



N-compounds speciation analysis in environmental samples using ultrasound-assisted solid–liquid extraction and non-chromatographic techniques

Ailton José Moreira · Carolina Dakuzaku Freschi · Ernesto Chaves Pereira · Gian Paulo Giovanni Freschi

Received: 19 October 2020 / Accepted: 19 April 2021
© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2021

Abstract A fast, efficient, and non-chromatographic method was presented in this study for nitrite, nitrate, and *p*-nitrophenol (N-compounds) extraction and speciation analysis of environmental samples. By applying ultrasound-assisted solid–liquid extraction (USLE), analytes were efficiently extracted from water, soil, or sediment collected in areas of environmental disaster. These analytes were selectively converted to $\text{NO}_{(\text{g})}$ through UV photolysis (NO_3^-), H_2O_2 /UV photocatalysis (PNP), and direct conversion (NO_2^-). Following conversion, $\text{NO}_{(\text{g})}$ was separated from the liquid phase and determined by high-resolution continuum source molecular absorption spectrometry (HR-CS MAS). The LODs obtained were

$0.097 \pm 0.004 \text{ mg L}^{-1}$ for nitrite, $0.119 \pm 0.004 \text{ mg L}^{-1}$ for nitrate, and $0.090 \pm 0.006 \text{ mg L}^{-1}$ for *p*-nitrophenol. On applying this speciation method to environmental samples, concentrations were found to be up to $0.99 \pm 0.03 \text{ mg L}^{-1}$ (NO_2^-), $49.80 \pm 2.5 \text{ mg L}^{-1}$ (NO_3^-), and $0.10 \pm 0.02 \text{ mg L}^{-1}$ (PNP). Finally, addition/recovery study of real water, soil, and sediment samples showed $101 \pm 2\%$ recovery for NO_2^- , $100 \pm 1\%$ for NO_3^- , and $96 \pm 5\%$ for PNP.

Keywords Spectroscopy · Extraction · Speciation · Environmental samples

Highlights

1. Application of a non-chromatographic method for speciation of N-compounds.
2. Fast and efficient extraction of N-compounds in environmental samples of soil and sediments.
3. Effective elimination of matrix interferences during the analytical process.
4. Accessible speciation method for the purpose of environmental monitoring of N-compounds.

A. J. Moreira (✉) · C. D. Freschi · G. P. G. Freschi
LAFFEQ, Institute of Science and Technology, Federal University of Alfenas, UNIFAL-MG, Poços de Caldas, MG 37715-400, Brazil
e-mail: aijomoquim@gmail.com

A. J. Moreira · E. C. Pereira
Chemistry Dept, Universidade Federal de São Carlos, UFSCar-SP, São Carlos, SP 13565-905, Brazil

Introduction

Environmental pollution caused by contaminants and noxious gases ranks as one of the most serious threats to modern society (Beyn et al., 2015; Moreira et al., 2020; Oiamo et al., 2015). Dyes—after degradation by different processes—are one such pollutant and are one of the leading producers of the nitrogen compounds (NO_x , NO_3^- , NO_2^-) introduced into ecosystems (Dong et al., 2020; Sharma, 2010). As a result, the monitoring of nitrogen compounds in the environment has been the object of numerous studies (Arif et al., 2016; Pani et al., 2020; Singh et al., 2019). Nitrogen is one of the most abundant elements in nature, and its inorganic forms such as nitrate and nitrite are continuously introduced into the

environment, through natural and/or anthropogenic sources. However, the presence of nitrite and nitrate in natural waters, even at low concentrations (100 to 900 mg L⁻¹ for NO₃⁻, 2 to 10 mg L⁻¹ for NO₂⁻), indicates toxicity and pollution (Chen et al., 2012; Valencia-Castañeda et al., 2019), possibly from different sources: fertilizers, pesticides, explosives, paints, or domestic and industrial effluents.

Maximum permitted limits (MPL) of nitrite and nitrate in natural waters in Brazil, according to the Brazilian Environmental Council (Conselho Nacional de Meio Ambiente, CONAMA in Portuguese), are, respectively, 1.0 and 10.0 mg L⁻¹, expressed in nitrogen (Brazil, 2005). Likewise, the Brazilian Health Surveillance Agency (Agência Nacional de Vigilância Sanitária, ANVISA in Portuguese) stipulates the same limits for drinking water (Brazil, 2011a). Surprisingly, though current environmental regulatory limits range from 0.2 to 10 mg L⁻¹ for different classes of non-polluted surface water, the Brazilian health authorities deem this range unfit for human consumption (Brazil, 2005, 2011b). In addition to inorganic species, organic nitrogen compounds were listed as emerging contaminants on account of their insertion in different ecosystems through anthropogenic activities (Arif et al., 2016; Sharma, 2010). For example, N-compounds *p*-nitrophenol (PNP) and its derivatives are classified as emerging contaminants because they are found in dyes and pesticides (Nakatsuji et al., 2015; Wan et al., 2017). These molecules are also carcinogens and skin irritants and persist in the environment due to their low degradability (Datta et al., 2004; Lai et al., 2014). Environmental monitoring of different nitrogen species is therefore important since it permits the identification of each toxic form (organic N-compound > NO₂⁻ > NO₃⁻) and, consequently, the prevention of health and environmental risks. (Ahmed et al., 2015; Luo et al., 2016).

Among its harmful effects, nitrite, upon ingestion, can react with secondary or tertiary amines to form N-nitrosamines, known carcinogenic agents. Also, nitrite in the blood can react with the iron (II) in hemoglobin to form methemoglobin—which does not carry oxygen—leading to respiratory failure and anemia. On contact with reducing bacteria, nitrate reductase enzymes reduce nitrate to nitrite, giving rise to the same toxicological effects (Grosse et al., 2006). Another important class of toxic N-compounds is that of nitrogenous organic pollutants such as PNP,

commonly found in industrial waste. PNP is potentially carcinogenic, and its degradation pathway via oxidative processes takes a long time to process (Arif et al., 2016; Pani et al., 2020).

Owing to their instrumental simplicity, spectrophotometric methods are the methods of choice for N-compounds determination. However, these methods display some drawbacks, namely, low selectivity, matrix effect, and toxic waste generation (azo-compounds) during the analytic process (Singh et al., 2019). Seeking to improve analytical selectivity and decrease toxic waste generation, chromatographic methods were studied for N-compounds analysis. These techniques enable identification of N-compounds or structures by separation process; however, they require complex preparation of soil and sediment environmental samples, and more, the chromatographic technique has a low level of sensitivity (Pontes et al., 2012; Wang et al., 2017). Recently, the associated use of high-resolution continuum source molecular absorption spectrometry (HR-CS MAS) and a chemical vapor generator (CVG) was successfully applied in NO₂⁻, NO₃⁻, and PNP speciation analysis of food samples (Gouvêa et al., 2018). Different from the atomic absorption spectroscopy (AAS), which is limited to the metals and semi-metals determination, HR-CS MAS applies to the determination of all elements, including non-metallic elements (Bechlin et al., 2013; Pinheiro et al., 2016, 2020). Briefly, non-metallic elements can be converted chemically into their diatomic and gaseous species, which when absorbing the light from the continuous source exhibited a molecular absorption spectrum with characteristic lines for each type of chemical bond (Brandao et al., 2012; Resano et al., 2019). In addition, the high resolution of the technique allows the spectral lines of the analyte to be monitored individually or collectively seeking to increase selectivity, while the sensitivity is increased by the possibility of calculating the area of the absorption graph (absorbance versus reading time) for definite regions (Resano et al., 2014; Vieira et al., 2019).

This selectivity and sensitivity can be improved when CVG is coupled to the HR-CS MAS system. CVG can act selectively to convert the analyte of interest into its diatomic and gaseous species, promoting an efficient separation from the matrix (Gouvêa et al., 2018). Also, CVG allows selectively vaporized species to be pre-concentrated in the system,

increasing the analytical sensitivity (Issa et al., 2011; Pinheiro et al., 2017). These advantages of HR-CS MAS have already been reported in studies aimed at determining P, S, N, and Cl, while CVG is a process widely applied to determine As, Sb, and non-metallic species of N, P, and S using spectrometric techniques (Pinheiro et al., 2016; Resano et al., 2014, 2019; Vieira et al., 2019). Due to its lower operating costs compared to other hyphenated techniques (LC-ICP-MS, LC-AAS, ICP-MS), its application holds promise for N-compound quantification in complex matrices such as soils and sediments. In this method, measurement is rendered possible through the selective conversion of N-compounds to NO_2^- and, subsequently, the formation of nitrogen monoxide, a gaseous molecule. $\text{NO}_{(g)}$ is then separated from the aqueous phase and transferred to an atomization cell where it is detected by a specific absorption line (Brandao et al., 2012; Gouvêa et al., 2018).

Moreover, when choosing an analytical technique for speciation, the most appropriate extraction process must be selected to ensure that sample preparation is representative and that analytes of interest are not converted into other compounds (Nakatsuji et al., 2015; Singh et al., 2019). Thus, solid–liquid extraction affords an adequate alternative and can be optimized using ultrasound- or microwave-assisted processes (Picó, 2013; Pontes et al., 2012). However, some organic compounds like PNP can become degraded at high temperatures, rendering the microwave-assisted process less suitable. Therefore, ultrasound-assisted solid–liquid extraction (USLE) comes into the spotlight for its simplicity, cost-effectiveness, speed, and high yield under moderated conditions. Also, USLE uses small amounts of samples and generates little waste, meeting green analytical chemistry practice requirements (Tobiszewski, 2016).

Nitrate, nitrite, and PNP speciation in soil and sediment samples have been scantily reported in the literature; therefore, in this work, USLE was evaluated as a sample preparation method for N-compounds extraction in environmental samples. Specifically, the soil and sediment samples were collated from two mining areas in the state of Minas Gerais where environmental disasters by the mining toxic waste spill had occurred following tailings dam collapses, at one site in 2015, and the other in 2019 (Bottino et al., 2017; Pereira et al., 2019). For detection, the

online UV/PVG-CS MAS technique developed by our group (Gouvêa et al., 2018) was optimized and then applied for speciation analysis. To our knowledge, this was the first study to show N-compound levels (NO_2^- , NO_3^- , and PNP) in the ecosystems impacted by the respective environmental disasters. Furthermore, the efficiency of the non-chromatographic method in performing N-compounds speciation analysis allied with its speed and selectivity showed the method to be an alternative to more costly techniques like chromatography.

Material and methods

Equipment

The N-compounds determination was performed using an HR-CS MAS ContraAA 300 spectrometer with HS60A chemical vapor generation system (Analytik Jena, Jena, Germany) and high purity argon gas as carrier (White Martins 99.999%) at a flow rate of 6 L h^{-1} . The photochemical reactor was composed of 2 (two) low-pressure 10-W mercury lamps (Philips Lamp, UV-C (254 nm), CA, USA).

Reagents

Standard solutions of nitrite, nitrate, and *p*-nitrophenol (PNP) 1000 mg L^{-1} were prepared by dissolving 0.150 g of NaNO_2 , 0.137 g of NaNO_3 , and 0.100 g of PNP (all Sigma-Aldrich, St. Louis, MO, USA) in 100 mL of Milli-Q water $18.2 \text{ M}\Omega \text{ cm}^{-1}$ (Direct-Q® 3UV, Millipore, Burlington, MA, USA). Thereafter, the solutions were kept under refrigeration in high-density polypropylene bottles. The ascorbic acid solution 3.5% (m v^{-1}) was prepared daily by diluting 3.5 g of reagent (Sigma-Aldrich, St. Louis, MO, USA) in 100 mL of Milli-Q ultrapure water. The 3.0 mol L^{-1} hydrochloric acid (HCl) solution was also prepared daily by dilution of 25.7 mL of 37% (v v^{-1}) HCl (Sigma-Aldrich, St. Louis, MO, USA) in 100 mL of Milli-Q ultrapure water. The ammonium buffer solution was prepared by dissolving 10.75 g of NH_4Cl (Sigma-Aldrich, St. Louis, MO, USA) in 100 mL of Milli-Q water and adjusting the pH to 8.5 with 15 mol L^{-1} NaOH (Sigma-Aldrich, St. Louis, MO, USA) and a pH meter. The solution was stored under

refrigeration in a high-density polypropylene bottle (Nalgene®, Rochester, NY, USA).

Sample identification, collection, and storage

Environmental samples applied in this study were collected in areas impacted by anthropogenic activities of the mining industry. To this end, water (**Wat1**), soil (**Soil1**), and sediment (**Sed1**) samples were collected in Poços de Caldas, Brazil, in the state of Minas Gerais, where a number of active mineral extraction industries are located (Pedrobom et al., 2017). Other samples were also collected in-state, in the towns of Mariana (samples with digit 2) and Brumadinho (samples with digit 3): water (**Wat2** and **Wat3**), soil (**Soil2** and **Soil3**), and sediment (**Sed2**). It is noteworthy that the Mariana and Brumadinho samples were representative of impacted soils after mining dam ruptures, in 2015 and 2019, respectively (da Silva Junior et al., 2018; Pereira et al., 2019). The sediments were collected using a polyvinyl chloride (PVC) collector. The collector was inserted in the sediment to a depth of 30 cm and the samples collected. Soils were collected at the same depth. After collection, the samples were stored, refrigerated, and transported to the laboratory. Subsequently, all samples were dried, sieved (2-mm mesh), homogenized, and stored at room temperature (24 °C) without preservatives or reagents. The basic properties of surface water samples are listed in Table 1. However, soil and sediment samples were not characterized in this study, since their basic properties were completely altered in the sample preparation (extraction) stage. Also, the literature reports previous studies that deal

with the exhaustive characterization of waters, soils, and sediments collected in these areas impacted by the environmental disaster (Reis et al., 2019; dos Vergilio, 2020; Zanchi et al., 2021).

Extraction procedures

USLE was applied in this study for sample preparation purposes. This procedure was chosen based on the good results previously attained in speciating As(III), As(V), and DMA (Pinheiro et al., 2017). Thus, an ultrasonic bath, model USC-700 (Unique, Brazil), capacity 1 L, frequency 50 Hz, heating power 55 W, was employed in the present study. To ascertain the most efficient extraction solution for N-compounds, the following were applied: 3.0 mol L⁻¹ hydrochloric acid, 1.0 mol L⁻¹ acetic acid, 1.0 mol L⁻¹ citric acid or methanol: water (1:1). This procedure was performed on all soil/sediment samples used in the addition/recovery assays to ensure that after the preparation process, samples contained 0.5 mg L⁻¹ concentrations of NO₂⁻, NO₃⁻, and PNP each. Therefore, the extract contained 0.5 mg L⁻¹ (NO₂⁻) + 0.5 mg L⁻¹ (NO₃⁻) + 0.5 mg L⁻¹ (PNP).

Detailing the extraction process: 1 g of the soil or sediment sample was placed on a watch glass and fortified with 1 mL of a NO₂⁻, NO₃⁻, and PNP solution at 5 mg L⁻¹. This moistened sample was dried in an oven for 2 h at 60 °C, cooled to room temperature, and transferred to a 20-mL test tube. To the sample was added 10 mL of the extraction solution (3.0 mol L⁻¹ hydrochloric acid, 1.0 mol L⁻¹ acetic acid, 1.0 mol L⁻¹ citric acid or methanol: water (1:1)), ensuring sample was covered, and then, the system was transferred to the ultrasound bath where it remained for 2, 3, 4, or 5 min. Finally, the sample was filtered through a 0.45-µm filter; the liquid extract was transferred to a 50-mL volumetric flask and filled to the meniscus with ultrapure water. For each analyte, the final concentration for all fortified solutions was 0.5 mg L⁻¹. Considering the different speciation analysis conditions for NO₃⁻, NO₂⁻, and PNP, it was necessary to add other reagents, so the last 50 mL was divided into 3 portions (15 mL each) for quantification of N-compounds. Extraction of the real samples was done using the same process, but for these, the fortification step was not applied.

Table 1 Basic properties of surface waters

Parameter	Wat1	Wat2	Wat3
Temperatura (°C)	19.80 ± 0.22	24.57 ± 0.02	20.81 ± 0.04
OD (mg L ⁻¹)	5.60 ± 0.33	9.32 ± 0.25	10.1 ± 0.18
pH	6.40 ± 0.45	6.69 ± 0.78	8.01 ± 0.09
Condutividade (uS cm ⁻¹)	42.60 ± 3	60 ± 2	49.1 ± 1.1
Turbidez (NTU)	320 ± 12	497 ± 10	628 ± 29
TOC (mg L ⁻¹)	0.58	1.61	0.98

*Determined according to standard methods for the examination of water and wastewater. 22nd ed

Speciation analysis procedure

The entire speciation analysis system for N-compound quantification has been illustrated in Fig. 1. Photochemical conversion was required for NO_3^- and PNP speciation analysis by reduction/oxidation process, while NO_2^- speciation analysis occurred in the absence of light, as described by Gouvêa et al. (2018).

Therefore, the N-compounds extract was pumped into the photochemical reactor through a 43.7-cm-long PTFE tube wrapped around the UV light source. NO_3^- and PNP determinations were performed under irradiation (light on), and the NO_2^- determination was performed without irradiation (light off). For clarity, the analytic procedures used in the speciation of each analyte (NO_3^- , NO_2^- and PNP) have been detailed here:

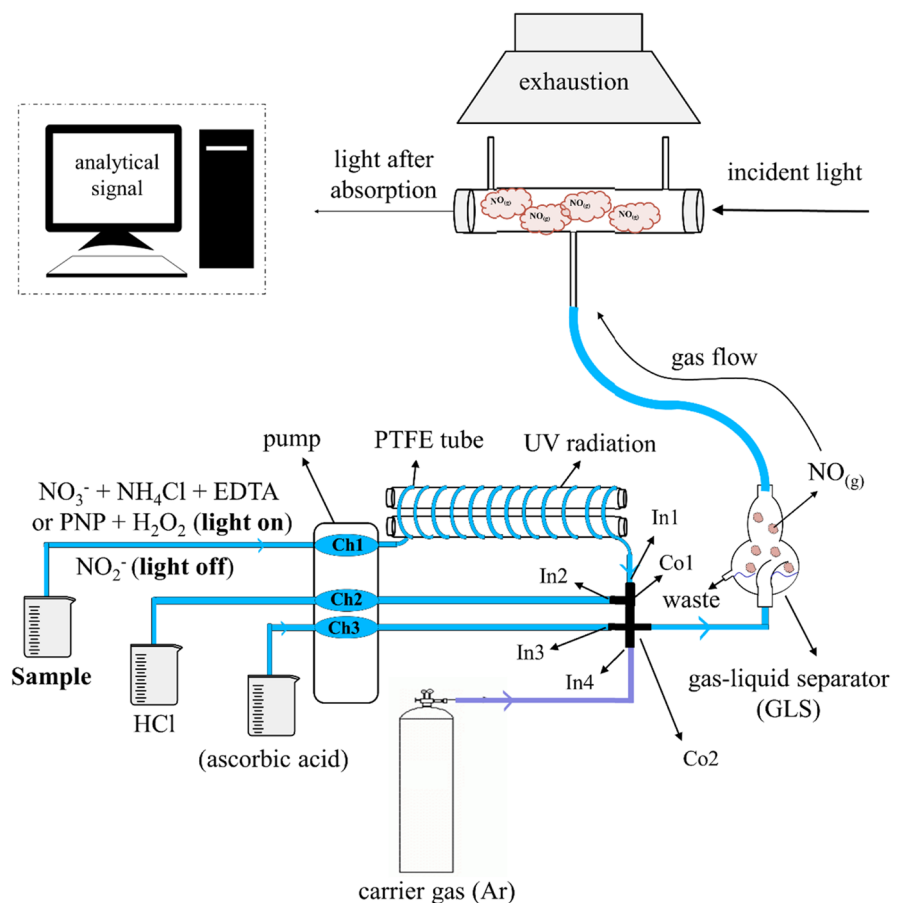
1. Nitrate ion determination: The extract was mixed with the carrier solution (EDTA + NH_4Cl buffer,

pH = 8.5) through channel 1 (**Ch1**). Here, a flow rate of 8.0 mL min^{-1} was applied; the sample was pumped through a PTFE tube under UV radiation for 20 s for photochemical reduction of NO_3^- to NO_2^- . After irradiation, the mixture reached inlet 1 (**In1**).

2. PNP determination: The extract was mixed with the $2 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ carrier solution through **Ch1**. Flow rate of 8.0 mL min^{-1} was applied, and the sample was pumped through the PTFE tube for 20 s under UV radiation for photochemical oxidation from PNP to NO_2^- . After irradiation, the mixture reached **In1**.

3. NO_2^- determination: The extract was loaded without carrier solution at 8.0 mL min^{-1} flow rate through **Ch1**. The sample was pumped through the PTFE tube for 20 s without UV radiation until it reached **In1**.

Fig. 1 Schematic diagram of the UV/CVG-CS MAS speciation system



Subsequently, the solution containing the NO_2^- formed was acidified with 3 mol L^{-1} HCl. The acid solution was transported through channel 2 (**Ch2**) at a flow rate of 8.0 mL min^{-1} and reached inlet (**In2**). After this, the sample containing NO_2^- ions was rapidly mixed at confluence 1 (**Co1**). In the next step, the acidified sample reached confluence 2 (**Co2**), and the NO_2^- ions were reduced to $\text{NO}_{(\text{g})}$ through reaction with the reducing agent (5% m v^{-1} ascorbic acid), which was transported to the reaction cell through channel 3 (**Ch3**), flow rate 8.0 mL min^{-1} , reaching inlet 3 (**In3**). At this point, the reduction reaction occurred in 20 s, and the $\text{NO}_{(\text{g})}$ formed was carried by the argon gas [inlet 4 (**In4**)] to the gas–liquid separator (GLS) at a flow of 6 L h^{-1} .

Upon reaching the GLS, the $\text{NO}_{(\text{g})}$ was separated from the aqueous phase and carried to the atomizer (quartz cell) by the inert gas (Ar). Finally, analytical signal was obtained through the molecular absorption process in a specific line for $\text{NO}_{(\text{g})}$. The conditions for speciation analysis were such that NO_3^- and/or PNP presence in the extract was not seen to be analytically interfering with each other and NO_2^- . As expected, NO_2^- signal was noted during the NO_3^- and PNP analysis, and for this reason, NO_3^- and PNP concentrations were calculated by subtracting NO_2^- concentration.

The optimized parameters for N-compound speciation analysis have been listed in Table 2. Here, temperature at 600 °C was selected because it

showed the highest absorbance signals (Gouvêa et al., 2018).

Testing the procedure and building the calibration curve

To evaluate the efficiency of the proposed analytic procedure, the steps described below were applied to the real and fortified samples. For all addition/recovery assays, matrices were fortified by the simultaneous addition of NO_2^- , NO_3^- , and PNP, so that the final extract would be constituted of a mixture of these analytes, simulating what is expected for real samples. However, for the construction of the calibration curves, the NO_2^- , NO_3^- , or PNP solutions were added individually to the matrices, so that only one of the analytes was found in the final extract.

Thus, 5 mL of water or extract (sediment/soil) was transferred to a 25-mL tube, to which was added 15 mL buffer solution, pH=8.5 (EDTA + NH_4Cl for NO_3^- determination), or 15 mL 2.0 mmol L^{-1} H_2O_2 (for PNP determination). All samples were diluted 1:4; ultrapure water was used for NO_2^- dilution. The samples are then submitted to N-compound speciation analysis in UV/PVG-CS MAS system (Fig. 1), under optimized conditions (Table 2). Calibration curves were constructed by adding different quantities each of NO_2^- , NO_3^- , or PNP solutions to the water (**Wat2**), sediment (**Sed2**), or soil (**Soil2**) matrices. Specifically, the respective matrices were fortified with different NO_2^- , NO_3^- , or PNP concentrations (0.3 to 5.0 mg L^{-1}) and submitted to the extraction process.

Statistical analysis

All samples were prepared in triplicate, and method precision was verified by calculating the relative standard deviation (% RSD) of the measurements ($n=3$ for sample and $n=10$ for the white) (Currie, 1995). The quality of the calibration curves was evaluated by the linear correlation coefficients obtained for the different data sets (concentration versus absorbance) of the respective analytes. Limits of detection (LOD) and limits of quantification (LOQ) were calculated using standard deviation of the absorbance measurements, obtained after 3 readings for LOD and 10 readings for LOQ, in agreement with the literature (Currie, 1995).

Table 2 Variables optimized for N-compounds speciation by UV/PVG-CS MAS system

Parameters	Optimized conditions
Absorption line	214.803 nm
Temperature of the quartz cell	600 °C
Flow of the PVG system reagents	8.0 mL min^{-1}
Flow of the carrier gas	6 L h^{-1}
HCl concentration	3.0 mol L^{-1}
Ascorbic acid concentration	5.0% (m v^{-1})
EDTA concentration	1.0 mmol L^{-1}
NH_4Cl concentration	2.5 mol L^{-1}
pH	8.5
H_2O_2 concentration	2.0 mmol L^{-1}
UV exposure time	20 s

Method accuracy was determined through addition/recovery assays. Matrices were fortified with N-compounds as follows: 0.5 mg g⁻¹ for the solid matrix or 0.5 mg L⁻¹ for the aqueous matrix. Further, in this work, method performance was also compared with that of the analytical method proposed by Pasquali et al. (2010) using addition/recovery assays and real unfortified samples analysis. Confirmation was obtained by *t* test (95% confidence level).

Results and discussion

Sample preparation: extraction procedure

The composition for the extraction solutions was chosen because HCl was already present as an acidifier in the speciation analysis stage, while acetic and citric acids were complexing agents capable of sequestering ions that can enhance the matrix effect. Methanol/water (MeOH:H₂O) solution was applied because it is widely used as a mobile phase in chromatographic speciation analysis and may enhance PNP extraction efficiency. All the characteristics of the reagents composing the extraction solution were in agreement with the literature (Singh et al. 2019). As the organic acids and MeOH could potentially compete in the photochemical stage (20 s duration), assays with all extraction solutions were performed. Mean recovery results for all fortified matrices show enhanced efficiency: HCl > C₆H₈O₇ > CH₃COOH > CH₃OH/H₂O (Table 3). These improved results for the HCl extraction solution were associated with its extraction capacity and especially with the non-interference of the speciation analysis in the photochemical stage.

It should be noted that addition/recovery procedure applied in this study cannot be compared to the real interaction behavior that occurs naturally between the analytes and the matrix. Nevertheless, this procedure complies to standards for this type of study, while the determination of ionic species in different samples by acid extraction has been widely reported in the literature (Singh et al., 2019; Wang et al., 2017). Consequently, the results indicate that the HCl extraction solution does not exhibit significant interference in the analyte-NO_(g) photochemical conversion mechanism. This hypothesis can be confirmed by the lower recovery values found for the C₆H₈O₇, CH₃COOH, and CH₃OH/H₂O extraction solutions.

According to the literature, organic species are easily oxidized by free radicals formed during the photochemical step (Baba et al., 2015); hence, methanol, acetic acid, and citric acid could act as competitors in the NO₃⁻ and PNP to NO₂⁻ conversion step (Liu et al., 2017; Mack & Bolton, 1999). Therefore, only the 3.0 mol L⁻¹ HCl solution performed significantly, with recovery values of over 95% for the different matrices. In view of the excellent performance of the HCl solution and considering that for each gram of sample, 0.5 mg of NO₂⁻, NO₃⁻, or PNP was added, the individual values found are shown in Fig. 2a.

The recovery of each analyte in different matrices was 99.6 ± 1.3 (NO₂⁻), 101.2 ± 1.0 (NO₃⁻), and 90.8 ± 4.2 (PNP). The data therefore showed that all species were recovered with > 90% efficiency using HCl extraction solution. The lowest recovery obtained for PNP suggests that the organic species needs optimizing in the photochemical oxidation stage. Considering that H₂O₂ was the oxidizing agent used in the photochemical conversion of PNP, the results obtained after changing oxidant concentration

Table 3 Efficiency of the different extraction solutions when USLE was applied to samples fortified with 0.50 mg g⁻¹ of each analyte (NO₂⁻, NO₃⁻, and PNP). Recovery values correspond to mean (n = 3) expressed as total extraction

Samples	Conc. added, mg g ⁻¹ of each analyte	Recovery (%)			
		CH ₃ COOH (1 mol L ⁻¹)	HCl (3 mol L ⁻¹)	C ₆ H ₈ O ₇ (1 mol L ⁻¹)	CH ₃ OH/H ₂ O (1:1/v/v)
Sed1	0.5+0.5+0.5	83.2 ± 4.9	98. ± 3.1	88.1 ± 3.9	68.3 ± 6.1
Sed2	0.5+0.5+0.5	88.7 ± 5.1	99.1 ± 2.8	87.6 ± 4.4	61.2 ± 6.4
Soil1	0.5+0.5+0.5	69.6 ± 6.2	96.7 ± 3.9	78.2 ± 5.2	45.2 ± 5.9
Soil2	0.5+0.5+0.5	68.4 ± 5.4	95.1 ± 4.0	74.2 ± 5.1	41.1 ± 6.2
Soil3	0.5+0.5+0.5	71.5 ± 5.6	96.6 ± 4.2	76.9 ± 4.8	43.2 ± 5.9
Average recovery	-	76.3 ± 7.7	97.3 ± 1.4	81.0 ± 5.5	51.8 ± 10.4

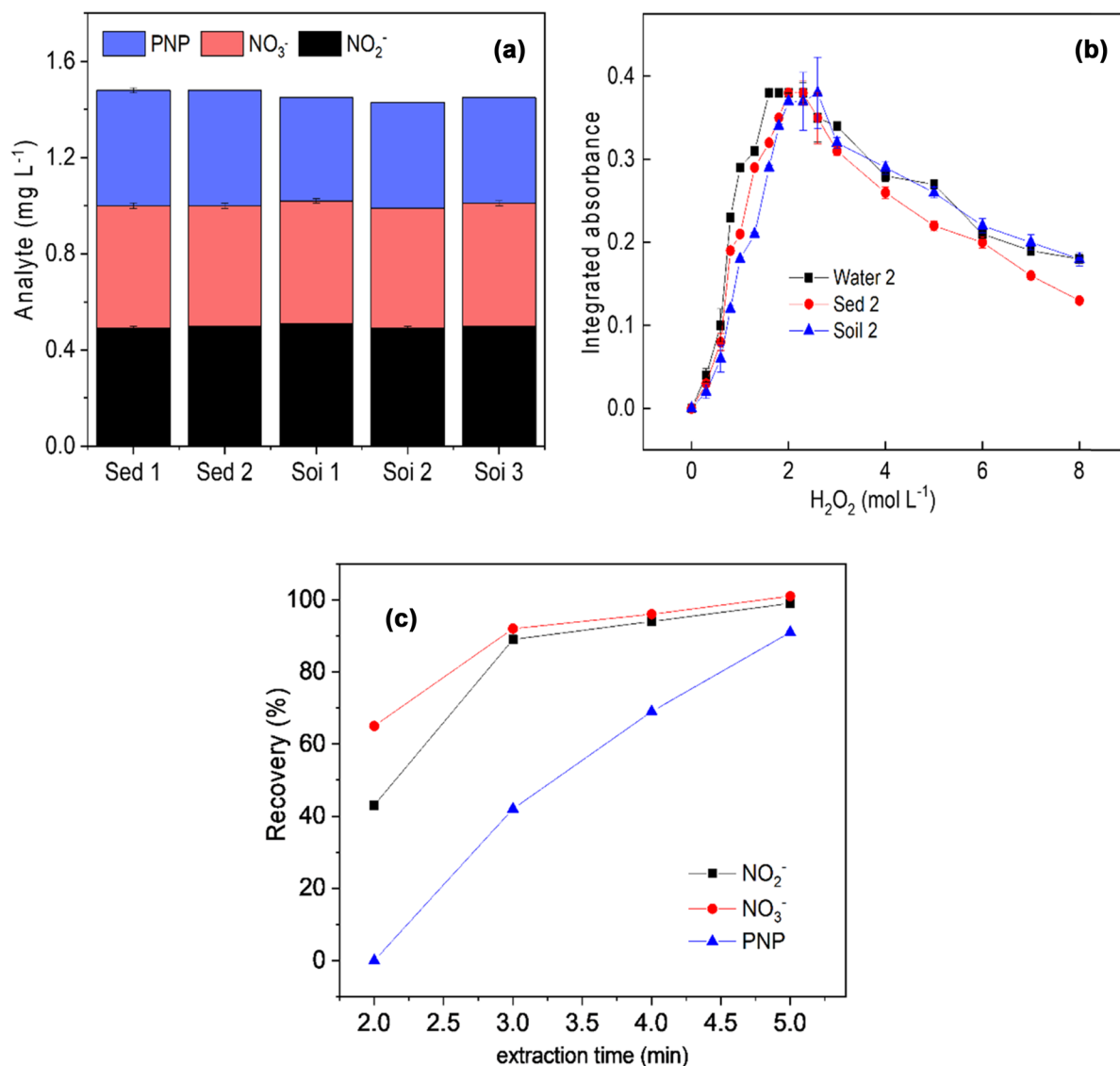


Fig. 2 Effect of sample matrix on recovery data ($\text{HCl}=3.0 \text{ mol L}^{-1}$) (a), influence of H_2O_2 concentration on photochemical oxidation of PNP (0.5 mol L^{-1}) (b), and extrac-

tion time study for samples identified as 2 (c) when the combined USLE and UV/PVG-CS MAS system was applied

are shown in Fig. 2b. Here, 2 mol L^{-1} was the optimized condition, while the $<2 \text{ mol L}^{-1}$ concentrations of H_2O_2 show that the lowest absorbance is due to incomplete PNP- NO_2^- conversion. Furthermore, for the $>2 \text{ mol L}^{-1}$ concentrations, excess $\cdot\text{OH}$ negatively affected photochemical conversion (Mack & Bolton, 1999).

Finally, using different extraction times, we show that inorganic species recovery was greater than

90% after 3 min, while PNP showed 91% recovery in 5 min (Fig. 2c). Thus, the extraction performed in up to 5 min was defined as the optimized condition and applied throughout all stages of this work. Here, we emphasize that extraction time was limited to 5 min so that the temperature of the extract would not rise high enough to cause PNP degradation; therefore, maximum temperature at the 5-min threshold was kept to $<40 \text{ }^\circ\text{C}$.

UV/PVG-CS MAS system optimization

The flow rates of the reagents in the photochemical vapor generation (PVG) system were analyzed to ascertain the amount of reagent required for the $\text{NO}_{(\text{g})}$ formation reaction. All the optimized parameters are shown in Table 2, and ascorbic acid is seen to be the main reagent responsible for NO_2^- to $\text{NO}_{(\text{g})}$ reduction in HCl. Thus, optimum acid concentrations were 3.0 mol L^{-1} for hydrochloric acid and 5.0% (m v⁻¹) for ascorbic acid, prioritizing the lowest possible chemical reagents consumption and the lowest associated standard deviation. Here, a higher concentration of ascorbic acid was used in comparison to our previous study, (Gouvêa et al., 2018). The change was necessary due to the characteristics of the environmental samples. Higher organic content in the soil and sediment possibly increased consumption of ascorbic acid—needed to reduce NO_2^- to $\text{NO}_{(\text{g})}$ in HCl medium.

At this stage, optimal amounts of EDTA, NH_4Cl , H_2O_2 , and reaction pH underwent little change compared to the previous study conducted to perform N-compounds determination in food samples (Gouvêa et al., 2018). The calibration curves and figures of merits associated with the N-compounds quantification in this work are shown in Table 4.

According to the American Environmental Protection Agencies (EPA, USA) and the Brazilian Health Surveillance Agency (Agência Nacional de Vigilância Sanitária ANVISA, in Brazil), MPLs for NO_3^- and NO_2^- in environmental matrices are 10 mg L^{-1} (NO_3^-) and 1 mg L^{-1} (NO_2^-), respectively (Brazil, 2011a; EPA, 2009). However, the European Environmental Agency (EEA) has determined 50 mg L^{-1} (NO_3^-) and 0.5 mg L^{-1} (NO_2^-) as the MPL for surface water, while the Brazilian

Environmental Council (Conselho Nacional de Meio Ambiente, CONAMA in Portuguese) enforces MPLs of 0.7 mg L^{-1} (NO_3^-) and 0.2 mg L^{-1} (NO_2^-) for class II water or brackish water (Brazil, 2011b; Fri, 1972). Therefore, the limits of detection (LOD), the limits of quantification (LOQ), and the linear correlation coefficients (R^2) obtained through the method proposed in this work can be applied and would fulfill legal requirements in different countries.

Moreover, due to its presence in the environment, PNP has been extensively investigated in advanced oxidation processes. However, its monitoring was generally done by spectrophotometric or chromatographic analytical techniques (Nakatsuji et al., 2015; Wan et al., 2017). These methods require complex sample preparation steps for elimination of analytical interference in most cases. Meanwhile, the method proposed in this work is suitable for fast, simple, and inexpensive monitoring of PNP in environmental matrices. Also, figures of merit (Table 4) are adequate for N-compounds quantification, and NO_2^- , NO_3^- , and PNP curves are obtained for each environmental matrix (Wat2, Sed2, or Soil2).

Linear range for each analyte was 0.3 to 3.0 mg L^{-1} (NO_2^-), 0.5 to 5.0 mg L^{-1} (NO_3^-), and 0.3 to 3.0 mg L^{-1} (PNP). As expected, the LOD found for water matrix (Wat2) was 12% (NO_2^-), 10% (NO_3^-), and 18% (PNP) lower compared to that found for soil matrix (Soil2), indicating weaker matrix effect in Wat2, since USLE was not needed. Furthermore, the LOD found for NO_3^- was 28% (Wat2), 24% (Sed2), and 20% (soil) higher than that found for PNP in the same matrices. This result was most likely due to the matrix effect and the greater difficulty in NO_3^- to NO_2^- photoconversion compared to PNP. Hence, the LOD results corroborate with the R^2 values obtained for the different analytes:

Table 4 Figures of merit obtained after Wat2, Sed2, and Soi2 matrices were fortified with N-compounds, recovered, and analyzed via the USLE and UV/PVG-CS MAS system

Parameters	NO_2^-			NO_3^-			PNP		
	Wat2	Sed2	Soil2	Wat2	Sed2	Soil2	Wat2	Sed2	Soil2
Slope (b)	0.368	0.345	0.321	0.221	0.212	0.202	0.384	0.369	0.346
Intercept (a)	-0.005	-0.004	-0.001	0.012	0.015	0.019	0.009	0.011	0.021
R^2	0.998	0.997	0.991	0.989	0.987	0.986	0.996	0.993	0.989
LOD (mg L^{-1})	0.09 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.11 ± 0.02	0.12 ± 0.01	0.13 ± 0.01	0.08 ± 0.01	0.09 ± 0.01	0.10 ± 0.02
LOQ (mg L^{-1})	0.30 ± 0.02	0.32 ± 0.01	0.34 ± 0.01	0.40 ± 0.01	0.40 ± 0.03	0.41 ± 0.02	0.27 ± 0.02	0.30 ± 0.04	0.33 ± 0.03

minimum values were $R^2=0.99$ for NO_2^- or PNP and slightly lower, $R^2=0.98$, for NO_3^- . With respect to non-conventional analytical systems that require multiple steps for final quantification, obtaining $R^2=0.98$ was not a new finding. In the literature, studies have already been reported wherein $R^2=0.98$ value was applied in different situations and, on validation, reliable results were exhibited (Chen et al., 2017; Devangad et al., 2016; Ding et al., 2019). In the present study, through addition/recovery assays, the applicability and efficiency of the proposed method were validated. Additionally, quantification in real samples allowed for further comparison with another method previously reported in the literature (Pasquali et al., 2010).

Applying the speciation analysis method to environmental samples

USLE was applied in the sediment and soil samples as described in Sect. 2.4. The extracts are analyzed by the method proposed in this work, and the results are showed in Table 5.

These results showed the presence of one or more analytes (NO_2^- and/or NO_3^-) in all the samples in this study; however, as expected, PNP was not found in any sample. NO_2^- concentration in real samples ranged from $0.33 \pm 0.01 \text{ mg L}^{-1}$ to $1.06 \pm 0.02 \text{ mg L}^{-1}$, while NO_3^- concentration in environmental samples ranged from $3.86 \pm 0.10 \text{ mg L}^{-1}$ to $52.29 \pm 1.75 \text{ mg L}^{-1}$. Bearing in mind that Brazilian environmental legislation defines MPL as 10 mg L^{-1} (NO_3^-) and 1 mg L^{-1}

(NO_2^-) for freshwater, it was possible to confirm that the respective ecosystems were not contaminated. Furthermore, no references were found in Brazilian legislation to the effect that soil and sediment samples with nitrate presence of $52.29 \pm 1.75 \text{ mg L}^{-1}$ and $9.05 \pm 0.27 \text{ mg L}^{-1}$ could be considered contaminated environments.

Specifically, for PNP, which was not found in any sample, it could be affirmed that the presence of organic species was uncommon in mining areas (Logov et al., 2015; Reis et al., 2017). Moreover, the oxidant character of the environmental matrices collected in bauxite mining areas (high acidity and $\text{Fe}^{2+/3+}$ presence) was as expected. This fact led to increased expectation concerning organic compound oxidation, due to the presence of the Fe_xO_y residues acting through the Fenton mechanism (Ren et al., 2017; Rodrigues et al., 2018; Tian et al., 2017). However, inorganic species (NO_2^- and NO_3^-) were also found in low concentrations at these sites, possibly due to lower plant density and microbial activity (Izquierdo et al., 2005). Also, it was possible to confirm that the highest concentrations for N-compounds were found in samples tagged with digits 2 or 3. These were the samples collected in the areas where dam collapse had caused vegetation destruction (da Silva Junior et al., 2018). Here, it could be suggested that the organic content from the native vegetation was incorporated into the soil and sediments, thereby raising NO_3^- and NO_2^- levels in the respective ecosystems.

Table 5 Concentrations found and addition/recovery tests (0.5 mg L^{-1} of each analyte) in environmental samples by two different methods

Sample	Determination by UV/PVG-CS AAS (this work)						Determination by spectrophotometric (Pasquali et. al)			
	Analyte (mg L^{-1})			Recovery (%)			Analyte (mg L^{-1})		Recovery (%)	
	NO_2^-	NO_3^-	PNP	NO_2^-	NO_3^-	PNP	NO_2^-	NO_3^-	NO_2^-	NO_3^-
Wat1	<LOD	3.86 ± 0.10	<LOD	93 ± 1	101 ± 2	100 ± 2	<LOD	3.89 ± 0.11	98 ± 1	100 ± 1
Wat2	<LOD	7.76 ± 0.20	<LOD	97 ± 3	99 ± 1	100 ± 3	<LOD	8.28 ± 0.21	98 ± 3	98 ± 2
Wat3	0.41 ± 0.01	9.43 ± 0.24	<LOD	99 ± 2	97 ± 3	98 ± 4	—	—	—	—
Sed1	0.33 ± 0.01	9.05 ± 0.27	<LOD	105 ± 3	99 ± 1	101 ± 3	0.34 ± 0.02	9.21 ± 0.45	96 ± 2	96 ± 3
Sed2	<LOD	8.12 ± 0.23	<LOD	99 ± 2	103 ± 2	97 ± 3	<LOD	8.19 ± 0.38	96 ± 4	100 ± 2
Soil1	0.54 ± 0.01	10.64 ± 0.31	<LOD	106 ± 3	101 ± 3	98 ± 1	0.52 ± 0.03	10.34 ± 0.51	102 ± 5	96 ± 4
Soil2	0.86 ± 0.02	26.35 ± 0.76	<LOD	108 ± 4	103 ± 2	87 ± 5	0.80 ± 0.04	25.56 ± 1.14	100 ± 3	104 ± 5
Soil3	1.06 ± 0.02	52.29 ± 1.75	<LOD	106 ± 3	103 ± 1	89 ± 2	—	—	—	—

The p-nitrophenol (PNP) quantification was not possible by spectrometric method (Pasquali et. al 2010)

Table 6 Comparative data from inorganic nitrogenous compound determination method/processes reported in the literature

Sample type	Extraction method	Extraction time (min)	Analytical method	LOD (mg L ⁻¹)	Recovery (%)	Reference
Soil	Ultrasonic extraction	30	Ionic chromatography	0.080 (NO ₂ ⁻); 0.060 (NO ₃ ⁻)	> 95 (NO ₂ ⁻) > 93 (NO ₃ ⁻)	Pontes et al. 2012
Water, wastewater, and food	MnO ₂ microcolumn	17	FAAS	0.07 (NO ₂ ⁻); 0.14 (NO ₃ ⁻)	> 96% for NO ₂ ⁻ / NO ₃ ⁻	Noroozifar et al. 2007
Groundwater	-	-	HR-CS ET MAS	0.10 (NO ₂ ⁻) and (NO ₃ ⁻)	> 96% for NO ₂ ⁻ / NO ₃ ⁻	Brandao et al. 2014
Food	-	15	Ionic chromatography	0.015 (NO ₂ ⁻); 0.046 (NO ₃ ⁻)	> 96 (NO ₂ ⁻) > 90 (NO ₃ ⁻)	Antczak-Chrobot et al. 2018
Environmental (water, soil, and sediments)	Ultrasonic extraction	5	UV/PVG-CS MAS	0.102 (NO ₂ ⁻); 0.125 (NO ₃ ⁻); 0.099 (PNP)	102 (NO ₂ ⁻) 101 (NO ₃ ⁻) 96 (PNP)	This work

All environmental samples were subjected to addition/recovery assays using the combined USLE and speciation analysis (UV/PVG-CS MAS) method proposed in this work. Additionally, we used the spectrophotometric method proposed by Pasquali et al. (2010) to compare the results found through different analytical methods (Table 5). Accordingly, the average recovery for all samples was 101 ± 4% (NO₂⁻), 101 ± 1% (NO₃⁻), and 96 ± 4% (PNP), applying the UV/PVG-CS MAS method, and 98 ± 2% (NO₂⁻) and 99 ± 2% (NO₃⁻), applying the method proposed by (Pasquali et al., 2010). As the comparative data showed a 95% confidence level (*t* test), > 96% recovery results reinforce the applicability of this method for N-compounds speciation analysis in environmental samples.

The advantages of USLE sample preparation and speciation analysis (UV/PVG-CS MAS) proposed in this work were: (1) fast and simple extraction by applying 3 mol L⁻¹ HCl, maximum sonication time 5 min; (2) efficient elimination of matrix effect by NO_(g) selective formation using speciation analysis method; and (3) effective quantification of NO₂⁻, NO₃⁻, and PNP using non-chromatographic method.

Table 6 shows, comparatively, the results obtained by the present method and those published in the literature for N-compounds analysis (Antczak-Chrobot et al., 2018; Brandao et al., 2014; Noroozifar et al., 2007; Pontes et al., 2012).

Having defined the optimal analysis conditions, the entire system was applied to determine N-compound concentration in the real samples. Moreover, system

efficiency was confirmed through the addition/recovery assays.

Conclusions

Ultrasound-assisted liquid extraction (USLE) and photochemical vapor generation (PVG) methods were efficiently applied to quantify NO₂⁻, NO₃⁻, and PNP in water, soil, and sediment environmental matrices. Notably, the entire analytical procedure (extraction and speciation analysis) to quantify NO₂⁻, NO₃⁻, and PNP took < 10 min, one of the advantages of the method. Analytical interferences usually present in complex matrices such as soil and sediments were easily eliminated/minimized by converting the N-compounds to NO_(g), which was selectively monitored using molecular absorption spectrometry. Further, under optimized conditions for extraction and speciation analysis, the method was validated through addition/recovery assays that showed > 96% for all analytes and confidence level > 95% (*t* test) when compared to another method reported in the literature. Therefore, the combined USLE and UV/PVG-CS MAS system was a good alternative for determination and speciation analysis of non-metal elements in environmental samples. Moreover, compared to other more expensive and inaccessible (chromatographic) methods, the current method has proven to be a real alternative in areas with limited laboratory infrastructure.

Authors' contribution All authors contributed to the study conception and design. Ailton José Moreira: writing and Methodology; Carolina Dakuzaku Freschi and Ernesto C. Pereira: writing-review and editing; Gian Paulo Giovanni Freschi: writing, conceptualization, supervision. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding This work was financially supported by Fundação de Amparo à Pesquisa do Estado de Minas Gerais (Fapemig), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, grant # 88887.368533/2019–00 and Code # 001; 88881.068088/2014–01 and Code # 001), Fundação de Amparo à Pesquisa do Estado de São Paulo (grants: 2013/07296–2, 2014/50249–8, 2017/11986–5), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Shell. J. A.

Availability of data and materials All data generated or analyzed during this study are included in this published article. The original (raw) experimental data can be requested from the corresponding author by email upon justification.

Declarations

Conflict of interest The authors declare no competing interests.

References

- Ahmed, E., Nagaoka, K., Fayez, M., Abdel-Daim, M. M., Samir, H., & Watanabe, G. (2015). Suppressive effects of long-term exposure to P-nitrophenol on gonadal development, hormonal profile with disruption of tissue integrity, and activation of caspase-3 in male Japanese quail (*Coturnix japonica*). *Environmental Science and Pollution Research*, 22(14), 10930–10942. <https://doi.org/10.1007/s11356-015-4245-9>
- Antczak-Chrobot, A., Bąk, P., & Wojtczak, M. (2018). The use of ionic chromatography in determining the contamination of sugar by-products by nitrite and nitrate. *Food Chemistry*, 240(February 2017), 648–654. <https://doi.org/10.1016/j.foodchem.2017.07.158>
- Arif, M. S., Riaz, M., Shahzad, S. M., Yasmeen, T., Buttler, A., Garcia-Gil, J. C., et al. (2016). Contrasting effects of untreated textile wastewater onto the soil available nitrogen-phosphorus and enzymatic activities in aridisol. *Environmental Monitoring and Assessment*, 188(2). <https://doi.org/10.1007/s10661-016-5112-y>
- Baba, Y., Yatagai, T., Harada, T., & Kawase, Y. (2015). Hydroxyl radical generation in the photo-fenton process: Effects of carboxylic acids on iron redox cycling. *Chemical Engineering Journal*, 277, 229–241. <https://doi.org/10.1016/j.cej.2015.04.103>
- Bechlin, M. A., Gomes Neto, J. A., & Nóbrega, J. A. (2013). Evaluation of lines of boron, phosphorus and sulfur by high-resolution continuum source flame atomic absorption spectrometry for plant analysis. *Microchemical Journal*, 109, 134–138. <https://doi.org/10.1016/j.microc.2012.03.013>
- Beyn, F., Matthias, V., Aulinger, A., & Dähnke, K. (2015). Do N-isotopes in atmospheric nitrate deposition reflect air pollution levels? *Atmospheric Environment*, 107, 281–288. <https://doi.org/10.1016/j.atmosenv.2015.02.057>
- Bottino, F., Milan, J. A. M., Cunha-Santino, M. B., & Bianchini, I. (2017). Influence of the residue from an iron mining dam in the growth of two macrophyte species. *Chemosphere*, 186, 488–494. <https://doi.org/10.1016/j.chemosphere.2017.08.030>
- Brandao, G. C., Lima, D. C., & Ferreira, S. L. C. (2012). The chemical generation of NO for the determination of nitrite by high-resolution continuum source molecular absorption spectrometry. *Talanta*, 98(2), 231–235. <https://doi.org/10.1016/j.talanta.2012.06.080>
- Brandao, G. C., Matos, G. D., Pereira, R. N., & Ferreira, S. L. C. (2014). Development of a simple method for the determination of nitrite and nitrate in groundwater by high-resolution continuum source electrothermal molecular absorption spectrometry. *Analytica Chimica Acta*, 806, 101–106. <https://doi.org/10.1016/j.aca.2013.11.031>
- Brazil. (2005). Ministério do Meio Ambiente. Conselho Nacional de Meio Ambiente (CONAMA). Resolução N° 357, de 17 de março de 2005. DOU n° 053, de 18/03/2005. pp. 58–63, Found in <http://www.mma.gov.br/port/conama/res/res05/res35705.pdf>. (Retrieved in 22/04/2020)
- Brazil. (2011a). Brazil, Ministério Da Saúde. Portaria n° 2914, de 12 de dezembro de 2011. Found in https://www.saude.mg.gov.br/images/documentos/Portaria_No-2.914_12_DEZEMBRO_2011.pdf, 2011, 16, (Retrieved in 22/04/2020)
- Brazil. (2011b). Brazil, Ministério do Meio Ambiente. Conselho Nacional de Meio Ambiente (CONAMA). Resolução n° 430 de 13 de maio de 2011. Found in <http://www2.mma.gov.br/port/conama/res/res11/res43011.pdf>. (Retrieved in 22/04/2020)
- Chen, G., Lai, B., Mei, N., Liu, J., & Mao, X. (2017). Mercury speciation by differential photochemical vapor generation at UV-B vs. UV-C wavelength. *Spectrochimica Acta - Part B Atomic Spectroscopy*, 137, 1–7. <https://doi.org/10.1016/j.sab.2017.09.007>
- Chen, W., Tong, H., & Liu, H. (2012). Effects of nitrate on nitrite toxicity to *Microcystis aeruginosa*. *Marine Pollution Bulletin*, 64(6), 1106–1111. <https://doi.org/10.1016/j.marpolbul.2012.04.006>
- Currie, L. A. (1995). Nomenclature in evaluation of analytical methods including detection and quantification capabilities. *Pure and Applied Chemistry*, 67(10), 1699–1723. <https://doi.org/10.1351/pac199567101699>
- da Silva Junior, C. A., Coutinho, A. D., de Oliveira-Júnior, J. F., Teodoro, P. E., Lima, M., Shakir, M., et al. (2018). Analysis of the impact on vegetation caused by abrupt deforestation via orbital sensor in the environmental disaster of Mariana, Brazil. *Land Use Policy*, 76(April), 10–20. <https://doi.org/10.1016/j.landusepol.2018.04.019>
- Datta, C., Naidu, R., & Yenkie, M. K. N. (2004). Photo-oxidative degradation of synthetic organic pollutant p-nitrophenol.

- Journal of Scientific and Industrial Research*, 63(6), 518–521
- Devangad, P., Unnikrishnan, V. K., Tamboli, M. M., Shameem, K. M. M., Nayak, R., Choudhari, K. S., & Santhosh, C. (2016). Quantification of Mn in glass matrices using laser induced breakdown spectroscopy (LIBS) combined with chemometric approaches. *Analytical Methods*, 8(39), 7177–7184. <https://doi.org/10.1039/c6ay01930g>
- Ding, Y., Liu, Y., Chen, Y., Huang, Y., & Gao, Y. (2019). Photochemical vapor generation for colorimetric speciation of inorganic selenium. *Analytical Chemistry*, 91(5), 3508–3515. <https://doi.org/10.1021/acs.analchem.8b05117>
- Dong, Y., Xu, L., Yang, Z., Zheng, H., & Chen, L. (2020). Aggravation of reactive nitrogen flow driven by human production and consumption in Guangzhou City China. *Nature Communications*, 11(1), 1–10. <https://doi.org/10.1038/s41467-020-14699-x>
- dos Vergilio, C., S., Lacerda, D., Oliveira, B. C. V. de, Sartori, E., Campos, G. M., Pereira, A. L. de S., et al. (2020). Metal concentrations and biological effects from one of the largest mining disasters in the world (Brumadinho, Minas Gerais, Brazil). *Scientific Reports*, 10(1), 1–12. <https://doi.org/10.1038/s41598-020-62700-w>
- EPA. (2009). National primary drinking water guidelines, *1cse*, 2009, 7. https://www.epa.gov/sites/production/files/2016-06/documents/npwdr_complete_table.pdf
- Fri, R. (1972). the Environmental Protection Agency1. *Journal of Milk and Food Technology*, 35(12), 715–718. <https://doi.org/10.4315/0022-2747-35.12.715>
- Gouvêa, L. F. C., Moreira, A. J., Freschi, C. D., Freschi, G. P. G. (2018). Speciation of nitrite, nitrate and p-nitrophenol by photochemical vapor generation of NO using high-resolution continuum source molecular absorption spectrometry. *Journal of Food Composition and Analysis*, 70 <https://doi.org/10.1016/j.jfca.2018.04.003>
- Grosse, Y., Baan, R., Straif, K., Secretan, B., El Ghissassi, F., Coglianò, V., et al. (2006). Carcinogenicity of nitrate, nitrite, and cyanobacterial peptide toxins. *The Lancet Oncology*, 7(8), 628–629. [https://doi.org/10.1016/S1470-2045\(06\)70789-6](https://doi.org/10.1016/S1470-2045(06)70789-6)
- Issa, N. B., Rajaković-Ognjanović, V. N., Marinković, A. D., & Rajaković, L. V. (2011). Separation and determination of arsenic species in water by selective exchange and hybrid resins. *Analytica Chimica Acta*, 706(1), 191–198. <https://doi.org/10.1016/j.aca.2011.08.015>
- Izquierdo, I., Caravaca, F., Alguacil, M. M., Hernández, G., & Roldán, A. (2005). Use of microbiological indicators for evaluating success in soil restoration after revegetation of a mining area under subtropical conditions. *Applied Soil Ecology*, 30(1), 3–10. <https://doi.org/10.1016/j.apsoil.2005.02.004>
- Lai, B., Zhang, Y., Chen, Z., Yang, P., Zhou, Y., & Wang, J. (2014). Removal of p-nitrophenol (PNP) in aqueous solution by the micron-scale iron-copper (Fe/Cu) bimetallic particles. *Applied Catalysis B: Environmental*, 144, 816–830. <https://doi.org/10.1016/j.apcatb.2013.08.020>
- Liu, M. J., Wiegel, A. A., Wilson, K. R., & Houle, F. A. (2017). Aerosol fragmentation driven by coupling of acid-base and free-radical chemistry in the heterogeneous oxidation of aqueous citric acid by OH radicals. *Journal of Physical Chemistry A*, 121(31), 5856–5870. <https://doi.org/10.1021/acs.jpca.7b04892>
- Logov, A. B., Oparin, V. N., Potapov, V. P., Schastlivtsev, E. L., & Yukina, N. I. (2015). Entropy analysis of process wastewater composition in mineral mining region. *Journal of Mining Science*, 51(1), 186–196. <https://doi.org/10.1134/S1062739115010251>
- Luo, S., Wu, B., Xiong, X., & Wang, J. (2016). Short-term toxicity of ammonia, nitrite, and nitrate to early life stages of the rare minnow (*Gobiocypris rarus*). *Environmental Toxicology and Chemistry*. <https://doi.org/10.1002/etc.3283>
- Mack, J., & Bolton, J. R. (1999). Photochemistry of nitrite and nitrate in aqueous solution: A review. *Journal of Photochemistry and Photobiology A: Chemistry*, 128(1–3), 1–13. [https://doi.org/10.1016/S1010-6030\(99\)00155-0](https://doi.org/10.1016/S1010-6030(99)00155-0)
- Moreira, A. J., Campos, L. O., Maldí, C. P., Dias, J. A., Paris, E. C., Giraldi, T. R., & Freschi, G. P. G. (2020). Photocatalytic degradation of Prozac® mediated by TiO₂ nanoparticles obtained via three synthesis methods: sonochemical, microwave hydrithermal, and polymeric precursor. *Environmental Science and Pollution Research*, 27, 27032–27047
- Nakatsuji, Y., Salehi, Z., & Kawase, Y. (2015). Mechanisms for removal of p-nitrophenol from aqueous solution using zero-valent iron. *Journal of Environmental Management*, 152, 183–191. <https://doi.org/10.1016/j.jenvman.2015.01.012>
- Noroozifar, M., Khorasani-Motlagh, M., Taheri, A., & Homayoonfar, M. (2007). Application of manganese(IV) dioxide microcolumn for determination and speciation of nitrite and nitrate using a flow injection analysis-flame atomic absorption spectrometry system. *Talanta*, 71(1), 359–364. <https://doi.org/10.1016/j.talanta.2006.04.009>
- Oiamo, T. H., Johnson, M., Tang, K., & Luginaah, I. N. (2015). Assessing traffic and industrial contributions to ambient nitrogen dioxide and volatile organic compounds in a low pollution urban environment. *Science of the Total Environment*, 529, 149–157. <https://doi.org/10.1016/j.scitotenv.2015.05.032>
- Pani, N., Tejani, V., Anantha-Singh, T. S., & Kandya, A. (2020). Simultaneous removal of COD and ammoniacal nitrogen from dye intermediate manufacturing industrial wastewater using fenton oxidation method. *Applied Water Science*, 10(2), 1–7. <https://doi.org/10.1007/s13201-020-1151-1>
- Pasquali, C. E. L., Gallego-Picó, A., Hernando, P. F., Velasco, M., & Alegría, J. S. D. (2010). Two rapid and sensitive automated methods for the determination of nitrite and nitrate in soil samples. *Microchemical Journal*, 94(1), 79–82. <https://doi.org/10.1016/j.microc.2009.09.005>
- Pedrobom, J. H., Eismann, C. E., Menegário, A. A., Galhardi, J. A., Luko, K. S., de Dourado, T., & A., & Kiang, C. H. (2017). In situ speciation of uranium in treated acid mine drainage using the diffusion gradients in thin films technique (DGT). *Chemosphere*, 169, 249–256. <https://doi.org/10.1016/j.chemosphere.2016.11.082>
- Pereira, L. F., Cruz, G. D. B., & Guimarães, R. M. F. (2019). Impactos do rompimento da barragem de rejeitos de Brumadinho, Brasil: uma análise baseada nas mudanças de cobertura da terra. *Journal of Environmental Analysis*

- and Progress, 4(2), 122. <https://doi.org/10.24221/jeap.4.2.2019.2373.122-129>
- Picó, Y. (2013). Ultrasound-assisted extraction for food and environmental samples. *TrAC - Trends in Analytical Chemistry*, 43, 84–99. <https://doi.org/10.1016/j.trac.2012.12.005>
- Pinheiro, B. S., Gimenes, L. L. S., Moreira, A. J., Freschi, C. D., & Freschi, G. P. G. (2016). Arsenic speciation in environmental samples using different acid concentrations and ultrasonic extraction for the determination by HG-FAAS. *Atomic Spectroscopy*, 37(2).
- Pinheiro, B. S., Gimenes, L. L., Moreira, A. J., de Araújo, A. F., Freschi, C. D., & Freschi, G. P. G. (2017). Speciation of As in environmental samples using the nano-TiO₂/PCHG-FAAS online system. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 52(11), 1089–1098. <https://doi.org/10.1080/10934529.2017.1340749>
- Pinheiro, B. S., Moreira, A. J., Gimenes, L. L. S., Freschi, C. D., & Freschi, G. P. G. (2020). UV photochemical hydride generation using ZnO nanoparticles for arsenic speciation in waters, sediments, and soils samples. *Environmental Monitoring and Assessment*, 192, 331. <https://doi.org/10.1007/s10661-020-08316-z>
- Pontes, F. V. M., Carneiro, M. C., Vaitsman, D. S., Monteiro, M. I. C., de Souza, E., & da MF Neto AA. (2012). Fast and simultaneous ultrasound-assisted extraction of exchangeable-NH₄⁺, NO₃⁻ and NO₂⁻ species from soils followed by ion chromatography determination. *Chemical Speciation and Bioavailability*, 24(4), 227–233. <https://doi.org/10.3184/095422912X13488406544054>
- Reis, D. A., Fongaro, G., da Silva Lanna, M. C., Dias, L. C. P., & da SantiagoF, A. (2019). The Relationship between human adenovirus and metals and semimetals in the waters of the Rio Doce, Brazil. *Archives of Environmental Contamination and Toxicology*, 77(1), 144–153. <https://doi.org/10.1007/s00244-019-00625-w>
- Reis, D. A., da Fonseca Santiago, A., Nascimento, L. P., & Roeser, H. M. P. (2017). Influence of environmental and anthropogenic factors at the bottom sediments in a Doce River tributary in Brazil. *Environmental Science and Pollution Research*, 24(8), 7456–7467. <https://doi.org/10.1007/s11356-017-8443-5>
- Ren, H., Su, Y., Han, X., & Zhou, R. (2017). Synthesis and characterization of saponin-modified Fe₃O₄ nanoparticles as heterogeneous Fenton-catalyst with enhanced degradation of p-nitrophenol. *Journal of Chemical Technology and Biotechnology*. <https://doi.org/10.1002/jctb.5139>
- Resano, M., Flórez, M. R., & García-Ruiz, E. (2014). Progress in the determination of metalloids and non-metals by means of high-resolution continuum source atomic or molecular absorption spectrometry. A critical review. *Analytical and Bioanalytical Chemistry*, 406(9–10), 2239–2259. <https://doi.org/10.1007/s00216-013-7522-9>
- Resano, M., García-Ruiz, E., Aramendía, M., & Belarra, M. A. (2019). Quo vadis high-resolution continuum source atomic/molecular absorption spectrometry? *Journal of Analytical Atomic Spectrometry*, 34(1), 59–80. <https://doi.org/10.1039/c8ja00256h>
- Rodrigues, C. S. D., Borges, R. A. C., Lima, V. N., & Madeira, L. M. (2018). p-Nitrophenol degradation by Fenton's oxidation in a bubble column reactor. *Journal of Environmental Management*, 206, 774–785. <https://doi.org/10.1016/j.jenvman.2017.11.032>
- Sharma, V. K. (2010). Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 45(6), 645–667. <https://doi.org/10.1080/10934521003648784>
- Singh, P., Singh, M. K., Beg, Y. R., & Nishad, G. R. (2019). A review on spectroscopic methods for determination of nitrite and nitrate in environmental samples. *Talanta*, 191(June 2018), 364–381. <https://doi.org/10.1016/j.talanta.2018.08.028>
- Tian, X., Liu, Y., Chi, W., Wang, Y., Yue, X., Huang, Q., & Yu, C. (2017). Catalytic degradation of phenol and p-nitrophenol using Fe₃O₄/MWCNT nanocomposites as heterogeneous Fenton-like catalyst. *Water, Air, and Soil Pollution*, 228(8). <https://doi.org/10.1007/s11270-017-3485-3>
- Tobiszewski, M. (2016). Metrics for green analytical chemistry. *Analytical Methods*, 8(15), 2993–2999. <https://doi.org/10.1039/c6ay00478d>
- Valencia-Castañeda, G., Frías-Espicueta, M. G., Vanegas-Pérez, R. C., Chávez-Sánchez, M. C., & Páez-Osuna, F. (2019). Toxicity of ammonia, nitrite and nitrate to *Litopenaeus vannamei* juveniles in low-salinity water in single and ternary exposure experiments and their environmental implications. *Environmental Toxicology and Pharmacology*, 70(May). <https://doi.org/10.1016/j.etap.2019.05.002>
- Vieira, A. L., Gonçalves, D. A., Virgílio, A., Ferreira, E. C., Jones, B. T., Donati, G. L., & Gomes Neto, J. A. (2019). Multi-energy calibration for the determination of non-metals by high-resolution continuum source molecular absorption spectrometry. *Journal of Analytical Atomic Spectrometry*, 34(5), 972–978. <https://doi.org/10.1039/c9ja00006b>
- Wan, D., Li, W., Wang, G., Lu, L., & Wei, X. (2017). Degradation of p-Nitrophenol using magnetic Fe₀/Fe₃O₄/Coke composite as a heterogeneous Fenton-like catalyst. *Science of The Total Environment*, 574, 1326–1334. <https://doi.org/10.1016/j.scitotenv.2016.08.042>
- Wang, Q. H., Yu, L. J., Liu, Y., Lin, L., Lu, R. gang, Zhu, J. ping, et al. (2017). Methods for the detection and determination of nitrite and nitrate: A review. *Talanta*, 165(December 2016), 709–720. <https://doi.org/10.1016/j.talanta.2016.12.044>
- Zanchi, C. S., Batista, É. R., Silva, A. O., Barbosa, M. V., Pinto, F. A., dos Santos, J. V., & Carneiro, M. A. C. (2021). Recovering soils affected by iron mining tailing using herbaceous species with mycorrhizal inoculation. *Water, Air, and Soil Pollution*, 232(3). <https://doi.org/10.1007/s11270-021-05061-y>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.