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The arsenic contamination event of Santana, Amapá State, Brazil, and the high values of arsenic in the brownish Amazon waters

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Abstract

The contamination with arsenic in Santana led to the perception that the brownish waters of the Amazon River carry arsenic, at a rate higher than 235,000 tonnes per year, and it seems important that this arsenic should be studied in detail. The anomaly was caused by the discharge of tailings of a pellet plant in an excavated sump. These tailings were composed of iron- and arsenic-rich minerals, crystallized at above 900°C in the metallurgical process, which become unstable when submersed in fresh water at pH 5.0-6.0. In the sump, iron, arsenic, manganese, and other metals were slowly solubilized from the minerals, entering the groundwater. When iron got in contact with the water organic compounds, it formed a gel, absorbing As, Mn, and other metals, as it normally happens during weathering in the Amazon. The sump has been built in practically impermeable clayey soil, which made the gel move slowly, giving time to form hard concretions of limonite, characteristic of the Amazonian soil. Iron, manganese, arsenic and other metals were retained in the concretions, and the arsenic-bearing iron gels went for a maximum of some hundreds of meters away from the sump. Soon after the identification of the contamination, the water of the sump was, under close control, discharged into the Amazon River, and the tailings were removed to high ground. In sequence, as it was impossible to properly isolate the tailings, they were sold and shipped away. In the meantime, there were complaints that persons have been affected by arsenic-contaminated water that flowed from a broken dam (that never existed) into a small creek that crossed a community, and that people that consumed the water had cancer. A large medical team was called by the local government, thousands of persons were examined, diseases were found, and none related to arsenic. Analysis of blood and hair presented arsenic in limits worldwide accepted as normal. As samples of the Amazon showed a conspicuous presence of arsenic, they led to the study of the river waters for arsenic. Information is presented to correct misunderstandings present in the literature. Two important points are commented on to understand the event. One is the geological affinity of arsenic with iron. The other is that the toxicity of a solid is determined by how much of the toxic element is liberated for contamination; the standards used for the proper definition of toxicity of a solid are presented.

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1. Introduction

For nearly 50 years, Indústria e Comércio de Minérios - ICOMI produced oxide and carbonate manganese ores in the State of Amapá, Brazil, shipping them to steel plants of all continents. The ores were exploited in Serra do Navio, located at latitude 0º55’ north and longitude 52º95’ west, and embarked in the company private port of Santana, located at latitude 0º03’ South and longitude 51º11’ West (Fig. 1). Initiated in 1957, the mining production ceased in 1998, in response to the exhaustion of the economically minable oxide ores. Serra do Navio still has resources of carbonate and low-grade oxide ores to be explored (Costa 1997; Scarpelli 2022).

After the closure of its mining activities, an environmental study done by ICOMI in the Industrial Area of the Santana port identified an unexpected and localized contamination of the groundwater with arsenic. While the company was taking action to eliminate the contamination, what was done in a short time, the anomaly identification led persons living in the proximity to complain about diseases which have resulted from arsenic contamination, what was never confirmed. The issue provoked a continuous flux of research and published papers dedicated to the incident, with some of them presenting unreal details.

A positive side effect of these studies was that they led to the identification of high grades of arsenic in the waters of the

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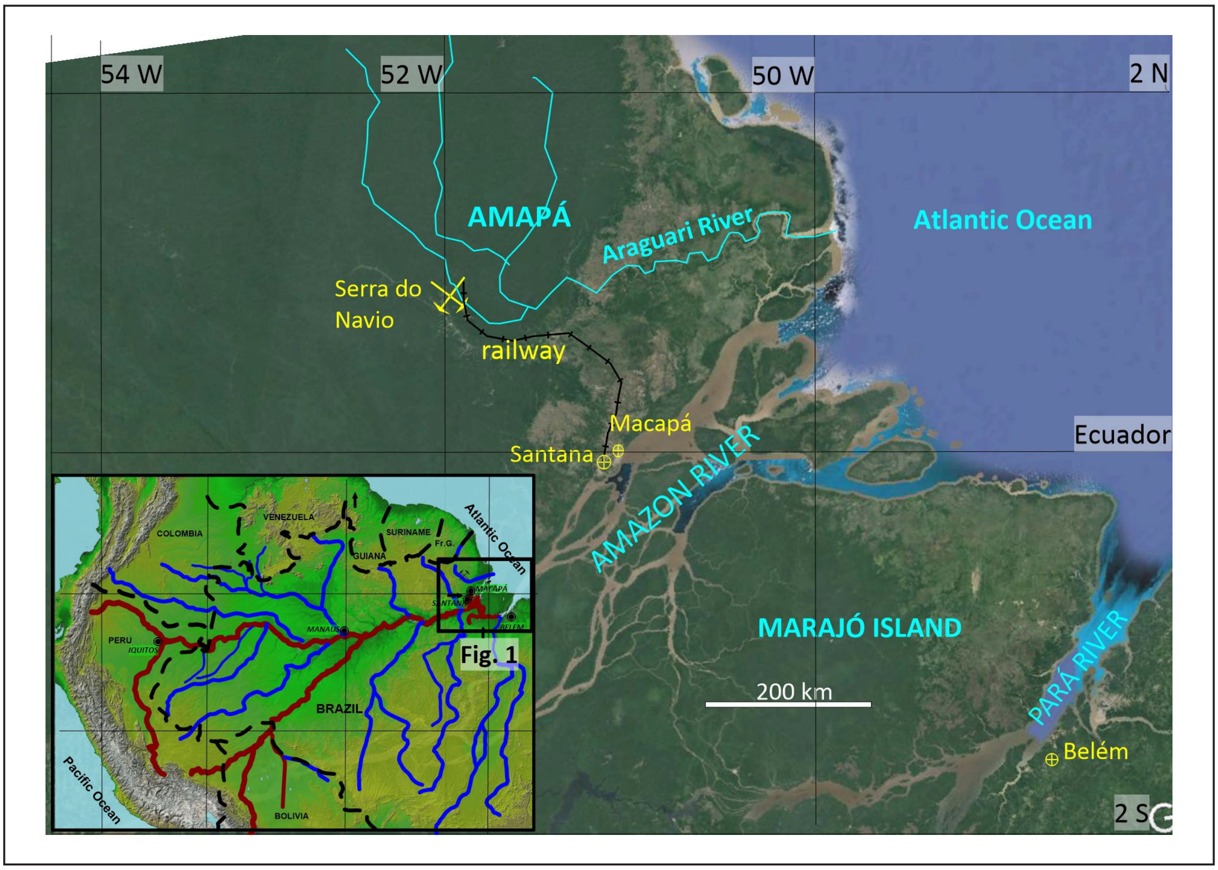

FIGURE 1. - – Location of the areas addressed in this review. The manganese ores were mined in Serra do Navio, from where the water flows directly to the Atlantic Ocean through the Amapari and the Araguari rivers. The ore was exported from the port of Santana, situated at the left margin of the Amazon River, near Macapá, the capital of the State of Amapá.

Amazon River, first observed by Pereira (2000), confirmed by Scarpelli (2005), and neglected by subsequent authors, who preferred to repeat not-confirmed information regarding the Santana contamination event. While it is obviously correct that the contamination be divulged, to avoid its repetition in other mining-metallurgical operations, it seems convenient to make it clear that it was neutralized.

The subject was discussed in 2002, in Macapá, during a conference open to the public and headed and sponsored by the NAEA (Núcleo de Altos Estudos Amazônicos), of the Universidade Federal do Pará, to examine 50 years of mineral exploration in the Amazon. Some of the presentations were made by professors of NAEA and by Environmental Organizations (NGO), mostly with a focus in possible problems brought by the mining done by ICOMI in Amapá, outlined by the arsenic contamination at Santana. The arsenic situation was presented and discussed in detail by Scarpelli (2003). At the end, in a session headed by the Environment Secretariat of Amapá, it was concluded that there was no longer an arsenic contamination in Santana. Unfortunately, no register was made of this session, besides the availability of the presentations in websites, as those of CETEC and NAEA (Monteiro 2003; Scarpelli 2003). Antonio Feijão, at the time Head of the Amapá District of the Agência Nacional de Mineração, confirmed that (free translation of his words): “the area of the port of Santana is free of contamination with arsenic” (Feijão 2012), actually exposing the conclusion of the mentioned conference.

With the intention to help in the understanding of what happened, this review starts with the methodology used to define the toxicity of an element in solids, follows through a summary of the main points of the literature referring to the Santana event, a short review of the geology and metallurgy of the manganese ores, the form of occurrence of arsenic in the ore, a description of how the Santana contamination was formed, and how it was eliminated, and cover the efforts made to get the greater context of what occurred. Comparison of water obtained from domestic water wells and from the Amazon River, and the examination of arsenic in blood and hair of inhabitants of the area, led to the perception, for the first time, of the high grades of arsenic present in the brownish waters of the Amazon River. The paper ends with the realization that the arsenic contamination of the Amazon River derives from sulfide mineralization in the Andes (Scarpelli 2005), the same cause of the strong arsenic contamination that occurs in the Mendoza and Sali rivers basins in Argentina (Gomez et al. 2019; Litter et al. 2019). This is a type of arsenic contamination which might be of interest of Geologists, Medical Doctors, Engineers, Metallurgists, Chemists, Environmentalists, Public Officials, Science Journalists and possibly other professionals.

2. Defining the toxicity of a material

The Health Ministry and other official institutions specify the maximum quantity that a soil or a water could have of a substance to be qualified as non-toxic on that substance. But, to define if a material is toxic in a substance, it is necessary to see how much of the substance contained in the material is actually available for ingestion, adsorption or absorption by an individual, an animal or a plant. If the material is a liquid where the substance is occurring in free form, the simple chemical analysis seems adequate for the definition of how much of the substance is available for contamination. Even so, the effective risk of damage varies according to factors like the valence of ions, if the substance is in organic or inorganic form, the personal resistance of the affected individuals etc.

In a sharp contrast, the toxicity of an element in a solid is not defined as the percentage of the element in the solid, but on how much of the element is, or could be, freely available, or available, for the possibly affected individual. In other words, by how much of the element of the solid can be liberated in a free form to the environment. If an element is firmly tied inside the crystalline structure of a mineral, from which it is not removable under natural chemical and physical conditions, that element, in that mineral, does not represent a risk of toxicity.

The quantification of how much an element, or a compound, in a solid is available, is obtained with the application of worldwide accepted techniques. In Brazil, they are prescribed by the ABNT standards (Associação Brasileira de Normas Técnicas - Brazilian Association of Technical Standards). Standard NBR-10.005 (ABNT 2004b) specify the procedures to be taken to quantify how much of the element is leached in a slightly acid environment, with a pH of 5, or of 3, while the standard NBR-10.006 (ABNT 2004c) details how much of the element is solubilized under a chemically neutral condition, of pH 7.0 (Table 1). These tests are usually done by accredited laboratories.

The actual limits of toxicity of a solid, due the presence of an element, are expressed with NBR-10004 (ABNT 2004a) using the results of the two tests above. Regarding arsenic, Table 1 shows that the solid is toxic in arsenic if the result of the leaching tests is higher than 1.0 mg/L, and inert, when it is smaller than 0.01 mg/L in the solubilization tests. Solids with less than 1.0 mg/L in leaching but more than 0.01 in solubilization are classified as non-inert (before 2004, the values in use were 10 times greater, of 5.0 mg/L for the leaching and 0.10 mg/L in the solubilization tests).

An interested person could ask “So, what is the reason for the limits established by the CONAMA (Conselho Nacional do Meio Ambiente – Brazilian National Environment Council), CETESB (Companhia Ambiental do Estado de São Paulo – São Paulo State Environment Company) and other organizations, defining the maximum percentages of the elements in soil”? Actually, the limits defined by these organisms intend to raise a signal of alertness, for an intervention. If the percentage of an element in a material is greater than the limit, the material should be submitted to the tests indicated by the standards NBR-10.005 and NBR-10.006, to check using standard NBR-10.004, whether it is toxic, non-inert or inert for the specific element.

3. Literature covering the Santana (Amapá State) occurrence

In the last 20 years, several authors presented papers dedicated to or making reference to the arsenic contamination in Santana. The work of Monteiro 2003 presents a good summary of the available information about the activities of ICOMI, including the financial, operational, administrative, and technical aspects. As far as arsenic is concerned, he mentions but did not comment the information available at the time, indicating that it required detailed studies. Scarpelli (2003) presented an overview of the contamination, its characteristics, origin, nature and what was being done to neutralize it. Santos et al. (2002, 2003) and Santos (2005) described the activities and results of the studies of the Instituto Evandro Chagas, of Belém, State of Pará, in the medical examination of individuals living near Santana for their eventual contamination by arsenic. Lima (2003) presents important results of sampling and assaying for arsenic of water from creeks and rivers of Santana.

At the same time, some authors presented descriptions, expectative and conclusions that were not supported by sound information, and, as a consequence, created conditions to raise negative views of their readers.

A few papers describe, inclusive mathematically, how the detected pocket of arsenic-contaminated groundwater of the Industrial Area would move uninterruptedly downslope towards the Amazon River (JPE 2001; Pereira 2000; Queiroz et al. 2001), albeit there is no sign that the contaminated groundwater reached the Amazon River (Scarpelli 2003). Even so, there was a suggestion that the entire delta of the Amazon River was contaminated by arsenic derived from the ICOMI operations (Pereira 2018), which is volumetrically impossible (Scarpelli 2005). Several papers called attention to arsenic causing cancer and other diseases in inhabitants of Elesbão (Pereira et al. 2009; Batista 2015), although no single case was identified. There are descriptions that the community of Elesbão was affected by surges of contaminated water, following the failure or the overflow of a dam that was storing tailings of a pellet plant (Pereira et al. 2009; Batista 2015); although such a dam never existed. The presence of arsenic in the air of inhabitants of Elesbão was attributed to contamination derived by the activities of ICOMI (Pereira et al. 2009; Batista 2015), without a demonstration and disregarding the possibility that arsenic was coming from the Amazon River (Scarpelli 2003, 2005), source of most of the drinking water used by the inhabitants of Elesbão. There is a citation of manganosis (Batista 2015), without any example of its occurrence, and ignoring the providences taken by ICOMI to avoid the disease in the only sites where it could have occurred, at the mine, specifically, during dry drilling (in shallow percussion drilling for geology), dry crushing (in some laboratory work) and in blasting (always done in the mine during lunch time, under open sky and far away from people). With chemical analysis of blocks of low-grade manganese ores paving some streets of Santana, Pereira et al. (2009) confirmed the expected presence of arsenic in these blocks, and, without any additional work, wrote that they are toxic and recommended their removal from the streets. Incidentally, Pereira et al. (2009) reported that the blocks presented arsenic grades from 48 to 1,713 mg/kg, with an average of 682 mg/kg, and, as this paper will show, these are quite normal results for the low-grade oxide manganese ores, which assay around 0.15% As, or 1.00 to 1.5 g/kg, without offering any health risk. They added that a portion of the pellet plant tailings, removed from their depository site, were also used to cover the streets, not considering the fact that the donation of ore blocks to the municipality occurred years before the removal

TABLE 1. Official parameters to define the toxicity of arsenic in Brazil. For liquids and solids, the limits for 'intervention' are used to verify if an accurate study is necessary. For water, the limits set by CETESB (2021) and CONAMA (2011) might suffice. For solids, the toxicity is defined with the treatment of the material with the tests detailed by norms NBR-10005 and 10006, and the qualification defined by norm NBR-10004.

ARSENIC TOXICITY IN SOLIDS (NORM NBR-10,004, updated in 2004 *)		
TOXIC MATERIAL	>1.00 mg/L in the leaching test	(NBR-10.005)
	<1.00 mg/L in the leaching test	
	>0.01 mg/L in the solubilization test	
INERT MATERIAL	<0.01 mg/L in the solubilization test	(NBR-10.006)

TESTS TO DEFINE THE TOXICITY OF ARSENIC IN SOLIDS (only the main details of the tests are presented)		
NBR-10.005	Leaching test	Agitation during 25 hours of a 100 g sample in 1 L of a natural acid at pH 5.0, or 3,0
NBR-10.006	Solubilization Test	Duplicate tests of agitation for 5 min of a 250 g sample in 1 L of deionized water at pH 7.0; wait for 7 days
In both tests, the resulting solution is assayed for the selected elements		

LIMITS OF ACCEPTANCE IN SOIL AND WATER							
CETESB (2021)					CONAMA (2011)		
SOIL					WATER		
mg/kg					(µg/L)		
Good quality	Call attention	Intervention			Potable	Inter-vention	Effluent
		Agricola	Residential	Industrial			
<3.5	>15	>35	>55	>150	<10	>10	>500

* Before 2004, the values defining Arsenic toxicity were, respectively, 5.0 mg/L in the

of the tailings from the sump (see details ahead). These authors also wrote that the Secretaria do Meio Ambiente of Amapá (Environment Secretariat), or SEMA, was informed of the arsenic problem by "an anonymous person", ignoring that SEMA had been previously informed of the execution of the environmental study, and that a copy of its report was personally handed to SEMA by a Director of ICOMI, in May of 1998 (Costa 1998). The majority of the mentioned authors wrote about the financial penalty applied to ICOMI by SEMA in July of 2000, but none of them mention that the payment was not reinforced, and not paid, since the problem was corrected. There are papers incorrectly informing that the arsenic came from wastes rich in arsenopyrite (Figueiredo et al. 2005), not considering that mine wastes only exist in the mines and not in Santana, and that arsenopyrite is a quite rare mineral in the Serra do Navio Formation, only seen in fresh rocks and never in the mine wastes, which are constituted by weathered rocks. A paper (Salgado et al. 2001) informs that a few unselected samples of rocks from Serra do Navio revealed arsenic in their composition, with a maximum value of 0.00054 mg/kg, and, without any other information, declares that the local population could be at risk, what is obviously not true. Other authors wrote that the population of Serra do Navio might be affected by arsenic contamination due to the presence of arsenic in the oxide ores (Pereira et al. 2009). Others wrote that local river waters transported sediments from the mine operations in Serra do Navio to the Amazon River (Seyler and Boaventura 2001; Nery and Bonotto 2011), albeit the fact that the waters of the mine area are discharged by the Araguari River directly into the Atlantic Ocean (Fig. 1), and that the water current of the coast of Amapá flows to the north, turning the assumption impossible.

An example of the consequences of the use of inappropriate descriptions is demonstrated by Teixeira et al. (2020), describing the Santana event in their article reviewing the problems of arsenic in Brazil. Describing the Santana event with information attributed to Monteiro 2003, Santos et al. 2003, Lima et al. 2007, and Brazil 2017, they initially confused the mine wastes with the tailings of the port area plants, albeit they are 192 kilometers apart and are completely different. They mention "arsenopyrite-bearing wastes", which never existed, "wastes incorrectly disposed at the mining vicinity", a topic that never raised a discussion, and "products of sintering collected around mining operation, waste dumps and processing sites", messing up words. They mix observation with wrong assumptions, as "toxic elements might have permeated into the aquifer or could have leached out through the cracks of dam walls, or during flooding events", and, culminating, with "arsenic contamination of two Amazon River tributaries, Elesbão 1 and Elesbão 2" which "cross a 129-hectare region inhabited by approximately 2,600 people", ignoring the fact that the 129-hectare area is the Industrial Area of ICOMI, where none of the mentioned 2,600 people live. An anonymous paper on the site of the Centro de Tecnologia Mineral - CETEM (CETEM 2011) expresses that overflows of the streams Elesbão 1 and 2 affected the inhabitants of Elesbão, mentioning, as an example, a series of diseases not related to arsenic. There is also the note that ore material was given to the municipality of Santana, for asphalt concrete, which is right, but also for "landfill in backyards and gardens, and in the construction of houses". There is too much biased and wrong information. In the end, when they agree with the suggestion of transforming Serra do Navio into a tourist area, they could have mentioned that ICOMI was ready to financially supports the installation of an Advanced Unit of the Universidade de São Paulo in Serra do Navio (Nogueira 1991), what was not executed due to the opposition of the Government of Amapá.

4. Summary of the ore geology and the arsenic contamination

The exploited manganese deposits occur in the Paleoproterozoic Serra do Navio Formation, formed by a sequence of carbonatic and silicate metasediments, and the commercial manganese oxide ores were formed during the weathering of queluzites (a silicate-bearing rhodochrosite marble), and occur only in the shallow and weathered portions of the rock (Scarpelli and Horikava 2017; Scarpelli 2022) (Fig. 2). The oxide ores were mined from 1957 to 1998, and the larger resources of manganese carbonates, which occur below the water table, remain practically untouched (Scarpelli 2022).

All minerals of the oxide ore are formed near the surface and, as such, are quite resistant to decomposition and dissolution under the conditions present on the surface. Firmly tied in the crystalline structure of the ore minerals, the arsenic is not available to contaminate mine workers and other persons. The presence of the element in the ore is known well before the beginning of the mining, and the assay of arsenic was routinely made in ore shipments.

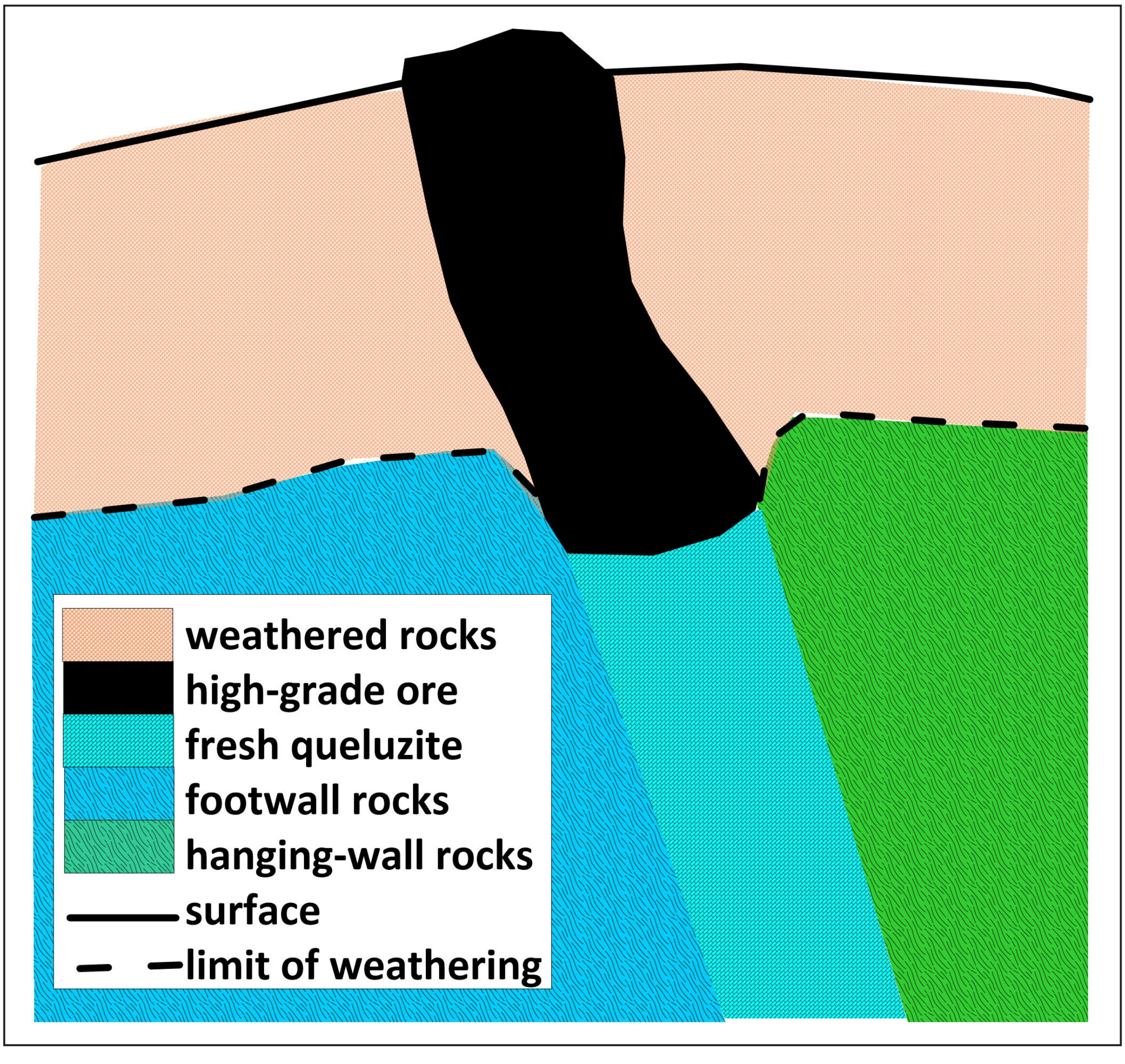

FIGURE 2. Geological section of the Serra do Navio manganese deposit, showing the manganese oxide ore replacing a weathered portion of a layer of queluzite protore, which is flanked by layers of quartzites and schists. Mining was done until the contact of the oxide ore with the fresh queluzite (adapted from Scarpelli and Horikava 2017; Scarpelli 2022).

In Serra do Navio, the extracted ore was treated in a plant installed next to the mine, where it was crushed, washed of clays and fines, and screened, after what the fragments varying from 8 cm to 0.8 millimeter were transported along a 192-kilometer railway to the port of Santana, for shipment to steel plants of Brazil, United States, Europe, Asia and Africa. The port is located in latitude 0º03' south and longitude 51º11' west, at the left margin of the Amazon River, at the southwest of Macapá, the capital of the Amapá State (Fig. 1). The screened-out fines, that is, the clean ore fragments smaller than 0.8 millimeter, were stockpiled in Serra do Navio.

The good stability of the arsenic of the oxide ores from Serra do Navio was disrupted in the Industrial Area of ICOMI in Port of Santana, when fines of the ore were used to produce pellets of manganese oxides. The required heating caused the recrystallization of the ore into a new group of minerals, some of them unstable under the present atmospheric conditions. A problem aroused when a portion of fragments with the new minerals were disposed in a sump of water, causing the liberation of a part of their content of arsenic, contaminating the groundwater (see details ahead).

While ICOMI was acting to eliminate the identified contamination, people living in Elesbão, a poor community at the west of the Industrial Area, started to present complaints of cancer and other health problems, which they attributed to the arsenic. Immediately, the government of Amapá called in the highly qualified Instituto Evandro Chagas, of Belém, State of Pará, to examine the medical situation of those people.

4.1. Geological details considering the arsenic of the ore

The queluzites, which are the primary source of the oxide manganese ores, are mostly made of carbonate (rhodochrosite) and silicates (picrotephroite, rhodonite, spessartite) of manganese. As accessories, they have minor percentages of sulfides, such as sphalerite and the arsenic-bearing sulfides of nickel and cobalt: cobaltite, niccolite and gersdorffite. They also contain iron, aluminum, silica, potash and other elements. As a reference, the fresh queluzite produced from the F-12 mine contained from 0.04 to 0.08% As, averaging 0.06% (Laranjeira 2000). Arsenic also can come from the other metasedimentary rocks (micaceous quartzites, limestones, biotite and graphitic schists) that occur above and below the queluzites, all of them containing minute percentages of pyrite, pyrrhotite and chalcopyrite, which normally are carriers of low quantities of arsenic. Conditioned by the high rainwater, high temperature, and by the action of the acid decay of the Amazon rainforest, which brings the pH of the groundwater to 4.5-5.5, the chemical weathering is quite intense, and the rocks are decomposed below the water table.

Some of the solubilized components, like manganese, iron, aluminum, and silicon, reprecipitate soon after the rock decomposition, forming supergene oxides and hydroxides of manganese (cryptomelane, lithiophorite and pyrolusite), of iron (limonite, goethite and hematite), aluminum (gibbsite), and silica (Scarpelli 2022). Some of the dissolved elements, such as potassium, cobalt and arsenic, have chemical affinities with manganese and iron, and stay in the crystalline structure of some of the supergene manganese and iron minerals, not representing a health problem for the mine workers and for the inhabitants of Serra do Navio. (The present author worked 12 years in the mines, from 1961 to 1972, normally grabbing fragments of the ore with his hand unprotected).

The ore minerals appear with three distinct textures and structures (Fig. 3). The most common is the massive ore, formed by the in-situ replacement, by cryptomelane, of rhodochrosite-rich portions of the queluzite. Next in frequency, the mammillary ore, formed in walls of cavities formed along fractures or by the leaching of masses of silicates of the queluzite. These mammillary bands are formed after repeated cycles of inflow of colloidal fluids rich in manganese, iron and other metals. Covering the surfaces of the caves, these flows led to the formation of very fine fibers of the ore minerals, that coalesce forming the mammillary bands (Valarelli 1967). The last and least common form is represented by euhedral pyrolusite, found in cavities not filled by the mammillary cryptomelane.

After the cessation of mine activities, samples of the piles of beneficiated but unsold ores left in Serra do Navio were submitted to leaching and solubilization tests, following the specifications of NBR-10.005 and NBR-10.006. The results, presented in Table 2, showed low values, of the order of <0.01 mg/L, for leaching and solubilization for all of the samples of oxide ore, demonstrating that arsenic is absolutely inert in these ores, not representing any risk to human beings. On the other hand, as expected, the carbonate, which is a fresh and not weathered rock, revealed 0.47 mg/L in the solubilization and 0.07 mg/L in the leaching test, indicating that the ore is non-inert, meaning that it is not toxic, but that attention should be given to its handling.

4.2. The loci of arsenic in the ore

To verify where the arsenic occurs in the ore, a sample of high-grade ore, containing iron, arsenic, aluminum, and silicon, was examined by X-ray spectrometry (Vlach 2002), for manganese, iron, arsenic, aluminum, silicon, and other elements. Vlach (2002) applied the WDS method (wave-length dispersive X-ray spectrometry) to get images (Fig. 3) of the distribution of manganese, iron, arsenic, alumina and silicon over a selected area of 90 x 90 μ, showing the three types of ore textures and structures: compact, mammillary and crystalline. The mammillary occupies most of the left-hand part of the sample. The compact and massive, replacing rhodochrosite, is at the far right, and, between the two, there is an open zone, with euhedral crystals of pyrolusite and dust-size lithiophorite (Vlach 2002).

The other five images in Fig. 3 represent the intensity of presence of manganese, iron, arsenic, aluminum and silica in the selected area. The colors that appear in the images of the elements were not calibrated to represent their actual grades, but just selected to show where the lower and higher grades are. White dots were included in the figures, to help in the visual comparison among the six images.

The zone with mammillary structure is rich in iron and poor in manganese, presenting a coincidence of higher and lower values of iron and arsenic, indicating a strong association between the two elements. In contrast, the manganese is lower where arsenic is higher, and higher values of iron and arsenic occur in a mammillary band poorer in manganese and aluminum. In the zones of pyrolusite and lithiophorite, and of massive cryptomelane, manganese is the dominant element, iron is almost absent, and arsenic appears with lower

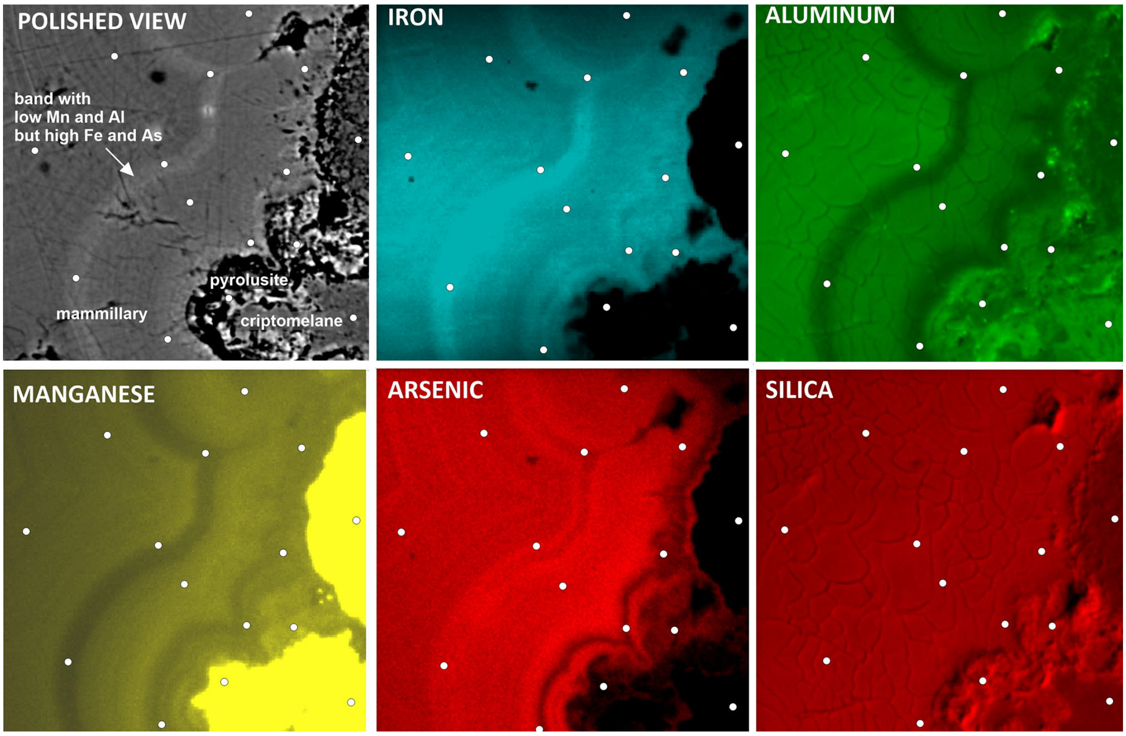

FIGURE 3. X-ray spectrometry of a selected 90 x 90 µ portion view of a sample of high-grade manganese ore, presenting a view of the distribution of iron, At the upper left, the photo-image of the sample, taken with the resolution of 512 x 512 pixels. The others were obtained by WDS (wave-length dispersive X-ray spectrometry) in the Inst. of Geosciences of the University of São Paulo, showing the intensity of iron, manganese, arsenic, aluminum and silica in the sample. At the center, iron and arsenic are greater in a zone with a mammillary structure. At the lower right, manganese is greater over pyrolusite and massive cryptomelane. The color images representing the elements are composed by 256 x 256 pixels, with the readings made over each pixel, for 2 seconds each, under a field of 20 KV and a current of 100 nA.

values in the pyrolusite-lithiophorite zone, possibly related to the lithiophorite. Aluminum follows the manganese in the mammillary zone. No clear pattern was seen in the silicon distribution.

Vlach (2002) also quantified the presence of these major elements in five selected spots of the sample, measuring the energy of X-rays dispersion (EDS method). The results (Table 3), emphasize the better association of arsenic with iron, in comparison with manganese, aluminum and silicon. Potash, which is a normal constituent of cryptomelane, is absent in pyrolusite and in the mammillary zone. No distribution pattern was seen for silicon and aluminum.

The association of arsenic to the iron explains the conclusion of a study conducted by the Battelle Memorial Institute, in Ohio, USA, demonstrating that in the steel furnaces most of the arsenic of the ore, arriving with the iron, remains with the iron, and goes with it to the steel (Presnell et al. 1968), not going to the slag with the manganese. As the arsenic introduces a small increase in the brittleness of the steel, some consumers used it to blend the Amapá ore with low-arsenic ores obtained from other sources.

4.3. The metallurgy and consequent recrystallization of the ores

The Industrial Area of ICOMI in Santana, located at W 51º11' - S 0º 3', occupies an area of 1,290,000 m^2 located at the margin of the Amazon River and adjacent to the city of Santana (Figs. 4 and 5). It was designed to host the port, ore piles, loading equipment and installations, the terminal of the mine railway, and buildings for maintenance, administration and other services. In 1970, as the pile of fines (clean ore fragments smaller than 0.8 millimeters, and assaying about 31% Mn) surpassed 1,000,000 tonnes, ICOMI was authorized to build in it a plant to use the fines to produce pellets. The Pellet Plant operated from 1972 to 1983, when it ceased activities due to increases in the cost of fuels. In the following years, the installations were modified to use the fines to produce a sinter for direct feed in electric-reducing furnaces. The production of sinter was initiated in 1986, and continued until 1996. In sequence, ICOMI installed an electric-reducing furnace, to use the sinter to produce a High-Carbon Iron-Manganese alloy (Figs. 4 and 5). This plant operated from 1990 to 1995. Albeit the high quality of their products, the sinter and the reducing furnace ceased activities in 1996, due to a high cost of electric energy. The commercialized products of these plants are shown in Table 4.

A manganese pellet is a porous sphere composed by manganese oxides. To get these oxides, the fines were mixed with coke or other carbonaceous fuel, and roasted to about 800-1,000 ºC in a vertical furnace with a fluidized bed (Chu 1972). During the roasting, the fines lost water of humidity, and part of the oxygen contained in the crystalline structure of the ore oxides and hydroxides of manganese and iron, which recrystallized into new minerals, richer of manganese

TABLE 2. Results of leaching and solubilization tests in samples of ore piles left in Serra do Navio after the cessation of mining activities. All al them assay about 1,500 ppm (0.15% As). All results of solubilization and leaching of the oxide ores were smaller than <0.01 mg/L, qualifying them as inert, without signs of toxicity. In contrast, the carbonatic ore revealed 0.47 mg/L in the solubilization test, and 0.07 mg/L, indicating that this ore is non-inert, requiring care during manipulation. Solubilization tests were done following NBR-10,006, in two equal half samples. Leaching tests were done following NBR-10,005, with 50 g samples, diluted to 800 mL. Hours represent how long took the leaching test.

Sample details								Solubilization			Leaching				
Ore name	Ore type	As%	Mn%	Fe%	SiO_2	Al_2O_3%	Characteristics	As (mg/L)	As (mg/L)	As (mg/L)	As (mg/L)	pH initial	pH final	Acid volume added	Hours
								(a)	(b)	Average					
Coarse30	oxide ore	0.1516	29.5	15.2	8.4	11.5	fragments smaller than 8 cm	<0.01	<0.01	<0.01	<0.01	5.08	5.02	0.0	25.75
Bitolado 36	oxide ore	0.1316	36.3	15.5	9.3	14.4	fragments smaller than 2.5 cm	<0.01	<0.01	<0.01	<0.01	5.12	4.89	0.0	28.75
Small 30	oxide ore	0.1558	30.5	14.3	7.9	11.5	fragments smaller than 2.5 cm	<0.01	<0.01	<0.01	<0.01	4.79	4.86	0.0	25.75
Small 28	oxide ore	0.1499	29.2	13.3	10.5	12.5	fragments smaller than 2.5 cm	<0.01	<0.01	<0.01	<0.01	4.93	4.93	0.0	25.75
Small 26	oxide ore	0.1549	26.5	14.6	11.4	13.7	fragments smaller than 2.5 cm	<0.01	<0.01	<0.01	<0.01	5.00	4.91	0.0	25.75
Small 20	oxide ore	0.1356	25.0	13.8	12.5	13.7	fragments smaller than 2.5 cm	<0.01	<0.01	<0.01	<0.01	5.14	4.99	0.0	25.75
CB/M	carbonate	0.1415	36.6	5.3	17.4	5.4	fragments smaller than 2.5 cm	0.49	0.45	0.47	0.07	6.42	4.98	15.0	31.50

TABLE 3. EDS analysis (Energy Dispersive X-ray Spectrometry) of a sample of high-grade manganese oxide ore. The analytical conditions where: 20 kV of voltage, 100 nA of current, 1 micron of diameter of the X-ray flux, and 100 s for the time of incidence. The obtained spectrum was treated with the software PROEZA and normalized for a total value of 100%, not considering the values of the not-analyzed elements. The actual values obtained for each point were adjusted to sum 100%.

Element	Massive cryptomelane	Massive cryptomelane	Pyrolusite - lithiophorite	Mammillary zone	Mammillary zone
Mn %	45.47	42.49	47.15	6.72	4.87
Fe %	0.30	0.46	0.17	58.02	54.86
As %	0.09	0.06	0.06	1.69	1.32
Al %	5.91	1.43	0.59	2.64	1.50
Si %	0.95	0.31	0.36	0.60	0.57
P %	0.11	-	-	0.75	0.79
K %	3.28	3.02	0.06	0.00	-
Cl %	0.84	-	-	-	-
O %	43.05	52.23	51.61	29.58	36.09
Total	100.00	100.00	100.00	100.00	100.00

TABLE 4. Commercialized products of the pellet and the iron-manganese alloy plant.

Years	Pellets (t)	Sinter feed (t)	Iron-manganese alloy (t)	Equivalent tonnes of oxide ore
1973-1985	1,273,883			1,465,000
1986-1996		575,356		633,000
1990-1995			100,319	240,000
Total tonnage of equivalent oxide ore:				2,338,000

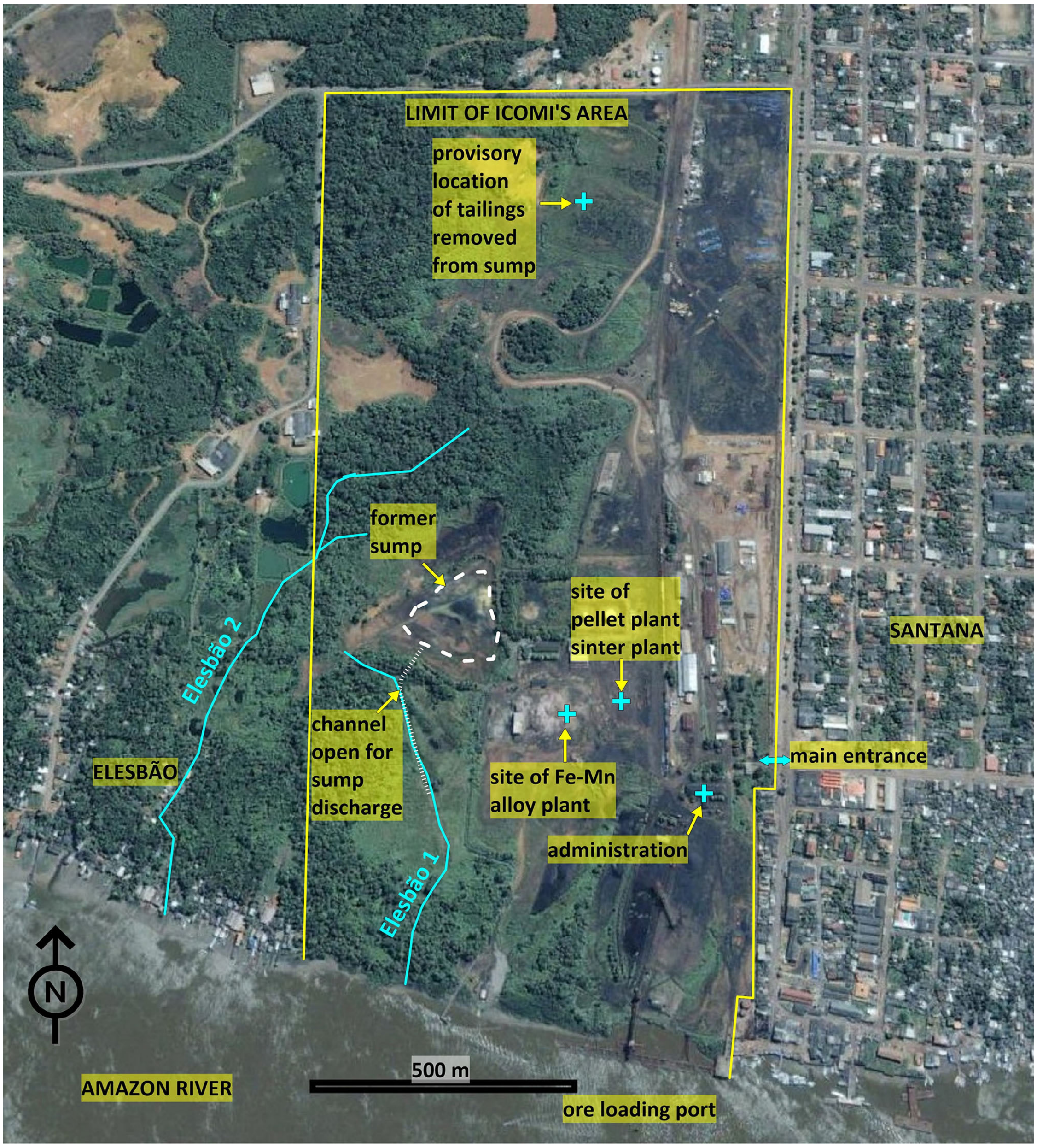

FIGURE 4. The Industrial Area of Santana sits between the town of Santana at east and the community of Elesbão at the west. The former site of the Pellet Plant and the sump is about its center; the plant was removed and the sump was filled, after its water discharged into the Elesbão 1 creek. The creek Elesbão 2 is at the north of the sump. A rim of compacted soil at the border of the sump avoids the flux of surface water into the sump. At its north, the site where, in 1998, the tailings of the sump were stockpiled after their removal from the sump.

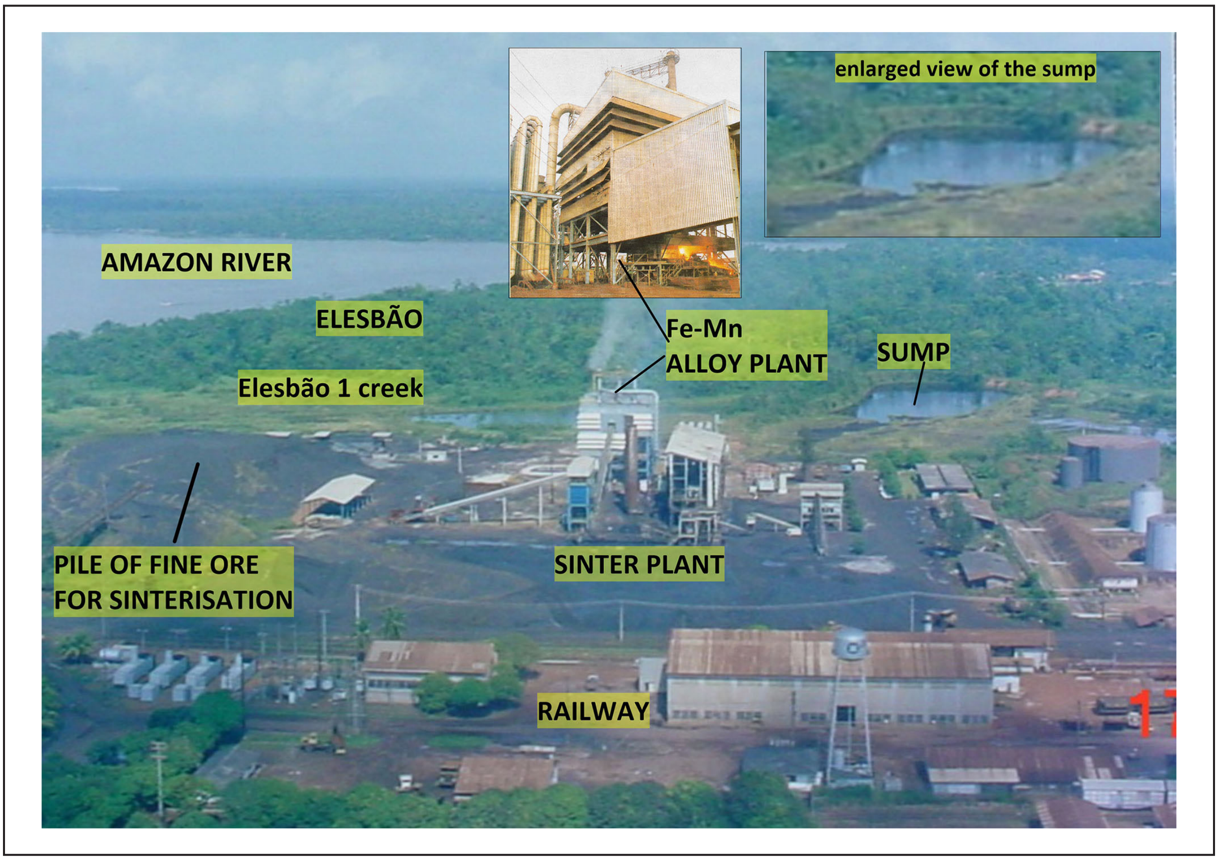

FIGURE 5. A west looking view of the Sinter and the Metallurgical Plants in operation. The sump appears at the upper right and the Elesbão 1 Creek at the left. It includes a view of the alloy plant from west and an enlarged view of the sump.

and iron, and poorer in oxygen, as MnO, Mn_3O_4, Fe_3O_4, and $(Mn,Fe)_3O_4$. The last two, containing iron, represent the magnetic minerals magnetite and jacobsite. To reduce the iron content of the mass, increasing its grade on manganese, the roasted material was milled, and more magnetic grains were removed with a magnetic separator, and discarded as tailings. The resulting mass of iron-poorer and manganese-richer particles was agglomerated to the pellet size in a rotating disc and was hardened by heating (Castro 2022). In contrast with the 30-35% Mn grade of the ore fines fed to the plant, the produced pellets assayed around 54% Mn, 7% Fe and 0.10% As, while the rejected magnetic tailings assayed around 38.5% Mn, 19.5% Fe, 7.0% SiO_2, 7.0% Al_2O_3, and 0.19% As (Laranjeira 2000). It is interesting to note that the grades of iron and arsenic of the tailings were about double those of the pellets, in another demonstration of the preferred association between these two elements.

During the production of sinter, the ore fines were mixed with fine-grained coke and a flux, and heated to ignition (Castro 2022). The resulting hot and reducing atmosphere provoked a partial reduction of the ores, which aggregates naturally into coarse and hard grains assaying 45-46% Mn and 7-8.6% Fe (Laranjeira 2000). There were no tailings in this process.

To obtain the desired high-quality of the Ferro-Manganese alloy, the installed reducing furnace operated at a 12.4 MWA capacity (Castro 2022), and fused a mixture of the sinter with manganese oxide ore assaying 40-45% Mn and carbonate ore assaying 32% Mn. As reducers, it used a mix of coke and charcoal produced in a private industrial forest. This plant also did not produce tailings.

4.4. The sump, the tailings of the pellet plant, and arsenic

To guarantee a permanent supply of water to the plant, an old sump (a shallow excavation, exposing groundwater used for industrial purposes), existing at the north of the creek Elesbão 1, was enlarged to hold about 200,000 cubic meters of water. Built in weathered clayey and siltic sediments of the Barreiras Formation (Lima et al. 1974), it had an upwards open concave bottom, occupied less than 25,000 square meters, and reached about 10 meters of depth. Its walls were not waterproof and it was naturally filled with groundwater of the phreatic level. A small wide and low rim, made of compacted soil, was built at its north, south and west areas, to avoid the entrance of running water with mud (a view of the sump and its rim in Fig. 5).

During its entire life, the upper surface of the stored water represented the upper surface of the groundwater, and never raised to the sump surface. Consequently, the stored water never overflowed the margins of the sump, exactly the opposite of what inexplicably wrote Pereira et al. (2009), Batista (2015), and others, that mentioned a “rupture of the tailings containment dam”.

From 1971 to 1983, the sump received the tailings of the pellet plant, that is, the discarded magnetic minerals formed during the roasting of the oxide ore fines, and, occasionally, badly-formed pellets. These particles were disposed in the deeper parts of the sump, where they stayed without exposition to the surface air.

A study of samples of these particles revealed minerals such as hausmannite (Mn_3O_4), bixbyite ($(Mn,Fe)_2O_3$), rhodonite ($(Mn,Fe)SiO_3$), tephroite (Mn_2SiO_4), jacobsite ($(Mn,Fe)_3O_4$), and quartz (SiO_2), followed by smaller quantities of pyrochroite ($Mn(OH)_2$), and hematite (Fe_2O_3) (JPE 2000b). The samples averaged 0.15% As.

The majority of these minerals did not occur in the natural ores, and a few, such as rhodonite and tephroite, appeared as constituents of the fresh queluzites, that gave origin to the supergene oxide ores of Serra do Navio. In the sump, in contact with water at the normal acid pH of the groundwater, they became unstable and started to weather, and, replicating what occurred during weathering in Serra do Navio, iron, manganese, arsenic and other elements started to be liberated. That dissolution was not immediate, like that of salt, but progressed slowly, acting first at the fresh surface of the grains, gradually progressing inwards.

As the sump water was connected with the phreatic level, the dissolved elements entered the groundwater, and slowly dispersed away of the sump. Fortunately, the velocity of the groundwater flux was very slow, conditioned by the low permeability of the argillaceous soil.

Regarding iron, as it happens when it is solubilized in the organic-rich soils of the Amazon Forest, it took the form of a gel, a form which has a strong capacity to retain other elements, such as arsenic, nickel and cobalt. The typical iron-rich gel gives to the pregnant water a turbid form and a yellowish color, and, obviously, had a very low velocity of lateral flow in the clayey soil. The gel moved very slowly through the argillaceous soil, and started to consolidate very soon, forming concretions of limonite, typical of the lateritic soil. The arsenic, nickel, cobalt and other metals present in the gel were retained and fixed in the internal structure of the concretions of limonite, in the same way as it happens with the Serra do Navio oxide ores and, as a consequence, drastically reducing the grade, in solution, of arsenic and the other associated elements.

4.5. Destination of the tailings of the pellet plant

Deposited at the north of the Industrial Area (Fig. 4), the tailings were covered with thick and impermeable sheets of black plastic, to protect them from rainwater. Unfortunately, these sheets did not resist much, as invaders of the property climbed and walked over the pile, tearing the plastic (Fig. 6), allegedly looking to get some infection due to arsenic, possibly to justify a quest for financial compensation. To protect the pile from invaders, and vice-versa, a post of permanent vigilance, 24 hours per day, was established next to the pile (Scarpelli 2003).

In 2001, five samples of the tailings were submitted to the CETEM (Centro de Tecnologia Mineral – Center of Mineral Technology), for determination of toxicity according to the standards NBR-10.004, 10.005, and 10.006. All of the samples presented concentrations lower than 0.65 mg/L in the leaching tests, and slightly greater than 0.5 mg/L in the solubilization tests, allowing to conclude that the samples contained arsenic in a non-inert form, not toxic for handling and transporting with caution (Ehrlich and Castro 2001).

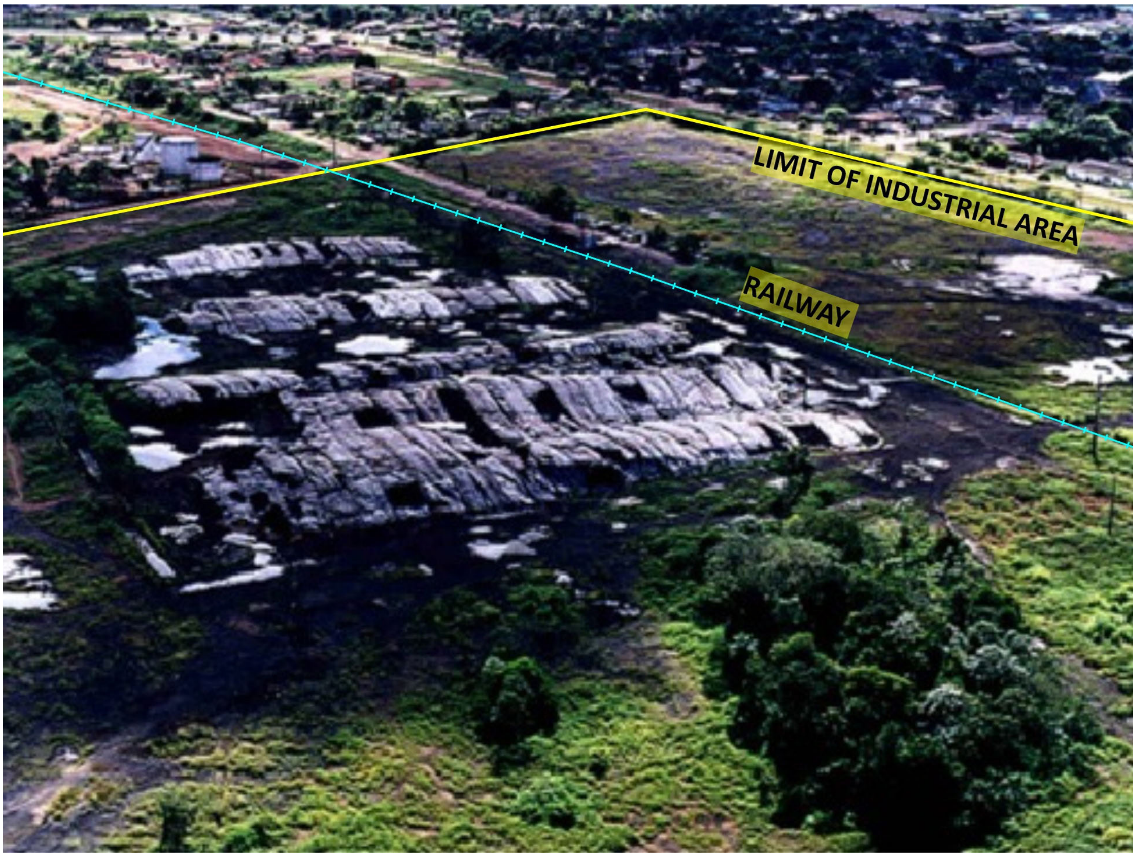

FIGURE 6. The pile of tailings removed from the sump was temporarily stockpiled at the north of the Industrial Area and covered by resistant plastic sheets. This photo of 1998-1999 shows the plastic cover partially dismantled and teared, due to invaders that climbed the pile.

Following the former recommendations of JPE Engenharia (JPE 1998b), and with the approval of SEMA, ICOMI programmed the neutralization of the tailings according to the ABNT standards NBR 10.004, NBR 8.418, NBR 10.157, and NBR 9.690, which specify how to dispose of toxic materials in covered landfills, made impermeable from below, above, and the sides by thick and special sheets of plastic, a cover with soil and a border with concrete ditches to divert rainwater, and other measures. In 2002, ICOMI contracted ERM Brasil Ltda. to perform this work and to review the results of the environmental studies.

After an early attempt to do it in Serra do Navio, the company chose an isolated and topographically high area near the Kilometer 34 of the Amapá Railway. Several wide excavations were opened there, of about 6 meters deep each. Their bottom and walls were filled and coated with a layer of clean sand and covered with the recommended thick and impermeable sheets of plastic. Unfortunately, soon after the plastic sheets had been properly set, people living far away from the site invaded the property and tore the plastic cover (Fig. 7). Anticipating other acts of vandalism, the work there was interrupted (Pereira 2004).

Facing these difficulties, ICOMI and SEMA gave up measures to isolate the tailings, which were sold to an interested merchant, who took them away by the sea, together with ore materials that formed the base of ore piles, and other remaining accumulations of oxide ore in the Industrial Area. There were 3 shipments, totaling 114,800 tonnes, done from the end of October 2003 to February 2004 (AMPLA Engenharia 2004).

FIGURE 7. Large excavations were opened near KM-34 of the railway to deposit the tailings, following all procedures indicated by the technical norms for the isolation of toxic solid materials. The preparation of the area was abandoned after the invasion and destruction of the first cover of the thick and impermeable plastic sheet.

5. Environmental study of the industrial area of Santana

In 1987, to justify the investments in the pellet plant, the federal government authorized ICOMI to obtain full control over the Industrial Area of Santana, and keep the domain over its installations after the end of the concession. In 1993, anticipating the exhaustion of the reserves of manganese ores, ICOMI considered the transference of these rights to Amapá Florestal e Celulose S.A. – AMCEL (Costa 1998). That transference would be very important to AMCEL, to improve its operations and exportations, and to the Amapá State, alleviating the public port of Santana.

To support the deal, ICOMI, in agreement with SEMA, conducted an environmental study of the Industrial Area, with the compromise to take the necessary measures to remove or neutralize eventual environmental problems. JPE Engenharia Ltda. (JPE) was contracted to carry out the study.

Most of the work of JPE was the opening and monitoring of 38 monitoring boreholes, 35 in the Industrial Area and 3 in an adjacent area of Elesbão. They were opened to a few meters into the groundwater, which was monthly examined and sampled, with a register of its color, cleanness, pH, temperature, electrical conductivity, etc. The samples of water were assayed for several chemical elements and compounds, many of them organic. This paper is limited to reviewing the situation of arsenic. To protect the water from contamination from above, the boreholes were maintained sealed between each observation and sampling.

The JPE monitoring work was done during 1997 and 1998, resulting in a report indicating (1) a higher content of iron and manganese in the areas where the ore was stockpiled and/or manipulated, (2) higher values of arsenic in the groundwater near the sump, and (3) higher content of organic materials in some of the industrial areas, where oils and combustibles were used. As soon as it received the report, ICOMI handed a copy to SAMA (Costa 1998), together with a program to intensify the study and define the actions to recover the affected areas (JPE 1998a). ICOMI retained JPE for this new work. Later, in 2001, the government of Amapá, based on arsenic contamination issued a financial sanction to ICOMI, that was not paid, since the contamination was eliminated.

5.1. Arsenic in the groundwater

The installation of the boreholes and the beginning of their monitoring occurred in 1997, two years after the cessation of the metallurgical plants activities. In the first sampling, done in June of 1997, four boreholes showed quite high values of arsenic, reaching 0.91, 2.19, 6.15, and 17.8 mg/L, quite higher than the maximum at the time allowed for potable water, that was 0.05 mg/L. As shown with Figure 8, all of these four boreholes were situated at less than 100 meters of the sump. All the other boreholes presented values below 0.05 mg/L, which was the limit of analytical detection at the time, with the exception of one near the Amazon River and the

Elesbão 1 creek, which presented a value of 0.06 mg/L, slightly above the limit of drinkability.

At the beginning of 1998, in a close review of the data collected by JPE, this author verified that the water of the four arsenic-rich boreholes was described as being yellowish and with waves of turbidity, a clear indication of iron associated with organic compounds, in a colloidal, or gelatinous, form. All the other boreholes were described as showing transparent and clear water.

Considering what was known in the mine about the arsenic-bearing colloidal iron, it was immediately considered that these colloids would not migrate easily through the clayey soil, in which they would be trapped, with the iron being precipitated as limonite, retaining the arsenic with it.

During 1998, when this idea became clear, ICOMI gradually opened a small channel to the south of the sump, allowing its water to flow in a controlled way to the Amazon River, via the Elesbão 1 creek. As this water was not sampled, it is difficult to say how much arsenic was liberated to the Amazon River with it. If a number is necessary, we might consider that if the liberated water reached 170,000 cubic meters (excluding the volume of the solids), and had 12.0 mg/l (average of the two highest values in the boreholes), the total of arsenic liberated to the Amazon would be of the order of 2 tons.

With the water removal, at the bottom of the sump, the remnants of pellets appeared as a mass "with a continuous and somewhat hardened and resistant cap, below which the solid grains were soaked in soft colloidal mass rich in water" (Rebouças 1998). The material, estimated to reach 50,000 cubic meters, was removed from the sump and stockpiled on dry land (Fig. 4).

The immediate result of these measures was *a* drop in the arsenic content of the groundwater near the sump, as shown by a comparison between the arsenic contents of the samples taken in June of 1997 and July of 2001 (Fig. 9). The borehole that in 1997 presented 17.8 mg/L, in 2001 showed 0.24 mg/L, that with 6.15 mg/L turned 0.142 mg/L, that with 2.19 mg/l turned 0.008 mg/L, and that with 0.91 mg/L turned below 0.002 mg/L. In contrast, one borehole near the rim of the sump, close to the opened channel, appeared with 1.22 mg/L, against less than 0.05 mg/L in 1997. Other two boreholes presented increases in the arsenic content: one at the south of the sump and near the channel, with 1.2 mg/L, and one at the north near the site where the pellets were stockpiled, with 0.025 mg/L (JPE 2000a, 2001). None of the other boreholes presented an increase in arsenic content, a demonstration that, actually, the arsenic did not spread out from the immediacies of the sump.

In 2001, ICOMI contracted AMPLA Engenharia, Assessoria, Meio Ambiente e Planejamento to continue with the boreholes monitoring. The sampling done in February of 2002 revealed an almost complete absence of values above the improved detection limit for arsenic, then of 0.002 mg/L (Fig. 8), with the only exception being a value of 0.03 mg/L near where the main stockpiles of manganese ores were maintained at the port area. Even so, this value is quite smaller than the accepted for an industrial effluent, which is 0.50 mg/L.

Those values of the arsenic in the groundwater indicate that it did not move significantly downslope and its concentration decreased as time went by, not with the distance, clearly retained in the clayey soil of the area. Being associated with colloidal iron, very possibly it precipitated with the iron in

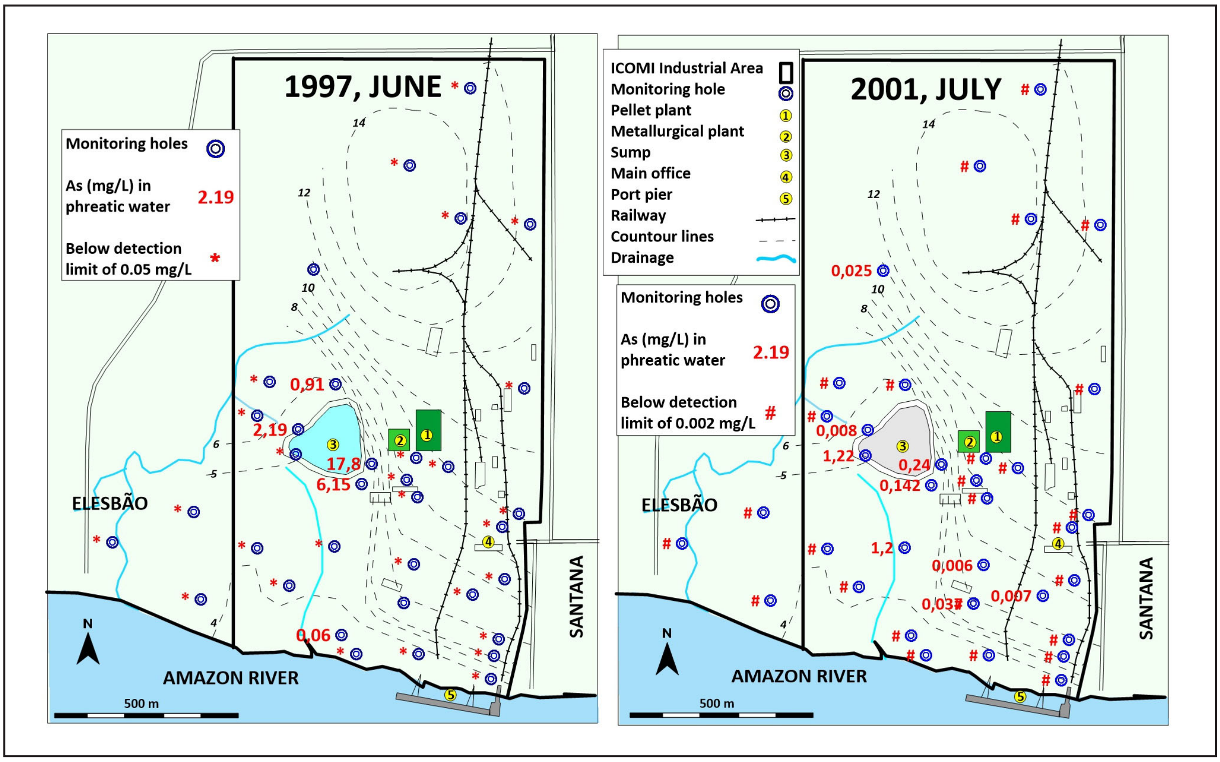

FIGURE 8. Arsenic grades in monitoring holes of the groundwater, as related by JPE in the months of June of 1997 and July of 2001. In 1997, high values of arsenic, reaching 0.91, 2.19, 17.8 and 6.15 mg/L appeared near the sump, while the samples of the other holes revealed values below the detection limit of 0.05 mg/L, with the exception of one hole with 0.06 mg/L near the margin of the Amazon River. In July of 2001, three years after the cleaning and filling of the sump, the greater values were of 1.22, 1.20, 1.02, and 0.24 mg/L, still near the former sump. At the north, a value of 0.025 mg/L was observed near the site where the tailings taken from the sump were stockpiled in 1998 (Fig. 4).

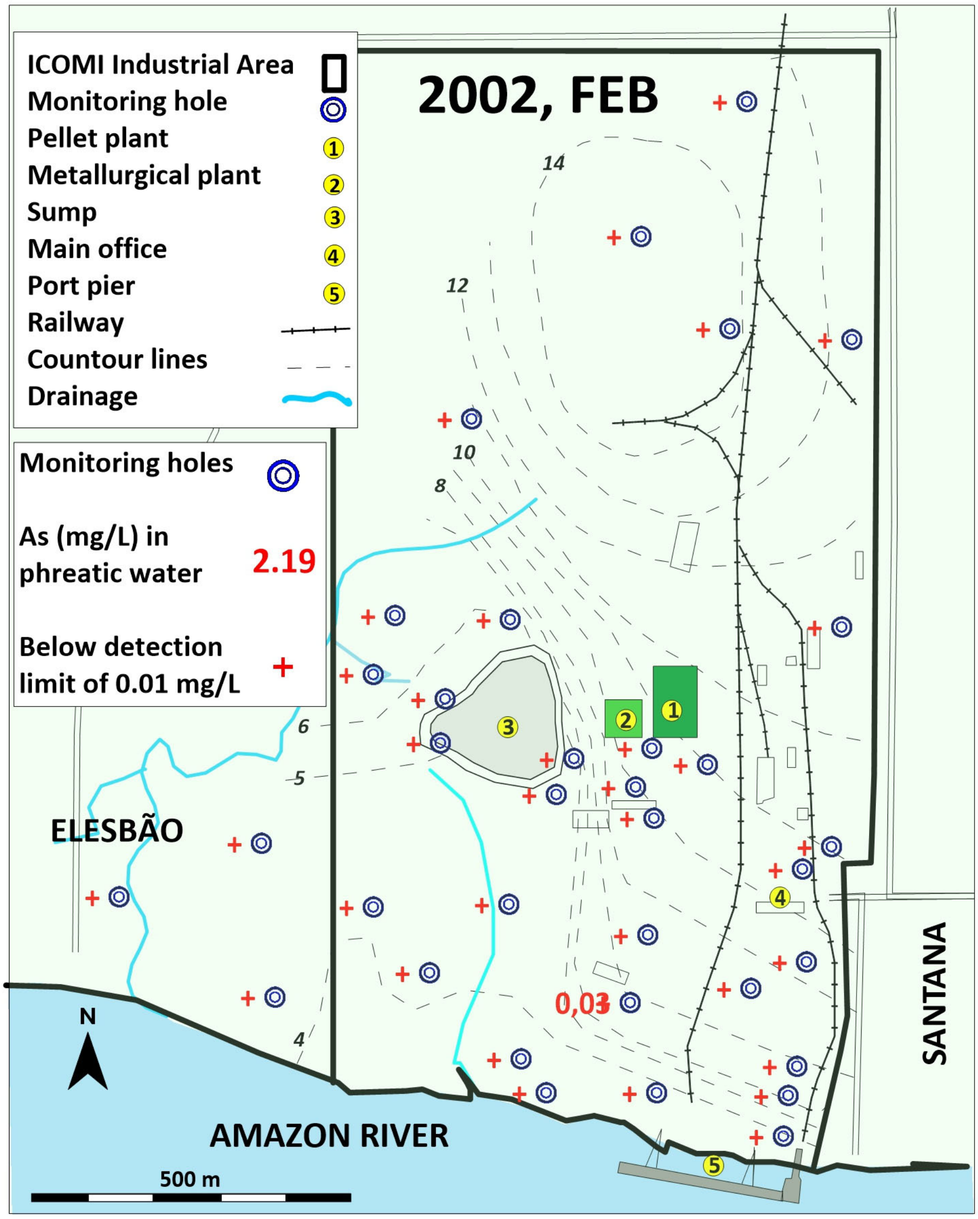

FIGURE 9. Water samples taken by ERM in February of 2002 showed that the high values of arsenic in the groundwater disappeared completely, inclusive in the sump area, with exception of one sample with 0.03 mg/L, at the south of the former sump.

concretions of manganese limonite, similar to that shown in Figure 3. Being so, it is quite acceptable that the anticipated down flow of the arsenic in the groundwater towards the Amazon River did not happen (Scarpelli 2003).

Values of <0.002 mg/L As in the groundwater were also obtained from samples of 6 private wells outside of the Industrial Area, opened by inhabitants to get potable water, 4 of which in the town of Santana and 2 in the community of Elesbão (Scarpelli 2003).

5.2. Arsenic in stream sediments

The Elesbão 1 and Elesbão 2 creeks drain the Industrial Area of ICOMI, both in its western side (Fig. 4). The shorter, Elesbão 1, is totally contained inside the Industrial Area. Its headwater is just south of the sump, and flows southwards, to the Amazon River. Two sample sites were chosen for this creek, one near the sump, and the other near the Amazon. In 1997 they presented, respectively, 0.57 and <0.05 mg/L and, in 2000, 0.117 and 0.82 mg/L, indicating a contamination with As (JPE 2000a). It seems reasonable to consider that the values of year 2000 were influenced by the use of this drainage for the discharge of waters of the sump towards the Amazon.

Elesbão 2 has its headwater north of the sump and flows southwestwards, reaching and crossing the community of Elesbão. It was sampled in 5 sites. In 1997, one value of 1.17 mg/L was obtained in one sample on the limit of the Industrial Area, and all the other samples, one upstream and 3 downstream, revealed 0.05 and 0.06 mg/L. The last sampling of ICOMI on these sites, done by ERM in August of 2002, presented values varying from 0.024 and 0.029 mg/L As at the border zone with the Industrial Area, followed downstream with two values of 0.002 mg/L, and, at the margin with the Amazon, 0.18% mg/L As (Pereira 2004), possibly influenced by the river.

Lima (2003) reports samplings done in December of 2000 and May of 2002, covering the Industrial Area and Elesbão, extended to the Matapi River, which discharges into the Amazon River at 1.5 km to the west of the Industrial Area. The work indicated the widespread appearance of values from 0.005 to 0.030 μg/L As in the area west of the Industrial Area, inclusive in the Amazon River itself. The distribution of the values seems to be a natural feature, regardless of the Industrial Area (Fig. 10). In the Industrial Area, higher values were seen near the sump (4,054 μg/L As in 2000, and 873 and 721 μg/L As in 2002) and the near the pile of tailings (695 and 926 μg/L As in 2002). All the other values observed are lower than the maximum specified for an industrial effluent, which is 500 μg/L (Table 1). It is quite probable that as time went by and the removal of these piles the values dropped to below the acceptable levels for industrial effluents.

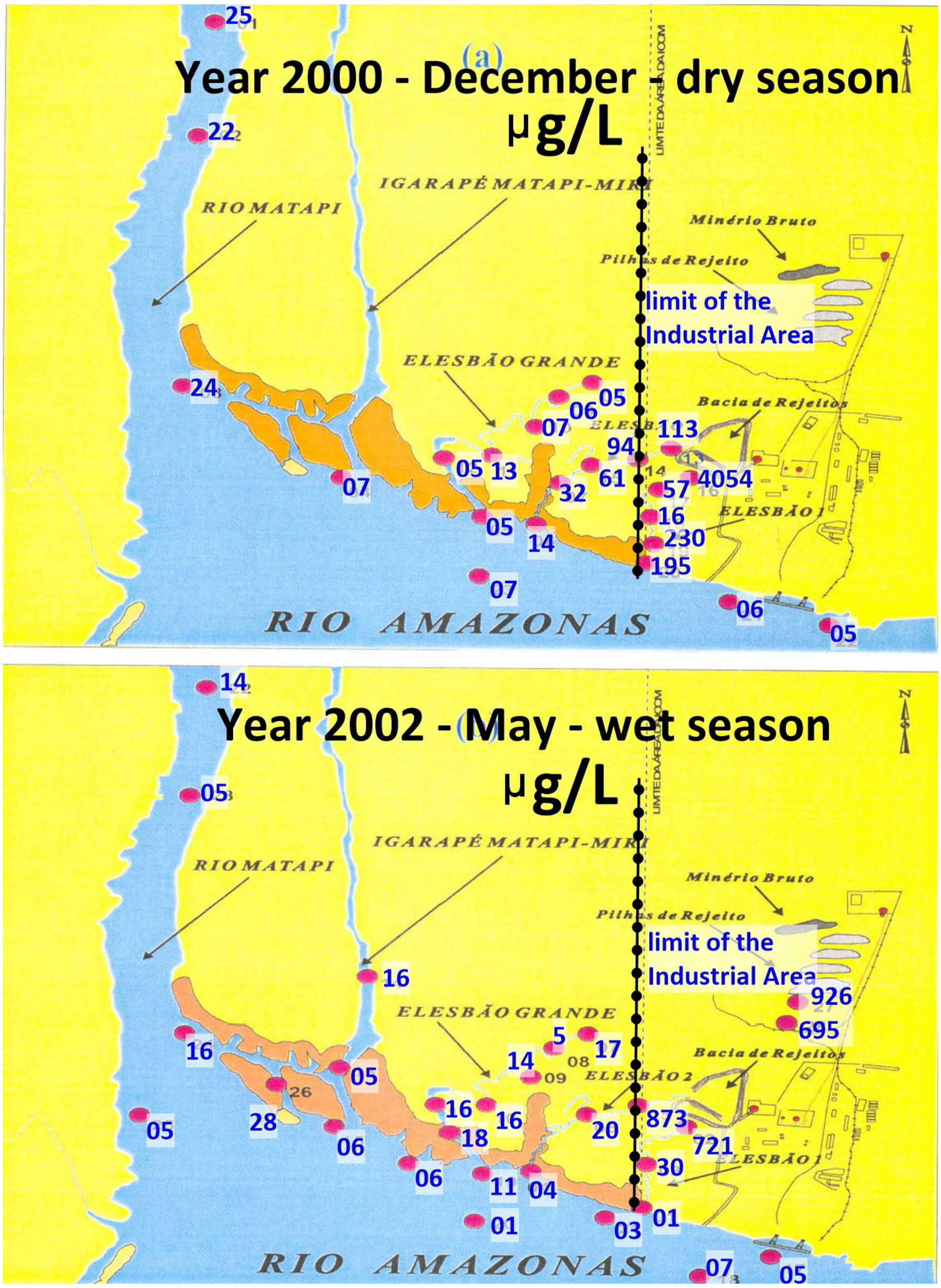

FIGURE 10. Copy of maps presented by Lima (2003) with results of arsenic in surface waters in December of 2000 and May of 2002. It confirms the high values near the sump, and their reduction with time. They show a wide distribution of significant values of arsenic to the west, in the community of Elesbão and in the Amazon and Matapi Rivers. some of which in places outside the area of influence of the Industrial Area.

6. Preoccupation of neighbors

6.1. Arsenic in the streets of the town of Santana

For many years ICOMI maintained in the Industrial Area a quantity of beneficiated oxide ores of low-grades (32 to 42% Mn), to attend the eventual consumers, to form the base of piles of higher-grade ores, and the pavement of working areas of heavy equipment. In 1997, the administration of the town of Santana asked ICOMI if the company could dispose of some quantity of this material to be mixed with asphalt in the paving of the streets of the town. In attention to the request, ICOMI supplied about 16,000 tonnes of a mixture of low-grade oxide ores, together with other materials that during the years have been placed in their piles. This supply of material was interrupted when it was observed that the municipality was using the material for direct pavement of streets, without the mixture with asphalt. Later, when the question of arsenic contamination near the sump was raised, the municipality of Santana and some inhabitants of these streets got themselves preoccupied with contamination by arsenic.

To help understand the situation in the streets of Santana, ICOMI took controlled drill core samples of the coated streets (following procedures indicated by ABNT norm NBR-10,007) and sent the samples to Lakefield-Geosol for solubilization and leaching tests. The sample description revealed that the majority were not homogeneous, containing, besides the oxide ore, fragments of different origins, including fragments of metals, slags and pellets (Table 5). Some samples contained grains of carbonate ores and a few presented soil and white clays, indicating a mixture with local materials. Their composition suggests that leftovers of old bases of ore piles, inclusive of the pellet and steel alloy plants, were included in the donated material. If this material had been mixed with asphalt, as initially considered, the situation would be acceptable, but that was not the case.

The tests indicated greater liberation of arsenic in the solubilization tests, done under pH 7, than in the leaching, and under pH 5. According to standard NBR-10004/2004, the tests indicate that none of the sampled material is toxic, as all presented less than 1.0 mg/L in the Leaching Tests. According to the standard, all the tested samples indicated non-inert materials, with the possible exception of that of Santana Avenue, with 0.01 mg/L in the solubilization, possibly indicating inertness (Scarpelli 2005).

Although the combined results of the Leaching and Solubilization tests of the sample of the Rio Branco Avenue indicate non-inertness, the high value of 1.80 mg/L obtained in the Solubility test suggests that it is adequate to accept some degree of toxicity to the sampled material. Considering that this test is done under a pH of 7.0, similar to that of rainwater, some arsenic is liberated if the area is covered by a standing blanket of rainwater for a period or hours or days. This street should be looked at with attention.

Pereira et al. (2009) described a spectrophotometric technique to determine the content of arsenic in the soil, using it to determine the presence of arsenic in Santana streets where the low-grade ore of manganese was used to pave the roads. They observed that the arsenic content varied from 0.048% to 0.171%, averaging 0.068% of the material assayed. These values actually are lower than the arsenic grade of the low-grade ore of manganese, suggesting a mixture with local soil. Comparing the two sets of assays, the arsenic values obtained by ICOMI in the 14 drilled areas were greater than those obtained by Pereira et al. 2009, varying from 0.0116 to 0.1937% As, with an average of 0.1215%.

6.2. Complaints of the community of Elesbão

Soon after the public disclosure of the arsenic contamination near the sump, representatives of inhabitants of the community of Elesbão, adjacent to the west, and downwind from of the Industrial Area, started to present complaints of diseases caused by arsenic. Most of the community is located at the margin of the Amazon River, with a few of the inhabitants living in stilt houses over the river. While some obtain water

TABLE 5. Tests done by ICOMI in the streets covered with material given by the company to the municipality to be mixed with asphalt for the pavement of streets. Based on tables of Scarpelli (2003), with description of the core samples and results of the tests.

Street/Avenue	Summary of sample description	As ppm	Mn %	Fe %	SiO_2 %	Leaching As mg/L	Solubilization As mg/L	Toxicity NBR 10,004 of 2004
Rio Branco	Fine-grain oxide ore, laterite, frags iron alloy	1,111	37.0	9.9	12.3	0.80	1.80	non-inert ?
1ª Avenida	Fine-grained oxide ore, frag pellets	1,785	40.7	14.8	5.8	0.12	0.48	non-inert
Brasília	Fine-grained oxide ore; frags slag	0,935	32.7	8.9	16.3	0.04	0.42	non-inert
Brasília	Fine-grained oxide ore; frags slag	0,339	26.6	3.5	25.7	0.03	0.40	non-inert
D. Pedro	Soil, oxide ore, fragments of carbonate ore	1,398	38.1	9.3	8.9	0.02	0.37	non-inert
Nações	Fine-grain oxide ore, fragments of pellets	1,566	32.1	18.0	10.5	0.04	0.35	non-inert
Salvador Diniz	Fine-grained oxide ore	1,996	42.3	13.9	6.0	0.06	0.31	non-inert
Rui Barbosa	Fine-grained oxide ore	1,777	37.5	13.4	11.2	0.07	0.29	non-inert
Coelho Neto	Earth, oxide ores, white clays, frags slag	0,291	23.4	3.3	29.7	0.01	0.24	non-inert
Machado Assis	Fine-grain oxide ore, few small pellets	1,937	39.9	16.5	5.4	0.08	0.23	non-inert
Coelho Neto	Earth, oxide ores, white clays, frags slag	0,116	17.2	1.7	35.6	0.01	0.19	non-inert
Machado Assis	Soil, fine-gr oxide ore, carbonate ore, frags slag	1,305	39.9	9.1	8.3	0.02	0.17	non-inert
D. Pedro	Oxide ore, carbonatic ore, frag slag	0,766	23.3	9.3	24.8	0.01	0.02	non-inert
Santana	Oxide ore, of medium to coarse size	1,684	41.8	7.7	6.7	0.01	0.01	inert

from wells, most of them use water from the Amazon River, with or without filtering and chemical treatment, for drinking, cooking, and hygienic needs (Santos et al. 2002, 2003). Overall, the conditions of sanitation are precarious, and these people need help. A part of the area is traversed by the creek Elesbão 2, which has its headwater in the Industrial Area, at the north of the sump. Several of the complainers said that they drank water from the Elesbão 2, but this does not seem logical, since the creek water lies practically at the same level as the Amazon River, where it debouches. This creek water flows very slowly, almost stagnant, with a muddy appearance, locally with a bad odor.

Further to the west, there is the larger creek, Elesbão Grande, not reaching the Industrial Area.

During 2003 and 2004, a sampling was made of the water actually consumed by the inhabitants of Elesbão (Lima et al. 2007). They were taken from 52 sites, and divided into three groups: (1) water from private shafts and local treatment, (2) water from the Amazon River, collected and treated by public service (CAESA), and (3) water taken from the Amazon River and treated by the consumer. In the three situations, the arsenic concentration in the water varied from 2 to 7 µg/L, which is lower than the 10 µg/L maximum limits accepted by the standards.

Called by the government of the Amapá state, a team of specialists of the Instituto Evandro Chagas, a high-level institution of the Health Ministry, examined the health situation of 2,045 Inhabitants of Elesbão, taking 1,927 samples of blood and 1,986 of hair for arsenic determination. In their final report (Santos et al. 2003, 183-184), they wrote (free translation): “*The arsenic levels in 1,927 samples of blood and 1,986 samples of hair, taken in the community of Elesbão, compared with the clinical examination of the sampled persons, allow us to conclude that, for the sampled persons, there is exposition (to arsenic), but without indications of intoxication. Overall, the observed averages coincide with averages of normality observed in the literature for non-exposed populations. No association was established between the clinic-laboratory observations and the content of arsenic in blood or hair*”.

It seems interesting to register that in a preliminary note, Santos E.C.O. et al., had shown one table with results of blood and hair with values slightly higher in inhabitants of the Matapi river than those obtained from Elesbão. As this river discharges in the Amazon River upstream from the Industrial Area, that observation raised the attention to “natural” high values of arsenic in the Amazon River itself (Scarpelli 2003).

6.3. Examination of arsenic in blood and in hair in the general area

Examination of arsenic in the blood is used as an indicator of arsenic absorbed during recent days or months, and arsenic in hair is used by an indicator of arsenic absorbed a longer time ago. According to the World Health Organization, values of arsenic of 1 to 5.1 µg/L and 1 to 2 µg/g are normal, respectively, for the blood and hair of persons not exposed to arsenic.

Two sampling campaigns examining arsenic in blood and hair were performed in several neighborhoods of the municipality of Santana, with the objective to identify differences that would help in the definition of the arsenic source in the examined persons. The first sampling was carried out in 2001 by the Instituto Evandro Chagas (Santos et al. 2001), for blood and hair, and the second by the LAQUANAM, a Lab. of Analytical and Environmental Chemistry, of the University of Pará, for hair (Pereira et al. 2010). The average values they obtained are shown in Figure 11.

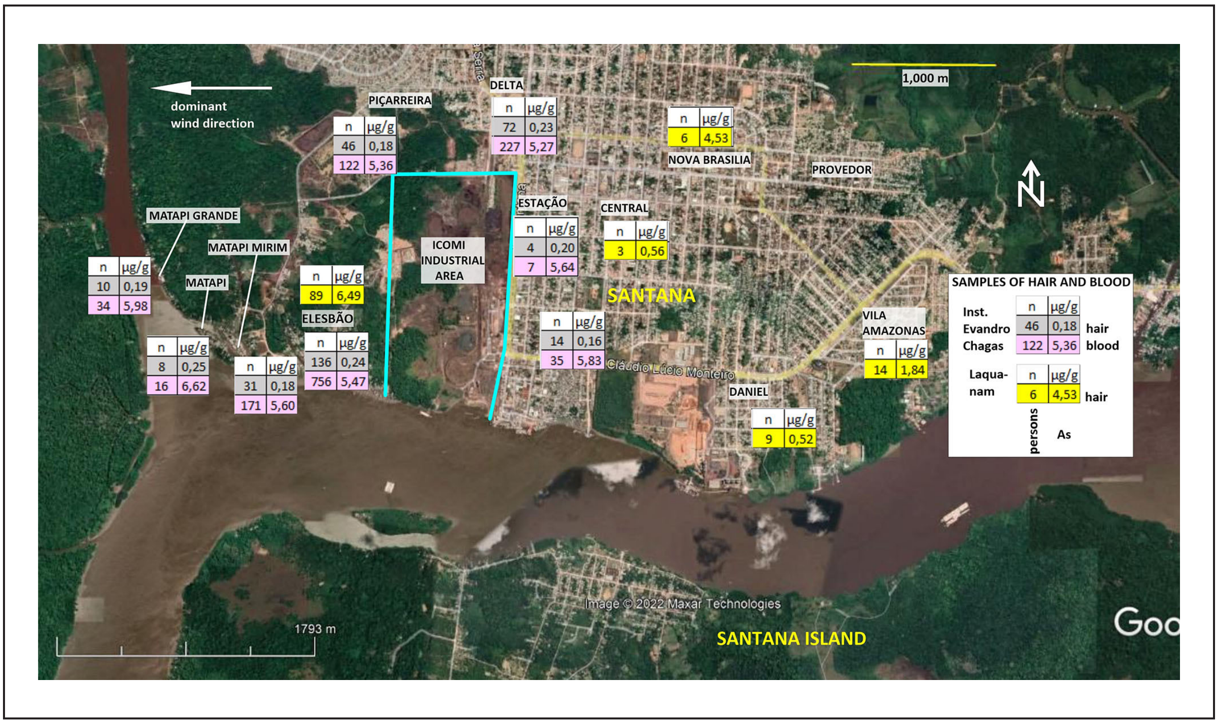

FIGURE 11. Results presented by the Inst. Evandro Chagas, for arsenic in hair and blood, and of LAQUANAM, for arsenic in hair, of inhabitants of several neighborhoods of Santana. There is not a pattern of the distribution of higher and lower values, but shows that arsenic in significative concentrations occur in all of the tested areas, possibly being related to the Amazon River. These studied did not include inhabitants of the Santana Island, situated in front of Santana.

For hair, while all the average grades obtained by Inst. Evandro Chagas in Elesbão were lower than 1 µg/g As, LAQUANAM observed average grades greater than 1 µg/g in Elesbão, and also in Nova Brasília and Vila Amazonas, the latter two sites at the east of the ICOMI Industrial Area. Pereira et al. (2010), called the attention that the groups living near the center of town presented lower values of arsenic.

For blood, the averages obtained by Inst. Evandro Chagas in eight areas of Elesbão, were close to 6 µg/L As, varying from 5,36 to 6,62 µg/L As, with the highest values appearing in individuals living closer to the Amazon River. Due to the small period of persistence of arsenic in blood, these concentrations of arsenic cannot be attributed to activities of ICOMI, which ceased years before the sampling.

Since the above information indicates that at least a large part of the observed arsenic seems to be related to the waters of the Amazon River, it is also important to sample blood and hair from other communities located on the banks of the Amazon River, such as the one that occupies the Santana island, located in front of Santana town, on the other side of the branch of the Amazon River (Fig. 11), and also of Macapá. Undoubtedly, this sampling could lead to actions to improve the health of the population that lives in these sites.

7. Arsenic in the Amazon River

One of the tasks of AMPLA, contracted by ICOMI in 2000, was the sampling of the water supplied to the population of the municipality of Santana. With this purpose, AMPLA sampled 5 private water wells, 4 in the east of the Industrial Area and 1 in Elesbão, plus in 4 points of the Amazon River from where water was being taken for treatment and human consumption. This sampling revealed that the grades of arsenic in the Amazon River were greater than in the 5 water wells (Scarpelli 2003).

One of the workings done by LAQUANAM for the government of Amapá was the sampling and analysis of arsenic in the waters of the Amazon, downstream from Santana, and, possibly for comparison, also in the Pará Rivers, near Belém, capital of the state of Pará. The results of the work revealed that both rivers are carriers of arsenic in solution, with 3 to 16 mg/m^3 (or µg/L) (Pereira et al. 2011; Pereira 2018) (Fig. 12). This work is quite remarkable, as it made public, for the first time, the presence of high values of arsenic in the two rivers, with increases of the grades towards the Atlantic Ocean. The number are impressive: The obtained grades, applied over the sampled areas of the two rivers would represent more than 40 tonnes of arsenic per vertical meter of water (Scarpelli 2005). That high tonnage and the similarity of

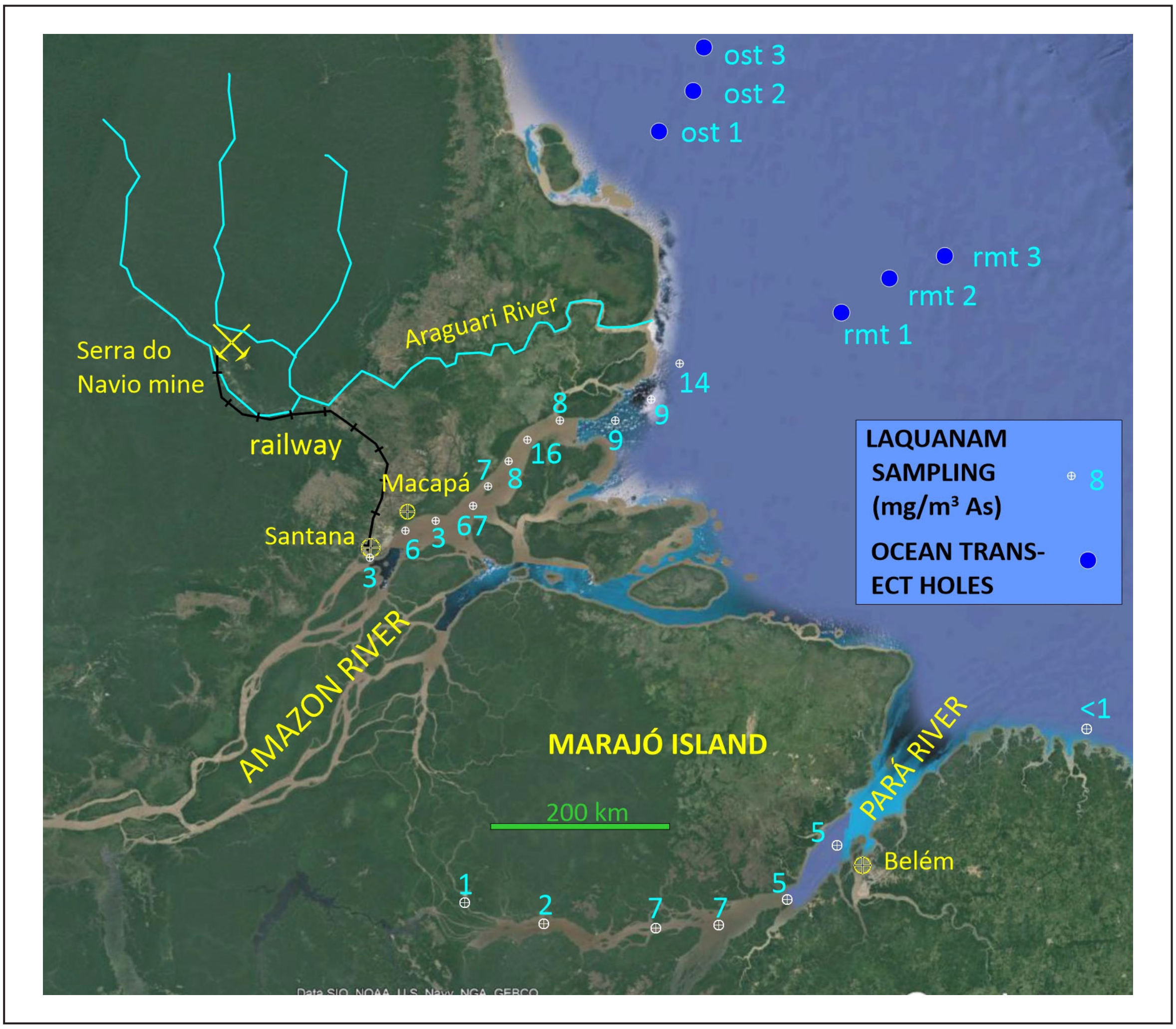

FIGURE 12. The first sampling of the Amazon River water for arsenic, done by LAQUANAM (Pereira 2000), revealed the significant presence of the element in the river, with values becoming greater in the delta of the river. The same set of results was found for the Pará River at the south, which receives water from the Amazon via several natural fluvial channels. Holes of the Ocean Transect Holes, mentioned in this paper, are marked in the figure.

results in both rivers eliminates the chance that the source of this arsenic was the Santana contamination event.

Considering the indications, a high effort was undertaken by this author in the search for information regarding arsenic in the waters of the Amazon River (Fig. 13). The best one found so far is in the tables by Seyler and Boaventura (2001), presenting the results of samples of water and suspended solids collected by the HYBAM Project (Hydrology of the Amazonian Basin), which was supported by Brazilian and French governmental institutions. The tables present, for the most important rivers of the basin, measurements of the flux of water and analytical results of samples of the water and of the sediments being transported (Scarpelli 2005).

The flux of water of the Amazon in Óbidos, Pará, was estimated to be of the order of 160,000 m^3/second, carrying 715,000,000 tonnes/year of sediments (Filizola and Guyot 2011), of which 65% from the Solimões River, 32% of the Madeira River, with only 3% of coming from the crystalline shield (Seyler and Boaventura 2001). Considering the reported grades obtained in Óbidos, of 7 mg/L of arsenic in solution and 2.8 mg/m^3 of arsenic in the transported solids (Seyler and Boaventura 2001), it is possible to see that, per year, the river might be transporting something like 35,000 tonnes of arsenic in solution and 200,000 tonnes in the solids.

A substantial volume of sediment does not reach the ocean, staying at the margins of the rivers, forming alluvial deposits containing arsenic. The famous mixings of brownish and silt water with darker and clean waters, which are points of touristic attractions of Manaus and Santarém, are just mixtures of arsenic-free waters with silt-clayey and arsenic-rich waters (Scarpelli 2005).

Near Iquitos and Pucalpa, in Peru, in the Ucayali River, a tributary of the Solimões, Meyer et al. 2017, examined a column of alluvial sediment, identifying four aquifers interlayered with impermeable layers. She found arsenic in all aquifers, with high values in two, whose water samples presented median values of 35 and 27 µg/L, well above the limits of drinkability; a value of 715 µg/L was seen in one of the water samples. In Madre de Dios, also in Peru, an affluent of the Madeira is intensely worked for gold by *garimpeiros* (artisanal gold miners), which are leaving back a large area clean of forest and the rivers full of mud, and possibly arsenic as well.

The situation of the Amazon, receiving an arsenical load of sediment from the Andes, seems similar to that of the Brahamaputra River, in Bangladesh, which receives a load of arsenical sediment from the Himalayas. That being the case, we should take in consideration the millions of cases of cancer due to arsenic in those persons that live in the floodplains of the Brahamaputra (Chowdhury et al. 2000).

7.1. Arsenic in the Amazon delta and fan areas

It seems important to consider that the arsenic grade of the Amazon waters increases in its delta, particularly in the

FIGURE 13. Presents a summary of figures from Scarpelli (2005) showing the arsenic being transported in the Amazon, presenting, for each sampled location, the values of arsenic in solution and in suspension, in mg/m3. It is quite clear that the major sources of the arsenic in the basin are the Madeira and the Solimões Rivers, bringing, from the foothills of the Andes, the arsenic, together with a high load of arsenic-bearing clay-silt sediment that gives to the water the typical brownish color (Scarpelli 2005).

fan area, where the shallow sediments are affected by marine currents. These sediments are described in papers of the *Ocean Drilling Program (ODP)* of the Amazon Delta (Scarpelli 2005). Supporting the observation of Gibbs (1967), that most of the transported sediment came from the Andes, a comparison of isotopes of lead and neodymium of Andean rocks and of fresh crystals of feldspars of the sediments led to the same conclusion (McDaniel et al. 1997; Nanayama 1997). Sullivan and Aller (1996), studying holes OST 1, 2 and 3, and RMT 1, 2 and 3 (see location in Fig. 12), inform that due to burial and the action of the salty ocean water, the iron oxides and hydroxides of the sediments were diagenetically replaced by sulfides, phosphates and carbonates of iron, liberating the arsenic in a free-form to the pore water of the sedimentary column, with the greater concentrations, varying from 2.0 to 4.0 μM/g As occurring between the depth of 0.5 to 2.5 m, dropping down below 3.0 m. They also observed that this arsenic is liberated to the overlying seawater when the sediments are disturbed by waves or marine currents (Scarpelli 2005), which seems to be the reason to explain the increase in arsenic in the waters of the delta and fan of the Amazon River.

8. Conclusion

The arsenic event in the Industrial Area of ICOMI, caused by technical neglect, was limited to the interior of that area and was corrected as soon as it became possible. Although some persons might be affected by the liberated arsenic, no one was identified yet, albeit the great work done to find someone. At this moment, attention should be maintained on some streets of Santana, such as Rio Branco Avenue, where the newly adopted values of standard NBR-10.004, updated in 2004, indicated non-inertness for the majority of the material used to pave the streets.

This arsenic event had a positive value as it exposed that the brownish waters of the Amazon Basin are carriers of arsenic in soluble and solid forms, coming down from the high Andes. All populations of the basin that obtain their drinking water from these rivers or from water holes opened in the alluvial deposit at the margins of these rivers should keep a degree of alertness for the arsenic. It might be adequate for health officials and universities to sample and analyze arsenic in the rivers, their alluvial deposits, and, also, the hair and blood of communities that drink their water. If there are health problems caused by arsenic in the water, providences might be taken to install equipment for the filtering of arsenic. For the government of Amapá, in particular, it seems adequate to do a preliminary investigative effort on Santana Island (in front of Santana) and in Macapá. Why not? The studies might be extended to arsenic in fish and other animals of the region.

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Authorship credits

Author	A	B	C	D	E	F
WS	▨	▨	▨	▨	▨	▨

A - Study design/Conceptualization **B** - Investigation/Data acquisition
C - Data Interpretation/ Validation **D** - Writing
E - Review/Editing **F** - Supervision/Project administration

Editor's note

All cited references can be obtained from the corresponding author "under request".

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