

NATURAL ATTENUATION OF BTEX CONTAMINANTS IN THE GROUNDWATER OF THE MOST POPULOUS CITY IN NORTHEASTERN BRAZIL

Paula Gimenez Bezerra¹
Joil José Celino²
Sarah Adriana R. Soares³
Karina Santos Garcia⁴

¹ Química, Mestre em Geoquímica do Petróleo e Ambiental. Doutoranda em Geologia, Instituto de Geociências, Universidade Federal da Bahia – IGEO/UFBA. pagimbezerra@gmail.com

² Geólogo, Dr. Geologia. Professor do Depto. de Oceanografia, pesquisador do Núcleo de Estudos Ambientais - NEA/IGEO/UFBA. joil@ufba.br

³ Química, Dra. Química Analítica. Técnica em Química dos Laboratórios de Pesquisa me Petróleo - LEPETRO-IGEO/UFBA. sarah.ufba@yahoo.com.br

⁴ Bióloga, Dra. Geoquímica. Coordenadora do LEPETRO-IGEO/UFBA. garciaks4@yahoo.com.br

ABSTRACT - In order to investigate the contamination and attenuation of BTEX compounds from fuel tank leaks into the Basin of Lucaia's river aquifer, Salvador, Bahia (Brazil), it was determined in samples of groundwater concentrations of volatile aromatics benzene, toluene, ethylbenzene and xylenes (BTEX), sulfate, nitrate and iron (II) in two distinct periods. The concentrations of compounds were compared to ascertain the yield reduction of BTEX in the sampling points up to 82%. Isotenor curves were generated by observing the behavior of composites and the relation of Eh and nitrate consumption with natural attenuation of BTEX, verifying that it does not occur in a wide spread critical levels and dangerous for the population.

Keywords: natural attenuation; contaminants; BTEX; groundwater; Brazil.

RESUMO – Atenuação natural de contaminantes de BTEX nas águas subterrâneas da mais populosa cidade do Nordeste do Brasil. A fim de investigar a contaminação e atenuação natural dos compostos BTEX dos vazamentos de tanques de combustível na Bacia do aquífero do rio Lucaia, Salvador, Bahia (Brasil), foi determinado em amostras de água subterrânea as concentrações dos voláteis aromáticos benzeno, tolueno, etilbenzeno e xilenos (BTEX), sulfato, nitrato e de ferro (II) em dois períodos distintos. As concentrações dos compostos foram comparadas e determinaram a redução no rendimento de BTEX nos pontos de amostragem em até 82%. Curvas de isoteor foram geradas do comportamento em relação ao Eh e consumo de nitrato com a atenuação natural de BTEX, verificando que não ocorre em níveis críticos pela ampla disseminação e nem perigosa para a população.

Palavras-chaves: Atenuação natural; contaminantes, BTEX; água subterrânea; Brasil

INTRODUCTION

The most serious groundwater contamination problems attribute to aromatic hydrocarbons, occurring in most cases from leaks in underground tanks that store petroleum-based fuels (FORTE et al., 2007). Among the constituents of gasoline, mainly derived from petroleum, the volatile monoaromatic hydrocarbons, benzene, toluene, ethylbenzene and xylene (BTEX), are of greater concern due to their toxicity (WANG et al., 2010) and water solubility (CORSEUIL; ALVAREZ, 1996). According to CONAMA Resolution 396/2008, the maximum allowable concentrations for benzene, toluene, ethylbenzene and xylenes are $5\mu\text{g L}^{-1}$, $24\mu\text{g L}^{-1}$, $200\mu\text{g L}^{-1}$ and $300\mu\text{g L}^{-1}$, respectively (BRAZIL, 2008). These compounds are major central nervous system depressants that may cause chronic toxicity, even in small concentrations. Among the BTEX compounds, benzene is

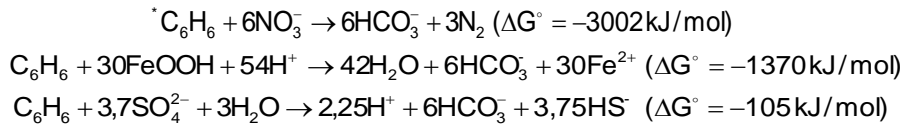
recognized as the most toxic and most soluble in water, with slow degradation under anaerobic conditions (CUNNINGHAM et al., 2001; COSTA et al., 2009).

The natural bioremediation of monoaromatic petroleum is the primary method of degradation for these compounds; studies indicate that more than 90% of BTEX is removed by natural degradation processes (FARHADIAN et al., 2007). Thus, the Monitored Natural Attenuation (ANM) is a technology that uses the natural attenuation processes that under favorable conditions act without human intervention, degrading and limiting the movement of contaminants in subsurface environments. (MALAMUD et al., 2005). In aquifers contaminated with petroleum compounds, the main degradation route for the anaerobic conditions is a redox reaction, in which organic compounds are generally oxidized by reducing an acceptor compound. In this type of

degradation, the preferred recipients of electrons are ones such as nitrate (NO³⁻), the iron ion (III), sulfate (SO₄²⁻), manganese (IV) and carbon dioxide (CO₂) (SILVA, 2002; ROYCHOUDHURY; MERRETT, 2006; CORSEUIL; NUNES, 2007).

When the amount of oxygen is low and nitrate is present (or other oxidized forms of nitrogen), some anaerobic microorganisms use nitrate (NO₃⁻) instead of oxygen as the final electron acceptor. Because of the low amounts of oxygen and nitrate, microorganisms can use ferric iron (Fe³⁺) as an electron acceptor, which is converted to its reduced

form Fe²⁺. Large amounts of iron in the ferric form are present in the sediments of many aquifers and may be a potential source for the biodegradation of these compounds. Sulfate reducers can potentially biodegrade the BTEX; however, it is a relatively slow process, and, when it occurs, it usually occurs in the center of the plume away from the uncontaminated (aerobic) groundwater (CORSEUIL; ALVAREZ, 1996; MARIANO, 2006). The possible routes of benzene degradation and their Gibbs free energy (lower values indicate a more favorable reaction) are:



(Data taken from ANDERSON, 1996).

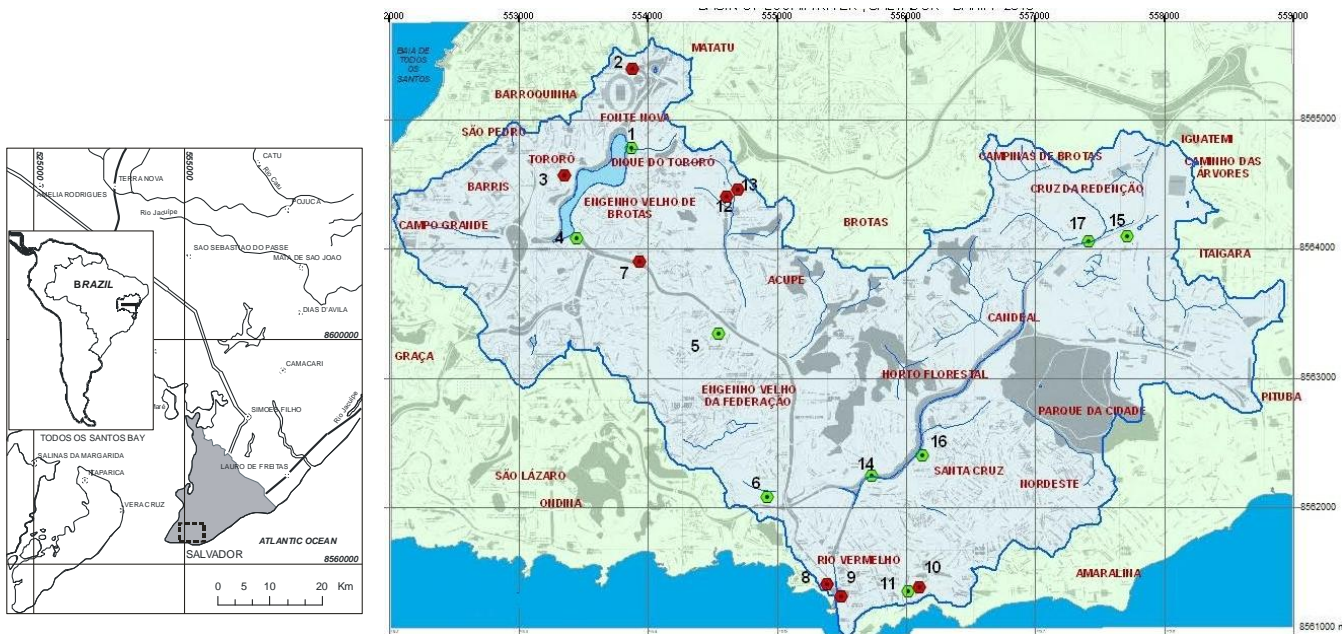
The Lucaia's River basin (Bahia, Brazil) is a densely populated area, and high exposure to agents and sources of anthropogenic contamination (SOARES et al., 2015) constitute a serious public health problem with serious risks and adverse effects on the population when its springs are used for domestic consumption (NASCIMENTO; BARBOSA, 2005). The objective of this study was to evaluate and monitor the groundwater aquifer contamination of the Lucaia's River by volatile organic compounds (BTEX) through water holes and wells, determining the degree of environmental contamination and the possible occurrence of the natural attenuation of these compounds.

MATERIALS AND METHODS

The area corresponding to Lucaia's river basin (Figure 1) located in the eastern portion of the state capital of Bahia. This region lies between the parallels 12°58'48" W and 13°00'58" S and meridians 39°32'05"W (approximately 14 km²) and is composed partially or fully by the following neighborhoods: Campinas de Brotas, Acupe de Brotas, Engenho Velho de Brotas, Itagara, Rio Vermelho, Federação, Ondina, Tororó, Santa Cruz and Fazenda Garcia.

Samples were collected at 17 locations from shallow wells and water-holes (Figure 1) with depths between 8 and 10 m.

Figure 1 – Location of groundwater holes within Lucaia's river basin districts, Salvador City, Bahia State, Brazil



During the rainy season, from July 5 to 13, 2010, 13 samples were obtained, and 11 samples were measured in the dry season, from December 17 to 22, 2010, with seven points coinciding with the first collection. Samples were obtained with a peristaltic pump (Solinst low flow, model 410) coupled to a flow cell (MicroPurge basics, model MP20) by Low Flow Sampling. The physical and chemical parameters measured for the water in the field are pH, Eh, temperature, conductivity and dissolved oxygen. After these measurements the samples were placed both in glass vials of 40 mL with a cap and a Teflon septum for BTEX determination and in polyethylene bottles of 500 mL for nitrate, sulfate and iron (II) determination. They were filled to the brim without bubbles, cooled to 4 °C and maintained at that temperature until they arrived at the LEPETRO (Laboratory of Petroleum Studies) of the Institute of Geosciences (IGEO) at the Universidade Federal da Bahia (UFBA); the samples were analyzed on the day they arrived. The determination of BTEX in water was performed using the EPA 8260C and 5030C methodologies. Analyses of volatile organic compounds in water were performed using the purge and trap, P & T, technique (Tekmar, model 3100) associated with a gas chromatography (Varian, CP-3800 SATUM) coupled with mass spectrometry (Varian, Saturn 2200), GC-MS, detector ion trap. The compounds of interest were quantified by the method of internal standardization, as recommended by the EPA (2003).

The calibration curve was obtained by mixing a standard BTEX in methanol solution with a concentration of 0.02 $\mu\text{g L}^{-1}$ and a stock solution of 0.1 $\mu\text{g L}^{-1}$ of BTEX to achieve concentrations ranging from 2,000 to 0.02 $\mu\text{g L}^{-1}$. A chlorobenzene solution (0.1 $\mu\text{g L}^{-1}$) obtained by diluting a standard 0.05 $\mu\text{g L}^{-1}$ solution was used as an internal

standard. The dilutions of the curve points were performed in Milli-Q ultrapure water. All the standards used were from AccuStandard. Samples were analyzed in duplicates and triplicates, 20% and 10% of the total samples, respectively; to evaluate the homogeneity of the points collected.

In parallel to the BTEX analysis, sulfate, nitrate and iron (II) analyses were performed with a UV-VIS spectrophotometer (Varian, model Cary 50 Probe) for ranges of 450, 400 and 510 nm, respectively. The sulfate determination used Hach kits and the second method SulfaVer 4, the nitrate analysis used Hach kits and the second method NitraVer 5 and the determination of the dissolved Fe^{2+} ion was done using the colorimetric method using 3500-Fe D. This substance is soluble in the reaction of iron with 1.10 – phenanthroline and forms a complex orange color intensity in direct proportion to the concentration of Fe^{2+} (EATON et al., 1995).

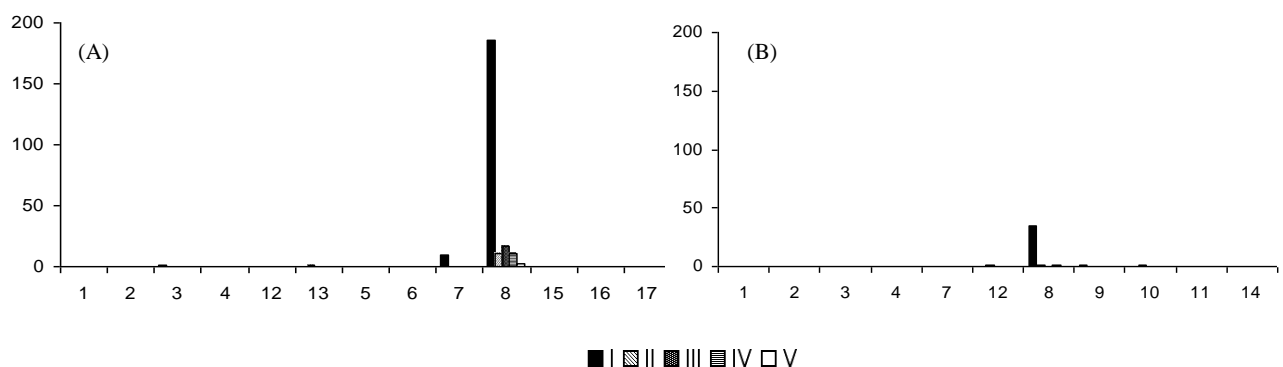
The curves generated from isotenor for BTEX compounds were made to the software Surfer Demo 9.

RESULTS AND DISCUSSION

According to CONAMA (Resolution n. 396/2008, art. 3, paragraph 4^o), the water analyzed can be classified as a water aquifer, a set of aquifer or a mixture of these. The water quality can be lowered by human activities and may require an appropriate treatment.

The concentration of BTEX, as shown in Figure 2, decreased from a range of 0 to 185.7 $\mu\text{g L}^{-1}$ (1st collection) to a range of 0 to 35.0 $\mu\text{g L}^{-1}$ (2nd collection); point 8 (a RIO) had the highest concentrations in the two campaigns.

Figure 2 - Concentration of BTEX ($\mu\text{g L}^{-1}$) at the points collected in the Lucaia's aquifer basin in July 2010: (I) benzene; (II) toluene; (III) ethylbenzene; (IV) m + p-xylene; (V) o-xylene



* Legend: (A) First collection, (B) Second collection, where: 1 - 1 DIQ 2 - DIQ 2, 3 - DIQ 3 4 - 4 DIQ; 5 - UA 1, 6 - VAS 2, 7 - VAS 3, 8 - RIO 1, 9 - RIO 2, 10 - RIO 3, 11 - RIO 4, 12 - OGU 1, 13 - OGU 2, 14 - ACM 1, 15 - ACM 2, 16 - ACM 3, 17 - ACM 4.

Bezerra et al. (2012) conducted a preliminary study on the natural attenuation of BTEX due to the electron acceptors nitrate, iron (III) and sulfate using statistical studies on the Eh of the compound degradation in contaminated locations. Thus, the more negative the Eh of the medium, the more favorable the BTEX oxidation.

The electron acceptors in the order of most favorable for BTEX degradation from a thermodynamic perspective are the nitrate (NO_3^-), the ion iron (III) and the sulfate (SO_4^{2-}). Low levels of nitrate are found for the first (0 to 8.42 mg L⁻¹) and the second (0.03 to 11.35 mg L⁻¹) collections, and higher values of Fe²⁺ in sites with the highest BTEX concentrations are found for the second collection (0.10 to 1.80 mg L⁻¹) than for the first collection (0 to 0.42 mg.L⁻¹), indicating the possible natural attenuation of these compounds. This natural attenuation is especially evident for nitrate and iron (III) and is more pronounced in year two. The sulfate concentrations for the second collection

(30.70 to 140.81 mg L⁻¹) are high compared to the first collection (5.09 to 86.77 mg L⁻¹), indicating that the sulfate acceptor was not consumed in the degradation of BTEX.

Isotenor curves for nitrate (Figure 3), Eh (Figure 4), and the BTEX (Figure 5) were generated from the data collected in the two campaigns, showing the dispersion of the compounds in the Lucaia's river basin.

The isolines indicate that the BTEX contamination in the groundwater is concentrated in the Red River region where the highest concentrations of benzene were found, 185.7 and 35.0 µg L⁻¹ for the first and second collections, respectively. The region with the highest BTEX levels had the lowest Eh, indicating a reducing environment more conducive to oxidation and degradation of BTEX. Similarly, low levels of nitrate were found in contaminated sites precisely because of its consumption for the attenuation of volatile compounds.

Figure 3 – Isolines of nitrate (mg L⁻¹)

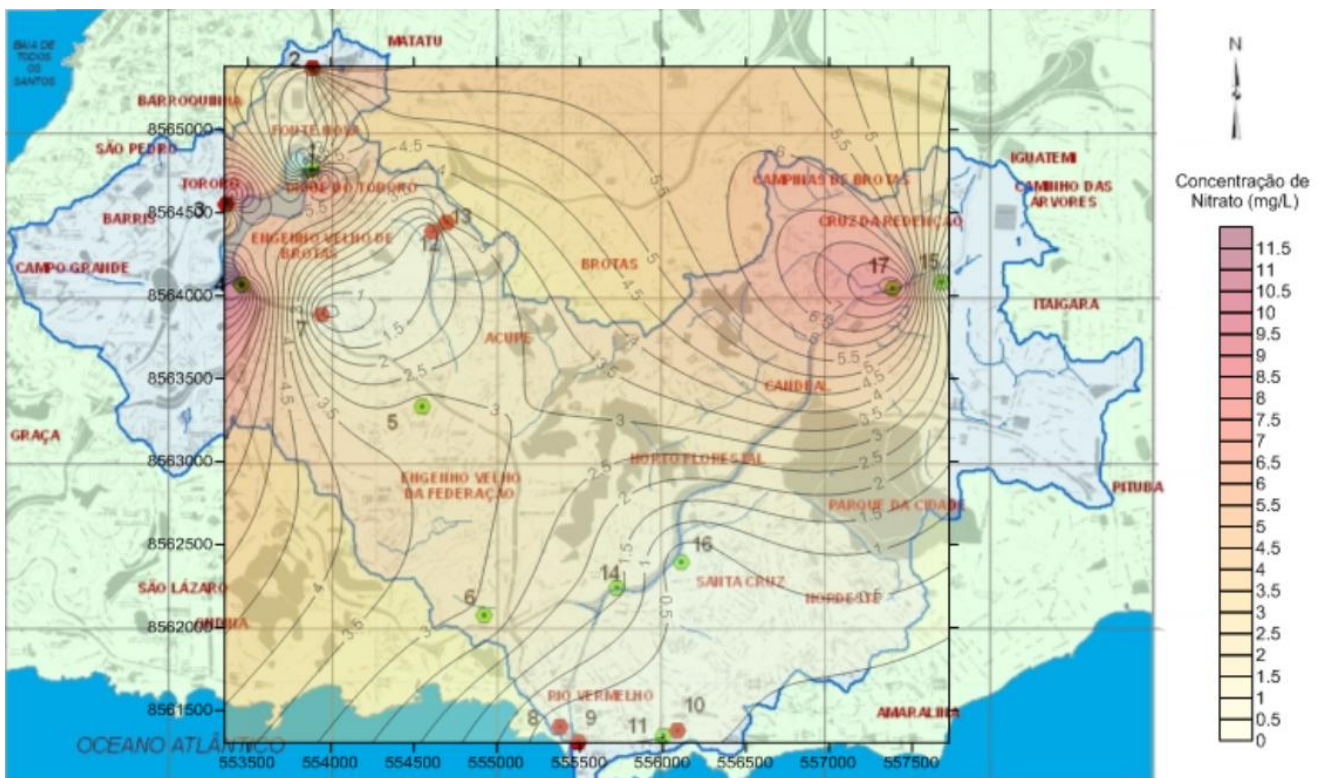


Figure 4 – Isolines for Eh (mV)

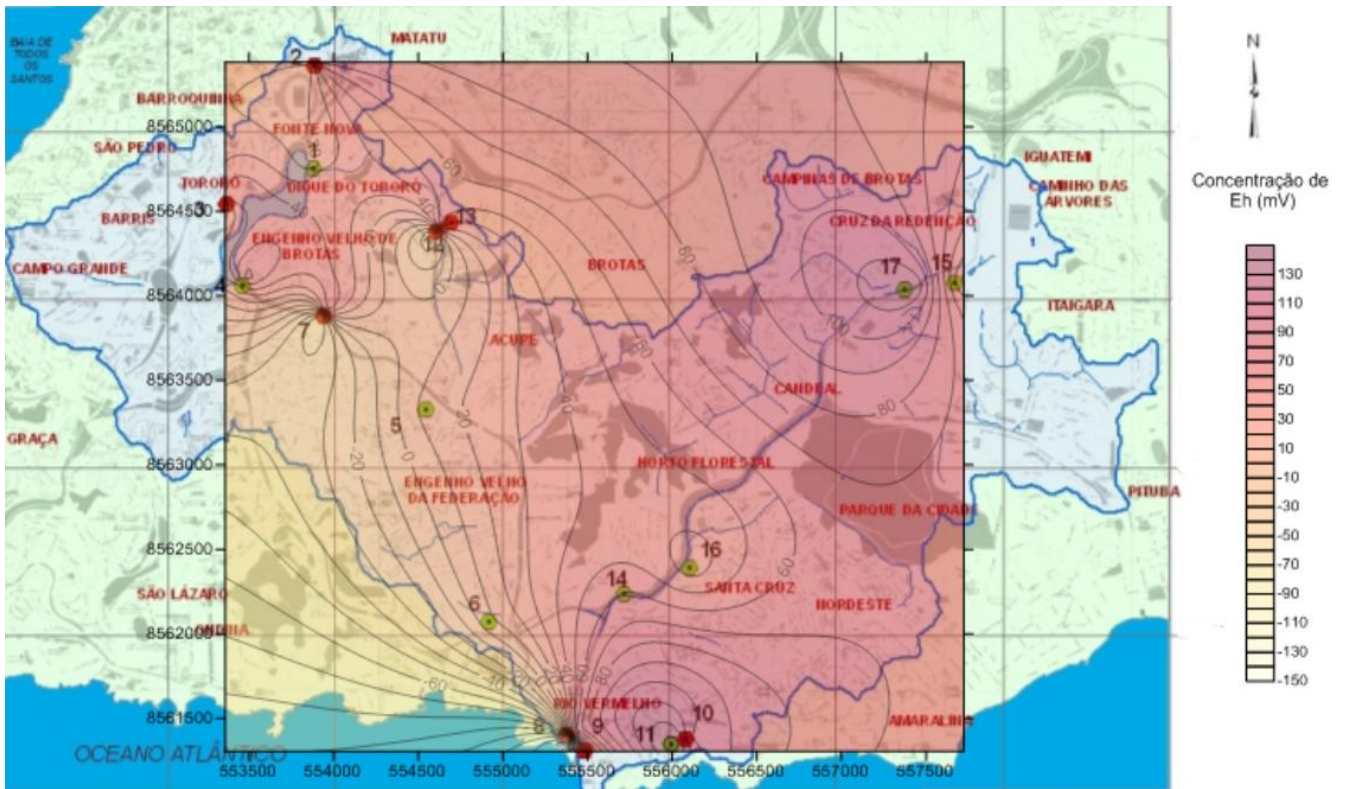
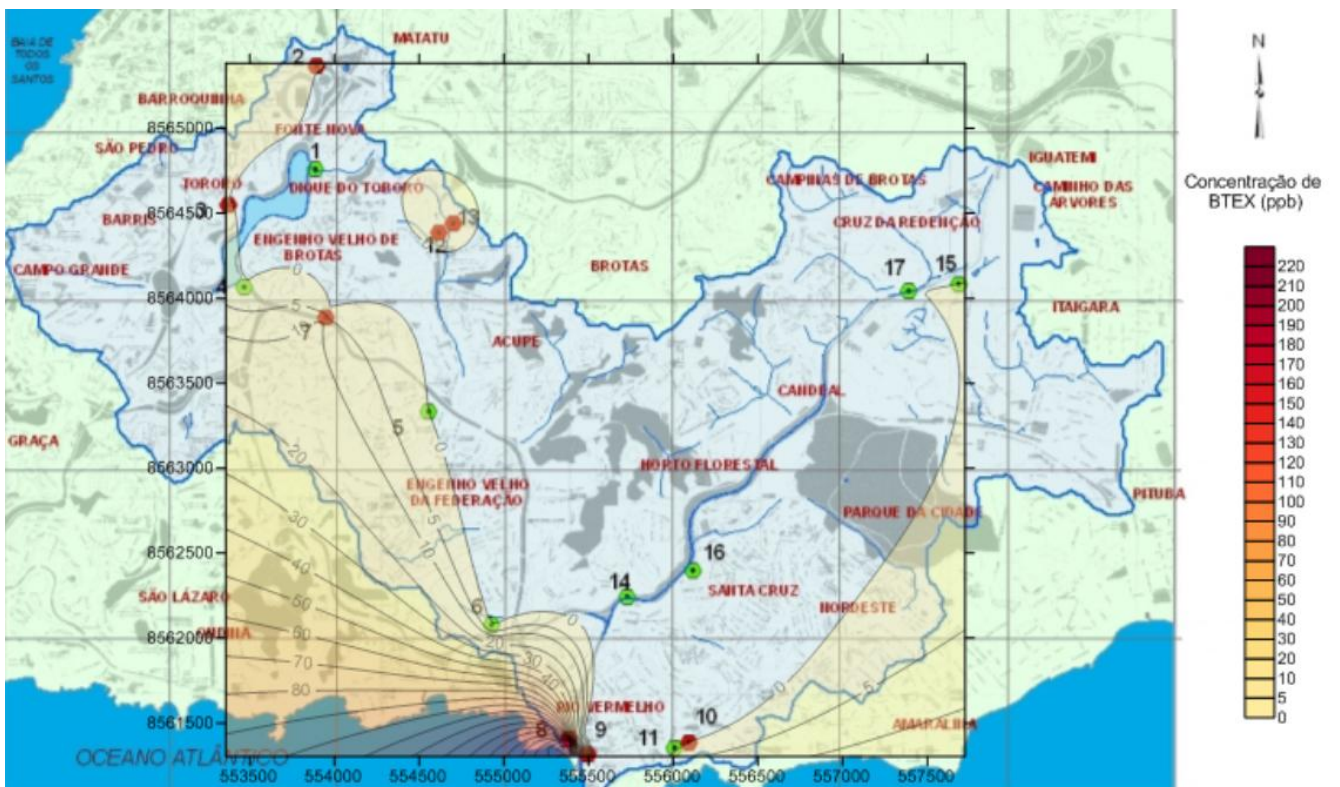


Figure 5 - Isolines of BTEX ($\mu\text{g L}^{-1}$)



CONCLUSION

A comparison of the two collections presented shows a significant reduction in the BTEX concentrations, especially for benzene, with a decrease of 82% in 6 months. Data collection has enabled the construction of isolines showing the dispersion of the nitrate, sulfate and iron (III), electron acceptors. The contamination, even centered on the Red River region, is not largely spread in the population at critical levels. The possible contamination source, the point RIO 1, had a greatly reduced BTEX concentration, and its surrounding areas have very low levels of BTEX (20 to 60 mg L⁻¹) below the CONAMA requirement.

REFERENCES

- ANDERSON G. M. **Thermodynamics of natural systems**. New Jersey: John Wiley and Sons Inc. 1996.
- BEZERRA, P. G.; CELINO, J. J.; GARCIA, K. S.; OLIVEIRA, M. R. Indicadores geoquímicos de contaminação por compostos orgânicos voláteis em águas subterrâneas da Bacia do Rio Lucaia, Salvador, Bahia. **Revista Brasileira de Geociências**, v. 42, p. 237-243. 2012.
- BRASIL. Ministério do Meio Ambiente. Portaria ministerial n. 396, de 3 de abril de 2008. Diário Oficial da União, 07 de abril de 2008, n. 66, seção I, p 64-68. Disponível in: < <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=562>>. Accessed: 12 nov. 2009.
- COSTA, A. H. R.; NUNES, C. C.; CORSEUIL, H. X. Biorremediação de águas subterrâneas impactadas por gasolina e etanol com o uso de nitrato. **Engenharia Sanitária Ambiental**, v. 14, n. 2, p. 265-274. 2009.
- CORSEUIL, H. X.; ALVAREZ, P. J. J. Natural biorremediation perspective for BTX – contaminated groundwater in Brazil: effect of ethanol. **Water Science & Technology**, v. 34, n. 7-8, p. 311-318, 1996.
- CUNNINGHAM, J. A. RAHME, H.; HOPKINS, G. D.; LEBRON, C.; REINHARD, M. Enhanced in situ bioremediation of BTEX contaminated groundwater by combined injection of nitrate and sulfate. **Environmental Science and Technology**, v. 35, p. 1663-1670, 2001.
- EATON, A. D.; CLESCERI, L. S.; GREENBERG, A. E. **Standard methods: examination of water and wastewater**. 19. ed. Washington, USA, 1995.
- EPA – ENVIRONMENTAL PROTECTION AGENCY. **Method 5030C: Purge-and-trap for aqueous samples**. Disponível em: <<http://www.epa.gov/SW-846/new-meth.htm>>. Acesso em: 13 out. 2012.
- FARHADIAN, M.; VACHELARD, C.; DUCHEZ, D.; LARROCHE, C. In situ bioremediation of monoaromatic pollutants in groundwater: a review. **Bioresource Technology**, n. 99, p. 5296-5308, 2008.
- FORTE, E. J.; AZEVEDO, M. S.; OLIVEIRA, R. C.; ALMEIDA, R. Contaminação de aquífero por hidrocarbonetos: estudo de caso na Vila Tupi, Porto Velho – Rondônia. **Química Nova**. v. 30, n. 7, p. 1539-1544, 2007.
- MALAMUD, E. S. T.; AMORIM JÚNIOR, C. J.; ROSÁRIO, M.; CORSEUIL, H. X. Avaliação da atenuação natural dos contaminantes BTEX e ETANOL em um derramamento controlado de gasolina através do balanço de massa. In: CONGRESSO BRASILEIRO DE ENGENHARIA SANITÁRIA E AMBIENTAL, 23. Campo Grande, 2005. **Proceedings...** [online]. Disponível in: <<http://www.remas.ufsc.br/Publicacoes/apcn034.pdf>>. Accessed in: 10 dez 2010.
- MARIANO, A. P. **Avaliação do potencial de biorremediação de solos e de águas subterrâneas contaminados com óleo diesel**. 147 p. Dissertação (Doutorado Profissional em Geociências e Meio Ambiente). – Universidade Estadual Paulista, Rio Claro, SP, 2006.
- NASCIMENTO, S. A. M.; BARBOSA, J. S. F. Qualidade da água do aquífero freático no alto cristalino de Salvador, Bacia do Rio Lucaia, Salvador, Bahia. **Revista Brasileira de Geociências**. v. 35, n. 4, p 543-550, 2005.
- NUNES, C. C.; CORSEUIL, H. X. Importância do etanol na atenuação natural de águas subterrâneas impactadas por gasolina. **Engenharia Sanitária Ambiental**, v. 12, n.3, p.259-265, 2007.
- ROUYCHOUDHURY, A. N.; MERRETT, G. L. Redox pathways in a petroleum contaminated shallow sandy aquifer: Iron and sulfate reductions. **Science of the Total Environment**, n.366, p.262-274, 2006.
- SILVA, R. L. B. **Contaminação de poços rasos no bairro Brisamar, Itaguaí, RJ, por derramamento de gasolina: concentração de BTEX e avaliação da qualidade da água consumida pela população**. 182 f. Dissertação (Doutorado em Ciências da Saúde pública) –

Escola Nacional de Saúde Pública da Fundação
Oswaldo Cruz, Rio de Janeiro, 2002.

SOARES, S. A. R.; COSTA, C. R.; ARAUJO, R. G. O., ZUCCHI, M. R., CELINO, J. J., TEIXEIRA, L. S. G. Determination of Polycyclic Aromatic Hydrocarbons in Groundwater Samples by Gas Chromatography-Mass Spectrometry After Pre-Concentration Using Cloud- Point Extraction with Surfactant Derivatization. **Journal of the Brazilian Chemical Society**, v. 26, n. 5, p. 955-962, 2015.

WANG, F.; COSTABILE, F.; LIU, F.; HONG, W.; FANG, D.; ALLEGRINI, I. Ambient BTX measurements in Suzhou, China. **Environmental Monitoring and Assessment**, v. 168, p. 21–31, 2010.