



Rapid analysis of 4-nonylphenol by solid phase microextraction in water samples



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ABSTRACT

Alquilphenols are considered to be endocrine disruptors and are mainly found as 4-nonylphenol (4-NP) in ecosystems. A chromatographic analytical method was developed using solid phase microextraction (SPME) combined with gas chromatography-mass spectrometry (GC-MS) for the extraction and quantification of 4-NP in sources of water in Mexico to establish environmental concentrations. A derivatization process with *N*-Methylbis(trifluoroacetamide) (MBTFA) was carried out in order to increase sensitivity in the method. The method was validated with a correlation coefficient above 0.99, and a limit of detection and quantification of $0.01 \mu\text{g L}^{-1}$ and $0.15 \mu\text{g L}^{-1}$ respectively, which were determined by a linear curve at low 4-NP concentrations. After demonstrating the feasibility of the method, an analysis in water samples was performed. Eighty-three percent of samples had detectable concentrations of 4-NP with a maximum concentration of $12.61 \mu\text{g L}^{-1}$, $12.2 \mu\text{g L}^{-1}$ and $6.08 \mu\text{g L}^{-1}$ in recreational water, wastewater discharges and drinking water respectively. Sixty-five percent of the samples presented concentrations above the limit established by the European Union ($2 \mu\text{g L}^{-1}$) and 17% above the limit by the Environmental Protection Agency ($6.6 \mu\text{g L}^{-1}$). Although the number of samples is not representative for the assessment of the real-world scenario, our data presents a general overview of the exposure levels and possible environmental and health risks. Continuous monitoring and regulation of this pollutant in Mexico is important in order to prevent exposure and thus, ecological and adverse health effects.

1. Introduction

Alquilphenol ethoxylates (APE) are non ionic surfactants widely used in detergents, plastic additives, emulsifiers, pesticides, among others. The APE most used is the nonylphenol ethoxylate (NPE), its use represents up to 80% of the total production [1]. The main characteristic of this compound is that is capable of generating micelles in solution. The amphiphilic structure of the surfactant molecule, which has a polar (hydrophilic) and a non polar (hydrophobic) end, is the cause for this activity. These chemicals are disposed directly into municipal and industrial wastewater discharges. In environmental conditions, NPE are degraded by microorganisms or ultraviolet light by transforming them into nonylphenol (NP) including the 4-nonylphenol (4-NP) [2].

4-NP is one of the most found organic pollutant in wastewater, effluents, rivers, drinking water, sediments and soil [3–7]. Several authors have reported that 4-NP possesses endocrine disruption activity

and is highly toxic to aquatic and terrestrial organisms because of its ability to mimic the female hormone 17β -estradiol [8]. Previous studies have shown a decrease in the gonadosomatic index in red seabream and black rockfish associated with the exposure of $50 \mu\text{g L}^{-1}$ of 4-NP [9]. Also, Japanese quail exposed to 4-NP presented a decrease in male spermatogenesis as well as pathologic injuries in male gonads [10]. The Water Framework Directive of the European Union has listed NP as a priority pollutant and allows a maximum concentration in water of $2 \mu\text{g L}^{-1}$ [11], while the Water Quality Criteria for the aquatic organisms protection of the Environmental Protection Agency (EPA) establishes $6.6 \mu\text{g L}^{-1}$ as the maximum concentration permitted [12]. Regulations in Mexico and Latin America that restrict the levels of NP in water are null. In addition, information on the presence of this pollutant in surface and treated waters do not exist. A study in Texcoco, which is a wastewater receptor of Mexico City, presented levels of 4-NP from 0.93 to $7.3 \mu\text{g L}^{-1}$ [13]. In addition, agricultural irrigation water used

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in Tula Valley in Hidalgo presented concentrations from 1.98 up to $7.3 \mu\text{g L}^{-1}$. Moreover, studies in drinking water of the Cutzamala system, which supplies 60% of water consumption in Mexico City, has registered concentrations of $0.089\text{--}0.655 \mu\text{g L}^{-1}$ [14]. Therefore, it is important to establish monitoring strategies in water in order to contribute to the generation of regulations in this respect, due to the toxicity associated to 4-NP and the wide use of NPE in Mexico.

An appropriate analytical method is necessary to quantificate 4-NP in different sources of water to be able to draw conclusions about the disposition and the possible threat and negative impacts that its use represents [15]. Some of the most used methods for the analysis of alquilphenol (AP) are liquid chromatography (LC), mass spectrometry (MS) or tandem mass spectrometry (MS/MS) [16]. NP extraction in water samples is commonly performed by liquid-liquid extraction (LLE) [17,18] nevertheless, its popularity has fallen because of the high consumption of time and solvents. To this extent, solid phase extraction (SPE) is primarily used for the extraction and pre-concentration of NP from several environmental matrices [19–21]. Although, compared to LLE, SPE reduces extraction time and solvent consumption, new analytical techniques that minimize costs, extraction time, organic solvents, quantity of sample and with high sensitivity, are being explored [22,23]. Pawliszyn reported solid phase microextraction (SPME) as a simple, rapid extraction method [24]. SPME employs an automatic device which contains a thin polymeric coating that is adapted to a microsyringe. There are two types of SPME: i) direct immersion (DI) and ii) headspace (HS). DI is mainly used to extract NP due to its non-volatile nature; however, HS has also been used combined with a derivatization process [25]. Derivative formation increases volatility, decreases polarity in organic compounds and improves the thermal stability of analytes. This causes a lower detection limit and/or better selectivity [26]. The aim of our study was to develop and validate an analytical method for the quantification of 4-NP in water samples using SPME with GC-MS with a previous derivatization process. Subsequently, an evaluation of 4-NP in different sources of water in Mexico was performed to demonstrate the effectiveness of the method as a monitoring technique of this contaminant in multiple scenarios.

2. Methods

2.1. Materials and reagents

Stock standard solution of 4-NP ($1000 \mu\text{g L}^{-1}$) was prepared in acetone and stored in the dark at -40°C until its further analysis. Standard working solution was prepared right before its use.

A 0.1 M hydrochloric acid (HCl) (JT Baker, Edo. Mexico) solution, sodium chloride (NaCl) (JT Baker, Edo. Mexico), Milli-Q deionized water (18.3 M Ω , Millipore) and *N*-Methyl-bis(trifluoroacetamide) (MBTFA) $\geq 97.0\%$ GC (Sigma Aldrich, Edo. Mexico) were used for derivatization process. Supelco supplied (Edo. Mexico) SPME fibers PDMS (100 μm polydimethylsiloxane); PA (85 μm polyacrylate) and DVB/CAR/PDMS (50/30 μm stableflex divinylbenzene/carboxen/polydimethylsiloxane) were tested for its performance. All three fibers were conditioned before use as manufacturer's instructions.

Samples and calibration curves were analyzed in a gas chromatograph (GC) (Agilent 6890) coupled to a mass spectrometry detector (MS) (Agilent 5975) in electron impact ionization mode (EI). The injection port was operated in splitless mode with a 0.75 mm liner without glass wool. Injection port temperature was 230°C ; helium used as carrier gas at a pressure of 36 psi with a constant flow of 1 mL min^{-1} . The chromatographic separation was carried through a HP 5MS (60 m \times 0.25 mm \times 0.25 μm) column (Agilent). Setting of the oven was as follows: 90°C (2 min), 180°C ($30^\circ\text{C min}^{-1}$), 200°C (1°C min^{-1}), 230°C ($30^\circ\text{C min}^{-1}$) and held for 5 min with a run time of 31 min. The tune parameters were: emission: 34.6; energy: 69.9; repeller: 26.6 and, EMVolts: 1341. SCAN mode (50–500 *m/z*) was employed in order to identify the compound, identification and quantification ions were

selected for SIM mode. The identified fragment ions were 203/316 *m/z*. Results were obtained and processed using Chemstation Software (Agilent).

2.2. Analytical procedure

The 4-NP quantification was performed with slight modifications of the methodology described by Basher & Lee [27]. For the calibration curves 1 mL of Milli-Q water was fortified with 4-NP using independent concentrations ranging from $0.5 \mu\text{g L}^{-1}$ up to $50 \mu\text{g L}^{-1}$ in amber glass vials. Sodium chloride (NaCl, 3%) and 0.1 M HCl (20 μL) were used to enhance ionic strength and to adjust pH, respectively. Standard working solutions were prepared right before its use. After sample extraction a derivatization process was carried out in order to improve volatility and sensitivity. This process consists on exposing the fiber to the headspace above a solution of acetone (1 mL) with MBTFA (100 μL) at 60°C for 10 min magnetically stirred at 600 rpm.

2.3. Establishing optimal conditions

Some parameters related with the adsorption of the analytes in the fiber were optimized to enhance the developed method: i) fiber coating, ii) temperature, iii) performance time and iv) ionic strength. For the optimization of the SPME procedure 1 mL of Milli-Q water was prepared fortifying with $1000 \mu\text{g L}^{-1}$ of 4-NP. NaCl and HCl (0.1 M) were added to adjust pH in an amber glass vial with magnetic agitation. Afterwards, the fiber was exposed to the headspace above the solution. Three types of fibers were evaluated for nonpolar, semipolar and polar compounds (PDMS, 100 μm , DVB/CAR/PDMS 50/30 μm , PA 85 μm). Assays were performed in triplicate to evaluate temperature (60, 80, 100°C), extraction time (5, 10, 20, 30, 40 and 60 min) and ionic strength (0, 3, 7%); averages are reported.

2.4. Statistical analysis

A multivariate two way ANOVA analysis was carried out to establish significant differences between the three fibers used considering two parameters: i) performance time (5, 10, 20, 30, 40 and 60 min) and ii) temperature (60, 80, 100°C). Determinations were performed in triplicate at a concentration of $1000 \mu\text{g L}^{-1}$ of 4-NP. The data distribution was evaluated using the Shapiro-Wilk test. Descriptive statistics parameters were calculated (mean, standard deviation, median, minimum and maximum). Differences between 4-NP concentrations reported in each scenario were established by the Kruskal Wallis test with a post hoc Dunn analysis using the statistic software GraphPad Prism 5.0 \circ .

2.5. Analytical Technique Validation

The validation of the method was performed based on the Guide for the Validation of Analytical Methods for the Determination of Organic Compounds at Trace Levels AOAC/FAO/IAEA/IUPAC [28] considering the following parameters, limit of detection (LOD), limit of quantification (LOQ), linearity (*r*), sensitivity, percentage of recovery and precision (repeatability and reproducibility), evaluating different concentrations in triplicate on the same day, and in duplicate five different days. LOD and LOQ were calculated using results obtained from five calibration curves determined in a concentration range of $0.5\text{--}50 \mu\text{g L}^{-1}$. The linearity expressed by the correlation coefficient (*r*) and the sensitivity determined by the slope of the working range curve (LOQ- $50 \mu\text{g L}^{-1}$) were obtained from the average of five curves obtained during three days.

2.6. Monitoring of 4-NP in water sources

A total of 29 samples were collected, from which 10 were of recreational use, 14 of wastewater discharges and 5 of drinking water.

Samples were collected in 1 L plastic recipients previously rinsed with Milli-Q water, no detergent was used in order to prevent contamination. After sampling, samples were stored in the dark at $-20\text{ }^{\circ}\text{C}$ until further analysis. The sampling sites were positioned using a Garmin GPS in UTM coordinates. Samples were collected mainly from the city of San Luis Potosí, México, in which the last decade its tourism has increased with the cooperation of national commissions and has a growing industrial zone where metal processing, auto part manufacturing, foundries and chemical industries are the principal performed economic activities [29]. A few samples were taken from *cenotes* (natural pits, or sinkholes, resulting from the collapse of limestone bedrock that exposes groundwater underneath) located in Merida, Yucatán, Mexico. The lack of an integral sewage and drainage networks makes this city highly vulnerable to anthropogenic contamination (mainly agricultural) due to the final disposition of wastewaters directly in the aquifer. Urban wastewaters are frequently impacted by septic tanks followed by infiltration wells causing pollution in the groundwater. The drinking water samples were collected randomly from water jugs of 5 different brands.

3. Results and discussion

3.1. Method optimization

Different parameters affect detection sensitivity for GC-based methods using SPME such as the fiber coating, extraction mode, and variables like temperature, stirring, ionic strength and extraction time [24]. Our method considered the fiber type, extraction temperature, extraction time and ionic strength for the extraction of 4-NP. Head space (HS) extraction mode was selected for the extraction of 4-NP due to the fact that unlike DI extraction mode, the HS prevents fiber damage that could be caused by direct contact with high molecular weight compounds and other non-volatile substances in the sample. Additionally, pH can be adjusted without damaging the fiber [24]. Even though, DI appears to be more adequate for 4-NP extraction, the HS extraction mode has been used successfully before in complex matrices [30] and has been assessed with a previous derivatization process in environmental samples [25]. SPME is based on the equilibrium between the quantity of analyte extracted by the fiber and the sample concentration, so the selection of the fiber coating is a key to determine the sensitivity, selectivity and repeatability of an analytical method [31]. To this extent, three different types of fibers were considered in this study: PDMS 100 μm (nonpolar compounds), DVB/CAR/PDMS 50/30 μm (semipolar compounds) and PA 85 μm (polar compounds).

The best conditions in the present study were achieved with a concentration of 3% NaCl. The overall detection response using the three SPME fibers is summarized in Fig. 1. Salt addition to samples has been frequently used in HS-SPME to moderately improve the extraction efficiency [23].

The distribution constant between the sample matrix and the fiber coating increases when a soluble salt is added to the sample, with increases in the sensitivity of the method. Aqueous solubilities of many organic compounds decrease when salt is added due to the -salting-out-effect that causes the analyte molecules to pass more easily from the sample to the HS and the fiber coating. Salt addition can increase or decrease the quantity of analyte extracted so it is necessary to evaluate the extraction efficiency by experimentation [32].

A temperature (60, 80, 100 $^{\circ}\text{C}$) and time (5, 10, 20, 30, 40 and 60 min) extraction study was performed using three types of fibers (PDMS, 100 μm ; DVB/CAR/PDMS 50/30 μm and PA 85 μm). Each assay was carried out in triplicate and averages were used for the corresponding analysis. The results of the two way ANOVA analysis (Table 1) show that there is no statistically significant difference between the parameters of time and temperature evaluated. The difference in the extraction lies in the polymeric fiber coating. Fig. 2 shows the profile of each evaluated fiber through a response surface graph as a function of

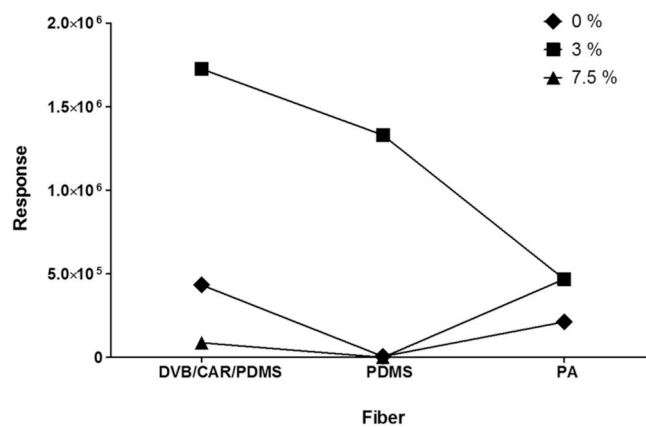


Fig. 1. Effect of salt addition for the extraction of 4-NP with different SPME fibers in fortified samples with $1000\text{ }\mu\text{g L}^{-1}$. PDMS: polydimethylsiloxane; PA: polyacrylate; DVB/CAR/PDMS: divinylbenzene/carboxen/polydimethylsiloxane.

Table 1

Details of the two-factor ANOVA test for abundances of 4-NP in water samples in response to the fiber and time factors. Conditions: (1) Time (5, 10, 20, 30, 40, 60 min) and (2) Fiber (PDMS, 100 μm ; DVB/CAR/PDMS 50/30 μm ; PA 85 μm).

Source of variation	% of total variation	P value
Interaction	16.44	0.7672
Fiber	23.78	< 0.0001
Time	5.77	0.0514
Source of variation	P value summary	Significant?
Interaction	ns	No
Fiber	**	Yes
Time	ns	No

Source of variation	Df	Sum-of-squares	Mean square	F
Interaction	40	8.208E+12	2.052E+11	0.8139
Fiber	8	1.187E+13	1.484E+12	5.887
Time	5	2.879 + E12	5.758E+11	2.284
Residual	106	2.672 + E13	2.521E+11	

ns: not significant.

the optimization variables (time and temperature). Fig. 2(A) describes the response of the extraction of 4-NP with PDMS fiber, where the best extraction was accomplished in 40 min at a temperature of 80 $^{\circ}\text{C}$. The image shows that this type of fiber provides a better homogeneity in the extraction although thermal stability was not achieved. The response of the fiber DVB/CAR/PDMS is presented in Fig. 2 (B). The best conditions for the extraction of 4-NP were obtained using an extraction time of 20 min at 80 $^{\circ}\text{C}$. PDMS fiber requires a very specific thermal extraction control, a high response was obtained, and therefore the quantity of 4-NP extracted increased. It has been reported that the DVB/CAR/PDMS fiber offers the best efficiency of extraction and this fiber has shown a better performance with compounds with high molecular weight [33]. The PA fiber (Fig. 2 C) showed the lowest extraction capacity compared with the other two evaluated fibers. This is probably due to the interaction with the compound because of the polarity of the fiber. The conditions that allowed a higher sample extraction for this fiber were 30 min of extraction time at 60 $^{\circ}\text{C}$. The type of fiber is then, the most important factor showing an increase in the adsorption of the compound that is proportional to the response of the GC-MS.

The extraction time selection depends on the objective of the analysis because there is always an engagement between length, sensitivity and repeatability. Equilibrium time is achieved when the maximum quantity of analyte has been extracted to the fiber [32]. It is expected that compounds with high molecular weight, such as 4-NP, have larger equilibrium times due to the low diffusion between the gas phase and

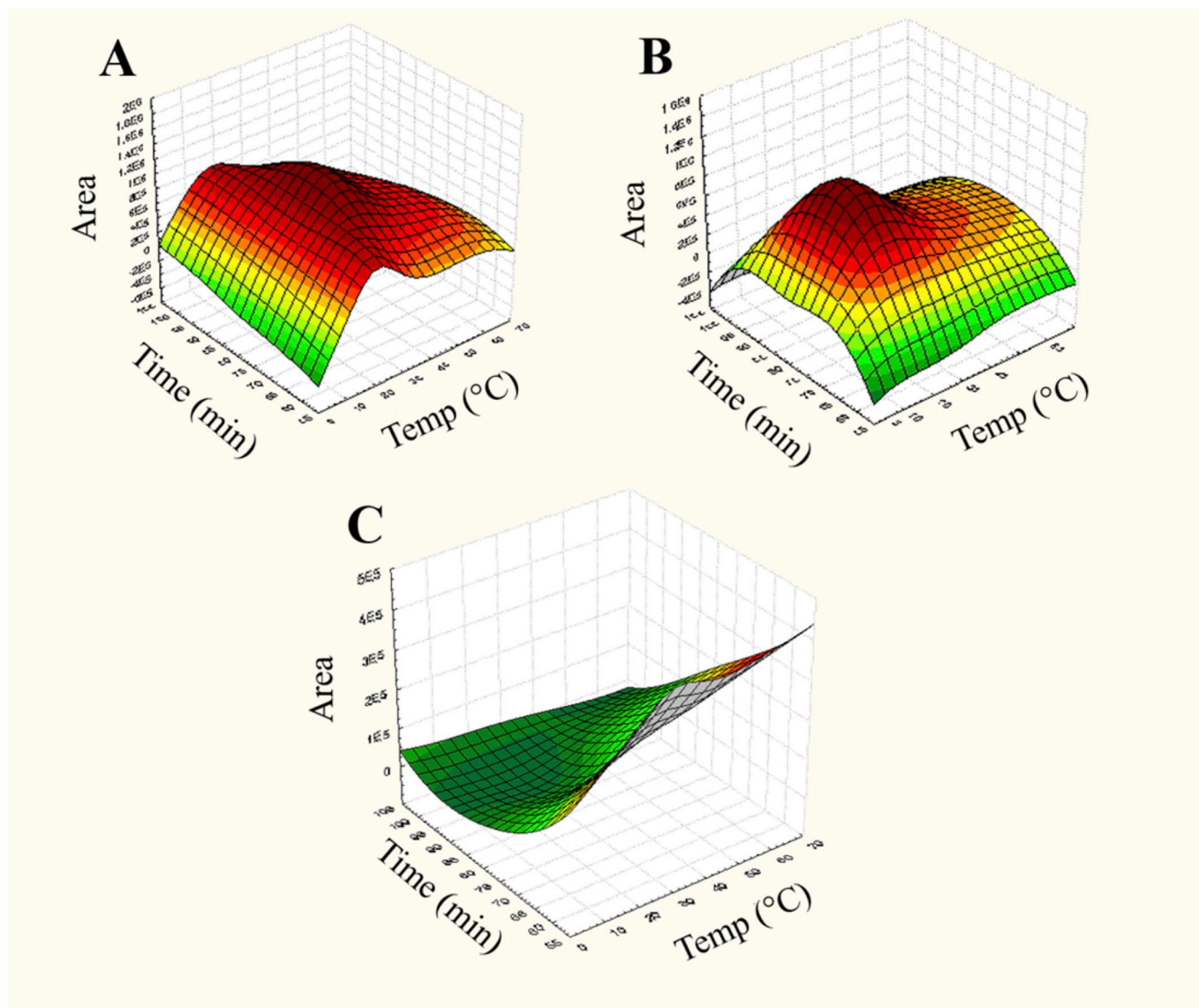


Fig. 2. Estimated optimization design based on temperature and time with different SPME fibers: (A) PDMS, 100 μm , (B) DVB/CAR/PDMS 50/30 μm , (C) PA 85 μm . Results were obtained at three different temperatures (60,80 and 100 $^{\circ}\text{C}$) and five different times (5, 10, 20, 30, 40 and 60 min) at a concentration of 1000 $\mu\text{g L}^{-1}$.

the fiber. The semivolatiles property of the compound along with the derivatization process allow an adequate extraction. An equilibrium time of 20 min with the DVB/CAR/PDMS fiber was obtained. This type of fiber is characterized by its thick coating which has been reported to offer greater efficiency and sensitivity in the extraction process [34].

Often a derivatization process is performed previous to the analysis to determine 4-NP. Derivatives typically have higher distribution constants toward the coating and the volatility of the compound is increased. Therefore, the derivatization process is used to improve extraction and separation efficiency as well as increasing detection sensitivity [24]. N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) is commonly used as derivatizing agent [35–37]. This study suggests the use of N-methyl-bis(trifluoroacetamide) (MBTFA) as a derivatizing agent because of the high reactivity of the obtained derivatives as well as the mild reaction conditions with products relatively inert, which prevents the gas chromatography column from damage, in addition it presents good reactivity with hydroxyl groups such as 4-NP [38]. It is possible that the choice of the derivatizing agent affects the sensitivity and capacity of extraction combined with the other considered parameters (e.g. temperature, coating of the fiber, exposure time, ionic strength). The silylation hyphenated in the derivatization process with

BSTFA is difficult due to the hidrolisis of the reagent and silylmethylated derivatives in aqueous solutions [39].

Optimal conditions were established as follows: one milliliter of water or sample, 3% of NaCl, 20 μL of 0.1 M HCl were added to a 10 mL sealed amber vial with gentle agitation. Subsequently the fiber DVB/CAR/PDMS was exposed to the headspace at 80 $^{\circ}\text{C}$ for 20 min magnetically stirred at 600 rpm. A derivatization process was carried out after each sample extraction. After derivatization, the device was inserted into the GC injection port for 3 min at 230 $^{\circ}\text{C}$. The conditions of extraction were sufficient to ensure a detectable concentration of the analyte. The resolution of the chromatographic peaks were adequate for the evaluation and quantification of the analyte of interest (Fig. 3).

3.2. Validation of the method

The method was validated in fortified samples to evaluate linearity, sensitivity, recovery percentage, repeatability and reproducibility. The calibration curves (Table 2) were linear over the working range (0.5–50 $\mu\text{g L}^{-1}$) and the correlation coefficient was above 0.99. LOD and LOQ were determined by a linear curve at low concentrations within a limit of confidence of 95% [40]. This method measures

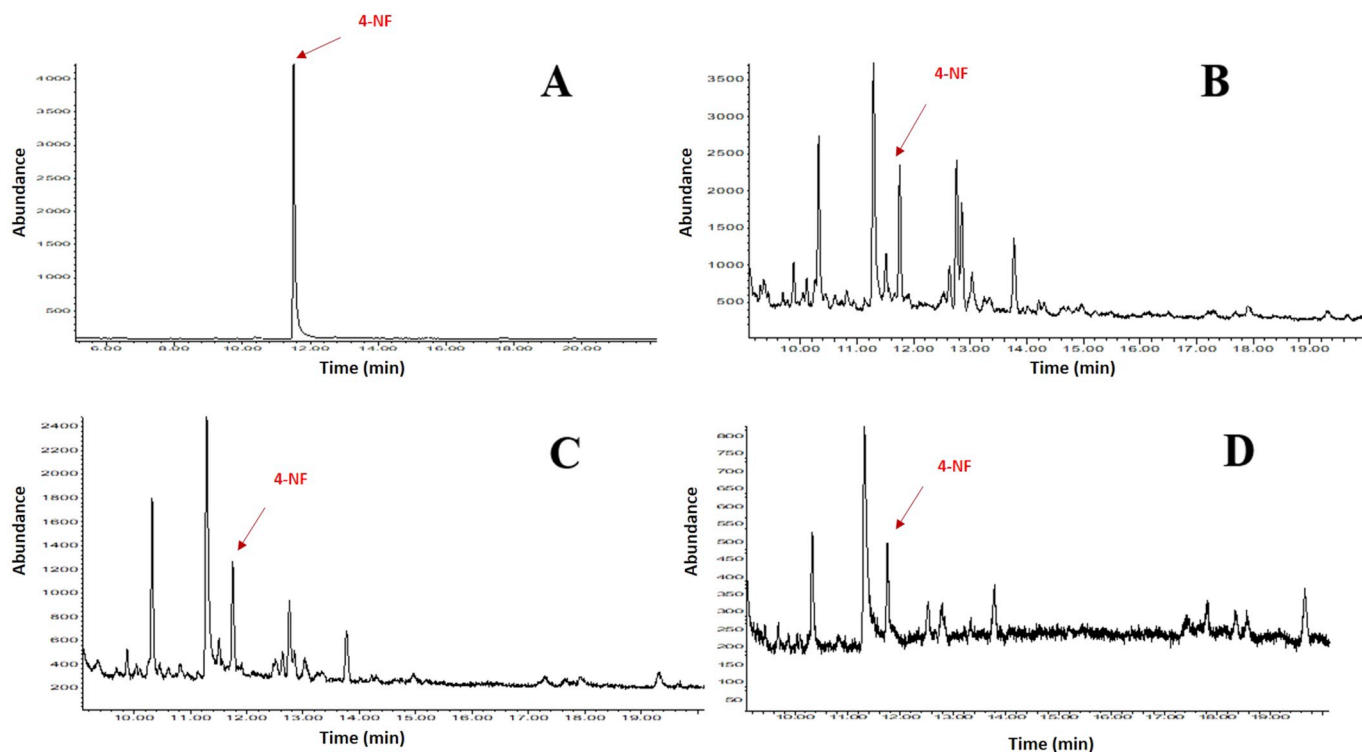


Fig. 3. Chromatograms of 4-NF (4-nonylphenol) HS-SPME-GC-MS (SIM mode) in water samples from different sources in Mexico and from a fortified sample. (A) Fortified sample with $1000 \mu\text{g L}^{-1}$, (B) Morales Lake, (C) San Jose Dam, (D) commercial brand 5.

Table 2

Validation parameters for HS-SPME-GC-MS analytical method in water samples.

Calibration curve	RSD% Repeatability	RSD% Reproducibility	Repeatability*	Reproducibility*
50	7.2	6.23	18.83	12.55
25	5.3	4.47	20.90	13.93
2.5	25.4	23.84	29.57	19.71
1	14.1	20.03	33.93	22.63
0.5	15.4	20.97	37.66	25.11
R^2	m	b	LOD*	LOQ*
0.9923	835.09	531.84	0.01	0.15

Units: $\mu\text{g L}^{-1}$; SD: standard deviation; CV: coefficient of variation; LOD: limit of detection; LOQ: limit of quantification; r: coefficient of correlation; m: sensitivity expressed as a linear slope. *Acceptable RSD% [49].

variations in the lowest values of the curve (where there is high uncertainty) to verify that the response of the obtained values are different than the blank. This is calculated from the intercept value (YB) plus the deviation that estimates random errors in the direction of the intersection (Sy/x), $YB + 3 Sy/x$ for LOD and $YB + 10 Sy/x$ for LOQ. The 95% of the limit of confidence of the variation of the slope in the interpolation zone is added to the obtained value, but the final value contemplates a high uncertainty in the lowest values of the curve and assures the presence of the analyte and its quantification with an acceptable precision. Our study reported a LOD of $0.01 \mu\text{g L}^{-1}$, this result is similar than the ones reported by Azzouz & Ballesteros [16] and Sanchez-Avila [30] with a LOD of $0.01 \mu\text{g L}^{-1}$ and $0.014 \mu\text{g L}^{-1}$ respectively. Another SPME methods report higher LOD; for example Ros et al. [35] and Moeder et al. [41] with LOD of $0.076 \mu\text{g L}^{-1}$ and $0.2 \mu\text{g L}^{-1}$ respectively. Table 3 shows a comparison between the developed method and other analytical techniques [42–48]. The method in the present study offers several advantages over other techniques. For example, only 1 mL of sample is needed and still low detection limits are obtained ($0.01 \mu\text{g L}^{-1}$). Additionally, the extraction time,

considering the derivatization process, is limited to 30 min. This allows the analysis of multiple samples in short time. And, for the first time to our knowledge, the feasibility of MBTFA as derivatizing agent to determine 4-NP was demonstrated.

The feasibility of the SPME method was assessed by analyzing fortified samples with different concentrations. 4-NP obtained recovery values were of 94%, 106% and 118% for samples of 1, 50 and $100 \mu\text{g L}^{-1}$ respectively. This values are in the acceptable range of the validation guide used for the validation of the method (70–120% for concentrations between $10 \mu\text{g L}^{-1}$ and $100 \mu\text{g L}^{-1}$) [28]. The obtained values are similar to the ones reported by Bina et al. [48]. Precision was measured as repeatability and reproducibility. Each point in the calibration curve was evaluated as the relative standard deviation (RSD%) of the area ratios. The compound (4-NP) has an acceptable RSD% which means that the developed method is reliable in different working days [49].

3.3. Monitoring of 4-NP in different sources of water in Mexico

It is difficult to determine the source of contamination in the 3 assessed scenarios: i) recreational water, ii) wastewater and iii) drinking water. However, the most common use of nonylphenol ethoxyolate is in detergents [50,51]; for example, in a study carried out in Taiwan, 41% of ninety domestic detergents contained from 0.2 to 21% of 4-NP [4]. This suggests that the presence of 4-NP comes mainly from the use of detergents.

In Table 4 the results of concentrations in the three analyzed scenarios are presented. Eighty-three percent of the analyzed samples presented concentrations above the LOD, of which sixty-five percent had concentrations above the allowed by the European Union (EU) ($2 \mu\text{g L}^{-1}$) and seventeen percent above concentrations recommended by the EPA ($6.6 \mu\text{g L}^{-1}$). Despite the fact that there is no statistically difference between the maximum concentrations in recreational and wastewater samples both were 2 times higher than the recommended level by EPA and 6 times higher than that allowed by the EU. The

Table 3
Chromatographic analytical methods for determination of Nonylphenol in water samples.

Compound	Sample volume (mL)	Extraction method	Derivatization	Analysis	Extraction time (min)	LOD ^a	Reference
4-NP	1	SPME	MBTFA (100 µL)	GC-MS	30	0.01	This study
NP	100	Continuous SPE	BSTFA (70 µL) + 1%TMCS	GC-MS	–	0.01	[16]
NP mixture	10	SPME	–	GC-MS	30	0.13	[23]
NP mixture	150	SBSE-PES	BSTFA(50 µL) + 1%TMCS + Pyridine(125 µL)	GC-MS	720	0.076	[32]
			–	LC-MS/MS	720	0.042	
4-NP	60	SPE	–	HPLC-DAD	40	0.34	[10]
4-NP	2500	MMF-SPME	–	HPLC-DAD	50	0.065	[42]
NP mixture	15	SPME	–	GC-MS/MS	40	0.014	[30]
4-NP	100	SBSE	BSTFA(2 µL) + 1%TMCS	GC-MS	900	0.021	[43]
4-NP	6	DLLME	BCEC-Cl (50 µL)	HPLC-MS	–	0.04	[44]
4-NP	500	SPE	BSTFA(30 µL) + TMCS(30 µL)	GC-MS/MS	–	0.020 (LOQ)	[45]
4-NP	2	SPME	MTBSTFA (100 µL)	GC-MS	40	0.00385	[46]
4-NP	20	PIL-SPME	–	GC-FID	60	0.0011	[47]
4-NP	5	DLLME	BSTFA + TMCS (10 µL + 10 µL)	GC-MS	–	0.00076	[48]
NP	4	SPME	BSTFA (100 µL)	GC-MS	90	0.2	[41]

^a Units: µg L⁻¹; SPME: solid phase microextraction; DLLME: dispersive liquid microextraction; SPE: solid phase extraction; SBSE-PES: stir bar sorptive extraction-polyether sulphone; MMF: multiple monolithic fiber; PIL: poly(VBHDIm⁺NTf₂)MBTFA: *N*-methyl-bis-trifluoroacetamide; BSTFA: *N*,*O*-Bis(trimethylsilyl)trifluoroacetamide; TMCS: Trimethylchlorosilane; BCEC-Cl: 2-(11H-benzo[*a*]carbazol-11-yl) ethyl carbonochloridate; MTBSTFA: *N*-Methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide; GC-MS: gas chromatography mass spectrometry; HPLC-MS: high performance liquid chromatography mass spectrometry; DAD: diode array detector; FID: flame ionization detector.

recreational water presented concentrations ranging from 0.83 to 12.61 µg L⁻¹ with a median of 3.61 µg L⁻¹; the wastewater from < LOD to 12.2 µg L⁻¹ with a median of 3.88 µg L⁻¹ and for drinking water from < LOD to 6.08 µg L⁻¹ with a median of 2.48 µg L⁻¹.

Concentrations of 4-NP in recreational water could be attributed to tourism, people washing clothes and illegal water discharges in rivers [52]. The reported values have reasonable similarities with other countries [21,48,53–61]. Nevertheless, these concentrations are much lower than the ones reported in Argentina (Table 5) [62]. Currently in Mexico the regulation of NP and its ethoxylates is not existent. So it is common to find these compounds in all types of detergents (industrial and domestic) because of its low cost and surfactant properties [63,64]. It is important to acknowledge that concentrations in recreational water were higher than in wastewater discharges. In this context, the exposure of 4-NP by skin contact has to be considered, as previous studies have reported skin absorption of NP in humans and other species [65–68]. Levels of 4-NP in drinking water in this study were higher than the reported by other authors. Tap water in Mexico is not potable, instead water jugs are used. The jugs are washed with any detergent each time before being refilled. A poor rinse may be the cause of the high concentrations of 4-NP in the reported samples. It is necessary to analyze drinking water before bottling in order to discuss this hypothesis. This ensures the need to monitor 4-NP and enforce the implementation of regulations in Latin America and Mexico.

The following limitations have been considered when interpreting the results of this study i) the limited number of water samples collected in each scenario and ii) the samples were punctual or taken at a specific time and place, so they are not representative of each scenario. However, the objective of assessing 4-NP in different sources of water was accomplished and results present a general overview of the current situation and allow to assess the exposure levels in this region. The real

Table 4
Location of the water samples collected from different exposure scenarios in Mexico.

Scenario	n	Median	Minimum	Maximum	P25	P75	% above reference EPA ^b	% above reference EU ^c
Recreational ^a	10	3.61	0.83	12.61	3.04	8.76	30	80
Wastewater ^a	14	3.88	< LOD	12.20	4.82	ND	7	57
Drinking water ^a	5	2.48	< LOD	6.08	ND	2.64	0	60

^a Units: µg L⁻¹; LOD: 0.01 µg L⁻¹.

^b The Environmental Protection Agency (EPA) recommends concentration of 4-nonylphenol in fresh water less than 6.6 µg L⁻¹.

^c The Water Framework Directive of the European Union allows a maximum concentration in water of 2 µg L⁻¹ of nonylphenol. Kruskal Wallis test-pos hoc Dunn, there is no statistically significant difference (p = 0.285).

Table 5
Exposure assessment of 4-NP in water samples from different scenarios in Mexico compared with data from different countries.

Scenario	Country	n	Minimum	Median	Maximum	Reference
Recreational	Mexico	8	0.83	3.05	12.61	This study
	France	12	0.006	0.058	0.55	[52]
	China	15	0.1	1.3	7.3	[53]
	Korea	18	0.01	0.9	41.3	[54]
	South Africa	7	0.38	1.655	2.61	[55]
	Argentina	14	1730.0	2020.0	2390.0	[62]
Wastewater	Spain	6	0.5	2	36.0	[56]
	China	21	0.093	0.161	0.332	[57]
	Mexico	12	< LOD	3.79	12.20	This study
	Spain	4	6.0	142	289.0	[58]
	Argentina	6	2390	2550	2680	[62]
	Iran	9	0.42	0.807	2.12	[48]
Drinking water	Belgium	10	0.25	0.745	2.5	[59]
	Italy	8	0.37	0.515	0.7	[59]
	Mexico	5	< LOD	2.48	6.08	This study
	China	15	0.01	0.05	2.7	[53]
	Czech Republic	6	0.029	0.0335	0.045	[21]
	China	62	ND	0.027	0.558	[60]
Italy	35	< 0.0077	0.0149	0.084	[61]	

*Units: µg L⁻¹.

source of contamination could not be defined; it is only possible to identify the final site in which the ecologic risk is presented. Mexico and Latin America do not have any regulations that establish minimum levels of NP in water. Therefore, there is scarce information about concentrations of this pollutant in surface and treated waters. The results presented in this investigation contribute with new information that

could help to identify the sources of contamination, as well to evaluate the ecologic and human risk that the exposure to 4-NP represents. This information could not be ignored by politicians, academics and companies as the ecologic and human implications are of great importance. This technique can support the continuous monitoring of this toxic in water samples.

4. Conclusions

A chromatographic analytical method was developed using HS-SPME combined with GC-MS for the extraction and quantification of 4-NP in water. Different parameters including type of fiber, extraction time, temperature and ionic strength were evaluated to optimize the analytical method. The feasibility of MBTFA as a derivatizing agent offering high sensitivity ensuring the detection of low concentrations was demonstrated. As the sensitivity and effectiveness of the method was proven, an analysis in water samples from different sources of water in Mexico was performed. In this study concentrations of 4-NP in water samples of recreational use and human consumption as well as in wastewater discharges were found. This pilot study detected 4-NP in eighty-four percent of the samples. Concentrations in recreational water, wastewater discharges and drinking water were up to $12.61 \mu\text{g L}^{-1}$, $12.20 \mu\text{g L}^{-1}$ and $6.08 \mu\text{g L}^{-1}$ respectively, which suggests the need to explore potential contamination sources. Environmental regulation measures are required to prevent the contamination in ecological receptors that could represent environmental harm. The ecological and health risk of 4-NP has been mainly related with endocrine disruption. As important concentrations of 4-NP in recreational water have been found in this study we recommend to consider skin exposure in humans and suggest further studies in this regard.

Concentrations of 4-NP found could cause a potential environmental impact and may represent a public health risk in Mexico. Thus, continuous monitoring and regulations are desired and recommended. The results obtained in this study provide an efficient analytical tool for future studies of 4-NP in environmental samples.

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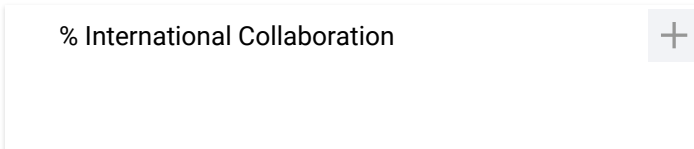
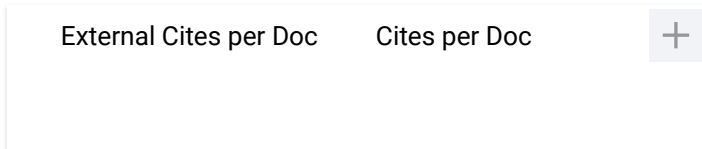
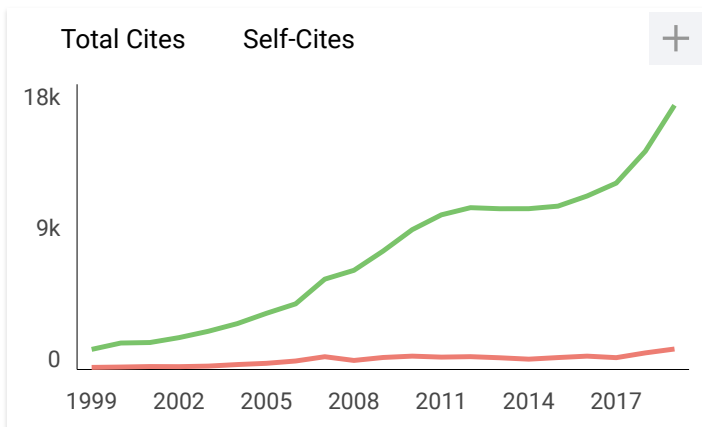
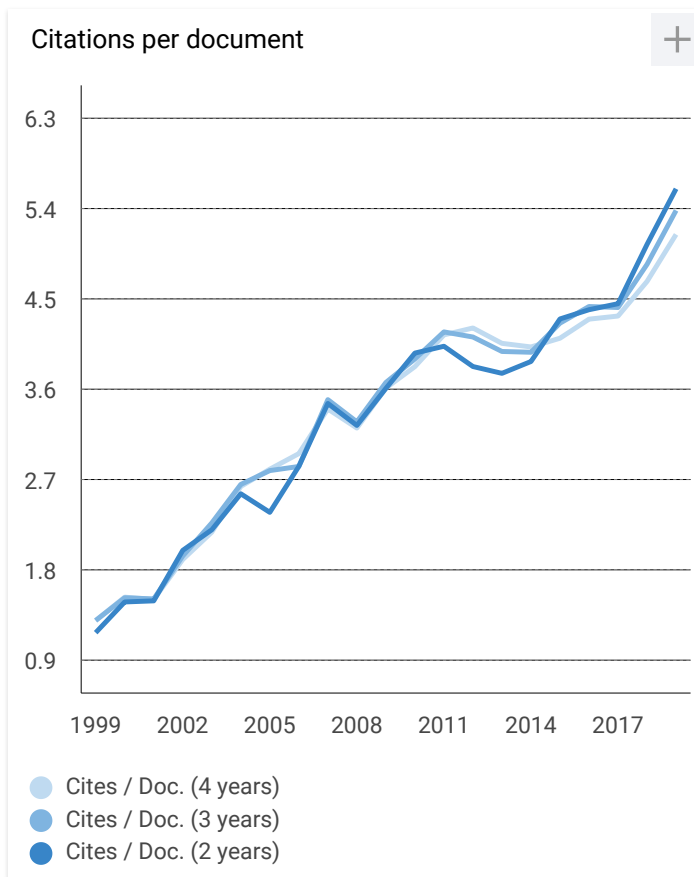
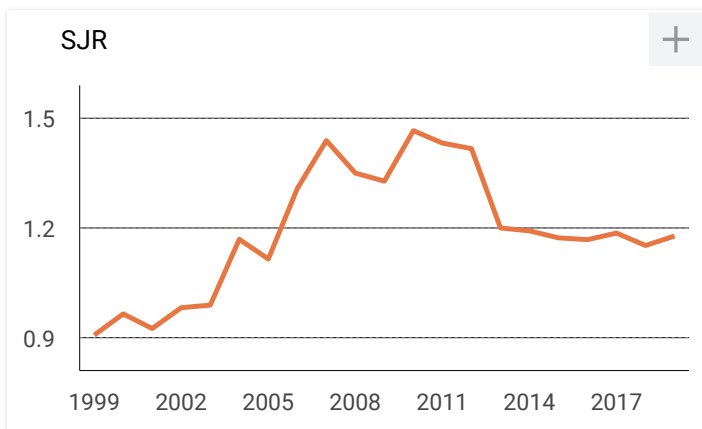
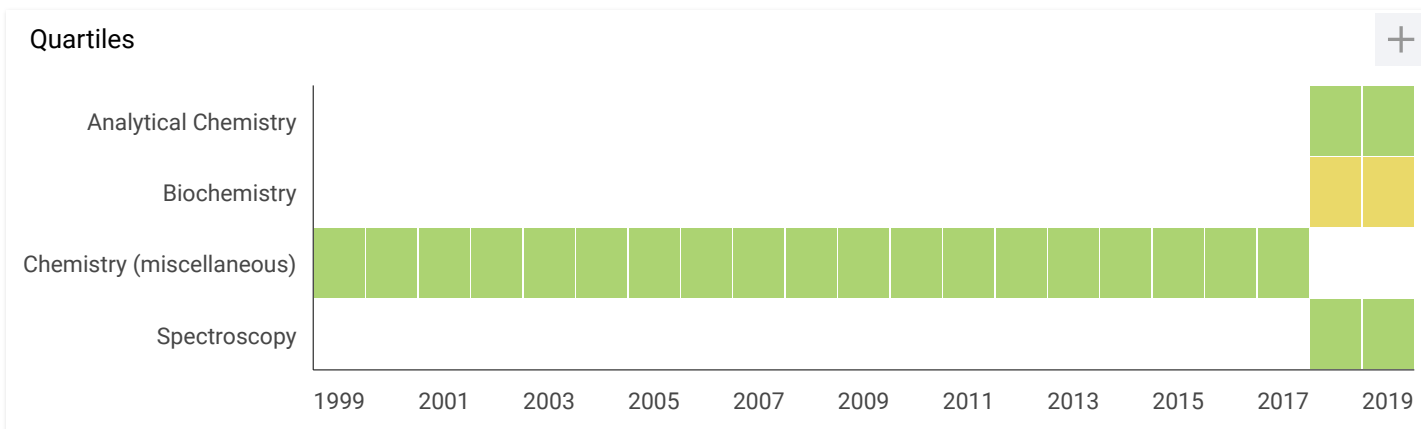


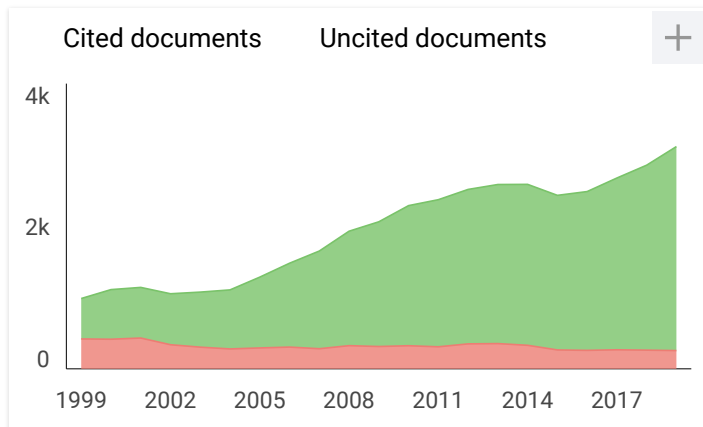
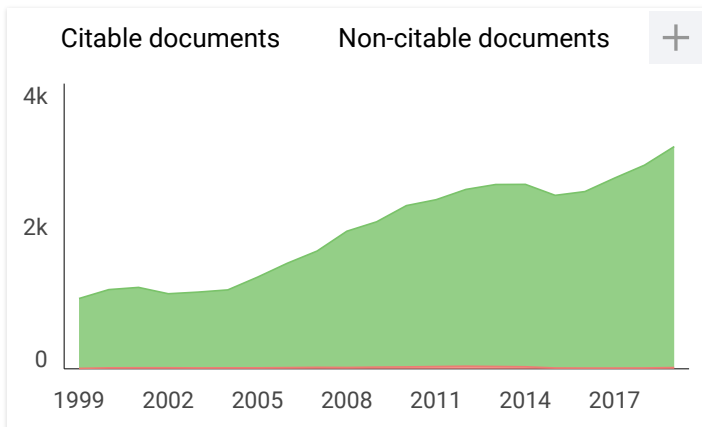
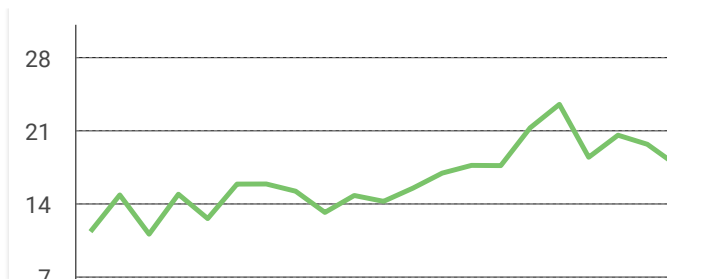
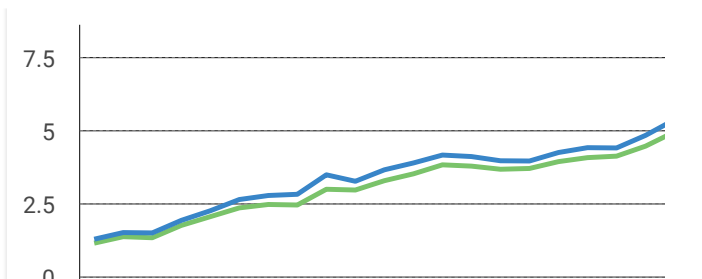
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Thank you for contacting us. We will proceed to analyze your query as soon as the current situation allows us. Best Regards, SCImago Team

SCImago Team

F **Fadhil** 7 months ago

Hi

reply

N **şükriye karabiberoğlu** 1 year ago

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