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ORIGINAL PAPER

Evaluation of potential human health risks from exposure to volatile organic compounds in contaminated urban groundwater in the Sava river aquifer, Belgrade, Serbia

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Abstract The oil pollutant in the Sava River aquifer in the residential area of Belgrade, Serbia was investigated in order to analyze the extent, origin and spatial distribution of the pollution, with the aim to estimate potential human health risks from exposure to the compounds detected. Analytical methods indicated that the dominant compounds in this oil pollutant were gasoline range organic compounds. Benzene, toluene, ethylbenzene and xylenes (BTEX) were identified as compounds of concern and quantified by headspace gas chromatography. The concentrations of benzene measured at all sampling points were higher than the remediation value while the maximum concentrations of BTEX quantified were among the highest concentrations of these compounds reported in the petroleum-contaminated aquifers in the world. The assessment of the human health risks from exposure to BTEX-covered industrial scenario for adult receptors and residential scenario for adult receptors and children. The exposure routes analyzed were dermal contact with and ingestion of contaminated water, considering both cancer and non-cancer effects. The analysis of the lifetime incremental cancer risk indicated the potential for adverse health effects for human exposure at the investigated location, and because of that it was interpreted as an unacceptable risk level or risks of high priority which required immediate consideration for remedial measures at this location. A complete set of mitigation measures was proposed including: groundwater decontamination treatment, installation of filters for tap water, development of the system for monitoring of BTEX in the groundwater and development of the emergency response capacities at this location.

Keywords Groundwater · Petroleum pollutant · BTEX · Human health risk assessment · Mitigation measures

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Introduction

Crude oil, as a natural resource, does not represent a polluting substance at the place of its origin. However, due to exploitation, processing, transport and use of petroleum products, but also due to accidental and incidental spills, crude oil and petroleum products are these days among the main pollutants of the environment (Yanxun et al., 2011).

Regarding the amount consumed, the most important crude oil derivatives are diesel oil and gasoline (Morrison, 2000). Hundreds of hydrocarbons are present in these petroleum fractions, and most of them can be generally classified as either aromatics or alkanes (Alfke et al., 2007). Large part of these fractions is composed from volatile organic compounds (VOCs) (IARC, 1989a, 1989b). Among them, the most investigated compounds are benzene, toluene, ethylbenzene and xylene (BTEX).

In the case of petroleum fuel spills, due to their relatively high water solubility and polarity, comparing to the other constituents of crude oil derivatives, BTEX can access groundwater at relatively high concentrations (López et al., 2008). Because of that, from the environmental and ecological point of view, BTEX compounds are the prime contaminants of surface- and groundwater in petroleum-contaminated areas (Duan & Li, 2017; Mitra & Roy, 2011; Cheng et al., 2016; Odermatt, 1994).

The aim of this study was to investigate petroleum pollutants in contaminated groundwater in the Sava River aquifer in the residential area New Belgrade, in the vicinity of the largest heating plant in Belgrade, the capital of Serbia. This research was conducted in order to investigate the oil contaminant which was detected at this location, with the aim to estimate the extent of this pollution, its origin and spatial distribution, with a special emphasis on the analysis of BTEX in this part of the aquifer and assessment of potential human health risks from exposure to these compounds.

Material and methods

Study area

The site investigated in this study is located on the left bank of the Sava River in Belgrade (the Capital of Serbia), approximately one kilometer from its confluence with the Danube (Fig. 1).

The investigated location is covering the surface area of 300.000 m^2 which is the property of the largest heating plant in this city. According to the installed capacity, this is also the largest single heating plant in Europe The main activity of this facility, which has been active since 1965, is steam supply for district heating in this part of Belgrade. Petroleum products have been used as fuel in this plant for decades. The most used derivatives are crude gasoline, eco diesel and heavy fuel oil, which are stored in several large storage tanks within the investigated area (Fig. 2; http://www.beoelektrane.rs/about_us.html).

According to the geological and hydrogeological characteristics, the investigated site is located in the alluvial plane of the Sava River. In this part of the alluvial plane, there is also a network of radial collector wells. The groundwater extracted from the aquifer by these wells is used for the city water supply system. The wells No 26 and No 27 are located within the areas investigated in this study (Fig. 2).

This location has been subject of our investigations for years. The previous extensive research of this locality was conducted in the period from 2015 to 2017. A large survey included analyzes of ground waters from this location and water samples from the Sava River (Vrvić, 2015). The results confirmed presence of diesel and heavy fuel oil in the groundwater, at the concentrations higher than the remediation intervention values (Avdalović et al., 2016). As a result, in situ bioremediation of the groundwater at this locality was recommended (Avdalović et al., 2016; Vrvić, 2015). The enhanced bioremediation of the groundwater under field conditions took twelve months. At the end of the remediation treatment, the TPH levels were lowered and below the threshold level regulated by the National legislation (Bulatović et al., 2020). During that project, a network of 15 bioremediation wells, 9 control wells, and bioreactor columns was constructed at the investigated location (Fig. 2).

During installation of that infrastructure, the lithological characteristics and the aquifer properties of the investigated location were analyzed. The results showed that the thickness of sandy-gravelly deposits in this area was in the range from several centimeters to several meters (Fig. 3; Bulatović et al., 2020). It is important to note that these porous unbound sediments

Fig. 1 Geographic position of the investigated area (Source: Vrvić, 2015; www.google.com/maps)

can facilitate transport of petroleum pollutants down to the groundwater level depths.

In September 2018, during a routine control, the existence of a new pollution at the locality of the heating plant was discovered. During the regular inspections of concrete channels for electric installation near the reservoir R-7 (Fig. 2), it was found that some of these channels were filled in with the oil pollutant that presumably accidentally leaked from the nearby reservoirs. This pollutant was dark in color, smelling of crude oil and had a thick sludge-like consistency. Because of that it was designated “oil sludge”. Cleaning of the concrete channels revealed that their bottoms were ruptured and perforated indicating that some constituents of this oil pollutant might have penetrated into the porous parts of the aquifer.

The aim of this study was to investigate the extent of this new pollution, its origin and spatial distribution, and especially to analyze BTEX compounds in this part of the aquifer in order to assess a potential human health risks from exposure to these compounds, and to propose the most appropriate mitigation measures.

Groundwater and sludge sampling

Groundwater samples (1 L of each) were collected from 28 hydrogeological boreholes (Fig. 2) from the depths of 8–11 m across the investigated profile of the alluvial sediments. The water samples were collected in amber air tight jars, put in the refrigerator at 4 °C, and immediately sent to the laboratory for instrument analyses.

The sludge samples (1 kg of each) were collected from two sampling points (U1 and U2) near reservoir R-7 (Fig. 2). They were kept and transported in the same way as the groundwater samples.

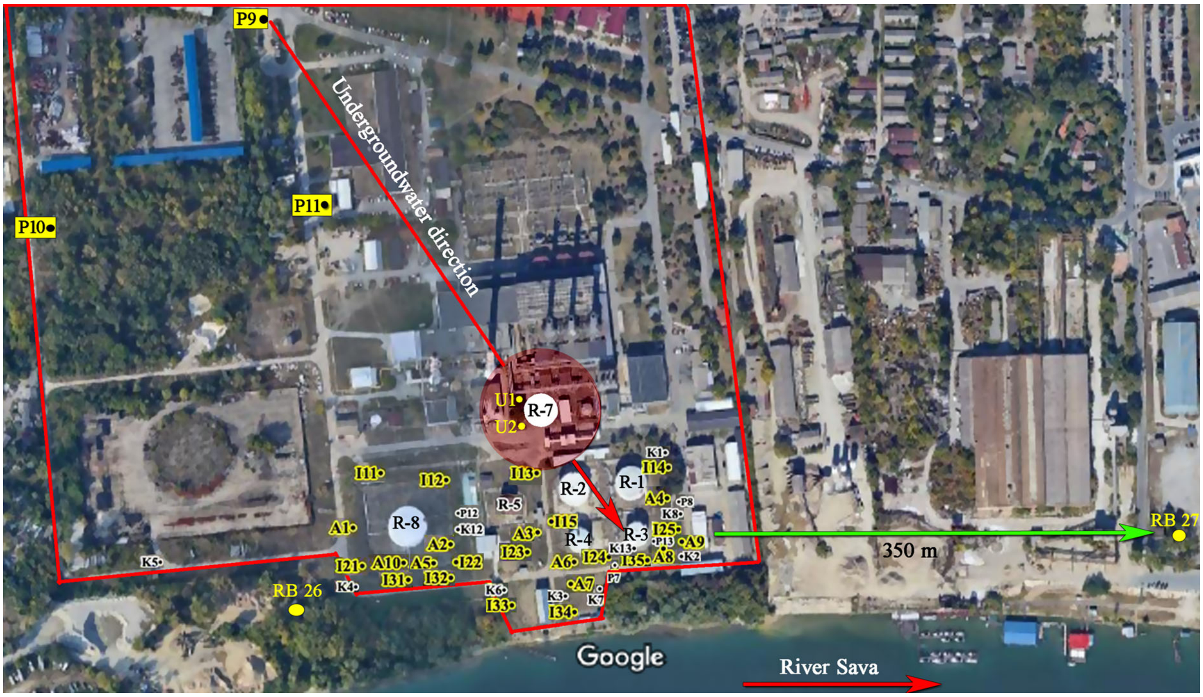

Fig. 2 Position of all sampling points and important facilities at the investigated location. I—infiltration pumping wells, K—control wells, P—piezometers, A—bioreactor columns, U—sampling points, R- reservoirs, RB 26—Radial Collector well No 26, RB 27—Radial Collector well No 27 (Source: www.google.com/maps)

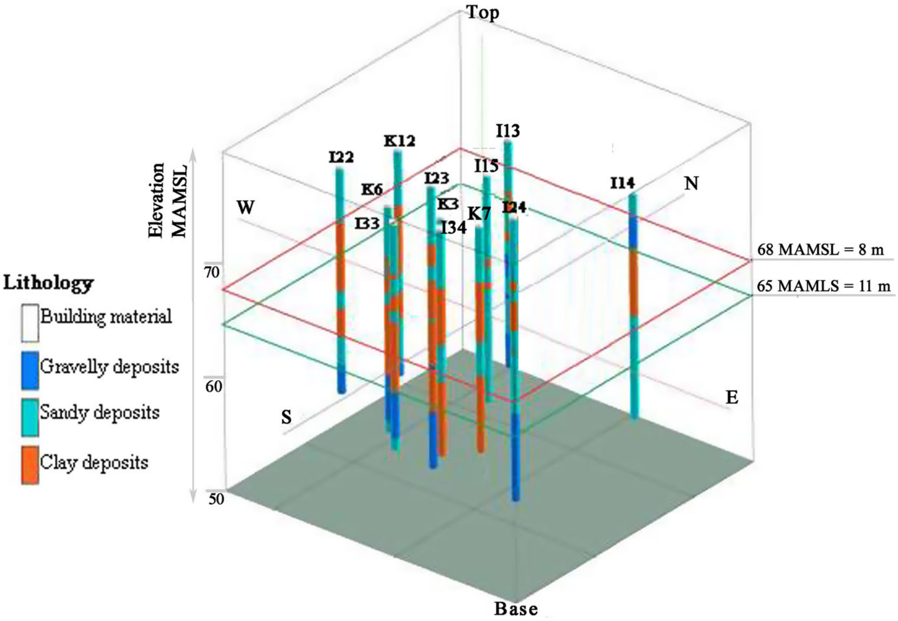

Fig. 3 Lithological profile of the investigated aquifer (3D model); I- infiltration pumping wells, K—control wells (The plains at 65 and 68 elevation (meters above mean sea level (MAMSL)) correspond to the depths of exploration wells, i.e., hydrogeological objects at 8 and 11 m in relation to the soil surface

Chemical analyses for sludge and groundwater characterization

The water content in the sludge samples was determined by coulometric Karl-Fischer titration. Analyses were performed according to the procedure of the standard SRPS EN ISO 12937 (2011), using 831 KF Coulometer, Metrohm. Ash at 550 °C was determined gravimetrically according to standard BS EN 12879 (2000). The contents of elements: carbon, sulfur, nitrogen and hydrogen were measured using an automatic analyzer Elementar, Vario EL III (Hanau, Germany) (Jednak et al., 2017). Total organic matter content was calculated by subtraction of the content of ash from the sum of the total content of elements (carbon, sulfur, nitrogen and hydrogen). The total nonpolar organic compounds extracted with *n*-hexane (*n*-Hexane Extractable Substances—HES) were determined with Extraction/Gravimetric method (EPA, 1999). Diesel fraction (C10–C28) and heavy hydrocarbon fractions of the oil fuel (C10–C40) were analyzed by GC-FID according to the standard BS EN ISO 16703 (2011). Total petroleum hydrocarbons (TPH) were determined by summing the VOCs and C10–C40 fractions.

Instrumental analyzes

Preliminary analyses of the organic compounds extracted from the sludge and from the groundwater samples were conducted by gas chromatography with flame ionization detection (GC-FID). The instrument employed was Agilent 7890A GC system equipped with a split-splitless injector and a flame ionization detector (FID). TG-5MT capillary column, 30 m × 0.25 mm × 0.25 µm was used. The GC parameters were as follows: 40 °C for 1 min, then increased at a rate of 15 °C/min to 100 °C and held at this temperature for 1 min, and then increased at a rate of 10 °C/min to 310 °C and held at this temperature for 15 min. The mode of injection was splitless. Hydrogen was used as the carrier gas with the flow rate of 30 ml/min.

In this study, volatile organic compounds (VOCs) were analyzed and identified by headspace gas chromatography with detection by mass spectrometry (HS-GC-MS). HS-GC-MS analysis was conducted by Agilent 19091S-433 gas chromatograph coupled with Agilent 5975C mass selective detector (70 eV). The analysis was conducted in a split mode. The instrument working parameters were: Equilibration Time: 0.5 min; Incubation Temperature: 90 °C/10 min; Oven Program: 35 °C for 5 min, then 3 °C/min to 50 °C for 0 min, then 10 °C/min to 150 °C for 0 min, then 50 °C/min to 250 °C for 4 min; Column: HP5-MS, 30 m × 0.25 mm, 0.25 µm film; The carrier gas: He, with constant flow rate (2 ml/min) and constant pressure (103 kPa); MS transfer line temperature: 280 °C.

Benzene, toluene, ethylbenzene and xylenes (BTEX) were quantified by headspace gas chromatography with flame ionization detector (HS-GC-FID). The instrument used was Agilent 7890B. The analyses were conducted in a split mode. The following working parameters were used for this instrument: Equilibration Time: 0.5 min; Incubation: 85 °C/30 min; Oven Program: 40 °C/2 min, then 8 °C/min to 120 °C for 1 min and 5 °C/min to 190 °C for 5 min; Column: HP5-MS, 30 m × 250 µm × 0.25 µm; The carrier gas: He, with constant flow rate (1.4 ml/min) and constant pressure (103 kPa); FID transfer line temperature: 350 °C.

Statistical analyses

All chemical analyses were conducted in triplicates, and the results were expressed as mean values ± standard deviation. A one-way analysis of variance (ANOVA) was used to examine statistical significance of differences in the mean concentrations for each of the Chemicals Of Concern (COCs) analyzed in this study (a level of $p < 0.05$ was considered significant). The Duncan's multiple range post hoc test for one-way ANOVA (at $p = 0.05$) was used to measure specific differences between the pairs of means. The software IBM® SPSS® Version 20 was employed for all statistical analyses.

Spatial analysis of BTEX

The software package used for the spatial analysis—contouring of contaminant data was Surfer 11 (Golden Software).

Chemicals of concern (COCs) selection

The COCs were selected from the list of the identified chemicals of potential concern (COPCs) using numerous screening and selection criteria such as: carcinogenicity, toxicity, endocrine disruption potential, environmental fate (such as: persistency, mobility, biodegradability), inclusion in the list of the priority pollutants, potential synergistic and/or antagonistic effect on other COPCs, emission characteristics, availability of the toxicity values and other relevant compound-specific data, concentration. Human health risks associated with exposure to the selected COCs were determined in the risk assessment.

Human health risk assessment

The assessment of risk to human health was conducted according to the US EPA Risk assessment guidance (EPA, 1989) including all relevant annotating and supporting documents. Where needed, World Health Organization (WHO) Human Health Risk Assessment Toolkit (WHO, 2010), and WHO Guidelines for Drinking-water Quality (WHO, 2017) were consulted as well.

Exposure assessment

The exposure assessment conducted in this study covered two scenarios: industrial and residential. In the industrial scenario, the excavation worker was recognized as the most exposed receptor. In the residential scenario, two sensitive receptor groups were considered: adults and children. For all these receptors, the main exposure routes analyzed were dermal contact with contaminated water, and ingestion of contaminated water, considering both cancer and non-cancer effects.

Chronic daily Intake for direct and indirect water ingestion was calculated according to Eq. 1 (EPA, 1989):

$$\text{Intake} = \frac{C_w \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (1)$$

where Cw is concentration of the individual COC in water (mg/L); IR is ingestion rate (L/day); EF is exposure frequency (days/year); ED is exposure duration (year); BW—body weight (kg); AT is averaging time (days).

Exposure levels as a consequence of dermal contact with contaminated water were expressed as Dermal Adsorbed Dose (DAD) and calculated according to Eqs. 2–4 (EPA, 2004):

$$\text{DAD} = \frac{\text{DA}_{\text{event}} \times \text{EV} \times \text{ED} \times \text{EF} \times \text{SA}}{\text{BW} \times \text{AT}} \quad (2)$$

where:

$$\text{If } t_{\text{event}} \le t^{*}, \text{ than DA}_{\text{event}} = 2\text{FA} \times K_{\text{p}} \times C_{\text{w}} \times \sqrt{\frac{6\tau_{\text{event}} \times t_{\text{event}}}{\pi}} \quad (3)$$

$$\text{If } t_{\text{event}} \ge t^{*}, \text{ than DA}_{\text{event}} = \text{FA} \times K_{\text{p}} \times C_{\text{w}} \times \left[\frac{t_{\text{event}}}{1+B} + 2\tau_{\text{event}}\left(\frac{1+3B+3B^2}{(1+B)^2}\right)\right] \quad (4)$$

where DA_{event} is absorbed dose per event (mg/cm^3-day); EV is event frequency (event/day); ED is exposure duration (year); EF is exposure frequency (days/year); SA is skin surface area (cm^3);; BW is body weight (kg); AT is averaging time (days); t_{event} is event duration (h/event); t^* is time to reach steady state (h); FA is fraction absorbed water (dimensionless); K_{p} is dermal permeability coefficient of compound in water (cm/h); C_{w} is chemical concentration in water (mg/ml); τ_{event} is lag time per event (h/event); B is ratio of the permeability coefficient of compound trough the stratum corneum relative to its permeability coefficient across the viable epidermis (dimensionless).

Risk characterization

In order to analyze the human health risk associated with exposure to volatile organic compounds from contaminated urban groundwater at the investigated location, lifetime incremental cancer risk and non-cancer health hazard quotient (and hazard index) were calculated and characterized.

Cancer risk characterization

In this research, benzene was the only carcinogenic COC, and the lifetime incremental cancer risk was calculated for this compound only.

The lifetime incremental cancer risk from exposure to benzene via ingestion ($\text{CR}_{\text{INGESTION}}$) was estimated by Eq. 5 (EPA, 1989):

$$\text{CR}_{\text{INGESTION}} = \text{Intake} \times \text{SF}_{\text{O}} \quad (5)$$

For estimation of the incremental cancer risk from exposure to benzene via dermal contact (CR_{DERMAL}) Eq. 6 (EPA, 2004) was used:

$$CR_{DERMAL} = DAD \times SF_D \qquad (6)$$

where SF_O (oral cancer slope factor $(mg/kg\text{-}day)^{-1}$) and SF_D (dermal cancer slope factor $(mg/kg\text{-}day)^{-1}$) are compound-specific constants. Estimates of the cancer potency (i.e., ingestion and dermal cancer slope factors) were used from the Integrated Risk Information System (IRIS) tabular values of the US EPA (IRIS, 2020).

Total cancer risk from exposure to benzene for each receptor was calculated by Eq. 7 (EPA, 2005a), assuming that the carcinogen accumulated via different exposure routes affects the same target organ to produce a cancer response (EPA, 2005b).

$$\text{Total Cancer Risk} = \text{Cancer Risk}_{INGESTION} + \text{Cancer Risk}_{DERMAL} \qquad (7)$$

For interpretation of the lifetime incremental cancer risk severity/acceptability, we used a reference cancer risk range of 1×10^{-4} to 1×10^{-6} as defined in the Volume 40 of the Code of Federal Regulations (40 C.F.R. § 300.340.): "For known or suspected carcinogens, acceptable exposure levels are generally concentration levels that represent an excess upper bound lifetime cancer risk to an individual of between 10^{-4} and 10^{-6}." The cancer risk equal to 1×10^{-6} means that a receptor's chance of developing cancer is 1 in 1.000.000 while the value for the cancer risk of 1×10^{-4} indicates that a receptor's chance of developing cancer is 1 in 10.000 (EPA, 1991). For carcinogens in drinking water, a lifetime incremental cancer risk of between 1 in 10.000 and 1 in 1.000.000 is interpreted as an acceptable risk level (EPA, 2013).

For a more detailed classification of the lifetime incremental cancer risks calculated for the investigated location, we used the criteria described by Kujlu et al. (2020) and Legay et al. (2011) where the cancer risks between 1×10^{-6} and 5.1×10^{-5} were designated as "acceptable low risks" and the cancer risks between 5.1×10^{-5} and 1×10^{-4} were labeled "acceptable high risks." The cancer risk levels $< 10^{-6}$ are considered as negligible and in these cases no action is needed, while the cancer risk levels $\geq 10^{-4}$ are risks of high priority which require immediate consideration for remedial measures (Hammonds et al., 1994).

Non-cancer hazard characterization

Non-cancer health hazard (expressed as Hazard Quotient, HQ) was estimated for human exposure to all COCs identified.

Hazard quotient for exposure via direct and indirect ingestion was estimated by Eq. 8 (EPA, 1989):

$$HQ_{INGESTION} = \frac{Intake}{Rf\ D_O} \qquad (8)$$

The dermal hazard quotient (HQ_{DERMAL}) for exposure via dermal contact was estimated by Eq. 9 (EPA, 2004):

$$HQ_{DERMAL} = \frac{DAD}{Rf\ D_D} \qquad (9)$$

where RfD_O (ingestion reference dose (mg/kg-d)) RfD_D (dermal reference dose (mg/kg-d)) are compound-specific constants obtained from the IRIS system (IRIS, 2020).

Total hazard index was calculated according to Eqs. 10–11 (EPA, 2005a), assuming that a single receptor was exposed to the COCs by all pathways identified in the corresponding scenario (EPA, 2000).

$$\text{Total Hazard Index} = \sum jHIj \qquad (10)$$

$$HI = \sum iHQi \qquad (11)$$

where Total Hazard Index is a total hazard index for an individual receptor for all COCs across all exposure pathways; HIj is a Hazard Index for exposure pathway j; HQ_i is a Hazard Quotient for COCi. For each receptor considered at the location investigated in this study, total hazard index was calculated as a sum of risks from the ingestion and dermal contact for all COCs.

For non-cancer hazard characterization, a threshold value of HQ = 1 was used for decision making. HQ values lower than 1 were interpreted as indicating acceptable risk for the exposed receptors (Tables 1, 2), while HQ values higher than 1 were interpreted as indicating unacceptable health risks with potential for adverse health effects in the exposed population (EPA, 2001).

Table 1 Summary of the factors and parameters used to assess the exposure to the selected COCs via the ingestion pathway

Factor	Value
Intake—daily water ingestion intake (mg/kg-day)	Equation (1)
C_w—chemical concentration in water (mg/l)	Table 4
IR—ingestion rate (L/day)	Workers: oral: 1; incidental during work: 0.02 Adult Residents: oral: 2; incidental during showering: 0.06 Children: 1
EF—exposure frequency (days/year)	Workers: 250 Adult residents: 350 Children: 350
ED—exposure duration (year)	For cancer risk: Workers: 25 Adult residents: 30 Children: 6 For non-cancer hazard: 1 year for all receptors
BW—body weight (kg)	Workers: 70 Adult residents: 70 Children: 15
AT—averaging time (days)	Non-cancerogenic effects: AT = ED*365 days/year Cancerogenic effects: AT = 70 year*365 days/year
Rf D_o—oral reference dose (mg/kg-d)	Benzene: 0.004 Toluene: 0.08 Ethylbenzene: 0.1 Xylenes: 0.2
SF_o—oral slope factor $(mg/kg/d)^{-1}$	Benzene: 0.055 Toluene: - Ethylbenzene: - Xylenes: -

Results and discussion

COPCs Identification

The sludge samples collected from the channels U1 and U2 (Fig. 2) were preliminary analyzed in order to identify the new pollutant found at this location. The results of these preliminary analyses are shown in Table 3.

These results demonstrated that this new pollutant was composed from almost only organic matter (99.64% in the channel U1 and 99.41% in the channel U2; Table 3). The instrumental analyses specific for petroleum products indicated that the sludge analyzed contained petroleum derivatives such as diesel and heavy fuel oil but also contained a high proportion of the volatile hydrocarbons.

In order to check whether the oil pollutant found in the investigated channels had reached the groundwater at this location, preliminary GC-FID analyses of the organic extracts from the ground waters were conducted. The profile of the compounds identified was also compared with the analytical standards for petroleum derivatives identified in the sludge samples: gasoline range organics, diesel range organics, heavy fuel oil and total petroleum hydrocarbons. The results

Table 2 Summary of the factors and parameters used to assess the exposure to the selected COCs via the dermal pathway

Factor	Value
DAD—dermally absorbed dose per event (mg/kg day)	Equation (4)
SA—skin surface area (cm^3)	Workers: 3300 Adult residents: 18,000 Children: 6600
EV—event frequency (event/day)	1
EF, ED, BW and AT	Defined in ingestion pathway
DA_{event}—absorbed dose per event (mg/cm^3 day)	Equations (5) and (6)
FA—fraction absorbed water (dimensionless)	Benzene: 1 Toluene: 1 Ethylbenzene: 1 Xylenes: 1
K_p—dermal permeability coefficient of compound in water (cm/h)	Benzene: 0.015 Toluene: 0.031 Ethylbenzene: 0.049 Xylenes: 0.053
C_w—chemical concentration in water (mg/cm^3)	Table 4
τ_{event}—lag time per ebvent (h/event)	Benzene: 0.29 Toluene: 0.35 Ethylbenzene: 0.42 Xylenes: 0.42
t_{event}—event duration (h/event)	Workers: 4 Adults residents: 0.58 Children:1
t^*—time to reach steady state (h)	Benzene: 0.70 Toluene: 0.84 Ethylbenzene: 1.01 Xylenes: 1.01
B—ratio of the permeability coefficient of compound trough the stratum corneum relative to its permeability coefficient across the viable epidermis (dimensionless)	Benzene: 0.1 Toluene: 0.1 Ethylbenzene: 0.2 Xylenes: 0.2
Rf D_d—dermal reference dose (mg/kg d)	Benzene: 0.0038 Toluene: 0.064 Ethylbenzene: 0.08 Xylenes: 0.16
SF_d – absorbed cancer slope factor $(mg/kg\ day)^{-1}$	Benzene: 0.06 Toluene: - Ethylbenzene: - Xylenes: -

of the analysis of the organic extract from the sludge sample with the highest content of the extract are shown in Fig. 4. These results indicated that the dominant compounds in these extracts were in the

Table 3 Results of the preliminary analyses of the sludge samples*

Analysis	Sample	
	U1	U2
Water content (%)	7.10 ± 0.52	9.84 ± 0.96
Ash at 550 °C (%)	0.36 ± 0.05	0.59 ± 0.08
Total organic matter (%)	99.64 ± 5.47	99.41 ± 7.63
Total carbon (C) (%)	85.51 ± 4.92	84.13 ± 6.18
Total sulfur (S) (%)	2.45 ± 0.11	1.97 ± 0.16
Total nitrogen (N) (%)	0.51 ± 0.02	0.45 ± 0.03
Hydrogen content (H) (%)	11.55 ± 0.62	10.98 ± 1.01
HES[a] (g/kg)	922.05 ± 47.34	964.28 ± 92.57
VOCs[b] (g/kg)	123.54 ± 6.13	248.15 ± 19.11
C10–C28[c] (g/kg)	274.93 ± 14.63	255.00 ± 20.91
C10–C40[d] (g/kg)	438.55 ± 27.49	420.10 ± 52.09
TPH[e] (g/kg)	562.09 ± 41.03	668.25 ± 75.19

*All chemical analyses were conducted in triplicates, and the results in this table are expressed as mean values ± standard deviation

[a] HES—*n*-Hexane extractable substances

[b] VOCs (Volatile organic compounds)

[c] C10–C28—diesel fraction of oil fuel

[d] C10–C40—heavy hydrocarbon fractions of oil fuel

[e] TPH—Total Petroleum Hydrocarbons (C6–C40)

range of gasoline range organic compounds and these compounds were identified as the COPCs at this location.

COCs selection

For the detailed analysis of the gasoline range organic VOCs and their possible identification, HS-GC-MS analytical technique was employed. The results of this analysis for the groundwater sample (K7), for which the GC-FID analysis demonstrated the highest content of the VOCs, are shown in Fig. 5. Identification of all compounds detected in this chromatogram is listed as well.

Using these results, and numerous selection criteria, benzene, toluene, ethylbenzene and xylenes (BTEX compounds) were selected as COCs in this study.

Concentration levels and spatial variations of COCs

Concentrations of crude gasoline and BTEX compounds in the investigated ground water samples are shown in Table 4. In 13 groundwater samples, the concentration of the crude gasoline was $\leq$ 0.01 mg/L. In 15 groundwater samples, the concentration of crude gasoline was $\geq$ 0.01 mg/L, and ranged from 0.01 to 10.02 mg/L. In these 15 samples, BTEX compounds were analyzed. The results showed that the total concentrations of BTEX in the groundwater samples ranged from 0.05 to 5.92 mg/L with an average value of 1.38 mg/L. In five samples concentrations of BTEX were higher than the remediation value (RS Official Gazette, 2010). The highest concentrations of BTEX were measured in the samples from the boreholes I15, K3 and K7 while the concentrations of these COCs were lower in the boreholes between them (Table 4; Fig. 2). These results indicate a possible existence of multiple sources of these pollutants in the investigated area or multiple discharges of these pollutants from the same source.

Statistical analyses of the results revealed significant differences between the concentrations of the individual BTEX at all sampling points except from those with the lowest concentrations. These results might confirm the assumption of the existence of multiple sources of these pollutants. However, in this study, significant differences between the concentrations of the individual BTEX can also be caused by large differences in the concentrations of these COCs at different sampling points and high precision of the instrumental method employed for the analysis of these compounds.

Concentration of benzene, which is the only carcinogenic COC in this study, was in range from 0.04 to 5.02 mg/L, averaging at 1.15 mg/L. The concentrations of benzene measured in all boreholes were higher than the remediation value. Considering the proximity of two Radial Collector wells (RB 26 and RB 27, Fig. 2), it is important to emphasize that all groundwater concentrations of benzene measured in this area exceeded the World Health Organization's guideline value for drinking water quality (0.01 mg/L; WHO, 2017). Furthermore, it should be noted that the maximum concentrations of BTEX quantified in this study are among the highest concentrations of these compounds reported in the petroleum-contaminated

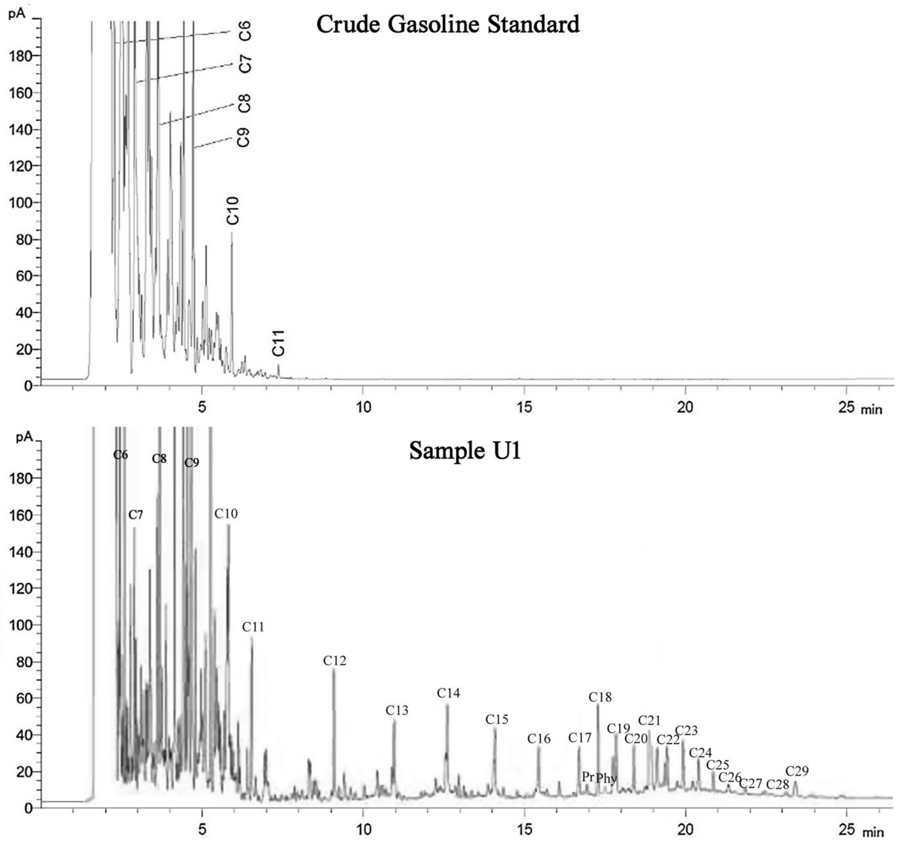

Fig. 4 GC-FID chromatogram of the sludge sample U1

aquifers in the world (Rajasekhar et al., 2020 and references therein). All these facts demonstrate the significance of a risk assessment study at this location.

Benzene is also the most abundant of all BTEX compounds investigated in the groundwater samples in this research. Its content in all samples is between 80 and 85% of all BTEX compounds quantified. This result can be explained by the higher solubility of benzene in water comparing to toluene, ethylbenzene and xylenes, but also by the higher content of benzene in the original crude gasoline pollutant.

Scenarios considered in the risk assessments and identification of potential human receptors

The site investigated in this study is located in a small restricted industrial area. On this property trespassing is forbidden. On the nearby riverbank, recreational activities such as swimming and fishing are not allowed. This is a typical industrial scenario where the most exposed potential human receptors are excavation/construction workers employed at this heating plant who might be exposed to the contaminated ground water during their regular working activities. This location has been allocated to them for one year, and after that period they will be transferred to some other activities. The exposure pathways for these receptors are ingestion of, and dermal contact with the contaminated water. Exposure of other employees to the COCs at this location is also possible but these cases belong to the short time occasional exposure, which we characterize as an acute health risk that will not be interpreted in this study.

In order to evaluate other scenarios such as a residential scenario involving a population living in the vicinity of this investigated area, which might be using potentially contaminated tap water, the gasoline content in the ground waters was investigated. Concentrations of the gasoline and BTEX compounds in the ground waters are shown in Table 4. Spatial

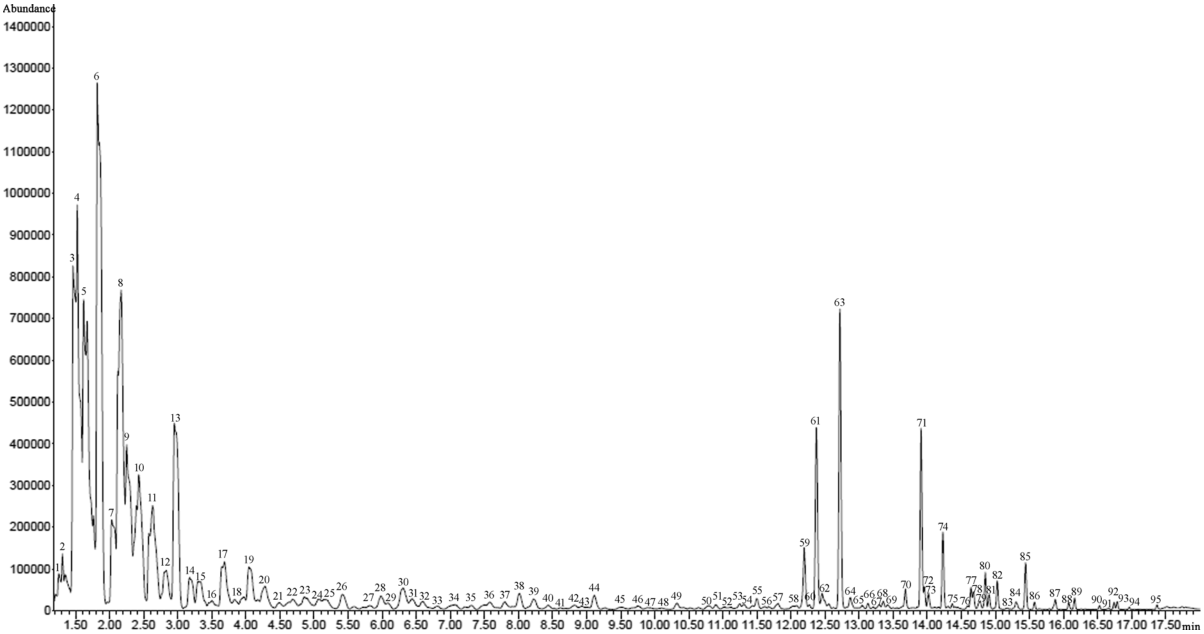

Fig. 5 HS-GC-MS chromatogram of the groundwater sample K7. The identified compounds are: 1) Pentane; 2) Methylene Chloride; 3) 2-methyl-Pentane, 3-methyl-Pentane; 4) Hexane, 2-Pentene, 2-methyl-Pentene; 5) Cyclopentane, methyl-Cyclopentane; 6) Cyclopentene, 1-methyl-Cyclopentene; 7) Benzene; 8) Cyclohexane; 9) Hexane, 3-methyl-Hexane; 10) Cyclohexene; 11) 1,3-dimethyl-Cyclopentane, cis-dimethyl-Cyclopentane, Heptane, Cyclopentene, 4,4-dimethyl-Cyclopentene, 2-Hexene, 2-methyl-Hexene; 12) 1,5-dimethyl-Cyclopentene; 13) methyl-Cyclohexane; 14) ethyl-Cyclopentane; 15) 4-methyl-Cyclohexen; 16) 1,2,3-trimethyl-Cyclopentane; 17) 2,4-Hexadiene, 2-methyl-Hexadiene; 18) NI; 19) Toluene, 1-methyl- Cyclohexene; 20) 1,3-dimethyl-Cyclohexane, cis-dimethyl-Cyclohexane; 21) 1,1-dimethyl-Cyclohexane; 22) 1-ethyl-3-methyl-Cyclopentane; 23) 1,2-dimethyl-Cyclohexane, trans-dimethyl-Cyclohexane; 24) NI; 25) 1,3-dimethyl-Cyclohexane, trans-dimethyl-Cyclohexane; 26) 4-Methyl-1,3-heptadiene; 27) 1,4-Hexadiene, 3-ethyl-Hexadiene; 28) 1,3-Dimethyl-1-cyclohexene; 29) 1,2-dimethyl- (cis/trans)-Cyclohexane; 30) ethyl-Cyclohexane; 31) 1,1,3-trimethyl-Cyclohexane; 32) Methyl-ethyl-Cyclopentene; 33) 1,6-dimethyl-Cyclohexene; 34) NI; 35) Pentalene, 1,2,3,3a,4,6a-hexahydro-Pentalene, Butane, 2-(ethylthio)-Butane; 36) 1,2,4,4-Tetramethyl-cyclopentene, Ethyl-benzene; 37) octahydro-Pentalene, cis-Pentalene; 38) m-Xylene, p-Xylene; 39) 1,2-dimethyl-Cyclohexene; 40) NI; 41) Thiophene, tetrahydro-2,5-dimethyl-Thiophene, cis-dimethyl-Thiophene; 42) tetrahydro-2,5-dimethyl-Thiophene, trans-dimethyl-Thiophene; 43) o-Xylene; 44) 2-ethylidene-1,1-dimethyl-Cyclopentane; 45) Dimethylthiophane; 46) Dimethylthiane; 47) 2H-Thiopyran, tetrahydro-2-methyl-Thiopyran; 48) Dimethylthiophane; 49) 1H-Indene, octahydro-Indene, trans-Indene; 50) tetrahydro-2-methyl-Thiopyran; 51) ethyl,methyl-Benzene; 52) NI; 53) 2,4-Dimethylthiane; 54) NI; 55) 2-ethyltetrahydro-Thiophene; 56) propyl-Benzene; 57) Dimethylthiane; 58) 1,1-dimethyl-2-(1-methylethylidene)-Cyclopentane; 59) 2-ethyl-4 methylthiophene; 60) Ethyltoluene; 61) 1-ethyl-4-methyl-Benzene; 62) 2-ethyl-5-methylthiophene; 63) 1-ethyl-2-methyl- Benzene; 64) 2,3,4-trimethyl-Thiophene, trans-2-Ethyl-3-methylthiophane; 65) cis-2-Ethyl-3-methylthiophane; 66) 1,2,4-trimethyl-Benzene; 67) NI; 68) 1-phenyl-1,2-pentadiene; 69) Ethylmethylthiophane, 2-methylpropyl-Benzene; 70) methylpropyl-Benzene, Trimethylthiophene, 3-(1,1-dimethylethyl)-Thiophene; 71) trimethyl-Benzene; 72) 1-methyl-4-(1-methylethyl)-Benzene; 73) 1-methyl-3-(1-methylethyl)-Benzene; 74) Indane; 75) 1-methyl-2-(1-methylethyl)-Benzene; 76) Indene; 77) propyl-Thiophane; 78) 1,3-diethyl-Benzene; 79) 1-methyl-4-propyl-Benzene; 80) 1-methyl-3-propyl- Benzene; 81) NI; 82) 1-ethyl-2,4-dimethyl-Benzene; 83) Ethyl-dimethyl-thiophene, methyl-propyl-Benzene; 84) methyl-propyl-Benzene; 85) 2-ethyl-1,4-dimethyl-Benzene; 86) 2-ethyl-1,3-dimethyl-Benzene; 87) 4-ethyl-1,2-dimethyl-Benzene, 1-ethenyl-3-ethyl-Benzene; 88) ethyl-dimethyl-Benzene; 89) ethyl-dimethyl-Benzene; 90) tetramethyl-Benzene; 91) tetramethyl-Benzene, Tetramethylthiophene; 92) 2,3-dihydro-5-methyl- Indene; 93) 2,3-dihydro-4-methyl-Indene; 94) tetramethyl-Benzene; 95) 1,2,3,4-tetrahydro-Naphthalene

distribution of BTEX concentrations in groundwater within the study is shown in Fig. 6. As can be seen, the gasoline is spreading from the source of pollution to the south-east, in the direction of the groundwater flow direction, toward the river bank (Fig. 2). This is the most undesirable possible scenario because, with the ground water flow, all these pollutants can be transferred to the Sava River, and further downstream, far from the original source of pollution. The second and the more important reason is that the COCs can be, by

Table 4 Concentrations (mg/L) of Crude Gasoline and BTEX in the groundwater samples collected from the hydrogeological boreholes in September 2018*

Sample	Crude Gasoline	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX
		Remediation Values**				
		0.03	1.00	0.04	0.07	1.25
I11	0.02 ± 0.00^{h}	ND	ND	ND	ND	ND
I12	0.10 ± 0.00^{h}	ND	ND	ND	ND	ND
I13	4.62 ± 0.14^{e}	1.06 ± 0.05^{d}	0.10 ± 0.00^{e}	0.04 ± 0.00^{d}	0.08 ± 0.00^{d}	1.28 ± 0.05^{d}
I14	< 0.01	–	–	–	–	–
I15	6.2 ± 0.15^{b}	5.02 ± 0.15^{a}	0.27 ± 0.01^{a}	0.27 ± 0.01^{a}	0.39 ± 0.02^{a}	5.92 ± 0.18^{a}
I21	< 0.01	–	–	–	–	–
I22	0.13 ± 0.01^{h}	0.04 ± 0.00^{g}	< 0.01	< 0.01	0.01 ± 0.00^{f}	0.05 ± 0.00^{g}
I23	0.16 ± 0.01^{h}	0.04 ± 0.00^{g}	< 0.01	< 0.01	0.01 ± 0.00^{f}	0.05 ± 0.00^{g}
I24	0.15 ± 0.01^{h}	0.04 ± 0.00^{g}	< 0.01	< 0.01	0.01 ± 0.00^{f}	0.05 ± 0.00^{g}
I25	< 0.01	–	–	–	–	–
I31	< 0.01	–	–	–	–	–
I32	0.10 ± 0.00^{h}	ND	ND	ND	ND	ND
I33	0.07 ± 0.00^{h}	0.04 ± 0.00^{g}	< 0.01	< 0.01	0.01 ± 0.00^{f}	0.05 ± 0.00^{g}
I34	0.96 ± 0.05^{g}	0.75 ± 0.04^{e}	0.04 ± 0.00^{g}	0.04 ± 0.00^{d}	0.05 ± 0.01^{e}	0.88 ± 0.05^{e}
I35	0.01 ± 0.00^{h}	ND	ND	ND	ND	ND
K1	< 0.01	–	–	–	–	–
K2	< 0.01	–	–	–	–	–
K3	5.96 ± 0.17^{c}	1.98 ± 0.06^{c}	0.13 ± 0.00^{d}	0.14 ± 0.00^{c}	0.15 ± 0.01^{c}	2.40 ± 0.07^{c}
K4	< 0.01	–	–	–	–	–
K5	< 0.01	–	–	–	–	–
K6	2.34 ± 0.07^{f}	0.52 ± 0.02^{f}	0.05 ± 0.00^{f}	0.03 ± 0.00^{e}	0.02 ± 0.00^{f}	0.62 ± 0.02^{f}
K7	10.02 ± 0.21^{a}	2.15 ± 0.06^{b}	0.15 ± 0.01^{c}	0.15 ± 0.01^{b}	0.20 ± 0.01^{b}	2.65 ± 0.05^{b}
K8	< 0.01	–	–	–	–	–
P9	< 0.01	–	–	–	–	–
P10	< 0.01	–	–	–	–	–
P11	< 0.01	–	–	–	–	–
K12	5.01 ± 0.13^{d}	1.05 ± 0.05^{d}	0.17 ± 0.01^{b}	0.02 ± 0.00^{f}	0.04 ± 0.00^{e}	1.28 ± 0.05^{d}
K13	< 0.01	–	–	–	–	–
Average	2.39	1.15	0.13	0.10	0.09	1.38

*All chemical analyses were conducted in triplicates, and the results in this table are expressed as mean values ± standard deviation; **Remediation values of BTEX were defined by National regulation for the systematic monitoring of soil quality, soil degradation risk assessment indicators and methodology for the development of remediation programs (Official Gazette of the Republic of Serbia (No88/2010)); The letters (a, b, c, …) represent the significant difference between the mean concentrations of Crude Gasoline and between the mean concentrations of the individual BTEX in the groundwater samples as computed by Duncan's multiple range post hoc test for one-way ANOVA ($p = 0.05$); < 0.01—Below the quantification limit (< 0.01 mg/L); "–" No data (not measured because the concentration of the crude gasoline in the sample was below the quantification limit); "ND" not detected

the groundwater flow, transferred to the area of the radial collector wells where they can enter the city water supply system, and in that way, tap water in the houses of the residents who live in this part of the city. Therefore, potential human receptors (adults and children) are residents who are exposed to the contaminated tap water via ingestion (drinking) and via dermal contact (bathing/showering). For the

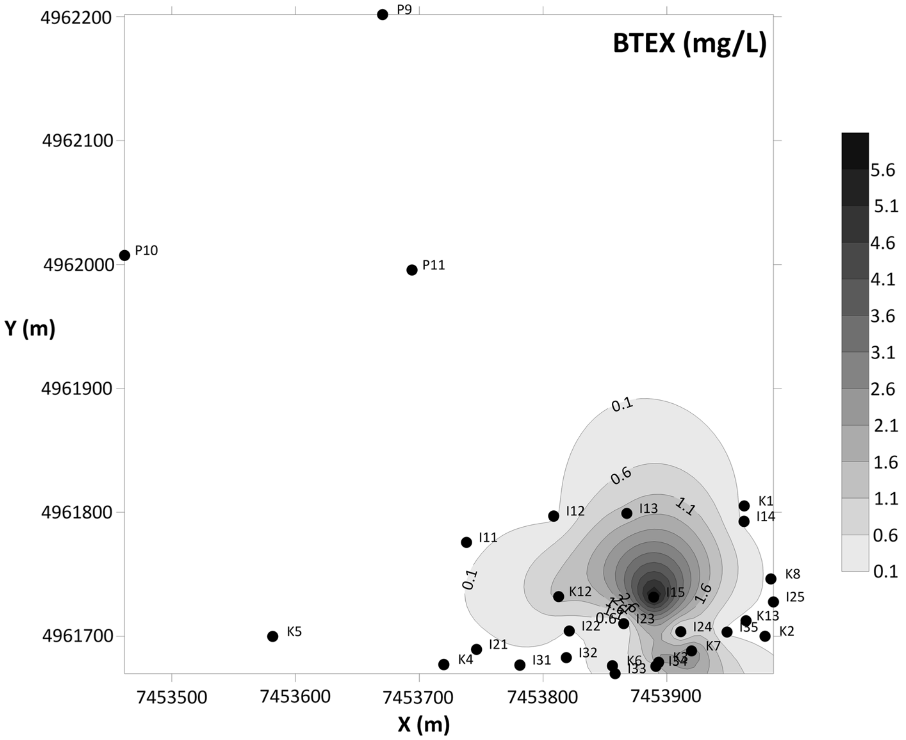

Fig. 6 Simulated two-dimensional groundwater transport of the BTEX in the investigated area

purposes of the risk assessment study, this scenario is marked as a Residential scenario.

Risk assessment

Residential scenario

This scenario refers to the local population of the municipality New Belgrade, which is supplied with the tap water originating from the investigated aquifer. The nearest residences are approximately 1.3 km away from the examined site (to the west: Heating plant - Block 70A: 1.4 km; to the north: Heating plant - Bellvile: 1.3 km; to the east Heating plant - Block 69: 1.2 km; GoogleMaps, 2021).

The territory of the municipality of New Belgrade covers an area of 41 km^2. The number of inhabitants in this municipality is 213.742, while the population density is 5.213/km^2. According to the 2011 census, the average age of the population in New Belgrade was 42.8 years (41.3 years for men, 44.4 years for women). The average life expectancy of this population was 77.6 years (77.5 years for men, 79.7 years for women). In 2018, the number of live births in this municipality was 2.248 (10.5 newborns per 1000 inhabitants), the number of deaths was 2.806 (13.1 deaths per 1000 inhabitants) while the natural increase was − 558 (− 2.6 per 1000 inhabitants; SORS, 2019).

Since this is an urban part of the city, the local population is not engaged in agricultural production. Because of that, the groundwater originating from the investigated aquifer is not used for irrigation of the crops.

As already explained, the sensitive receptors in the Residential scenario are residents who might be exposed to the contaminated tap water sourced from the investigated groundwater. Considering differences in the concentrations of the COCs measured at different sampling points but also the effects of flow and mixing in the groundwaters, we assumed that the average concentrations of the individual pollutants would best describe the reasonable maximum exposure expected to occur at this site. Because of that, for the health risk assessment of the population in this scenario, the average concentrations of COCs measured at all sampling points (Table 4) were used: 1.15 mg/L for benzene, 0.13 mg/L for toluene, 0.10 mg/L for ethylbenzene, and 0.09 mg/L for xylenes. It should be stated that the gasoline transport from the source of pollution in the groundwater in the form of a non-aqueous phase liquid is also possible. However, since the occurrence of the gasoline as a non-aqueous phase liquid in the groundwater saturated zone was not detected at this location, this case will not be considered in this study.

According to US EPA (EPA, 1989), in the residential scenarios volatile organic compounds from the tap water are probably completely lost during traditional cooking of food and drinks. Because of that, ingestion of the tap water is the only oral exposure pathway of the sensitive receptors to the COCs in this study. In this pathway, we can distinguish between two cases for ingestion of the tap water. One is the intentional direct ingestion of water through drinking of the tap water, and the other one is accidental ingestion of the tap water during showering/bathing. The latter is much lower in quantity than the former but in order to simplify the discussion in this study, these two values are combined and shown in the tables as one numerical value.

Exposure of residents to the pollutants in the tap water through the dermal exposure pathway can occur during numerous household activities such as: showering/bathing, laundering, dishwashing, handwashing, etc. In the scientific literature which is covering this subject area (López et al., 2008; Maurice et al., 2019; Rajasekhar et al., 2020; Zhang et al., 2016) it is generally accepted that among all mentioned activities in the dermal exposure pathway, the highest exposure to BTEX is during showering/bathing, while the contribution of all other activities to the total dermal risk is considered negligible. In our present study, we will follow the same principle and interpret showering/bathing as the highest contributor to the dermal exposure risk in the residential scenario.

One part of the exposure of the excavation/construction workers will also be evaluated in this scenario, and that is their exposure to the contaminated tap water which they might ingest during their working hours at this location.

All parameters used for this exposure assessment are listed in the Tables 1 and 2.

Estimated non-carcinogenic health risk associated with BTEX exposure for adults and children in the residential scenario is presented in Table 5. Estimated lifetime incremental cancer risks for the sensitive receptors in the residential scenario are shown in Table 6.

Table 5 Non-carcinogenic risk associated with exposure of adults (residents and workers) and children to BTEX from the tap water in the residential scenario

	Adults	Children	Workers
Oral exposure[a]			
HQ Benzene	8.14	19.54	2.82
HQ Toluene	0.03	0.07	0.01
HQ Ethylbenzene	0.02	0.04	0.01
HQ Xylenes	0.01	0.03	0.00
HI oral exposure	8.20	19.68	2.84
Dermal exposure			
HQ Benzene	1.33	2.28	–
HQ Toluene	0.02	0.03	–
HQ Ethylbenzene	0.02	0.03	–
HQ Xylenes	0.01	0.02	–
HI dermal exposure	1.38	2.36	–
Total hazard index	9.58	22.04	–

[a] Oral exposure for residents is a sum of hazard quotients from ingestion of tap water and accidental ingestion during showering/bathing

Table 6 Carcinogenic risk associated with exposure of adults and children to benzene from the tap water in the residential scenario

	Adults	Children	Workers
Oral exposure[a]	7.67E-04	3.69E-04	2.00E-04
Dermal exposure	1.23E-04	7.11E-05	–
Total risk	8.90E-04	4.40E-04	–

[a] Oral exposure for residents is a sum of cancer risks from ingestion of tap water and accidental ingestion during showering/bathing

The results indicate that, for all sensitive receptors in the residential scenario, the estimated non-carcinogenic health risk from exposure to benzene accounts for more than 99%, and more than 96% of the total non-carcinogenic risk associated with exposure to the BTEX compounds via oral and dermal pathway respectively. This result is a consequence of the high concentration of benzene comparing to the other BTEX compounds (Table 4) but also very low values of the parameters RfD_O and Rf $D_{D,}$ which are in denominators of the equations for oral and dermal non-carcinogenic health risk (Eqs. 8, 9).

The non-carcinogenic risk associated with exposure to BTEX from tap water in this scenario is mainly due to the ingestion (more than 85% of the total hazard index). These results are in agreement with the results of other authors, who investigated the human health risk from exposure to BTEX form petroleum-contaminated ground waters (López et al., 2008; Zhang et al., 2016), and concluded that in these cases ingestion dominates over other exposure pathways.

The HQ calculated for toluene, ethylbenzene and xylenes for ingestion and dermal pathways are <1. These results indicate that these COCs, if they reach the tap water in these concentrations, will not pose any adverse health effect for local population. However, estimated HQ values for benzene are much higher than 1 for both pathways considered. According to these results it can be concluded that, if benzene reaches the tap water in these concentrations, it could pose a serious adverse health effect for local consumers through these exposure pathways.

In the both of the exposure pathways analyzed, ingestion and dermal, the estimated values for hazard indexes for children are more than twice as high as the estimated values for hazard indexes for adults for the same period of exposure. These results are in agreement with the results of Rajasekhar et al. (2020) who concluded that children under age of five were the most susceptible age group in the assessments of the exposure to BTEX from water.

The assessment of the carcinogenic risk associated with exposure of adults and children in the residential scenario showed that this risk is primarily caused by ingestion and to the lower extent by dermal exposure (Table 4). In all cases, the estimated carcinogenic risk for children is lower than the risk for adults. However, the results of this study revealed that the total cancer risks for all receptors in the residential scenario were higher than 1×10^{-4}. These results are interpreted as an unacceptable risk level (EPA, 2013), or risks of high priority which require immediate consideration for remedial measures (Hammonds et al., 1994).

Industrial scenario

In the industrial scenario, the only sensitive receptors considered in this study are construction/excavation workers employed at the heating plant on the investigated location. The exposure of these receptors to BTEX from the groundwater might vary depending on the location within the property of this facility. In this scenario, we analyze their exposure when they are working in close proximity of the hydrogeological boreholes (Fig. 2). Because of that, for this part of the risk assessment, for each of the hydrogeological boreholes the mean value of the measured concentrations for that borehole was used (Table 4). Two exposure pathways are considered: oral exposure (incidental ingestion of the contaminated water during work) and dermal exposure. In the case when they ingest tap water at this location, they might be additionally exposed via the ingestion pathway. This case is explained in the residential scenario.

All parameters used in this exposure assessment are listed in the Tables 1 and 2.

Estimates of the non-carcinogenic risk, associated with exposure of construction/excavation workers in the industrial scenario to BTEX from ground water via oral exposure, are shown in Table 7 for oral exposure, and in Table 8 for dermal exposure. Hazard Indexes for oral and dermal exposure pathways and Total Hazard Index for exposure of construction/excavation workers to BTEX from ground waters in the industrial scenario are shown in Table 9. Calculated carcinogenic risks, associated with exposure of construction/excavation workers to benzene from ground water in the industrial scenario, are listed in Table 10.

The results show that, at all locations investigated in the industrial scenario, the calculated non-carcinogenic health risk from exposure to benzene accounts for more than 99% of the total non-carcinogenic risk

Table 7 Non-carcinogenic risk associated with exposure of construction/excavation workers to BTEX from the ground water via oral exposure in the industrial scenario

Sample	Benzene	Toluene	Ethylbenzene	Xylenes
I13	0.05	2.45E-04	7.83E-05	7.83E-05
I15	0.25	6.60E-04	5.28E-04	3.52E-04
I22–I33	1.96E-03	2.45E-05	1.96E-05	9.78E-06
I34	0.04	9.78E-05	7.83E-05	4.89E-05
K3	0.10	3.18E-04	2.74E-04	1.47E-04
K6	0.03	1.22E-04	5.87E-05	1.96E-05
K7	0.11	3.67E-04	2.94E-04	1.96E-04
K12	0.05	4.16E-04	3.91E-05	3.91E-05

Table 8 Non-carcinogenic risk associated with exposure of construction/excavation workers to BTEX from the ground water via dermal exposure in the industrial scenario

Sample	Benzene	Toluene	Ethylbenzene	Xylenes
I13	0.53	3.23E-03	1.04E-03	1.04E-03
I15	2.67	8.74E-03	6.99E-03	4.66E-03
I22–I33	0.02	3.24E-04	2.59E-04	1.30E-04
I34	0.40	1.29E-03	1.04E-03	6.48E-04
K3	1.06	4.21E-03	3.63E-03	1.94E-03
K6	0.28	1.62E-03	7.77E-04	2.59E-04
K7	1.15	4.86E-03	3.88E-03	2.59E-03
K12	0.53	5.50E-03	5.18E-04	5.18E-03

Table 10 Carcinogenic risk associated with exposure of construction/excavation workers to benzene from the ground water in the industrial scenario

Sample	Ingestion	Dermal contact	Total cancer risk
I13	4.07E-06	4.20E-05	4.60E-05
I15	1.93E-05	2.10E-04	2.29E-04
I22–I33	1.54E-07	1.68E-06	1.83E-06
I34	2.88E-06	3.15E-05	3.44E-05
K3	7.61E-06	8.31E-05	9.07E-05
K6	2.00E-06	2.18E-05	2.38E-05
K7	8.26E-06	9.02E-05	9.85E-05
K12	4.04E-06	4.41E-05	4.81E-05

associated with exposure to the BTEX compounds via oral and dermal pathways. As already explained, this result is due to both, high concentration of benzene relative to the other BTEX compounds in the investigated groundwater and low values of the parameters Rf D_O and Rf D_D which are in denominators of the Eqs. 8 and 9.

In this scenario, the non-carcinogenic risk associated with exposure to BTEX from the contaminated groundwater is mainly due to the dermal exposure and almost ten times higher than the risk from the accidental ingestion. If the workers ingest tap water at this location during their working hours, the non-carcinogenic risk via ingestion will be much higher, as estimated in the residential scenario (Table 5), but it will be of the same order of magnitude as the dermal risk in the industrial scenario (Table 7).

Hazard index for oral exposure in this scenario is < 1 at all locations (Table 9) and it can be interpreted as acceptable risk for the exposed receptors (EPA, 2001). However, hazard index for dermal exposure varies considerably between the sampling points (Table 9). At most of the hydrogeological boreholes, hazard index for dermal contact is <1, and belongs to the category of acceptable risks. In the vicinity of the boreholes where the highest concentrations of benzene were detected (I15, K3 and K7) the hazard index for dermal contact is ≥ 1 which is interpreted as an unacceptable risk. As a result of the high values for hazard index via dermal exposure pathways, values for total hazard index at these three points are much higher than 1, which indicates unacceptable health risks with potential for adverse health effects for the exposed workers (EPA, 2001).

Table 9 Hazard Indexes for oral and dermal exposure pathways and Total Hazard Index for exposure of construction/excavation workers to BTEX from the ground waters in the industrial scenario

Sample	HI oral exposure	HI dermal exposure	Total Hazard Index
I13	0.05	0.54	0.59
I15	0.25	2.69	2.94
I22	2.01E-03	0.02	0.02
I23	2.01E-03	0.02	0.02
I24	2.01E-03	0.02	0.02
I25	2.01E-03	0.02	0.02
I34	0.04	0.40	0.44
K3	0.10	1.07	1.16
K6	0.03	0.28	0.31
K7	0.11	1.16	1.27
K12	0.05	0.54	0.59
Mean Value	0.06	0.61	0.62

The estimates of the lifetime incremental cancer risk associated with exposure of construction/excavation workers in the industrial scenario show that this risk is mainly caused by dermal contact with benzene from ground water, while the value of the carcinogenic risk caused by incidental ingestion is approximately ten times lower (Table 10).

Total cancer risk for workers' exposure to benzene at almost all sampling points in the industrial scenario is in the range from 9.85×10^{-5} to 1.83×10^{-6}. According to the US EPA classification (EPA, 2013), these values can be interpreted as an acceptable risk level. Furthermore, most of these points are within the cancer risks between 1×10^{-6} and 5.1×10^{-5} and can be designated as "acceptable low risks." Only two of these sampling points resulted in the cancer risks between 5.1×10^{-5} and 1×10^{-4} which is labeled "acceptable high risk" (Kujlu et al., 2020; Legay et al., 2011). It is necessary to emphasize that due to the high concentration of benzene in the hydrogeological borehole I15 (Table 2), the lifetime incremental cancer risk associated with exposure of construction/excavation workers to the groundwater in the vicinity of this sampling point is estimated to 2.29×10^{-4}. These results indicate the potential for adverse health effects for the exposed workers at the investigated location, and because of that they are interpreted as an unacceptable risk level (EPA, 2013), or risks of high priority which require immediate consideration for remedial measures at this location (Hammonds et al., 1994).

Proposed mitigation measures

As already stated, the main aim of this study was to estimate the risks to the human health from the exposure to the BTEX in the investigated groundwater and, accordingly, to propose the most appropriate mitigation measures.

Based on the results of the human health risk assessment in this research, several mitigation measures can be proposed.

First of all, the results of this study revealed that the total cancer risks for all receptors in the residential scenario, and for exposure of construction/excavation workers to the groundwater in the vicinity of one sampling point in the industrial scenario were higher than 1×10^{-4}. These risks values were higher than the interval between 10^{-4} and 10^{-6} that represents acceptable exposure levels (40 C.F.R. § 300.340.), and because of that they were interpreted as unacceptable risk levels. According to Hammonds et al. (1994), these results were interpreted as risks of high priority which required immediate consideration for remedial measures at this location. Accordingly, in order to decrease health risk associated with exposure to BTEX at this location, it is necessary to design and conduct a groundwater decontamination treatment with low environmental impact and, preferably, low usage of energy. Bioremediation approach has already been proven effective and potent for remediation of groundwater contaminated with petroleum hydrocarbons (Fayemiwo et al., 2017; Kuyukina & Ivshina, 2019). Therefore, we suppose that bioremediation is a method of choice for clean-up of the pollution investigated in this study. Contaminated aquifers are usually oxygen depleted and facultative and/or obligate anaerobic bacteria are expected to dominate in petroleum aromatic compounds-degrading communities (Lovley, 2001). Because of that, properly selected microbial communities adapted to the specific pollutants should be used as microbiological agents for decontamination (Lješević et al., 2020; Sperfeld et al., 2018). Aerobic microorganisms can also be used for bioremediation treatment in this area. However, stimulation of oxidation processes by injection of H_2O_2 into the aquifer might be necessary (Marić et al., 2015).

Since the bioremediation techniques can be time consuming, temporary measures are foreseen as well. For the receptors in the Residential scenario, the most appropriate temporary measure can be installation of efficient BTEX filters for the residential tap water. For this purpose, the most suitable might be adsorbents with both, high adsorption capacity for BTEX, and high regeneration efficiency (such as zeolite and carbonaceous adsorbents) (Gallup et al., 1996; Ranck et al., 2005).

In the industrial scenario, dermal contact with BTEX from the contaminated groundwater was identified as the main exposure route for construction/excavation workers employed. According to these results, the mandatory measures that should be introduced are the proper selection and use of the appropriate personal protection equipment as obligatory for construction/excavation workers during their working hours.

As already discussed, exposure of other employees to the BTEX at this location is also possible through the short time occasional exposure, which was characterized as an acute health risk. In the case of the accidental contact with high volume of the contaminated water, human receptors in this scenario might be seriously endangered. Because of that it is necessary to further develop emergency response capacities at this location which should provide a proper human health protection in the case of the accidents.

In addition to all these proposed measures, it is necessary to develop a system for monitoring of BTEX in groundwater, river water but also in the municipal tap water at this location. This monitoring system should help to control the emissions of these pollutants to the groundwater but it also requires a maintenance plan that can ensure that the monitoring system is functioning properly.

Further research should be designed to collect data relevant for other types of receptors, such as terrestrial and aquatic life communities at this locality. In that respect, the results of this study might be a good starting point for a complete environmental risk assessment at this location.

Conclusions

The oil pollutant in the Sava River aquifer in the residential area of Belgrade, the capital of Serbia, was investigated in order to estimate potential human health risks from exposure to the compounds detected. Gas chromatographic analyses specific for petroleum products indicated that the main pollutant at this location was composed from gasoline range organic compounds. Benzene, toluene, ethylbenzene and xylenes (BTEX) were identified as COCs in this study. The results indicated a possible existence of multiple sources of these pollutants in the investigated area or multiple discharges of these pollutants from the same source. The concentrations of benzene measured at all sampling points were higher than the national remediation value while the maximum concentrations of BTEX quantified were among the highest concentrations of these compounds reported in the petroleum-contaminated aquifers in the world.

The human health risk exposure assessment revealed that in the residential scenario, the health risk was primarily caused by ingestion and to the lower extent by dermal exposure. The estimated values for hazard indexes for children were more than twice as high as the estimated values for hazard indexes for adults for the same period of exposure. The estimated carcinogenic risk for children was lower that the risk of this kind for adults.

In the industrial scenario, the non-carcinogenic risk and the lifetime incremental cancer risk associated with exposure of workers to BTEX from the contaminated groundwater was mainly due to the dermal exposure and almost ten times higher than the risk from the accidental ingestion.

The results of the human health exposure analysis demonstrated the potential for adverse health effects for human exposure at the investigated location, and because of that the risk was interpreted as an unacceptable risk level or risks of high priority which required immediate consideration for remedial measures at this location.

Based on the results of the human health risks assessment in this research, it was concluded that serious mitigation measures were necessary to protect human health and the environment at this location.

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Code availability Not applicable.

Declarations

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