

Monitoring of Pesticides and Polycyclic Aromatic Hydrocarbons in Water from Paraíba do Sul River, Brazil

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Estudou-se a qualidade da água do Rio Paraíba do Sul através da determinação das concentrações de alguns poluentes orgânicos prioritários, a saber, hidrocarbonetos policíclicos aromáticos (HPAs) e pesticidas. Duas cidades foram selecionadas, Resende e Campos dos Goytacazes, três sítios em cada, por apresentarem atividades industriais e agrícolas. O estudo foi desenvolvido entre Julho de 2001 a Março de 2002. O método envolveu a extração de 200 mL de amostra por extração em fase sólida utilizando cartucho polimérico OASIS, seguido pela análise por cromatografia gasosa acoplada a espectrometria de massas (CG/EM). A recuperação e o desvio padrão para amostras de água real não poluída dopada com padrões de pesticidas foi de 82-119% e menos de 20%, respectivamente. Para os HPAs, a recuperação e o desvio padrão foram de 56-78% e menos de 18%, respectivamente, com exceção do acenafileno, 23% e 2,7%. Atrazina foi detectada em uma concentração média de $0,231 \mu\text{g L}^{-1}$ em dois sítios em Campos dos Goytacazes, nas proximidades de usina e plantações de cana de açúcar, enquanto em Resende não foi detectada. Irgarol foi observado no centro de Campos dos Goytacazes a uma concentração de $0,138 \mu\text{g L}^{-1}$, uma área com atividades de barcos de pequeno porte. Benzo[a]pireno foi detectado em Resende a uma concentração de $0,255 \mu\text{g L}^{-1}$, próximo a rodovia Presidente Dutra. HPAs não foram detectados nas amostras de água de Campos dos Goytacazes.

The Paraíba do Sul River, in the State of Rio de Janeiro, was studied for its water quality, by determining the levels of selected polycyclic aromatic hydrocarbons (PAHs) and pesticides from six sites in two cities, Resende and Campos dos Goytacazes, as they have industrial and agricultural activities. This study was carried out between July 2001 and March 2002. The method involved 200 mL samples taken by off-line, solid phase extraction by OASIS polymeric cartridges followed by gas chromatography-mass spectrometry (GC-MS). Recoveries and standard deviation of pesticides in non polluted real water sample spiked with a standard mixture were 82-119% and less then 20%. For PAH, recoveries and standard deviation were 56-78% and less then 18%, respectively, with exception to acenaphthylene, 23% and 2.7%. Atrazine was detected in the average concentration of $0.231 \mu\text{g L}^{-1}$ in two sites in Campos dos Goytacazes, near the sugar-cane power plants and plantations area, while no detection was observed in Resende. Irgarol was observed in Campos dos Goytacazes downtown at $0.138 \mu\text{g L}^{-1}$, an area of small boating activities. Benzo[a]pyrene was detected at $0.255 \mu\text{g L}^{-1}$ in Resende, near the Presidente Dutra highway. PAHs were not detected in the water samples from Campos dos Goytacazes.

Keywords: atrazine, water, PAHs, pesticides, GC-MS

Introduction

National and international pressure is growing for water quality improvement and better management. The need for monitoring some important groups of dangerous organic pollutants, such as polyaromatic hydrocarbons (PAHs), pesticides, phenolic compounds, alkyl and aromatic sulfonates in surface waters is essential for

achieving good water-quality objectives. The European list of the priority organic compounds to be monitored from discharges is the Directive EC 76/464¹ while Brazilian regulations are CONAMA no. 20 from the Environmental Ministry and regulation no. 1469 from the Health Ministry. Regulations for drinking water are well defined in North America with given analytical procedures, whereas in Europe the regulation for each pesticide is set at $0.1 \mu\text{g L}^{-1}$ and for polyaromatic hydrocarbons, total of 6 compounds is set at $0.2 \mu\text{g L}^{-1}$.^{2,3}

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Atrazine was introduced in the 1950s, and since that has become a commonplace in agricultural and forestry applications. For instance, atrazine is used to control annual grasses and broad-leaved weeds in selected vegetable and cereal crops, vines, sugar cane, grassland, fruit orchards, citrus groves, and forestry. It is the most widely used herbicide in the world, with between 70,000 and 90,000 tons applied per year. It is one of the most effective and inexpensive herbicides in the world and is consequently used more frequently than any other herbicide. In recent years, concerns have been raised regarding its persistence within the environment and entry into groundwater and the aquatic environment. Atrazine is most effective in wet soils and is therefore usually applied after significant winter rain when soils are at field capacity.⁴ Banning atrazine completely would cost \$240 million, with no improvement in water quality. Banning all triazines would improve water quality, but it would cost nearly \$740 million. The most effective policies appear to be atrazine restrictions based on federal health limits of $3 \mu\text{g L}^{-1}$ or $100 \mu\text{g L}^{-1}$, water quality was greatly improved at a cost of between \$160-\$230 million.⁵

Polycyclic aromatic hydrocarbons are widespread contaminants throughout the environment arising mainly from anthropogenic sources such as the combustion from fossil fuels and the direct release of oil and oil products. These widespread environmental contaminants have been intensively studied owing to their mutagenic and carcinogenic properties. Some of the PAHs are classified as priority pollutants by both the US EPA and the European Community.⁶

This study aims to carry out a survey of selected organic micropollutants in the water samples from Paraíba do Sul River, focusing on three sites each in two important cities in the State of Rio de Janeiro, Resende and Campos dos Goytacazes, that suffers industrial and agricultural impact, and also to carry out a partial validation of the used methodology.

Experimental

Sampling sites

The city of Campos dos Goytacazes (latitude $21^{\circ}45'15''\text{S}$ and longitude $41^{\circ}19'28''\text{W}$) with about 398,547 inhabitants, is the most important city in the northern part of the state of Rio de Janeiro. It is basically an agricultural area, in which the sugar cane plantation is the main economic activity with sugar/alcohol power plants.

The city of Resende (around latitude $22^{\circ}28'\text{S}$ and longitude $44^{\circ}27'\text{W}$) with about 120,000 inhabitants and

an area of 407 km², is an important city in the southern part of the state of Rio de Janeiro. It is an industrial area with agricultural (tomato, corn, rice, bean) and ecological activities. Some industries in this area are Clariant, Volkswagen Brazil, Norvartis and Cyanamid Brazil.

Three sites were chosen in each city for sampling: sites 1 and 4, just before downtown; 2 and 5, downtown the cities; 3 and 6, after passing through downtown. The unpolluted river water sample was sampled from an ecological site, Lumiar, Nova Friburgo (RJ; latitude $22^{\circ}16'55''\text{S}$ and longitude $42^{\circ}31'52''\text{W}$). Figure 1 shows the Paraíba do Sul River map, with the two cities in study.

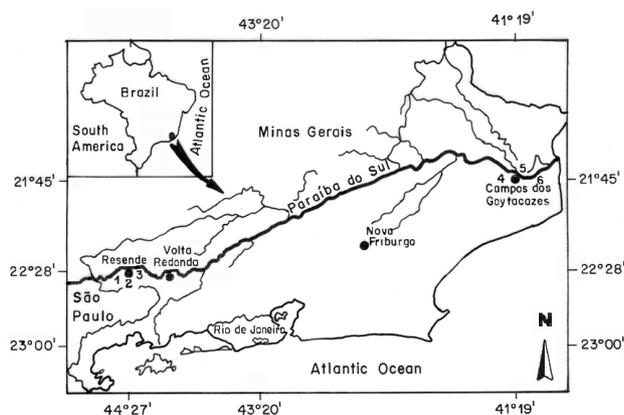


Figure 1. Map from the selected sampling sites.

Chemicals

The standards used were 98-99% pure. It was studied 10 compounds (Table 1). Pesticides standards were obtained from Promochem (Wesel, Germany) and Riedel-de Haën (Seelze, Germany). Irgarol was from Ciba-Geigy (Barcelona, Spain). Polycyclic aromatic hydrocarbons standard as Phenanthrene, Fluoranthene, Pyrene, Chrysene and Benzo[a]pyrene are from Sigma/Aldrich (USA). Stock solutions of $1000 \mu\text{g mL}^{-1}$ were prepared by weighing 10

Table 1. Retention time, diagnostic m/z ions, calibration equation and coefficients of correlation (R^2) in SIM mode of organic compounds using SPE followed by GC/MS

Compounds	t_r	m/z	Calibration equation	R^2
Simazine	24.6	186/201	$Y = 117951X - 3430$	0.999
Atrazine	24.8	173/200	$Y = 203607X - 45917$	0.994
Alachlor	27.7	160/188	$Y = 58162X + 659$	0.999
Irgarol	30.4	182/238	$Y = 11767X - 2048$	0.999
Acenaphthylene	18.7	152	$Y = 723244X - 4774$	0.999
Phenanthrene	25.5	178	$Y = 886338X - 184998$	0.993
Fluoranthene	30.5	202	$Y = 484806X + 11008$	0.995
Pyrene	31.3	202	$Y = 802262X - 13653$	0.994
Chrysene	36.6	228	$Y = 431547X - 10253$	0.994
Benzo[a]pyrene	41.7	252	$Y = 188424X - 6306$	0.997

mg of each of the solutes and dissolving them in 10 mL of chromatographic-grade dichloromethane or acetonitrile (TediaBrazil, Rio de Janeiro). They were then stored at $-20\text{ }^{\circ}\text{C}$. Dichloromethane and acetonitrile ABSOLV (chromatographic grade) were from TediaBrazil, acetic acid was purchased from Grupo Química (Rio de Janeiro, Brazil).

Sampling

The samples were collected at July and October/2001 and March/2002. All the water samples were sampled at 20 cm depth using 1 L precleaned amber glass bottles (avoiding the surface micro-layer). Samples were acidified with acetic acid to pH 4.0, filtered through 1.2 and $0.45\text{ }\mu\text{m}$ glass fiber filters in order to remove suspended particles and kept at $4\text{ }^{\circ}\text{C}$ in the dark until analysis.

SPE extractions

The OASIS cartridges (60 mg, Waters, USA) were washed sequentially with 6 mL of dichloromethane, 6 mL of acetonitrile and 6 mL of water. A 200-mL aliquot of sample was passed through the cartridge and then washed with 1 mL of water. Water residues from cartridges were eliminated by 30 min vacuum. Elution was carried out with 2.5 mL of acetonitrile-dichloromethane (1:1) followed by 3.2 mL of dichloromethane.⁷

The C18 (200 mg, PR-COLA) and the Bond-Elut Certify (130 mg, Varian, PN: 1211-3054) cartridges were washed sequentially with 6 mL of methanol and 6 mL of bidistilled water. A 200 mL aliquot of sample was passed through the cartridge and then washed with 1 mL of water. Water residues from cartridges were eliminated by 30 min vacuum. Elution was carried out with 6 mL of methanol for the C18 cartridges and with 2 mL dichloromethane/isopropanol (8:2) with 2% ammonium hydroxide solution (make fresh daily) for the Bond-Elut Certify.

Evaporation of the solvents was performed under a stream of nitrogen. The final sample volumes were $200\text{ }\mu\text{L}$.

GC/MS conditions

Gas chromatography-mass spectrometry analysis were performed in a Hewlett Packard 5890 gas chromatography coupled to a Hewlett Packard 5972 MSD Instrument utilizing helium as carrier gas and the following conditions: fused silica column DB-5 (J & W, 30 m X 0.25 mm, $d_f = 0.25\text{ }\mu\text{m}$), $60\text{ }^{\circ}\text{C}$ for 2 min to $300\text{ }^{\circ}\text{C}$ at $6\text{ }^{\circ}\text{C min}^{-1}$, splitless injection mode (time of 1 min), temperature of injector was set at $280\text{ }^{\circ}\text{C}$. Electron impact at 70 eV was

used. All samples were analysed in Single Ion Monitoring (SIM) mode for quantification purposes of the compounds, Figure 2 (major ions corresponding to the typical fragments of the compounds were selected, Table 1).

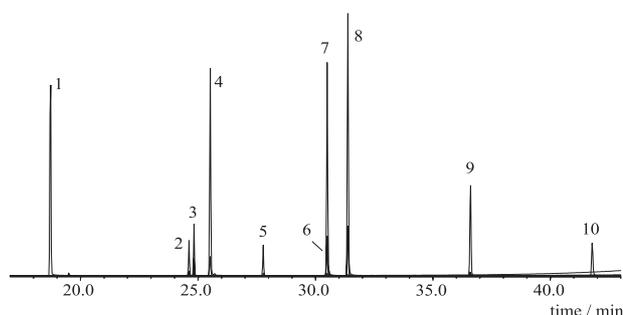


Figure 2. Overlaid mass fragmentograms in SIM mode from the standard compounds in study at $0.7\text{ }\mu\text{g L}^{-1}$. (1) Acenaphthylene (m/z 152), (2) Simazine (m/z 201), (3) Atrazine (m/z 200), (4) Phenanthrene (m/z 178), (5) Alachor (m/z 160), (6) Irgarol (m/z 182), (7) Fluoranthene (m/z 202), (8) Pyrene (m/z 202), (9) Chrysene (m/z 228), (10) Benzo[a]pyrene (m/z 252).

Recoveries

Recoveries obtained with distilled water samples spiked with standard compounds were tested in different conditions. Three different SPE cartridges were evaluated: C18 (PR-COLA, Brazil), Bond-Elut Certify (Varian, Harbor City, CA, USA), OASIS (Waters). The water pH was also evaluated; water sample with and without addition of acetic acid (pH 4.0).

Unpolluted river water samples were also used for OASIS SPE cartridge. The compounds were spiked in 200 mL of water to give a final concentration of $1.0\text{ }\mu\text{g L}^{-1}$ and subsequently the water was acidified at lower pH (pH 4.0). Immediately after this operation, the water samples were extracted.

The recovery were determined by comparison of peak areas from water samples spiked with known amount of organic pollutants ($1.0\text{ }\mu\text{g L}^{-1}$), processed according to the described method versus non-extracted pure standards which represent 100% recovery.

External calibration was used to the quantification of the extract after SPE with the standard mixture. The calibration equations for the different compounds were constructed and were linear ($R^2 > 0.99$) over the range $0.05\text{-}1.0\text{ }\mu\text{g L}^{-1}$. The quantification of the water was achieved using SIM with the ions indicated in Table 1. The limits of detection (LODs) were calculated by using a signal-to-noise ratio of 3 (the ratio between the peak intensity under SIM conditions and the intensity of the noise was used) and are presented in Table 2. Recoveries are presented in Table 3.

Table 2. Limits of detection (LOD) in $\mu\text{g L}^{-1}$ of the standard compounds in study with different cartridges tested: C18 (PR-Cola), Bond-Elut Certify (Varian) and Oasis (Waters). Unpolluted river water spiked with $1.0 \mu\text{g L}^{-1}$ of organic pollutants

Compounds	C18	Bond-Elut	Oasis
Simazine	0.02	0.04	0.0005
Atrazine	0.016	0.003	0.0005
Alachlor	0.0006	0.0006	0.001
Irgarol	0.004	-	0.0002
Acenaphthylene	0.20	0.04	0.0009
Phenanthrene	0.0004	0.0001	0.0003
Fluoranthene	0.002	0.0001	0.0003
Pyrene	0.002	0.0001	0.0002
Chrysene	0.0007	0.0004	0.0002
Benzo[a]pyrene	0.004	0.004	0.001

Limits of detection for OASIS cartridges

A calibration curve consisted of six concentration points from 0.01, 0.025, 0.05, 0.10, 0.20 to $0.50 \mu\text{g}$ of organic pollutants per 1 L of unpolluted river water. These spiked water samples were passed through the OASIS cartridges. The calibration equations for the different compounds were constructed and were linear ($R^2 > 0.99$) over the range $0.01\text{--}0.5 \mu\text{g L}^{-1}$. The limits of detection (LODs) were calculated by using a signal-to-noise ratio of 3 and the constructed calibration curve (Table 4).

Table 3. Mean recovery, \bar{x} (%), confidence limits, CL (%), coefficient of variation, CV (%), standard deviation, SD (%), for replicates ($n = 4$; 3 degree of freedom), using Student *t*-test (95%; $t_{\text{tab}} = 3.182$). Spiked sample at $1.0 \mu\text{g L}^{-1}$. River water volume: 200 mL

Atrazine	$\bar{x} \pm \text{CL}$ (%)	CV (%)	SD (%)	Fluoranthene	$\bar{x} \pm \text{CL}$ (%)	CV (%)	SD (%)
Oasis d	117.2± 12.3	6.6	7.7	Oasis d	105.2± 12.3	7.3	7.7
Oasis d/pH=4	94.9± 24.4	16.1	15.3	Oasis d/pH=4	87.0± 25.5	18.4	16.1
Oasis r pH=4	106.3± 19.7	11.7	12.4	Oasis r pH=4	78.3± 22.4	18.0	14.1
C18 d/pH=4	80.6± 3.3	2.6	2.1	C18 d/pH=4	71.4± 20.8	18.3	13.1
C18 d	91.1± 13.6	9.4	8.5	C18 d	44.2± 18.2	25.9	11.4
BE d (n=2)	73.8± 49.4	42.1	31.0	BE d (n=2)	50.2± 35.3	44.3	22.2
BE d/pH=4	87.1± 10.9	7.9	6.9	BE d/pH=4	47.5± 11.6	15.4	7.3
Simazine				Pyrene			
Oasis d	101.8± 15.4	9.5	9.7	Oasis d	72.4± 16.4	14.3	10.3
Oasis d/pH=4	95.2± 19.0	12.5	11.9	Oasis d/pH=4	84.8± 25.5	18.4	16.1
Oasis r pH=4	81.6± 16.6	12.8	10.4	Oasis r pH=4	72.8± 13.0	11.2	8.1
C18 d/pH=4	91.6± 19.1	13.1	12.0	C18 d/pH=4	34.7± 4.3	7.8	2.7
C18 d	80.7± 22.4	17.5	14.1	C18 d	51.6± 14.3	17.4	8.9
BE d (n=2)	71.4± 43.5	38.3	27.4	BE d (n=2)	62.2± 39.2	39.6	24.6
BE d/pH=4	24.8± 7.1	17.9	4.5	BE d/pH=4	74.7± 36.7	30.8	23.0
Irgarol				Chrysene			
Oasis d	112.1± 33.1	18.5	20.8	Oasis d	104.7± 38.1	22.9	24.0
Oasis d/pH=4	98.6± 32.8	20.9	20.6	Oasis d/pH=4	84.2± 27.0	20.2	17.0
Oasis r pH=4	119.4± 25.6	13.5	16.1	Oasis r pH=4	77.7± 5.1	4.1	3.2
C18 d/pH=4	47.9± 16.9	22.2	10.6	C18 d/pH=4	12.4± 2.0	10.2	1.3
C18 d	88.9± 20.7	14.6	13.0	C18 d	25.7± 8.4	20.6	5.3
BE d (n=2)	nd	nd	nd	BE d (n=2)	13.7± 4.6	20.9	2.9
BE d/pH=4	nd	nd	nd	BE d/pH=4	32.5± 7.6	14.6	4.8
Alachlor				Benzo[a]pyrene			
Oasis d	84.4± 43.0	32.2	27.01	Oasis d	76.4± 11.4	9.4	7.2
Oasis d/pH=4	99.4± 19.0	12.5	11.9	Oasis d/pH=4	108.2± 14.1	8.2	8.8
Oasis r pH=4	117.0± 32.5	17.4	20.4	Oasis r pH=4	55.6± 5.0	5.7	3.2
C18 d/pH=4	81.0± 31.2	24.2	19.6	C18 d/pH=4	31.0± 16.9	34.3	10.6
C18 d	39.9± 25.8	40.6	16.2	C18 d	14.1± 2.5	11.2	1.6
BE d (n=2)	146.8± 71.2	30.5	44.7	BE d (n=2)	nd	nd	nd
BE d/pH=4	55.8± 20.6	23.2	13.0	BE d/pH=4	nd	nd	nd
Phenanthrene				Acenaphthylene			
Oasis d	77.1± 34.1	27.8	21.4	Oasis d	41.3± 31.2	47.5	19.6
Oasis d/pH=4	69.9± 36.7	33.0	23.1	Oasis d/pH=4	26.9± 23.7	55.7	14.9
Oasis r pH=4 (n=3)	62.5± 12.8	12.8	8.0	Oasis r pH=4 (n=2)	23.2± 4.2	11.5	2.7
C18 d/pH=4	48.2± 36.7	33.0	27.3	C18 d/pH=4	8.5± 9.7	71.7	6.1
C18 d	46.2± 3.7	5.0	2.3	C18 d	8.6± 3.2	23.5	2.0
BE d(n=2)	50.2± 26.5	38.4	16.6	BE d (n=2)	3.5± 3.2	23.5	2.0
BE d/pH=4	60.9± 46.6	48.1	29.3	BE d/pH=4	4.9± 9.7	71.7	6.1

d = distilled water; r = unpolluted river water; in bold = the conditions used with the real water samples.

Table 4. Limits of detection (LOD) in $\mu\text{g L}^{-1}$, calibration equation and coefficients of correlation (R^2) in SIM mode of the standard compounds using OASIS cartridges. Unpolluted river water spiked with organic pollutants at 0.01, 0.025, 0.05, 0.10, 0.20 and $0.50 \mu\text{g L}^{-1}$

Compounds	LODs	Calibration equation	R^2
Simazine	0.01	$Y = 194858X + 1950$	0.9968
Atrazine	0.008	$Y = 285362X - 1508.8$	0.9996
Irgarol	0.003	$Y = 361595X - 274$	0.9985
Acenaphthylene	0.0005	$Y = 370727X + 597$	0.999
Phenanthrene	0.01	$Y = 864858X + 7159$	0.9991
Fluoranthene	0.005	$Y = 1000000X - 4485.4$	0.9995
Pyrene	0.006	$Y = 1000000X - 5442.4$	0.9996
Chrysene	0.025	$Y = 514641X + 6775$	0.9992
Benzo[a]pyrene	0.025	$Y = 174736X + 1269$	0.9965

Quantification

External standard calibration was used for quantification of the extracts. Calibration graphs for SIM mode was plotted using 4-6 points in the concentration 0.05, 0.10, 0.25, 0.5, 0.75 and 1 mg mL^{-1} . Calibration equations obtained in SIM mode and R^2 values are presented in Table 1 for GC/MS.

Results and Discussion

Partial validation

Data obtained with standard compounds are presented in Table 3. Recovery (%), confidence limits (CL, %), coefficient of variation (CV, %), standard deviation (SD, %), for replicates ($n = 4$; 3 degree of freedom), using Student t -test (95%; $t_{\text{tab}} = 3.182$) were determined. These parameters were well within the acceptance criteria of the accuracy of 70-130% and precision of 30% for organic compounds at trace level in water samples, according to the US-EPA methods general characteristics.³

The calibration curves constructed were linear over the range of interest. The correlation coefficients were in all cases higher than 0.99, indicating good performance of the chromatographic method (Table 1). Recoveries with OASIS cartridges for real water samples were around 82-119% and standard deviation were no more than 20 for pesticides standards and 56-78% and 18% for polycyclic aromatic hydrocarbons, respectively. Detection limits (Table 2) were in the range of 0.0002 - $0.001 \mu\text{g L}^{-1}$ obtained for distilled water spiked with standard compounds and percolated through the cartridges (far below $0.1 \mu\text{g L}^{-1}$) being good enough for trace levels determination, taking into account that 200 mL of water were percolated through the cartridges. Low recovery value was observed for

acenaphthylene, 23% as it is a volatile compound and it is lost at the evaporation steep.

The choice for working with OASIS cartridges was based on the recoveries data obtained also with the other tested cartridges. Recoveries and standard deviation for distilled water spiked with the standard mixture and with C18 cartridges were 40-91% (SD = 16%) for pesticides and 14-46% (11%) for PAH, while in pH 4.0 were 58-92% and 20% for pesticides and 12-71% and 27% for PAH (Table 3). Recoveries for Bond-Elut Certify were from not detected to 147% (SD = 45%) for pesticides and nd to 62% (25%) for PAH without acetic acid addition and from nd to 87% (13%) for pesticides and nd to 75% (29%) for PAH in pH 4.0. The data for Oasis cartridges and distilled water samples spiked with standard mixture were 84-117% (27%) for pesticides and 72-105% (24%) for PAH and 95-99% (21%) for pesticides and 84-105% (25%) for PAH in pH 4.0.

It is easy to observe that worse results were obtained with Bond-Elut Certify in the conditions tested. The C18 cartridges generated worse results mainly to PAH. Oasis cartridges presented better results to both class of studied compounds: pesticides and PAH, as we were looking for a SFE cartridges that would permit to analyse both class of compounds. Data with real water sample spiked with the standard mixture showed a reduction in the recoveries values, as would be expected, although still being the better results.

Detection limits of polycyclic aromatic hydrocarbons are in the $0.010 \mu\text{g L}^{-1}$ range.¹ In this study we observed values in the range 0.0005 up to $0.025 \mu\text{g L}^{-1}$ (Table 4) when unpolluted river water samples spiked with the standard mixture at different concentrations were analysed. The pesticides gave detection limits in the range 0.003 - $0.01 \mu\text{g L}^{-1}$, below the observed values in a previous paper.⁷

Application to a case study

Water samples from the Paraíba do Sul River were analyzed following the proposed method in six sites from two cities, in three distinct dates. The analytical protocol was applied to the analysis of real environmental samples. Analytes monitored in this study were chosen because they are commonly detected in surface waters and they are on the priority lists of the Brazilian Environmental Ministry (CONAMA no. 20/1986) and Health Ministry (regulation no. 1469/2000) and also of the United State Environmental Protection Agency (US-EPA) and European Community (e.g., Directive 76/464/EEC).

Triazines

Highest reported concentrations of atrazine are associated with the first rainfall after application. The level of atrazine in river water varies seasonally with the highest concentrations found in the spring and summer months. The impact of atrazine on fish physiology occurs at concentrations as low as $3 \mu\text{g L}^{-1}$. Atrazine has been detected in drinking water reservoirs up to $88.4 \mu\text{g L}^{-1}$, and in rivers up to $100 \mu\text{g L}^{-1}$.⁴

Atrazine showed a rather constant concentration over time in two sites in Campos dos Goytacazes, in a average concentration of $0.231 \mu\text{g L}^{-1}$. These sites are near the sugarcane power plants and plantations area. No detection was observed in downtown of Campos dos Goytacazes and in Resende. Figure 3 presents summaries of atrazine concentrations found in freshwater bodies around the world and in Campos dos Goytacazes, this work.

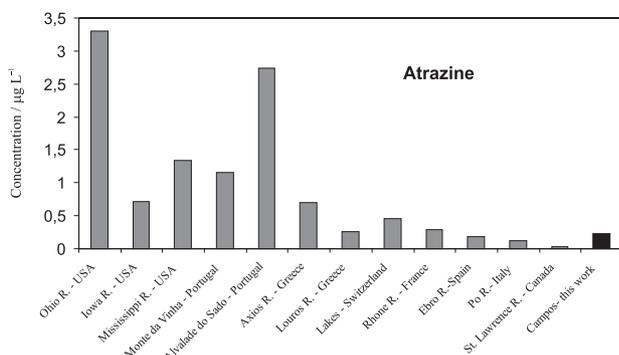


Figure 3. Reported values for atrazine concentrations in water bodies ($\mu\text{g L}^{-1}$) around the world and in this study.

Irgarol, the herbicide 2-(methylthio)-4-(tert-butylamino)-6-(cyclopropylamino)-s-triazine (tradename Irgarol 1051) was also detected. Irgarol 1051 is effective mostly against freshwater and seawater algae and less against animal organisms. Some studies showed that the substance is very toxic to all microalgae tested; EC_{50} values range from 0.45 to 2.12 mg L^{-1} .⁸ This compound is used in antifouling paints as a biocide agent. The herbicide is added in paints in order to inhibit the primary growth of fouling organisms such as algal slimes and seaweeds.^{9,10} Data are available concerning Irgarol contamination of aquatic environment. Studies had been undertaken in Côte d'Azur,¹⁰ the southern coastal of the U.K.,¹¹ Lake Geneva,⁸ seawater from Mediterranean Spanish Coast^{9,10} and river and coastal water from Portugal.⁷ Irgarol are added to ship/boat paints to prevent fouling and diffuse into the surrounding waters and contaminate environments.

The observed concentration of Irgarol in downtown of Campos dos Goytacazes water (138 ng L^{-1}) was only three

times lower than the lowest EC_{50} reported for algae (450 ng L^{-1}). Figure 4 presents summaries of Irgarol concentrations found in water bodies around the world and in Campos dos Goytacazes, this work. Figure 5 shows mass fragmentogram in SIM mode for atrazine (Figure 5A; m/z 200) and Irgarol (Figure 5B; m/z 182) in river water samples from downtown of Campos dos Goytacazes and from standard compounds spiked at a final concentration of $0.20 \mu\text{g L}^{-1}$ in an unpolluted river water sample (Figures 5D and 5E).

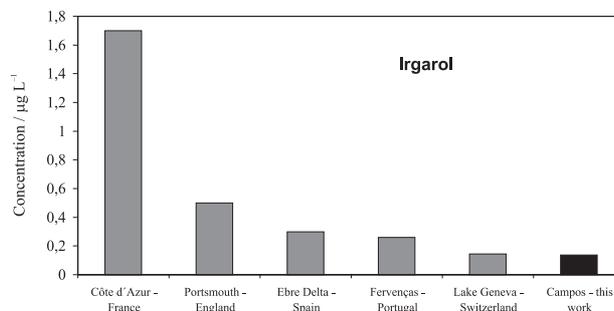


Figure 4. Reported values for Irgarol concentrations in water bodies ($\mu\text{g L}^{-1}$) around the world and in this study.

Polycyclic aromatic hydrocarbons

Benzo[a]pyrene was detected only at $0.255 \mu\text{g L}^{-1}$ in Resende (July/2001), near the Presidente Dutra highway. This is illustrated in Figure 5C, while Figure 5F shows the m/z 252 mass fragmentogram from the corresponding benzo[a]pyrene standard spiked at a final concentration of $0.20 \mu\text{g L}^{-1}$ in an unpolluted river water sample. PAHs were not detected in the water samples from Campos dos Goytacazes. In a previous work regarding PAHs in the Paraíba do Sul River, concentration values of benzo[a]pyrene were from $0.03 \mu\text{g L}^{-1}$ up to $1.2 \mu\text{g L}^{-1}$ near the CSN industry (National Siderurgical Company, the most important industry in this area with metallurgical activities), in the Volta Redonda city¹² (see map).

The Brazilian regulations (CONAMA n° 20/1986) specify that benzo[a]pyrene detection should not exceed $0.01 \mu\text{g L}^{-1}$ in drinking water, while Brazilian Health Ministry (regulation n°. 1469/2000) specify a value of $0.70 \mu\text{g L}^{-1}$. Lethal concentration (LD_{50}) down to less than $10 \mu\text{g L}^{-1}$ for total PAHs (ΣPAHs) has been reported for various organisms and is used as a threshold value.¹³ Imperative and maximum admissible concentration of polycyclic aromatic hydrocarbons (total of 6 compounds; fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) in surface water for drinking water purposes is $0.2 \mu\text{g L}^{-1}$ in the EC regulations.¹

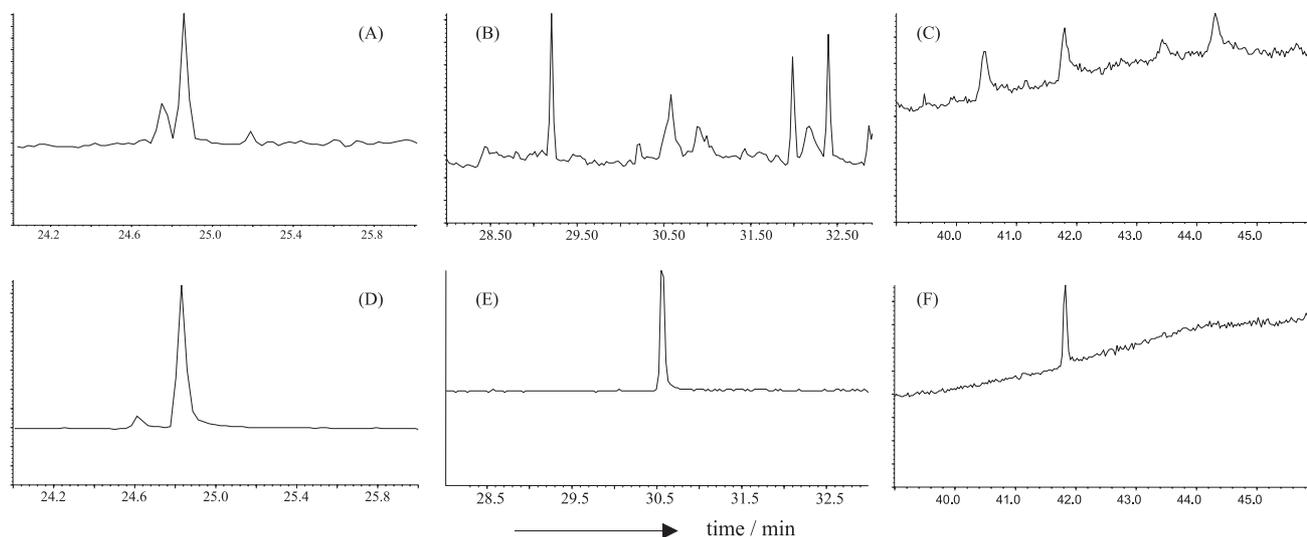


Figure 5. Paraíba do Sul River water samples: (A) m/z 200 mass fragmentogram, atrazine characteristic ion, from downtown of Campos dos Goytacazes (October/2001); (B) m/z 182 mass fragmentogram, Irgarol characteristic ion, from downtown of Campos dos Goytacazes (July/2001); (C) m/z 252 mass fragmentogram, benzo[a]pyrene characteristic ion, from Resende (July/2001); Unpolluted water sample spiked with $0.20 \mu\text{g L}^{-1}$ of each standard, after passing through the Oasis cartridges; (D) m/z 200 mass fragmentogram of Atrazine; (E) m/z 182 mass fragmentogram of Irgarol; (F) m/z 252 mass fragmentogram of Benzo[a]pyrene.

Total parent PAH concentrations (ng L^{-1}) in sub-surface water from various marine sites in the world were: $0.300\text{--}0.594 \text{ ng L}^{-1}$ in the Baltic Sea, $4\text{--}36 \text{ ng L}^{-1}$ in Seine River and Estuary (France), $106\text{--}945 \text{ ng L}^{-1}$ in Western Xiamen Bay¹⁴ (China), $4228\text{--}29325 \text{ ng L}^{-1}$ in Daya Bay¹³ (China).

Conclusion

Precision, accuracy, linearity, specificity and limits of detection were determined for four pesticides and six polycyclic aromatic hydrocarbons investigated in this study using Oasis cartridge solid phase extraction followed by GC/MS analysis. This methodology was applied to real river water samples from the Paraíba do Sul in two distinct cities where the main pollution would be from industrial and agricultural activities. The detected compounds were atrazine and Irgarol (triazines pesticides) in downtown of Campos dos Goytacazes and benzo[a]pyrene in Resende. The detected concentration values were around $0.2 \mu\text{g L}^{-1}$.

Among the organic pollutants determined in this study, atrazine is caused by agricultural contamination, mainly from sugar-cane crops; Irgarol is used in boating paints and benzo[a]pyrene has an fossil fuel origin.

Although this analytical method were optimised and applied for analysing 75 organic compounds, mainly pesticides, halogenated compounds and phenols, in river water samples from Portugal in a previous paper,⁷ in the present one we extended the method to the detection of polycyclic aromatic hydrocarbons and applied for analysing Brazilian river water samples.

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References

- Hennion, M.-C.; Pichon, V.; Barceló, D.; *Trends Anal. Chem.* **1994**, *13*, 361.
- Barceló, D.; Hennion, M.-C.; *Trace Determination of Pesticides and Their Degradation Products in Water*; Elsevier: Amsterdam, 1997.
- Barceló, D.; *J. Chromatogr.* **1993**, *643*, 117.
- Greymore, M.; Stagnitt, F.; Allison, G.; *Environ. Int.* **2001**, *26*, 483.
- Lakshminarayan, P.G.; Bouzaher, A.; Shogren, J.F.; *J. Environ. Manage.* **1996**, *48*, 111.
- Zhou, J.L.; Hong, H.; Zhang, Z.; Maskou, K.; Chen, W.; *Wat. Res.* **2000**, *34*, 2132.
- Azevedo, D.A.; Lacorte, S.; Vinhas, T.; Viana, P.; Barceló, D.; *J. Chromatogr. A* **2000**, *879*, 13; Azevedo, D.A.; Lacorte, S.; Viana, P.; Barceló, D.; *J. Braz. Chem. Soc.* **2001**, *12*, 532.
- Tóth, S.; Becker van Slooten, K.; Spack, L.; de Alencastro, L. F.; Tarradellas, J.; *J. Bull. Environ. Contam. Toxicol.* **1996**, *57*, 426.
- Ferrer, I.; Barceló, D.; *J. Chromatogr. A* **1999**, *854*, 197.
- Tolosa, J.; Readman, J. W.; Blaevet, A.; Ghilini, S.; Bartocci, J.; Gorvat, M.; *Mar. Pollut. Bull.* **1996**, *32*, 335.

11. Gough, M. A.; Fothergill, J.; Hendrie, J. D.; *Mar. Pollut. Bull.* **1994**, 28, 613.
12. COPPE/UFRJ. Programa Estadual de Investimentos da Bacia do Rio Paraíba do Sul - RJ. Análise Ambiental. MPO/SEPURB/PQA-ABC-PNUD-UFRJ/COPPE. BRA/96/017 PROJECT, 1999. (www.hidro.ufrj.br).
13. Zhou, J.L.; Maskaoui, K.; *Environ. Pollut.* **2003**, 121,269.
14. Maskaoui, K.; Zhou, J.L.; Hong, H.S.; Zhang, Z.L.; *Environ. Pollut.* **2002**, 118, 108.

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