



Evaluation of the effects of exposure to heavy metals in rescue dogs and their role as environmental biomonitors after the Brumadinho disaster, Minas Gerais, Brazil

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ABSTRACT

In January 2019, a mining dam collapsed in Brumadinho, Minas Gerais, Brazil. Numerous professionals from fire brigades from several states in Brazil and trained dogs worked to rescue the victims of this tragedy and maintained direct contact with the dam's tailings. To understand the consequences generated by this exposure, a cross-sectional observational study, heavy metals, cytokines and clinical signs were correlated, was carried out with the aim of identifying biological biomarkers and the presence of metals in trained dogs. Hair and serum samples from 30 rescue dogs from the Military Fire Brigade were used to analyze heavy metals, trace elements and cytokines. Among these, 20 dogs were exposed to tailings and 10 were not involved in mining disasters. Cadmium metal obtained a significant result ($p = 0.013$) when compared with the exposure to waste and a negative correlation (-0.58) with IL-15 ($p = 0.01$). The clinical signs that presented significant values were dermatological ($p = 0.011$) and locomotor ($p = 0.003$). Of the exposed dogs (6/20) 30 %, had neoplasms in the skin and reproductive system. The dogs in the exposed group showed a positive correlation (0.49) between Lead and the number of hours worked ($p = 0.02$) and a positive correlation (0.48) with Chromium ($p = 0.03$). The correlation between clinical signs, presence of metals and inflammatory cytokines indicates that dogs can be a promising tool for characterizing long-term occupational exposures and highlights the importance of bio-monitoring the health of firefighters who suffer constant environmental exposures.

1. Introduction

Biomonitoring studies have helped to understand the occupational effects on firefighters' health in order to improve the characterization of risk factors and their association with work-related diseases, for the implementation of surveillance programs [6].

The spillage of mining tailings can cause an increase in the bioavailability of a series of toxic components in the environment [44]. The mining sector is an activity of great economic representation in Brazil and operates among the largest world powers [14]. The state of Minas Gerais (MG) was the target of two major natural disasters resulting from the collapse of mining company tailings dams. The

Fundão tailings dam, which failed in the municipality of Mariana, in 2015, and the collapse of the Brumadinho dam in Córrego do Feijão, in 2019 [3].

The Brumadinho disaster was considered the biggest work accident ever to occur in Brazil. The rescue searches involved approximately 1500 military firefighters from Corporations in varerigious States, forming the largest rescue operation ever to take place in the country [39]. This type of disaster releases chemical substances, contaminating the environment and exposing the population to risk and morbidity scenarios [40]. Environmental toxic variation and exposure to mining tailings can affect health in several ways. Metals trigger a series of consequences for the body, including damage to neurological functions,

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changes in the immune system, liver and kidney damage, among others [44].

Metals/metalloids are characterized into three categories, namely: I- nutrient elements that perform essential functions in metabolic processes and are not considered environmental contaminants; II- nutrient elements that act on metabolic functions and can also be considered environmental contaminants; III- elements that induce damage and are considered environmental contaminants [9].

Cadmium (Cd), Mercury (Hg), Arsenic (As) and Chromium (Cr), are characterized as non-essential and highly toxic metals, also Lead (Pb) even in low concentrations [37]. They can induce oxidative stress through the generation of free radicals. Furthermore, long-term exposure can result in apoptosis, affect signaling and generate changes in DNA, lipids, proteins, enzymes and Ca and Na ion homeostasis [22]. They play an important role in the development of chronic degenerative diseases [26].

Exposure to environmental pollutants induces inflammatory changes characterized by the release of cytokines and mediators [29]. Cytokines are bioactive proteins produced by cells of the immune system that mediate the inflammatory response, act in communication and interaction between cells, signal sites of injury, infection and inflammation [30]. They are classified as pro-inflammatory, anti-inflammatory, chemotactic or growth regulatory and exert a function on cells that have specific receptors for them to act on [38].

Organic pollutants have the ability to interfere with biological systems and cause negative effects on the health of humans, dogs and other living beings [17]. Dogs can be considered “guardians of life,” as they are early indicators of environmental pollution. They are part of human life, share the same environment, and are exposed to the same environmental agents [5]. Just like humans, dogs are susceptible to a variety of diseases, related to age and environmental risks such as cancer [11], for example, cancer of the bladder, mammary glands, testicles and ovaries, lymphoma, mesotheliomas and carcinomas [19]. For this reason, in recent decades companion animals have been observed as biomonitors of human exposure [17].

Because they share the same environment as humans and are exposed to the same pollutants, dogs can be good bioindicators for environmental pollution [4,27,35]. In this sense, aiming to understand the risks to human and animal health, inherent to the exposure of the environmental disaster in the city of Brumadinho/MG, this work aimed to identify biological biomarkers, cytokines and chiomycins, metals and trace elements, and evaluate their correlation with the clinical changes in working animals of Military Fire Brigade Corporations.

2. Materials and methods

2.1. Type of study

This is a cross-sectional study carried out using dogs from Military Fire Brigades from different states of the Brazilian Federation. The data was collected between the period from May to September 2022. The source population consists of working dogs from the Military Fire Brigades, among them, a group that worked to rescue victims and bodies in the rupture of Dam I of the Córrego do Feijão mine in Brumadinho, Minas Gerais, Brazil. The second group of rescue dogs did not act in dam collapses.

2.2. Population study

All dogs used in this study are working dogs from Fire Departments, with 20 animals involved in the tragedy of the Córrego do Feijão dam collapse in Brumadinho/MG and were exposed to the mining company's tailings, in the same way as the firefighters, who worked to rescue bodies and people. This group was called the exposed group. The dogs that

worked in Brumadinho belonged to or were owned by various fire brigades. Working dogs from the states of Minas Gerais, Mato Grosso, Goiás and Distrito Federal were included in the study. They were working dogs between 5 and 10 years old, regardless of sex, of the Blue Heller, Border Collie, Labrador, German Shepherd and Malinois breeds.

The second group, the unexposed group, is represented by working dogs from fire departments who live the same routine as the exposed group. They live in the same place, feed on the same food, but have not been involved in mining disasters. They were aged between 8 months and 8 years, without sex distinction, being of Labrador, German Shepherd and Malinois breeds.

2.3. Data collection

Data collection from both groups was carried out simultaneously, on the premises of the Fire Departments in the states of their origin or at the home of the firefighter responsible for the canine, after 3 years of exposure to waste. Animal data were cataloged using a clinical record.

For a better understanding of the clinical changes, a medical history and a physical examination were performed on each dog. Specific questions were asked about different systems (respiratory, reproductive, integumentary, locomotor, nervous, cardiovascular, and endocrine), and the presence or history of oncological conditions were assessed. Additionally, the guardians were interviewed about the dog's employment history, hours worked per day, and clinical signs over the three years following their employment. To evaluate the unexposed group, the same questionnaire was used, investigating their length of service in the Fire Department and the work performed.

2.4. Collection of biological samples

Samples of 3 mL of blood were collected by venipuncture of the cephalic vein, after cleaning with 70 % alcohol, stored in an SST® tube. After collection, the material was centrifuged at 3500 rpm for 10 min. At the end of the centrifugation, the centrifuge tubes kept in a vertical position were removed and 400 µL of blood serum was pipetted into a tube with a thread suitable for freezing and stored in a gallon of nitrogen.

Hair samples were collected from the dogs, in the abdominal region (10 × 10 cm of hair), using a trichotomy device and stored in identified plastic bags.

2.5. Metal analysis

Analysis of metals and trace elements, Aluminum (Al), Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Mercury (Hg), Manganese (Mn), Nickel (Ni) and Lead (Pb) were carried out by the Toxicological Information and Assistance Center – CIATOX (IBB-UNESP-Botucatu, São Paulo) on dog hair samples according to the analytical protocol recommended by the manufacturer (Provecto Análise 2000). 0.5 g of hair was weighed on an analytical balance, decontamination was carried out by washing the material in detergent (Extran®) and then dried in an oven after it was adequately homogenized, weighed and added to the reaction vessel (PTFE) of the microwave (PROVECTO-®DGT 100 plus). 6 mL of nitric acid (HNO₃ 65 % Merck®) was added and mineralization was ramped for 2 h in the microwave. The analyzes were carried out using an atomic absorption spectrometer (GBC® model AA 932). Certified primary standards (Fluka®, Merck® and Sigma/Aldrich®) were used for each chemical element and the respective specific standard curves according to their detection and quantification limits (Table 1). The optimization of the programming of the GBC 932 equipment was carried out specifically for each chemical element (manufacturer's recommendation).

Table 1

- Limits of detection and quantification of the GBC AA 932 technique for analyzing metals in the fur of working dogs in Fire Departments.

Metals	LOD	LOQ	Metals	LOD	LOQ
Al	0,55	25,0	Fe	0,05	2,0
As	0,64	30,0	Hg	0,001	0,01
Cd	0,009	2,0	Mn	0,02	1,0
Cr	0,05	2,0	Ni	0,04	1,8
Cu	0,02	1,0	Pb	0,05	2,5

LOD – limit of detection and LOQ - limit of quantification of the technique. Unit = µg/g (PPM).

2.6. Immunological markers analysis

Quantification of immunological and inflammatory biomarkers was performed using the Luminex® assay (Merck Milliplex®). The Luminex assay methodology is based on fluorescent beads, which involve antibodies to various cytokines and chemokines. The kit (MAP Canine Cytokine/Chemokine premixed Magnetic Bead Kit, Millipore, USA) was used to evaluate the cytokines IL-2, IL-6, IL-8, IL-10, IL-15, IL-18, MCP1 and TNF-α, with a sensitivity range between 12.2 and 50,000 pg/mL used to measure the amounts of cytokines.

The assay was carried out according to the manufacturer's instructions (Merck Milliplex®). All samples were analyzed individually, and the results were quantified according to the standard curve. Mean fluorescence intensities were analyzed using Milliplex Analyst software (Millipore®, Billerica, MA). Therefore, to determine the concentration values of each sample, a software logistic model was used with 5 parameters to adapt the standard curve. All standards and controls were within expected concentration ranges.

2.7. Statistical analysis of data

All data were evaluated based on the clinical changes presented by each canine studied. SPSS version 23 software was used for statistical analyses. To analyze significant differences between groups, normality between groups was first assessed using the Shapiro-Wilk test. Subsequently, the Mann-Whitney or Kruskal-Wallis tests (in the non-parametric context). The correlation test was performed using the Spearman test. For all analyzes a significance level of $p < 0.05$ was considered. Ni and Hg were excluded from the analysis as they did not present variance.

3. Results

A total of 30 working dogs were recruited for the study, of which 20 dogs worked in rescuing bodies from tailings in Brumadinho, forming the exposed group and 10 dogs that had no work history in mining tailings rescuing, with the group not being exposed. Table 2 shows the socio demographic data of the groups. There was a significant difference ($p < 0.001$) in age between the groups. This characteristic occurred due to the retirement of many dogs after working in Brumadinho and new dogs were placed in training. Due to the large proportion of victims, all trained and healthy dogs at the time of the tragedy were made available for this activity. To be part of the unexposed group, it was assumed that they had not worked with the tailings, which led to a restriction of dogs for the group, leading to the use of dogs that had recently undergone search and rescue training.

When evaluating the number of females and males, there was a greater number of females than males, which characterized (12/20) 60 % of females in the exposed group and (7/10) 70 % in the unexposed group (Table 2).

Table 2

Characteristics of exposed and unexposed groups of working dogs in Fire Departments, characterized by age, sex, State of origin and breed.

Variables	Exposed group (n = 20)	Unexposed group (n = 10)	p-value
Ages, years average ± SD* (min-max)	7,75 ± 1,77 (5,00–10)	3,47 ± 2,12 (0,67- 8,00)	< 0,001
Source location (States of the Federation/BR) N (%)	N (%)	N (%)	
DF	6 (30 %)	5 (50 %)	0,506
GO	3 (15 %)	2 (20 %)	
MT	7 (35 %)	3 (30 %)	
MG	4 (20 %)	0 (0 %)	
Sex	N (%)	N (%)	
Female	12 (60 %)	7 (70 %)	0,592
Male	8 (40 %)	3 (30 %)	
Race	N (%)	N (%)	
Blue Heeler	1 (5 %)	0 (0 %)	0,326
Border Collie	3 (15 %)	0 (0 %)	
Labrador	9 (45 %)	4 (40 %)	
German Shepherd	1 (5 %)	3 (30 %)	
Malinois Shepherd	6 (30 %)	3 (30 %)	

SD* - Standard Deviation; Significant value: ($p < 0,05$).

Table 3

Quantification of periods worked and working hours per day of working dogs that worked in the dam collapse in Brumadinho-MG.

Variable	Exposed group (n = 20)	p-value
Period worked	N (%)	
0 period	0 (0 %)	< 0,001
1 period	10 (50 %)	
2 period	7 (35 %)	
3 period	3 (15 %)	< 0,001
Worked hours average ± SD (min-max)	9,6 h ± 2,16 (6,00–14 h)	

Significant value: ($p < 0,05$).

The dogs worked on the search for 15 consecutive days, after which they returned to their original corporation to rest. There was no pattern of periods worked, the vast majority worked only 1 period 50 % (10/20), however 15 % (3/20) worked 3 periods corresponding to a total of 45 days which on average worked 9.6 h (6.00–14.00) (Table 3). The variable of periods worked and hours worked presented significant values.

The exposed dogs showed a wide range of clinical signs after the exposure period, such as lameness, skin wounds, uterine infections, heart disease, among others (Fig. 1).

These clinical signs were cataloged and quantified (Table 4). The analyzes were carried out based on the characteristics arranged in the affected systems. Dermatological clinical signs showed significant results ($p = 0.003$), as well as clinical signs of the locomotor system ($p = 0.011$).

After quantifying the oncological manifestations, each tumor type was evaluated and they did not show significant differences (Table 5).

Cd presented significant values ($p = 0.013$) in the exposed group in the Mann-Whitney test (Fig. 2, Table 6).

A Spearman correlation was performed to evaluate the correlations. Cd showed a strong correlation (0.54) with Mn ($p = 0.01$) and a negative correlation (-0.58) with IL-15 ($p = 0.01$). IL-15 showed a strong correlation (0.76) with IL-2 ($p = 0.001$), a strong correlation (0.82) with IL-6 ($p < 0.001$), a strong correlation (0.54) with IL-18 ($p = 0.03$), strong correlation (0.62) with MCP1 ($p = 0.01$) and strong correlation (0.81) with TNF-α ($p < 0.001$) (Fig. 3).

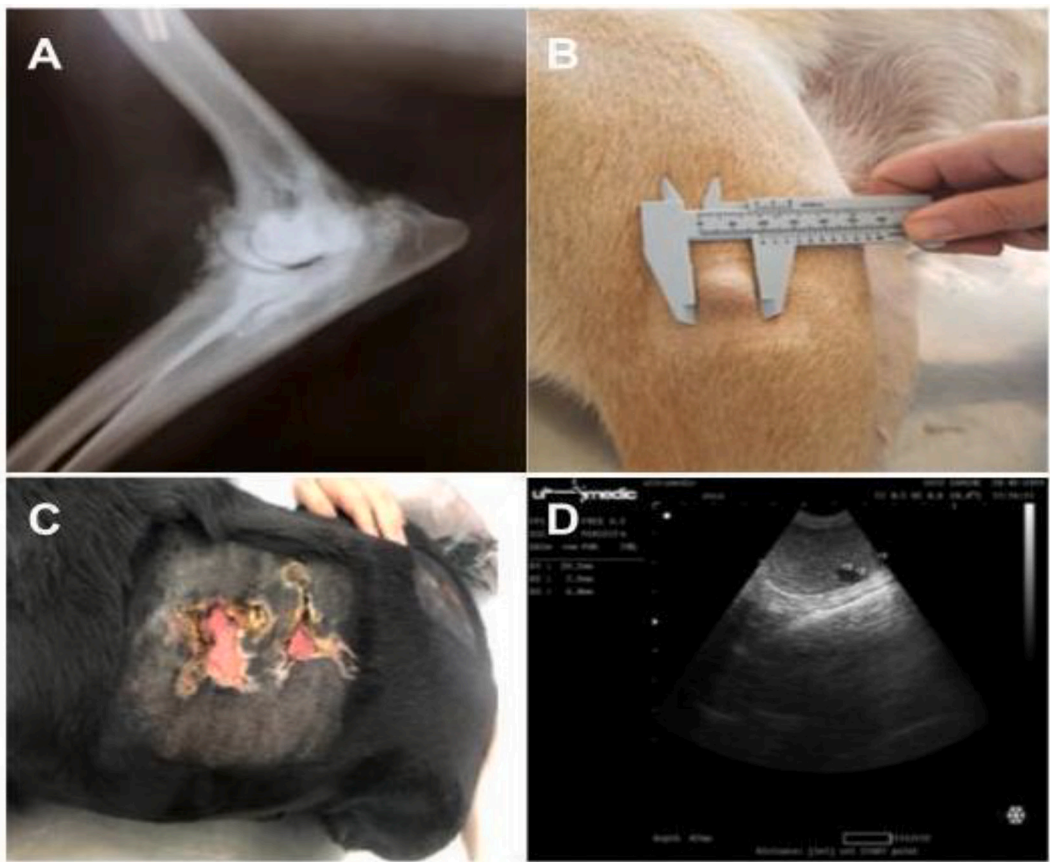


Fig. 1. (a) Radiographic image of the humeroradial joint with evidence of arthrosis. (b) Skin nodulation in a working canine. (c) Scarring process of skin lesion in a working canine after contact with mining company tailings. (d) Ultrasound image of the testicle showing an anechoic area suggestive of a testicular nodule. Photos: By the author, 2019.

Table 4
Quantification of clinical signs, classification by absence or presence in the dermatological, digestive, locomotor, respiratory, cardiac, genitourinary, oncological systems and infectious diseases of Fire Department dogs.

Variable		Exposed group	Unexposed group	p-value
System affected		N (%)	N (%)	
Dermatological	presence	11 (55 %)	0 (0 %)	0,003*
Digestive	presence	1 (5 %)	1 (10 %)	>0,999
Locomotor	presence	9 (45 %)	0 (0 %)	0,011*
Respiratory	presence	1 (5 %)	0 (0 %)	>0,999
Cardiac	presence	2 (10 %)	0 (0 %)	0,540
Genitourinary	presence	6 (30 %)	0 (0 %)	0,074
Oncology	presence	6 (30 %)	0 (0 %)	0,074
Infectious	presence	4 (20 %)	0 (0 %)	0,272

* Significant value: ($p < 0,05$).

Table 5
Quantification of the occurrence of neoplasms in the skin, testicles and mammary glands of Fire Department dogs.

Variable		Exposed group	Unexposed group	p-value
		N (%)	N (%)	
Oncology				
Skin	presence	10 % (2/20)	0 (0 %)	
Testicle	presence	10 % (2/20)	0 (0 %)	
Mammary gland	presence	10 % (2/20)	0 (0 %)	0,353

Significant value: ($p < 0,05$).

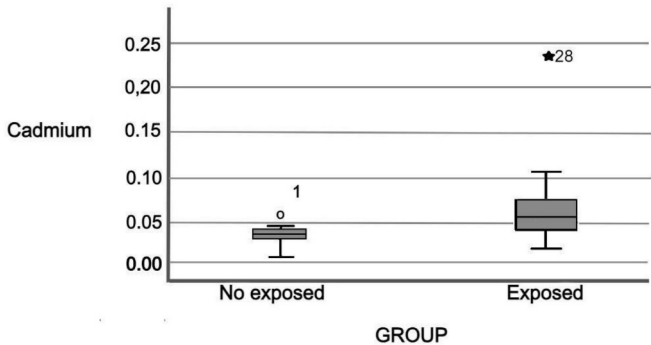


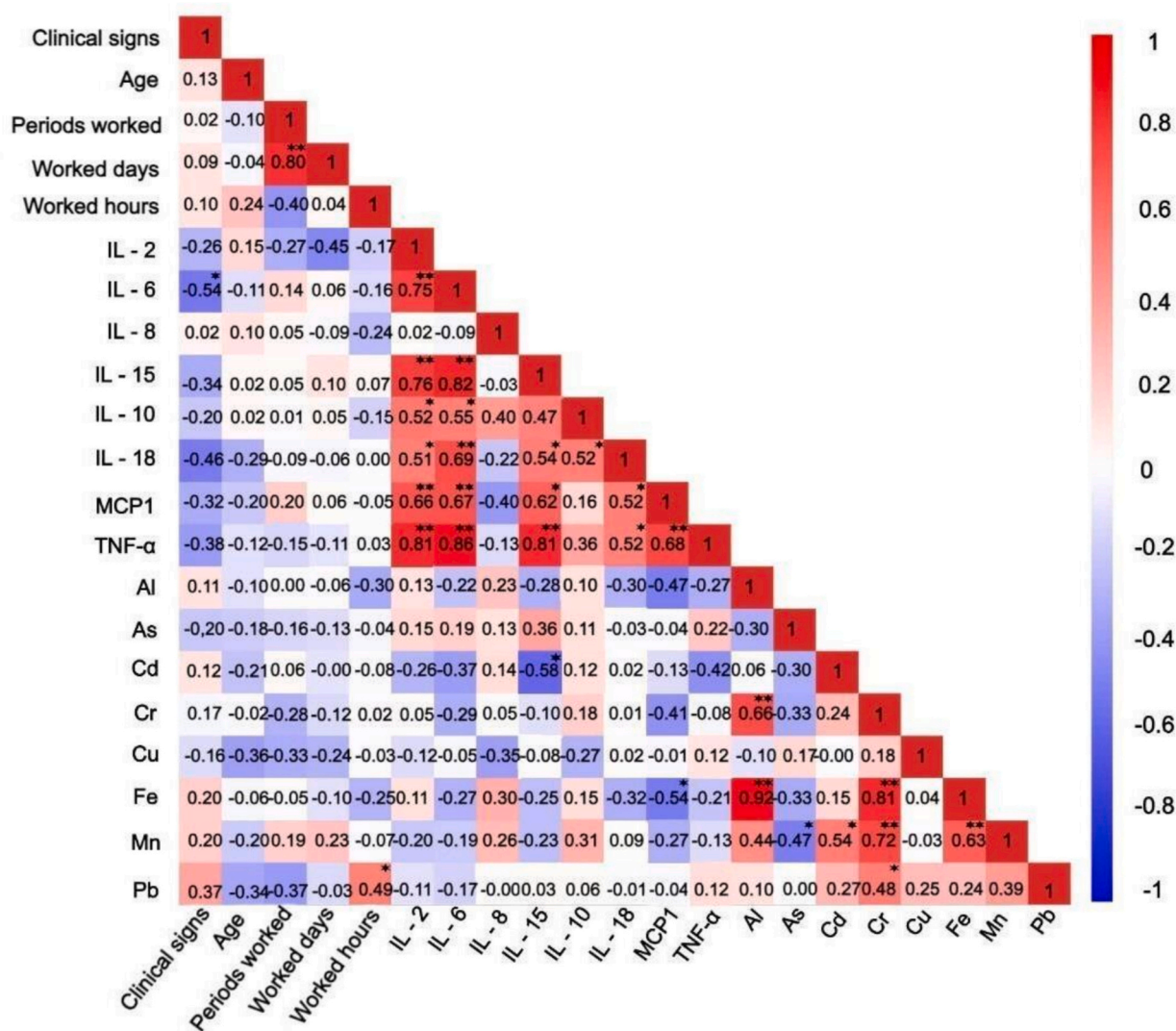
Fig. 2. Box plot of heavy metal concentration in the hair of working dogs 3 years after working in mining waste sludge. Cadmium (Cd), with a higher average in the exposed group (0.06) than the unexposed group (0.04).

Pb showed a strong correlation (0.49) with the number of hours worked per day ($p = 0.026$) and a moderate correlation (0.48) with Cr ($p = 0.03$). MCP1 showed a strong correlation (0.66) with IL-2 ($p = 0.005$), a strong correlation (0.67) with IL-6 ($p = 0.004$), a strong correlation (0.62) with IL-15 ($p = 0.011$), strong correlation (0.52) with IL-18 ($p = 0.03$), strong correlation (0.68) TNF- α ($p = 0.003$) and negative correlation (-0.54) with Fe ($p = 0.029$). Fe showed a strong correlation (0.92) with Al ($p < 0.001$), a strong correlation (0.81) with Cr ($p < 0.001$) and a strong correlation (0.63) with Mn ($p = 0.003$).

Table 6

Result of the assessment of metals Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni and Pb (ug/g or ppm) of Fire Department working dogs.

Variable	Exposed group				Unexposed group				p-value
	Average	Maximum	Minimum	*SD	Average	Maximum	Minimum	*SD	
Al	544,97	1372,66	55,28	357,98	430,98	657,79	117,18	153,70	0,681
As	4,43	12,86	0,21	3,60	2,46	3,07	1,55	0,51	0,196
Cd	0,06	0,24	0,01	0,05	0,04	0,06	0,01	0,01	0,013**
Cr	1,52	12,23	0,39	2,56	0,86	1,53	0,42	0,32	0,611
Cu	9,91	12,82	7,58	1,17	9,98	11,75	7,64	1,37	0,581
Fe	551,88	1600,00	132,65	342,49	428,58	571,84	178,54	122,11	0,559
Mn	3,11	9,64	0,99	2,05	2,81	4,49	1,75	0,92	0,991
Pb	0,39	0,86	0,05	0,32	0,19	0,74	0,05	0,21	0,227

* *SD - Standard Deviation; **Significant value: ($p < 0,05$).**Fig. 3.** Spearman correlations between metal biomonitoring results. The correlation coefficient is designated by color, with blue designating negative correlations and red designating positive correlations. Asterisks denote significant correlations at $p < 0.05$ (*) and $p < 0.01$ (**). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

4. Discussion

Cd metal obtained a significant result ($p = 0.013$) when compared with exposure to waste (Table 6, Fig. 3). A study carried out on 3080 people living in Brumadinho, heavy metals in peripheral blood were evaluated, after the period of waste spillage, found increases above the reference values of Mn (38.08 %), As (5.04 %), Pb (5.04 %), Hg (0.76 %)

and Cd (0.17 %) [32]. This study shows an increase in Cd levels in residents, corroborating the metal accumulated in exposed dogs.

Cd has a long half-life in humans of 20–30 years, accumulates in organs, leading to a continuous response to the immune system, contributing to injuries and dysfunctions in tissues and organs [1]. Data like these can justify the presence of the heavy metal Cd in dog hair even three years after the Brumadinho disaster.

Another study investigated the effects of subchronic Cd exposure in mice and demonstrated increased IFN γ and IL-10 which suggested that Cd exposure may affect multiple T cell subsets [43]. Olszowski [34] reports that Cd has a positive effect on inflammation mediators (NF- κ B, IL-6, TNF- α , IL-1 β , IL-8, ICAM-1, VCAM-1, PECAM-1, COX-2, PGE-2). However, IL-15 showed a strong correlation with IL-2, IL-6, IL-18, MCP1 and TNF- α . IL-15 is a pleiotropic cytokine of the 4- α -helix bundle that includes IL-2, IL-3, IL-4, IL-6 and IL-21 and regulates the proliferation, survival and secretory activity of different cells, being characterized as a bioregulator that modulates adaptive immune responses [8]. The strong correlations with IL-2 and IL-6 reinforce its role in adaptive immunity, while the negative association with Cd suggests that the metal may suppress IL-15 while favoring pro-inflammatory activation, which may be related to immune dysregulation and chronic inflammation.

The main organs negatively affected by exposure to Cd are the kidneys, bones, vascular system and lungs, altering genetic expression and the transduction of signals recognized as carcinogenic [24]. In this study, the clinical signs that presented significant values were dermatological ($p = 0.003$) and locomotor ($p = 0.011$).

It is noteworthy that (6/20) 30 % of the dogs in the exposed group showed oncological changes in the skin and reproductive system in females and males. Cd is classified by IARC [20] as a potentially carcinogenic heavy metal (Group 1). Study carried out by Mouro [33] in mice demonstrates Cd-induced testicular toxicity with increased apoptotic cell labeling, degeneration of the seminiferous epithelium, damage to Leydig cells, and death of germ cells.

Chronic exposure to heavy metals can harm female reproductive health. Cd has been described as causing endometriosis, endometrial cancer and miscarriages in human health [15]. In a comparative study of breast cancer in humans, a significant accumulation of Fe, Ni, Cr, Zn, Cd, Hg and Pb was evidenced when compared to the group without breast cancer. Data suggest that the accumulation of metals in breast tissue may be related to the growth of malignant neoplasms [21].

In a systematic review carried out by Rauf [36] the presence of Cr, Co and Ni was related to cases of dermatitis and eczema in humans and Cd, Pb and Hg with chronic diseases such as psoriasis and skin cancer. Dogs exposed to waste had higher Cd values, which may justify the development of skin lesions and skin cancer in this group.

Studies incriminate Cd as a heavy metal that is involved in the disturbance of bone homeostasis and the development of osteoporosis, it has been suggested that it acts to inhibit bone formation and increase resorption mediated by the activity of osteoblasts and osteoclasts [45]. Another factor that must be considered is that several canines in the exposed group had significant increases in Fe in their fur (Table 6). Studies in mice demonstrate that Fe may be a risk factor for osteoporosis, due to the accumulation of Fe inhibiting multipotent osteoblast precursor cells and inducing their apoptosis through the activation of Caspase 3 [48].

The dogs in the exposed group showed a moderate correlation (0.49) of the heavy metal Pb (Graph 2) with the number of hours worked ($p = 0.02$) and a moderate correlation (0.48) with Cr ($p = 0.03$). Lourenço [28] carried out eco-toxicological analysis of the material disposed of in the soil and water systems after the collapse of the Brumadinho dam. The presence of tailings increased the density of particles, the concentration of Fe, compromised the organic matter content, increased the contents of heavy metals Hg, Pb, Zn and Cu with values that exceeded the limits of current legislation. This fact may characterize that a longer period of exposure to tailings results in a greater increase in Pb in dog hair, with the average of the exposed group (0.39) being relatively higher than that of the unexposed group (0.19) (Table 6). It is noteworthy that the correlation between Pb and Cr can contribute to the appearance of skin lesions. Kim [23] incriminates Cr for the development of skin allergies and dermatitis.

Urine and blood samples were collected by the Ezequiel Dias Foundation - FUNED from search and rescue professionals (State Fire Department, National Security Force) and analyzed by the Evandro

Chagas Institute - IEC. As, Al, Cr, Ni, Mn and Hg in urine and Pb in urine were evaluated during two periods of time after work. In the first period there was an increase in As and Ni above the reference values and in the second period As and Al [31]. Likewise, in the present study, an increase in metal values in Al, As, Cd, Cr, Fe, Mn and Pb was observed in the hair of the group of exposed dogs.

The work activity carried out by military firefighters exposes them to various contaminants, which can increase the risk of developing different types of cancer [25]. IARC [20] classified the occupational exposure of firefighters as potentially carcinogenic. Firefighters are exposed to construction materials, fire combustion products, chemicals such as firefighting foams such as *per*- and polyfluoroalkylates (PFAS) [13]. The present study highlights exposure to mining tailings due to the work activity of rescuing people and bodies after the collapse of the Brumadinho dam.

According to the Epidemiological Bulletin of the Health Surveillance Secretariat, Ba and Cu had higher values than those recommended by current legislation [40]. Chemical analyzes of 10 samples were carried out along the route of the tailings, the results of the heavy metal analyzes were compared with Prevention Values (VP), determined by Resolution of the National Environmental Council (Conama) n $^{\circ}$ 420 of 2009. These data can corroborate the results of the Mann-Whitney test to characterize clinical signs, heavy metals and cytokines. Cu presented a significant value ($p = 0.042$) for clinical signs of disorders in the cardiac system.

The Cu is an essential trace element, but its excess is potentially toxic, its characteristic of circulating between two oxidation states is an important factor for several physiological processes associated with enzymes linked to it. Its cellular bioavailability is tightly controlled by Cu transporters, which play an essential role in cardiovascular responses, including cell growth, migration, angiogenesis and damage repair [16]. Studies indicate that increased Cu may be associated with increased cardiovascular disease, atherosclerosis [10,42], heart disease, ischemic disease and heart failure [47]. This set of evidence reinforces the importance of monitoring Cu levels in dogs exposed to tailings, as the cardiac alterations was observed in two animals from the exposed group. The cardiac disease in these animals was diagnosed by echocardiography, after presentation of clinical signs.

Fe showed a strong correlation (0.92) with Al ($p < 0.001$), a strong correlation (0.81) with Cr ($p < 0.001$) and a strong correlation (0.63) with Mn ($p = 0.003$) and weak correlation (-0.54) with MCP1 ($p = 0.029$). Al has the potential to alter the systemic content of regulatory factors, which provides changes in Fe-related proteins, causing an accumulation of this trace element [46]. This data can justify the values of exposed dogs that presented high Al results and also showed an increase in Fe (Table 6). TNF- α induces the acquisition of Fe by macrophages and inhibits the export of this metal to ferroportin, together with the action of interleukins (IL-1, IL-6 and IL-10), promoting storage in the nuclear phagocytic system, generating an elevated Fe stores and deficient erythropoiesis, which may justify anemia in chronic diseases [18]. The increase in intracellular free Fe leads to increased oxidative stress and overaccumulation of lipid peroxides, leading to cell death called ferroptosis. This event may be associated with the development of various pathologies [2].

Analysis of 1847 water samples were collected by health professionals from the Unified Health System (SUS), resulting from campaigns to monitor the quality of water for human consumption, whose sources are at a distance of up to 100 m from the Paraopeba River (an area potentially affected), totaling 16 municipalities. Results above the maximum value allowed by the standards were evidenced, for potability of iron in 336 samples, aluminum in 117 samples, manganese in 207 samples, it is noteworthy that in 38 samples all these metals were above the maximum value allowed [40].

A study on *Coxiella burnetii* seropositivity in working dogs from Brazilian police K-9 units raised awareness about the possibility of cross-exposure as an alarming occupational risk to One Health and a concern

for the workers' health [12]. This perspective is different from the present study, but it emphasizes the interconnectedness of agent exposure and harm shared between dogs and humans. This study also highlights that the health of working dogs can be indicators of human exposure.

In Granite City, Illinois, USA, a study was conducted near a former lead smelter. Blood lead levels were measured in 827 humans, 84 dogs, and 26 cats. A significant relationship was found between blood lead concentrations in domestic animals and children, supporting the hypothesis that pets could be used to monitor lead exposure in children [7]. In addition, a cross-sectional study of pet dogs living near high-risk environmental pollution sites in the United States found a higher frequency of micronuclei in peripheral blood lymphocytes compared with the control group [5]. These findings corroborate with those of the present study and reinforce the possibility that using dogs as biomonitors, because they share the same environment, may have a similar metabolism to humans and a shorter lifespan, allows earlier observations of toxic effects.

The concept of biomonitoring is not limited to domestic species. Wildlife has also been employed to detect environmental contamination. In Iran, for example, small mammals (*Meriones persicus*) were studied at the iron mining company by evaluated tissue samples, which showed significant levels of Cu and Cd in the kidneys and liver [41]. The metals characterized in this study were similar in the exposed group (Cd) and the metal that showed significance in cardiac clinical signs (Cu). These results reinforce the use of dogs as biomonitors for environmental pollution, both to assess the exposure of the local wild population and for worker exposures and highlight exposure to heavy metals in mining areas.

This study had some limitations. The dogs representing the exposed group were older than the dogs in the unexposed group. This was due to the retirement of some of the rescue dogs in Brumadinho and their deaths after their work period. These dogs were replaced by young dogs in training, which comprised part of the unexposed group. Older dogs can develop tumors independent of heavy metals exposure; therefore, further studies, such as genetic testing, should be conducted to analyze the true effect of metals on the dogs' health. Another factor that should be considered regarding age is the bioaccumulation of metals, which can occur from different sources of exposure to pollutants throughout the dog's working life. An older dog may have a higher exposure rate compared to a younger dog. However, during the interviews, the missions performed by each study participant were discussed, and dogs that worked in other events involving mining tailings were excluded from the unexposed group. It is worth noting that military firefighters' working dogs perform various activities in which they are exposed to other pollutants. A relevant fact that needs to be addressed regarding this study's limitations is the material analyzed, which was hair. Metal bioaccumulation is specific and the metals accumulate in different organs, such as the liver, kidneys, and bones, which would require biopsies of these animals or postmortem studies. Finally, a factor that can cause differences in metal levels is the type of diet each animal receives, a fact not inferred from this study.

5. Conclusion

The study shows that, even in the long term, significant Cd values were identified in the group of working dogs exposed to Brumadinho waste. Dermatological and locomotor clinical signs showed significant results. Despite the limitations of the study, the correlation between clinical signs, presence of metals and inflammatory cytokines indicates that dogs can be a promising tool for characterizing long-term occupational exposures and highlights the importance of biomonitoring the health of firefighters who suffer constant environmental exposures. Chronic exposure to heavy metals and trace elements suppresses the immune system, promoting the development of pathologies.

6. CEUA and authorizations

The project was submitted and approved by the Ethics Committee on the Use of Animals (CEUA) of the Faculty of Agricultural and Veterinary Sciences (FCAV) of the São Paulo State University "Júlio de Mesquita Filho" - Unesp - Jaboticabal Campus - SP. Executed in accordance with the standards required by CONCEA (National Council for the Control of Animal Experimentation). Protocol n°. 1178/21. A request was made via authorization letter for working dogs to participate in the research, through the Fire Departments of each State.

Consent to participate

Not applicable.

Consent to publish

All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

Statements and declarations

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Fabiana Sperb Volkweis, Andriago Barboza De Nardi, Henrique C. S. Silveira and Paula Rohr. The statistics performed by Bruno Stéfano Lima Dallago. The first draft of the manuscript was written by Fabiana Sperb Volkweis and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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CRediT authorship contribution statement

Fabiana Sperb Volkweis: Writing – original draft, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Paula Rohr:** Methodology. **Bruno Stéfano Lima Dallago:** Formal analysis. **Henrique C.S. Silveira:** Writing – review & editing, Supervision. **Andriago Barboza De Nardi:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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