the electrodeposition; and four polishers that handle all the items before the electrodeposition, polishing them either manually or mechanically. The items prepared to be plated have usually been previously covered with other metals, such as gold, silver, chromium and copper.

Airborne particulate matter sampling

Stationary air sampling was carried out in order to evaluate the level of elemental concentration in the indoor environment of the plants. The sampling of airborne particulate matter (APM) was conducted by using 0.8-μm pore size, 37-mm diameter, and 5.0-μm pore size, 37-mm diameter, housed in polystyrene cassettes. The respective cassettes were attached to constant air flow sampling pumps, SKS, Eighty Four, PA 15330, USA, PCXR8KD. Both air-sampling pumps were calibrated before use to ensure accuracy of the volume of air sampled to 4 $l \cdot min^{-1}$. Each pair of sampler, one with 0.8-μm and another with 5.0-μm pore size, collected the APM simultaneously at the same place. As the primary objective of the study was to obtain information regarding workmen's exposure, the samples collected came from places that would reflect, as much as possible, the indoor environment: near the polishing activities, as close to the chrome and copper baths as possible and in office 2. The sampling was performed for 8 hours during two days. After the sampling, the cassettes were carefully opened. The air filters were folded and inserted into their respective polyethylene tubes for irradiation.

Biomonitors sampling and preparation

The sampling of the Workers' Group was carried out after the physicians had explained to workers the aims of the project and how it would be performed. The volunteer workers donated their toenail clippings and also hair samples. The scalp hair samples were collected according to IAEA instructions[7,12] from the nape with scissors. All hair samples were washed following the IAEA procedure.[7,12]. After being washed the samples were dried at 40 °C and weighed in the irradiation container. The toenails samples were washed according to the literature.[11] After being washed the samples were air dried and weighed in the irradiation container.

The same biomonitors collecting and preparing procedures were applied to the Comparative Group samples.

Irradiation, gamma-spectroscopy and calculations

The irradiation was performed in the Triga Mark I IPR-R1 in the CDTN reactor at 100 kW, neutron flux $6.6 \cdot 10^{11} n \cdot cm^{-2} \cdot s^{-1}$. The samples were irradiated simultaneously accompanied by Au and Na standards as comparators, and Human Hair Reference Certified Material,[14] GBW 09101, from the Shanghai Institute of Nuclear Research Academy.

The usual neutron activation analysis and gamma-spectroscopy comprise three schemes: 5 minutes of irradiation time, 2 to 15 minutes of decay time and 600 seconds of measuring time to determine Al, Cl, Cu, Mn, Ti and V; 4 hours of irradiation time, 12 hours of decay time and 3 hours of measuring time to determine As, Au, Br, La and Na; 20 hours of irradiation time, 10 days of decay time and 4 hours of measuring time to determine Ag, Co, Cr, Fe, Hf, Hg, Sb, Sc, Ta and Zn. After a suitable decay time, gamma-spectroscopy was performed with a HPGe detector ORTEC, 10175-P, resolution of 1.85 keV for the 1332 keV peak of ^{60}Co. The spectra obtained were analyzed using the Genie PC, Canberra software, and the k_0 method of instrumental neutron activation analysis[12–18] was applied to determine the elemental concentrations. The quality control was done using the Human Hair Reference Certified Material analyzed with the samples and replicates of samples, when possible. The quality assurance of the analytical results was evaluated by analyzing several certified reference materials. The overall accuracy[13] was 1–5%. The participation in a relevant interlaboratory comparison study[19] organized by International Atomic Energy Agency on determining trace elements in filters loaded with airborne particulate matter, urban dust and filters loaded with welding fume was another quality control procedure.

Results and discussion

In a previous work[12,20] a pilot sampling was carried out before the galvanizing on focus. The objective was to verify the metal exposure level inside the workplace and so scalp hair and fingernail samples were collected. The results from washed samples pointed out that all the elemental concentrations in the workers' hair were higher than those in the Human Hair Reference Material. They showed a higher concentration in unwashed hair compared to washed hair samples, and a high elemental concentration in fingernail samples, proving the indoor polluted environment. Visiting the factory, it was possible to foresee the contamination because of the dust from polishing impregnated on the walls and floor and was visible on the dirty appearance of the workers.

Concerning the airborne particulate matter, the results of the air filters are presented in Table 1. The breathable fraction corresponds to APM having an equivalent aerodynamic diameter of less than 5 μm and inhalable fraction, more than 5 μm. The Table also shows the Threshold Limit Values, TLV, that "refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without any adverse health effects" according to the definition of the American Conference of Governmental Industrial Hygienists, ACGIH.[21]

The results point out that the polishing area presented the highest elemental concentrations. Observing the table, it is possible to verify the following: Ag was not detected anywhere. Really, this galvanizer usually does not plate with silver, besides at that time no item previously covered with silver was polished. In the polishing area, the elements Al, Co, Fe, Mn, Sc and Zn came possibly from the metal structure of the items to be galvanized; As, Au and Cu from the previous coating on the items; Cr, came not only from the previous coating, but, possibly, also from the bath area; Cl and Na came from the bath and the item cleaning areas. In the bath area, Al, As, Au, Fe, Mn and Zn, possibly came from the polishing procedure; Cr came from the bath itself; Cu was not detected and Cl came from the bath and acid cleaning. In office 2, Al, Fe, Mn, Sb and Zn presence, at very low concentration, possibly came from outside but Cr concentration higher than in the bath, possibly came not only from outside but also from the bath as mist formed during the plating process. As there is no window in the office and the communication is only through the reception desk, in front of the street, the mist has been retained in office 2.

It is possible to observe that at the time when the samples were collected only the Polishing Area presented real risk for the workers, because of the Cu breathable fraction concentration and Fe in both fractions, inhalable and breathable, were higher than TLV. However, for better evaluation of the risks it should be considered that the breathable fraction presents additive toxic effects. The ACGIH suggests to calculate the TLV for mixtures. It means to calculate the sum of the reasons between the elemental concentration determined and the TLV foreseen for this element concerning the breathable fraction. The sum should be equal to unity. It means that the additive effects will be in a security range of concentration. But if the sum is higher than unity it means that the security limits were exceeded. The TLV for mixtures were calculated for each element but for some elements there were TLV foreseen in general, not specific for breathable fraction.

Table 1. APM elemental concentrations (in mg·m^{-3})

Element	TLV	Office 2		Bath area		Polishing area	
		Breathable fraction	Inhalable fraction	Breathable fraction	Inhalable fraction	Breathable fraction	Inhalable fraction
Ag metal	0.1	ND	ND	ND	ND	ND	ND
Al fume	5	0.025 ± 0.003	ND	0.18 ± 0.04	0.40 ± 0.02	1.82 ± 0.04	2.36 ± 0.04
Dust	10						
As metal and compounds	0.01	ND	ND	0.0002 ± 0.0001	ND	0.0012 ± 0.0002	ND
Au	NF	ND	ND	0.000002±0.000002	0.0000004±0.0000004	0.00004±0.00001	0.00007±0.00001
Cl chlorine	14	ND	ND	0.13 ± 0.01	ND	4 ± 1	ND
Co metal and compounds	0.02	ND	ND	ND	ND	0.003 ± 0.001	0.0010 ± 0.0005
Cr metal and Cr(III) compounds	0.5	0.070 ± 0.001	0.060 ± 0.001	0.014 ± 0.001	0.013 ± 0.001	0.040 ± 0.004	0.007 ± 0.005
Water-soluble Cr(VI) compounds	0.05						
Insoluble Cr(IV) compounds	0.01						
Cu fume	0.2	ND	ND	ND	ND	0.24 ± 0.04	ND
Dust and mist	1						
Fe oxide dust and fume	5	0.030 ± 0.003	0.15 ± 0.08	1.2 ± 0.1	0.23 ± 0.03	15 ± 1	6 ± 1
Mn metal and compounds	0.2	0.003 ± 0.001	0.0013 ± 0.0001	0.0010 ± 0.0005	ND	0.09 ± 0.01	0.12 ± 0.04
Na	NF	0.004 ± 0.002	0.027 ± 0.002	0.034 ± 0.001	ND	ND	0.27 ± 0.02
Sb metal and compounds	0.5	0.0003 ± 0.0001	ND	ND	ND	ND	ND
Sc	NF	ND	ND	ND	ND	0.0001 ± 0.00005	0.0001 ± 0.00002
Zn fume	5	0.007 ± 0.004	0.011 ± 0.003	0.015 ± 0.001	ND	0.013 ± 0.005	0.19 ± 0.01
Dust	10						

ND: Not detected.
NF: Not foreseen.
TLV: Threshold limit value.

Then, these values were applied to calculate the TLV for Mixtures.[10] Concerning chromium, there are three values of TLV depending on the class of compound. This element is among those that are responsible for the great majority of injuries caused to galvanizing workers in a short time. The toxicity of Cr[22] is well known: the oxidizing agent chromic acid and the dichromate salts cause several injuries and, in some instances they perforated the septum. Cr(III) is considered as an essential bioelement but Cr(VI) is toxic. With respect to hexavalent compounds, in industrial activities, one of the highest exposures to Cr(VI) occurs during chrome plating.[22] As during this study the total Cr was determined without information about its valency, the TLV for mixture, TLVM, were calculated foreseeing the three possibilities of occurrence of Cr. Table 2 brings these results and shows that 66.7% of the TLVM values exceed unity. It reflects the conditions for health risk.

Calculating TLVM, chromium's TLV was decisive for classifying the risk. Though it is possible to verify the individual contribution of each element for the risk. Table 3 summarizes the general assessment of risks for office 2, bath and polishing areas, showing how many elemental concentrations were determined, how many of the elements determined have TLV, how many of these determinations exceeded the corresponding TLV, calculated by means of the ratio elemental concentration by foreseen TLV, and their percentage: 25.6% of the elements, for which TLV are foreseen, exceeded the limits, offering insecure conditions for workers' health, mainly in the polishing area. There is no information about the limits of the other elements and, consequently, their risks.

The elemental concentrations determined in the samples from non-exposed people,[23] the Comparative Group – are in Table 4. Reference 1[24] scalp hair values is about individuals living in São Paulo city, Brazil, and Reference 2[25] reports about fingernail clippings. As reference values for toenails were not found, it was decided to compare them with fingernail matrices only to give an idea about the concentration levels. Comparing the results, it is possible to verify that in general there are no significant differences between the values. The variations are due to diet, personal hygiene habits, environment and other influences.[24]

Table 5 shows the elemental concentrations determined in hair samples from the Workers Group organized by activity and Table 6 the results obtained for toenail samples. At first glance the results for workers are higher than those for the non-exposed subjects. Table 7 summarises the concentration comparison by means of the ratio between elemental concentrations of the Workers Group and the Comparative Group. A qualitative analysis of the results can be seen in Table 8. In the air filter 13 elements were detected, Al, As, Au, Cl, Co, Cr, Cu, Fe, Mn, Na, Sb, Sc and Zn, and except As, Co and Sc, those elements were also determined in the hair and toenail samples.

Table 2. Threshold limit values (TLV) for mixture inside the galvanizing factory

	Office 2	Bath area	Polishing area
Metal and Cr(III) compounds	0.14	0.31	5.5
Water-soluble Cr(VI) compounds	1.3	0.56	6.2
Insoluble Cr(IV) compounds	6.6	1.7	9.4

Table 3. General assessment of risks

Workplace	Number of elemental determinations	Number of elemental determinations with correspondent TLV	Exceeding the TLV	
			Number of occurrences*	Correspondent percentage
Office 2	12	10	2	20
Bath	13	10	2	20
Polishing	20	15	5	33.3
Total	45	35	9	25.7

* Related to element which has correspondent TLV.

Table 4. Comparative group: concentrations (in $\mu g \cdot g^{-1}$) determined and values presented in literature

Element	Scalp hair				Nail		
	Comparative group (22 individuals)		Reference 1[24] (35 individuals)		Comparative group - toenail (22 individuals)		Reference 2[25] fingernail
	Range	n	Range	n	Range	n	Range
Al	5–104	21	1.60–37.4	35	ND	–	$(132–927)\cdot10^{-6}$
As	ND	–	(0.0067–0.126)*	35	ND	–	$(0.2–1.05)\cdot10^{-6}$
Au	0.002–0.27	12	ND	–	0.001–0.036	6	$(0.03–0.78)\cdot10^{-6}$
Br	0.08–2.1	22	0.42–85.4	28	ND	–	$(9–10)\cdot10^{-6}$
Cl	23–809	19	40.7–1339	33	ND	–	$(109–357)\cdot10^{-7}$
Co	ND	–	(0.008–0.325)*	33	0.2–0.3	5	$<0.2\cdot10^{-6}$
Cr	0.7–17	6	(0.068–0.753)*	32	1.6–4	3	$6.2\cdot10^{-6}$
Cu	3–46	21	4.0–56	35	ND	–	$(11.2–53)\cdot10^{-6}$
Fe	ND	–	7.2–37	33	78–323	4	$(27–347)\cdot10^{-6}$
Hg	0.3–5	15	0.08–4.75	35	0.2–1.4	5	$(0.07–7.27)\cdot10^{-6}$
Mn	1.2–1.7	2	(0.105–2.50)*	35	ND	–	$(0.04–2.1)\cdot10^{-6}$
Na	0.7–22	19	1.50–30	35	ND	–	$(332–3010)\cdot10^{-6}$
Sb	ND	–	(0.003–0.85)*	33	ND	–	$(0.03–0.75)\cdot10^{-6}$
Sc	ND	–	(0.0012–0.006)*	14	0.004–0.1	15	NI
V	ND	–	(0.0015–0.054)*	9	ND	–	$<0.15\cdot10^{-6}$
Zn	120–280	22	105–264	32	57–2100	19	$(73–304)\cdot10^{-6}$

ND: Not detected.
n: Number of individuals whose samples presented the element.
NI: Not informed.
* $\mu g \cdot kg^{-1}$.

Table 5. Elemental concentrations (in $\mu g \cdot g^{-1}$) determined in comparative's and workers scalp hair samples

Element	Comparative group (22 individuals)			Item cleaners (2 workers, 2 samples)			Platers (3 workers, 3 samples)			Polishers (5 workers, 4 samples)		
	$x_G \times\div s_G$	Range	n	$x_G \times\div s_G$	Range	n	$x_G \times\div s_G$	Range	n	$x_G \times\div s_G$	Range	n
Ag	ND	–	–	8±1		1	3×÷1	3–2	2	4×÷1	3–7	4
Al	18×÷1	5–104	21	42±2		1	175×÷1	88–285	3	531×÷4	45–2190	4
Au	0.02×÷3.4	0.002–0.3	12	0.03±0.01		1	0.1×÷1.1	0.069–0.1	3	0.1×÷1.4	0.02–0.1	4
Br	0.5×÷1.5	0.08–2.1	22	0.3×÷1	0.23–0.3	2	1×÷1	0.7–1	3	1×÷1	0.5–1.2	3
Cl	127×÷2	23–809	19	133±10		1	560×÷1	523–600	2	144×÷2	60–346	2
Co	ND	–	–	0.4×÷1.9	0.2–1	2	0.04×÷9	0.01–0.2	2	0.20×÷0.01	0.1–0.2	3
Cr	3×÷2	0.7–17	6	3±1		1	9×÷1	7–14	3	4×÷1	2–7	4
Cu	13×÷1	3–46	21	36×÷1	23–56	2	127×÷1	76–314	3	335×÷2	66–590	4
Fe	ND	–	–	86×÷1	83–89	2	257×÷1	180338	3	841×÷4	75–3050	4
Hf	ND	–	–	ND	–	–	1.4±0.5		1	4±1		1
Hg	1×÷2	0.3–5	15	ND	–	–	1×÷1	0.6–0.8	2	0.8±0.2		1
La	ND	–	22	0.04		1	0.1×÷0.1	0.11–0.13	2	0.3×÷1.6	0.07–0.7	4
Mn	1.5×÷0.5	1.2–1.7	2	1±1		1	9×÷6	3–76	3	9×÷2	1.5–21	4
Na	2×÷2	0.7–22	19	2×÷1	1.8–1.9	2	5×÷1	4.6–6.7	3	16×÷2	2.8–37	4
Sb	ND	–	–	ND	–	–	0.5×÷2.1	0.2–2	3	0.2×÷0.1	0.2–0.3	2
Ta	ND	–	–	ND	–	–	ND	–	3	0.2±0.1		1
Ti	ND	–	–	ND	–	–	254±80		1	380±80		1
V	ND	–	–	ND	–	–	ND	–	3	11×÷1	6–17	3
Zn	235×÷1	120–280	22	126×÷1	96–165	2	119×÷1	60–212	3	121×÷1	73–250	4

$x_G \times\div s_G$: Geometric mean and standard deviation.
n: Number of individuals whose samples presented the element.
ND: Not detected.
As and Sc were not detected.

Table 6. Elemental concentrations (in $\mu g \cdot g^{-1}$) determined in comparative's and workers toenail samples

Element	Comparative group (22 individuals)			Item cleaners (2 workers, 1 samples)			Platers (3 workers, 2 samples)			Polishers (5 workers, 3 samples)		
	$x_G \times \div s_G$	Range	n	$x_G \times \div s_G$	Range	n	$x_G \times \div s_G$	Range	n	$x_G \times \div s_G$	Range	n
Al	ND	–	–	298±7		1	295×÷1	136–638	2	138×÷1	94–282	3
Au	0.002×÷4	0.001–0.04	6	0.03±0.01		1	0.1×÷1.9	0.03–0.15	2	0.01×÷1.1	0.008–0.02	3
Br	ND	–	–	ND	–	–	ND	–	–	1×÷1	0.5–0.9	2
Cl	ND	–	–	ND	–	–	650±40		1	473×÷1	292–684	3
Co	0.2×÷1	0.2–0.3	5	ND	–	–	ND	–	–	ND	–	–
Cr	3×÷1	1.6–4	3	ND	–	–	21×÷3	8–56	2	5×÷1	3.4–11	3
Cu	ND	–	–	ND	–	–	64×÷1	40–101	2	ND	–	–
Fe	150×÷1	78–323	4	ND	–	–	183±100		1	393×÷1	349–430	3
Hg	0.4×÷1.3	0.2–1.4	5	ND	–	–	ND	–	–	ND	–	–
Mn	ND	–	–	2.3±0.2		1	ND	–	–	4×÷1	3.4–5.5	3
Na	ND	–	–	182±6		1	302×÷1	182–500	2	301×÷1	227–496	3
Sb	ND	–	–	ND	–	–	0.9±0.5		1	ND	–	–
Sc	0.02×÷1.6	0.004–0.1	15	ND	–	–	ND	–	–	ND	–	–
Zn	132×÷1	57–220	19	54±10		1	234×÷1	192–285	2	104×÷1	94–119	3

$x_G \times \div s_G$: Geometric mean and standard deviation.
n: Number of individuals whose samples presented the element.
ND: Not detected.
Ag, As, Hf, La, Ta, Ti and V were not detected.

Table 7. Concentration comparison

Element	Ratio: Workers group/comparative group					
	Scalp hair			Toenails		
	Item cleaners	Platers	Polishers	Item cleaners	Platers	Polishers
Ag	+*	+*	+*	–*	–*	–*
Al	2	10	30	+*	+*	+*
Au	2	5	5	15	50	5
Br	0.6	2	2	–*	–*	+*
Cl	1	4	1	–*	+*	+*
Co	+*	+*	+*	–	–	–
Cr	1	3	1	–	7	2
Cu	3	10	26	–*	+*	–*
Fe	+*	+*	+*	–	1	3
Hf	–*	+*	+*	–*	–*	–*
Hg	–	1	1	–	–	–
La	1	3	10	–*	–*	–*
Mn	1	6	6	+*	–*	+*
Na	1	3	8	+*	+*	+*
Sb	–*	+*	+*	–*	+*	–*
Sc	–*	–*	–*	–	–	–
Ta	–*	–*	+*	–*	–*	–*
Ti	–*	+*	+*	–*	–*	–*
V	–*	–*	+*	–*	–*	–*
Zn	1	1	1	1	2	1

+: Element detected in worker sample.
–: Element not detected in worker sample.
*: Element not detected in comparative group.

Table 8. Qualitative analysis

Matrix	Al	As	Au	Cl	Co	Cr	Cu	Fe	Mn	Na	Sb	Sc	Zn
Hair	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓		✓
Toenail	✓		✓	✓		✓	✓	✓	✓	✓	✓		✓
Air filter	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
All matrixes	✓		✓	✓		✓	✓	✓	✓	✓	✓		✓

✓: Element determined in this matrix.

Conclusions

The highest elemental concentrations in airborne particulate matter collected were determined in the polishing area. These results point out this workplace as offering the highest pollutant exposure risks to workers. The results of TLV for mixtures calculated in function of chromium prove the polluted environment inside the factory. Besides, the general assessment of risks reveals the level of exposure for those elements that present foreseen TLV. This assessment exposes the danger hidden for elements about which there is neither knowledge of related security limits of exposure neither of risks to health.

Except Br and Hg, the workers' concentrations of which in hair and toenails biomonitors are similar to those determined for the Comparative Group, the other elements, in general, present higher values demonstrating the high pollutant exposure. In fact, Br and Hg are not associated with the galvanizing processes and they were not detected in air filter samples.

The majority of elemental concentrations determined in the workers' hair and toenail samples were higher than in the Comparative Group samples. Besides, the presence of other elements in the workers' samples, not detected in the comparative samples, evidenced the general contamination, in special the Item Cleaners, that do not handle the contamination sources directly but work under the same roof. Observing the tables, sometimes the Polishers present the highest concentrations, sometimes the Platers. All these results confirm the data revealed by the air filters: the pollutants are dispersed inside the factory. Besides, it is common for the workers to carry out other activities in the factory despite their function, exposing themselves to several sources of contaminants.

This investigation project was the first action in order to assess the elemental concentration level in a galvanizing factory. Many studies have been developed concerning this industrial process broaching many aspects including chromium and nickel contamination consequences, but so far none has pointed out the detection and measurement of other elements such as silver, gold, arsenic, elements not considered essential for human being. Other considered to be essential as Fe, Cr, were determined but in high concentrations, playing, maybe, a toxic role. Nickel was not determined because of the analytical nuclear technique applied is not suitable to determine this element.

The results confirmed and reinforced the need of action in order to minimize the hazardous work conditions. This first assessment alerts for the need of assessing the influence of a long-term exposure and will support the establishment of guidelines and data basis for the next occupational program for this specific workplace. The results confirmed the medical suspicions of workers' contamination and the medical recommendations, aimed at minimizing the hazardous condition at the workplace and its effects. Besides the recommendations the main actions were: to install exhausts over the bath and the polishing areas; close the communications between polishing and bath areas making them independent workplaces.

Qualitative analysis showed that 77% of the elements determined in airborne particulate matter, Al, Au, Cl, Co, Cr, Cu, Fe, Mn, Na, and Zn were also determined in hair and toenail samples. This evidences the efficiency of these matrixes as biomonitors indicating endogenous contamination and the importance to carry out the airborne particulate matter sampling in parallel to scalp hair and toenail as biomonitors mainly in occupational epidemiological studies.

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