The Study of Groundwater Contamination with Volatile Organic Micropollutants (Trichloroethylene) in Northern Bucharest

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The potential severity of some incidents regarding groundwater contamination within urban areas has recently led to the intensification of national concerns for complex identification and assessment of risks in contaminated areas and of their effects on human and environmental health. Urban groundwater protection in line with environmental objectives directly depends on the implementation of the legal and technical regulations in force in a proactive manner, aiming at the appropriate treatment of pollution situations and the effective management of the related risks. Given the massive industrial use of volatile organic compounds, their accumulation in the environment poses a major threat to the environment and public health, including through water pollution. This paper presents the results of a study on the presence of trichlorethylene (TCE) in groundwater and drinking water in a residential area of Bucharest (Pipera-Tunari area), highlighting TCE contamination found in some cases in concentrations well above the required limit set by Law 458 on Drinking Water Quality. The study analyzes the seasonal variations of TCE contamination, while addressing the effectiveness of applicable depollution solutions. The results of the study provide the most useful information for water quality authorities, and can be regarded as a benchmark for similar analyzes in other urban areas.

Keywords: TCE, groundwater, tap water, pollution, residential area

Environmental care is a constant concern of both companies in the polluting industries and of other entities that initiate various research and social responsibility programs [1], outlining a significant orientation of different stakeholders towards environmental issues [2].

Volatile Organic Compounds (VOCs) are a heterogeneous class of compounds derived from aliphatic hydrocarbons originating from both biogenic (e.g. from volcanoes, bacteria and marine organisms) [3-5] and human origin [6]. In fact, the compounds are derived from many products, including fuels, paints, adhesives, deodorants and refrigerants and/or from solvents used in industrial processes. Moreover, many VOCs are used in agriculture as herbicides and fumigants [7]. Some of these compounds (e.g. benzene) are formed during the transport, handling, storage and combustion of petroleum products, while others (e.g. trihalomethanes, vinyl chloride) are produced during disinfection treatments (chloroform, 1,2-dichloroethane, etc.) of raw water for potabilization, from gases containing large amounts of organic substances [8] or from contact with plasticizers containing polyvinyl chloride (PVC) or other polymers [9]. For this reason, VOCs are often responsible for the degradation of organoleptic water parameters, such as taste and smell.

The most volatile halogenated compounds, even at low concentrations, are carcinogenic or mutagenic agents [10, 11]. VOCs are non-biodegradable substances, representing a long-term risk to human health and the ecosystem [12-14]. Because of their affinity for electrons, these compounds form photochemical oxidants, which interrupt the electrons transport in cells, causing acute blood and liver poisoning and neurological damage to the central nervous system [15].

Numerous articles and studies in the literature suggest that these substances, when adsorbed through the skin, may favor the development of inflammatory processes [16], skin cancers [17] or leukemia [18] in the case of benzene. Moreover, VOCs are accumulated in fatty tissues in relation to their chemical properties, thus causing chronic illness especially to industrial workers [18]. VOCs can impact the ecosystem in various ways. Because they are extremely mobile, having sufficient vapor pressure against atmospheric pressure, they can significantly volatilize, being released into the atmosphere and implicitly becoming potential contaminants of soil and groundwater.

Trichlorethylene (TCE) is a frequent contaminant of groundwater in industrial areas [19], which has led to many studies regarding the decontamination of TCE-containing waters [20]. Under favorable microbial and hydro-geochemical conditions, underground waters experienced a major decrease in TCE from high concentrations to regulated limits, but under other conditions, TCE proved to be very difficult to degrade [18]. Specialty literature indicates that thousands of wells have been affected by volatile industrial contaminants (VOCs), including the TCE, in the US [21].

Trichlorethylene is mainly used as a solvent to remove grease from various metallic parts, as extraction solvent for oils, waxes and tar, to clean cotton, wool, and other fabrics in the textile processing industry or in the synthesis of other chemical substances. Trichlorethylene can also be found in some household products including correction fluid, paint stripper, adhesives, and stain removal products.

The present study highlights the presence of trichlorethylene in underground and drinking water in a residential area of Bucharest (Pipera-Tunari area) at values above the maximum allowed by environmental legislation, a situation due either to the development of some polluting industrial activities or to accidental pollution.

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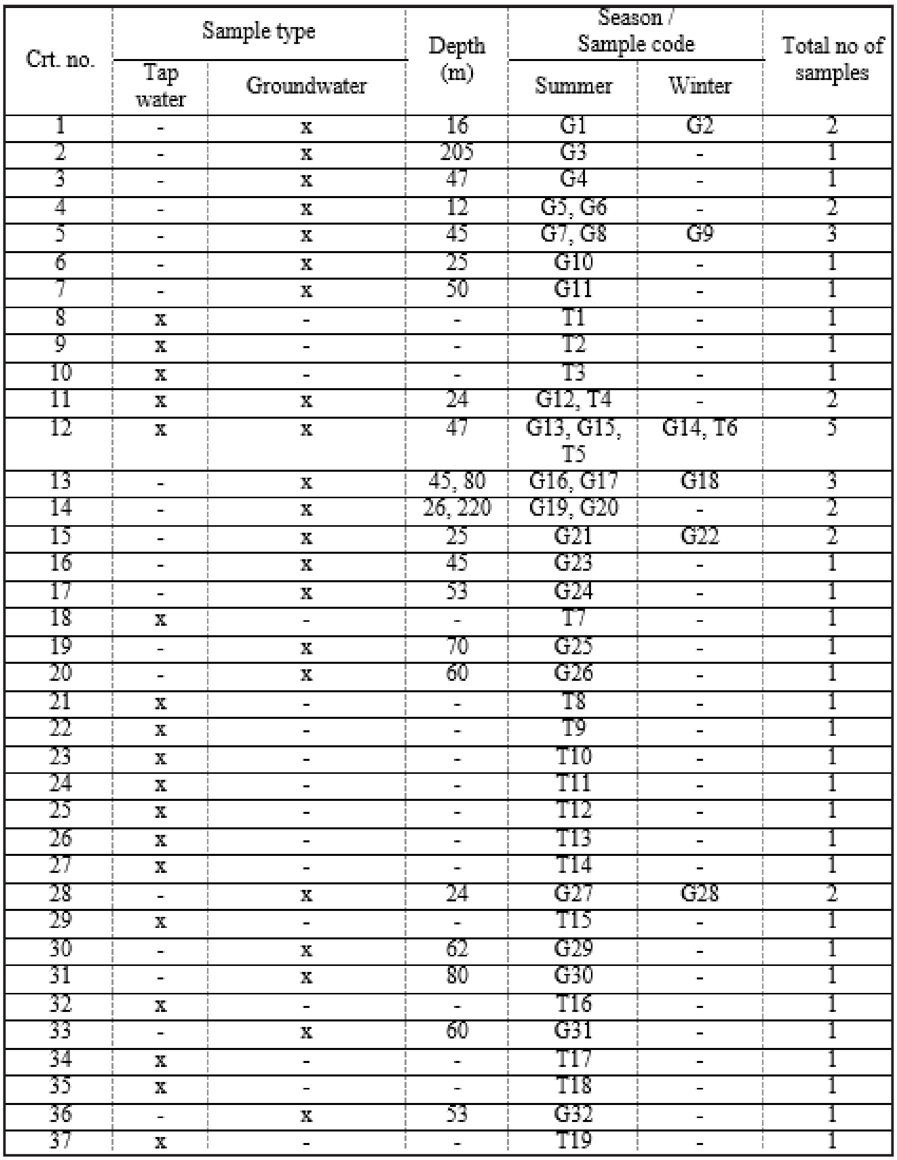

Table 1
TYPE OF SAMPLES

Crt. no.	Sample type		Depth (m)	Season / Sample code		Total no of samples
	Tap water	Groundwater		Summer	Winter	
1	-	x	16	G1	G2	2
2	-	x	205	G3	-	1
3	-	x	47	G4	-	1
4	-	x	12	G5, G6	-	2
5	-	x	45	G7, G8	G9	3
6	-	x	25	G10	-	1
7	-	x	50	G11	-	1
8	x	-	-	T1	-	1
9	x	-	-	T2	-	1
10	x	-	-	T3	-	1
11	x	x	24	G12, T4	-	2
12	x	x	47	G13, G15, T5	G14, T6	5
13	-	x	45, 80	G16, G17	G18	3
14	-	x	26, 220	G19, G20	-	2
15	-	x	25	G21	G22	2
16	-	x	45	G23	-	1
17	-	x	53	G24	-	1
18	x	-	-	T7	-	1
19	-	x	70	G25	-	1
20	-	x	60	G26	-	1
21	x	-	-	T8	-	1
22	x	-	-	T9	-	1
23	x	-	-	T10	-	1
24	x	-	-	T11	-	1
25	x	-	-	T12	-	1
26	x	-	-	T13	-	1
27	x	-	-	T14	-	1
28	-	x	24	G27	G28	2
29	x	-	-	T15	-	1
30	-	x	62	G29	-	1
31	-	x	80	G30	-	1
32	x	-	-	T16	-	1
33	-	x	60	G31	-	1
34	x	-	-	T17	-	1
35	x	-	-	T18	-	1
36	-	x	53	G32	-	1
37	x	-	-	T19	-	1

Experimental part

Studied area

The study was conducted in the Pipera-Tunari area, in the vicinity of a former electronics and electrotechnical equipment company, in the perimeter bounded by Erou Iancu Nicolae Street and the adjacent streets. The collections and analysis of the samples was carried out during a calendar year, covering both the hot (summer) and the cold (winter) seasons. A number of approximately 75 groundwater samples and tap water samples were taken from various points located within the mentioned perimeter in order to perform necessary analyzes to determine the degree of TCE pollution.

Table 1 presents the collected samples (as codes), their type, the season and the well's depth in case of underground samples.

Sampling and preservation of samples

For groundwater sampling, sampling bales were used to prevent the TCE contaminant from being lost by forced volatilization, while sampling of tap water was performed after 5-10 min of water flow, filling the sampling container completely. The transport and preservation of the samples was carried out at a 4°C temperature using cooling boxes. Prior to performe the chromatographic analysis, the internal standard mixture of 1-chloro-2-bromopropane was added to each sample.

Analytical method

Extraction of volatile organic compounds

The headspace extraction technique was applied, using an automated autosampler, the samples being analyzed in 20 mL sealed vials, which were heated to 60° C and shaken for 10 min. The vapors above the sample were drawn using a 2.5 mL sealed syringe, heated to 80° C, the vapors being then transferred to the gas chromatograph injection port.

Determination by GC / MS

VOC separation and quantification was performed using GC-MS Agilent Technologies 7010B Triple Guad on a ZB-5ms, 60m, 0.25 mm, 0.25 μm non-polar column, with a helium flow rate of 1 mL/min. The temperature program used for the capillary column started at 35° C with a 16 minute range, while the heating ramp was gentle at 5° C/min to a final 165° C temperature where there was no range.

The detector, a low-resolution mass spectrometer had the source temperature at 230°C, the quadrupole having a temperature of 150°C. The voltage on the filament was 70 eV and the voltage on the multiplier was maintained around 1300 V. The mass spectrometer operated in SIM mode, with the monitoring of specific mass ions.

The performance parameters of the method used [22, 23], namely the detection limit (LOD), the quantification limit (LOQ), the precision and uncertainty measurement are presented in table 2.

Parameter	Value (µg/L)	Parameter	Value (%)
Calibration curve range	0.1 - 50	Intermediate precision	3.88
LOD	0.05	Repeatability	2.78
LOQ	0.20	Uncertainty	14.0

Table 2
PERFORMANCE PARAMETERS OF THE APPLIED METHOD FOR TCE DETERMINATION

Results and discussions

The limits imposed by the Law no. 458(R1)/2002 on drinking water quality require a maximum admissible concentration of 10 µg / L for the sum of trichlorethylene and tetrachlorethylene (maximum admissible value - MAV). Out of the total of 51 samples analyzed initially, 20 samples (39.2%) of both groundwater and drinking water collected from the tap showed values above this limit.

Table 3 shows the TCE values recorded in groundwater samples, and table 4 shows the TCE values obtained from drinking water samples.

With regard to groundwater, a high percentage (46.9%) of samples had TCE concentrations above the limit set by the law in force, ranging from tens of µg / L to tens of mg / L, due to the variation in TCE solubility in water, which is directly proportional to temperature rise (water solubility of TCE at 20-25°C may range from 900 to 1463 mg / L).

It was observed that the samples collected during the warm season showed higher concentrations compared to those taken during the cold season, marking an increase in TCE content of 8.3% (G21, G22 samples), 18.9% (G8, G9 samples), 28.6% (G13, G14 samples), 34.5% (G27, G28 samples) and 36.1% (G1, G2 samples).

Regarding the depth of wells from which the samples were collected, it was not possible to establish a correlation between the measured concentration and the depth of the well. Thus, very high concentrations of TCE (tens of mg / L) were detected in samples taken at a depth of 25 m (G21, G22) and from 45 to 47 m (G7, G13, G14). TCE concentrations of thousands of µg / L were detected at depths of 20-24 m (G12, G27, G28) and at 45 m (G8, G9). Concentrations of hundreds of µg / L were detected at depths of 16 m (G1, G2), 47 m (G15) and 53 m (G24) were also detected.

At depths between 60 and 220 m, TCE was not found, or concentrations were at a maximum level of 7 µg / L. The displacement of the underground water front allowed the spread of contamination over an extended area in terms of surface and depth.

With regard to tap water samples, the concentration range was much narrower (below LOQ ÷ 1157µg / L), the percentage of non-conforming samples being 31.6%.

There was also a 33.6% increase in TCE content in the T5 sample collected in the warm season compared to the T6 sample collected in the winter. This set of samples recorded the highest TCE content of the 19 analyzed samples of tap water.

Considering that some of the inhabitants of the affected area have installed equipment for water purification based on different technologies (adsorption on activated carbon, reverse osmosis, aeration), TCE analyzes for other 12 samples of water have been carried out after the application of different depollution processes.

Table 5 presents the results of groundwater and drinking water analyzes before and after a decontamination

Sample code	Value	Sample code	Value	Sample code	Value
G1	**381**	G12	**1720**	G23	<0.20
G2	**280**	G13	**39301**	G24	**335**
G3	<0.20*	G14	**30558**	G25	4.39
G4	<0.20	G15	**652**	G26	2.10
G5	<0.20	G16	**39.5**	G27	**2001**
G6	<0.20	G17	6.91	G28	**1488**
G7	**11747**	G18	5.50	G29	<0.20
G8	**3994**	G19	<0.20	G30	3.10
G9	**3358**	G20	1.30	G31	<0.20
G10	<0.20	G21	**67652**	G32	<0.20
G11	1.00	G22	**62452**		

*LOQ

Table 3
TCE VALUES IN GROUNDWATER SAMPLES (µg/L)

Sample code	Value	Sample code	Value	Sample code	Value
T1	**31.5**	T8	<0.20	T15	<0.20
T2	**312**	T9	<0.20	T16	<0.20
T3	**18.7**	T10	<0.20	T17	0.80
T4	7.50	T11	<0.20	T18	<0.20
T5	**1157**	T12	<0.20	T19	<0.20
T6	**866**	T13	1.58		
T7	**124**	T14	<0.20		

Table 4
TCE VALUES IN TAP WATER SAMPLES

Sample code	TCE before treatment (µg/L)	TCE after treatment (µg/L)		
		Activated carbon	Reverse osmosis	Aeration
G13	39301	41127	-	-
G7	11747	14246	-	0.31
G12	1720	1542	-	-
T2	312	407	< 0.20	-
T7	124	42.2	< 0.20	-
T5	1157	1214.5	-	-
G17	6.91	3.21	< 0.20	-
G27	2001	2005	-	-

Table 5
TCE VALUES DETERMINED BEFORE AND AFTER WATER TREATMENT

procedure. There is an increase in the TCE content of treated waters using activated carbon adsorption. The groundwater decontamination process through activated carbon adsorption is not suitable for waters with concentrations higher than 200 μg / L, as these filters collapse in a very short period of time, leading to subsequent recontamination of the water source due to the release of excess TCE from the carbon filter. It can be observed that at low concentrations, TCE is adsorbed on carbon, followed by the decrease in TCE content, but not in all cases under MAV (T7 after activated carbon treatment).

A significant decrease in TCE content is observed in aerated water (sampling point G7) and reverse osmosis (sampling points T2, T7, G17).

The treatment methods for removing VOCs include air stripping, high temperatures incineration, photocatalytic and catalytic oxidation, adsorption and absorption, distillation, anaerobic/aerobic biological treatment, pervaporation and supported liquid membrane [24-28]. But, no single method can be used in all cases; combined methods are used, for example - adsorption and absorption, pervaporation and air-stripping [29].

Conclusions

As a result of the research, it was found that in the studied area of the Pipera-Tunari residential district, both groundwater and tap water showed a strong TCE contamination, with concentrations above the limit imposed by the legislation in force in 39.2% of cases.

The one-year study, carried out by sampling during both hot and cold season, allowed the characterization of the contamination level of Pipera-Tunari phreatic zone. The trichlorethylene concentrations determined in the studied area were in the range of <0.02 ÷ 67650μg / L.

A higher number of groundwater samples with high TCE levels have been identified in the immediate vicinity of a former electronic component manufacturing company that used TCE during the production processes but also in areas remote from this probable cause of pollution, which is why it cannot be firmly concluded that pollution in the area was due to former industrial activities.

An increase in the trichlorethylene concentration has been observed when the temperature rise during warm season, due to increased TCE solubility in water at temperatures above 20-25° C.

Treating samples by reverse osmosis as well as aeration resulted in a drastic decrease in TCE content, making water suitable for human consumption.

The results of the study on groundwater contamination with trichlorethylene were transferred to Apa Canal Ilfov Company, which manages the water quality of the Pipera-Tunari area.

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