Hydrocarbon Pollution in Aquifers: An Overview on its Mechanisms and Solutions

Ana Letícia Araszewski Gomes da Silva

Academic Department of Civil Construction, Federal University of Technology – Paraná, Curitiba, Brazil, anaaraszewski@gmail.com

Abstract. Petroleum is one of the most valuable goods in our society, revered for its economic significance and pivotal role as a primary energy source. Alongside the process of modernization and urbanization, the explanation and influence of oil continue to increase in our world. Unfortunately, the usage and the refining processes of petroleum generate a series of environmental challenges. One of them is the pollution of aquifers caused by hydrocarbons of the BTEX type (Benzene, Toluene, Ethyl-Benzene and Xylenes) - typically encountered in petroleum, these compounds are well-documented for their carcinogenic properties. In the pursuit to better conserve groundwater, this article aims to highlight the contamination that the BTEX causes in aquifers, as well as the solutions and remediations methods used in the preservation of groundwater. In pursuit of this objective, the article draws upon an analysis of empirical discoveries and studies conducted on the remediation of aquifers contaminated by petroleum.

Keywords. Petroleum, hydrocarbons, pollution, contamination, aquifers, groundwater.

1. Introduction

Groundwater, predominantly found in aquifers, constitutes approximately 97% of the Earth's total water volume. Consequently, its conservation holds great significance, not just for today´s people and the generations to come, but also for the vast ecosystem of organisms inhabiting its domain [1].

Since the dawn of civilization, aquifers have played an important role in the history and progress of humankind. It was through the exploration of wells and springs that facilitated the advancement of human understanding in the realms of geology, agriculture and even technology [2]. The use of wells and springs as a catchment of fresh water originated from aquifers, remains as a common practice in rural Brazil, for example [3,4].

Nonetheless, with the accelerated industrialization and urbanization process that commenced in the 18th century, negative environmental impacts accompanied by the depletion of natural resources, have become ordinary problems [5]. One of the most current and concerning environmental issues is the pollution of groundwater by BTEX-type hydrocarbons (Benzene, Toluene, Ethyl-Benzene, and Xylenes) [6], which are prevalent constituents of petroleum. The persistence of such pollutants in aquifers and other bodies of water, has been continuously documented by scholars [5]. The petrochemical contamination of water tables and aquifers can occur in multiple ways, including the percolation from both subterranean and surface storage facilities, improper disposal of petroleum wastes and accidental spills [7].

Given these considerations, this article aims to provide a bibliographical review encompassing the aquifer contamination process, as well as an overview of different remediation methods, including Air Sparging and Bioremediation.

2. Methodology

To conduct this study, a bibliographic review was undertaken, in order to provide a comprehensive overview of hydrocarbon pollution in aquifers, as well as exploring potential remediation strategies. Groundwater pollution remediation strategies exhibit considerable diversity, with new approaches continually emerging. However, the focus of this article centers on air sparging and bioremediation, due to their environmental character [7].

To analyze and investigate the articles, it was used Google Scholar as the principal research tool, implementing keywords such as "hydrocarbons," "aquifers," and "pollution" in the search bar. Articles discussing the microbial degradation of hydrocarbons in the environment, with a specific focus on aquifer pollution caused by oil leakage, were analyzed. The selected articles offered distinct perspectives on groundwater pollution and remediation, approaching varying techniques and research methodologies regarding air sparging and bioremediation.

This bibliographic approach was adopted to furnish a synthesis of ideas, and to present a comprehensive understanding of aquifer pollution and its potential remedies. It is necessary to note that a variety of sources were consulted, but this article draws its main analysis from the works: *Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview* (Nadim et al., 2000) [7] and *Técnicas para remediação de aquiferos contaminados por vazamentos de derivados de petróleo em postos de combustíveis* (Coutinho; Gomes, 2007) [8].

3. Aquifers and Petroleum: Formation and Characteristics

Before understanding the process of hydrocarbon pollution of aquifers, it is necessary to understand the concept and formation of the two main parts of this study – aquifers and petroleum.

3.1 Aquifers

Groundwater can be found in various environments, but its primary reservoir is in aquifers. Recognized for their geological formation characterized by permeability, rainwater can percolate through soil and rocks, thus resulting in a large subterranean reserve of water that naturally flows within it [3, 9]. Aquifers possess two main characteristics: the capacity for groundwater storage (storativity) and the capacity for groundwater flow (wide variation); such characteristics are highly influenced by the geological formation of the aquifer [10].

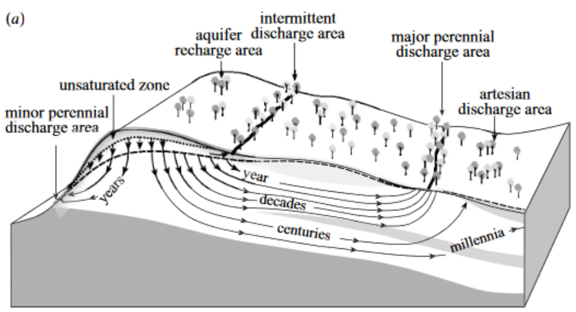

Fig. 1 – Common groundwater structures and systems in humid regions [10].

Often conflated, it is important to highlight the distinction between aquifers and water tables. Aquifers are subterranean water formations [3], whereas a water table is a natural aquifer, which has variable water levels throughout the year. Water tables serve as a representation of the groundwater level, dividing the saturated zone from the unsaturated zone. The saturated zones, in this case, are voids between rocks and soil beneath the surface filled with water, lying above the aquifers and below the water tables [9, 11].

3.2 Petroleum Compounds

The geological and chemical formation of petroleum occurred millions of years ago, upon specific conditions of pressure and temperature. This process involves the accumulation of organic matter, such as plants, algae, and plankton, in several layers of sedimentary basin subsoils [12, 13]. It is known that the oil refining process is a distinct procedure. After all, in its raw state, oil has few applications, therefore for its commercial use crude oil needs to go through several improvement stages [14].

Hydrocarbons are the fundamental constituents of oil. Although their quantities within the petroleum structure may change, it is understood that they constitute approximately 70% of its composition [15, 16]. Such hydrocarbons mainly consist of varying proportions of carbon and hydrogen, occasionally incorporating elements such as nitrogen, sulfur, and oxygen [17].

Crude oil can be classified into 4 different groups: Saturates (aliphatics), Aromatics (ringed hydrocarbons), Resins and Asphaltenes; each component has its own intensity of biodegradability in relation to the environment [12, 17]. Saturates are the most common types found in the structures of crude oil. They are characterized by a lack of double bonds [12]. Aromatic hydrocarbons feature one or more aromatic rings [18], whereas resins and asphaltenes have an intricate and partially unknown structure [12, 17].

BTEX (benzene, toluene, ethylbenzene, and xylene) represent volatile constituents commonly present in petroleum. They are hydrocarbons arranged in a condensed aromatic ring, generally consisting of carbon and hydrogen atoms [19, 20]. They are of significant concern due to their toxicity and mobility in aqueous environments. Their environmental significance is further accentuated by BTEX carcinogenic content, as well its potential to quickly seep into aquifers, which can lead to groundwater pollution [20, 21].

Benzene (C_6H_6) is a volatile organic compound found in gaseous emissions from volcanoes and forest fires, but it can also be emitted in industrial activities. Research on benzene and the human immune system show that chronic exposure to this pollutant can cause damage to the immune function [22]. Toluene (C_7H_8) is known for its volatile and flammable characteristics, its main sources of emissions into the environment are fossil fuels. Exhibition of toluene can affect the central nervous system of living beings such as humans and animals, on top of causing fatigue, drowsiness, headache and nausea [20, 23]. Ethylbenzene (C_8H_{10}) is an organic compound used in the manufacture of paints, varnish solvents, printing inks, insecticides, synthetic rubber and manufactured cellulose. Moreover, contact with ethylbenzene leads to eye and throat irritation, in addition to potentially inducing respiratory complications [20, 24]. Xylenes (C_8H_{10}) are structured with a six-carbon ring that has two attached methyl groups, comprising a set of three isomers: ortho-xylene, meta-xylene and para-xylene. They are used in fragrances, paints, varnishes and rubber. Its constant exhibition can cause harm to the immune system [25].

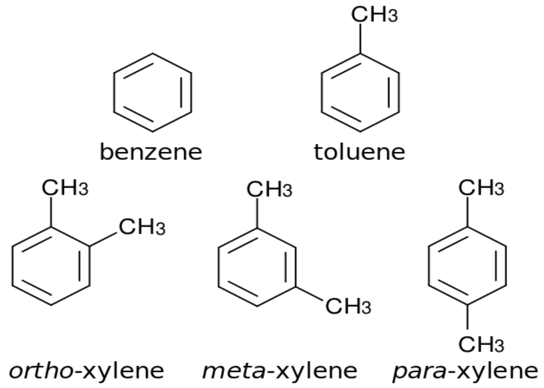

Fig. 2 – Chemical structure of BTEX compounds [26].

4. Contamination Processes

The BTEX compounds are considered the main contaminants of groundwater in aquifers and water tables, due to their solubility and mobility in water [8]. This phenomenon occurs because although hydrocarbons are generally known for their ability to dissolve in aqueous solutions, hydrocarbons with lower molecular weights possess better solubility levels compared to those of a higher molecular weight [27]. As a result of this atribute, BTEX compounds can easily dissolve and locomote in water, considering that their molecular masses are – 78.1 (benzene), 92.4 (toluene), 106.16 (ethylbenzene) and 106.2 (xylene) [20].

BTEX can be released into aquifers in several ways: mining activities, use of agricultural pesticides and herbicides, accidents involving oil pipelines, radioactive waste in repositories located in deep geological formations, among others [8, 21, 28, 29]. It is important to emphasize that the primary prompter of groundwater contamination is caused by leakage of underground storage tanks utilized by gas stations and industries on a global scale [7].

The distribution of hydrocarbons in groundwater highly depends on its hydrogeological conditions (vertical and lateral extensions of the underlying parts of the water level). After BTEX percolates into the soil, it is necessary to analyze units of an aquifer considered strategic for the movement of groundwater, as well as its fluctuations in water levels. These characteristics play a pivotal role in the dispersion of hydrocarbons, distributing their compounds in unsaturated and saturated zones of the aquifer [30].

5. Remediation Techniques

Although there are many aquifers and water table remediation methods, the techniques that this article intends to overview are bioremediation and air sparging. Both methods are known for their minimal environmental impact in the intended application environments.

5.1 Air Sparging

In situ air sparging (IAS) is a hybrid technology created in the late 1980s, with the aim of treating dissolved volatile organic compounds (VOC) by introducing air below the water table. It relies on the mechanisms of biodegradation and volatilization, which can either work together or separately [31, 32]. This method can be implemented in both saturated and unsaturated polluted parts of the aquifer [8]. Air sparging entails the pressurized injection of air, generating air bubbles that are intersected horizontally and vertically through the soil column, thus displacing water and generating air-filled pores within the saturated soil [8, 33]. IAS not only aids in the volatilization of VOCs, but also increases aerobic bacteria in saturated zones of the aquifer [7]. As a result, both physical removal and aerobic biodegradation of contaminants from the saturated zone are increased [33].

Air sparging allows aquifer remediation without the use of active groundwater pumping. Occasionally, it has been proven that the use of IAS significantly and permanently reduces BTEX contaminants in groundwater, which has increased its use as a propitious remediation technique over the years [33].

Some factors that may limit the applicability and efficiency of IAS are: interaction between the injected air and the polluted groundwater, the volatility and solubility of the contaminant, gas permeability in the unsaturated zone, water flow rate and the absorption of the aquifer [8].

5.2 Bioremediation

Bioremediation involves harnessing natural processes to address environmental contamination. Some examples of bioremediation techniques are bioventing, landfarming, bioreactor, compositing, bioaugmentation, biostimulaiton, among others [34]. Although studies to improve this technique are contemporary, bioremediation has been used since ancient times. When applied to aquifers, this technique is used to break down BTEX compounds by specialized microorganisms (also known as bioremediators). Bioremediation is known for its eco-friendly, sustainable, and economically viable characteristics. This process uses microorganisms, such as bacteria and fungi, to generate energy through a redox reaction. These reactions include vital biological functions such as respiration and reproduction. After these substances are utilized, they are converted into carbon dioxide and water [8, 34, 35, 36]. The fungi species Penicillium, Fusarium, and Rhizopus are among the most commonly employed microorganisms in the bioremediation of aquifers and other environments contaminated by BTEX [35].

A variety of microbial electron acceptors can be used in the bioremediation process: oxygen-, nitrate-, manganese-, iron (III)-, sulfate-, or carbon dioxide-reducing, and their corresponding redox potentials [35].

It is important to understand that, in order for bioremediation to work, the environment in which the process occurs must have adequate permeability to facilitate the flow of oxygen and nutrients. These characteristics are essential not only to properly remediate the aquifer, but also to prevent the production of toxic substances harmful to living beings [7, 8].

Some factors to take in consideration when applying the bioremediation process are: contaminant concentrations (when concentrations are too high, it might create a toxic environment, whereas if the concentration is too low, it might not cause a difference in the environment at all), contaminant bioavailability (microbial reactions have their bioavailability reduced when contaminants are firmly bound to solids) and redox potential (redox potential is impacted by the presence of electron acceptors like nitrate) [34].

The bioremediation process occurs in 4 stages:

1) Identify and characterize microorganisms native to the region where the process intends to be applied.
2) Cultivating these microorganisms in a controlled laboratory environment to establish viable populations.
3) Analyze catabolic activity that such microorganisms carry out in contaminated material through small-scale experiments.
4) Monitor and assess the progress of bioremediation using chemicals by performing toxicity tests in a chemically-polluted environment [36].

6. Discussion and Conclusion

Resources on our planet are finite, and it is vitally important to conserve what nature has to offer us. The conservation of aquifers is extremely important for humankind, it is estimated that 80% of the world's population depends on groundwater for survival [7]. Having around 97% of all fresh water in its domain, aquifers and water tables represent a crucial resource for humanity. With the advent of modernity, the use of petroleum is continually growing, with no sign of imminent decline. Both the direct and indirect use of oil, as well as its manufacturing, cause various environmental damages. The pollution of aquifers by BTEX has a certain urgency on its remediation, since the hydrocarbons present in petroleum are incredibly toxic due to their solubility and mobility in aqueous environments. Due to these factors, along with persistent groundwater pollution, it may take years of remediation processes to restore the aquifers to their previous state. Unfortunately, as long as governments fail to recognize the influence and significance of aquifers for living beings, problems such as groundwater contamination by BTEX will continue to be ignored by society.

As stated in the article, the main form of aquifer pollution is caused by leakage of underground storage tanks used by gas stations and industries. Such stations and tanks suffer from wear and lack any form of inspection, exacerbating the issue. Leaks from underground tanks and other incidents reported in the petroleum industry are not visible on the surface, which leads to slower remediation processes.

Current remediation methods have several implicit limitations. The selection of a remediation technology depends on both the specific attributes of the aquifer and the types of contaminants. Although bioremediation has the potential for ex-situ application and is more economically available (especially in developing countries) than air sparging, it is important to consider that bioremediation requires comprehensive studies to prevent the generation of toxic chemicals that can potentially impact both the aquifer and human health. Despite its negative side, it is essential to highlight that bioremediation, as well as air sparging, don´t cause damage to the environment. Additionally, both remediation processes have already been shown to be extremely effective in numerous researches.

The best approach to address hydrocarbon pollution in aquifers, would be to prevent BTEX contaminants to make contact with the soil. This can be achieved through several ways, as global awareness of environmental impacts continues to grow. Perhaps with such an approach, one day nature will be able to free itself from anthropogenic pollution.

7. References

[1] Gilbert, J., Danielopol, D. L., & Stanford, J. A. (Eds.). *Groundwater ecology* (Vol. 1). Academic Press, San Diego, 1994; 561 p.

[2] Kingston, P. F. Long-term environmental impact of oil spills. *Spill Science & Technology Bulletin*, *7*(1-2), 2002; 53-61.

[3] DE CONTAMINAÇÃO, I. E. R. ÁGUAS SUBTERRÂNEAS E AQUÍFEROS: IMPORTÂNCIA E RISCOS DE CONTAMINAÇÃO. *Dicionário de Saneamento Básico: pilares para uma gestão participativa nos municípios*; 2022, p 54.

[4] Fogaça, P. H. D. C. Contaminação do lençol freático por hidrocarbonetos na região de Avaré-SP. 2015.

[5] Antoci, A., Galeotti, M., & Sordi, S. Environmental pollution as engine of industrialization. *Communications in Nonlinear Science and Numerical Simulation*, *58*, 2018; 262-273.

[6] da Costa, M. S., Gomes, M. D. C. R., & de Morais Nascimento, S. A. Vulnerabilidade de aquíferos à poluição: uma revisão metodológica. *Revista de Geociências do Nordeste*, *8*(1), 2022; 60-76.

[7] Nadim, F., Hoag, G. E., Liu, S., Carley, R. J., & Zack, P. Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview. *Journal of Petroleum Science and Engineering*, *26*(1-4), 2000; 169-178.

[8] Coutinho, R. C. P., & Gomes, C. C. Técnicas para remediação de aquíferos contaminados por vazamentos de derivados de petróleo em postos de combustíveis. *XVII Simpósio Brasileiro de Recursos Hídricos*. 2007.

[9] Todd, D. K., & Mays, L. W. *Groundwater hydrology*. John Wiley & Sons. 2004.

[10] Foster, S. S. D., & Chilton, P. J. Groundwater: the processes and global significance of aquifer degradation. *Philosophical Transactions of the Royal Society of London. Series B: Biological Sciences*, *358*(1440), 2003; 1957-1972.

[11] Baird, A. J, & Low, R. G. The water table: Its conceptual basis measurement and its usefulness as a hydrological variable. *Hydrological Processes*, *36*(6), 2022; 14622

[12] Varjani, S. J. Microbial degradation of petroleum hydrocarbons. *Bioresource technology*, *223*, 2017; 277-286.

[13] Turgeon, A., & Morse, E. Petroleum. *National Geographic Society*, *5*. 2018.

[14] Mariano, J. B. Impactos ambientais do refino de petróleo. *Rio de Janeiro*. 2001.

[15] Atlas, R. M. Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiological reviews*, *45*(1), 1981; 180-209.

[16] Petrov, A. A. *Petroleum hydrocarbons*. Springer Science & Business Media, 2012.

[17] Chandra, S., Sharma, R., Singh, K., Sharma, A. Application of bioremediation technology in the environment contaminated with petroleum hydrocarbon. Ann. Microbiol. 63, 2016; 417–431

[18] Abbasian, F., Lockington, R., Mallavarapu, M., & Naidu, R. A comprehensive review of aliphatic hydrocarbon biodegradation by bacteria. *Applied biochemistry and biotechnology*, 176, 2015; 670-699.

[19] Lovley, D. R. Potential for anaerobic bioremediation of BTEX in petroleum-contaminated aquifers. *Journal of Industrial Microbiology and Biotechnology*, *18(2-3),* 1997; 75-81.

[20] Anjos, R. B. D. *Avaliação de HPA e BTEX no solo e água subterrânea, , em postos de revenda de combustíveis: estudo de caso na cidade de Natal-RN* (Master's thesis, Universidade Federal do Rio Grande do Norte). 2012.

[21] da Silva, G. S. Contaminação do subsolo por hidrocarbonetos do petróleo. *Caderno de Graduação-Ciências Exatas e Tecnológicas-UNIT-ALAGOAS*, 3(1), 2015; 57-64.

[22] Ferreira da Costa, M. A., & Barrozo da Costa, M. D. F. Benzeno: uma questão de saúde pública. *Interciência, 27(4),* 2002; 201-204.

[23] Forster, L. M., Tannhauser, M., & Tannhauser, S. L. Toluene toxicology: abuse aspects. *Revista de Saúde Pública*, 28, 1994; 167-172.

[24] Banton M. Ethylbenzene, Encyclopedia of Toxicology (Third Edition), *Academic Press*, 2014; 516-518.

[25] Kandyala, R., Raghavendra, S. P. C., & Rajasekharan, S. T. Xylene: An overview of its health hazards and preventive measures. *Journal of oral and maxillofacial pathology: JOMFP, 14(1),* 2010; 1.

[26] Fayemiwo, O., Moothi, K., & Daramola, M. BTEX compounds in water–future trends and directions. *Water Sa*, *43*(4), 2017; 602-613.

[27] Curl, H. C., & O'Donnell, K. Chemical and physical properties of refined petroleum products. 1977.

[28] Marquezan, R. G., Luna Caicedo, N. O., Bastos Neto, A. C., & Azambuja Filho, N. C. D. Análise da vulnerabilidade do lençol freático à contaminação por hidrocarbonetos em cenário de vazamentos na área do oleoduto Orsul II, Refap-Copesul, Refap-Copesul, RS. *Rbrh: revista brasileira de recursos hídricos. Porto Alegre, RS. Vol. 15, n. 1 (jan./mar. 2010),* 2010; p. 101-109.

[29] Bear, J., & Verruijt, A. *Modeling groundwater flow and pollution* (Vol. 2). Springer Science & Business Media. 1987

[30] Lee, J. Y., Cheon, J. Y., Lee, K. K., Lee, S. Y., & Lee, M. H. Factors affecting the distribution of hydrocarbon contaminants and hydrogeochemical parameters in a shallow sand aquifer. *Journal of contaminant Hydrology*, 50(1-2), 2001; 139-158.

[31] Hinchee, R. E. Air sparging state of the art.

Air sparging for site remediation, 1994; 1-13.

[32] Johnson, R. L., Johnson, P. C., McWhorter, D. B., Hinchee, R. E., & Goodman, I. An overview of in situ air sparging. *Groundwater monitoring & remediation*, 13(4), 1993; 127-135.

[33] Bass, D. H., Hastings, N. A., & Brown, R. A. Performance of air sparging systems: a review of case studies. . *Journal of Hazardous Materials, 72*(2-3), *2000; 101-119.*

[34] Ossai, I. C., Ahmed, A., Hassan, A., & Hamid, F. S. Remediation of soil and water contaminated with petroleum hydrocarbon: : A review. *Environmental Technology & Innovation*, *17*, 100526, 2020.

[35] Adams, G. O., Fufeyin, P. T., Okoro, S. E., & Ehinomen, I. Bioremediation, biostimulation and bioaugmention: a review. *International Journal of Environmental Bioremediation & Biodegradation*, 3(1), 2015; 28-39.

[36] Kensa, V. M. Bioremediation-an overview. *Journal of Industrial Pollution Control*, 27(2), 2011, 161-168.