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Methodology for volatile organic compounds determination in water from wells and springs in Mexico state, Mexico

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RESUMEN

Se utilizó el método 524.2 recomendado por la EPA para analizar compuestos orgánicos volátiles (VOC's) presentes en muestras de agua. Los análisis se realizaron con un sistema de purga y trampa con cromatografía de gases acoplado a masas, equipado con detectores de ionización electrónica y de flama. Con este sistema se determinó la presencia de VOC's en muestras de agua, de manantial y de pozo, del estado de México. Los resultados preliminares de siete sitios de muestreo confirman la presencia de VOC's procedentes de insecticidas utilizados en la zona .

PALABRAS CLAVE: agua subterránea, contaminación, GC-MS purga-trampa, VOC's.

ABSTRACT

The EPA 524.2 method using purge and trap capillary gas chromatography, electron ionization and flame ionization detection was used to determine volatile organic compounds (VOC's) in water samples from wells and springs in Central Mexico. The sampling technique was improved to assess the presence of VOC's in the samples. The preliminary results obtained in 7 sites from the State of Mexico, confirmed the presence of VOC´s from pesticides used in the zone.

KEYWORDS: Groundwater, pollution, VOC's, GC-MS purge and trap method.

INTRODUCTION

Considerable quantities of volatile organic compounds (VOC's) are produced in the synthetic organic chemistry manufacturing industry. The compounds are contained in many products, including paints, adhesives, gasoline and plastics. Other sources are emissions and evaporation from mobile or fixed sources such as automobiles, fuel stations, leaking from underground storage tanks, etc. VOC's can be important environmental contaminants because many are mobile, persistent and toxic; they do not necessarily remain in the medium where they originate. In certain media VOC's can have a very short half-life of a few hours due to degradation, whereas in others they can be very persistent and show little degradation over periods of years. In urban areas they are associated with toxic air pollutants (Squillace *et al.,* 1999). The occurrence of VOC's in drinking water from surface and groundwater has also been reported (Westrick, 1990). Trace organic compounds analysis has always been a major challenge to environmental chemistry. Amendments for safe reservoir and drinking water have required to set more strict regulations for the presence of the VOC's down to the μg/L level (USEPA, 1996). In rural areas, reports in groundwater from wells of different type have shown the presence of VOC's originating from solvents, gasoline, aromatic hydrocarbons and fumigants (Lanchote *et al.,* 2000; Polkowska *et al.,* 2000).

The main purpose of the present study was the assessment of VOC's concentration levels in groundwater from springs and wells located around the Lerma river basin. For this purpose the EPA 524.2 method using purge and trap capillary gas chromatography (GC-MS), electron ionisation and flame ionisation detection were used. Sampling techniques were improved to obtain VOC's concentrations lower than μg/L level.

EXPERIMENTAL

The water samples were taken in seven sites in the northern part of the State of Mexico, belonging to the Mexican Volcanic Belt. Four springs and 3 wells, located in urban and agricultural zones, where pesticides are frequently used, were monitored for VOC's. The geographical location, some characteristics of the sites and the average temperature of the water are indicated in Table 1. The sampled zone is surrounded by oaks and coniferous forests and the agriculture consists basically of corn, wheat and beans on 45% of the land (INEGI, 1999).

A first sampling at Tultenango and Las Fuentes was performed in September 2000, during the rain season. At this occasion the sampling was performed using polyurethane bottles, that were only rinsed with deionized water. The bottles were immersed in the spring and, eventually, the water

Table 1

An overview of the geographical features of the 7 sites and the average water temperatures

Place	Site	T (°C)	Coordinates	Altitude (m)	Site characteristics
El Oro (volcanic and mine zone)	Tultenango	24.2	19º 50’ 45"N 100° 07’ 47"W	2675	Borehole 200 m deep, in a valley where the main activity in the zone is agriculture and animal breeding.
	Plaza de Sta. Cruz	17.3	19° 48’ 35" N 100° 07’ 47"W	2772	Spring near a village, used for drinking water supply.
	Cuauhtemoc	15.8	19° 46’ 52"N 100° 08’ 24"W	2753	Artesian well 7 m deep located in a farm, agricultural zone producing maize.
	La Venta	19.5	19° 48' 13" N 100° 07’ 11"W	2630	Borehole near downtown El Oro City.
Jocotitlán volcano (agricultural zone)	Las Fuentes	18	19° 43’ 41"N 99° 41’ 05"W	2882	Group of springs used for drinking water supply, agricultural zone.
	Tiacaque	17.9	19° 40’ 19"N 99° 42’ 38"W	2857	Spring near Jocotitlán volcano.
	Pasteje	18.13	19° 40’ 59"N 99° 46’ 40"W	2818	Spring used for drinking water supply. Cattle and agricultural area in an industrial zone.

was put in a plastic pot before being transferred to the sampling bottles.

In April 2001, the sampling procedure was improved. For each site, two glass vials (25 ml) were prepared. They were washed with liquid soap and rinsed with deionized water. They were then dried at 110°C for 72 hours, in an impurities free oven. The oven cavity was also carefully washed before use with liquid soap and rinsed with deionized water. After drying the vials were quickly closed to produce a vacuum effect. They were stored until used in the field. The sampling was performed, using gloves to avoid contamination, by immersion of the vial in the water where it was opened, filled and closed. The seven sites were sampled. April corresponds to the dry season.

LABORATORY MEASUREMENTS

Many of the VOC’s found in water spring samples, are present at µg/L and ng/L levels. To identify and quantify these species, pre-concentration must be achieved. The use of purge and trap system (P & T) to concentrate VOC’s prior to analysis has been established as a proven technique for their detection (Rood, 1995).

In the present work a Tekmar™ 3000 (GC-MS) equipment was used, consisting of VOC’s purge and trap concentrator that allows automatic processing of liquid samples for analysis by gas chromatography. The concentrator operates and interfaces with the gas chromatograph (GC) under microprocessor control.

The equipment has a sample glassware for processing single samples; a front panel trap pressure gauge that shows the current system pressure (in psi) for each mode; a liquid crystal detection screen displays information about the ON/OFF switch.

The EPA method 524.2 (USEPA,1993) permits to determine halogenated, aliphatic and aromatic compounds as well as simple hydrocarbons using a P&T extraction technique interfaced with capillary gas chromatography for high resolution capabilities. The direct interfacing is accomplished without splitting of the purge and trap desorption carrier flow. The process of sampling, purging and trapping, injection and analysis of the sample, is manual and takes around 75 minutes.

To detect the presence of fertilizers in water samples, the standard 47582-U was used. Detection of 60 VOC's was performed using the serie EPA 4S 8775, 4S 8777, 4S 8779, 4S 8786, 4S 8797 and 4S 8799 standards. Calibration was performed with standard solutions at 0.1, 1.0, 5.0 and 10 µg/mL concentrations. The chemical standards used in this work were Supelco "standard grade". Stock standards made from pure analytes were prepared by placing 9.8 mL methanol (LiChro Solv. Merck, Germany) into a 10 mL ground-glass, stupider volumetric flask. The flask was allowed to stand, unstoppered, for about 10 min or until all methanol wetted surfaces were dried. The flask was weighed. At ambient temperature, one or two drops of the pure liquid standard were added to the flask using a 100 µL syringe. Care was taken to hold the tip of the needle just above the methanol surface without contacting the neck of the flask. The flask was re-weighted, and the solution was diluted to volume, stoppered and mixed by inverting the flask several times. The concentration of the analyte standard in µg/mL was calculated.

From the natural waters samples, 10 mL aliquots were injected into the P & T system simultaneously with the equipment starter. This activates the precooling of the fused -silica-trap to 120°C. Using the luer lock syringe, a time and temperature program for precooling the trap, purging, trapping and injecting the sample could be set. The purge vessel was then purged with helium carrier gas at a flow rate of 40 mL/min at 23°C. For the desorption step the trap was flash heated to 150°C within 30 s and held at this temperature for a total of 3 minutes.

At the moment of the injection, gas enters the equipment at the carrier inlet, flows trough the six port valve, back-flushes and the concentrated analytes on the trap are rapidly heated. The heated trap is then back-flushed with gas to deliver a tight band of organic analytes to the gas chromatograph. With 10 mL water sample, concentrations ranging from 0.1 to 10 µg/L of the individual compounds are analyzed. The accuracy of the method varies from 99 to 105 % and its precision varies from 3.6 to 9.6. With the exception of some analytes, the method detection limits ranges from 0.09 to 0.01 µg/L.

RESULTS AND DISCUSSION

The qualitative results from the September 2000, Tultenango and Las Fuentes samples, are shown in Table 2: the retention time (min) and the flame ionization detection (FID) are indicated for each VOC's together with its m/z value. The first interpretation of the presence of these contaminants in the water samples was the use of pesticides and the dissemination of industrial and urban waste affecting the zone. These compounds, seem to originate from gasoline or diesel spilling or oily from waste and residual matter.

However, Tultenango is a borehole protected by a special construction and the origin of the presence of VOC's was interpreted as an underground pollution due to antropogenic causes or to a mishandling of the sample. The sampling technique using plastic devices with a 24.2°C water temperature, could probably contaminate with VOC's the Tultenengo, September 2000, sample.

On the other hand, Las Fuentes is a spring opened to the free air and located in an agriculture zone. The VOC's obtained in the September 2000 sample could come from human activities such as the use of pesticides and fertilizers in the fields around. Since the sampling was performed when heavy rain occurred, the transport of pollutants drained by surface water could be the origin of the presence of the VOC's at this particular site. Results in rain water (Polkowska *et al.,* 2000) have shown that the presence of pesticides and fertilizers in trace amounts is a recognised environmental problem. This, together with the surface transport of VOC's by the precipitation water indicates the necessity to monitor the VOC's contents.

The results obtained in April 2001, during the dry season, in the samples from the 7 sites are shown in Table 3.

Except at La Venta, no VOC's were found in this occasion at the studied springs and wells, including Tultenango and Las Fuentes.

The April 2001 sampling, during the dry season, had no influence of the surface water in the transport of pollutants. The lack in this occasion of the compounds found in September 2000 at Tultenango and Las Fuentes indicate that the sample handling and the possible contamination by excess surface water were responsible for the presence of Table 2 VOC's in September results.

La Venta well consists of a 30 cm diameter tube where water flows to the surface at a low flux of approximately 2 L/s during the dry season. The water drains to a nearby (3 m away) river. The shore tube is only protected with a concrete cover. The well is located in the middle of a grass field at 300 m of the limit of the urban zone of El Oro. A grease layer is systematically observed at the top of the water due to local contamination. The top water of this spring is particularly sensitive to surface contamination from the surrounding fields.

Table 2

The retention time (min) and the flame ionisation detection (FID) are indicated for each VOC's together with its m/z value

Site	Compound	FID	RT(min)	m/z
Las Fuentes	Bromoethane	7.00	6.92	108
Las Fuentes	Dichloromethane	10.70	10.70	84
Las Fuentes	1,2,3,trichlorobenzene	57.60	57.00	180
Las Fuentes	Chloroform	15.00	15.50	83
Las Fuentes	Trichloroethane	18.00	18.01	132
Las Fuentes	1,2,dichloroethane	18.91	18.91	98
Tultenango	Chloromethane	5.70	5.80	50
Tultenango	Dibromomethane	24.00	24.20	172
Tultenango	Tetrachloroethene	30.48	30.47	164
Tultenango	1,2,dibromoethane	32.15	32.00	186
Tultenango	Chlorobenzene	35.00	35.00	112
Las Fuentes &Tultenango	Heptane	20.00	20.30	100
LasFuentes &Tultenango	Bromobenzene	42.33	42.34	156
Las Fuentes &Tultenango	2,chloro,1,3,butadiene	13.18	13.15	124
Las Fuentes &Tultenango	Benzene	19.56	19.54	78

Table 3

VOC's obtained at the 7 sites in April, 2000

Site	Tultenango	Sta. Cruz	Cuauhtemoc	La Venta	Las Fuentes	Tiacaque	Pasteje
VOC's	<DL	<DL	<DL	3.8µg/L Phorate 10G	<DL	<DL	<DL

*DL=0.01 µg/L

At La Venta, results indicate the presence of trace amounts of Phorate 10G, product used as a pesticide in a restricted way in Mexico. The trace amount of this product in the water can originate from the top soil pollution since the spring has no protection, it is very shallow and vulnerable to the close environment in such a way that any antropogenic contribution in the soil of chemicals from fertilizers or pesticides can affect the top water layer of the spring.

The differences between the rain and dry season observed in the studied sites indicates that the method has shown adequate sensitivity. Results reported in the environmental control of drinking water from streams related to recharging points of aquifers located in intensive agricultural zones (Lanchote *et al.,* 2000) have shown the capability of the method to measure VOC's at concentrations lower than 0.1 µg/L. Several results (Pollowska *et al.,* 2000; Lanchote *et al.,* 2000; Dobosiewicz *et al.,* 2000) indicate qualitative and quantitative changes in the occurrence of organic compounds in rain and drinking water during various seasons. When precipitation water reaches the soil, it drains and dilutes the compounds that are carried on through the slopes of terrain transporting compounds, specially to the surface discharge of groundwater.

CONCLUSIONS

The conclusions of the present preliminary results indicate that the samples handling played a role in the presence of certain VOC's, but that the characteristics of the springs and wells, where the surficial water can suffer a contamination by the draining of precipitation water that mixes at the surface, can give results that differ considerably as a function of the season. No evidence indicating groundwater pollution is obtained from the present results.

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