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CONTAMINATION OF GROUNDWATER WITH PHENOL DERIVATIVES AROUND A DECOMMISSIONED CHEMICAL FACTORY

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Abstract

In this study, the concentrations of 15 phenol derivatives were analyzed from the phreatic and groundwater wells surrounding a decommissioned chemical factory in a village from the western part of Romania. An UPLC-MS method was used to assess the concentrations of the chemical target compounds in the water samples. The most frequent compounds were 4-chlorophenol, 4-tert-octylphenol and 4-nonylphenol, being detected in 17 of the 19 sampling sites, while the least frequent compound was 2,4,6-trichlorophenol, that was found in only 7 samples. The highest mean concentration was obtained for bisphenol A ($47.54 \text{ ng}\cdot\text{mL}^{-1}$), while 2,4-dinitrophenol was found with the lowest mean concentration ($9.38 \text{ ng}\cdot\text{mL}^{-1}$). The most contaminated water samples were found in the monitoring wells placed downstream of the factory. With the exception of the samples taken from the municipal drinking water system, the samples from phreatic water wells contained the target phenol derivatives, at various concentrations. Although the platform has ceased completely, the hazard caused by decades of continuous phenolic pollutant leakage is still significant to the present day.

Key words: monitoring wells, phenol derivatives, water contamination

Received: September, 2013; *Revised final:* June, 2014; *Accepted:* June, 2014; *Published in final edited form:* March 2018

1. Introduction

Due to the ubiquitous development of the chemical industry, many organic contaminants can be found in water streams, at μg per liter levels or below (Ericson et al., 2009). The chemical factories that do not have water resource recovery facilities are the most likely sources of contamination of the aquatic environment. In many cases, these factories use large ponds to “dilute” their wastewaters. As the ponds produce leakages containing hazardous compounds, the aquatic environment becomes contaminated with highly toxic or even carcinogenic chemicals (Mahugo Santana et al., 2009; Zhou et al., 2009). Various

studies have been conducted on sustainable alternatives for petrochemical wastewaters containing phenols and aliphatic organic compounds, produced by the petrochemical industry (Teodosiu and Fratila-Apachitei, 2002). Therefore, the monitoring of organic pollutants is required to estimate the degree of pollution of surface, phreatic and groundwater.

Some phenols are registered as priority pollutants in the European Council Directive 2013/39/EU (EC, 2013) and the US Environmental Protection Agency (ATSDR, 2008). The current European legislation, European Council Directive 98/83/EC (amended by Regulation EC No 596/2009), and European Council Directive 2013/39/EU, does not

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mention about total phenolic concentration in water, but states that each member state can regularly monitor supplementary parameters (such as phenol content) as a quality index (EC, 1998, 2013). According to Romanian legislation: HG 352/2005 (Ro Gov, 2005), correlated with Law 311/2004 (Ro Parliament, 2004), local water management authorities can establish a normal maximum limit ($1.00 \mu\text{g}\cdot\text{L}^{-1}$ for phenol) and an exceptionally allowed limit ($2.00 \mu\text{g}\cdot\text{L}^{-1}$ for phenol) until the upgrade of a wastewater treatment plant. These limits correspond to the natural background concentration of phenols in waters upstream of the studied source of pollution (ANAR-DAB, 2008). The problem of phenols is an important issue because phenols may be present in all types of waters, industrial wastewater, natural and drinking water. During chlorination of water, phenols are easily converted to chlorophenols, compounds with a higher toxicity potential (Yousef and El-Eswed, 2009). It is known that bisphenol A, nonylphenols and octylphenols are main endocrine disrupting chemicals (WHO, 2012), that can be detected in sewage effluents, in drinking water sources (even tap water), rivers, sediments, whose adverse effects may be cumulative and irreversible (Jiang et al., 2013).

The objective of this paper is to investigate the presence of 15 phenol derivatives in groundwater (wells at depth from 3 to 200 m) in order to assess the pollution with these compounds from an old factory that used to produce chemicals for almost a century and that was decommissioned for more than 10 years. For this purpose, an analytical strategy consisting in analyzing the water samples extracted from the nearest points to the chemical plant and establishing a list of target contaminants was applied. Another objective of the paper is to find out the possible causes for compounds remanence in Bega watershed.

The petrochemical platform of Solventul Margina, near Făget city (Timiș county), with a surface of 37.6 ha, was mainly known for wood distillation and the production of retort charcoal, as well as acetates, solvents, vinegar, thinner, alcohol (<http://www.solventul.ro/margina.html>). As a result of the technological process, the insufficiently treated wastewaters were either discharged into the Bega river, stored in tanks that were leaking on the ground, or directly scattered on “dispersal fields”. These faulty practices for both water and soil by the disposal of pyroligneous water caused serious groundwater pollution in the area (Marinov et al., 2002).

The technological processes used at Margina plant, that included dry distillation of the wood, have produced many byproducts that are included in the group of persistent organic pollutants, like most of the phenol derivatives, part of the tar (a major byproduct of the industrial unit) and of the pyroligneous waters (Boukis et al., 2004; Ghețiu, 2008). Tar is a complex mixture of phenols, polycyclic aromatic hydrocarbons, heterocyclic compounds, and hundreds of other substances (Gangadhar et al., 2002), proven carcinogen (NTP, 2011). Creosote present in both tar and pyroligneous acids, also contains phenol,

methylphenols, ethylphenols, xylenol (Allen, 1909; Lee et al., 2005). Phenol is soluble in most organic solvents: aromatic hydrocarbons, aliphatic hydrocarbons, ethers, alcohols, ketones, acids, halogenated hydrocarbons (CRC, 2009; Weber et al., 2005). At the same time phenol forms azeotropic mixtures with water and other substances (Busca et al., 2008).

2. Experimental

2.1. Chemicals and reagents

As the optimization of sample preparation and chromatographic analysis of phenol derivatives was presented elsewhere (Preda et al., 2013), here we only mention the names of the studied analytes: phenol, 2,4-dinitrophenol, 4-nitrophenol, 4-methylphenol, 2-methyl-4,6-dinitrophenol, 3,5-dimethylphenol, 4-chlorophenol, 3-methyl-4-nitrophenol, 2,4,6-trimethylphenol, 4-chloro-3,5-dimethylphenol, bisphenol A, 3,5-dichlorophenol, 2,4,6-trichlorophenol, 4-tert-octylphenol, 4-nonylphenol (for more details see the Supplementary File).

2.2. Sampling and sample pretreatment

Various types of water samples were collected around the area of the old chemical factory “Solventul” SA, Margina branch: one sample was collected from a pollution monitoring well, with a depth of about 10 m (point P2). Other 3 samples were collected from monitoring wells for groundwater levels, wells with depths between 12 and 40 m (points F2, F3, F4). Six samples were collected from various sources from Sintești village, located downstream of the chemical factory (points S1 till S6). From Margina village (where the factory was located) there were collected 7 samples, from various points around the perimeter of the chemical plant (points M1 till M7). Two other samples were collected from Făget city, located 5 km downstream of the chemical factory. A global positioning system (GPS) was used to locate the exact site during the sampling. Water samples were placed in amber glass bottles previously cleaned with nitric acid (1:1; v/v) and usual precautions were taken to avoid contamination. Two-liter water samples were collected in duplicate for every sampling site and the bottles were flushed at least twice by the same water sample before collection. Samples were centrifuged at 4500 rpm (Centrifuge Rotofix 32A Hettich, Germany) for 10 min, filtered through a 0.22 μm PTFE syringe disk filter and stored in the dark at 4°C, until treatment was performed, which occurred in all cases within 48 h after sample collection. The analysis was performed with the minimum possible delay. Two analyses were performed for each sample: one without spiking and the other one after spiking with analytes at $30.00 \text{ ng}\cdot\text{mL}^{-1}$. In this way a quality control (QC) was applied for every sample analyzed. Phenol extraction (sample preparation) of water samples collected from the contaminated area was achieved by off-line phase of solid phase extraction

(SPE) (Preda et al., 2013). All the water samplings (n=19) were performed in September 2012 from different locations in Timis county, in order to make a

complex assessment of the selected area around the source of pollution: Margina, Sintești, Zorani, Făget, crossroads downstream Bega River (Fig. 1, Table 1).

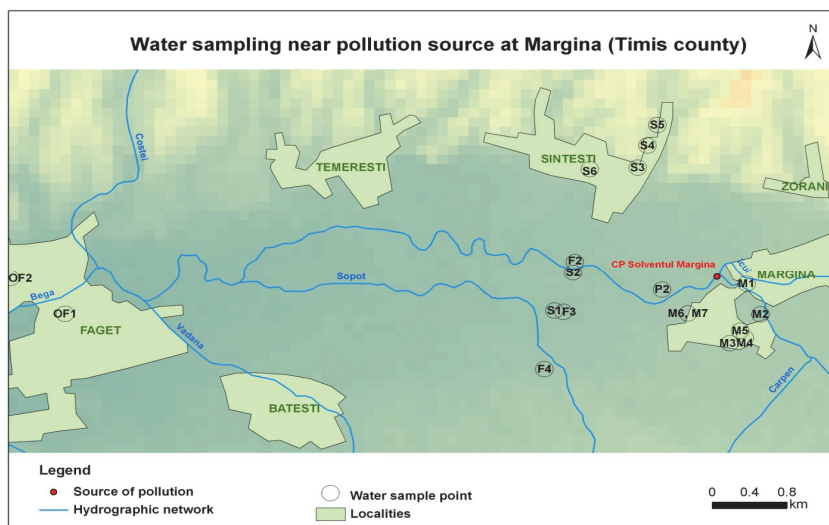


Fig. 1. The map of the investigated region

Table 1. Details about the sampling sites

No.	Sample name	Location of the collection point	Type of water	GPS coordinates	Point depth	Source of water
1.	P2	Margina village, nearest sampling point to the pollution source - pollution dispersion field	drilling point for pollution monitoring	45°51'39.38"N 22°15'31.00"E	10	phreatic water
2.	F2	Sintești bridge, downstream of the chemical plant, right bank of Bega river	drilling point for phreatic water monitoring	45°51'49.21"N 22°14'47.22"E	26	phreatic water
3.	F3	Sintești crossroads, 1 km downstream the chemical plant	drilling point for phreatic water monitoring	45°51'29.56"N 22°14'42.47"E	28	phreatic water
4.	F4	Sintești crossroads, 2 km downstream the chemical plant	drilling point for phreatic water monitoring	45°51'7.24"N 22°14'34.19"E	23	phreatic water
5.	S1	Sintești crossroads, artesian well, 1 km downstream the chemical plant	drinking water	45°51'29.94"N 22°14'38.02"E	60	average groundwater depth
6.	S2	Bridge to Sintești village, 1 km downstream of the chemical plant, left bank of Bega river	Bega river	45°51'44.98"N 22°14'46.62"E	2-3	surface water
7.	S3	NE of Sintești village, private well	drinking water	45°52'26.49"N 22°15'16.53"E	3	phreatic water
8.	S4	Sintești village, artesian well, low flow	drinking water	45°52'35.19"N 22°15'20.95"E	160	deep groundwater
9.	S5	Sintești village, water supply	drinking water	45°52'43.22"N 22°15'25.51"E	120	deep groundwater
10.	S6	Sintești village, middle of the village, draw well	drinking water	45°52'25.35"N 22°14'52.87"E	10	phreatic water
11.	M1	Margina village, private well, near the bridge over Bega river	drinking water	45°51'42.63"N 22°16'12.77"E	6	phreatic water
12.	M2	Margina village, private well, near the railway	drinking water – not used	45°51'30.93"N 22°16'20.28"E	5	phreatic water
13.	M3	Margina village, private well, close to the pollution source	drinking water	45°51'19.43"N 22°16'5.48"E	4	phreatic water
14.	M4	Margina village, water supply, private house near the pollution source	drinking water	45°51'21.64"N 22°16'12.91"E	200	deep groundwater
15.	M5	Margina village, artesian well, low flow	drinking water	45°51'24.39"N 22°16'10.56"E	100	deep groundwater
16.	M6	Margina village, water supply, private house across the street from the chemical plant	drinking water	45°51'30.43"N 22°15'44.36"E	200	deep groundwater
17.	M7	Margina village, the same location as M6, artesian well, low flow	drinking water	45°51'30.58"N 22°15'44.00"E	>50	average groundwater depth
18.	OF1	Făget city, water supply, central park	drinking water	45°51'22.76"N 22°10'35.45"E	30	phreatic water
19.	OF2	Făget city, water pump, manually operated, bridge over Bega river	drinking water	45°51'35.87"N 22°10'7.53"E	10-15	phreatic water

2.3. Sample Analysis

Ultra – High - Performance Liquid Chromatography technique was preferred in this study for the separation of organic compounds, due to its high resolution and reduced separation time. The chromatographic analyses were performed with an AcquityUPLC system (Waters, USA) using BEH C18 column, coupled to a XevoTQD (T-wave quadrupole) mass spectrometer with an orthogonal Z-spray–electrospray interface (Micromass, UK) for detection, according to (Preda et al., 2013).

2.4. Edaphic background

Because one of the main issues stands for the qualitative aspect of phreatic water as a prime resource in everyday life, including agricultural practice, the compliance with the maximum phenol limits for surface and groundwater is vital. In order to get a good interpretation of the data, a map of the soils surrounding the chemical plant was prepared. The soil map of the area was made based on cartographic sketches of Banat soils (Ianoş and Puşcă, 1998) and adapted to the current soil taxonomy (Florea and Muntean, 2012).

2.5. Geology and hydrogeology

The studied land surface contained deposits of silty and sandy clays, boulders, gravel and sand. Due to the granular disposition of the components of sediments, there are fast water movements between gravel and coarse sand within the phreatic aquifer that in the studied site is located between 4-10 m depth (ANAR-DAMB, 1983).

3. Results and discussion

Before the analysis of water samples from the selected wells, a simple procedure was carried out to optimize the parameters for detection of some phenol derivatives using a Xevo TQD MS/MS detector (Preda

et al., 2012). Nineteen water samples (see Table 1 and Fig. 1) were then analyzed with the optimized method (Preda et al., 2013). With the exception of the samples taken from the municipal drinking water system, the samples from phreatic water wells contained the target phenol derivatives, at various concentrations. In seven sampling sites (P2, F2, F3, F4, S3, S6, M3) all the target compounds were found in the waters samples. As P2, F2, F3, F4 are drilling wells and are situated downstream of the contamination point, the high concentration and the diversity of the polluted compounds are not surprising. Although the high levels and number of contaminants in the sampling points S3, M3 and S6, may be a surprise, as these are homemade wells to collect the phreatic water, this situation can be understood considering the historical contamination of the groundwater in this region. The sampling sites S1 and S2 have a lower level of contamination with phenols derivatives perhaps due to the vicinity to the Bega River. In the sites S4 and S5, the water samples were collected from relatively high depth, reason why the contamination was relatively low. In Table 2, there are presented the mean and median levels of the 15 analyzed target phenol derivatives, minimum and maximum values, as well as the number of water samples in which the respective compounds were not detected. Bisphenol A has the highest mean concentrations ($47.54 \text{ ng}\cdot\text{mL}^{-1}$) while 2,4-dinitrophenol has the lowest mean concentrations ($9.38 \text{ ng}\cdot\text{mL}^{-1}$). The maximum individual concentration corresponded to 4-tert-octylphenol ($172.00 \text{ ng}\cdot\text{mL}^{-1}$), while the 2,4,6-trichlorophenol was not detected in 12 samples (see also the Supplementary File).

Although studies have been performed regarding the slow biodegradability of dimethylphenols compounds (Kahru et al., 2002), our results indicate the persistence in phreatic water mostly of nitro- and chloro- phenolic groups as median concentration of phenols residues (Table 2). The concentration of the target analytes in the waters samples collected from the sampling sites is presented in Table 3.

Table 2. Concentration of phenols residues ($\text{ng}\cdot\text{mL}^{-1}$) in analyzed samples: mean, median, minimum and maximum values, and percentage of samples in which the corresponding phenol residues were detected

Analytes	Mean	Median	Min	Max	% of detected
phenol	20.25	13.50	8.00	56.00	42.10
2,4-dinitrophenol	9.38	8.50	6.00	15.00	42.10
4-nitrophenol	15.00	12.00	6.00	35.00	47.36
4-methylphenol	13.38	6.00	5.00	44.00	68.42
2-methyl-4,6-dinitrophenol	11.00	6.00	5.00	28.00	47.36
3,5-dimethylphenol	12.70	7.00	5.00	34.00	52.63
4-chlorophenol	37.18	11.00	5.00	148.00	89.47
3-methyl-4-nitrophenol	15.13	9.50	4.00	42.00	42.10
2,4,6-trimethylphenol	13.50	8.50	4.00	33.00	42.10
4-chloro-3,5-dimethylphenol	11.50	9.50	5.00	26.00	42.10
bisphenol A	47.54	13.00	5.00	164.00	68.42
3,5-dichlorophenol	13.10	9.50	5.00	36.00	52.63
2,4,6-trichlorophenol	12.57	11.00	4.00	25.00	36.84
4-tert-octylphenol	37.35	10.00	5.00	172.00	89.47
4-nonylphenol	36.81	9.00	5.00	165.00	84.21

Table 3. The quantities of the phenol derivatives (ng·mL⁻¹) in the analyzed water samples

LOQ	OF2	OF1	M7	M6	M5	M4	M3	M2	M1	S6	S5	S4	S3	S2	S1	F4	F3	F2	P2	
5	*	*	*	*	*	*	10	*	*	9	8	*	12	*	*	15	22	30	56	phenol
5	*	*	*	*	*	*	9	*	*	8	6	*	7	*	*	8	10	12	15	2,4-dinitrophenol
5	*	*	*	*	*	*	11	*	6	8	9	*	12	*	*	14	18	22	35	4-nitrophenol
5	*	*	*	*	5	5	14	5	5	6	6	*	11	6	*	16	22	31	44	4-methylphenol
3	*	*	*	*	5	*	5	*	6	5	*	*	6	*	*	10	14	20	28	2-methyl-4,6-dinitrophenol
3	*	*	*	*	*	*	6	6	8	5	6	*	5	*	*	11	19	27	34	3,5-dimethylphenol
3	*	*	5	5	9	10	28	13	11	8	11	9	35	10	14	89	102	125	148	4-chlorophenol
3	*	*	*	*	*	*	*	*	6	5	6	*	4	*	*	13	17	28	42	3-methyl-4-nitrophenol
3	*	*	*	*	*	*	5	8	*	6	*	*	4	*	*	9	14	29	33	2,4,6-trimethylphenol
5	*	*	*	*	*	*	9	*	*	6	5	*	5	*	*	10	13	18	26	4-chloro-3,5-dimethylphenol
5	*	*	*	*	9	*	35	*	6	9	13	5	15	13	12	75	108	154	164	bisphenol A
5	*	*	*	*	*	*	13	6	*	6	5	*	5	5	*	14	17	24	36	3,5-dichlorophenol
5	*	*	*	*	*	*	10	*	*	5	*	*	4	*	*	11	15	18	25	2,4,6-trichlorophenol
5	*	*	5	5	9	6	32	6	6	16	9	8	23	11	10	76	97	144	172	4-tert-octylphenol
5	*	*	5	6	8	*	45	5	9	17	8	5	18	8	9	63	86	132	165	4-nonylphenol
	0	0	15	16	45	21	232	49	63	119	92	27	166	53	45	434	574	814	102	Total conc.

In general terms, the most polluted water samples were those collected from phreatic water and average groundwater depth (confined aquifer) (4 till 30 m deep) and situated nearby or downstream of the contamination point (the old chemical factory). This is the case of sampling points P2, F2, F3, F4, S3, S6 and M3. The cleanest was the tap water collected after being treated at the water treatment plant. The samples collected from various homemade shallow wells have intermediate levels of pollution (considering both the

number of the target compounds found and their concentrations). As Figs. 1-2 show, the majority of the soils are included in the riparian area, often marshy, of the Bega River. The studied perimeter is located practically within or along floodplains. Most of the communities from the studied area are located on soils where surface and phreatic layers are strongly bonded, especially during rainy seasons, river overflowing or flooding, increasing the potential danger of pollution with phenols (ARPM-TM, 2011; Ceaușescu, 2004).

From the chromatographic analysis of the water samples, it can be noticed that phenolic compounds in the case of P, F and M -type wells are concentrated around the pollution source or downstream on the flow direction of the Bega River and its tributaries. The infiltration of phenolic compounds is strongly connected to soil texture. The contaminated area is covered mostly by luvisols, fluvisols and gleysols, characterized by water excess. Aquifer ranges from sands and gravel type rocks, a lithology allowing easy infiltration of pollutants. Gleyic subtype soil, also predominant in the area, is an indicator of permanently waterlogged soils, where groundwater is rising and oxidation-reduction processes take place. Stagno- or pseudogleyic soils were formed as a consequence of prolonged stagnation of water over an impermeable or poorly permeable horizon, and also as a result of temporary stagnation of rain water in the soil profile. Amfigleyic combines both subtypes (Ianoş, 1999).

During the practice of direct disposal on the ground of pyrolyneous solutions, water content from wastewater solutions was initially absorbed by the clay structural units, as natural clay is a well-known adsorbent (Arellano-Cárdenas et al., 2005; Djebbar et al., 2012), and subsequently evaporated in dry seasons. In contrast, after water evaporation, pollutants remained trapped in the clay structure. This could be an explanation for the high levels of contaminants detected in F3 monitoring well. On the other hand, the sandy soils like fluvisols and regosols are poor soils, with a high permeability to water a possible cause for the highest levels of contaminants in P2, F2), meaning that residual solutions could have percolated at high depths. Neither luvisols, nor fluvisol stood for a viable solution because aquifers were in a permanent direct exchange with surface water, at a depth of up to 2 meters.

The degradation of chemicals in soil depends on numerous factors, such as soil temperature, oxygen

concentration, the content of microorganisms, the presence of other contaminants (UKEA, 2009). At Margina, a cold and wet weather prevails, so only a reduced percentage of phenol contents could have easily evaporated in these climatic conditions.

There is also a robust association between the concentrations of phenols and the depth of aquifers. The phreatic film is supplied both by penetration of precipitation through the soil layer and also by drainage among the clays. Along with this percolating water, the residue from the sludge pits leaks underground. Specifically, in dry periods, water rises from greater to shallow depth (DAMB-Tm, 1983), thus “dragging” the contaminants through layers (ARPM-TM, 2011). Three types of aquifers were observed in this zone: deep groundwater between 100-150 m; average groundwater depth between 50-100 m; while phreatic layer resides at less than 1 m to a max of 40-50 m.

There is an inverse relation between the concentration of phenol and the depth of the sampling point from the phreatic layer. The highest amounts of contaminants are mostly found in the shallow depths, as it may be seen in Fig. 3. The resemblance of variation can also be seen in the case of the average groundwater depth and of the deep groundwater.

The terrain has elevated landform energy, sharp morphological slopes and a quick drainage of surface and groundwater. The general east-west orientation undergoes spectacular variations in the studied area, from NNE-SSW on the right bank of Bega river, to the SSE-NNW on the left side. The hydrogeology of the area indicates that the Bega river represents the ultimate collector of surface and groundwater, hence the direction of flow (drainage) is directed towards the hydrographic artery (DAMB-Tm, 1983; RoCSG, 1968). That is why we can affirm that pollution coverage moves along with groundwater flow, as it may be seen in Fig. 4.

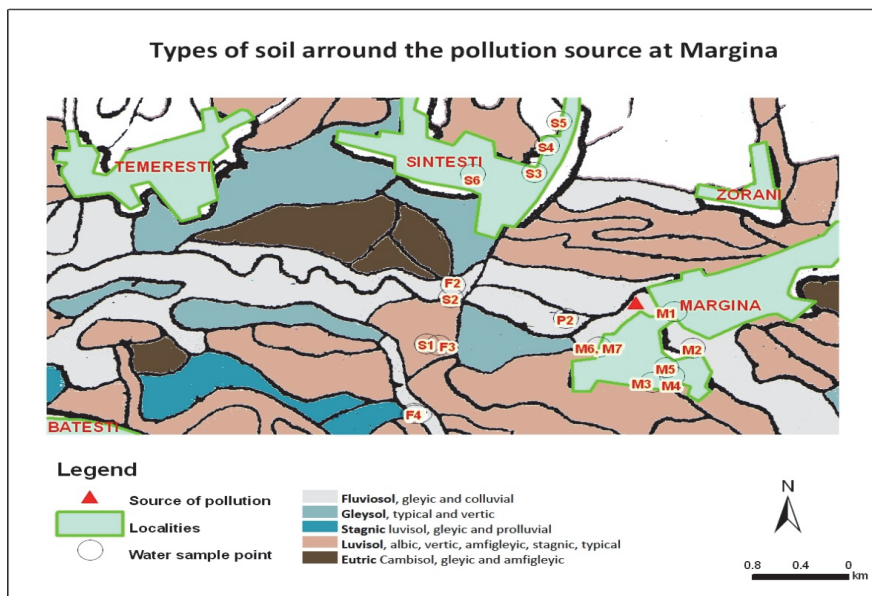


Fig. 2. Soil map of the contaminated area

The variation of phenolic concentrations depending on the distance from the source reveals that there is a connection between some points of similar concentrations: P2 and F2, F3 and F4, etc. From a statistical point of view, a dendrogram for all the sampling points can indicate the agglomerative hierarchical clustering of phenolic concentrations (see Supplementary File). It is highly possible that, at Margina, the phenols detected with UPLC-MS/MS method were not entirely produced by the industrial activity of the plant, but, in time, they might have been a result of the microorganism's activity in soil aqueous phase. Neither the biodegradation potential of bacteria, nor the aging factor could minimize the effect of degradation proved by chromatographic data.

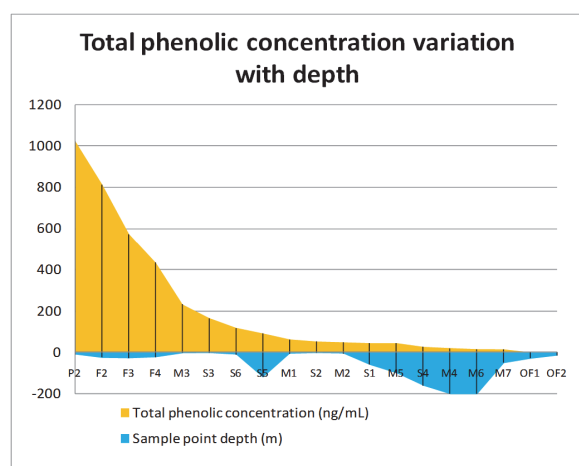


Fig. 3. Variation of phenolic concentration with depth of sampling site

The local population is situated very close to the decommissioned chemical plant. The land is permanently exposed to the risk of water contamination, since there is a strong hydrodynamic and hydro-chemical connection between surface water and groundwater. Moreover, most of population is aged (a common tendency for Romanian rural people), fact that makes inhabitants be more vulnerable to the aggressive toxic effects of phenol derivative contaminants.

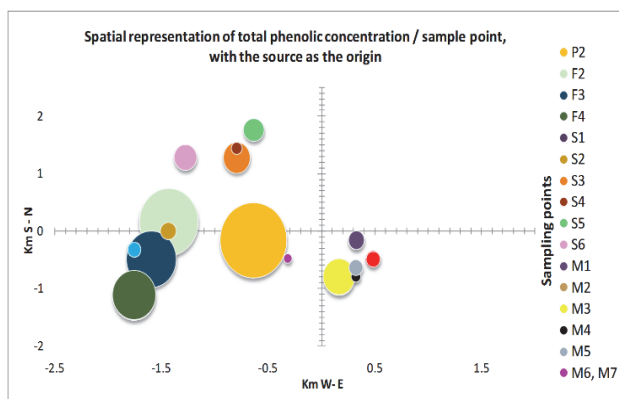


Fig. 3. Spatial representation of total phenolic concentration

Regarding the geographic area studied within this paper, further studies can be developed in two main directions. First, health and safety of the local people from Margina, Sintești and Zorani should be evaluated, as practice of using water from private wells for agricultural activities is still a common habit. Second, effective remediation methods to the contaminated area are imperatively needed to be applied using suitable adsorbent materials, that are low-cost, environmental friendly and with a high affinity for target compounds as phenols (Bizerea Spiridon et al., 2013).

4. Conclusions

The main objective of this paper was to investigate the current quality of the Bega superior watershed after the leakages from an old chemical factory had entered in the surrounding groundwater, in order to see the present state of pollution. This study provides new data regarding the occurrence of 15 phenols derivatives in phreatic and groundwater in the vicinity of the chemical plant "Solventul" Margina after more than 10 years since the industrial platform was demolished. The results suggest that the target compounds exist widely in this studied area, waters of phreatic aquifer being the most polluted, as it was the most exposed and exploited layer in this area. The decrease of phenol concentrations is due to the filtration and natural decontamination of the water when passing through more or less permeable layers, horizontally as well as vertically. But natural attenuation is not enough to compensate for a century-old contamination, and this can be proved by the analytical data indicating total phenolic concentrations of tens or hundreds of times higher than permissible limit.

The site of the former chemical plant and of the sludge pits made the distance covered by various chemical compounds from their place of origin to the Bega river to be very short, with no economic or social obstacles in their way.

The existence of significant amounts of phenolic compounds is related to the large amounts of residue from the former pits that were not neutralized. Thus, groundwater is always "fed" with phenolic leakage from pits, after rainfall. Therefore, in sandy areas, phenols are not retained in groundwater, but their presence is caused by the continuous intake of phenolic compounds from the source. The existing quantities of phenols at a certain moment in water flow with it, but are permanently replaced with other amounts coming from the source, amounts that seep into groundwater continuously.

Acknowledgments

This work was supported by the project 464 RoS-NET financed by the EU Instrument for Pre-Accession (IPA) funds, under the framework of the Romania-Republic of Serbia IPA Cross-border Cooperation Programme. The authors thank to Banat Water Directorate for valuable help in sample collection, especially to Mr. hydro-geologist E.

Stanciu for his significant contribution. Likewise, we wish to thank Dr. R. Reisz for his considerable help in the statistic interpretation of agglomerative hierarchical data.

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