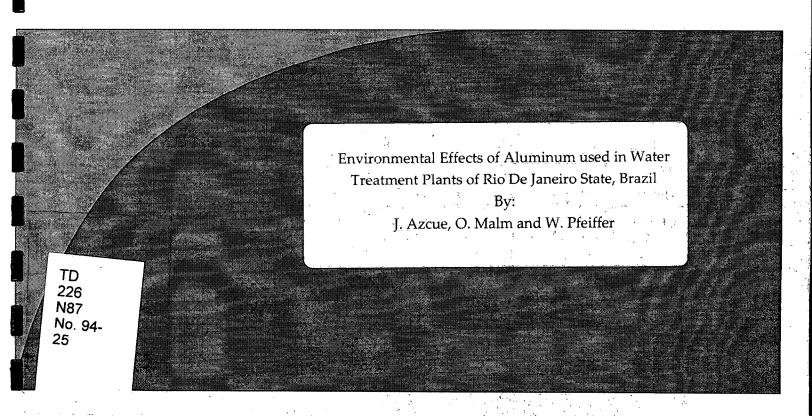
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ENVIRONMENTAL EFFECTS OF ALUMINUM USED IN WATER TREATMENT PLANTS OF RIO DE JANEIRO STATE, BRAZIL

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Manuscript: Environmental Effects of Aluminum used in Water treatment Plants of Rio de Janeiro State, Brazil

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MANAGEMENT PERSPECTIVE

Aluminum (as aluminum sulfate) has been used as the predominant chemical coagulant in water treatment plants since the ancient Romans of 2000 B.C. The discharge of the wastes from the municipal water treatment plants to a watercourse has been considered standard practice worldwide. The potential effects of alum sludge discharge on receiving bodies of water is a controversial topic in environmental pollution. An increasing number of studies point to a relationship between aluminum and both Alzheimer's disease and dialysis encephalopathy in humans. High concentrations of aluminum in drinking water could come from the treatment characteristics.

The present manuscript is the product of an international collaboration and study the effects of the extended use of alum on the concentration of aluminum in water treatment plants of Rio de Janeiro State in Brazil. The system investigated is an irreplaceable source of water to more than 40 cities, among them Rio de Janeiro (11 million inhabitants). The concentrations of aluminum found were near and sometimes over the values recommended by the World Health Organization, with an average concentration of 306 μ g/L, reaching seasonally maximum values of 877 μ g/L and 2,100 μ g/L in household taps. The discharge of alum sludge back to the river system is the predominant pathway in the aluminum cycling in the study area, followed by sedimentation and enhanced availability to the biota. The possible effects of aluminum discharge on aquatic life, that is close to 1.7 tones/yr in some treatment plants, justify an effort for national and international development or update of disposal guidelines or alternatives.

Key words: Aluminum, water treatment, sludge, Brazil.

Abstract

The effect of the extended use of alum in water treatment on the concentration of aluminum in treated water was investigated. Water from the Paraiba do Sul-Guandu River (PSR-GR) system, collected after conventional treatment, was analyzed from the six main Water Treatment Plants (WTP). Among the studied WTP was the Guandu-WTP which provides water to the city of Rio de Janeiro (11 million inhabitants) with a flow of 40 m³/s. The concentrations of aluminum found were near and sometimes over the values recommended by the World Health Organization (200 μ g/L), with an average concentration of 306 μ g/L, reaching seasonally maximum values of 877 μ g/L at the WTP and 2,100 μ g/L in the house tap. The discharge of alum sludge back to the river system is the predominant pathway in the aluminum cycling in the study area, followed by sedimentation and enhanced availability to the biota.

Introduction

The most conventional water treatment processes have been originally designed for treatment objectives other than the removal of trace inorganic contaminants. The main purpose of drinking water purification was to remove Ca²⁺ and Mg²⁺, and to oxidize and clean up turbid waters (Förstner and Wittman 1979). However, most trace inorganic contaminants can be adequately removed from raw water by the physical-chemical treatment processes of coagulation, settling and filtration. Removal of the particulate matter and/or colloidal substances that are not removed rapidly by sedimentation, is accomplished through the mechanisms of adsorption-precipitation between the coagulant added and the contaminants present in the raw water.

Alum, aluminum sulfate, has been used as the predominant chemical coagulant in the clarification of water since the ancient Romans of 2000 B.C. (Faust and Aly 1983). The aluminum content of commercial alum is typically >50,000 mg/L (Cornwell et al. 1987). Ferric sulfate or ferric chloride and lime have also been employed alone, or with alum, as an aid to sedimentation of particulate matter (Amirtharajah and Mills 1982; Johnson and Amirtharajah 1983; Dempsey et al. 1985). The essential purpose of alum (coagulant agent) is to produce a voluminous, adsorptive hydrolysis product of low solubility, that will settle quickly within an hour or two and /or will be filtered by sand (Faust and Aly 1983).

The wastes of these industrial processes must be discharged into the environment. Therefore, one of the major sources of aluminum in freshwater, surpassing industrial users, is the discharge of alum sludge from municipal water treatment plants (Moore 1991). Even though directly discharging alum sludge (including filter backwash water) to a watercourse has been standard practice worldwide, at the present time this mode of operation is being questioned (Cornwell et al. 1987). The potential effects of alum sludge discharge on receiving bodies of water is a controversial topic in environmental pollution. Several groups have attempted to quantify the effects of alum sludge discharge into surface waters, Roberts and Diaz (1985) measured phytoplankton productivity during alum sludge discharge, and observed a depression of production by the high suspended solids associated with the discharge. Simulations of episodic increases in aluminum concentrations during acidic snowmelt suggested that added aluminum can associate preferentially with organic functional groups, rendering DOC more hydrophobic and less soluble (Hall et al. 1985). In 1987 the Sludge Disposal Committee of the AWWA published one report entitled "Research needs for alum sludge discharge" (Cornwell et al. 1987), providing a summary of the existing research in the area. The committee concluded that "significant research must be completed before alum sludge discharge practices can be supported or eliminated".

There is an increasing number of studies pointing to a relationship between aluminum and both Alzheimer's disease and dialysis encephalopathy in humans (Bowdler et al. 1979; Marlowe et al. 1985; Perl and Good 1988; Krishnan et al. 1988). High concentrations of aluminum in drinking water could come from the treatment characteristics. Miller et al. (1984) concluded that when alum is used as a coagulant agent, there is a 40-50 percent chance that the concentration of aluminum will increase above the original concentration in raw water. Laboratory and field data are required to better understand the role of aluminum, and the different aluminum species, in health terms.

The PSR-GR system, situated between the two largest Brazilian cities (Sao Paulo and Rio de Janeiro), is of great social and economical importance since it supplies water to neighbouring cities (about 40 altogether). It is an irreplaceable source of water to the city of Rio de Janeiro (11 million inhabitants) after conventional treatment. The purpose of this study was to assess the concentration of aluminum in drinking water after conventional treatment by the six main Water Treatment Plants (WTP) in the State of Rio de Janeiro, Brazil. The six WTP utilize surface water from the Paraiba do Sul-Guandu River (PSR-GR) system and treat it by coagulation and flocculation with aluminum sulfate, sedimentation, rapid sand filtration and chlorine disinfection (Azcue et al. 1987).

Earlier studies performed in this area (Pfeiffer et al. 1986; Malm et al. 1988) concluded that the Paraiba do Sul-Guandu River system can be considered moderately to strongly polluted in terms of total metal concentrations. Results presented in a preliminary survey suggested that aluminum can be considered as a potentially critical element to the local biota related to its uses in the water treatment processes (Azcue et al. 1988a). Aluminum toxicity to biota is closely related to its chemical speciation, which is function of several factors, such as, the presence of humic and fulvic acids (Truitt and Weber 1979; Pankey and Patterson 1988) and pH (Driscoll et al. 1980).

Methodology

Study Area

The Paraiba do Sul-Guandu River (PSR-GR), with a total length of 1060 km, flows for approximately 400 km of its length alongside the main railroad and highway linking the cities of Sao Paulo and Rio de Janeiro. The study area is situated in the State of Rio de Janeiro and has a total length of 200 km starting from the border with the state of Sao Paulo at the Funil Dam. The river, at the study area, has an average flow rate of 250 m³/s. In Barra do Pirai city, at the Santa Cecilia pumping station, 70% of the total water of the PSR is pumped into the Santana Dam, which releases this volume into the Guandu River.

In this study, water was analyzed after conventional treatment at the six main WTP, located in Resende, Barra Mansa, Volta Redonda, Barra do Pirai, Pirai, and Guandu. Three WTP were along the PSR and the last two in the Guandu River. The Guandu-WTP holds two water treatment facilities which are named in the present paper as Old-Guandu and New-Guandu, and provides water to the city of Rio de Janeiro with a flow of about 40 m³/s. The six WTP utilize surface water from the PSR-GR system and treat it by coagulation and flocculation with aluminum sulfate, sedimentation, rapid sand filtration and chlorine disinfection. In Volta Redonda and Guandu-WTP, water is also fluoridated prior to distribution. The water flows (L/s) treated by the different WTP are: (25)in Pirai, (<200) in Resende, Barra Mansa and Barra do Pirai, and (40,000) in Guandu.

Sample Collection

Water and sludge samples were collected from the six water treatment facilities. Water samples were collected after the treatment and to avoid stagnation problems, the treated water samples were collected after flowing for five minutes from the stored tanks or from the domestic taps. Tap water samples (5 L) were collected in polyethylene bottles and immediately transported to the laboratory and maintained at $\pm 4^{\circ}\mathrm{C}$ until filtration. Samples were filtered (~15 h later) through previously weighed 0.45 $\mu\mathrm{m}$ Millipore nitrocellulose filters, reduced in volume by low

temperature evaporation (about 50x), and digested at $\pm 100^{\circ}\text{C}$ with an acid mixture of HCl:HNO₃:HClO₄ (3:3:1) (Malo 1977). The residue was brought to a final volume of 50 ml in HCl 0.1 M. The filters containing the suspended particles were dried, weighed, and digested with the same acid mixture stated above and dissolved in 0.1 M HCl. Metals in the sludge from the WTP were extracted with H_2O_2 and 0.3 N HCl, and considered as the available fraction (Malo 1977). The residue was dissolved in an HNO₃:HF (4:5) acid mixture, and was considered as the residual or mineralogical fraction.

Metal concentrations in all samples were determined by flame atomic absorption spectrophotometry using a Varian Model AA1475 spectrophotometer, following recommended standard procedures (Varian A.A. 1981). Internal standards were used to check for interference problems. The reagents used were from Merck, p.a. quality including metal standards (Tritrisol). Reagent blanks were performed with the same amounts of reagents used in the analytical steps. The metal concentrations were usually determined in triplicate samples and reagent blanks of each process were always carried out through the procedure together with the samples. The detection limit determined for Al was 40 μ g/L (Slavin et al. 1972). Accuracy of results from our measurements were confirmed by analyzing standard samples in national and international intercomparison programs, mainly with the British Geological Survey Agency.

Results and Discussion

The average concentration and range of aluminum in the sludge from the different WTP, in the available and in the total fractions are presented in Table 1. The total concentrations of aluminum associated with the sludge was relatively constant in the different WTP, approximately 20 mg/g. However, notable differences can be observed in the concentrations of aluminum present in the available fraction in the different WTP. Aluminum in the available fraction of the sludge of Pirai and Barra do Pirai-WTP can reach concentrations of 6.7 mg/g. The importance of the interaction between the available fraction of sedimented sludge and the water column in treatment plants has already been discussed in a previous paper (Azcue et al. 1988b).

Little research has been done on the periodical discharge of sludge into the surface waters. The time interval between the sludge discharges as well as the calculated aluminum discharged by the different WTP of this study are shown in Table 1. In the Volta Redonda-WTP, approximately every 75 days, some 19 tonnes of sludge from the WTP are discharged in the main stream; while in the Guandu-WTP almost 4 tonnes of sludge are discharged daily. This represents that approximately 1.77 tonnes/y of aluminum are discharged in the Paraiba River.

The alum sludge discharge in the PSR-GR may represent a serious threat to the freshwater aquatic life. The mean concentration of aluminum in edible portion and intestines of fish from the PSR varied from 14 to 1,350 mg/kg wet weight, respectively. (Azcue et al. 1988a). Similar distribution of aluminum in fish organs was observed by Brumbaugh and Kane (1985). However, there is a lack of information regarding the toxic effects of alum sludge discharge in this area in other aquatic organisms, such as benthic invertebrates.

The concentrations of dissolved and total aluminum in the drinking water after the treatment are summarized in Table 2. These results show that the concentration of aluminum in the dissolved fraction was very little affected by the treatment, remaining close to 100 μ g/L in all the WTP. Although there is no Maximum Permissible Concentration in the Brazilian legislation aluminum, the drinking water analyzed in Barra do Pirai and Resende-WTP always reached concentrations higher than the 200 μ g/L guideline level recommended by the W.H.O. (WHO 1993). The total aluminum in the treated water, reached values as high as 877 μ g/L in Barra do Pirai-WTP, and 627 μ g/L in Resende-WTP, with average total concentrations of 591 and 556 μ g/L, respectively. Aluminum present as suspended particles, as well as with the other heavy metals except iron (Azcue et al. 1988b), are the critical compartment to be removed by the WTP. Similar observations of the need of effective removal of particulate matter to minimize

residual aluminum was reported by Letterman and Driscoll (1988). The observed discrepancies in the aluminum concentrations among the different WTP in this study were probably due to operational differences (amount of alum, pH adjustment, and residence time) once the aluminum concentration in the raw water was almost constant.

It is well known that after the treatment, during the further transport of water, particularly in the water piping of individual house-holds, an increase in the heavy metal concentration of drinking water can take place (Gordon and Rusell 1974). Therefore, some domestic tap water were analyzed. The results are presented in Table 2. The average concentration of aluminum in tap water in Barra do Pirai reached the significant level of 980 μ g/L (reaching 2,100 μ g/L). A vast number of samples would be required before reaching any definitive conclusion in this matter. However, these scattered results are enough to confirm the importance of the transport and distribution of the water after the treatment. In further aluminum toxicity studies, the haemodialysis patients, that use 50-100 L of water per day, can be considered as the most critical group.

Conclusions

Although all the WTP of this study were subjected to the same physicochemical treatment, the concentrations of aluminum in treated water reported present large differences with concentrations higher than those recommended by other agencies and countries. The Volta Redonda and Guandu-WTP have presented the best performance in terms of aluminum level, and the WTP of Barra do Pirai and Resende presented the worst one, with an aluminum average concentration in treated water close to 600 μ g/L. The home tap water analyzed confirmed the high levels observed in Barra do Pirai with an average aluminum concentration of 980 μ g/L.

The alum sludge from the water treatment, which concentrates many water pollutants, is periodically discharged again into the surface water downstream. The possible effects on the aquatic life of aluminum discharge, that is close to 1.7 tones/y in Volta Redonda, deserve a thorough study and monitoring at the time of discharging, for developing disposal alternative or guidelines for discharging. Although for monitoring purposes measuring the total aluminum can be considered adequate, the role of the different aluminum chemical species in the freshwater aquatic organisms has to be investigated further. The potential toxic effects of the discharge of alum sludge into the river justify an effort on the national and international development or update of guidelines for the disposal or alternatives.

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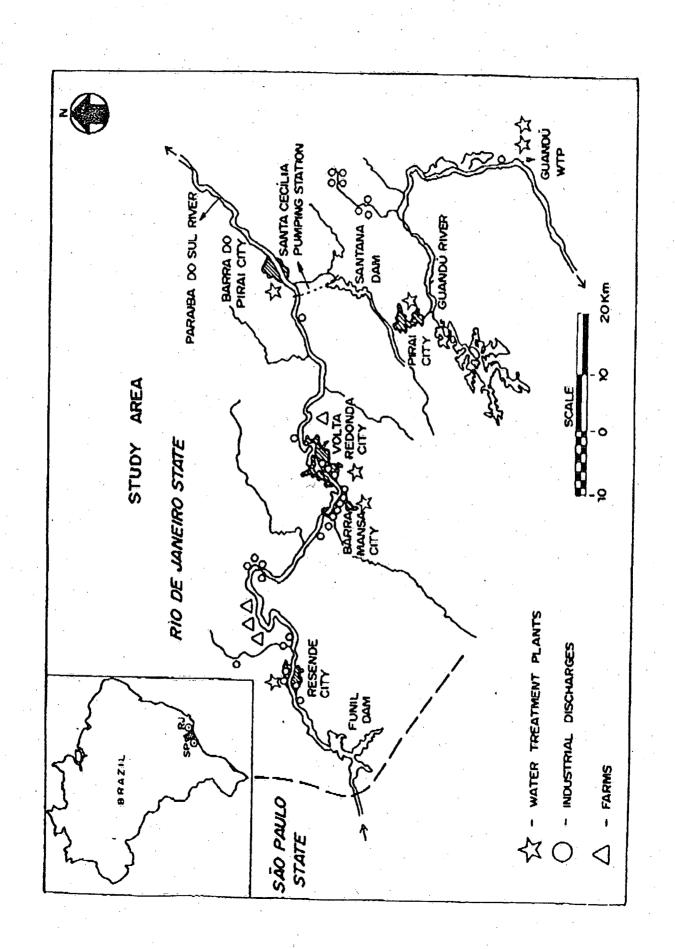


Table 1. Concentration of aluminum in sludge (mg/g) and mass discharged (kg) into surface water after cleaning procedure. Interval in between cleaning expressed in days.

	Resende	Barra Mansa	Volta Redonda	Pirai	Barra Pirai	01d Guandu	New Guandu
Available							
mean	2.9	3.12	1.5	4.5	3.3	2.2	2.5
range	2.0-3.8	2.0-3.9	1.4-1.5	1.6-6.7	1.0-6.6	1.2-3.2	1.9-3.8
Total			*				
mean	24.2	20.8	19.1	23.1	18.6	20.4	19.4
range	3.1-29.4	18.6-24.3	11.3-26.2	14.0-42.4	13.4-23.8	16.2-24.7	17.7-23.5
Sludge discharge	290	610	19,110	5,395	277	3,8	3,874
Interval	30	30	75	120	120	on'	06

Table 2. Dissolved (<0.45 μ m) and total aluminum concentrations (in μ g/L) in drinking water after treatment in the WTP and in local domicilies after distribution.

	Resende	Barra Mansa	Volta Redonda	Pirai	Barra Pirai	01d Guandu	New Guandu
Dissolved							
mean	129	57	88	121	87	116	96
range	66-180	53-66	34-140	45-220	46-200	20-203	36-204
Total						٠.	
mean	556	275	128	232	591	207	156
range	473-627	156-389	38-234	46-465	406-877	59-345	83-243
Homes							
mean	372	410	290	280	086	200(")	(*)
range	120-790	130-1,030	110-1,300	120-570	60-2,100	70-590	290

(") The water from the old and new Guandu-WTP are mixed after the treatment, before the distribution

Aluminum Maximum Permissible Concentrations $(\mu g/L)$:

- World Health Organization : 50
- European Economic Community: Guidance Level 50 and Maximum permissible 200



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