

Total hardness of surface waters in São Paulo State (Brazil).

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ABSTRACT: Total hardness of surface waters in São Paulo State (Brazil). **The aim of this study was to determine the total hardness of surface waters from 112 sampling sites in São Paulo State, using the EDTA Titrimetric Method, in order to assess the appropriate water conditions for toxicity tests with aquatic organisms. Freshwaters from São Paulo were classified as soft waters (mean total hardness of 31 mg/L CaCO₃) and it allows the use of soft water with total hardness between 40-48 mg/L CaCO₃ in aquatic organism culturing and toxicity testing in São Paulo State.**

Key-words: hardness, surface waters, toxicity tests, *Daphnia*, *Ceriodaphnia*.

RESUMO: Dureza total em águas de superfície do estado de São Paulo (Brasil). **O objetivo deste estudo foi determinar a dureza total das águas superficiais de 112 pontos de amostragem no Estado de São Paulo, utilizando o método titulométrico do EDTA, com finalidade de estabelecer condições apropriadas para cultivo e execução de testes de toxicidade com organismos aquáticos. Os resultados obtidos permitiram classificar as águas como moles, com dureza média de 31 mg/L CaCO₃. Além disso, possibilitaram justificar a utilização de água mole, com dureza entre 40 e 48 mg/L CaCO₃, no cultivo e realização de testes de toxicidade com organismos aquáticos no Estado de São Paulo.**

Palavras-chave: dureza, águas superficiais, testes de toxicidade, *Daphnia*, *Ceriodaphnia*.

Introduction

The total hardness is an attribute of freshwater and can be defined, in general, by the total concentration of calcium and magnesium. The main source of water hardness is the dissolution of limestone, so it varies according to the soil composition of each region.

In terms of ecotoxicological studies the hardness of the dilution water used in toxicity tests is an important factor which can affect the toxicity of some chemicals, mainly metals (Sprague, 1985). Toxicity tests, in turn, are important in establishing products register, impact evaluation, interlaboratory studies and water quality criteria. Furthermore, some standard procedures (Weber, 1993) recommend that the culture and dilution water hardness be similar to that of water samples, because expressive differences between them can influence test results.

According to the law n° 9034/94 (São Paulo, 1994), the State of São Paulo is divided in 22 Units of Hydric Resource Management (UHRM), as shown in Figure 1. Although a great amount of water quality data is available for each UHRM, very few are about total water hardness. So, the aim was to compile data of the total hardness of freshwaters from São Paulo State, in order to establish, the appropriate water conditions for aquatic organisms culturing and toxicity testing.



Figure 1: Map of São Paulo State. Numbers denote locations of UHRM (see Table II).

Material and Methods

During the period of 8 years (1993 to 2000), the total water hardness from 112 sampling sites located in rivers, lakes and reservoirs, distributed in 20 UHRM of São Paulo State, were determined through EDTA Titrimetric Method (Eaton et al., 1995). The number of samples ranged between 3 and 22 for each sampling site. The mean value of total water hardness was then calculated for each UHRM, as well as the pooled mean for the whole State.

Results and Discussion

The total hardness of freshwaters in São Paulo State varied from 7 to 69 mg/L CaCO_3 with a pooled mean of 31 mg/L CaCO_3 , being classified according to Sprague (1985, Tab.I) as soft waters (Tab.II).

The importance of determining the total water hardness is due to the fact that many chemicals (mainly metals) have their toxicity influenced by this characteristic. In CETESB (1980), it was verified that the toxicity of copper, zinc, barium, chromium and mercury to *Daphnia similis* in soft water (40-48 mg/L as CaCO_3) was higher than in moderately hard water (± 100 mg/L as CaCO_3).

Table I: Classification of water by total hardness (Sprague, 1985).

mg/L as CaCO_3	classification
0 - 75	Soft
75 - 150	Moderately hard
150 - 300	Hard
> 300	Very hard

Kszos et al. (1992) in experiments with *Ceriodaphnia dubia* using water with a hardness of 40 mg/L CaCO_3 , observed that a concentration of 7.5 mg nickel/L was lethal to the organisms within 7 days. When water with a hardness of 177 mg/L CaCO_3

Table II: Means of total water hardness for UHRM of São Paulo State.

UHRM	Main rivers and reservoirs	Mean total water hardness, as mg/L as CaCO ₃ , (min.- max.)
2	Paraíba river, Jaguari river	12 (9-17)
4	Pardo river (Ribeirão Preto)	18 (16-21)
5	Piracicaba river, Corumbataí river, Capivari river, Atibaia river	30 (16-52)
6	Tietê river (Mogi das Cruzes) Juqueri river, Cotia river, Jundiá Reservoir., Billings Reservoir, Guarapiranga Reservoir.	30 (7-57)
7	Cubatão river, Mogi river	37 (14-69)
8	Sapucaí-Mirim river	16 (11-20)
9	Mogi-Guaçu river	19 (18-22)
10	Sorocaba river, Tietê river (Laranjal Paulista), Barra Bonita Reservoir., Itupararanga Reservoir.	43 (16-68)
11	Juquiá river, Ribeira de Iguape river	27 (7-44)
12	Pardo river (Barretos)	19 (19-20)
13	Tietê river (Bariri), Jacaré-Guaçu river, Jacaré-Pepira river	30 (16-43)
14	Taquari river, Itararé river	30 (17-47)
15	Grande river, Turvo river, Preto river	33 (15-39)
16	Tietê river (Ibitinga), Promissão Reservoir.	36 (34-39)
17	Pardo river (Ourinhos)	28 (23-32)
18	São José dos Dourados river	48 (36-58)
19	Tietê river (Promissão)	30 (19-34)
20	Aguapeí river, Tibiriçá river,	52 (48-61)
21	Peixe river	53 (47-64)
22	Paraná river, Paranapanema river, Santo Anastácio river	25 (19-39)
	Pooled mean	31

was used, the concentration of nickel necessary to kill all the animals was 15 µg/L. Chromium, zinc and cadmium were less toxic to daphnids in hard water than soft water, possibly due to the competition of these metals with magnesium for adsorption sites in biological tissues (Paulauskis & Winner, 1988; Persoone et al., 1989).

With regard to manganese, the acute and chronic toxicity to *Ceriodaphnia dubia* were affected by total hardness of water (Lasier et al., 2000). In soft water, LC50 and IC50 values were 6.2 mg Mn/L and 3.9 mg Mn/L respectively. For hard water, these values were 15.2 mg Mn/L and 11.2 mg Mn/L, respectively.

Moreover, the toxicological response of the organisms may vary if the hardness of culture and dilution waters are very different (Berglind & Dave, 1984). These authors observed that *Daphnia magna* reared in hard water (300 mg/L CaCO₃) was more sensitive than organisms reared in soft water (50 mg/L CaCO₃), when they tested DDT using dilution water with a hardness of 250 mg/L CaCO₃.

Although the results obtained in this study point out a mean hardness of these freshwaters of approximately 31 mg/L CaCO₃, a standard method used in Brazil recommends total water hardness ranging from 40 to 48 mg/L CaCO₃ in culturing and toxicity testing with aquatic organisms (ABNT, 1995). This range corresponds to that of the "soft reconstituted water", which is one of the types recommended in some toxicity test guidelines (U.S.EPA, 1993; U.S.EPA, 1994). Furthermore, this difference between mean total hardness of freshwaters from São Paulo State and the standardized water seems insignificant, since experiments conducted at CETESB (1986) using water of total hardness ranging from 5 to 75 mg/L CaCO₃ had no effects on the rate of immobility or survival of *Daphnia similis*.

As a result, these data allowed the classification of freshwaters from São Paulo as soft waters, which justifies the use of water hardness between 40-48 mg/L CaCO₃ as representative for aquatic organisms culturing and toxicity testing.

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