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ORIGINAL ARTICLE

Effect of disposal of aluminum recycling waste in soil and water bodies

Mirian Chieko Shinzato[1] · Raphael Hypolito[2]

Abstract This study evaluated environmental contamination by disposal of waste from tertiary aluminum industry in soil and water bodies. The main wastes of this industry are dross, non-metallic waste (product of dross leached with water) and liquid effluent. The water at the bottom of the pond, where the alkaline and saline aluminum effluent is discharged, presented high values of pH (>9) and high concentration of ammonia ($N\text{-}NH_3$). However, dross disposal in soil decreased pH (<4) of groundwater and increased concentrations of Al^{3+}, Na^+, K^+, Ba^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+}. The $N\text{-}NH_3$ produced from the reaction with water and some components of dross (aluminum nitride) probably promoted the increase of the nitrifying microbial activity in soil, which was responsible for the decrease in pH. In this condition, many components of dross were also easily leached into groundwater. The disposal of non-metallic waste into soil did not change the groundwater pH, but increased concentrations of Mn^{2+}, Ba^{2+}, Pb^{2+}, Fe^{3+} and Ni^{2+}. The disposal of aluminum recycling wastes without any treatment can change the quality of groundwater and surface waters, mainly due to high level of $N\text{-}NH_3$, which modifies the pH of these waters and is very toxic to aquatic organisms.

✉ Mirian Chieko Shinzato
    mirianshinzato@hotmail.com

    Raphael Hypolito
    rhypo@igc.usp.br

[1] Instituto de Ciências Ambientais, Química e Farmacêutica da Universidade Federal de São Paulo (UNIFESP–Campus Diadema), Rua São Nicolau, 210, Diadema, SP 09913-030, Brazil

[2] Instituto de Geociências da Universidade de São Paulo (USP), Rua do Lago, 562, São Paulo, SP 05508-80, Brazil

Introduction

Many areas in Brazil are contaminated by disposal of industrial wastes directly in the soil. This is a concern for groundwater protection, since this method is used in many cities in Brazil.

The aluminum industry is one important sector, which has increased in Brazil and is responsible for the disposal of large volumes of wastes. In the last two decades, recycling activity, one sector of this industry, has emerged as one of the largest in the world (ABAL 2014). Indeed, recycling of aluminum has become an important activity, which requires less energy and produces less waste compared to primary production. According to Tsakiridis (2012), aluminum recycling has grown consistently and in 1990, over 8 million tons of this metal had been produced from scrap, and this number was raised to 18 million tons in 2010. This author expects that around 31 million tons of aluminum will be produced from recycled scrap in 2020.

The aluminum recycling industry in Brazil consists of two sectors (Fig. 1). In the first sector (secondary aluminum industry), metal is recovered from primary aluminum dross (in addition to other aluminum scraps, like cans) by fusion and produces another kind of dross. Since this material contains aluminum, many companies (tertiary aluminum industry) recover the metal by leaching with water. In the work of Shinzato and Hypolito (2005), there is a detailed description of the Brazilian tertiary industry,
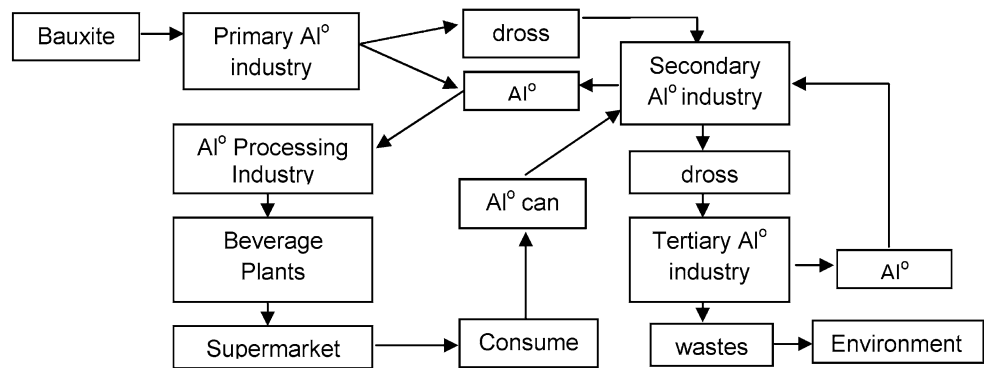
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Fig. 1 Diagram of aluminum recycling in Brazil

as well as the characterization of the wastes generated by this activity.

Since some components of dross, such as nitrides, carbides and aluminum metal, react quickly with water to form ammonia (1), methane (2) and hydrogen (3), respectively (Bruckard and Woodcock 2007), this waste is considered a hazardous material and, in many cases, is disposed of in appropriate landfills.

$$AlN_{(s)} + 3H_2O_{(l)} \leftrightarrow Al(OH)_{3(s)} + NH_{3(g)} \qquad (1)$$

$$Al_4C_{3(s)} + 12H_2O_{(l)} \leftrightarrow 4Al(OH)_{3(s)} + 3CH_{4(g)} \qquad (2)$$

$$Al_{(s)} + 3H_2O_{(l)} \leftrightarrow Al(OH)_{3(s)} + 3/2H_{2(g)} \qquad (3)$$
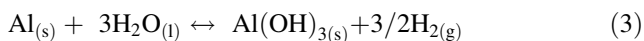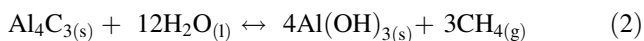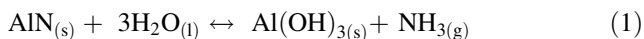
Considering that this material is very reactive and contains large amounts of water-leachable salts, it can contaminate the groundwater and air, and its disposal in landfills is not a risk-free option (Tsakiridis 2012; Stark et al. 2012). Another problem is that aluminum reactions in alkaline water are highly exothermic, increasing the temperature of the surroundings, which can consequently lead to combustion, compromising the structural stability of the components of the landfill (Calder and Stark 2010). Contrastingly, David and Kopac (2012) demonstrated that the rate of hydrogen produced from dross is similar to that generated by the hydrolysis of pure aluminum. Therefore, they concluded that this material can be used for hydrogen production.

To resolve the issues of dross storage, bad odor (caused by ammonia production) and safety related to burial of this waste, Liu and Chou (2013) presented a simple and economical method that consists of stabilizing aluminum dross through the addition of ferrous chloride solution. According to the authors, this solution depresses the evolution of ammonia and prevents the leaching of heavy metals.

Nevertheless, many companies do not comply with the environmental legislation and do not seal the soil surface for disposal of dross, and even fewer companies protect the dross from weathering.

Despite the lack of information about the environmental impacts caused by aluminum recycling activity, there are many works related to the impacts caused by ammonia (the main product generated by this industry) in the ecosystems. The ammonia may be provided by different sources, as sewage effluent (Murto et al. 2004), organic and inorganic fertilizer (Webb et al. 2010; Fan et al. 2011), intensive poultry unit (Jones et al. 2013) and roaster chicken houses (Shah et al. 2014). The main damages associated to the ammonia emission is in the eutrophication of lakes and also in the decreasing diversity of vegetation (Jones et al. 2013). Paoli et al. (2010), for example, verified that high ammonia concentrations may reduce the lichen photosynthetic capacity.

Therefore, considering the increase in aluminum recycling in Brazil, we performed an analysis of some parameters, such as physicochemical and chemical composition of groundwater and surface water reservoirs, to assess the impact of the disposal of aluminum recycling waste in the environment.

Materials and methods

This study was conducted in the area of a small recycling company during its operation, approximately 10 years ago, which was located in the metropolitan area of São Paulo and some time ago, moved to another location. The studied area (23°29′05″S/46°20′32″W) has a tropical humid climate with an annual average temperature of 20 °C and total of precipitation ranging between 1100 and 2000 mm (Rocha 2005). The rainy season occurs from October to March, and the dry season, from April to September. This recycling company is part of the tertiary aluminum industry, which recovers aluminum from dross from secondary aluminum industries by leaching with water. It has operated for more than 10 years (almost until 2005) in the area of floodplain of the Tietê River, which was considerably modified by sand mining.

The material that covers this area consists of sediments of a sand mining tailing and, although being not natural, in this work, it will be called as soil. Previous studies revealed

that this soil has silty sand texture, pH around 5 and is formed by minerals of quartz, feldspar, kaolinite and gibbsite (Shinzato 1999).

This company uses aluminum from dross produced from industries that recycle the metal by melting Al cans and other Al-based materials in the presence of salts (NaCl/KCl). The dross and waste (non-metallic material) from this industry were previously described by Shinzato and Hypolito (2005). According to these authors, dross consists of soluble salts (such as Na, K and Cl), aluminum metal, and alloying elements (such as Mg, Si, Fe, Ca, Ti, Mn), and the waste generated by leaching is mainly composed of Al, Si, Mg and Fe. Figure 2 outlines the main components of

Fig. 2 Photo extracted from Google Maps showing locations in the pond where waters were collected (**a**). Schematic drawing of the industrial components of the recycling company and locations of monitoring wells (*PM1, PM2* and *PM3*) drilled for this study (**b**)

this company and shows the locations where the groundwater and surface waters were collected.

This company received tons of dross from secondary Al recycling companies from all over the São Paulo State, and this material was stored in contact with the soil (D in Fig. 2). These wastes have the shape of blocks, which were broken with sledgehammers and manually put into a rotating drum (B in Fig. 2) to be leached with water. The leaching solution accumulated in decantation tanks (C in Fig. 2) up to saturation and then it was discarded back into the pond. It is noteworthy that this process consumed about 40,000 L of water every 10 h, producing a liquid effluent, toxic gases (ammonia and methane), and a solid waste. Periodically, the waste accumulated in decantation tanks was removed and disposed of in the soil (E in Fig. 2), and pond water, contributing to siltation. About 20 tons of dross were treated per day, producing 4 tons of aluminum metal and 16 tons of new waste per day.

The waters of the pond, which were used by the recycling company and for discharging effluent, were collected at each of the five locations, on the surface and at a different depth (Fig. 2a). Measurements of pH, Eh and conductivity were analyzed on the spot using a probe coupled to field measurement equipment (DM-PV/DIGIMED and DMCM010/DIGIMED). After filtration with cellulose membrane filters of 45 μm pore size, samples of pond waters and also of the industrial liquid effluent were chemically analyzed. The euphotic zone of each locations was determined using a Secchi disk. According to Bouton et al. (2014) this zone corresponds to about three times the Secchi depht.

To study the effect that the disposal of aluminum dross has on soils and on groundwater quality, three monitoring wells (PM1, PM2 and PM3)—constructed according to Brazilian regulation NBR-13895 (ABNT 1997)—were strategically installed in the area of the tertiary aluminum recycling company (Fig. 2b). PM1 was drilled near the site where the dross was stored; PM2 was drilled near the area where solid waste from decantation tanks was disposed, and PM3 was the reference monitoring well located in an uncontaminated area, away from the other wells and topographically above the other wells.

During the drilling of the monitoring wells, soil sampling was conducted from the auger holes at three depth intervals: 0–50, 50–100 and 100–150 cm. The groundwater table level measured in each well were 1.5 m in PM1, 1.0 m in PM2 and 0.5 m in PM3.

The soil samples of each interval were mixed thoroughly in a clean plastic bucket to obtain a composite sample and was taken to a laboratory, air-dried and sieved (2 mm). These samples were treated using a single extractant of $0.1 \ mol \ L^{-1}$ HCl to leach the soluble and adsorbed ions present in the soils. In this extraction 100 mL of
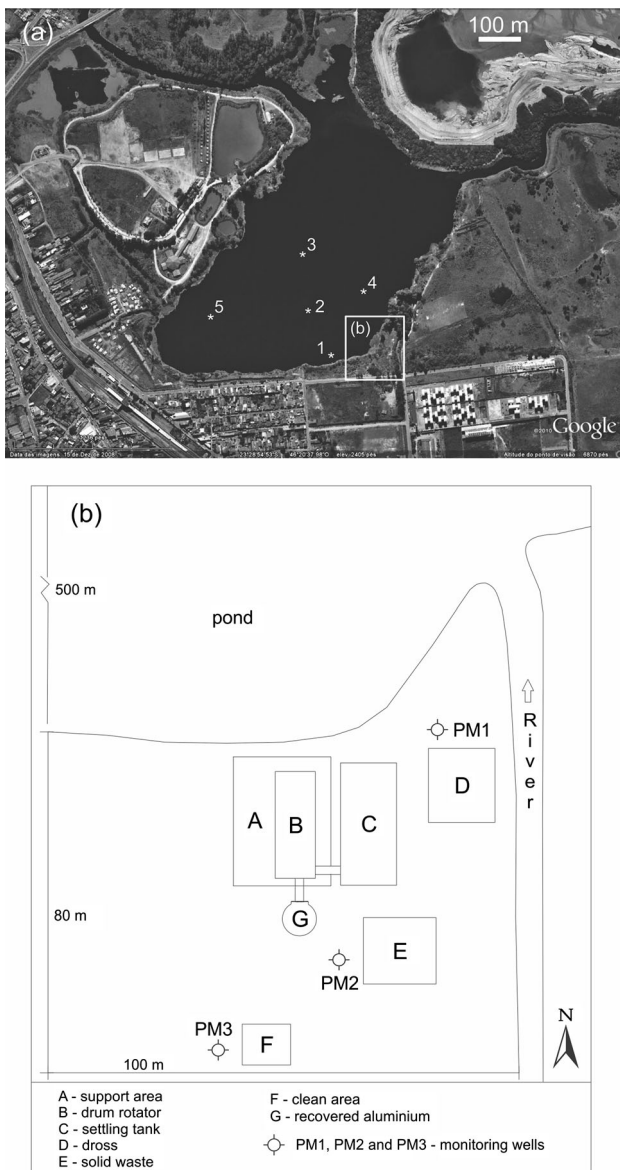
0.01 mol L^{-1} HCl was added to 5 g of soil sample, which was digested at 40 °C for 5 days. After filtration with cellulose membrane filters of 45 μm pore size the digester solution was chemically analyzed. The pH of these soils was determined using a digital pH meter (DIGIMED/DM-PV), after 10 g of soil being agitated with 25 mL of distilled water for 15 min and decanted for 30 min.

Periodically over a year, the groundwater from monitoring wells (PM1, PM2 and PM3) were chemically analyzed. Prior to sampling, the water table was measured and then the monitoring well was purged at a low flow rate to remove all the stagnant water. Parameters as pH, Eh (DIGIMED/DM-PV) and conductivity (DIGIMED/DMCM010) were also determined in loco and, after filtration with cellulose membrane filters of 45 μm pore size, these solutions were preserved with nitric acid for metal analysis.

The chemical parameters of the studied materials (soils and waters) were analyzed in the laboratories of Instituto de Geociências da Universidade de São Paulo (USP) using some techniques:

- Atomic absorption spectrometry method (CG/AA7000BC) for Al^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe_{total}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} determination. The detection limit levels of this equipment are: 0.01 mg L^{-1} for Ni^{2+}, Mg^{2+}, Ca^{2+} and Mn^{2+}; 0.02 mg L^{-1} for Al^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}; and 0.04 mg L^{-1} for Fe^{3+}, Sr^{2+} and Ba^{2+}.
- Flame emission spectroscopy (MICRONAL/B262) for Na^+ and K^+ analysis which detection limit levels for both ions is 0.02 mg L^{-1}.

- Nessler method using UV–vis spectrophotometer (DR2000/HACH) for $N-NH_3$ concentration analysis, which detection limit level of this compound is 0.02 mg L^{-1}.

The results obtained in these chemical analysis were the average of two determinations. Blank absorbance values were monitored throughout the period of the experiment and were subtracted from the readings before the results were calculated.

Results and discussion

Effluent and pond waters analysis

The mean values of the chemical parameters of the effluent produced during leaching of the dross and the pond water analyzed in the study area are shown in Table 1.

The effluent of the aluminum recycling company is very alkaline and saline since has high concentrations of Na^+, $N-NH_3$, Mg^{2+}, Ca^{2+}, K^+ and Al [as $Al(OH)_4^-$], and very low concentrations of heavy metals. The pH of the effluent is alkaline (9.8) due to the ionization of part of ammonia [formed during the reaction (1)], leading to a high content of $N-NH_3$ (110 mg L^{-1}) in solution. The others components (Na^+, K^+, Mg^{2+} and Ca^{2+}) were solubilized during the leaching process of dross, also contributing to the high electrical conductivity of the pond water. Low levels of heavy metals (all below the limits required by the environmental regulation) are present in the effluent due to high

Table 1 Mean values of pH, Eh, electrical conductivity and ion concentration measured in the water samples collected at each of the five locations in the pond (L1–L5), near the surface (sur) and at a different depth (dep), and liquid effluent

Pond points	Euphotic zone/ lake depth (m)	pH	Eh (mV)	Electrical condut. (mS cm^{-1})	Na (g L^{-1})	K (mg L^{-1})	Al (mg L^{-1})	Ca (mg L^{-1})	Mg (mg L^{-1})	Cu/Zn/Pb (mg L^{-1})	$N-NH_3$ (mg L^{-1})
L1											
Dep	0.31	6.72	−142	0.31	37.5	4.7	<0.02	16.2	2.1	<0.02	4.25
L2											
Sur	–	6.87	−0.5	0.31	36.3	4.4	<0.02	17.0	1.8	<0.02	3.28
Dep	1.89/4.65	8.78	−104	0.37	35.0	4.5	1.43	16.9	1.7	<0.02	13.55
L3											
Sur	–	6.87	+101	0.29	35.0	4.4	<0.02	18.4	2.1	<0.02	3.48
Dep	2.64/17.7	9.41	−220	0.50	50.0	6.3	4.15	17.8	1.9	<0.02	65.75
L4											
Sur	–	6.77	+188	0.28	42.5	5.9	<0.02	18.9	1.9	<0.02	3.30
Dep	2.16/17.0	9.10	−220	0.38	45.0	6.0	6.88	18.6	2.0	<0.02	30.25
L5											
Sur	–	6.79	+202	0.27	35.0	4.6	<0.02	19.0	2.1	<0.02	3.25
Dep	2.28/21.0	6.71	+204	0.28	40.0	5.5	<0.02	18.9	1.8	<0.02	4.55
Effluent	–	9.79	–	80.0	52.8	9.0	5.20	28.0	86.0	0.11/0.13/ 0.72	110.0
CONAMA 430/2011	5.0–9.0	–	–	–	–	–	–	–	–	≤1.0/≤5.0/ ≤0.5	≤20.0

CONAMA 430/2011 = limits of permitted effluent discharge levels of some chemicals

pH conditions, that promote their precipitation as hydroxides. These heavy metals come from the melting of beverage cans together with aluminum dross.

As this effluent was discharged through underground pipes inside the pond, the quality of the bottom waters was mostly affected than the surface waters. In the upper water column, ammonia concentrations were low and the pH is near 6 (Table 1). Meanwhile, in the bottom waters, where the Eh values are negative (L2–L4), the concentration of ammonia remain high since the pH is around 9 and the rate of its oxidation by microorganisms is low (Joye et al. 1999). According to Arana (2004), depending on water pH and temperature, free ammonia (NH_3) and ionized-ammonia (NH_4^+) can exist in equilibrium; but this balance is mainly affected by pH (Lin and Wu 1996; Jofre and Karasov 1999). A one-unit increase in pH rises ten-fold the concentration of unionized ammonia (Enviroment Canada and Health Canada 2001). So the presence of unionized ammonia in the bottom of the pond may be favored by the high pH of these waters (Table 1).

According to the Brazilian Environmental Regulation (CONAMA 2011), the maximum level of $N-NH_3$ in the industrial effluent allowed to be discharged in water bodies is 20 mg L^{-1}, and the pH range must be within 5 and 9. If pH is around 9 (as occurs in the bottom of L2–L4), the level of free ammonia (NH_3) increases, being toxic to aquatic organisms (Baird 1995), since it can diffuse across biological membranes more readily than other forms (US EPA 1998). The presence of ammonia in the environment also increases biochemical oxygen demand (BOD) in water, which is caused by the nitrifying bacteria during the breakdown of NH_3 into NO_3^- (since this reaction requires a lot of dissolved oxygen) (Wang et al. 2006). Considering that nitrogen compounds are essential for living organisms, they also lead to an increase in oxygen demand and eutrophication (Lei et al. 2008).

The limit of ammonia concentration for drinking water regulated by Brazilian Regulation (Ministério da Saúde 2011) is 1.5 mg L^{-1} and, according to the Guidelines for drinking-water quality of World Health Organization (WHO 2003), the surface waters may contain up to 12 mg L^{-1} of ammonia. Nevertheless, the recommended water quality criteria for ammonia established by US Environmental Protection Agency (US EPA 2013a) is a magnitude of 17 mg L^{-1} at pH 7 and 20 °C for a 1-h average duration (not to be exceeded more than once every 3 years on average). EPA also recommends a chronic criterion magnitude of 1.9 mg L^{-1} for a 30-day average duration (not to be exceeded more than once every 3 years on average).

Since the pH of the bottom waters are above 9, aluminum ions [mainly as $Al(OH)_4^-$] was also detected in these solutions, revealing its origin from the recycling industry effluent. Other ions which are in high concentrations, as Na^+, Ca^{2+} and K^+, come from this effluent and, due to its high solubility, they are homogenously distributed in all surface and bottom waters of the pond (Table 1). On the other hand, the presence of heavy metals in pond waters was not detected, probably because of the alkaline pH of the effluent, which may precipitate these metals as hydroxides in the decantation tanks, during the leaching process of dross.

Groundwater and soil analysis

During this study, the water table of groundwater varied between 1.25 and 2.75 m at PM1, between 1.1 and 2.3 m at PM2, and between 0.5 and 1.95 m at PM3. This variation reflects the precipitation indices and the topography of the area where these wells were drilled.

Comparing the mean values of chemical composition of water samples of reference well (PM3) with those collected in monitoring well PM1, it is possible to verify that the quality of groundwater was obviously impacted by the dross disposal in the soil, whereas the impact caused by non-metallic waste (PM2) was relatively minor (Fig. 3).

As the dross were deposited directly in the soil without any protection, many components were promptly leached, increasing the values of electrical conductivity and the concentration of many ions in groundwater, including some heavy metals (Fig. 3).

Although the pH of the liquid effluent produced by leaching the dross with water was strongly alkaline (around 10) and has affected the pH of pond waters, this condition was not observed in water samples from PM1. Contrastingly, groundwater of PM1 was more acidic (around 4), with higher values of Eh (mean of 249.57 mV) and conductivity (mean of 60.14 mS cm^{-1}), and with concentrations of Al^{3+}, Na^+, K^+, Ba^{2+}, Fe_{total}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} greater than those measured in PM2 and PM3.

The decrease in groundwater pH at PM1 was probably due to oxidation of ammonium (Eq. 1) by nitrifying microbial communities in the soil, according to Eqs. (4) and (5).

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{4}$$

$$2NH_4^+ + 3O_2 \leftrightarrow 2NO_2^- + 2H_2O + 4H^+ \tag{5}$$

Despite the nitrate content was not analyzed in this study, higher Eh values detected in the PM1 groundwater can indicate the occurrence of ammonia oxidation—since the most common nitrogen compound found in groundwater in oxidizing conditions (positive Eh values) is NO_3^-, and the NH_4^+ form can be found in groundwater with strongly reducing environments (Lindenbaun 2012).

It is noteworthy that this phenomenon is very common in soils treated with ammonium fertilizers or urea (Bolan et al. 1991; Barak et al. 1997). Princic et al. (1998) also
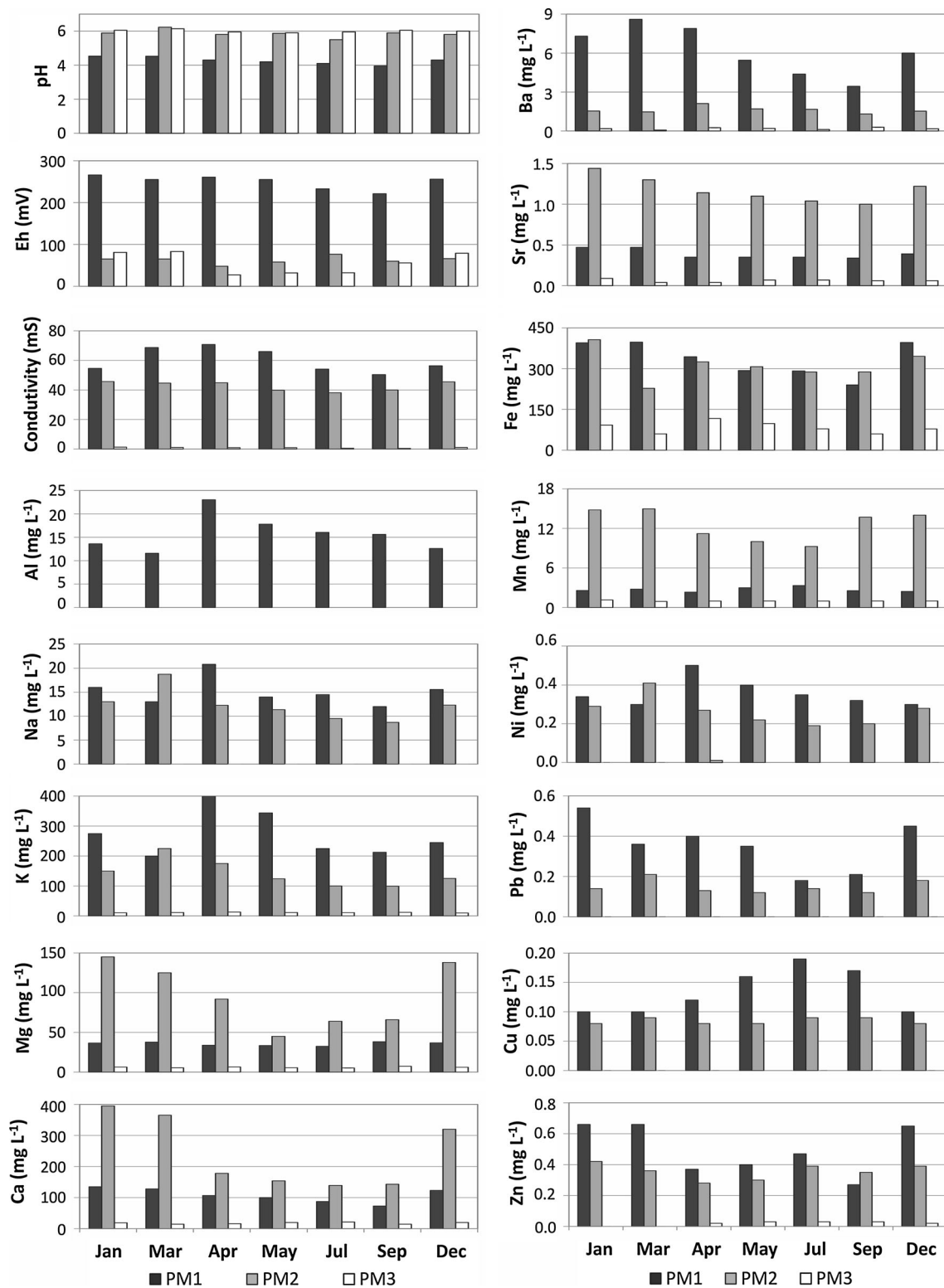
Fig. 3 Mean values of some physicochemical and chemical parameters of groundwater collected for a year from the saturated zone at PM1, PM2 and PM3

observed the increase in the oxygen uptake and the lower of pH in environments with high inputs of ammonium. Despite ammonium can occur naturally in groundwater, as

the product of decay of natural organic compounds, its presence in high concentration is a common indicator of anthropogenic impact (Lingle 2013).

Table 2 Mean concentrations of some ions present in groundwater samples collected in monitoring wells (PM1, PM2 and PM3)

	Al^{3+} (mg L^{-1})	Pb^{2+} (mg L^{-1})	Cu^{2+} (mg L^{-1})	Fe_{total} (mg L^{-1})	Ni^{2+} (mg L^{-1})	Zn^{2+} (mg L^{-1})	Ba^{2+} (mg L^{-1})	Mn^{2+} (mg L^{-1})
PM1	15.75	0.36	0.14	336.36	0.36	0.5	6.15	2.72
PM2	0.17	0.15	0.08	312.32	0.27	0.36	1.62	12.56
PM3	<0.02	<0.02	<0.02	83.32	<0.01	0.03	0.18	1.01
CETESB[a]	0.2	0.01	2.0	0.3	0.02	5.0	0.7	0.4
WHO[b]	Nil	0.01	2.0	Nil	0.07	Nil	0.7	Nil
US EPA[c]	Nil	0.015	1.3	Nil	Nil	Nil	2.0	Nil

[a] Limits concentrations for groundwater quality established by the São Paulo State Environmental Agency, Brazil (CETESB 2014)

[b] WHO Drinking Water Standards (WHO 2011)

[c] US EPA maximum contaminant level allowed in drinking water (US EPA 2009)

The decrease in pH would thus enhance the dissolution of some metals, such as Al^{3+}, Fe_{total}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Ba^{2+}, and Mn^{2+}, increasing their concentrations (except for Cu^{2+} and Zn^{2+}) in PM1 groundwater above the limits established by the São Paulo State Environmental Agency (CETESB 2014) for groundwater quality (Table 2). These values are also above the limit established by US EPA (2009) and WHO (2011) for drinking water.

In water samples from PM2, pH was always close to neutral, and concentrations of Mg^{2+}, Ca^{2+}, Sr^{2+} and Mn^{2+} were higher than those measured in samples from PM1 and PM3 (Fig. 4). Concentrations of Mn^{2+}, Ba^{2+}, Pb^{2+}, Fe_{total} and Ni^{2+} were above the limits established by CETESB for groundwater quality and by WHO (2011) and US EPA (2009) for drinking water (Table 2). The enrichment of these ions occurred mainly in wet months (December, January and March), indicating that they may have been leached from the waste at the surface, and penetrated deeper into the saturated zone of the soil. Beyond the high concentration of these ions in the waste composition, the properties of soil (silty sand texture and minerals with low cation exchange capacity) may also promoted their mobilization until groundwater level.

The main toxicity of the ions, which are above the limits of CETESB, refers to their exposure to living lives. According to Barbeau (1984) excessive Mn can cause irreversible nervous system damage to human; while for people who consume Ba in excess for many years, could have their blood pressure increased (US EPA 2013b). The effects caused by the exposure to Cu are gastrointestinal distress and liver or kidney damage, as to Pb exposure (US EPA 2013b), which is stored in soft tissues (Mudipalli 2007). According to Yumoto et al. (2001) the intake of Al in high levels is highly neurotoxic and may inhibits pre-natal and postnatal development of the brain in humans and animals. Finally, the excess exposure of Ni for humans also may increase cancer risk, as this element is hematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, hepatotoxic and carcinogenic agent (Das et al. 2008).

The concentration of ions in groundwater at PM3 was always lower than that in other wells, which was expected, since PM3 is the reference monitoring well. All chemical parameters measured in this well are below the limits set by CETESB for groundwater quality, except for Fe and Mn, which may have been leached out of the structure of some minerals. In short, the variability in groundwater composition shows a strong influence of the chemical composition of the materials disposed of in the soil.

The chemical parameters measured in the acid (0.01 mol L^{-1} HCl) extracted solution of soils refer to the ions released from the soluble and adsorbed phases of soil. However, this extraction can also mobilize part of elements originally found in the structure of soil components, as some minerals (Beckett 1989). The soil pH of samples collected in PM1 did not change by the disposal of dross, but the concentration of some ions (Na^+, K^+, Ni^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) increased mostly in upper level of the soil profile (Fig. 4).

The high concentration of ions near the PM1 soil surface indicates that they were leached from dross and were retained by some soil components (illite, kaolinite and gibbsite) and/or were precipitated as hydroxides (except for Na^+ and K^+). Nevertheless, these two cations are very soluble and can easily cross the silty sand soil to reach the groundwater level, so their concentration in PM1 groundwater composition remained high all over the year (Fig. 3).

The main heavy metals present in soil collected in PM1 were Cu and Zn, which maximum concentration were, respectively, 115.9 and 24 mg kg^{-1} (Fig. 4). These metals are commonly used as aluminum-alloys, so they may be leached from the dross disposed in this area.

The small aluminum concentration found on the surface of soil collected in PM1 may indicate that this ion was leached from dross and mobilized as anion $[Al(OH)_4^-]$. For this reason, the concentration of this ion increased in the soil deeper level, where the soil pH is more acid and may promote its precipitation as hydroxide.
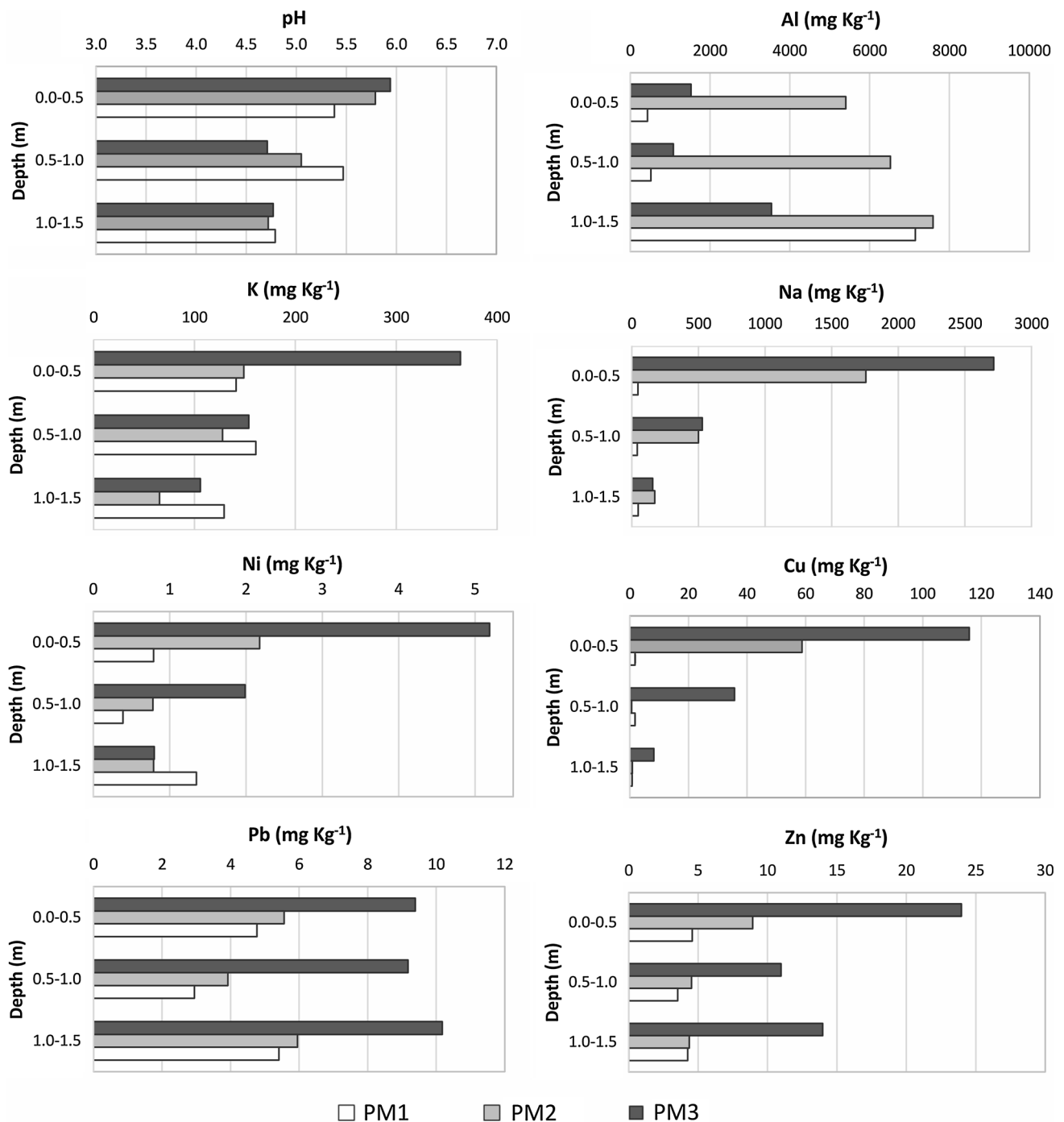
Fig. 4 Mean values of pH_{H2O} and chemical parameters of the extracted solution of soils samples collected at PM1, PM2 and PM3 in depths of 0–1.5 m

The soil samples collected in PM2 (where the non-metallic residue from tertiary aluminum industry was stored) presented more aluminum than the composition of soils samples of PM1 and PM3. This result may be related to the composition of the waste deposited in this area, which is rich in aluminum hydroxide.

Conclusions

The effluent produced by the tertiary aluminum industry has high concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, $N-NH_3$ and is very alkaline—which pH of almost 10 promote the precipitation of heavy metals (released during the aluminum dross leaching process).

The discharge of a saline and alkaline effluent in surface waters affects the quality of this environment, since the ammonia oxidation rate decreases at reducing conditions found in bottom waters of lakes—keeping this compound unionized (NH_3), which is very toxic to aquatic organisms.

The ions leached from aluminum dross disposed directly on soil can contaminate the surface levels of soils and also affect the quality of groundwater. In this case, the pH of groundwater decrease (around 4), probably by the activity of soil nitrifying bacteria that breaks ammonia molecule. In acid pH many ions become soluble, as Al^{3+}, Fe_{total}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Ba^{2+} and Mn^{2+}, exceeding the limits for groundwater quality.

The non-metallic waste disposal in PM2 area did not affect the quality of soil, but it increased the concentration of aluminum, since this material is rich in $Al(OH)_3$. Nevertheless, the concentration of some components of this waste (Mn^{2+}, Ba^{2+}, Pb^{2+}, Fe_{total} and Ni^{2+}) exceeded the limits established by environmental agencies.

Since the aluminum dross and the non-metallic waste are very reactive with water and can contaminate the environment, the recycling industries should concern with the correct storage of these materials, placing them in a sealed and protected area. To avoid the contamination of surface water, the liquid effluent generated by this industry should be properly treated to decrease the pH and remove the ammonia content.

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