NATURAL ATTENUATION AND MICROBIAL DEGRADATION OF MTBE IN THE SANDSTONE MATRIX OF THE PATIÑO AQUIFER, PARAGUAY

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Abstract

This study investigates the natural attenuation and microbial degradation of methyl tert-butyl ether (MTBE) in the Patiño Aquifer, Paraguay, following the phase-out of MTBE in gasoline in 2016. The aquifer's sandstone matrix, characterized by interconnected pores and redox-active minerals, facilitates microbial colonization and abiotic degradation. Sampling campaigns revealed a decline in MTBE detection from 44% to 17.8% of monitored wells, alongside increased detection of degradation products tert-butyl formate (TBF) and tert-butyl alcohol (TBA) in 72% and 21% of samples, respectively. MTBE decline in Patiño Aquifer linked to discontinued use (halting inputs), enhanced microbial degradation (aerobic/anaerobic pathways producing TBA/TBF), natural attenuation (first-order kinetics aided by hydrology/redox shifts), and minor abiotic oxidation. Adsorption was negligible due to MTBE's low sandstone affinity. The metabolite shifts reflect reduced anthropogenic inputs, biological breakdown, and hydrogeochemical dynamics. This interplay underscores the aquifer's capacity for MTBE transformation via integrated microbial activity, environmental conditions, and source cessation.

Keywords: *sandstone, MTBE, TBA, TBF, natural attenuation, microbial degradation*

1. INTRODUCTION

1.1. MTBE Contamination and Remediation Challenges

Methyl tert-butyl ether (MTBE), a gasoline oxygenate, has been widely used since the 1970s to enhance combustion efficiency (Rosell et al., 2007). However, its high solubility and low soil adsorption affinity make it a persistent groundwater contaminant (Johnson et al., 2000). MTBE plumes often outpace other gasoline components due to slow biodegradation and weak soil retention (Lindsey et al., 2017). Health risks include carcinogenic potential, with animal studies linking MTBE to kidney and liver tumors (Burns & Melnick, 2012). In Paraguay, MTBE usage in gasoline peaked in 2014 (18.5% by volume) but was phased out by 2016, halting new inputs (Facetti et al., 2019). Remediation challenges stem from MTBE's recalcitrance under anaerobic conditions and limited abiotic degradation in iron-poor aquifers (Schoonen et al., 2004).

1.2. Hydrogeological Framework of the Patiño Aquifer Sandstone Matrix

The Patiño Aquifer serves as the primary drinking water source for 1.8 million people (Wehrle, 2017). Composed of Cretaceous sedimentary rocks, specifically sandstones of the Asunción Group—including the Patiño Formation (conglomerates) and Yaguarón Formation (sandstones)—the aquifer originates from eroded Misiones magmatism and local sources, with mineralogy dominated by quartz, feldspar, and aluminosilicates (e.g., clays) (DeGraf & Orue, 1984; DeGraff, 1985; Bartell, 1994). Accessory minerals include iron/manganese oxides, which drive redox reactions but occur in low concentrations. The aquifer's porosity and permeability are governed by interconnected pores in the sandstone matrix, facilitating groundwater flow and microbial activity. Hydraulic behavior is stratified (SENASA–TNO-NTG, 2001): in Upper layers (unconfined to semi-confined): Transmissivity = 10–30 m2/day; horizontal hydraulic conductivity = 0.3–0.6 m/day (vertical conductivity 2–5 times lower); effective porosity = 10–20%; elastic storage coefficient = 10^{-3}–10^{-5}; while in Lower layers (semi-confined):

Transmissivity = 30–200 m²/day; horizontal hydraulic conductivity = 1–4 m/day (vertical conductivity 2–5 times lower); effective porosity = 10–20%; elastic storage coefficient = 10^{-4}–10^{-7}.

Iron/manganese oxides drive Fenton-like redox reactions, albeit weakly due to low iron content (Strathmann & Stone, 2001). Vulnerability to contamination arises from fractures, urban development, unregulated gasoline stations, leaking septic/sewer systems, and fuel spills (Martínez & Pérez, 2011; Facetti et al., 2019).

1.3. Hydrogeological Assessments

- Redox Conditions: Piezometer data identified aerobic/anaerobic zones (Wehrle. 2007 y Wehrle A.; Lopez D. 2007).

- Recharge Dynamics: Annual rainfall (2015–2020) averaged 1,500 mm but fluctuated significantly (2015: 1,450 mm; 2016: 1,600 mm; 2017: 1,780 mm; 2018: 1,350 mm; 2019: 1,500 mm; 2020: 1,700 mm). The 2018 drought (1,350 mm) was linked to El Niño effects (MADES, 2019).

2. MATERIALS AND METHODS

2.1. Study area

The Patiño Aquifer, located in Paraguay's Central and Paraguarí Departments, spans 1,770 km² and reaches depths of up to 600 m. It stretches 65 km in length and 30 km in width, forming a triangular area bordered by the Paraguay River. Elevations range from 62 m (near the river) to 200–300 m above sea level. Studies highlight its hydrogeological significance and structure, with key references from Wehrle (2017) and Bartel (1994). The Patiño Aquifer, composed of Cretaceous sedimentary rocks from the Asunción Group, formed during tectonic events linked to the South Atlantic (100.5–66 Ma) and Andean (65–23 Ma) cycles. Bartel (1994) describes it as a NW-SE semi-graben from Gondwana's breakup. The Asunción Group is divided into the basal Patiño Formation (conglomerate) and Yaguarón Formation (sandstone). Geochemical studies (Facetti-Masulli et al., 2006/2010) identify two sandstone types: one with Misiones magmatism signatures and another resembling Misiones Formation sandstones.

2.2. Sampling Campaigns and materials

Two sampling campaigns were conducted in May – June 2017 and in December 2017. During the first sampling campaign, there was accumulated rainfall of 200 mm during the second sampling campaign the accumulated rainfall was 406 mm; the accumulated rainfall between both sampling campaigns was 477 mm (Dirección General de Meteorología e Hidrografía, 2019).

Duplicate samples of the 90 wells (80–206 m depth) were collected in duplicate according to the Method 1060 of the Standard Methods for the examination of water and wastewater, 22nd (APHA, 2012). To avoid redox conditions all samples were collected in sodium thiosulfate-treated vials (APHA Method 1060, 2012).

2.3. Analytical Techniques

MTBE and its degradation products were extracted via headspace SPME (30 min, 35°C) from 5 mL samples with 1.8 g NaCl, using a Shimadzu AOC 5000 autosampler with a 75 µm PDMS/Carboxen fiber. Method validated at 21–25°C. Detection limits of MTBE, TBA, and TBF were 0.009 µg/L, 0.029 µg/L, and 0.010 µg/L, respectively (Nuñez et al., 2017). Analytes were separated via GC-MS (Shimadzu QP-2010 Plus) using a Restek VMS column (30m×0.25mm×1.4µm) in split mode (1:10). Desorption at 200°C. Temperature program: 35°C (7min), 4°C/min to 90°C, then 35°C/min to 220°C (2min). MS detection used EI ionization (70 eV, 230°C), monitoring ions from 4–20min. Calibration involved MTBE, TBA, TBF (99.9–99% purity) and MTBE-d3 internal standard. Solutions were prepared in ultra-pure methanol and boiled water.

3. RESULTS

3.1. Decrease in MTBE and Increase in TBF/TBA

The detection frequency of MTBE decreased from 44% to 17.8% after 2016, while the detection of TBF and TBA increased to 72% and 21%, respectively (Facetti et al., 2019).

3.2. Hydrogeochemical Dynamics

Redox changes: Anaerobic zones were correlated with increased production of TBF, which is consistent with the findings of Youngster et al. (2010). The presence of both aerobic (TBA-dominated) and anaerobic (TBF-dominated) degradation products suggests potential redox variability within the aquifer. This interpretation is supported by: the co-occurrence of MTBE, TBA, and TBF in some wells (e.g., well P87 contained all three compounds); seasonal recharge patterns that may create oxygen gradients (Wehrle, 2007; Wehrle A. & Lopez D., 2007); and previous studies indicating the accumulation of TBF under anaerobic conditions (Youngster et al., 2010). However, no direct measurements of redox potential were performed in this study.

The distribution of degradation products may alternatively reflect: spatial variability in microbial communities; differences in diffusion times from contaminant sources; and localized variations in aquifer geochemistry. First-order kinetics are also relevant, as the average half-life of MTBE was estimated at 7.3 months (Metcalf et al., 2016), consistent with natural attenuation models. Finally, aquifer recharge driven by seasonal precipitation variability in Asunción exhibits significant interannual differences.

4. DISCUSSION

In the studies conducted by Facetti et al., the first sampling campaign detected MTBE in approximately 44% of wells, while the second campaign reported a decline to 17.8%, along with a notable increase in the detection of degradation products—particularly TBF (up to 72% of wells) and, to a lesser extent, TBA. Several processes and factors appear to contribute to these observations:

Reduction in MTBE inputs. In Paraguay, MTBE usage peaked around 2014 and was virtually phased out by 2016, ceasing continuous inputs via gasoline. The removal of the source allowed natural attenuation processes to act upon residual MTBE over time (Facetti et al. 2022).

Enhanced microbial degradation. Prolonged dry seasons reduce recharge, leading to MTBE concentration and promoting anaerobic conditions conducive to degradation. Recent studies have shown that mixed microbial consortia can degrade MTBE more effectively than previously assumed. Bastida et al. (2010) demonstrated that consortia including key degraders such as Methylibium petroleiphilum play a central role in MTBE biodegradation. Youngster et al. (2010) reported that while aerobic degradation proceeds with relatively mild fractionation, anaerobic processes can result in more pronounced changes—suggesting that anaerobic pathways (which may yield intermediates like TBF) may be more active in oxygen-limited aquifer zones. Reviews on MTBE biodegradation (e.g., Fiorenza and Rifai, 2003) confirm that both aerobic and anaerobic pathways are viable, with TBA as the primary intermediate and subsequent transformation leading to compounds such as TBF. These findings support the hypothesis that the observed increase in TBF is associated with ongoing microbial degradation of residual MTBE.

Natural attenuation kinetics and aquifer dynamics. MTBE natural attenuation can be accurately described by first-order kinetics. Metcalf et al. (2016) estimated MTBE half-lives ranging from a few weeks to several years, with an average of approximately 7.3 months in affected wells. This kinetic framework aligns with the observed decline in MTBE concentrations over time. Moreover, the hydrogeological characteristics of the aquifer, as detailed in technical reports on piezometric and exploratory well drilling (Wehrle, 2007; Wehrle A. & Lopez D., 2007), indicate that variations in aquifer volume—driven by recharge and seasonal fluctuations—can lead to dynamic redox conditions. Such changes may promote the transition from aerobic to anaerobic conditions in specific zones, thereby facilitating the degradation of MTBE into metabolites such as TBF and TBA.

Chemical transformation and minor contributions from abiotic processes. Although microbial processes represent the primary pathway for MTBE attenuation, studies on Fenton-like oxidation suggest that chemical oxidation may also contribute under specific conditions. However, within the context of the Patiño Aquifer—characterized by a sandstone matrix and iron concentrations around 15% (Facetti-Masulli et al., 2010)—the microbial pathway is likely predominant. Adsorption studies further support that MTBE is only weakly retained by soils due to its low partition coefficient, meaning that dilution and biodegradation are more influential than sorption in determining its fate (Kamalan et al., 2009).

Additionally, research indicates that although MTBE is relatively persistent, prolonged residence time in the subsurface, combined with microbial activity, leads to its gradual removal from groundwater (Hamann et al.), aligning with the trend observed in this investigation of the Patiño Aquifer.

5. CONCLUSIONS

The reduction in MTBE detection and the concurrent appearance of degradation products during the second sampling campaign in the Patiño Aquifer can be attributed to: the discontinuation of MTBE use, which halted new inputs into the system; increased activity of specialized microbial consortia capable of transforming MTBE—both aerobically and anaerobically—into intermediates such as TBA and TBF; natural attenuation processes following first-order kinetics, facilitated by the aquifer's dynamic hydrology and redox variability; and minor contributions from abiotic oxidation processes, with adsorption playing an insignificant role due to MTBE's low affinity for the sandstone matrix.

This integrated perspective reinforces the conclusion that the observed changes in MTBE and its metabolites are the result of a complex interplay among reduced anthropogenic inputs, biological degradation pathways, and the inherent hydrogeochemical dynamics of the aquifer.

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