EVALUATION OF THE INPUT OF PHTHALATES IN PUBLIC WATER SUPPLY OF THE METROPOLITAN REGION OF SAO PAULO, BRAZIL: GUARAPIRANGA DAM

Juliana Ikebe Otomo [1*]
Elâine Arantes Jardim Martins [1]
Larissa Limeira da Silva [1]
Marycel Elena Barboza Contrim [1]
Maria Aparecida Faustino Pires [1]

Abstract

Many studies that assess the presence of endocrine disruptors in surface waters for public supply of major metropolises increase every year due to the effects of these substances can cause to human and wildlife even when in concentrations of µg and ng L^{-1}. This study determined dibutyl phthalate and diethyl phthalate in surface waters from the Guarapiranga dam, one of the largest reservoirs which supply the city of Sao Paulo, Brazil. The study indicates the presence of these compounds at concentrations between 0.33 µg L^{-1} and 12.92 µg L^{-1}. In treated water sample the concentrations were 0.36 µg L^{-1} for DBP and 0.27 µg L^{-1} for DEP. Even with low values of concentrations for these compounds it is very important further studies to be conducted in order to know the real health risk to the population served by these waters.

Keywords: dibutyl phthalate, diethyl phthalate, endocrine disruptors compounds, GC-MS, surface water

[1] Centro de Química e Meio Ambiente - Instituto de Pesquisas Energéticas e Nucleares/Comissão Nacional de Energia Nuclear.
**Autor corresponsal:* Centro de Química e Meio Ambiente, Instituto de Pesquisas Energéticas e Nucleares. Av. Lineu Prestes, 2242 - Cidade Universitária, São Paulo, SP. CEP 05508-000. Brasil. Email: julianaikebe@gmail.com

AVALIAÇÃO DO APORTE DE FTALATOS EM ÁGUAS DE ABASTECIMENTO PÚBLICO NA REGIÃO METROPOLITANA DE SÃO PAULO, BRASIL: REPRESA GUARAPIRANGA

Resumo

Estudos que avaliam a presença de interferentes endócrinos em águas superficiais destinadas ao abastecimento público de importantes metrópoles crescem a cada ano devido ao efeito que essas substâncias podem ocasionar nos seres vivos mesmo estando em concentrações de µg e ng L^{-1}. Este trabalho determinou dibutilftalato e dietilftalato em águas superficiais da represa do Guarapiranga, uma das maiores represas que abastecem a cidade de São Paulo, Brasil. O estudo aponta para a presença desses compostos em concentrações entre 0.33 µg L^{-1} e 12.92 µg L^{-1}. Em amostra de água tratada foram encontradas concentrações de 0.36 µg L^{-1} de DBP e 0.27 µg L^{-1}de DEP. Mesmo sendo valores baixos de concentrações é de suma importância que estudos complementares sejam realizados a fim de se conhecer o real risco à saúde da população abastecida por essas águas.

Palavra chave: água superficial, dibutilftalato, dietilftalato, GC-MS, interferente endócrino.

Introduction

After the Industrial Revolution society became to have a better quality of life where electronics are more present in day-to-day as well as a higher intake of processed foods, cosmetics and pharmaceuticals. As a consequence, it can be seen that there was a rapid and intense increase in production and generation of new chemicals (Otomo, 2010; Souza, 2011).

As a result of new consumption habits of the population there was also a change in the composition of the effluent released in water bodies and thus the concern with the quality of surface water intended for public supply increased. Different studies have been developed to understand the distribution, behavior and action of substances that, even in concentrations of µg e ng L^{-1}, are potentially harmful to living beings. Named as emerging micropollutants and including the endocrine disruptors compounds that are represented by estrogens, natural and synthetic female hormones, natural substances and a large amount of synthetic chemicals widely used by modern society (Bila, 2003; Girotto, 2007; Ghiselli, 2006; Reis Filho, 2006; Otomo, 2010; Souza, 2011).

The endocrine disruptors compounds are synthetic or natural chemical substances that have the ability to act on the endocrine system of humans and wildlife by mimicking natural hormones stimulating different responses from those which would originally generated by blocking the receptors in cells, preventing production of correct responses by stimulating the production of greater quantities than required or by inhibiting the production of natural hormones causing its deficiency (USEPA, 1997; ISTAS, 2002).

Environmental agencies from different countries with recognized influence like UKEA (United Kingdom Environment Agency), USEPA (United States Environmental Protection Agency), OSPAR (Oslo and Paris Commission), JEA (Japan Environmental Agency) and WWF (World Wildlife Fund) classified, among other substances, phthalates as endocrine disruptors, which are the subject of this work (Birkett & Lester, 2002).

Phthalates are present in a wide variety of products and consumer goods like cosmetics, personal care products, drugs capsules, medical and hospital supplies, toys, food packages, cleaning and construction supplies, solvents and lubricating oil. There are multiples routes of human exposure to phthalates due to the widespread use of these compounds, which may occur by ingestion, inhalation, dermal absorption and others. Contamination can also occur through breast milk and migration from the body of the mother to the baby through the placenta (Souza, 2011).

The determination of phthalates in aquatic matrices can be performed by different techniques, like gas chromatography and liquid chromatography, both coupled to mass spectrometry detector (GC-MS and LC-MS) which are the most widely used because of the great sensitivity and selectivity of these techniques (Grover, 2012; Souza, 2011).

Many studies indicate that this contamination is coming from various sources of pollution, but the main route of entry into the aquatic environment is via domestic and industrial wastewater, other routes are run-off in the streets of cities and agriculture, atmospheric deposition, hospital waste and pharmaceuticals industries, illicit drugs, fish-farming, leaking of landfills and deliberate disposition of disuse drugs and others (Sodré, 2011; Grover, 2012). The contamination worsens in large urban centers, especially due to use and occupancy of irregular areas near reservoirs.

In this context, this work aimed to evaluate the occurrence and distribution of anthropogenic input of phthalates, dibutyl phthalate and diethyl phthalate in surface waters of the Guarapiranga dam as well as treated water, using the technique of solid phase extraction followed by GC-MS analysis.

The Guarapiranga dam is considered one of the largest and most endangered among the 8 reservoirs that compose the integrated water supply system of Metropolitan Region of Sao Paulo. The reservoir is located in a highly populated region causing major environmental impact on water quality. This scenario is caused mainly due to the release of untreated sewage in the reservoir from neighborhoods by illegal settlements and disorderly occupation in your surroundings. The sewage and diffuse pollution are the main sources of pollution of the reservoir, with serious consequences for public supply much of the MRSP (Whately & Cunha, 2006).

Methodology

Study area

Guarapiranga Dam is located in the Metropolitan Region of Sao Paulo city, in Sao Paulo State, southeast Brazil (23°42'S, 46°43'W) at altitude of 737 m, an area of 36.18 km^2, a mean depth of 7 m and water volume of 253 10^6 m^3. This reservoir has been eutrophic for several decades and is characterized by environmental impacts from urban invasion, industrial and sewage wastes, all of which seriously affect its water quality (Fontana et al, 2014). In Table 1 geographic coordinates are shown for the 14 sites (Figure 2) chosen for sampling. The sampling was conducted on August 2011. Sampling of the water column was made with bottled van Dorhn, at 10 cm below the surface and transferred to 1 liter amber glass bottle previously decontaminated. Samples were kept refrigerated until they arrived at the laboratory.

Figure 1. Location of Guarapiranga Dam in the Metropolitan Region of Sao Paulo.

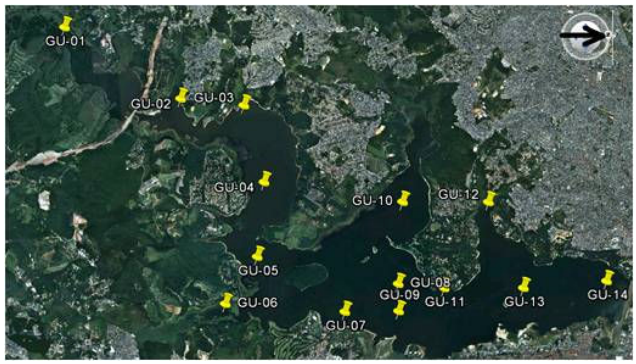

Figure 2. Location of 14 sample sites of superficial water in Guarapiranga Dam.

Table 1. Geographical coordinates of the sampling sites in Guarapiranga Dam.

Sampling site (Fig 1)	Geographical Coordinate	
GU-01	23°46'49.6"S	46°47'22.0"W
GU-02	23°45'29.5"S	46°46'18.7"W
GU-03	23°44'52.2"S	46°46'13.6"W
GU-04	23°44'44.6"S	46°45'25.8"W
GU-05	23°44'57.5"S	46°44'24.2"W
GU-06	23°45'01.2"S	46°43'61.5"W
GU-07	23°43'64.7"S	46°43'42.3"W
GU-08	23°42'96.9"S	46°43'61.2"W
GU-09	23°43'04.6"S	46°43'34.0"W
GU-10	23°42'89.9"S	46°44'68.7"W
GU-11	23°42'53.4"S	46°43'44.9"W
GU-12	23°41'88.5"S	46°44'67.3"W
GU-13	23°41'58.0"S	46°43'57.3"W
GU-14	23°40'78.2"S	46°43'55.9"W

Solid Phase extraction and CG-MS

In the laboratory, samples were subjected to the preparation procedure including filtration through glass fiber membrane with 0.45 µm porosity, acidification to pH 3 with hydrochloric acid solution (v/v 1:1) and extraction in a solid phase extraction cartridge filled with octadecyl (C_{18}). Initially, the cartridge was conditioned with ethyl acetate and methanol/H_2O (v/v1:9). One liter of the sample was percolated and the clean up was made with methanol/H_2O (v/v 1:9). For complete removal of water, the cartridge was placed under vacuum and then centrifuged for 25 minutes at 2500 rpm (rotation per minute). The elution of the analytes was made twice with 4 mL ethyl acetate/methanol (v/v 6:4). The extract was blow dried in a smooth flow of N_2 until 1 mL.

Sample analysis was performed by gas chromatography with detection by mass spectrometry (GC-MS) and the parameters defined in the equipment were: injector temperature 270°C; interface temperature 290°C; heating ramp from the column from 80°C to 280°C with isotherms at 210°C, 240°C and 280°C; column flow at 1.6 mL min^{-1}, injection 1µL extract using capillary column DB-5 (5% phenyl and 95% dimethylpolysiloxane, 30 m length, 0.25 mm internal diameter and 0.25 mm thick film of stationary phase) and data acquisition on SIM mode (single ion monitoring) by monitoring three mass fragments of each compound (149, 150, 223 to dibutyl phthalate and 149,176, 177 to diethyl phthalate). The method for determination of phthalates was developed and validated by Souza (2011), showing $r^2 > 0.99$ in the linearity range from 0.05 to 0.55 µg L^{-1}, precision of 3.1 to 11.8 for repeatability and 2.0 to 11.6 for reproducibility, limit of detection of 0.010 µg L^{-1} for DBP and 0.007 µg L^{-1} for DEP. Limit of quantification of 0.034 and 0.023 µg L^{-1} for DBP and DEP respectively, and recovery from 72 to 105%.

Results and discussion

In 100% of analysed samples were found concentrations of dibutyl phthalate (DBP) and diethyl phthalate (DEP) above their respective limits of quantification 0.05 µg L^{-1} e 0.01 µg L^{-1}. The obtained results are shown in Table 2, and the point 12 had the highest concentration of dibutyl phthalate as much as diethyl phthalate. During the sampling was found strong smell of sewage at this point, which corroborate with the results.

Table 2. Concentration of dibutyl phthalate and diethyl phthalate, in surface water samples from 14 sites of Guarapiranga dam, as well as treated water from August 2011.

Sampling sites	Dibutyl Phthalate (µg L^{-1})*	Diethyl Phthalate (µg L^{-1})*
GU-01	0.92±0.18	0.49±0.05
GU-02	0.94±0.06	0.56±0.03
GU-03	0.46±0.06	0.33±0.04
GU-04	0.51±0.05	0.36±0.04
GU-05	3.46±0.23	0.91±0.11
GU-06	1.44±0.23	0.86±0.14

GU-07	4.41±0.74	1.31±0.22
GU-08	2.99±0.28	0.90±0.07
GU-09	5.69±0.31	1.28±0.08
GU-10	9.15±0.94	1.06±0.09
GU-11	5.57±0.78	1.07±0.13
GU-12	12.92±0.54	1.88±0.20
GU-13	7.06±0.55	1.28±0.10
GU-14	4.02±0.48	0.70±0.10
Concentration range in surface water	0.46 to 12.92	0.33 to 1.88
Treated water	0.36±0.01	0.27±0.02

* average of three replicates with their respective measurement uncertainty (k=2 and 95% of confidence).

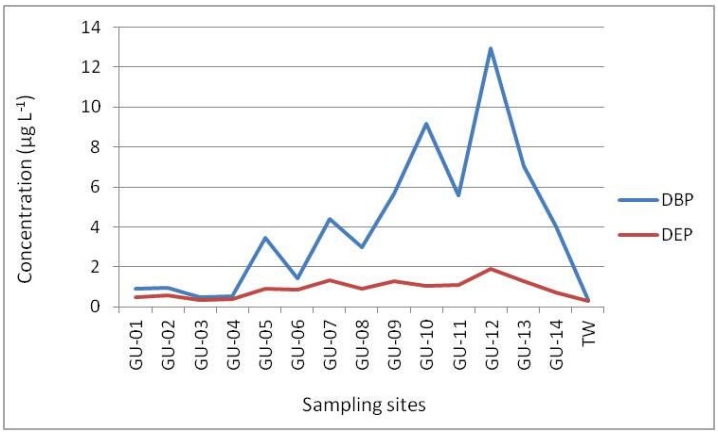

Figure 3. Concentration profile of DBP and DEP through the sampling sites

By results shown on Figure 3 can be concluded that the profile of dibutyl phthalate and diethyl phthalate had the same behavior. The concentrations of those pollutants increase as the points approach the urban area near the reservoir (Figure 1). Studies that assess the quality of surface water from reservoirs located in metropolitan regions show that high concentrations of these compounds are usually due to the presence of raw sewage from illegal discharges (Ghiselli, 2006; Sodré, 2011; Serôdio, 2006; SMA, 2008).

Other studies reported concentrations of DBP and DEP in superficial water for public supply at levels from 0.26 µg L^{-1} to 1.25 µg L^{-1} for DBP and 0.03 to 0.44 µg L^{-1} for DEP at Vale do Paraíba (Souza, 2011); 0.39 to 2.4 µg L^{-1} for DBP and 0.22 to 3.2 µg L^{-1} for DEP at Metropolitan Region of Campinas (Ghiselli, 2006); from <0.03 to 33.1 µg L^{-1} for DBP at Atibaia river (Raimundo, 2007). In treated water analysed in those studies concentration of 0.07 µg L^{-1} for DBP at Vale do Paraíba (Souza, 2011) and 1.75 µg L^{-1} at RMC (Ghiselli, 2006) were found, for DEP concentrations ranged from <0,02 µg L^{-1} (Souza, 2011) and 0.23 µg L^{-1} (Ghiselli, 2006). A group of 16 phthalates was assessed in a lake situated in the most urbanized city in southern China and the concentrations ranged from 0.01 to 0.32 µg L^{-1} for DEP and from 0.94 to 3.6 µg L^{-1} for DBP.

Considering that G000-14 is the capture point of the water treatment company, at that point was observed a reduction around 90% to 60% in concentration for dibutyl phthalate and diethyl phthalate respectively, comparing with concentration of those compounds in treated water. Even though the conventional treatment employed for the water company is not specific for these compounds.

Currently there are no limits for the presence of dibutyl phthalate and diethyl phthalate into surface water or water for public supply. However, due to the widespread production and use of dietilhexilftalato (DEHP) in industry on a larger scale, when compared to other phthalates, this compound was incorporated in the list of priority substances by the European Union (EU) and the World Health Organization (WHO), taking the limit of 8 µg L^{-1} established for

drinking water. USEPA (Environmental Protection Agency of the United States) regulates the Safe Drinking Water Act, with a maximum of 6 $\mu g\ L^{-1}$ for this same compound in drinking water (Serôdio, 2006).

Conclusion

The results obtained in the analysis of surface water in the Guarapiranga dam showed significant concentrations of dibutyl phthalate and diethyl phthalate, mainly near the dense urban settlement areas. Considering informations that only 50% of households in the vicinity of study area are served by sewage network, its possible associate the values found to raw sewage discharges at the reservoir.

The concentrations of phthalates in drinking water are about 20 times below the international limits established (EU and USEPA) for DEHP. However low concentrations of these compounds do not guarantee the health protection of the population, since the main characteristic of the endocrine disruptors class is causing adverse effects even in concentrations of $\mu g\ L^{-1}$ and $ng\ L^{-1}$. It is also important to consider that endocrine disruptor concentration on the environment must be evaluated along with their estrogenic potential. Furthermore, the organisms rarely interact with a single substance in the environment. Considering that, in general, the biota is exposed simultaneously to several compounds with different potential hazards present in the medium at different concentrations (Harris, 1997; Sodré, 2011). In this context, it's reinforced the idea that complementary studies such as in vitro tests to evaluate the estrogenic activity of the sample, are needed for a complete assessment of the risk posed to the population.

Acknowledgment - *The authors acknowledge the support of FAPESP funding through the Thematic Project 2009/53898-9 and CNPq nº 310214/2013-0.*

References

Bila, D. M.; Dezotti, M.(2003) Fármacos no meio ambiente. *Quimica. Nova* **26**(4), 523-530.

Birkett, J. W.; Lester, J. N. (2002) *Endocrine Disrupters in Wastewater and Sludge Treatment Processes*, IWA Publishing, Lewis Publishers CRC Press LLC: USA.

Fontana, L.; Albuquerque, A. L. S.; Brenner M.; Bonotto D. M.; Sabaris T. P. P.; Pires M. A. F.; Cotrim M. E B.; Bicudo D. C. (2014) The eutrophication history of a tropical water supply reservoir in Brazil, *J. Paleolimol.* **51**, 29-43

Girotto, G.; Nogueira, K.L.; Moura, J.A.; Souza, J.B.; Giacometti, L.L.; Marchi, M.R.R.; Tognolli, J.O. (2007) Estrógenos em água: otimização da extração em fase sólida utilizando ferramentas quimiométricas. *Eclética Química* **32**(2), 61-67.

Ghiselli, G. Avaliação da qualidade das águas destinadas ao abastecimento público na região de Campinas: ocorrência e determinação dos interferentes endócrinos (IE) e produtos farmacêuticos e de higiene pessoal (PFHP). Tese de doutorado, UNICAMP, Campinas, 2006.

Harris, C. A.; Henttu, P.; Parker, M. G.; Sumpter, J. P. (1997) The estrogenic activity of phthalate esters *in vitro*. *Environmental Health Perspectives*. **105**(8), 802-811.

ISTAS – Instituto sindical de trabajo ambeinte y salud. Curso de introdución a los disruptores endocrinos. 2002. Disponível em < http://www.istas.net/ma/decops/>. Acessado em 08 de fevereiro de 2010.

Raimundo, C.C.M. Ocorrência de interferentes endócrinos e produtos farmacêuticos nas águas superficiais da bacia do rio Atibaia. Dissertação de mestrado – Universidade Estadual de Campinas, UNICAMP, Campinas, 2007.

Reis Filho, R. W.; Araújo, J. C.; Vieira, E.M. (2006) Hormônios sexuais estrógenos: contaminantes bioativos. *Química Nova,* **29**(4), 817-822.

SMA (Secretaria do Meio Abiente) (2008) *Guarapiranga - Caderno Ambiental*, SMA/CEA, 84 p.

Serôdio, P.; Nogueira, J. M. F. (2006) Considerations on ultra-trace analysis of phthalates in drinking water. *Water Research,* 40, 2572–2582.

Sodré, F. F.; Montagner, C. C.; Locatelli, M. A. F.; Jardim, W.F. (2007) Ocorrência de interferentes endócrinos e produtos farmacêuticos em águas superficiais da região de Campinas (SP, Brasil). *J. Braz. Soc. Ecotoxicol*., **2**(2), 187-196.

Souza, R. R. Desenvolvimento e validação de metodologia analítica para determinação de disruptores endócrinos resultantes de atividades antrópicas nas águas da região do rio Paraíba do Sul, SP. Dissertação de mestrado, Instituto de Pesquisas Energéticas e Nucleares/USP, São Paulo, 2011.

Otomo, J. I. Desenvolvimento e validação de metodologia analítica para determinação de hormônios, considerados disruptores endócrinos, nas águas destinadas ao abastecimento público na região do rio Paraíba do Sul, SP. Dissertação de mestrado, Instituto de Pesquisas Energéticas e Nucleares/USP, São Paulo, 2010.

USEPA-United States Environmental Protection Agency; Special Report on Environmental Endocrine Disruption: An effects assessment and analysis, Washington, 1997

Whately, M.; Cunha, P. M. (2006) Guarapiranga 2006: como e porque São Paulo está perdendo este manacial: resultados e diagnóstico. São Paulo: Instituto Sócio Ambiental. 51p