Phthalate contamination in potable waters of Rio de Janeiro City

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Abstract

Phthalates are the most used plasticizers in industrial products. They have low toxicity, but have frequently been an object of environmental concern because of their worldwide distribution in ecosystems. Their presence and concentrations in the environment indicate a region's industrialization degree. Phthalates have also been investigated as an endocrine disruptor, especially in the reproductive system. This work studies phthalate contamination levels in tap water from thirteen different regions of the city of Rio de Janeiro. The samples were solid phase extracted in C_{18} disks and the obtained acetone extracts were analysed by gas chromatography with electron capture detection. Extraction recoveries were calculated using surrogate standards, diphenyl phthalate and di- isophenyl phthalate, and provided values between 89.3 to 98.7%. Phthalate standards were used to identify the analyte peaks, and to determine respective detector response factors. Benzyl benzoate was used as internal standard. Di-ethyl hexyl phthalate (DEHP) was the only one found in all water samples, in the concentration range of 2.94 to 9.67 $ng.L^{-1}$. The results allowed correlation according to the city water distribution net. Samples from the southern region provided the highest values. For comparison purposes, a commercial natural mineral water and one sample collected directly in its spring were also analysed using the same procedure. All results obtained were compared to phthalate contaminations reported for other cities.

1 Introduction

Phthalate esters are used as plasticizers and are by far the largest class of plastic additives. Their production increases with the growth of the plastic industry.

Among them, di (2-ethyl hexyl) phthalate (DEHP) is the most used and, in Brazil, it accounts for 90% of the plasticizer consumption [1].

Due to several antropogenic inputs, phthalates have been detected everywhere in the world, contaminating aquatic systems, wildlife, plants, sediments and soil [2-25]. Their presence in the environment usually indicates the industrial contamination extent of a region.

In spite of this long use, the harm that phthalates can cause to living organisms remains controversial. They have been suspected of causing endocrine disruption, especially in the male reproductive system [4-5,11,26-27]. In 1974, EPA included phthalate esters in its priority pollutants list [28]. DEHP and butyl benzyl phthalate (BBP) have been reported as causing positive evidence for carcinogenicity [26].

In 1997, EPA [29] withdrawn all phthalates but dibutyl phthalate (DBP) of its priority pollutants list. In 1999, American Council on Science and Health concluded that DEHP is not harmful to medical patients even to highly exposed ones. Almost simultaneously Health Care Without Harm released literature review reaching opposite conclusion [30].

Endocrine disruptive properties were observed for some phthalates, including DEHP and BBP, in *in vitro* and *in vivo* tests [11]. Also embryotoxic and teratogenic effects had been detected for both phthalates [27].

The fact is that phthalates are hard to replace and their ubiquity and quantities discharged in the environment justify all concerns that motivate several studies all over the world.

This study investigates the occurrence of phthalates in the potable water system of the city of Rio de Janeiro, in a commercial mineral water and in a sample collected in its spring, located at the surrounding mountains of the city.

2 Study area

Rio de Janeiro City was chosen for being the second industrial center of the country and also the most important touristic city of Brazil.

Potable water was defined as the one that reaches the residences by the public water distribution system.

The samples were collected in 13 residential areas (quarters) with high demografic density, selected among the 120 quarters of the city. The location of those regions and the water distribution net are shown in figures 1 and 2 respectively.

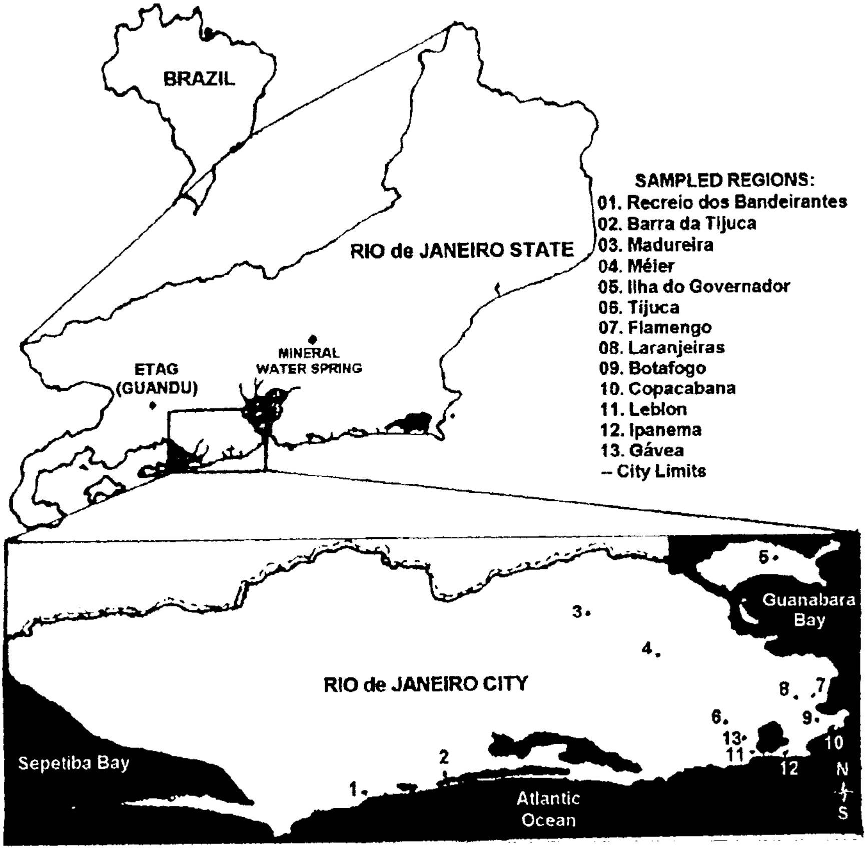

Figure 1: Location of sampled quarters

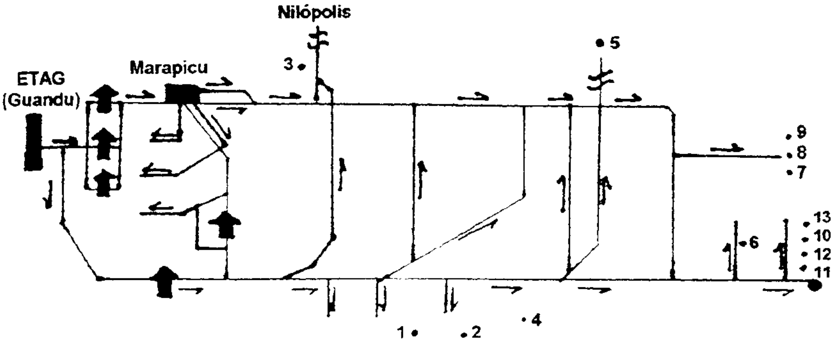

Figure 2: ETAG - Water Treatment Station of Guandu

3 Experimental

3.1 Sampling

Sampling was carried on along the first week of January/2001, using 1L glass bottles previously decontaminated at 450°C for 4hrs [10,12-18,20-21,31-33] and collecting the tap water after 1 minute of continuous water flush.

The mineral water sample was colleted in a spring situated in the surrounding mountains, about 80 Km far from Rio de Janeiro City. The mineral water source is commercially explored and is sold in polythylene terephthalate (PET) recipients. A fifth teen day bottled water was used as the commercial mineral sample.

3.2 Extraction

The samples brought to the laboratory were kept refrigerated for a maximum period of 12 hours, before being extracted.

Solid phase extraction (SPE) was used for all samples with C_{18} disks (3M Empore High Performance Extraction Disks). According to the manufacturer instructions for phthalates in drinking water analysis [33], the disks were conditioned with 5mL of methanol for few minutes; afterwards 1L volume sample spiked with surrogate standards was filtered. The sample flask was washed out with 5mL of acetonitrile and this volume was added to the filter. The filter was then washed with two successive portions of 5mL dichloromethane to recover the extracted phthalates. The extracts were combined and filtered through anhydrous sodium sulphate in order to eliminate residual water, and were evaporated until dryness under N_2 flow. The residue was dissolved in 1mL of acetone for gas chromatographic analysis. All the solvents used were pesticide residue grade.

Surrogate standards, di phenyl phthalate (DPP) and di iso-phenyl phthalate (DPIP) from Accustandard (New Haven,CT,USA) were added to the sample before the extraction, in order to verify the extraction recovery. All the standards were recommended by the EPA Method 8061A [32] for phthalates determination in environmental samples.

3.3 Chromatographic Analysis

The analyses were performed in a gas chromatograph HP 5890 (Palo Alto, CA,USA), equipped with electron capture detector and a capillary column DB-5 (J&W, Folsom,CA,USA) 30m x 0.25mm and phase thickness of 0.25μm.

The injector and detector temperatures were 250°C and 300°C, respectively. Column temperature was kept isothermal at 190°C for 40min and then programmed at a rate of 20 $°C.min^{-1}$ until 210°C, where it was held for 12 min. Total analysis time was 53min. Nitrogen was used as carrier and make-up gas at flow rates of 4mL.min^{-1} and 26mL.min^{-1}, respectively. Sample volume was 1μL, injected in splitless mode.

The qualitative analysis was based on the comparison of the retention times of the sample peaks with the retention times of a standard mixture (Accustandard, New Haven, CT, USA) containing 16 phthalates of interest, according to the EPA Method 8061A.

The quantitative analysis was accomplished with the aid of calibration curves (area versus concentration), where the area of each phthalate standard was divided by the area of the internal standard, benzyl benzoate (Accustandard, New Haven, CT, USA), added to the standard mix solution at the concentration of 10, 25, 50 and 100 ng.L^{-1}. Each point in the curve represented the average value of five replicate analyses of each standard solution.

4 Results and Discussion

The extractions recoveries ranged from 89.3 to 98.7%.

Though the method could screen 16 phthalates, DEHP was the only one found in all water samples. This result was confirmed by GC-MS.

Since the gas chromatographic conditions were not suitable to detect trace amounts of dimethyl phthalate and diethyl phthalate, this same GC-MS screen was used to verify the occurrence of both substances in all samples, with negative results.

Minimum detection limits were defined as the minimum concentration of a phthalate that could be quantified. The limits were determined by analyzing successively diluted standard phthalate solutions. For the sixteen phthalates, detection limits ranged from 0.5 to 5.0 ng.L^{-1}. For DEHP the minimum detection limit was 0.5 ng.L^{-1}.

Six whole procedure blank tests were performed and no phthalate peaks were detected. When blanks were spiked with surrogate standards, one peak of DEHP was obtained, obviously an impurity of the surrogates. This impurity was quantified and the average result (n=6) of 4.38 ng.L^{-1} was subtracted from the concentrations found for the water samples.

Tables 1 and 2 present the analytical results.

The DEHP concentrations can classify the quarters in three groups: quarters 1-6, which exhibited the lowest concentrations; quarters 7-9, which presented about twice the previous values and quarters 10-13, with the highest values, approximately three times the first ones.

Quarters 1-6 are located in the western (1,2) and northern (3-6) areas of the city, whereas 7-9 and 10-13 are in the southern region, but are fed by two different distribution lines. The supply line that reaches 7-9 is shorter then the one feeding 10-13 quarters, which are located at the end of the distribution net.

Table 1: Potable waters results ($ng.L^{-1}$)

Sample	DEHP	Sample	DEHP
1 - Recreio dos Bandeirantes	3.13	8 - Laranjeiras	6.19
2 - Barra da Tijuca	3.14	9 - Botafogo	6.20
3 – Madureira	2.94	10 - Copacabana	9.65
4 – Méier	3.16	11 - Leblon	9.66
5 - Ilha do Governador	3.40	12 - Ipanema	9.67
6 – Tijuca	3.65	13 - Gávea	9.63
7 – Flamengo	6.18		

The results were very consistent and showed that the DEHP contamination increased with the distance of the sampled area from the Water Treatment Plant (Guandu), in spite of being all pipelines of the water system made of concrete and/or forged iron. Future studies concerning larger number of quarters may confirm this tendency.

Table 2: Mineral waters results ($ng.L^{-1}$)

Sample	DEHP concentration
commercial	1.26
Spring	1.21

Mineral water samples presented very low contamination levels, and the bottled product practically exhibited the same content of the one from the natural spring. The mountain water source is possibly contaminated from air particulate from the neighboring industrial city areas.

The potable water results showed considerably lower phthalate contamination levels (both qualitative and quantitative) for Rio de Janeiro, when compared to the values reported for European [10] and American [14,15] cities. The mineral water commercialized in the city also evidenced lower DEHP levels than those reported in the literature for similar products [10, 25].

5 Conclusions

DEHP was the only one phthalate contaminating the potable waters of highly populated quarters of Rio de Janeiro. Measured values, from 2.94 to 9.67 $ng.L^{-1}$ were considerably lower than those detected for cities in Europe and USA.

Samples of commercial and spring mineral water, with DEHP concentration levels of 1.26 and 1.21 $ng.L^{-1}$, respectively, also showed the same tendency.

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