

## A THEORETICAL MODEL FOR PREDICTING THE BEHAVIOUR OF BTEX IN THE UNSATURATED ZONE AND GROUNDWATER

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### Abstract:

Fuelling stations are one of the most important forms of soil and groundwater contamination in urban areas around the world. In this work, a mathematical model was applied to assess the risk of physical media contamination (water, air and soil). The model is based on the chemical fuel and hydrological properties of each site. The group of hydrocarbons selected for applying the model were monoaromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX). A mathematical model was used to evaluate the behavior of each compound in each partitioning phase (non aqueous liquid phase, dissolved, volatile and retained). Furthermore, it was analyzed which compound has more affinity for each phase. Finally, mass flux of BTEX reaching groundwater was calculated according to steady flow under two different conditions: (1) considering only sorption and volatilization, and (2) adding biodegradation. In this study, it could be demonstrated that modeling BTEX behavior in soil gave good results for urban areas. The methodology applied in this work could be extrapolated to any site of the world with the same problematic. Particularly, the model could be used to determine the distribution of BTEX in the soil profile. Moreover, results exhibit that dissolution is the main process affecting BTEX transport in areas containing reduced unsaturated zones (less than two meters). Otherwise, when water table is placed at deeper depths, contaminants are predominately retained in soil. In all cases, the lowest proportion of BTEX were in the volatile phase. Using this information, zones with high and low risk of contamination could be easily defined in the city of Bahía Blanca, Argentina.

**Keywords:** Mathematical model; fuelling station; BTEX; risk of contamination; unsaturated zone; groundwater; Bahía Blanca.

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## INTRODUCTION

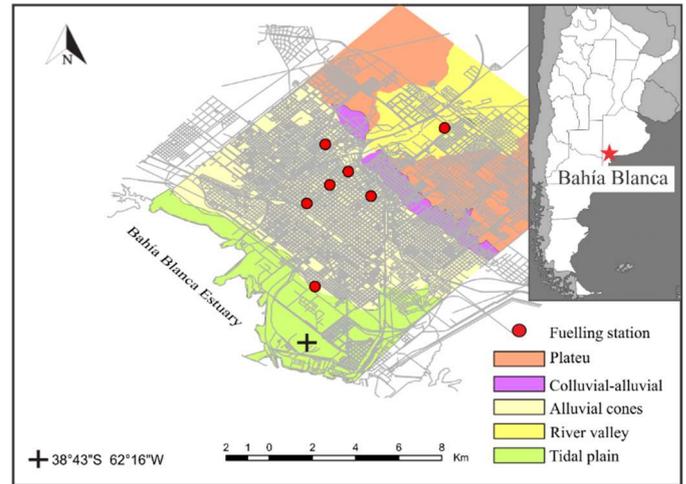
Fuelling stations are one of the main sources of contamination of the unsaturated zone (UZ) and groundwater in urban areas. In 1990, a census done in Bahía Blanca revealed that 90% of fuelling stations had leaks in their underground hydrocarbon storage system (UHSS) and pipes (Lexow, 1994). Nowadays, there are 40 registered fuelling stations (active and inactive) on a 2 247 km<sup>2</sup> surface. To assess the risk of contamination for the physical environment (water, air and soil) a mathematical model can be applied. The model is based on chemical properties of petroleum fuels and any site-specific hydrologic properties. Bahía Blanca has five geomorphologic regions, characterized by variations in their topographic, lithological and hydrological conditions. Therefore, under certain natural conditions, the presence of fuelling stations could generate a greater or lesser hazard to the environment and humans.

The main objective of this study was to use a theoretical model to recognize the behavior of BTEX in the subsoil and groundwater after a petrol leak is occurred. Furthermore, the model assesses to determine which areas are more or less susceptible to contamination. Theoretical model will serve as a basis to analyze and propose a remediation plan, according to the natural conditions of each site under study.

### Study area

Bahía Blanca is located in the Southwest sector of the Buenos Aires Province, Argentina. The city is placed more precisely between 38°39' and 38°48' S latitudes and 62°21' and 62°10' W longitudes. The subsoil is characterized by variations in its sedimentological qualities. Hence, the hydrodynamic behavior varies for each sector. According to the geomorphologic zone, water table is located at depths that fluctuate between two and 30 meters (Caló et al., 1999).

The centric area of the city is located over an alluvial fan, between 10 and 30 a.m.s.l. topographic heights. In the northeast, there is a plateau whose elevation slightly exceeds 80 a.m.s.l. and which descends moderately to the west and south to heights no greater than 60 a.m.s.l.. The edge of this plain is continued by a slope, included between 10 and 60-80 a.m.s.l. elevations, which constitutes a colluvial-alluvial complex and coalescent alluvial cones. In the south, a zone that extends between 0 and 10 a.m.s.l. altitudes forms the coastal area, corresponding to an emerged old tidal plain (Caló et al., 1999). Different geomorphological zones are shown in **Fig. 1**. The aquifer recharge zones are located in the highest topographic region while discharge zones are next to the coast. The main groundwater direction is NW-SE (Caló et al., 1996). Despite its saline to hypersaline characteristics (Bonorino & Sala, 1983), the phreatic aquifer is usually used for irrigation and recreation.



**Fig. 1** Map of the geomorphologic zones map of Bahía Blanca (Modify from Pérez Marfil et al., 2019).

## THEORETICAL FRAMEWORK

### Behavior and properties of petroleum hydrocarbons in the ground

Leaks produced over the years, from UHSS and associated pipes generate a gradual accumulation of hydrocarbons in the UZ. If the quantity of petroleum fuel is enough, gravity and capillary forces cause the movement of fuel. Part of the hydrocarbon is retained in pores and fractures of soil as a residual phase. Another part, depending on Henry's constant, can also volatilize. The mobile non-aqueous liquid phase (NAPL) will continue to migrate until it reaches capillary fringe. In this place, competition with water begins. NAPL is a non-humidifying phase that is less dense than water, therefore, a plume is generated. NAPL floats above the water table and moves laterally depending on the hydraulic gradient. Dissolution of chemical compounds occurs in contact between petroleum fuel and groundwater (Kim & Corapcioglu, 2003).

Mobility and transport of NAPL is controlled by different parameters. These parameters include: properties of liquid phase (density, viscosity, solubility, vapor pressure, volatility and interfacial tension), characteristics of soil in which it is propagated (capillary force or pressure head, pore size distribution, initial moisture content, strata geological structure, and groundwater velocity) and saturation functions (residual saturation and relative permeability) (Celis, 2009).

Each petroleum fuel is a mixture of a large quantity of hydrocarbons. There are typical hydrocarbons that are used as indicators of their presence. In particular, those who may represent a risk to people are considered. The most used are aromatic hydrocarbons, mono- and polynuclear, that are toxic and several of them have been shown to be carcinogenic. BTEX are the most common group of monoaromatic and, due to their

mobility and dissolution, are difficult to trap and easily biodegradable.

The leakage of UHSS or pipes corresponds to oil or diesel. The percentages of each compound in BTEX group will vary according to the predominant petroleum fuel. Weight percentage of each compound according to oil type is listed on **Table 1**. Each compound has specific chemical and partitioning properties. The properties considered at 20°C are listed in **Table 2**, taken from Thomas & Tellam (2004).

### BTEX partition and solute transport in the ground

Contaminants partition in soil-water, air-water or NAPL-water interfaces depends on chemical properties and solubility of each compound (Cipullo et al., 2018). Behavior of petroleum fuels in soil can be described based on mathematical equations. Distribution and partition of BTEX during their transport in UZ can be modelled by the following means.

Once leak is generated, phases present in soil pores are water, air and hydrocarbon. The partition percentage of each phase can be expressed according to the porosity occupied. Thus, soil total porosity ( $n$ ) in UZ is composed of:

$$n = \theta_w + \theta_a + \theta_{NAPL} \quad (1)$$

where  $\theta_w$  is volumetric water content;  $\theta_a$  is volumetric air content;  $\theta_{NAPL}$  is volumetric NAPL content.

According to Clapp and Hornberger method (Clapp & Hornberger, 1978) average volumetric water content in UZ ( $\theta_w$ ) can be calculated as:

$$\theta_w = \theta_s * \left(\frac{V_d}{K_s}\right)^{\frac{1}{2b+3}} \quad (2)$$

where  $\theta_s$  is saturated water content of the soil (total porosity);  $V_d$  is recharge rate (m/d) and  $K_s$  is saturated hydraulic conductivity (m/d). Constant  $b$  is an empirical parameter whose value depends directly on soil texture. It could vary from 4.5 for a sandy soil to 11 for a clay soil.

When a petroleum fuel leak occurs, certain pores will become occupied by hydrocarbon. Assuming that Clapp & Hornberger method is valid when NAPL is present, volumetric water content in UZ can be estimated and volumetric air content ( $\theta_a$ ) would be:

$$\theta_a = n * (\theta_{NAPL} + \theta_w) \quad (3)$$

Condition:  $n > (\theta_{NAPL} + \theta_w)$  and deep  $UZ > 0$ . When saturated air content in profile soil is zero.

Volumetric NAPL ( $\theta_{NAPL}$ ) content in UZ can be estimated as:

$$\theta_{NAPL} = \frac{n * \theta_{rNAPL}}{100} \quad (4)$$

Measuring residual saturation ( $\theta_{rNAPL}$ ) in field is complex. Some laboratory studies (Mercer & Cohen, 1990) indicated that it could vary from 10% to 20% depending on the type of product. In this work 10% of total porosity was considered. Under these considerations, total mass of each compound ( $m$ ), expressed by soil volume, can be calculated from:

$$m = \theta_w * C_w + \theta_a * C_a + \theta_{NAPL} * C_{NAPL} + \delta_a * C_s \quad (5)$$

where  $\delta_a$  is the soil bulk density.

**Eq. (5)** also requires definition of concentration of each compound in each phase present in UZ: water ( $C_w$ ), air ( $C_a$ ), NAPL ( $C_{NAPL}$ ) and solid ( $C_s$ ) phases. Distribution of each solute is defined by partition coefficients: soil-water ( $K_d$ ), water-air ( $K_h$ ) and water-NAPL ( $K_o$ ) respectively.

The soil-water partitioning coefficient ( $K_d$ ) is estimated using the following relationship:

$$K_d = K_{oc} * F_{oc} \quad (6)$$

where  $K_{oc}$  is organic carbon partitioning coefficient and  $F_{oc}$  is organic carbon fraction.

This approach accepts that contaminants will only be absorbed by organic matter. Although this affinity is very strong, there are other soil components, such as clays or oxides, which will interact with petroleum fuels. This interaction could modify the contaminants mass of the system in transfer processes (Balseiro-Romero et al., 2018).

**Table 1.** Percentage of BTEX in petroleum fuel. Taken from Gustafson et al. (1997).

BTEX	Carbon number	Weight percent in oil	Weight percent in diesel
Benzene	6	0.12–3.5	0.003–0.10
Toluene	7	2.73–21.8	0.007–0.70
Ethylbenzene	8	0.36–2.86	0.007–0.20
o-Xylene	8	0.68–2.86	0.001–0.085
m-Xylene	8	1.77–3.87	0.018–0.512
p-Xylene	8	0.77–1.58	0.018–0.512

**Table 2.** Specific chemical properties and partitioning coefficients of BTEX.

BTEX	Weight percentage in oil (%)	Molecular weight (g/mol)	Water solubility (mg/L)	Vapor pressure at 25°C (atm)	Henry's constant (atm·m <sup>3</sup> /mol)	$K_{oc}$ (L/kg)	Half-life $T_{(1/2)}$ days
Benzene	1.9	78.11	1780	0.125	5.59E-03	83	720
Toluene	8.1	92.14	515	0.037	6.37E-03	30	28
Ethylbenzene	1.7	106.17	152	0.013	6.43E-03	1100	228
Xylenes	9	106.17	175	0.012	5.10E-03	830	360

Volatilization process can be explained by applying of Henry's Law, water-air partitioning coefficient ( $K_h$ ) is represented by:

$$K_h = \frac{K'_h}{R \cdot T} \quad (7)$$

where  $K'_h$  is Henry's constant for BTEX compound ( $\text{atm}\cdot\text{m}^3/\text{mol}$ );  $R$  is the universal gas constant ( $\text{atm}\cdot\text{m}^3/\text{mol}\cdot\text{K}$ ) and  $T$  is temperature ( $^\circ\text{K}$ ).

Raoult's law is valid according to Cline et al. (1991) if we assume that: (1) the source in study is dissolving in equilibrium, (2) an ideal behavior of the components and (3) a large area of contact between residual NAPL and groundwater. This law can be used to define water-NAPL partition coefficient ( $K_o$ ) given the concentration of different constituents in NAPL (Feenstra et al., 1991). Even if the constituents of NAPL change over time due to occurrence of processes such as dissolution, volatilization, degradation and sorption, value of  $K_o$  is presumed constant for calculation of this model.

$$K_o = \frac{\text{average MW of compound} \cdot \text{average MW of NAPL}}{S_{\text{effective}}} \quad (8)$$

The effective solubility ( $S_{\text{effective}}$ ) of an organic substance in a mixture is calculated using Raoult's law (Feenstra et al., 1991). The effective solubility is estimated multiplying molar fraction of the compound in the mixture by solubility of pure substance ( $S$ ).

$$S_{\text{effective}} = \frac{\% \text{ by weight of NAPL compound} \cdot \text{average MW of NAPL} \cdot S}{\text{average MW of NAPL} \cdot 100} \quad (9)$$

where MW is molecular weight.

The amount of each compound shall be distributed in different phases present in soil: dissolved phase, volatile phase, adsorbed phase and liquid phase. The terms of Eq. (5) can be estimated as follows:

$$C_w = 100 \cdot \left( \frac{\theta_w}{B_w} \right) \quad (10)$$

$$C_a = 100 \cdot \left( \frac{\theta_a \cdot K_h}{B_w} \right) \quad (11)$$

$$C_s = 100 \cdot \left( \frac{\delta_a \cdot K_d}{B_w} \right) \quad (12)$$

$$C_{\text{NAPL}} = 100 \cdot \left( \frac{\theta_{\text{NAPL}} \cdot K_o}{B_w} \right) \quad (13)$$

Parameter  $B_w$  is bulk water partitioning coefficient (l.gr-1), defined as:

$$B_w = \theta_w + (\theta_a \cdot K_h) + (\theta_{\text{NAPL}} \cdot K_o) + (\delta_a \cdot K_d) \quad (14)$$

Once the leakage occurs, petroleum fuels concentrations in the pore system volume ( $M_i$ ) can be calculated according to Eq. 15 for each BTEX. It is required: average density ( $\delta_{\text{fuel}}$ ) between oil and diesel ( $765 \text{ kg/m}^3$ ), total soil porosity ( $n$ ) and molar fraction of each compound ( $FM_i$ ).

$$M_i = n \cdot \delta_{\text{fuel}} \cdot FM_i \quad (15)$$

When analyzing the transport of solutes in a multiphase system, it is usual to express concentrations in each phase in relation to a reference phase. Charbeneau & Daniel (1992) considered it advisable to take water phase ( $d_w$ ) as a reference phase to analyze leaching of contaminant. Therefore:

$$d_w = \frac{m}{B_w} \quad (16)$$

Thus, estimation of concentration of dissolved BTEX ( $C_i$ ) in poral water can be calculated from the following relationship:

$$C_i = \frac{V \cdot \theta_w \cdot d_w}{\theta_{\text{NAPL}}} \quad (17)$$

where  $V$  is the volume of petroleum fuel leakage.

As a result, the initial contaminant mass flux ( $F_i$ ) present in the leaching per unit area is estimated by combining Eq. 17 with convective transport equation for unsaturated media:

$$F_i = C_i \cdot \frac{V_d}{\theta_w} \quad (18)$$

Based on steady flow in UZ, two scenarios for solute transport could be modeled: (a) considering processes of sorption and volatilization; and (b) considering processes of sorption, volatilization and biodegradation.

In the first case, final concentration of compounds in recharge could be accepted as equal to initial concentration of leachate. Adsorption and volatilization processes are represented by a retardation factor ( $R$ ).

$$R = 1 + \frac{\delta_a \cdot K_d + (\theta_s - \theta_w) \cdot K_h}{\theta_w} \quad (19)$$

Consequently, transit time ( $T$ ) of a given solute, without considering dispersion, can be calculated as:

$$T = \frac{z \cdot \theta_w \cdot R}{V_d} \quad (20)$$

where  $z$  is the depth of UZ. Finally, contaminant velocity is:

$$V_c = \frac{V_d}{\theta_w \cdot R} \quad (21)$$

Considering contaminant velocity ( $V_c$ ) (Eq. 21) and BTEX concentration in poral water (Eq. 17), mass flux per unit of time and space is obtained as:

$$F = V_c \cdot C_i \quad (22)$$

In the second case, biodegradation is incorporated into processes described above. In aerobic environments, biodegradation of petroleum fuels can be explained mathematically according to a first-order decay model as:

$$C_2 = C_1 \cdot e^{-T\lambda} \quad (23)$$

where  $C_1$  is initial concentration of applied contaminant;  $C_2$  is concentration of contaminant in UZ and  $\lambda$  is the first order degradation coefficient ( $t^{-1}$ ).

If expression above (Eq. 23) is combined with transit time (Eq. 20) and in terms of half-life ( $t_{1/2}$ ) for each compound, it can be expressed:

$$C_2 = C_1 \text{EXP}\left(\frac{-0.693 * R * Z * \theta_w}{V_d * t_{1/2}}\right) \quad (24)$$

Equation 24 is used to calculate final concentration of leachate reaching water table. Hence, mass flux per unit area considering biodegradation is equal to:

$$F = Vd * C_2 \quad (25)$$

## METHODOLOGY

Background data of fuelling stations located in Bahía Blanca (Table 3) were used to run the model. Sites were selected based on depth of water table and its distribution respect to geomorphological zones (Fig. 1). Historical rainfall in the city was estimated as 555 mm (Caló et al., 2004). Recharge rate was considered as 11% of historical rainfall (Carrica & Lexow, 2006) for fuelling stations located in a tidal plain (sites A) without impermeable surface. For the rest of the fuelling stations, recharge rate was considered to be 7% of rainfall.

Depth of water table was conservatively considered at the lowest value recorded. To run the model, UHSS

were located at a depth of two meters for sites B, E and G. In these cases water table is located at depths deeper than two meters. Otherwise, UHSS were placed at 1.40 meters underground for sites A, C, D and F.

The mathematical model used corresponds to the one developed by Thomas & Tellam (2004). To start running the model it is necessary to know the volume of petroleum fuel leaked. For this purpose information of dimensions of the UHSS is required. Normally, in the city, each fuelling station have four to six UHSS, with store capacity from 100 000 to 120 000 liters of petroleum fuel. Information available is listed in Table 4. For this study, it was considered a thickness of one meter for UHSS and an affected area of 25 liters per square meter. Initially, concentration of dissolved BTEX in poral water system ( $C_i$ ) was estimated from Eq. (17). The percentage of each BTEX compound in different phases were calculated using Eqs. 10 ( $C_w$ ), 11 ( $C_a$ ), 12 ( $C_s$ ) and 13 ( $C_{NAPL}$ ) respectively.

Initial contaminant mass flux ( $\text{mg}/\text{m}^2/\text{y}$ ) for each fuelling station was calculated based on Eq. (18). Final contaminant flux in the recharge ( $\text{mg}/\text{m}^2/\text{y}$ ) was calculated considering: (1) only sorption and volatilization processes (Eq. 22) and (2) sorption, volatilization and biodegradation processes (Eq. 25). Results were presented graphically as maps developed within QGIS tool (version 3.4.8).

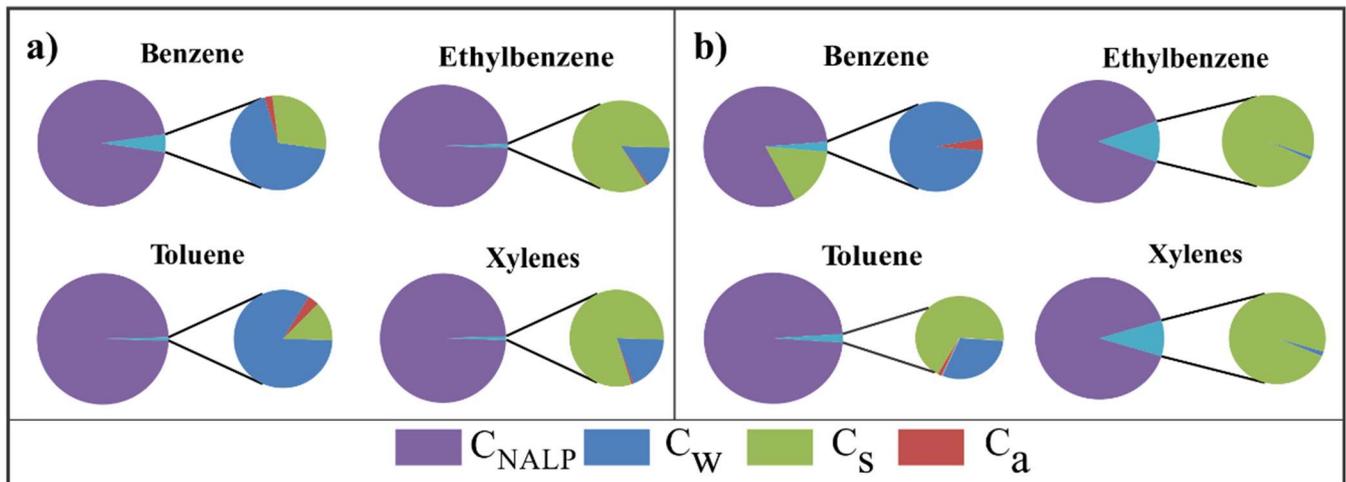


Fig. 2 (a) Distribution of BTEX in different phases in fuelling station A, and (b) Distribution of BTEX in different phases in the rest of fuelling stations.

Table 3. Physical properties of fuelling station

Fuelling stations	Texture	Total porosity % <sup>(1)</sup>	Effective porosity % <sup>(1)</sup>	Bulk density ( $\text{g}/\text{cm}^3$ )	Permeability ( $\text{m}/\text{d}$ ) <sup>(2)</sup>	Constant b <sup>(3)</sup>
A	Clay loam	40	10	1.59	0.086	8.52
B	Sandy loam	30	15	1.86	0.864	4.90
C	Clay loam with calcareous cement	25	5	1.99	0.090	8.52
D	Sandy clay loam	40	12	1.59	0.864	7.12
E	Sandy loam	30	15	1.86	0.864	4.90
F	Sandy clay loam	40	12	1.59	0.864	7.12
G	Loamy sand	35	15	1.72	0.864	4.38

(1) Sanders (1998), (2) Freeze & Cherry (1979), and (3) Clapp & Hornberger (1978).

**Table 4.** Information for UHSS at fuelling stations.

Fuelling stations	N° installed tanks	Affected area (m <sup>2</sup> )	Spill volume (L)
A	6	120	3000
B	4	100	2500
C	6	120	3000
D	4	80	2000
E	7	140	3500
F	4	80	2000
G	5	100	2500

## RESULTS AND INTERPRETATIONS

### BTEX partitioning in different phases

When petroleum fuel leakage occurs in UZ, compounds are distributed in different phases according to their partitioning constants and soil physical properties. Distribution of BTEX in NAPL, dissolved, volatile and retained phases are illustrated in **Fig.2**. Results are presented in two groups: **Fig.2a** represents fuelling station A, with its tanks arranged nearly above the water table; **Fig.2b** represents the rest of the fuelling stations, which had the same response despite differences in thickness of UZ.

It is logical that all BTEX concentrate mostly on NAPL. In fuelling station A, benzene and toluene are distributed more in the dissolved phase than in retained and volatile phases (**Fig.2a**). This effect could be explained by their high solubility into water. BTEX with greater solubility begins to dissolve when NAPL is placed above the water table. Otherwise, ethylbenzene and xylenes are mostly concentrated in the solid phase, given its affinity for organic particles and its high octanol-water partition value ( $K_{oh}$ ).

In contrast, on the rest of fuelling stations (**Fig.2b**) compounds tend to concentrate in the following order  $C_{NAPL} > C_s > C_w > C_a$ . When thickness of UZ increases, moisture content present in soil decreases obstructing the solubility of compounds. While migrating through soil, compounds are retained by solid particles. Hence, there is a delay in transit time during transport to groundwater. Finally, in all cases, smallest proportions of BTEX are in volatile phase. The causes may be related to low values for Henry's constants.

BTEX are partitioned in dissolved, volatile and retained phases according to the chemical properties and hydrogeological conditions of each fuelling station. Percentages of dissolved benzene, toluene, xylenes and ethylbenzene are presented in **Fig. 3a**. Highest percentage of dissolved elements are present in sites A, G and C. Fuelling stations A and C have the shallowest water table (less than two meters). However, in fuelling station G, water table was displaced to three meters of depth. High percentages of dissolved compounds in site G could be related to subsoil texture. Sandy silt texture is characterized by higher moisture retention contents.

In other areas of the city, water table is at similar depths but UZ is composed of coarse grain sizes (predominantly sand) with lower moisture contents average. Behavior of elements in the volatile phase is described in **Fig. 3b**. Fuelling stations A, C and G present the lowest volatilization percentages. In sites A and C this may be due to proximity to water table that causes the compounds to dissolve before volatilization could occur. Otherwise, the highest volatilization percentages are observed in fuelling station B and E. Still these sites present the lowest dissolution percentages. This could be explained by the greater thickness of UZ that allows elements to volatilize more easily.

Retained elements percentages in soil are illustrated in **Fig. 3c**. Fuelling station A exhibits the lowest percentage of retained elements. Similarly sites D and G present low values. This condition, in the same way could relate to the proximity of water table. Moreover, the highest values of retained components are observed in fuelling stations C, B, E and F. Although in the sites C and F water table is shallow, the fraction of organic carbon present in the soil matrix is high. Thus, the affinity for solid phase would increase.

Graphs demonstrated that BTEX distribution in soil is in the order:  $C_s > C_w \gg C_a$ . Exception is site A, where leaks from their UHSS influence directly to the water table. As expected, the most quantity of BTEX is founded in NAPL.

### Assessment of risk of contamination

The mathematical model allowed calculation of contaminant load for each fuelling station. A hypothetical scenario was considered given the occurrence of a petroleum fuel leakage from the UHSS. Thereby, the model could be used to recognize sites that have better qualities for attenuating the contaminating effects to soil and groundwater.

Initial contaminant mass flux generated from UHSS is represented in **Fig. 4**. Fuelling stations with highest initial BTEX mass flux into UZ correspond to the sites that had the higher underground storage capacity. In this case, fuelling stations are A, C and E, which have an affected area of 120, 120 and 140 m<sup>2</sup> respectively. As mentioned in previous section, compounds that could be easily dissolved and transported with water correspond to benzene and toluene. Presence of xylene and ethylbenzene is negligible.

The model final output corresponds to the contaminant mass flux that is transported to the groundwater. Two scenarios were evaluated: considering only processes of sorption and volatilization (**Fig. 5**) and considering the previous ones plus biodegradation (**Fig.6**). The first scenario is the most conservative one. Only the occurrence of sorption and

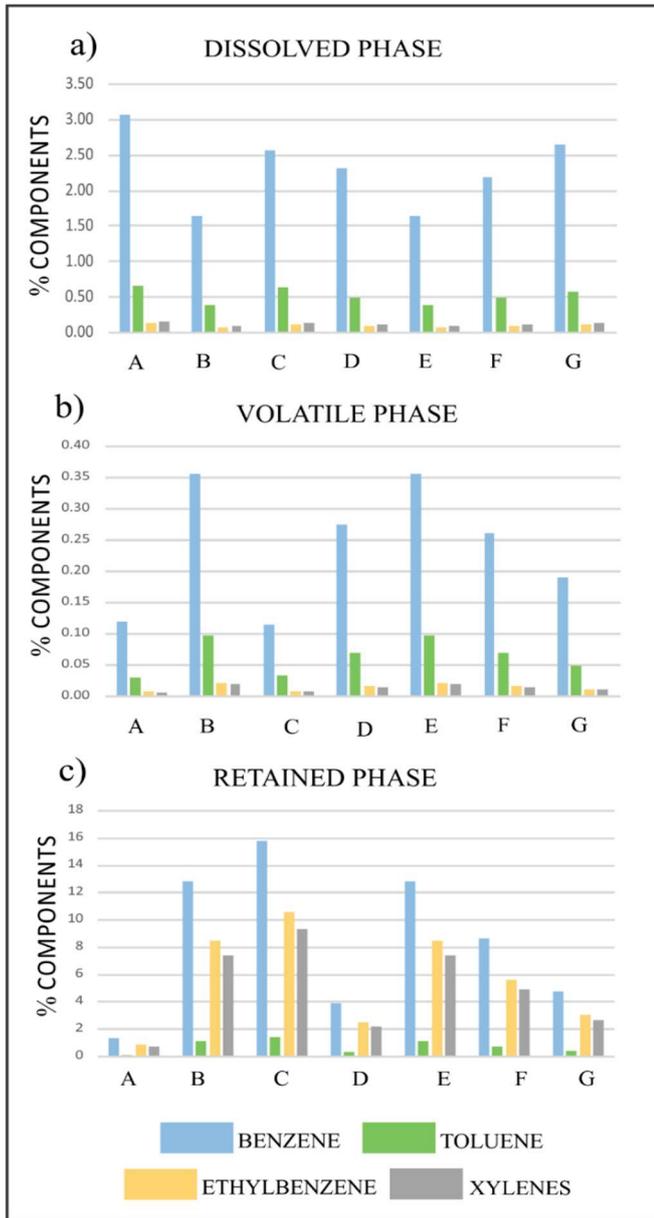


Fig. 3 Behavior of BTEX components in each fuelling station for phase a) dissolved b) volatile and c) retained.

volatilization during transport are considered. These processes are represented by retardation factor. The inclusion of this parameter in the transport equation generates a delay in transit time, increasing the time necessary for BTEX to reach groundwater. Calculated values for each fuelling stations are presented in Table 5. The order for arrival of compounds is toluene > benzene > xylene > ethylbenzene in every case under study. In addition, fuelling stations A exhibits the greatest mass flux of contaminant (391 mg/m<sup>2</sup>/y). It is followed by fuelling stations G with a mass flux of 140 mg/m<sup>2</sup>/y. Meanwhile, sites C, D, B and F have lowest values with respect to the previous ones. Values are similar to each other, being 108, 99, 86 and 62 mg/m<sup>2</sup>/y respectively.

In the second scenario, biodegradation effects generate an increase in attenuation capacity of UZ. Final contaminant flux to groundwater is greatly reduced for all fuelling stations. Only sites A has values greater than 50 mg/m<sup>2</sup>/y recorded. Sites C and D have values of 0.70 and 0.40 mg/m<sup>2</sup>/y respectively. While fuelling stations E and F have values < 0.1 mg/m<sup>2</sup>/y and B and G do not register the presence of BTEX.

**CONCLUSIONS**

Application, in our study area, of the theoretical model proposed by Thomas & Tellam (2004) gave good results. Through its use, it was possible to establish the distribution of BTEX in the subsystems of unsaturated zone (dissolved phase, retained phase and volatile phase). Model can delimit areas of low and high risk of contamination. Thus, it can be used as a first instance in a remediation plan, or for urban planning. It should be noted that the more field data is supplied to the model, the more accurate the results will be. Theoretical model can be adapted to other cities, allowing decision making according to conditions of each site.

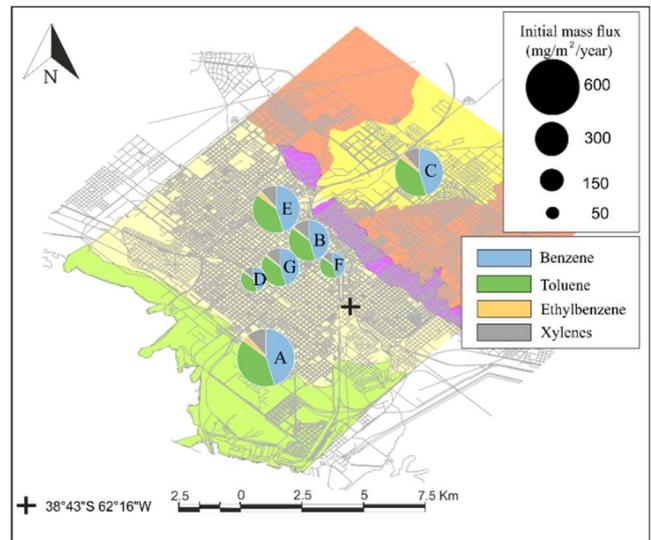


Fig. 4 Map of initial mass flux.

Table 5. Calculated values of retardation factor and velocity of benzene (B), toluene (T), ethylbenzene (E) and xylenes (X) for each fuelling station.

Fuelling stations	Retardation factor = R				Velocity of contaminant (m/d)			
	B	T	E	X	B	T	E	X
A	1.5	1.2	6.8	5.4	3.6E-04	4.4E-04	8.0E-05	1.0E-04
B	9.0	4.1	103.7	78.5	8.5E-05	1.9E-04	7.4E-06	7.7E-06
C	7.2	3.3	82.3	62.4	7.8E-05	1.7E-04	6.9E-06	1.1E-06
D	2.8	1.8	23.3	17.8	1.6E-04	2.5E-04	1.9E-05	2.5E-05
E	9.0	4.1	103.7	78.5	8.5E-05	1.9E-04	7.4E-06	7.7E-06
F	5.0	2.6	52.8	40.1	8.9E-05	1.7E-04	8.5E-06	1.1E-05
G	2.9	1.8	24.8	19.0	1.5E-04	2.5E-04	1.8E-05	2.3E-05

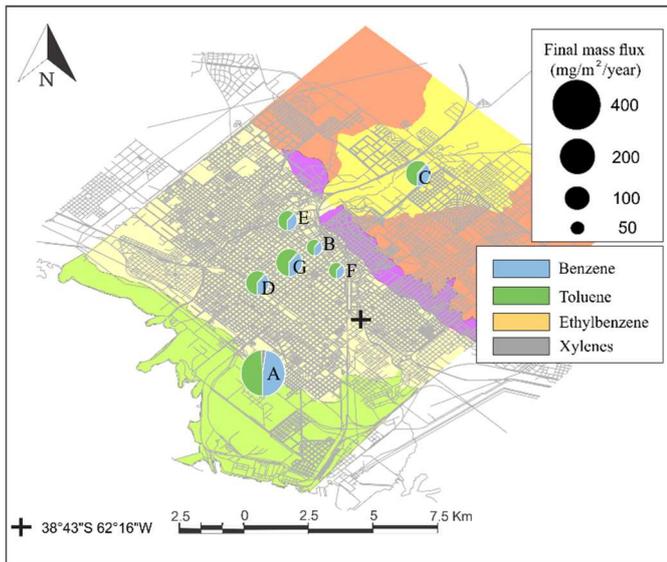


Fig. 5 Map of final mass flux considering only sorption and volatilization.

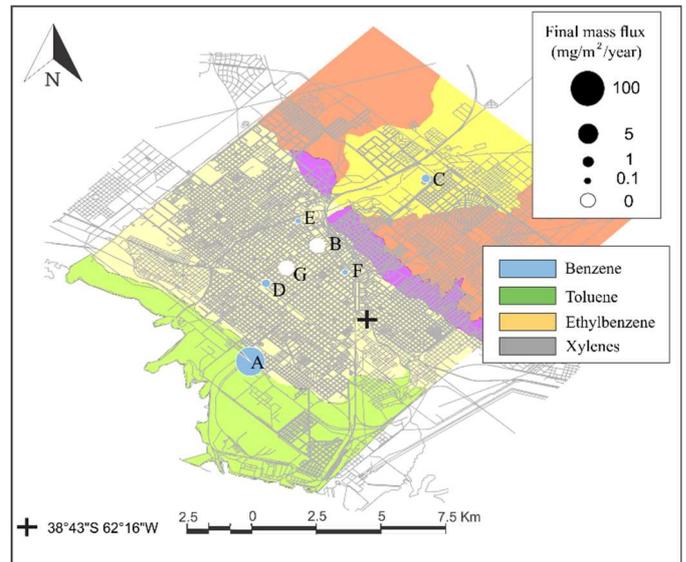


Fig. 6 Map of final mass flux considering sorption, volatilization and biodegradation.

Particularly, it was observed that when thickness of UZ is reduced (less than two meters) the main process that affects BTEX is dissolution. This is important when designing a remediation plan. After extraction of NAPL is concluded, the volume of groundwater that is in direct contact with it should be extracted and treated. In areas where the UZ is greater than two meters, dominant process over BTEX is soil retention. Volatilization process turned out to have the less importance over BTEX transport. In general, BTEX distribution order in soil is:  $C_s > C_w \gg C_a$ . Exception is site A, where leakage from their UHSS influence directly to water table.

Model allows to establish contaminant mass flux into groundwater. Tidal plain is the geomorphological zone that presents a greater danger for soil and groundwater contamination. The main reason is due to the proximity of water table to the surface. For the rest of the geomorphological zones (plateau, colluvial-alluvial and river valley) study should be more detailed, considering several factors such as lithology, thickness of UZ, impermeable surface of surrounding soil, etc. In these places, sorption and volatilization processes generate an attenuation effect. Biodegradation plays a fundamental role as an attenuator for this kind of contaminants. However, extensive studies are required to ensure the existence of degradation bacterias in the unsaturated media.

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