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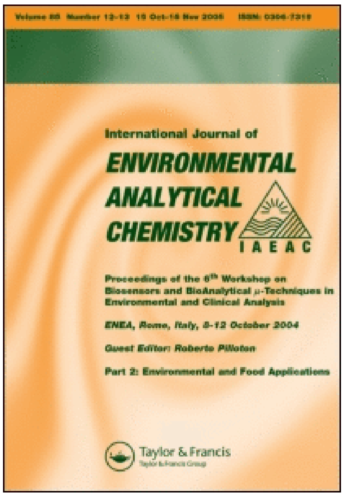

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Monitoring and Evolution of the Pollution by Volatile Organic Compounds (Vocs) in the Groundwaters of The Najerilla River Basin (Spain)

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Online publication date: 17 September 2010

To cite this Article Pons, Begoña , Fernández-Torroba, Miguel A. , Ortiz, Gustavo and Tena, María Teresa(2003) 'Monitoring and Evolution of the Pollution by Volatile Organic Compounds (Vocs) in the Groundwaters of The Najerilla River Basin (Spain)', International Journal of Environmental Analytical Chemistry, 83: 6, 495 — 506

To link to this Article: DOI: 10.1080/0306731031000111724

URL: http://dx.doi.org/10.1080/0306731031000111724

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Intern. J. Environ. Anal. Chem.
Vol. 83, No. 6, pp. 495–506, June 2003

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MONITORING AND EVOLUTION OF THE POLLUTION BY VOLATILE ORGANIC COMPOUNDS (VOCs) IN THE GROUNDWATERS OF THE NAJERILLA RIVER BASIN (SPAIN)

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(Received 6 May 2002; in final form 17 February 2003)

VOCs were detected and identified in the water of several wells in the area of Nájera (La Rioja). The past uncontrolled spills from an important painting and varnishing industry and from other smaller ones devoted to the manufacture of furniture and varnishing activities were the sources of the VOCs plume detected in this aquifer. This article shows the results obtained in the monitoring and assessment of the pollution at 18 sampling points for more than a year. It has allowed us to study the evolution of the different pollutants and the influence of a remediation process applied by the company in the main pollution source. The analytical method is based on headspace-solid-phase microextraction (SPME) using a 75-μm carboxen-polydimethylsiloxane fibre. Quantification was carried out by gas chromatography with flame ionization detection. This method has allowed us to determine the 13 VOCs identified in the polluted underground samples providing good sensitivity (LOD between 0.1 and 6.0 ng/mL) and reproducibility (r.s.d. less than 10%).

Keywords: VOC; BTEX; Groundwater pollution; SPME

INTRODUCTION

The presence of toxic pollutants is the most significant health concern for people using underground water as their drinking water supply [1]. Volatile organic compounds (VOCs) were detected and identified in the water of several wells in the area of Nájera (La Rioja). The past uncontrolled spills from an important painting and varnishing industry and from other smaller ones devoted to the manufacture of furniture and varnishing activities were the sources of the VOCs plume detected in the aquifer of the river Najerilla [2].

Preliminary studies showed that the source of the pollution could be a localized point. After studying several remediation processes, the company discovered an old

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ISSN 0306-7319 print: ISSN 1029-0397 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0306731031000111724

deposit that had been used as an uncontrolled dumping site for solvents and residues. The company removed this deposit and all the soil around this saturated area.

The objective of this article is to determinate the concentration level of VOCs in the underground water of the Najerilla aquifer, the paths through which they flow and other factors that affect their presence in the aquifer, after applying the previous remediation process.

Volatile organic compounds are difficult to analyse owing to their great volatility. Nowadays, volatile compounds are analysed using either headspace (HS) [3] or purge-and-trap [4–6] techniques, while for semi-volatile and non-volatile compounds, liquid–liquid extraction (LLE) [7] and solid-phase extraction (SPE) [8–10] are commonly used. All these techniques are effective but have some limitations [4,5,11]. Headspace is an excellent method to analyse complex or environmental samples, although the analysis is restricted to those volatile compounds with relatively high concentrations. Purge-and-trap is recommended by the United States Environmental Protection Agency (USEPA) coupled with full-scan mass spectrometry. The purge-and-trap method applied to volatile compounds can be affected by a contaminated trap, requires large amounts of liquid nitrogen and is highly susceptible to leaks. In LLE, the main problems are the difficulties in automating the methods and the high volume of expensive solvents necessary, which must also be of high purity. Besides, many of these solvents are toxic and even carcinogenic, and their disposal is difficult. LLE has been largely replaced in the last few years by SPE using different sorbents [12]. SPE can be automated and uses very little solvent; however, it is still a multi-step process, prone to losing analytes if it is not fully automated, and still needs toxic organic solvents for the elution step. Moreover, a large volume of sample is required for trace analysis, and it is susceptible to high baseline blanks, channelling and, if the sample contains particles, plugging of the sorbent beds. Furthermore, SPE is restricted to semi-volatile compounds since the boiling points of the analytes must be substantially above that of the solvent.

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Solid-phase microextraction (SPME) is a relatively new extraction technique developed by Pawliszyn and co-workers [13–15]. SPME is a valuable advance in sample preparation and has a number of advantages compared to the conventional techniques used to extract organic compounds from environmental samples. It does not require organic solvents, which are often expensive and harmful to both health and the environment. The technique is very simple and fast, the whole extraction and analyte transfer process usually only takes a few minutes [13] and it is easily automated, portable and inexpensive [14].

The analytical method developed in this work is based on SPME and gas chromatography with flame ionization detection (GC-FID). This technique is based on an immobilized phase (polydimethylsiloxane or polyacrylate polymers) as a stationary phase and is used for the direct extraction of organic trace compounds by simply dipping the fibre into the matrix or into its headspace. Thus sampling, extraction and concentration are focused in a single step, and this method is particularly suitable for volatile analytes since it reduces losses during sample preparation. Some of its advantages over the classical techniques are speed, simplification of the analytical process and automation. SPME is a very efficient technique for analysis of relatively volatile compounds from different environmental matrices including air, water and soil [16–21].

One group of organic pollutants of interest in aqueous samples is composed of the volatile organic compounds (VOCs) including benzene, toluene, ethylbenzene and xylene isomers (BTEX). These compounds were the first ones studied by SPME [22–29]. Often the pollution sources of BTEX are residues of hydrocarbon fuels [27–29]; however, in the case of the Najerilla aquifer, other VOCs were involved owing to the use of solvents in the factory: acetone, methyl isobutyl ketone, ethyl acetate, methyl *tert*-butyl ether, trimethylbenzenes and naphthalene.

In the laboratory, we developed an analytical method based on headspace-SPME and GC-FID [2,30,31] that allowed us to determine the 13 VOCs identified in the polluted underground samples: acetone, ethyl acetate, methyl isobutyl ketone (MIBK), methyl *tert*-butyl ether (MTBE), 1,3,5-trimethylbenzene (1,3,5-TMB), 1,2,4-trimethylbenzene (1,2,4-TMB), benzene, toluene, ethylbenzene, *m*-, *p*-, and *o*-xylene and naphthalene. These contaminants were identified by GC-MS. The behaviour of five fibres coated with different stationary phases and mixed phases, i.e., poly(dimethylsiloxane) (PDMS), poly(acrylate) (PA), poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB), divinylbenzene/Carboxen/poly(dimethylsiloxane) (DVB/CAR/PDMS) and Carboxen/poly(dimethylsiloxane) (CAR/PDMS), for the determination of the above-mentioned compounds had already been studied, both by direct extraction and by headspace-SPME (HS-SPME). The best results were obtained with a CAR/PDMS coating fibre in mode of headspace. Validation of the optimized method was carried out by analysing synthetic samples and by comparison with the HS technique [30,31].

Using this headspace-SPME method with a 75-µm CAR/PDMS fibre, we monitored the pollution at 18 sampling points of the aquifer for more than a year. This article shows the evolution of the different pollutants at the most significant sampling points and the influence on the aquifer of the remediation process implemented by the company in the main pollution source.

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EXPERIMENTAL

Sampling Procedure

To collect the underground water, Grunfoss pumping equipment of 6-cm diameter with an electric generator was used. The pump was submerged below the piezometric level and the sample of water was pumped at 0.5 L/s until the pH and conductivity parameters remained constant. In this way, the homogeneity of the samples was assured, since the saturated zones in the wells have low depth (approximately three metres). Then, the samples of water were collected in glass bottles and hermetically sealed, preventing the formation of bubbles and without free headspace. Finally, the samples were acidified at $pH = 2$ and preserved at 4°C until the analytical determination (never for more than a week).

Reagents and Chemicals

The calibration solutions were prepared in purified water MilliQ from the following standard stock solutions supplied by Supelco: Petroleum Volatile Organic Compounds/Gasoline Range Organics (PVOC/GRO), a mixed solution of 2000 µg/mL of benzene, toluene, ethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, methyl-*tert*-butyl ether, *m*-xylene, *o*-xylene, *p*-xylene and naphthalene in methanol; a standard solution of 2000 µg/mL of ethyl acetate in methanol; and a standard solution of 2000 µg/mL of acetone in methanol:water (90:10); and a standard solution of 5000 µg/mL of MIBK in methanol. NaCl(s) RPE (for analysis) supplied by Carlo Erba was used as matrix modifier. The SPME fibres of 75-µm CAR-PDMS were supplied by Supelco.

Instrumentation

A Varian 3800 gas chromatograph with a flame ionization detector and a Combipal autosampler (CTC Analytics), which allows for an automated static headspace and SPME injections, were used.

Chromatographic Conditions

The GC-FID was equipped with a CP-Select 624 column (30 m × 0.32 mm i.d. with 1.8 µm phase). For the gas chromatography, an initial temperature of 35°C was used for 5 min, followed by an increase in the temperature at a rate of 10°C/min up to 225°C and up to a final hold at 225°C for 1 min. The carrier gas used at 1.7 mL/min was helium. The detector temperature was 300°C, with a make-up flow of 25 mL/min, an H_2 flow of 30 mL/min and an airflow of 300 mL/min. The conditions in the SPME injections were an injector temperature of 280°C and a splitless mode at the initial time, followed by a 1:50 split ratio at 0.5 min. A 0.8 mm i.d. insert was used. The sorption time of the fibre in the headspace was 15 min, and the desorption time in the injector was also 15 min in order to ensure that the fibre was cleaned. Note that although the desorption was completed in less than 0.5 min, the fibre was left inside the injector at 280°C for a longer period (15 min) with the split valve open to ensure that no compound remained in the fibre coating that might appear in subsequent analyses (carry-over effect).

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Sample Preparation

An aliquot of 0.6 mL of the water sample was transferred to a 2 mL glass vial (Scharlab), and then 0.15 g of NaCl was rapidly added and the vial was capped (with screw caps) and taken to the GC autosampler. According to the literature [32,33], this salting out has a significant influence on the extraction of BTEX and favours the extraction of polar compounds such as acetone, MTBE, MIBK and ethyl acetate [34,37]. Moreover, the salting out equals the matrix of the sample solutions and the calibration solutions, since the quantification is carried out from an external standard calibration. The calibration solutions were prepared from the standard stock solutions diluted with purified water milliQ and with the same concentration of NaCl.

A 75-µm CAR-PDMS fibre was equilibrated at room temperature for 15 min with the headspace above a 0.6 mL sample placed in a 2-mL sealed vial. The use of this kind of fibre allowed us to develop a multiresidue method capable of quantifying the 13 analytes, which were very different in terms of polarity and volatility [30,31]. This headspace-SPME method provided good sensitivity (detection limit (LOD) between 0.1 and 6.0 ng/mL) and reproducibility (RSD less than 10%) [31].

Samples that exceeded the highest quantification limit had to be diluted to an appropriate extent with water milliQ containing the same concentration of NaCl.

All the samples were analysed in triplicate.

RESULTS AND DISCUSSION

Analytical Features

Previous studies [2,30,31] performed in this laboratory showed that the CAR-PDMS fibre was the most suitable for the simultaneous determination of the 13 analytes, whereas other fibres (such as PDMS, which have a wider linear range) proved to be more suitable for non-polar compounds, and others (e.g., polyacrylate) for very polar compounds. The kinetics and behaviour of five different fibres, i.e., PDMS, PA, PDMS/DVB, DVB/CAR/PDMS and CAR/PDMS were studied and the final choice of CAR-PDMS was a compromise decision for determination of the 13 VOCs identified in the contaminated underground water [2,31]. This fibre proved to have a good extraction efficiency for VOCs of medium polarity [20,38] and, although its concentration range is not extensive [16,38], it showed an acceptable repeatability (less than 10% RSD, $n = 15$) [31,32].

Figure 1 shows a chromatogram of a calibration solution and a chromatogram of an underground sample. It can be seen that *m*-xylene and *p*-xylene eluted simultaneously, so these two compounds were quantified together.

The SPME method developed was validated against a more conventional method such as the headspace method [31] and proved to have good sensitivity and reproducibility. Table I shows the features of the analytical method and it can be seen that the LODs, defined as the concentration of the mean peak area three times the standard deviation of a blank, were within the range of 0.1 ng/mL for MTBE, benzene and 1,3,5 TMB, and 6.0 ng/mL for acetone. The method also showed a good reproducibility too; the RSDs were between 4 and 10% ($n = 15$).

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Monitoring and Evolution of the Pollution

Eighteen sampling points were monitored once a month for more than a year. The sampling points were control wells located in the Najerilla aquifer. Figure 2 shows a map of the sampling points and the pollution source. It is difficult to classify the points according to their concentration level, since the concentration varies greatly between the different pollutants. Nevertheless, the sampling points were classified according to their pollution levels. The points with only a few parts per billion (ppb, ng/mL) of pollutants or close to the quantification and/or detection limits were considered as ‘low pollution’ points. The points with concentrations of up to 300 ppb in some contaminant were considered as ‘moderate pollution’ points and those with concentrations higher than 300 ppb were considered as ‘high pollution’ points; the latter even reached parts per million levels (ppm, µg/mL). The moderate and high pollution points were divided into two categories: those whose pollution was decreasing and those whose pollution remained constant. The predominant flow of the aquifer is shown in Fig. 2, and it can be seen that the point NS-17 is located in the opposite direction to this predominant flow, and thus NS-17 was considered as a blank point.

Figure 3 shows the evolution of the pollution by VOCs at some sampling points. The remediation process began in November 2000 and continued until the summer of 2001. The wells S-6 and S-7 were built in April 2001. It can be seen that the concentration of pollutants is decreasing in many wells. However, at some points,

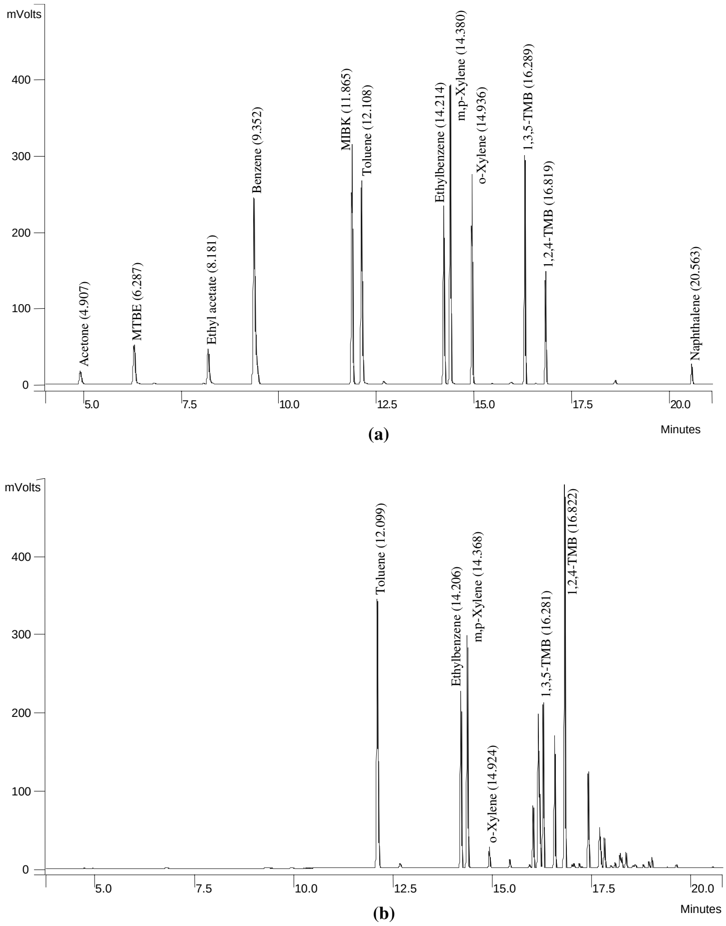

FIGURE 1 Chromatogram of the headspace-SPME obtained in: (a) a calibration solution of 500 ng/mL for each compound; (b) a sample of underground water at the point NS-14 in October 2001.

TABLE I Features of the HS-SPME method: limits of detection (LOD) and relative standard deviation (RSD) obtained by the HS-SPME method using a CAR/PDMS coated fibre, for the compounds studied

Compound	*Linear range* (ng/mL)	*L.O.D* (ng/mL)	*% RSD* (*n* = 15)
Acetone	10–750	6	9
Methyl *tert*-butyl ether	10–750	0.1	5
Ethyl acetate	10–750	1	9
Benzene	10–750	0.1	6
Methyl isobutyl ketone	25–1875	0.2	10
Toluene	10–750	4	4
Ethylbenzene	10–750	0.4	5
m,*p*-Xylene	10–750	1	6
o-Xylene	10–750	1	5
1,3,5-Trimethylbenzene	10–750	0.1	7
1,2,4-Trimethylbenzene	10–750	0.5	9
Naphthalene	10–750	1	7

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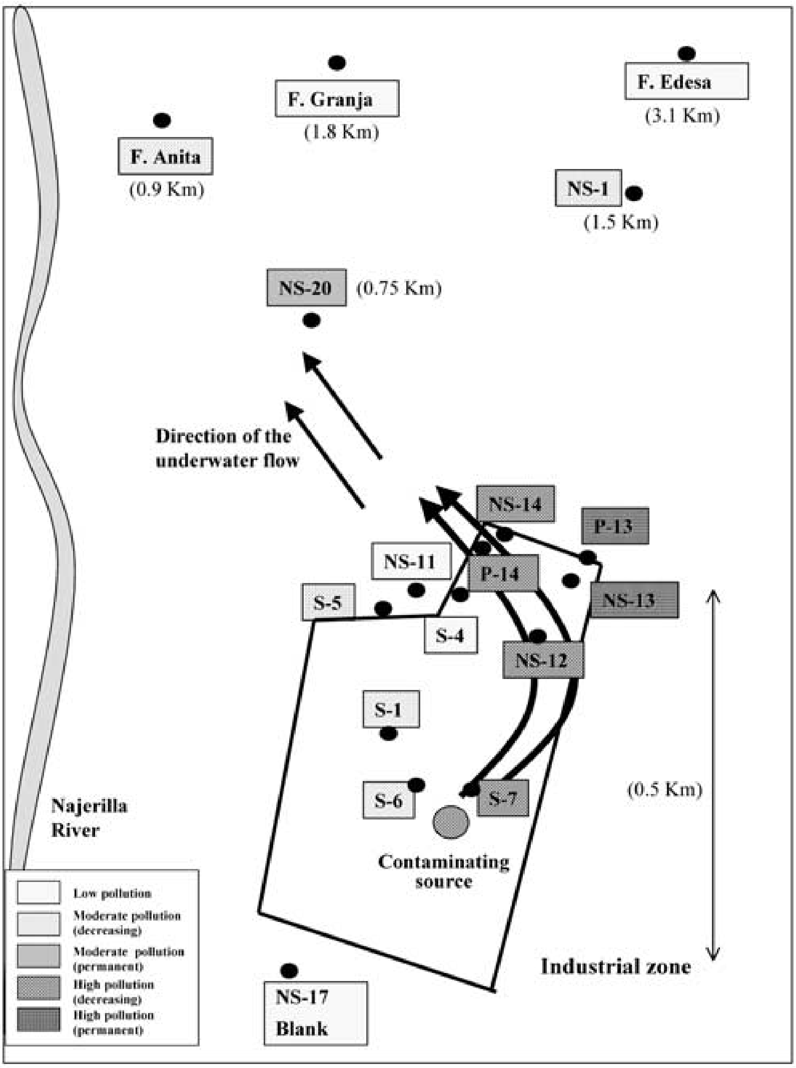

FIGURE 2 Map of the sampling points in the industrial zone including a classification by pollution.

i.e. NS-20 and NS-13, no decrease is detected, and this may indicate that the water has a preferential flow through S-7, NS-12 and NS-14, whereas the points NS-13 and NS-20 seem to be somehow isolated. These preferential flows might be due to the existence of areas with different hydraulic conductivity in the alluvium aquifer of Najerilla caused by the great heterogeneity of the terrain. On the other hand, the point NS-20 presents a higher concentration of TMBs (and other alkylbenzenes have also been identified). Figure 4 shows the excessive concentration of TMBs at the points S-5 and NS-20 compared with the concentration of other pollutants, and at the points NS-14 and NS-11, a fact that might be due to the recalcitrant nature of the TMBs and their high adsorption distribution coefficients (K_d) between the soil and the water. Nevertheless, other pollution sources cannot

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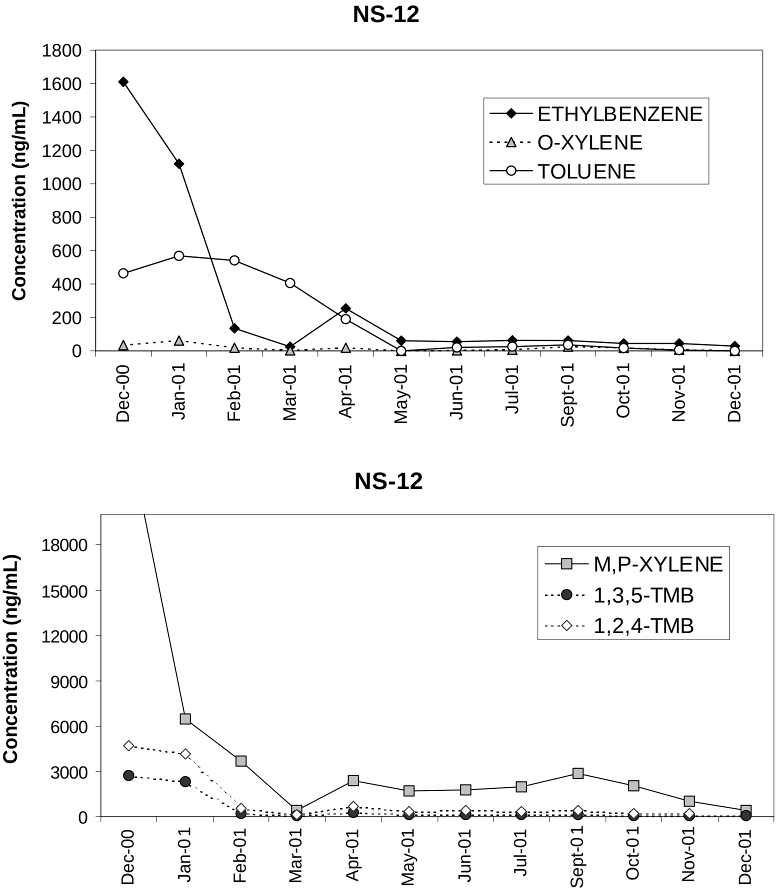


(a)

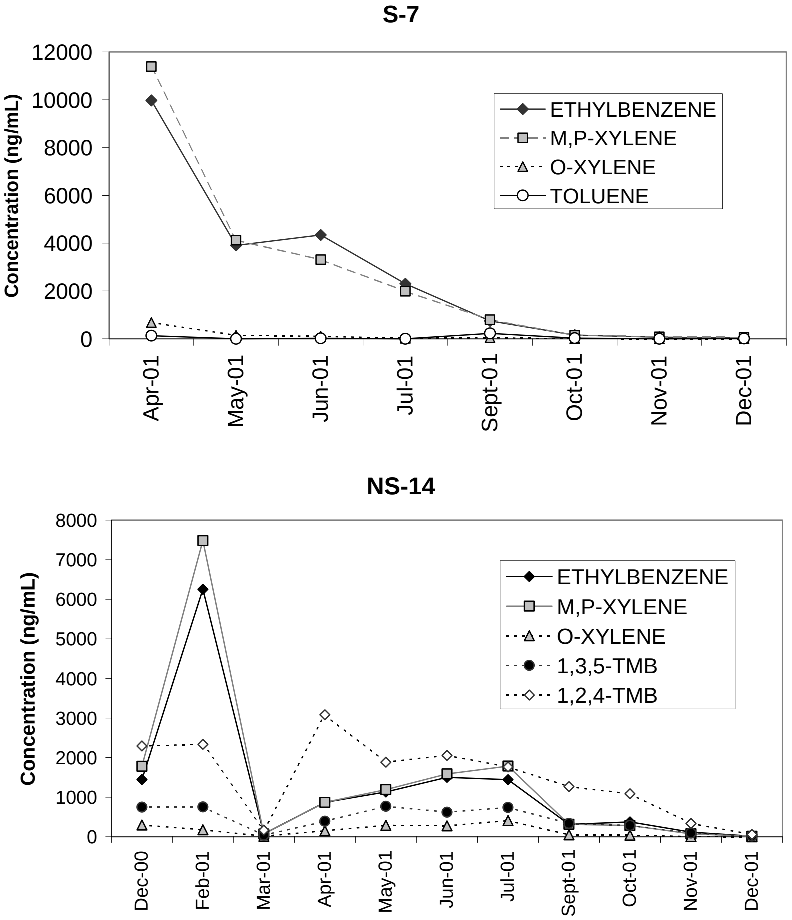
FIGURE 3 Evolution of the pollution by VOCs at some sampling points. (a) The pollution has decreased at NS-12; (b) the pollution has decreased at S-7 and NS-14; (c) the pollution remained constant at NS-20; (d) the pollution remained constant at NS-13.

be ruled out [39]. A similar result is obtained, though to a lesser extent, at the point NS-1.

CONCLUSIONS

The analytical method is adequate to determine simultaneously the 13 analytes described in these water samples.

After the remediation process, as expected, the pollution by VOCs is decreasing at most of the sampling points, but there are some sampling points (NS-13, NS-20) where the pollution does not seem to decrease. The behaviour of these points is anomalous, since their pollution level remains constant. It is at least possible that these points may be somehow isolated from the rest of the flow of the aquifer. Some road-building had occurred near the point NS-20, and this could be the cause of the isolation since the



(b)

FIGURE 3 Continued.

flow might have been diverted through another path. It may be necessary to build a new piezometer or well near this point to follow the flow of the aquifer.

The water flow must have preferential paths through S-7, NS-12, NS-14 and P-14, since the nearby points have low pollution levels. These preferential flows may be due to the existence of areas with different hydraulic conductivity in the alluvium aquifer of Najerilla caused by the great heterogeneity of the terrain.

Point NS-20 has a higher TMBs concentration, which might be due to the recalcitrant nature of the TMBs and the high adsorption distribution coefficients (K_d) between the soil and the water. Nevertheless, other pollution sources cannot be discounted [39].

Currently, the pollution of the wells is still monitored and it is necessary to continue the study because the concentration level is still high at some points. If the pollution does not decrease at these points, it would be advisable to look for other sources of pollution and the company will have to apply a new remediation process.

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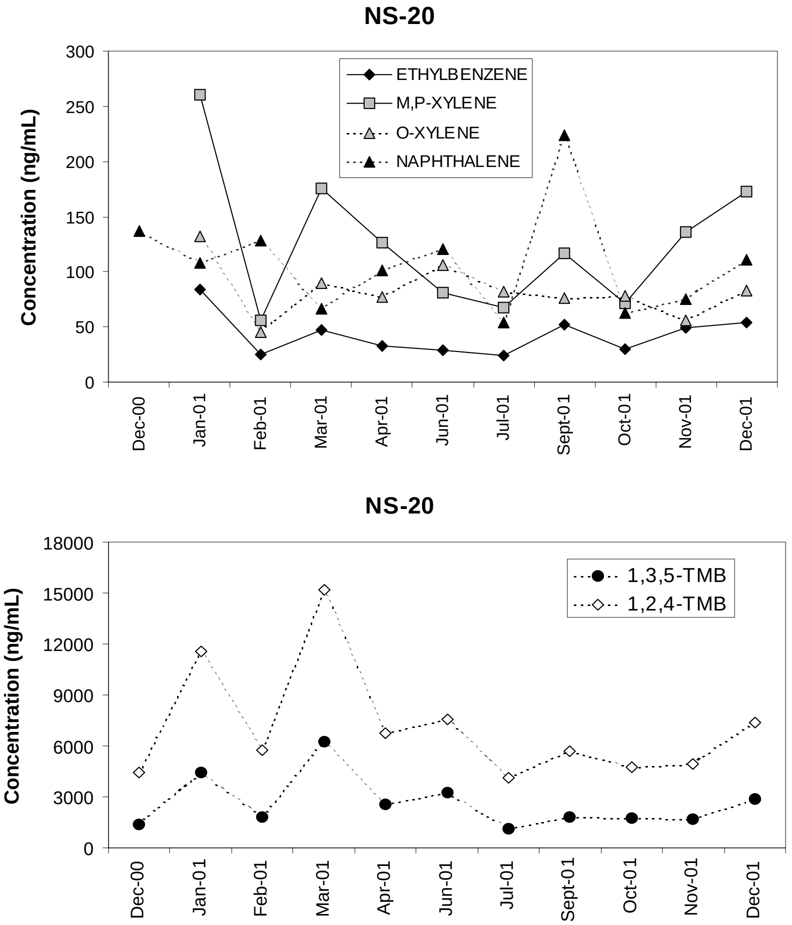
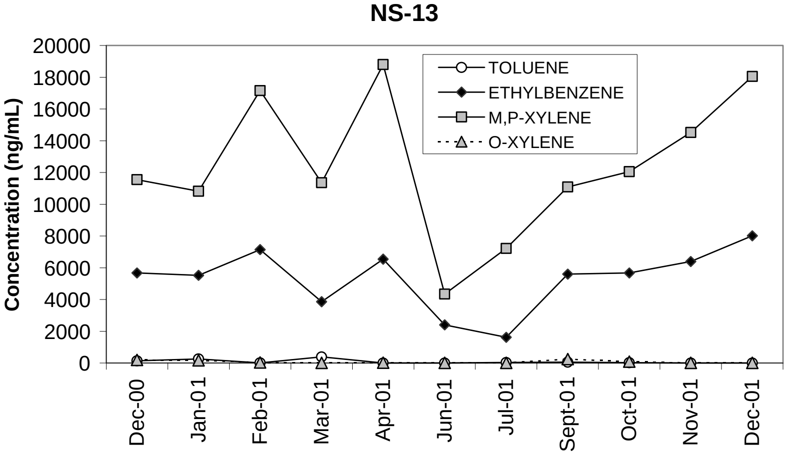
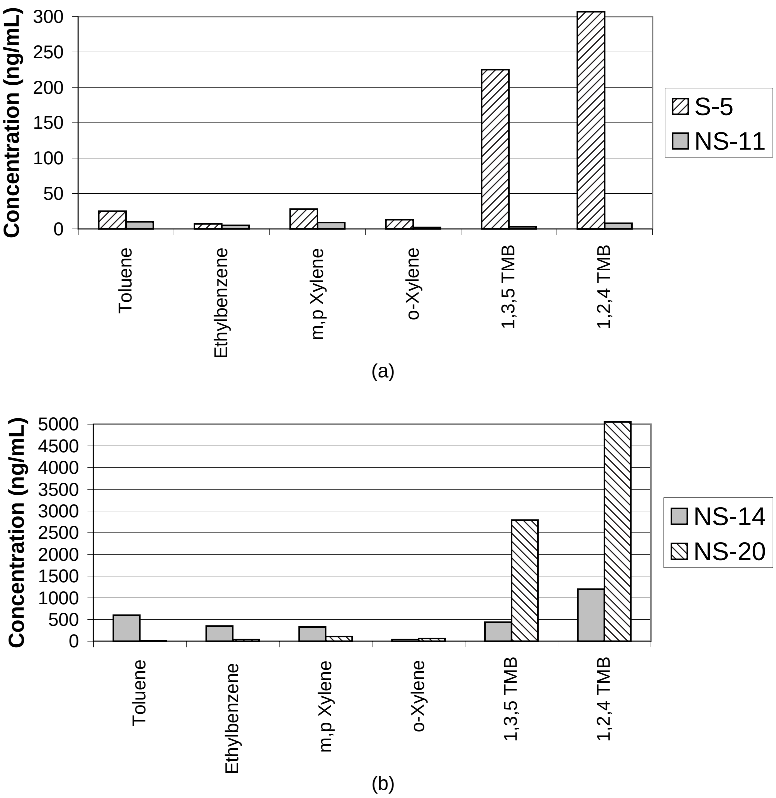


(c)



(d)

FIGURE 3 Continued.



(a)

(b)

FIGURE 4 Comparison of the relative concentration of TMBs at the points S-5, NS-20 vs. the points NS-11 and NS-14.

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Acknowledgements

This work was supported by the Research Project 2FD97-1708 within the *Plan Nacional de I + D* cofinanced with FEDER funds, and the Research Project ANGI-b-2001 within the *I Plan Riojano de I + D*. Further, we thank the Dirección General de Calidad Ambiental del Gobierno de La Rioja for its collaboration.

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