SHORT COMMUNICATION

Evaluation of polar phenolic compounds in water samples close to shale exploitation area: a case study

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Abstract

Polar phenolic compounds of anthropogenic sources are widely studied by the scientific community since their effects are considered harmful to aquatic biota. From an environmental point of view, information regarding the presence of these contaminants allows promoting broader studies of environmental assessment. An evaluation of the presence of phenol, *o*-cresol, *m*-cresol, *p*-cresol, and 2,4-dimethylphenol in aqueous samples was carried out, to investigate the possibility of contamination owing to the shale mining activities in the most important Brazilian oil shale reserve, in the region of São Mateus do Sul, Paraná State, Brazil. Ten water samples were collected near this region and the five mentioned phenolic compounds were preconcentrated using a previously validated liquid-phase microextraction procedure. Their quantitation was realized by liquid chromatography coupled with diode array detector. The presence of phenol was estimated in some samples below 3.3 μg L^{-1} and 2,4-dimethylphenol was determined (4.7 μg L^{-1}) in one sample, whereas the cresols were not found in any sample. To confirm the presence or the absence of the analytes, the samples were spiked with the phenolic compounds, and satisfactory recovery values between 52.2 and 120.5% and relative standard deviations less than 17.2% for triplicate samples of these compounds were observed, suggesting that this chromatographic/extraction method was adequate for quantitation of these compounds in environmental samples and wastewater from shale mining area. The results suggested no contribution of the phenolic compounds as pollutants of the rivers and streams for the studied area owing to the shale activities.

Keywords Mining operations · Rivers · Phenol · Cresols · Liquid-phase microextraction · Liquid chromatography

Introduction

The shale industry has afforded a relevant alternative source of fossil fuels concerning the conventional sources, since its abundance in nature. The shale is a complex mixture of organic and inorganic components, mainly marl and clays, in which the organic matter and the kerogen are distributed as a fine and heterogeneous form (Tian et al. 2018; Wang et al. 2018). However, the exploitation of shale may have undesirable effects on the environment. The various stages of mining and processing can generate residues rich in highly toxic organic and inorganic substances, which can cause adverse effects in the environmental compartments and the different life forms (Zhong et al. 2018a). Among these species, a variety of phenolic compounds (PC) can be released in soils and water bodies, affecting the entire balance of the ecosystem.

These PC correspond to a wide range of organic compounds, whose structures present one or more hydroxyls groups directly bonded to an aromatic ring. These compounds are found naturally in plants, mainly as flavonoids, stilbenes and lignins, and have several biological functions in human beings: anticarcinogenic, antioxidant, antidiabetic, antiproliferative and present immune-stimulating properties

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(Hajji et al. 2018; Rai et al. 2018). Also, PC have an important role in the industrial branch, in synthesis of resins, flavorings and perfumery items (Cesari et al. 2017).

However, in addition to the natural occurrence, synthetic PC can be introduced into aquatic environment through anthropogenic activities that include oil refinery wastewater, fossil fuels combustion, industrial activities like steel, plastics, pharmaceutics and others (Lavilla et al. 2012; Salcedo et al. 2019; Dörter et al. 2020), being detected in waters of several countries. Their presence in natural waters becomes a worldwide concern due to their toxicity and bioaccumulation in plants and animals, providing adverse effects in the most diverse forms of life (Zhong et al. 2018a). Many of these PC eventually converge to the environment due to the industrial activities, like food, petrochemical and pesticides industries, increasing their concentrations in all environment (Duan et al. 2018).

Because of the importance of the presence of PC in different environmental matrices, recent reports have been published. Zhong et al. (2018b) studied fifty PC in samples from three different Chinese rivers, and seventeen PC were found in water samples, in higher concentrations in water than sediments and suspended particulate. This fact points out the needing for a more rigorous evaluation of water quality. Another research group (Wang et al. 2016) determinates the presence of a variety of PC with properties of endocrine disruptors in water and sediment samples from various points of an urban river in China. According to the authors, the presence of PC compounds in river water was mainly related to the high population, the industrial sources and the sewage. Acosta et al. (2018) determined the total concentration of PC in samples of river water from Argentina, and higher concentrations than those permitted by the Argentine legislation for waters to recreational use (5.0 μg L^{-1}) were observed, which showed that the total PC presented a significant contribution as pollutant in the water samples.

Despite of these works, little attention has been dedicated to the PC with low molar mass and high polarity as phenol and cresols under the environmental perspective (Michałowicz et al. 2008; Roots and Roose 2013; Zhong et al. 2018b), although some reports devoted to the validation of analytical methods have been published, including for determination of these PC (Dolatto et al. 2016; Zhao and Lee 2001).

The PC are usually found in relatively low concentrations in water samples, therefore the preconcentration step of these compounds is necessary to accomplish quantifiable levels and reliable results. For this purpose, several procedures have been employed, such as conventional liquid–liquid extraction (LLE), solid-phase extraction (SPE) and the miniaturized procedures as the liquid-phase microextraction (LPME), dispersive liquid–liquid microextraction (DLLME), solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE) (Dolatto et al. 2016; Kovács et al. 2011).

The presence of PC in water samples has been reported mainly based on industrial, agricultural and domestic activities (Anku et al. 2017; Raza et al. 2019). However, to the best of our knowledge, no studies related to the possibility of water contamination by polar PC from shale mines exploitation activities were reported so far in the literature. Considering this lack of information about the presence and quantitation of PC in waters related to shale exploitation, in the present work was proposed a method that might be used preliminarily, for diagnosis and possible monitoring of PC contamination present inside and around a shale exploitation area. This evaluation was based on a spatial analysis, through the determination of (Ph), *o*-cresol (*o*-Cr), *m*-cresol (*m*-Cr), *p*-cresol (*p*-Cr) and 2,4-dimethylphenol (2,4-DMPh) in water samples. In this work, it was used the LPME technique for preconcentration of the previously mentioned PC in water samples collected near a shale exploitation area, and it used the liquid chromatography coupled to diode array detector (LC-DAD) technique for quantitation of these compounds.

Materials and methods

Equipments, reagents and solutions

The analytical standards of Ph, *o*-Cr, *m*-Cr, *p*-Cr and 2,4-DMPh (purity higher than 99.0%) and the solvent for extraction (*n*-octanol) used in this work were acquired from Sigma-Aldrich®. For the preparation of the mobile phase the solvent acetonitrile (HPLC grade) was purchased from Carlo Erba (Rodano, Italy). Other reagents used in this work were of analytical grade and were supplied from Carlo Erba, J.T Baker, Merck or Sigma-Aldrich. A reverse osmosis system from Quimis (Diadema, SP, Brazil) model Q842-210, was used to produce water for the Simplicity UV water purifying system from Millipore (Molsheim, France). This water presented resistivity higher than 18 MΩ cm and was designed as ultrapure water that was employed for the preparation of all solutions in this work. All glassware was previously decontaminated with alkaline detergent solution, rinsed with tap water, distilled water, ultrapure water and dried in a place protected from dust. The stock standard solutions of Ph, *o*-Cr, *m*-Cr, *p*-Cr and 2,4-DMPh were prepared in methanol (HPLC grade) individually at 1000 mg L^{-1} and maintained into amber glass at 4 °C. Some physicochemical properties of the studied PC are shown in Table 1 that shows high solubility and polar character of the analytes, due their log of octanol/water partition coefficient K_{ow} values (lower than 3).

Table 1 Physicochemical properties of phenol (Ph), *o*-cresol (*o*-Cr), *m*-cresol (*m*-Cr), *p*-cresol (*p*-Cr) and 2,4-dimethylphenol (2,4-DMPh)

Parameter	Ph	*o*-Cr	*m*-Cr	*p*-Cr	2,4-DMPh
Solubility (g L^{-1} at 20 °C)	93.0	25.0	23.0	23.5	5.0
pK_a (25 °C)		9.89	10.20	10.01	10.17	10.60
log K_{ow} (25 °C)		1.46	1.95	1.98	1.94	2.35

Chromatographic analysis

Quantitation of the PC was carried out via LC-DAD, using the chromatographic system from Waters (Milford, MA, USA). The LC-DAD modules consisted in: a quaternary pump (Waters 600E), a heated compartment to maintain the column temperature at 40 °C, an automatic sampler (Waters 717 Plus) with a volume of 20 µL, a degasser (In Line AF), and a DAD (Waters 2998) at the wavelength of 270 nm, using the software Empower 2 for the acquisition of the signals. For the PC separation, an octadecylsilane column (Kromasil AkzoNobel, Bohus, Sweden) with the dimensions of 250×4.6 mm and particle size of 5 µm was used. The isocratic elution was carried out using a mobile phase 60:40 composed by acetic acid solution 1.0% (v v^{-1}) and acetonitrile at a flow rate of 1.0 mL min^{-1}. The mobile phase was previously filtered through a 0.45 µm PTFE membrane (47 mm), whereas the samples were filtered using 0.45 µm disposable PTFE membrane (13 mm), before the injections. All analyses were carried out in triplicate.

Sampling and preparation of water samples

The surface water samples were collected in April of 2015 from the city of São Mateus do Sul, state of Paraná, South of Brazil, which is located in latitude 25°53′S–50°20′W and longitude 25°46′S–50°26′W, approximately 150 km away from the city of Curitiba, capital of the state of Paraná. At this location, the Irati pyrobituminous oil shale (Irati formation), which is the most important Brazilian oil shale reserve, is exploited by Oil Shale Industrialization Business Unit of Petrobras Inc.

The water samples were collected from rivers, streams and effluents, in ten different points, near this shale exploitation area. Table 2 shows the identification of the collection points (P1–P10) and the approximate distance from the active mine (Dois Irmãos Mine), whereas Fig. 1 shows the sampling sites. All samples were collected in 1 L amber glass bottles with polyethylene lids which were previously decontaminated using alkaline detergent and exhaustively rinsed with tap water, followed by 10 mL of acetonitrile, distilled water (10 times), ultrapure water (5 times) and dried in an oven at 40 °C for 24 h. The water samples were collected from the surface (30 cm depth) of the collection points. The 1-L flasks were filled and transported in an ice bath to minimize the risks of degradation and volatilization of the analytes. These samples were filtered under vacuum using cellulose nitrate membranes (0.45 µm, 47 mm), stored under refrigeration (4 °C) and all the determinations were performed before 7 days.

Extraction of the phenolic compounds

A miniaturized extraction procedure (LPME) was employed to extract the PC from the aqueous samples, according to the previous paper (Dolatto et al. 2016). Briefly, 50.0 mL of aqueous solution containing mixed solution of the standards PC prepared in NaCl ionic medium (15.0% w v^{-1}) was added in a 50.0 mL volumetric glass flask and acidified with HCl to provide a final concentration of 0.01 mol L^{-1}, and next, it was added 900 µL of *n*-octanol. With the aid of a magnetic stirrer, the aqueous and organic phases were stirred for 5 min at 600 rpm, and after a rest of 5 min for the phases

Table 2 Points of collection of water samples in the region of São Mateus do Sul, Paraná State, Brazil

Code	Place	Samples information	Distance from DIM (km)
P1	Taquaral River	Downstream DIM	2.8
P2	Effluent of DIM	Upstream DIM	0.3
P3	Iguaçu River	Downstream DIM	8.6
P4	Iguaçu River	Upstream DIM	11.2
P5	Canoas Stream	Downstream Sul Lake area	2.8
P6	Sul Lake (effluent)	Upstream Sul Lake area	6.2
P7	Jaguatirica Stream	Downstream RPM	0.5
P8	RPM (effluent)	Upstream RPM	0.4
P9	Plant (effluent)	Industrial effluent of the plant	6.7
P10	Stream of experimental area	Stream near Shale area	2.0

DIM Dois Irmãos Mine, *RPM* Rio das Pedras Mine

Fig. 1 Sampling sites of the superficial water in the region of São Mateus do Sul. The codes P1–P10 are identified according to Table 2
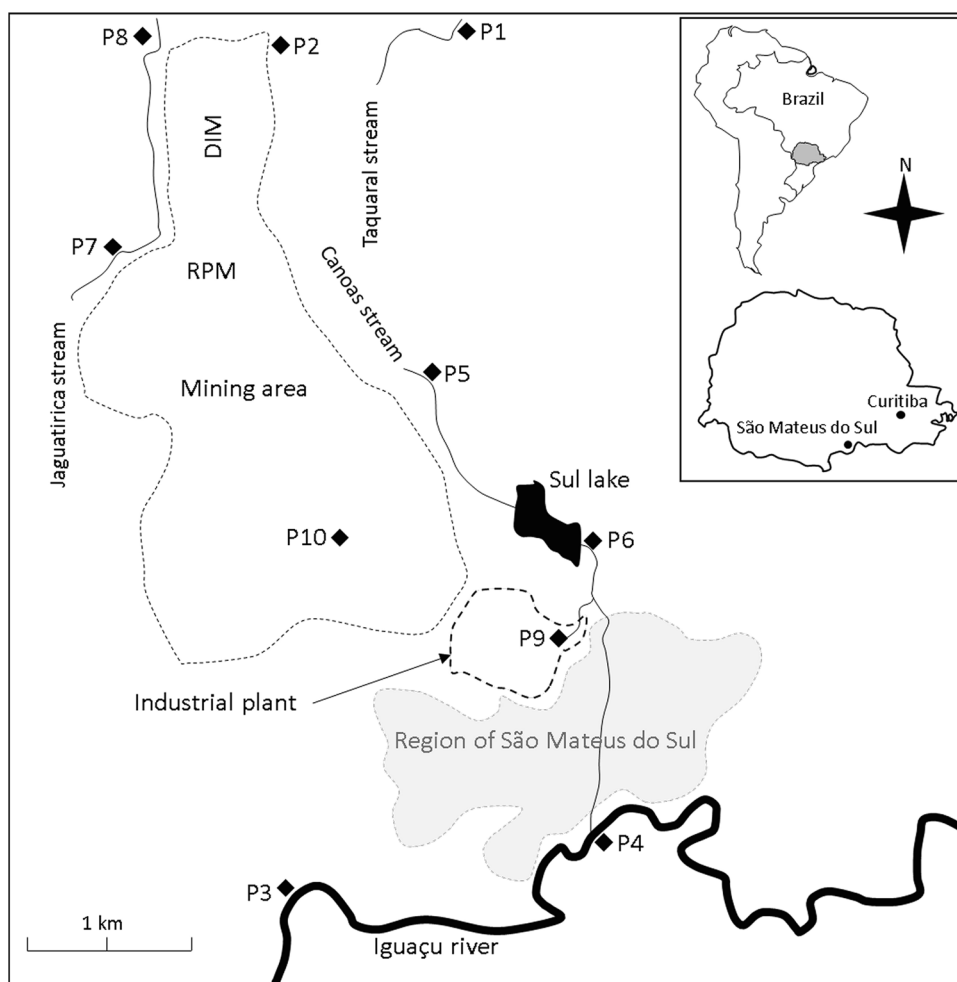
separation, an aliquot of 650 μL of the organic phase was withdrawn and transferred to a 15 mL glass centrifuge tube containing 250 μL of 0.60 mol L^{-1} NaOH solution. A vortex was used to accomplish the mixture of the phases for 1 min, and then, the suspension was centrifuged at 2800 rpm (5 min). An aliquot of 230 μL of the alkaline aqueous solution was transferred to a chromatographic vial containing a mixture of 200 μL of acetonitrile plus 70 μL of concentrated acetic acid.

This same procedure was used to prepare the analytical curves (five points) in the concentration range from 2.50 to 50.0 μg L^{-1} (Ph, m-Cr + p-Cr and o-Cr) and from 12.5 to 100.0 μg L^{-1} for 2,4-DMPh. These analytical curves were generated in our previous work, and, among the figures of merit, were obtained LOQ of 1.4, 1.2, 1.2 and 11.4 μg L^{-1} for Ph, $o + m$-Cr, p-Cr and 2,4-DMPh, respectively, with r^2 higher than 0.9970 in all cases.

Subsequently, a recovery study using the LPME method was performed using the water samples (except samples P5 and P7). Aliquots of the samples (25 mL) were fortified with 100 μL of a working solution containing the mixture of phenolic compounds spiked at the concentration levels: 3.0, 15.0 and 40.0 μg L^{-1} (Ph, o-Cr and m-Cr + p-Cr) and at 15.0 and 40.0 μg L^{-1} (2,4-DMPh). Then the solution was stirred for 30 min, filtered through a syringe with PTFE membranes with a porosity of 0.45 μm. The filtered solution was subjected to a microextraction procedure. All the experiments were carried out in triplicate. The results were evaluated in terms of the statistic parameters such as correlation coefficient (r), mean ± standard deviation (SD) and relative standard deviation (RSD).

Results and discussion

In the present study, the interest was related to the presence of the more polar PC (Ph, o-Cr, m-Cr, p-Cr and 2,4-DMPh) in water samples. Because of the physicochemical properties, such as low molar mass, log K_{ow} values and high solubility in water (Table 1), these analytes present high mobility in waters and soils. These compounds could arise in the water samples due to the proximity to the industrial area of oil shale extraction and processing. Based on a previous study (Dolatto et al. 2010), the PC here studied seem not to

be sorbed by soils, but highly susceptible to biodegradation process in this environment. Their physicochemical characteristics suggest that these PC compounds could be more susceptible to remain in the aqueous medium rather than in the soils, and for these reasons, our focus was to investigate the water bodies.

The analytical LPME procedure was not studied in the present work, but the optimization of the extraction conditions was carefully investigated in our previous paper (Dolatto et al. 2016), as well as the respective figures of merit applied to different natural waters, tap water and soil extract. Thus, the LPME method was applied to the surface waters identified in Table 2, aiming to develop a way for monitoring of PC in wastewater from an industrial plant for shale exploitation, and different natural water bodies around this plant. This kind of work had never been related in the literature.

It is important to inform that, in chromatograms, no separation between the chromatographic peaks of m-Cr and p-Cr was possible, and for this reason, both cresols were quantified together (Dolatto et al. 2016).

No presence of m-Cr + p-Cr was verified, as well as for o-Cr, based on the absence of chromatographic peaks for these PC. This suggests that these compounds were absent, or below the limit of quantitation of the method (LOQ) that was previously determined as 1.2 µg L^{-1}, or even below the limit of detection (LOD), between 0.3 and 0.4 µg L^{-1} since no distinction was verified between the chromatograms in comparison with the baseline of the blank experiments. For 2,4-DMPh, only for the sample P4 (Iguaçu River, upstream mining area) it was possible to estimate the concentration close to 4.7 µg L^{-1}, but this value was also below the LOQ (11.6 µg L^{-1}) and below the first concentration from the analytical curve (12.5 µg L^{-1}), and, hence, should be evaluated with caution. For Ph, no signal was observed for samples P1 and P2 suggesting the absence of this compound in these samples. For the samples P3, P4, P6, P8, P9 and P10, it was verified some chromatographic peaks, but below the concentration of the first point of the analytical curve (2.50 µg L^{-1}) and also below the LOQ (1.4 µg L^{-1}), suggesting the Ph presence, but without the possibility of its quantitation. For samples P5 (Canoas Stream) and P7 (Jaguatirica Stream), the concentrations of 3.3 ± 0.7 and 2.6 ± 0.4 µg L^{-1} were observed, respectively, being sample P5 downstream Sul Lake and P7 downstream Rio das Pedras Mine, that could explain the presence of Ph in these samples; or even they could be due to the natural lignin biodegradation in soils (Datta et al. 2017), or still from other industrial activities (Abdelkreem 2013; Duan et al. 2018). These results were close to the values established for total PC in waters destined for public water supply, according to Brazilian regulation (3 µg L^{-1}), but much lower than the limit for discharge of effluents in Brazil (500 µg L^{-1}) (CONAMA 2011). Because of the suspicion of water contamination by PC in the region,

the sample P9 (effluent from the plant) was included in the study, but as already commented, the concentrations were also below the LOQ. It is important to inform that the samples P7 and P8 were collected in the vicinity of Rio das Pedras Mine, which is no longer active. The absence of PC in Iguaçu River downstream Dois Irmãos Mine (DIM) (sample P3) and upstream DIM (sample P4), suggested that the DIM do not cause impact in terms of PC in the region. In general, if one considers all the results observed for the PC (samples P1–P10), they were indicative of no surface water bodies contamination, even under the shale mining activities in the industrial area. Perhaps, the absence of the PC in the water samples is related to the half-life of these species in aquatic medium. The half-lives for Ph and 2,4-DMPh in water reported in the literature is 55 h and 77 h, respectively (Wang et al. 2012), while for o-Cr, m-Cr and p-Cr, values up to 50 days, 49 days and 6 days were reported (U.S. National Library of Medicine 2019). Moreover, the PC are easily biodegraded in soils (Dolatto et al. 2010; Wang et al. 2012; U.S. National Library of Medicine 2019) and this aspect could contribute to minimize the concentrations of these compounds in the water samples.

There are no specific studies about the PC here studied related to the evaluation of water contamination owing to shale exploitation. Despite this, some studies aiming the determination of these compounds in a diversity of waters samples were carried out, and a great variability in terms of concentration can be observed as shown in Table 3.

Although in most of the works presented in Table 3 other PC were evaluated (mainly chlorophenols and nitrophenols), we presented only the results for the compounds investigated in the present work for comparison purposes. For most of the samples, PC were not detected, agreeing with our results, although some relatively high concentrations of cresols were observed for one river in China, up to 269 and 271 µg L^{-1} for m-Cr and p-Cr, respectively (Zhong et al. 2018b).

Despite the PC concentrations were not significant, and the LPME method was previously validated (Dolatto et al. 2016), an additional recovery study was carried out using eight water samples, except samples P5 and P7, in which the PC concentrations were above the LOQs of the LPME method. For this study, three levels of Ph, o-Cr and m-Cr + p-Cr concentration were investigated, one close to the first point of the analytical curves, in the middle of the curves and near the highest concentration, whereas for 2,4-DMPh the concentrations of 15.0 and 40.0 µg L^{-1} were evaluated.

In Table 4 are shown the recovery results between 52.2% (Ph, 40.0 µg L^{-1}, sample P9) and 120.5% (o-Cr, 3.0 µg L^{-1}, sample P3). If only the lower concentration were considered (3.0 or 15.0 µg L^{-1}), results between 78.0 (sample P8) and 114.1% (sample P1) for Ph, 75% (samples P9 and P10) and 118.0% (sample P2) for m-Cr + p-Cr, 71.9% (sample P9) and 120.5% (sample P3) for o-Cr, and from 59.7% (sample P6) to

Table 3 Range or values of concentration for phenol (Ph), *o*-cresol (*o*-Cr), *m*-cresol (*m*-Cr), *p*-cresol (*p*-Cr) and 2,4-dimethylphenol (2,4-DMPh) in some waters samples, reported in the literature

Water sample	Ph	*o*-Cr	*m*-Cr	*p*-Cr	2,4-DMPh	References
Rivers	ND–15.5	ND–52.6	ND–269	ND–271	ND–90.6	Zhong et al. (2018b)
Rivers	ND–0.773	NE	NE	ND–0.097	NE	Michałowicz et al. (2008)
Rivers	NI	NI	2.1	2.3	NI	Roots and Roose (2013)
Tap and reservoir	NE	NE	ND	NE	ND	Zhao and Lee (2001)
Tap, river and mineral	ND	NE	NE	NE	ND	Faraji et al. (2009)
Wastewater	ND–15.5	NE	NE	NE	ND–3.3	Saraji and Marzban (2010)
Well, river and tap	ND	NE	NE	NE	NE	Alcudia-León et al. (2011)
Groundwater and river	0.28–14.41	0.02–0.33	ND–0.16	0.02–0.85	NE	Kovácz et al. (2011)
River and lake	ND–<4.09	ND–<0.77	NE	<0.78–1.72	NE	Shang et al. (2014)
River and lake	ND	NE	NE	NE	ND	Zhong et al. (2016)
Tap, sea, river and groundwater	ND	ND	ND	ND	ND	Dolatto et al. (2016)
Rivers and streams	ND–3.3	ND	ND	ND	ND–<11.6	This work

ND not detected, or concentration between LOD and LOQ, *NE* not evaluated, *NI* not informed

Table 4 Evaluation of accuracy in terms of recovery percentages (REC, %) and the relative standard deviation (RSD, %) for the determination of phenol and cresols in surface water samples from the region of São Mateus do Sul, PR, Brazil. The codes (P1–P10) are according to Table 2

Spike	P1	P2	P3	P4	P6	P8	P9	P10
µg L^{-1}	REC %							
Ph								
3.0	114.1 (6.1)	90.0 (1.4)	90.1 (3.0)	79.1 (2.0)	90.4 (3.4)	78.0 (7.3)	80.8 (1.4)	87.5 (3.0)
15.0	95.8 (2.3)	101.7 (7.7)	94.0 (2.0)	84.1 (3.8)	93.7 (6.4)	93.1 (5.3)	79.4 (2.7)	82.4 (7.3)
40.0	86.2 (2.6)	96.3 (8.9)	93.8 (9.5)	78.8 (5.3)	84.9 (9.0)	84.2 (9.6)	52.2 (8.6)	91.9 (3.5)
m-Cr+*p*-Cr								
3.0	93.5 (5.8)	118.0 (2.2)	83.2 (7.9)	75.5 (0.1)	92.3 (0.1)	75.2 (2.7)	75.0 (5.9)	75.0 (5.9)
15.0	79.6 (6.5)	80.0 (7.4)	83.8 (3.9)	78.4 (1.4)	81.9 (6.0)	81.9 (2.1)	83.1 (0.4)	83.1 (0.4)
40.0	80.4 (4.7)	77.0 (7.9)	82.5 (9.4)	75.0 (4.4)	74.2 (8.1)	80.8 (2.4)	77.1 (8.6)	77.1 (8.6)
o-Cr								
3.0	100.7 (10.5)	94.2 (7.4)	120.5 (1.6)	85.1 (7.4)	90.0 (8.3)	77.9 (9.6)	71.9 (0.3)	98.9 (9.1)
15.0	95.8 (10.7)	100.6 (7.2)	96.7 (2.4)	79.8 (3.2)	92.6 (6.5)	86.9 (3.5)	108.2 (4.6)	104.1 (1.0)
40.0	92.4 (5.1)	96.2 (8.4)	92.2 (10.1)	75.8 (3.6)	83.2 (9.1)	84.2 (1.6)	84.6 (8.6)	95.0 (0.9)
2,4-DMPh								
15.0	73.5 (7.6)	89.5 (13.0)	75.5 (0.7)	88.6 (3.1)	59.7 (6.7)	74.6 (1.3)	109.5 (11.5)	74.2 (17.2)
40.0	82.9 (3.0)	91.0 (6.3)	79.3 (5.3)	78.1 (2.7)	71.9 (3.3)	81.3 (5.1)	97.1 (5.5)	57.7 (4.9)

Relative standard deviation values, RSD % in parentheses

109.5% (sample P9) for 2,4-DMPh were verified. Although it would be an important evaluation in lower concentrations, this aspect was limited by the LPME method and the LC-DAD technique, and for this reason concentrations lower than 3.0 µg L^{-1} were not investigated. It is important to mention that this method was selected owing to its simplicity of execution and robustness. The LOQ values of the protocol were considered adequate for the application, since for total phenols in effluents (500 µg L^{-1}) and waters for public supply (3 µg L^{-1}), they are below those values established by Brazilian environmental legislation (CONAMA 2011).

The results here obtained, indicated that a future evaluation of the PC presence in the region would be essential and requires the application of strategies with superior detectability. Most of the samples presented relative standard deviation (RSD) lower than 10% (Table 4). The highest RSD value was 17.2% for 2,4-DMPh at concentration of 15.0 µg L^{-1} (sample P10). In general, the recovery and RSD results are in good agreement with the literature employing dispersive liquid–liquid microextraction to extract the same analytes in refinery effluents, being determined recoveries between 74 and 96% with RSD values up to 14% (Salcedo

et al. 2019). For this study, ten samples were considered enough in order to evaluate the presence of PC in rivers, streams and effluents with high probabilities of the presence of the analytes. In addition, recovery studies were carried out mostly to increase the reliability of the evaluation. The results may be considered satisfactory in terms of accuracy and precision, mainly if one considers the complexity of the LPME method and samples, suggesting an appropriate reliability for the determination of the PC evaluated; and, hence, corroborate that there is not contamination by PC in the waters surrounding the shale mines.

Although PC were not detected in most samples, the method used in this work had already been shown to be appropriate for the determination of these compounds in several environmental samples (Dolatto et al. 2016). However, the present study showed that this method is also suitable for the determination of these compounds in wastewater from the shale exploration industry, since the spiking and recovery experiments have showed, in most of the water samples, acceptable results and low RSD values in determination of the studied PC.

This work proposed the determination of PC based only on a spatial study. For a better understanding of the presence and distribution of PC in this industrial area, however, it would be necessary to carry out a larger spatial study, with more collection points, and a temporal study, so that the concentrations of species are constantly verified throughout longer times. As this study aimed to propose the possibility of using a previously validated method as a possible way for monitoring PC, and not effectively monitoring, the number of samples was relatively small ($n = 10$ samples) and the temporal study was not carried out.

Conclusion

Shale mining activities in the region of São Mateus do Sul, Paraná State, Brazil do not cause water contamination by phenolic compounds of rivers and streams located about mines. Despite this, two out of ten samples presented phenol concentration values close to the maximum value established by the Brazilian current legislation, considering the total PC concentration. Based on the results here presented, and despite no water contamination in the vicinity of the active and inactive mines, we consider relevant to extend the investigation of water resources on this region focused not only in PC but also in other potential contaminants that could be present owing to shale mining and processing.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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