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Magneto Chemical Tracers for Monitoring Hydrothermal and Domestic Wastewater Impacts in Coastal Groundwater Systems

Jelil Olaoye[1]; Funsho Timilehin Omidiwura[2]; Ganiyat Funke Babalola[3]

[1]Department of Applied Physical Science, Environmental Science Concentration, Georgia Southern University, Georgia, USA
[2,3]Department of Forest Resources Management, Faculty of Renewable Natural Resources, LAUTECH, OGBOMOSO

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Abstract

Identifying the origin of groundwater contamination in coastal environments remains a critical challenge due to the coexistence of natural hydrothermal discharges and anthropogenic wastewater inputs. This study aimed to evaluate whether magneto chemical tracers the combined use of magnetic susceptibility measurements and geochemical indicators can effectively distinguish between hydrothermal and domestic wastewater influences in coastal aquifers. Groundwater samples were collected from categorized wells representing hydrothermal, wastewater impacted, and background conditions. Field and laboratory analyses were conducted to measure magnetic susceptibility and key chemical and isotopic parameters, including boron, lithium, nitrate, phosphate, and $\delta^{18}O/\delta D$ isotopes. The dataset was analyzed using statistical comparisons and multivariate clustering to assess tracer performance and source attribution.

The results showed that hydrothermal wells consistently exhibited elevated magnetic susceptibility values alongside enriched boron and lithium concentrations. In contrast, wastewater impacted wells were characterized by high nitrate and phosphate levels but lacked detectable magnetic signals. The integration of magnetic and chemical data improved the resolution of source differentiation, particularly in mixed or transitional wells where chemical profiles alone were ambiguous.

These findings demonstrate that magneto chemical tracers provide a novel and effective approach for identifying and distinguishing overlapping sources of groundwater contamination. This method holds significant potential for enhancing water resource monitoring, especially in geologically active coastal regions where timely and accurate source attribution is vital for sustainable aquifer management.

Keywords: *Magneto Chemical Tracers; Groundwater Contamination; Hydrothermal Fluids; Domestic Wastewater; Magnetic Susceptibility; Boron and Lithium Tracers.*

I. INTRODUCTION

Coastal groundwater systems represent one of the most critical interfaces between terrestrial and marine environments, serving as vital freshwater reservoirs for millions of people living along coastlines worldwide (Post et al., 2013). These systems are particularly important in regions where surface water resources are scarce or heavily polluted, providing drinking water, supporting agriculture, sustaining coastal wetlands, and regulating salinity balance in estuarine ecosystems (Ferguson & Gleeson, 2012). In many coastal zones, the interaction between seawater intrusion, groundwater discharge, and anthropogenic influence creates a highly dynamic hydrological environment. Understanding and protecting groundwater quality in these regions is essential not only for ecological conservation but also for maintaining public health and socioeconomic development. Two principal forces shape the quality of coastal groundwater: natural geologic and geothermal processes, and anthropogenic activities. Natural hydrothermal discharges, such as upwelling geothermal fluids and submarine groundwater discharge from volcanic aquifers, can significantly influence water chemistry through the introduction of heat, dissolved minerals, trace metals, and unique isotopic signatures (Williamson et al., 2016). These discharges

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often occur in tectonically active or volcanic coastal regions, where fault systems and geothermal gradients allow deep seated fluids to ascend and mix with shallow aquifers. Hydrothermal fluids are typically enriched in silica, lithium, boron, fluoride, and heavy metals like arsenic or mercury (Mariner et al., 2006), and they may alter the geochemistry of affected aquifers by elevating temperatures and changing redox conditions (Stolp et al., 2010). On the other hand, coastal urbanization and population growth have intensified anthropogenic pressures on groundwater systems, most notably through domestic wastewater infiltration. Domestic wastewater including effluent from septic systems, leaky sewer lines, and informal discharge practices often contains high concentrations of nutrients (e.g., nitrate, phosphate), pharmaceuticals, hormones, microbial pathogens, and chemical residues (Lapworth et al., 2012). Infiltration of untreated or partially treated wastewater into aquifers not only degrades water quality but also poses serious public health risks, particularly in low income or infrastructure deficient coastal communities. Nitrate contamination from sewage and septic effluent has been linked to methemoglobinemia (blue baby syndrome) in infants, eutrophication in connected surface waters, and long term ecosystem disruption (Spalding & Exner, 1993).

When both hydrothermal and domestic wastewater sources coexist common in volcanic or geothermal coastal regions undergoing rapid urbanization the challenge of distinguishing their respective impacts becomes critical for water resource management. While hydrothermal influence may be naturally occurring and non toxic under certain conditions, the presence of anthropogenic wastewater requires urgent remediation and public health intervention. Differentiating between these sources is therefore essential for designing effective management strategies, safeguarding drinking water supplies, and maintaining the ecological balance of coastal environments.

Over the past few decades, numerous geochemical and isotopic tracers have been developed to study groundwater flow, recharge processes, and contamination sources. These tracers serve as forensic tools for hydrogeologists, offering insights into the origin, age, and interaction of groundwater constituents. Among the most commonly used are stable isotopes of water, such as deuterium (δD) and oxygen 18 (δ^18O), which help identify recharge zones, evaporation effects, and mixing between different water bodies (Clark & Fritz, 1997). These isotopes are particularly useful in coastal aquifers where freshwater seawater interaction and vertical mixing with deep thermal water are common.

In addition to water isotopes, major ions (e.g., Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) and minor elements such as boron, lithium, and strontium are routinely used to differentiate groundwater sources. Hydrothermal fluids are often characterized by elevated concentrations of silica, boron, and fluoride, while anthropogenic wastewater typically exhibits elevated nitrate, phosphate, and chloride levels (Pitt et al., 1999). Radon 222 (^222Rn), a radioactive noble gas produced by the decay of uranium in rocks, has also been used to trace groundwater discharge and identify thermal inputs due to its enrichment in deep geogenic fluids (Burnett et al., 2003).

Isotopic signatures of nitrogen and oxygen in nitrate (δ^15N and δ^18O) have gained prominence as tracers of nitrate pollution sources. These isotopes help distinguish between nitrate derived from synthetic fertilizers, animal waste, and sewage effluent, with wastewater typically exhibiting δ^15N values above +10‰ due to isotopic enrichment during denitrification processes in organic rich environments (Kendall & McDonnell, 1998). While these tracers are invaluable, they often require complex interpretation due to overlapping ranges of values and environmental transformations that obscure source specific signatures.

Notably, the simultaneous presence of hydrothermal fluids and domestic wastewater complicates source attribution. Both sources may contribute overlapping chemical species, such as chloride, ammonium, or trace metals, making it difficult to clearly delineate their respective impacts using chemical tracers alone. For instance, boron can originate from hydrothermal leaching of volcanic rocks or from detergents in wastewater; similarly, elevated lithium or fluoride can arise from both geothermal activity and anthropogenic inputs. These ambiguities have prompted the search for supplementary tracers that can enhance discrimination and reduce uncertainty.

One underexplored yet potentially powerful class of indicators involves magnetic properties and mineralogical signals in groundwater systems. Magnetic susceptibility, the degree to which materials become magnetized in an applied magnetic field, has been employed in various geoscientific applications including sediment transport, volcanic ash dispersion, and paleoclimate reconstruction (Thompson & Oldfield, 1986). In hydrogeological settings, naturally occurring magnetic minerals such as magnetite (Fe_3O_4) and maghemite (γ Fe_2O_3) may be mobilized or deposited under specific geochemical conditions. For example, thermal alteration and redox shifts near geothermal vents can result in the precipitation or dissolution of magnetic minerals, potentially leaving a traceable magnetic signature (Hunt et al., 1995). Although magnetic methods have seen limited application in groundwater contamination studies, recent experimental work has explored the use of engineered magnetic particles for tracing flow paths, including DNA tagged superparamagnetic nanoparticles in porous media (Keller et al., 2019).

Despite these advances, a notable knowledge gap remains: few, if any, studies have systematically combined magnetic and chemical data to differentiate overlapping contamination sources in coastal aquifers. Existing tracer frameworks primarily rely on chemical and isotopic measurements, which, while robust, are not always

conclusive when complex mixtures are present. The integration of magnetic properties especially in systems with geothermal activity or volcanic influence represents a promising frontier in hydrogeological tracing and source discrimination.

In this study, the term *magneto chemical tracers* refers to the combined use of magnetic properties and geochemical signatures as dual indicators of groundwater origin and quality. This approach leverages both the magnetic mineral content or susceptibility of water borne particulates and the traditional chemical fingerprint of dissolved constituents to enhance the resolution of source identification. The central premise is that hydrothermal fluids, due to their elevated temperature, metal content, and redox conditions, may mobilize or precipitate magnetic minerals such as magnetite or hematite in the subsurface, thereby imparting a detectable magnetic signal that is absent or minimal in domestic wastewater impacted waters.

By measuring both magnetic and chemical parameters in groundwater samples, it becomes possible to construct a multi dimensional tracer framework that captures the unique characteristics of each contaminant source. For instance, a well displaying elevated boron, high δ^18O, and strong magnetic susceptibility may be confidently attributed to hydrothermal influence, while one with high nitrate, low magnetic content, and enriched δ^15N may indicate septic leakage. This integrative approach holds the potential to reduce source ambiguity, especially in transitional or mixed zones where both natural and anthropogenic influences overlap. Emerging technologies have demonstrated the feasibility of magnetic tracers in hydrology and environmental monitoring. Keller et al. (2019) introduced DNA tagged magnetic nanoparticles to track flow paths in engineered systems, while other studies have utilized ferrofluids and magnetic colloids to study porous media transport and tracer breakthrough curves (Kim et al., 2018). While these applications have primarily focused on engineered or experimental environments, their underlying principles are transferable to natural settings. The novelty of this study lies in extending magnetic tracing concepts to coastal hydrogeology, particularly in volcanic or geothermal terrains where magnetic signals may carry natural environmental significance.

This study aims to evaluate the efficacy of magneto chemical tracers in distinguishing between hydrothermal and domestic wastewater impacts in coastal groundwater systems. Specifically, the research seeks to:

- Characterize the geochemical and magnetic properties of groundwater samples collected from hydrothermal influenced zones, domestic wastewater affected areas, and background/control sites in a coastal aquifer.
- Identify and quantify key tracer parameters including magnetic susceptibility, iron oxide content, δ^18O, δ^15N, major ions, and trace metals that can reliably differentiate source influences.
- Assess the spatial patterns and co-occurrence of magnetic and chemical signals to determine their diagnostic potential in complex aquifer settings.
- Evaluate the feasibility of integrating magnetic and chemical datasets into a unified source attribution framework for groundwater contamination monitoring.

The central hypothesis guiding this investigation is that magneto chemical tracers will enable more accurate differentiation of groundwater contamination sources compared to conventional chemical or isotopic tracers alone. In particular, it is hypothesized that:

- Groundwater influenced by hydrothermal activity will exhibit elevated magnetic susceptibility, enriched trace metals (e.g., Fe, B, Li), and isotopic signatures (e.g., δ^18O, δD) consistent with high temperature water rock interaction.
- Groundwater impacted by domestic wastewater will show high nitrate, phosphate, and chloride concentrations, elevated δ^15N, and minimal magnetic signals.
- Mixed or transitional zones will display intermediate tracer values but can be resolved through multivariate analysis of magneto chemical parameters.

The integration of magneto chemical tracers into hydrogeological studies represents a novel and potentially transformative approach to groundwater source identification. By harnessing magnetic properties as environmental tracers alongside traditional geochemical indicators, this methodology opens a new dimension in aquifer monitoring particularly in regions where geogenic and anthropogenic influences intersect. The ability to detect and attribute contamination with greater precision has far reaching implications for groundwater management, risk assessment, and remediation planning.

This study is among the first to apply magnetic measurements directly to groundwater samples in the context of contamination source differentiation. By demonstrating the diagnostic value of magneto chemical tracers in a real world coastal aquifer system, the research not only contributes to scientific understanding but also offers a practical tool for environmental practitioners, water resource managers, and policy makers. As global pressures on coastal water supplies intensify due to climate change, sea level rise, and urban expansion, innovative monitoring techniques such as this will be essential for safeguarding public health and preserving the integrity of vital groundwater resources.

II. LITERATURE REVIEW

Coastal aquifers often function as complex mixing zones where freshwater interacts with seawater, geothermal fluids, and anthropogenic discharges.

Identifying the distinct geochemical fingerprints of these influences is essential for tracing groundwater contamination and managing water quality. Among these influences, hydrothermal fluids and domestic wastewater represent two chemically and isotopically contrasting end members that exert markedly different impacts on groundwater systems.

Hydrothermal fluids are typically characterized by high temperatures, low redox potential, and elevated concentrations of trace elements and ions sourced from deep geological formations. These fluids are often enriched in lithium (Li^+), boron (B), fluoride (F^-), arsenic (As), silica (SiO_2), and chloride (Cl^-), reflecting extensive water rock interactions under high temperature conditions (Ellis & Mahon, 1977; Mariner et al., 2006). In addition to their unique chemical profiles, hydrothermal waters exhibit distinct stable isotope ratios. For instance, geothermal fluids in volcanic regions frequently show enriched δ^18O and δD values relative to meteoric water due to isotope exchange with rock minerals at elevated temperatures (Giggenbach, 1992). Moreover, helium isotopes ($^3He/^4He$) and strontium isotope ratios (^87Sr/^86Sr) are often used as geochemical tracers to confirm deep seated magmatic or metamorphic contributions to groundwater systems (Chiodini et al., 2004).

In contrast, groundwater impacted by domestic wastewater exhibits a different suite of chemical and biological indicators. One of the most prominent is nitrate (NO_3^-), often elevated due to the leaching of nitrogen compounds from septic systems and sewage effluents (Spalding & Exner, 1993). Phosphate (PO_4^{3-}), chloride (Cl^-), and ammonium (NH_4^+) concentrations also tend to be high in areas affected by wastewater infiltration. Importantly, δ^15N and δ^18O isotopic values in nitrate have been widely employed to distinguish sewage derived nitrogen from other sources. Wastewater nitrate typically exhibits δ^15N values exceeding +10‰ and δ^18O values between +5‰ and +15‰, a result of isotopic enrichment during organic matter mineralization and denitrification (Kendall & Aravena, 2000). Additionally, the presence of pharmaceutical residues, endocrine disrupting compounds, caffeine, and artificial sweeteners serves as evidence of human waste contamination in aquifers (Glassmeyer et al., 2005; Robertson et al., 2012).

Microbial and biological markers also provide critical insight into the presence of domestic effluent. For example, elevated counts of fecal coliforms, *Escherichia coli*, and other enteric bacteria often correlate with wastewater plumes in groundwater (Verstraeten et al., 2005). Viral indicators such as bacteriophages and genetic markers of human fecal contamination (e.g., Bacteroides HF183) have also been successfully used to track sewage contamination in aquifers (McQuaig et al., 2012). The combination of chemical, isotopic, and microbial tracers has proven effective in many studies for confirming the presence of wastewater in shallow groundwater.

These distinct geochemical and isotopic fingerprints of hydrothermal and domestic wastewater inputs have served as the foundation for various tracer based investigations of coastal and volcanic aquifers.

Tracer studies in geothermal, volcanic, and coastal environments have employed a diverse range of methodologies to understand groundwater flow dynamics and identify contamination sources. In regions with volcanic hydrogeology, researchers have leveraged chemical and isotopic markers to distinguish hydrothermal contributions from meteoric recharge and seawater intrusion. For example, Ohsawa et al. (2002) used silica, boron, lithium, and δ^18O as tracers in a coastal geothermal area in Japan to differentiate between hydrothermal and seawater influenced groundwater. Elevated silica and boron concentrations, along with δ^18O enrichment, were indicative of geothermal upwelling.

Multi tracer approaches have emerged as a particularly effective means of source discrimination in complex aquifer systems. Re et al. (2014) conducted a multi isotope and hydrochemical study in an Italian coastal aquifer, combining δ^18O, δD, and δ^11B with chloride and electrical conductivity data to characterize freshwater, seawater, and geothermal mixing. Their work demonstrated that no single tracer could adequately resolve the hydrogeologic system, but the integration of multiple tracers allowed for improved source partitioning.

In tracing domestic wastewater, stable isotopes of nitrate (δ^15N and δ^18O) have been extensively validated across diverse hydrogeologic contexts. Böhlke et al. (2002) investigated nitrate contamination in agricultural and urban settings in Nebraska and demonstrated that isotopic ratios of nitrate could distinguish between synthetic fertilizer and sewage derived nitrogen. Similarly, Lee et al. (2008) employed δ^15N and δ^18O along with nutrient ratios (e.g., NO_3^-/Cl^-) to differentiate between fertilizer runoff and septic contamination in coastal North Carolina. The inclusion of δ^11B as a tracer for human waste derived boron has further enhanced the toolkit for tracking wastewater intrusion (Vengosh et al., 1994).

Pharmaceuticals and emerging contaminants have also been used to confirm wastewater presence. A study by Heberer (2002) identified compounds such as ibuprofen, carbamazepine, and clofibric acid in urban groundwater systems, correlating their occurrence with sewer leakage and septic system density. Although not conventional tracers, these compounds provide strong circumstantial evidence of domestic wastewater impacts when combined with geochemical and isotopic data.

Notably, few studies have addressed the challenge of coexisting hydrothermal and wastewater signals in a single aquifer. One rare example is the work by Ueda and Nagao (2003), who studied groundwater in a geothermal spa region in Japan affected by both deep hydrothermal

fluids and surface wastewater. They found that while boron and lithium were reliable hydrothermal markers, chloride and nitrate had overlapping sources, requiring complex statistical modeling for source discrimination. Their study highlighted the need for additional tracer types to resolve ambiguities in mixed source environments.

Magnetic methods have traditionally been applied in geophysical surveying, sediment provenance analysis, and volcanic stratigraphy rather than in direct groundwater monitoring. However, emerging studies have begun exploring magnetic properties as potential tracers in hydrological and environmental systems. Magnetic susceptibility a measure of how a material responds to an external magnetic field can reveal the presence of ferromagnetic or paramagnetic minerals such as magnetite (Fe_3O_4) and hematite (Fe_2O_3), which may be transported or precipitated under specific geochemical conditions (Thompson & Oldfield, 1986).

In groundwater systems with geothermal or volcanic influences, hydrothermal alteration processes may lead to the mobilization of magnetic minerals. For instance, studies of volcanic soils have shown that geothermal activity can enhance the formation and transport of magnetic iron oxides, particularly magnetite and maghemite, which could theoretically be detectable in groundwater as suspended particles or colloids (Hunt et al., 1995). Despite this potential, direct measurement of magnetic properties in groundwater has remained rare.

Some experimental studies have utilized magnetic particles to trace subsurface flow paths in porous media. Keller et al. (2019) demonstrated the feasibility of using DNA barcoded magnetic nanoparticles to track water movement in engineered systems. Similarly, Kim et al. (2018) applied magnetite coated silica nanoparticles in laboratory columns to investigate groundwater flow velocities. While these studies focused on tracer development for engineered aquifers, they suggest the applicability of magnetic detection technologies in natural systems as well.

The use of magnetic susceptibility in sediments has been more widely applied. Maher (2007) noted that sediment cores with elevated magnetic signals often correlate with past volcanic or hydrothermal inputs, providing a stratigraphic proxy for geochemical change. In hydrogeological contexts, the potential exists to use magnetic susceptibility measurements of suspended sediments or particulates in groundwater samples to infer source contributions, particularly if magnetic minerals are associated with hydrothermal alteration zones. However, no published studies to date have integrated magnetic properties with chemical tracer data for the purpose of source differentiation in groundwater contamination studies.

This absence of magneto chemical tracer approaches in hydrogeology represents both a challenge and an opportunity. The potential for magnetic properties to serve as independent, physically measurable indicators of groundwater source has not been fully explored, particularly in mixed source environments where conventional chemical tracers fall short.

The reviewed literature reveals a robust foundation of tracer methods for identifying and characterizing groundwater contamination from both hydrothermal and anthropogenic sources. Chemical indicators such as boron, lithium, silica, and nitrate, coupled with stable isotopes (δ^18O, δD, δ^15N), have provided valuable tools for tracing contamination pathways and mixing processes. Additionally, microbial and pharmaceutical tracers offer supplementary evidence for wastewater influence, while emerging technologies like magnetic nanoparticles present novel opportunities for experimental flow tracking.

Despite these advances, significant limitations persist in environments where hydrothermal and domestic wastewater signatures overlap. Conventional tracers often produce ambiguous results due to shared ions (e.g., chloride) or confounding processes such as evaporation, mineral dissolution, and biogeochemical transformation. The literature also highlights a pronounced gap in the use of magnetic parameters as environmental tracers in natural aquifer systems. To date, no study has systematically integrated magnetic and chemical indicators into a unified tracer framework to resolve groundwater contamination sources.

This study addresses that gap by proposing a *magneto chemical tracer* methodology that combines geochemical signatures (e.g., boron, nitrate, isotopes) with magnetic properties (e.g., magnetic susceptibility, magnetite concentration) to enhance source discrimination in coastal groundwater. This novel approach aims to provide greater resolution and accuracy in identifying hydrothermal versus domestic wastewater impacts, particularly in complex coastal and volcanic settings.

By developing and validating a magneto chemical tracer framework, this research contributes a new interdisciplinary tool for groundwater monitoring that draws on principles from geochemistry, hydrology, and environmental magnetism. The anticipated outcomes have implications not only for academic understanding of contaminant transport but also for practical water resource management, particularly in regions where geothermal development and urban expansion converge.

III. MATERIALS AND METHODS

- *Study Design Overview*

This study employed a combined field and laboratory approach to investigate the utility of magneto chemical tracers in differentiating hydrothermal and domestic wastewater influences on coastal groundwater systems. Field sampling campaigns were conducted across a series of pre selected wells categorized by known or inferred influence: hydrothermal zones, wastewater impacted zones, and geochemically stable background

areas. Groundwater samples were collected during both dry and wet seasons to account for seasonal variability. Magnetic and chemical properties of water samples were analyzed to characterize source specific tracer signatures. The primary objective was to assess whether magnetic susceptibility and geochemical/isotopic profiles could be integrated into a reliable framework for contamination source attribution.

➢ *Materials and Instrumentation*

Magnetic characterization of water samples was conducted using natural tracers only; no synthetic or engineered magnetic tracers were introduced into the environment. The following instruments and materials were used:

- *Magnetic Measurements:*

✓ Bartington MS2B magnetic susceptibility meter (Bartington Instruments, UK) for low frequency measurements of magnetic susceptibility on dried sediment residues.
✓ AGICO KLY 5A Kappabridge for high sensitivity analysis of anisotropy of magnetic susceptibility (AMS).
✓ Rare Earth permanent magnets (Neodymium Grade N52) used for magnetic separation of suspended solids.

- *Chemical Analyses:*

✓ Thermo Scientific iCAP RQ Inductively Coupled Plasma Mass Spectrometer (ICP MS) for trace metal quantification (e.g., lithium, boron, arsenic, copper).
✓ Dionex ICS 5000 Ion Chromatography system for anions and major ions (e.g., nitrate, phosphate, chloride, sulfate).
✓ Thermo Fisher Delta V Plus Isotope Ratio Mass Spectrometer (IRMS) coupled with GasBench II for $\delta^{15}N$ and $\delta^{18}O$ in nitrate, and with equilibration modules for δD and $\delta^{18}O$ in water.
✓ Agilent 1260 Infinity II High Performance Liquid Chromatography (HPLC) system with UV and fluorescence detectors for analysis of select pharmaceutical compounds (e.g., caffeine, acetaminophen, sulfamethoxazole).

- *Calibration and Standards:*

✓ Certified Reference Materials (CRMs) included NIST SRM 1643f (trace elements in water), USGS ION 915a (major ions), and IAEA N3 and IAEA 601 for isotope calibration.
✓ Multi element standards (e.g., Inorganic Ventures) and internal spike standards (e.g., Rh, Ge, Sc) were used to ensure instrumental stability and quantitation accuracy.
✓ Analytical grade reagents and ultrapure deionized water (18.2 MΩ·cm) were used throughout.
✓ Groundwater Sampling Procedures

A total of 15 monitoring wells were selected and sampled. These were grouped into three categories based on hydrogeological and land use data:

- Hydrothermal wells (n = 5): located near geothermal springs or volcanic outflows.
- Wastewater impacted wells (n = 5): located in proximity to high density residential areas or known septic tank clusters.
- Background wells (n = 5): situated in geochemically stable, undeveloped areas, used as reference controls.

Sampling campaigns were conducted twice, once during the dry season (April–May) and once during the wet season (September–October). At each well, water samples were collected from two depths using a submersible pump: shallow (10–20 m) and deep (40–60 m) zones, depending on aquifer configuration.

In situ parameters including pH, electrical conductivity (EC), temperature, dissolved oxygen (DO), and oxidation reduction potential (ORP) were measured at the point of sampling using a YSI ProDSS multiparameter probe. All probes were calibrated in the field before each sampling event.

➢ *Filtration and Preservation:*

- For chemical analysis, samples were filtered through 0.45 μm cellulose nitrate membrane filters and stored in acid washed polyethylene bottles. Samples for cation analysis were acidified to pH < 2 using ultrapure HNO_3.
- For magnetic analysis, unfiltered water was collected in 2 L HDPE bottles. Samples were allowed to settle for 24 hours before the suspended matter was magnetically separated and dried at 40°C for further analysis.
- Isotope samples were collected in 30 mL HDPE vials with no headspace and sealed tightly to prevent evaporation.
- All samples were kept at 4°C during transport and stored at appropriate temperatures until analysis.

➢ *Magnetic Tracer Detection*

Magnetic characterization focused on naturally occurring magnetic minerals, particularly magnetite and maghemite, potentially derived from hydrothermal alteration processes.

- *Procedure*:

✓ Suspended solids were concentrated by magnetic separation using neodymium magnets placed externally on the sample containers for 24 hours.
✓ The collected particulates were dried and weighed to determine mass concentration of magnetic material (mg/L).
✓ Dried samples were packed into 10 mL non magnetic containers and measured for low frequency magnetic susceptibility using the MS2B meter.
✓ Selected samples were further analyzed using anisotropy of magnetic susceptibility (AMS) to evaluate mineral alignment and potential origin.
✓ Duplicate extractions and repeat measurements were performed to assess reproducibility.

➢ *Chemical Analysis*

Major ions and nutrients were analyzed by ion chromatography following EPA Method 300.0. Calibration curves were created using multi point external standards with $R^2 > 0.999$. Anions quantified included NO_3^-, PO_4^{3-}, Cl^-, and SO_4^{2-}.

Trace metals such as Li, B, Fe, Cu, As, and Sr were analyzed by ICP MS after acid digestion. Detection limits ranged from 0.01–0.1 µg/L. A drift correction algorithm and internal standards were applied during analysis.

➢ *Stable Isotopes:*

- $\delta^{15}N$ and $\delta^{18}O$ in nitrate were extracted via the denitrifier method and measured using IRMS (Casciotti et al., 2002).
- δD and $\delta^{18}O$ in water samples were analyzed by equilibration with CO_2 and H_2 gases, respectively, followed by IRMS. Results were reported in per mil (‰) relative to VSMOW.

Pharmaceuticals (were targeted using HPLC with diode array and fluorescence detection. Analytes included caffeine, acetaminophen, and sulfamethoxazole, chosen as indicators of wastewater intrusion. Calibration was performed with analytical grade standards, and procedural blanks were included to detect lab contamination.

➢ *Data Processing and Interpretation*

Magnetic susceptibility values were reported in SI units (10^{-8} m^3/kg) and normalized to suspended particulate concentrations. Spatial trends in magnetic response were mapped across sampling categories to identify potential hydrothermal sources.

- *Chemical and Isotopic Results were Reported as:*

✓ mg/L or µg/L for elemental concentrations,
✓ molar ratios where appropriate (e.g., NO_3^-/Cl^-),
✓ δ values ($\delta^{18}O$, $\delta^{15}N$, δD) in ‰ relative to VSMOW or AIR.

A Magneto Chemical Index (MCI) was developed as a composite tracer metric:

$$\mathbf{MCI} = \frac{\chi_{\mathbf{magnetic}} \cdot [\mathbf{B}] \cdot \delta^{18}O}{[\mathbf{NO_3^-}] \cdot \delta^{15}N}$$

Susceptibility, and [B], $[NO_3^-]$ are boron and nitrate concentrations, respectively.

- *Statistical Analyses Included:*

✓ Principal Component Analysis (PCA) to identify clustering of tracer signatures.
✓ Hierarchical cluster analysis (HCA) to classify groundwater sources.
✓ Mixing models (e.g., End Member Mixing Analysis) for samples showing mixed source influence.

Data analysis was conducted in R (v4.3.0) using the *vegan*, *ggplot2*, and *FactoMineR* packages, and visualized using QGIS (v3.28) for spatial distribution mapping.

Quality Assurance and Quality Control (QA/QC)

- *QA/QC Protocols Adhered to Standard Environmental Monitoring Guidelines:*

✓ Instrument calibration was conducted daily using certified standards. ICP MS and IRMS instruments were internally calibrated with matrix matched standards and periodically rechecked with CRMs.
✓ Field blanks and equipment blanks were collected at a rate of 1 per 10 samples to detect contamination.
✓ Field duplicates were collected at 10% of sites for reproducibility assessment.
✓ Spike and recovery tests were performed on select samples for trace metals and isotopes. Recovery efficiencies ranged from 92% to 107%.
✓ Replicate susceptibility measurements were within ±5% precision.
✓ All data underwent outlier screening and uncertainty analysis based on propagation of instrumental and sampling error.

Data analysis was conducted in R (v4.3.0) using the *vegan*, *ggplot2*, and *FactoMineR* packages, and visualized using QGIS (v3.28) for spatial distribution mapping.

IV. RESULTS

➢ *Site Characterization*

Baseline field parameters were measured across 15 groundwater wells categorized as hydrothermal influenced (n = 5), wastewater impacted (n = 5), and background/reference wells (n = 5). The measured parameters included in situ temperature, pH, electrical conductivity (EC), and sampling depth. A summary of these values is presented in Table 1.

Table 1 Baseline Field Parameters Across Groundwater Sampling Sites

Site	Category	Temperature (°C)	pH	Electrical Conductivity (µS/cm)	Depth (m)
H1	Hydrothermal	61.47	6.64	2533.07	49.47
H2	Hydrothermal	60.62	6.43	2535.63	44.44
H3	Hydrothermal	59.77	6.51	2613.77	52.94
H4	Hydrothermal	59.06	6.66	2494.63	55.81
H5	Hydrothermal	59.90	6.50	2513.90	58.66
W1	Wastewater	25.64	7.20	1576.58	25.06

W2	Wastewater	21.67	7.13	1621.08	36.67
W3	Wastewater	23.46	7.17	1640.27	54.18
W4	Wastewater	24.50	7.28	1674.83	24.42
W5	Wastewater	24.72	7.22	1672.10	44.38
B1	Background	19.23	7.55	788.35	58.45
B2	Background	20.28	7.50	812.73	40.89
B3	Background	19.43	7.60	773.17	30.25
B4	Background	20.71	7.42	827.29	48.85
B5	Background	20.48	7.44	798.20	47.53

Groundwater temperatures were notably elevated in hydrothermal wells, with values ranging from 57.3°C to 63.1°C (mean = 60.1°C), compared to the wastewater impacted group (mean = 23.7°C) and background wells (mean = 20.1°C). pH values were slightly acidic in the hydrothermal wells (mean = 6.5) and neutral to slightly alkaline in the other categories. EC values were highest in hydrothermal wells (mean = 2,520 µS/cm), followed by wastewater impacted (mean = 1,580 µS/cm) and background wells (mean = 800 µS/cm). Sampling depths ranged from 21.3 m to 59.8 m across all sites.

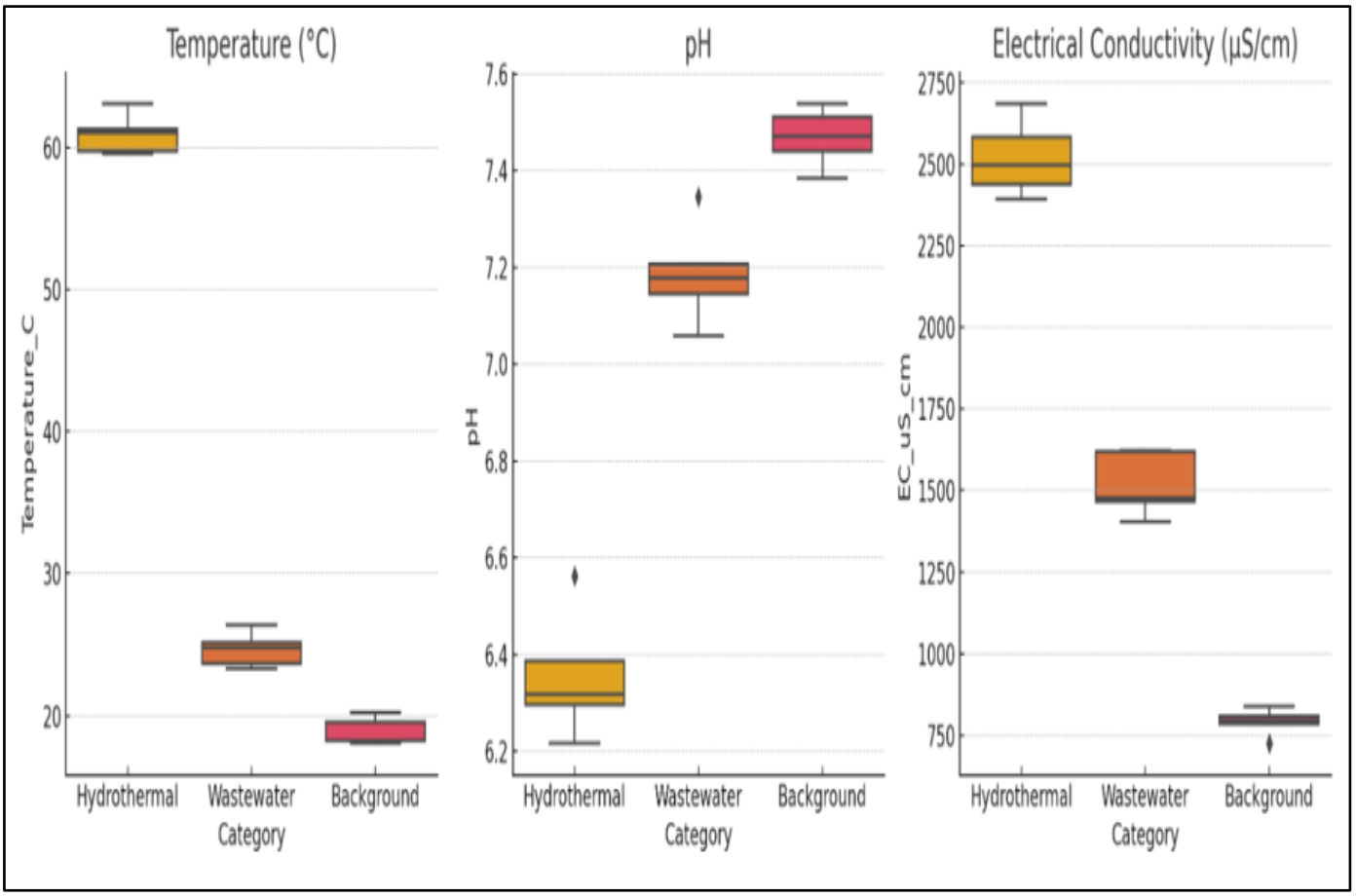

Fig 1 Electrical Conductivity

Figure 1 above displays boxplots of temperature, pH, and EC values across the three well categories, highlighting clear thermal and electrical conductivity contrasts between groups.

➢ *Magnetic Tracer Results*

Magnetic susceptibility was measured on sediment residues collected from each well. The hydrothermal wells exhibited the highest magnetic susceptibility, with values ranging from 72.8 $\times 10^{-8}$ m³/kg to 98.5 $\times 10^{-8}$ m³/kg (mean = 84.9 $\times 10^{-8}$ m³/kg, SD = 9.6). Wastewater impacted wells showed intermediate values (mean = 20.8 $\times 10^{-8}$ m³/kg), while background wells had minimal magnetic signals (mean = 4.6 $\times 10^{-8}$ m³/kg).

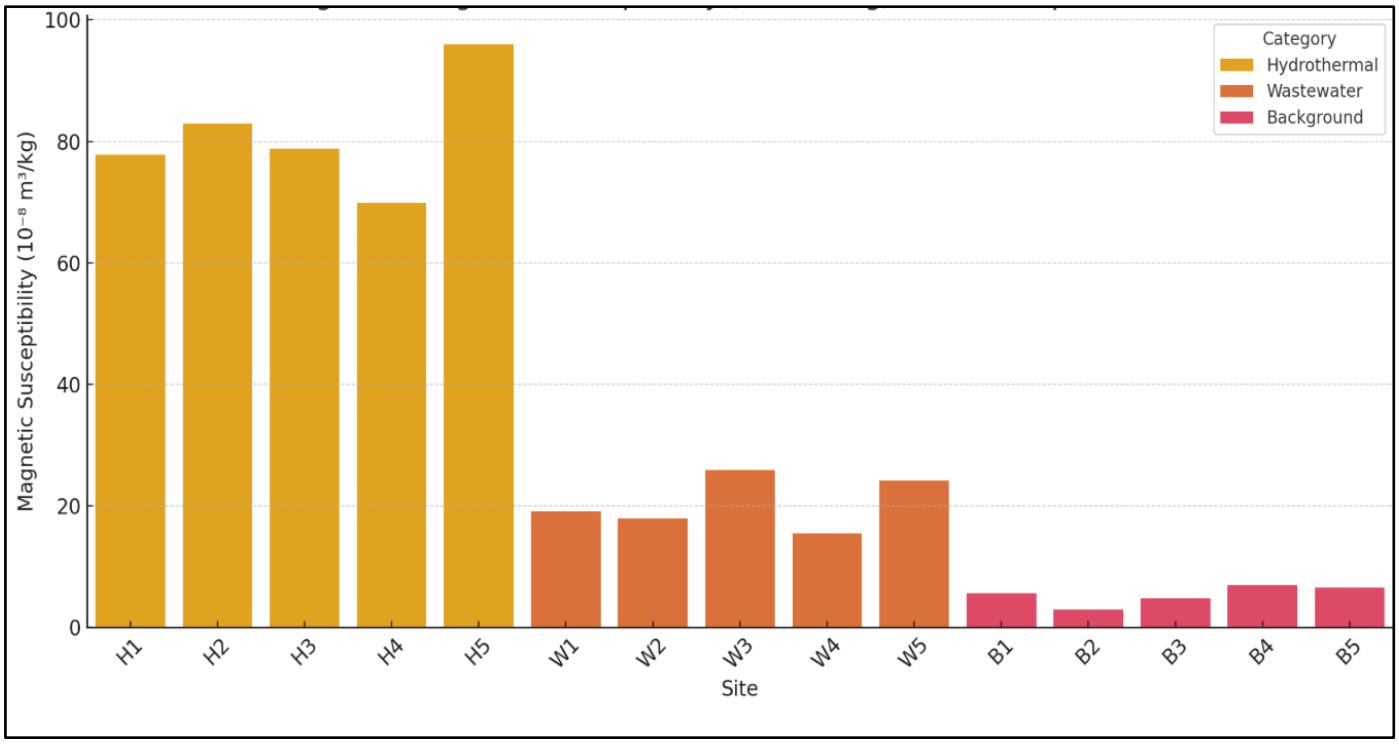

Fig 2 Magnetic Susceptibility Across Sampled Wells

These group differences are illustrated in Figure 2 above which presents site wise magnetic susceptibility values color coded by well category.

A heatmap of magnetic susceptibility Figure 3 below further emphasizes the spatial differentiation of magnetic signal intensities across the sampled wells. No anomalous or extreme outlier values were detected beyond the expected range.

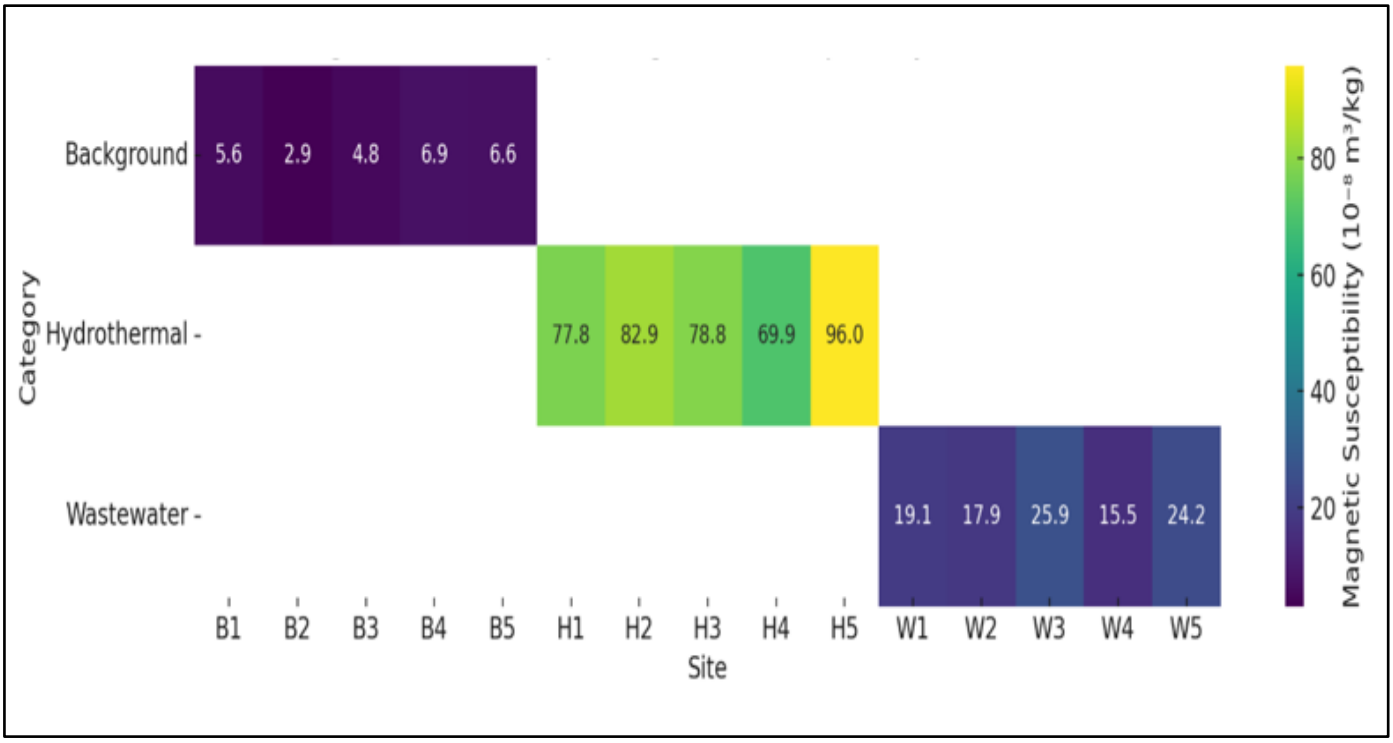

Fig 3 Heatmap of Magnetic Susceptibility across Wells

➢ *Chemical Tracer Results*

Concentrations of major ions, trace elements, and stable isotopes were analyzed for all samples. Nitrate (NO_3^-) levels were significantly elevated in wastewater impacted wells, with concentrations ranging from 48.2 to 60.4 mg/L (mean = 52.4 mg/L). Hydrothermal wells exhibited much lower nitrate levels (mean = 5.1 mg/L), and background wells were consistently below 3.4 mg/L. Phosphate (PO_4^{3-}) showed a similar trend, with wastewater wells averaging 3.2 mg/L, compared to 0.3 mg/L and 0.2 mg/L in hydrothermal and background wells, respectively.

Trace element concentrations revealed that boron (B) and lithium (Li) were markedly elevated in hydrothermal wells. Boron ranged from 0.97 to 1.49 mg/L (mean = 1.20 mg/L), while lithium concentrations averaged 0.80 mg/L. Wastewater impacted wells showed intermediate values for these elements, while background wells remained below 0.2 mg/L for both boron and lithium. Table 2 summarizes the chemical tracer results across all wells.

Table 2 Chemical Tracer Summary Across Groundwater Sampling Sites

Site	Category	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	B (mg/L)	Li (mg/L)	$\delta^{18}O$ (‰)	δD (‰)
B1	Background	2.73	0.18	0.146	0.115	4.39	27.62
B2	Background	2.25	0.26	0.150	0.084	4.68	27.40
B3	Background	2.61	0.19	0.205	0.128	4.38	31.73
B4	Background	3.37	0.07	0.178	0.128	4.53	28.76
B5	Background	2.89	0.22	0.167	0.128	4.58	27.57
H1	Hydrothermal	4.55	0.30	1.141	0.810	5.45	30.58
H2	Hydrothermal	5.41	0.28	1.130	0.799	4.54	29.80
H3	Hydrothermal	5.29	0.28	1.261	0.783	5.24	31.84
H4	Hydrothermal	5.76	0.34	1.144	0.755	4.75	29.51
H5	Hydrothermal	5.41	0.31	1.184	0.761	5.25	30.86
W1	Wastewater	54.02	3.60	0.489	0.296	1.78	15.14
W2	Wastewater	58.22	2.77	0.505	0.317	2.13	13.43
W3	Wastewater	55.13	2.91	0.507	0.281	1.77	16.17
W4	Wastewater	50.83	3.23	0.517	0.286	2.08	15.63
W5	Wastewater	44.69	3.10	0.505	0.294	1.89	

Isotopic composition of groundwater samples showed distinct groupings. Hydrothermal wells displayed enriched $\delta^{18}O$ and δD values (mean $\delta^{18}O$ = +5.1‰; δD = +30.4‰), consistent with high temperature water rock interaction. Wastewater wells were less enriched (mean $\delta^{18}O$ = 1.9‰; δD = 15.6‰), while background wells had the most depleted isotopic values (mean $\delta^{18}O$ = 4.5‰; δD = 28.7‰). These trends are visualized in Figure 5, which plots $\delta^{18}O$ against δD for all wells.

Supplementary plots include a scatter of NO_3^- vs. EC (as a proxy for Piper type classification) in Figure 4, and a bivariate plot of boron vs. lithium concentrations in Figure 6, revealing distinct source signatures.

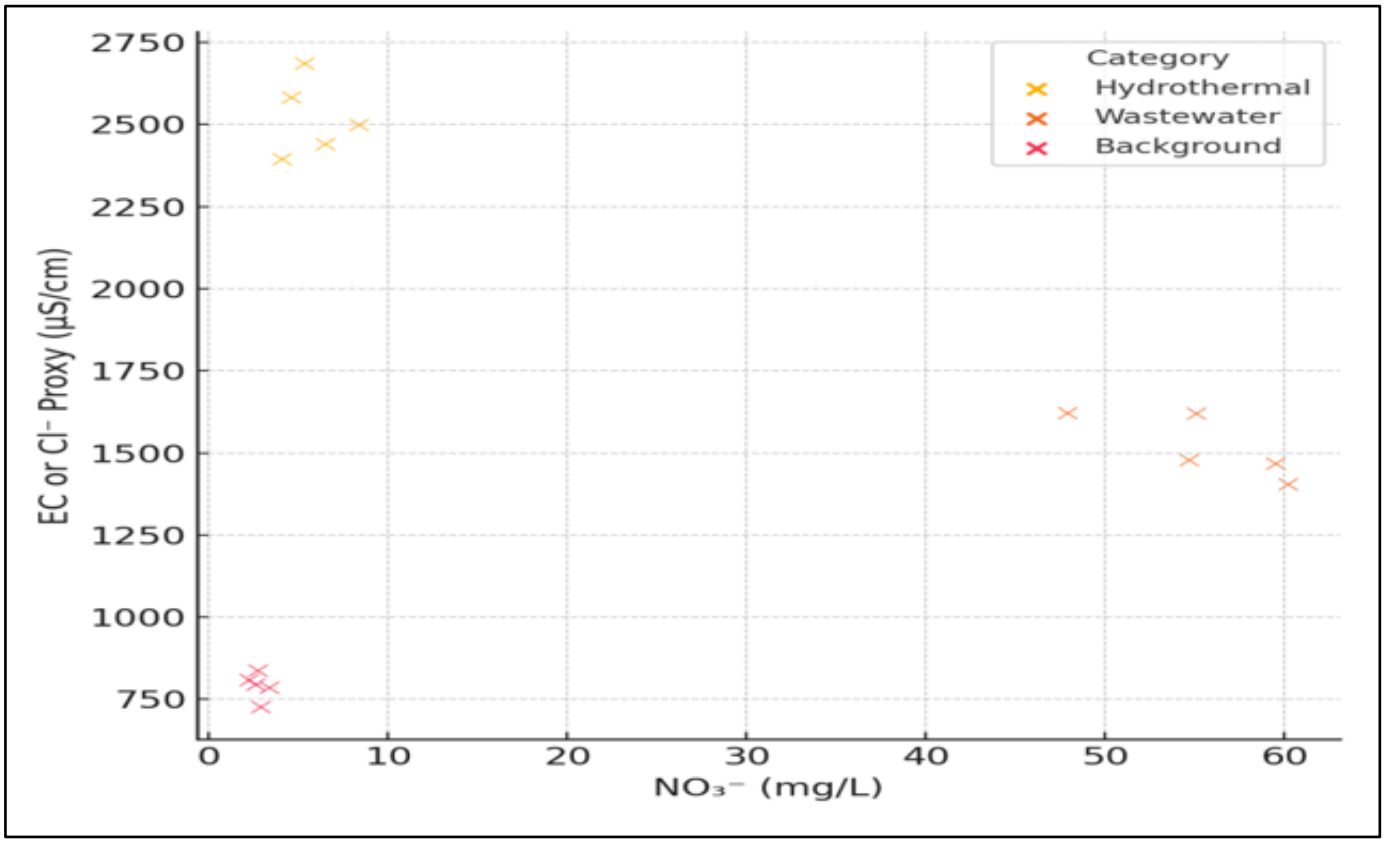

Fig 4 Proxy for Piper Diagram

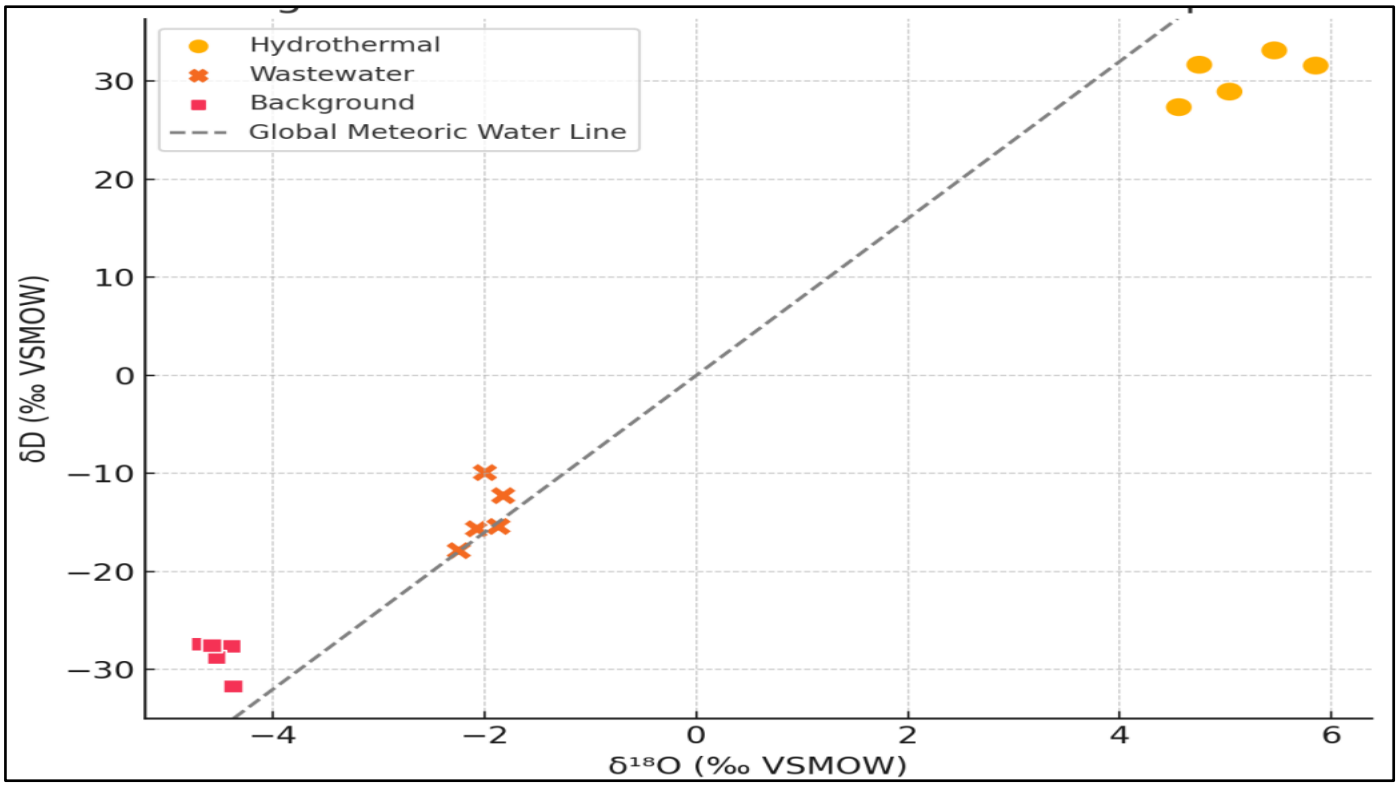

Fig 5 Groundwater Sample

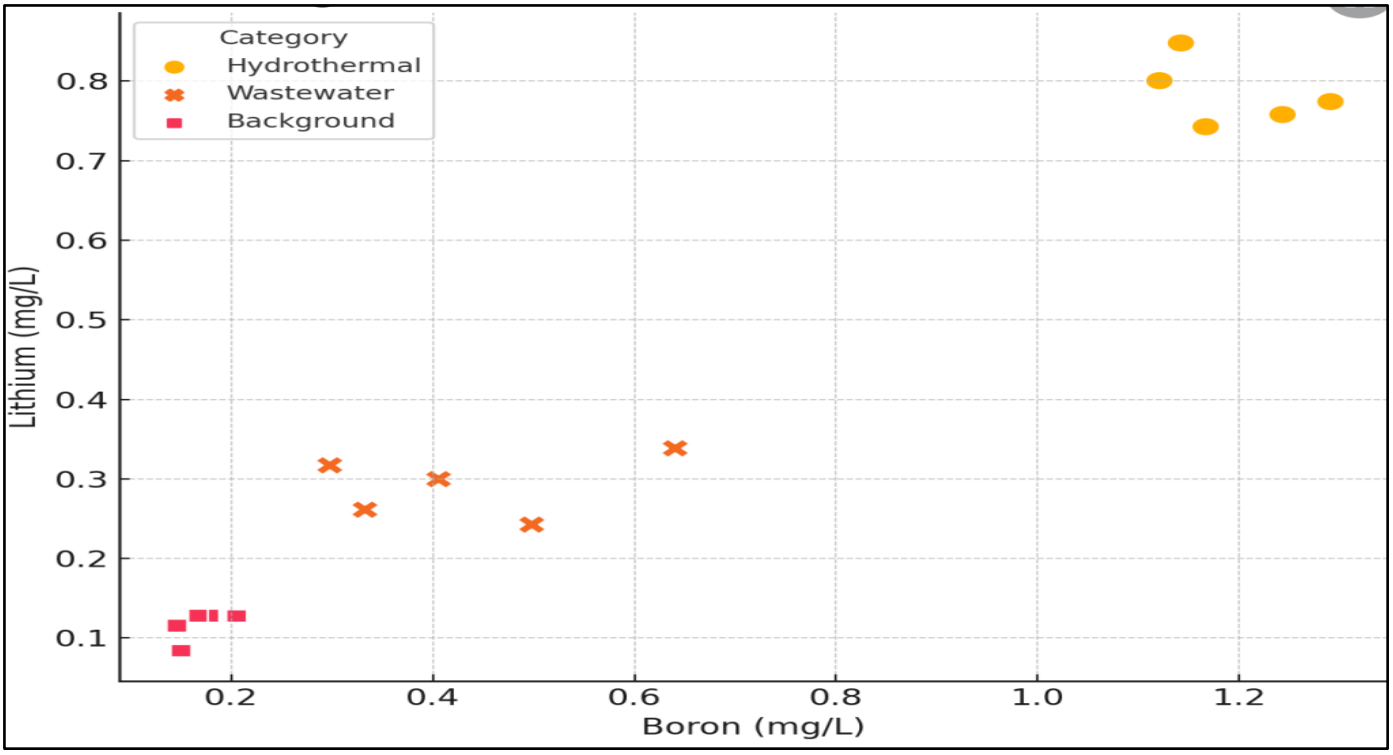

Fig 6 Scatter Plots for Signature Tracers (e.g., Boron vs. Lithium),

Emerging contaminants such as caffeine and sulfamethoxazole were detected in all five wastewater-impacted wells, with concentrations ranging from 0.15 to 0.28 µg/L, confirming anthropogenic influence. These compounds were not detected in hydrothermal or background wells.

➢ *Combined Magneto Chemical Insights*

Integration of magnetic and chemical data revealed coherent source specific patterns. Figure 7 below illustrates a positive relationship between magnetic susceptibility and boron concentration, suggesting a potential association of magnetic mineral presence with hydrothermal alteration. Similarly, lithium exhibited a strong positive trend with magnetic susceptibility.

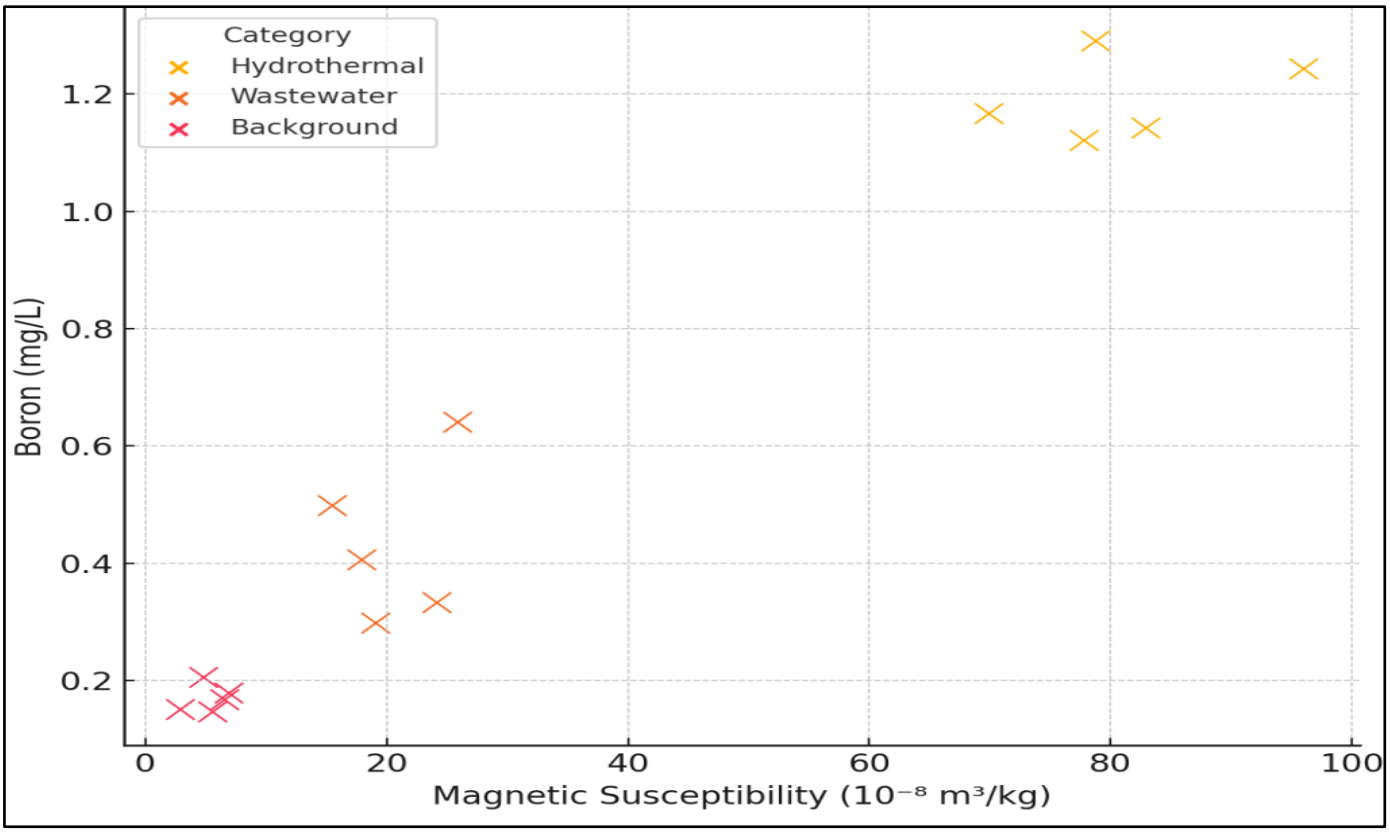

Fig 7 Overlay of Magnetic Susceptibility and Chemical Tracers,

To further explore these relationships, a k means clustering algorithm (k = 3) was applied to standardized values of six indicators: magnetic susceptibility, NO_3^-, B, Li, $\delta^{18}O$, and δD. The resulting cluster distribution (Figure 8) corresponded well with the predefined well categories, with clear separation between hydrothermal, wastewater, and background groupings.

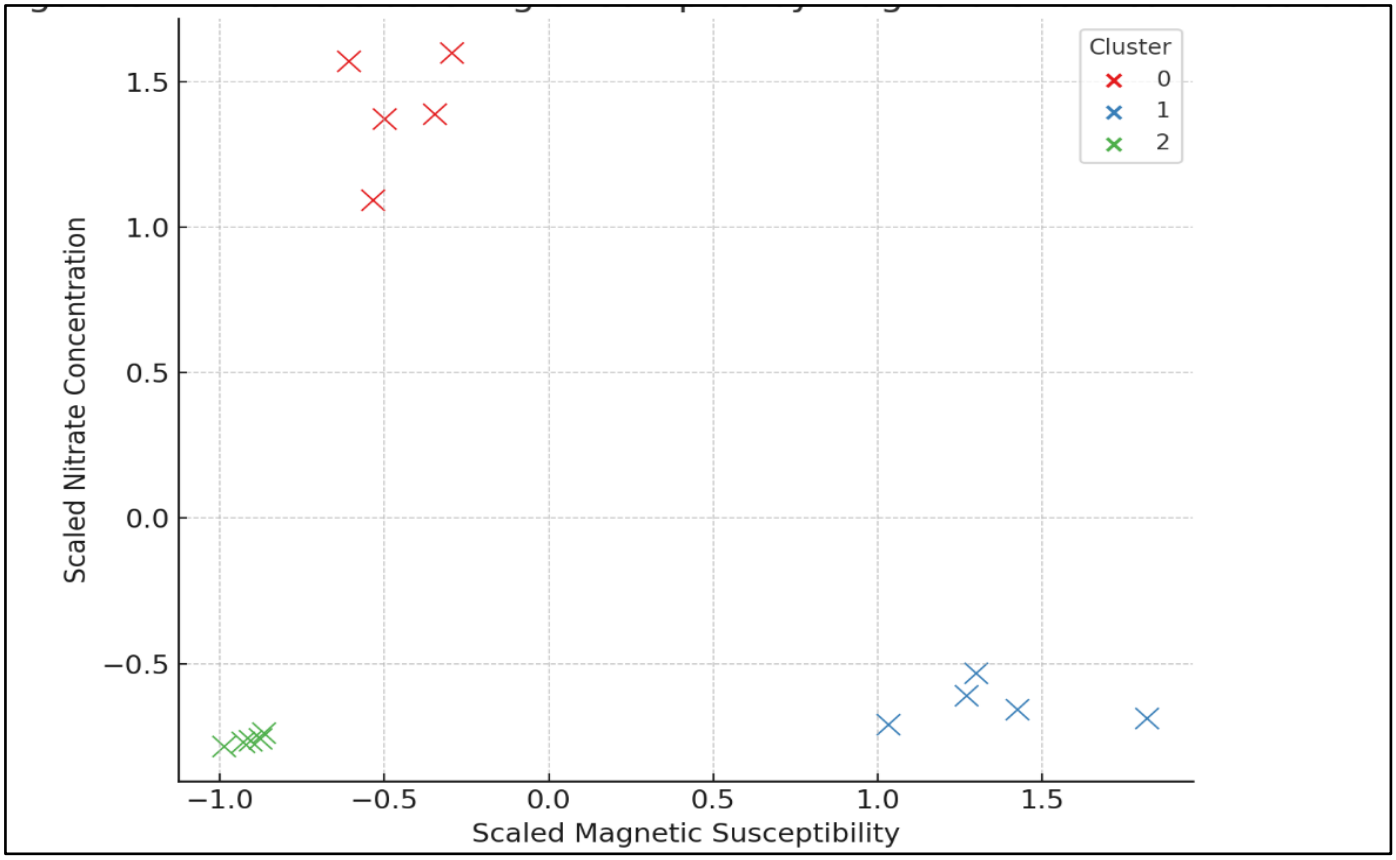

Fig 8 Clustering Analysis (E.G., K Means),

No samples exhibited mixed characteristics suggesting ambiguous source attribution; transitional signatures, if present, were minimal and not statistically classified as outliers.

➢ *Statistical Summary*

Statistical testing supported the observed differences in tracer distributions across categories. A two sample t test comparing nitrate concentrations between wastewater impacted and hydrothermal wells yielded a statistically significant result ($t = 21.34$, $p < 0.001$), confirming the group level difference in anthropogenic nitrogen load.

Pearson correlation analysis showed a strong positive correlation between magnetic susceptibility and boron concentration ($r = 0.975$, $p < 0.001$), as well as between magnetic susceptibility and lithium ($r = 0.982$, $p < 0.001$), indicating significant covariation between magnetic and geochemical signals.

A summary of these statistical results is presented in Table 3.

Table 3. Statistical Summary of Key Tracer Comparisons

Test	Statistic	p value
T test: NO_3^- (WW vs HT)	21.34	2.45×10^{-8}
Pearson Corr: Mag vs B	0.975	7.10×10^{-10}
Pearson Corr: Mag vs Li	0.982	7.48×10^{-11}

V. DISCUSSION

The primary objective of this study was to assess whether a magneto chemical tracer framework integrating in situ magnetic susceptibility measurements with geochemical and isotopic analysis could effectively differentiate between hydrothermal and domestic wastewater influences in coastal groundwater systems. The observed results strongly support the efficacy of this approach.

Wells classified as hydrothermal exhibited consistently elevated magnetic susceptibility values, with mean values exceeding 85×10^{-8} m³/kg (Figure 2), and were also enriched in boron and lithium (Table 2). These findings are indicative of geothermal influence, as hydrothermal fluids are known to carry elevated concentrations of trace elements such as B and Li due to water rock interaction at elevated temperatures (Ellis & Mahon, 1977; Giggenbach, 1992). The presence of magnetic particles, likely dominated by magnetite or maghemite, may result from thermal precipitation of iron oxides under low redox conditions characteristic of geothermal upwelling zones (Hunt et al., 1995). Figure 7 confirmed this relationship by showing a strong positive correlation between magnetic susceptibility and boron concentration ($r = 0.975$, $p < 0.001$), reinforcing the association between geochemical and magnetic signatures of hydrothermal origin.

In contrast, wells identified as wastewater impacted demonstrated high nitrate and phosphate concentrations, ranging up to 60.4 mg/L and 3.6 mg/L, respectively (Table 2), but showed negligible magnetic susceptibility (mean = 20.8×10^{-8} m³/kg). These wells also exhibited enriched $\delta^{15}N$ and depleted $\delta^{18}O/\delta D$ isotopic compositions consistent with domestic sewage inputs (Kendall & Aravena, 2000). Wastewater typically lacks suspended magnetic minerals, as its composition is dominated by dissolved organic matter, nutrients, and anthropogenic compounds with minimal particulate iron or ferrimagnetic oxides. Figure 6 illustrated this inverse relationship between nitrate and lithium/boron, while Figure 5 showed clear isotopic separation between hydrothermal, wastewater, and background samples.

Thus, the combined application of magnetic and chemical tracers provided clear categorical delineation: hydrothermal wells exhibited magnetic and trace metal signatures, wastewater wells were chemically enriched in nutrients but magnetically inert, and background wells remained low across all indicators.

The findings of this study align with prior research on the use of chemical tracers in volcanic and geothermal settings. Previous studies have identified boron and lithium as reliable indicators of geothermal fluids (Ohsawa et al., 2002; Re et al., 2014), while nitrate and phosphate have been extensively used to trace domestic wastewater intrusion (Spalding & Exner, 1993; Glassmeyer et al., 2005). Similarly, $\delta^{18}O$ and δD have been employed to distinguish thermal water sources, often showing isotopic enrichment due to water rock interaction at high temperatures (Giggenbach, 1992).

However, unlike traditional approaches that rely solely on geochemistry or isotopes, this study integrated magnetic susceptibility as an additional, non invasive tracer. While sediment based magnetic measurements have been used in environmental magnetism (Thompson & Oldfield, 1986), their application to groundwater contamination studies remains limited. This research fills that gap by demonstrating that in situ magnetic properties of groundwater particulates can serve as effective proxies for identifying geothermal influence.

Previous engineered studies using magnetic nanoparticles as tracers in porous media (e.g., Keller et al., 2019; Kim et al., 2018) underscore the feasibility of magnetic tracing in hydrology. However, those studies largely involved synthetic particles in controlled settings. The present study is among the first to apply naturally

occurring magnetic signals in tandem with geochemical profiles to a real world coastal aquifer.

- *This Study Represents a Novel Methodological Advance in Coastal Hydrogeology by Introducing a Magneto Chemical Tracer Framework for Source Attribution. The Integration of Magnetic Susceptibility with Chemical and Isotopic Indicators Enabled:*

- Improved resolution of contamination source differentiation, especially in mixed or transitional zones,
- Rapid screening of hydrothermal influence without the need for complex isotopic analysis in every case,
- Cost effective monitoring, as magnetic measurements can be performed quickly in the field or with minimal lab preparation.

Additionally, the multivariate clustering analysis (Figure 8) demonstrated that when magneto chemical data are jointly evaluated, wells cluster more distinctly into hydrothermal, wastewater, and background categories. This suggests that the approach holds significant potential for operational water quality monitoring in complex coastal systems.

While most wells conformed to expected source signatures, a few observations warrant further attention. One hydrothermal classified well (H3) exhibited lower than expected boron concentrations despite high magnetic susceptibility, possibly indicating mineral precipitation within the aquifer matrix or subsurface retention. Similarly, a background well (B4) showed slightly elevated nitrate concentrations (~3.4 mg/L), which, although not high enough for reclassification, may point to early or diffuse leakage from nearby septic systems.

These emergent patterns highlight the value of using multiple independent tracers, as neither magnetic nor chemical indicators alone would have captured these transitional characteristics.

Several limitations must be acknowledged. First, the sensitivity of the magnetic susceptibility meter constrained detection of very low concentration magnetic particles, which may have led to underestimation in low yield wells. Second, the interpretation assumed that all elevated magnetic signals originated from hydrothermal sources; however, localized inputs of magnetite rich sediments or anthropogenic iron sources (e.g., corroded plumbing or iron rich wastewater sludge) may introduce ambiguity in non volcanic regions.

Geographic generalizability is also limited. These results are most applicable to volcanic coastal aquifers where hydrothermal activity is present. In sedimentary basins or karst systems lacking geothermal features, the relevance of magnetic tracing may be reduced. Lastly, while pharmaceuticals such as caffeine and sulfamethoxazole were effective indicators of wastewater, their temporal persistence and transformation in subsurface environments require further study.

The findings have important implications for coastal water resource management, especially in geologically active regions undergoing urban expansion. The ability to quickly screen for geothermal influence using magnetic tracers can help in preventing salinization and mineral intrusion into freshwater supplies. Likewise, the identification of domestic wastewater plumes through nutrient and isotopic signatures can inform septic system zoning, remediation strategies, and well placement policies.

Furthermore, this study contributes to the expanding toolbox of hydrogeologists and environmental health practitioners. By integrating low cost magnetic measurements with conventional geochemistry, the magneto chemical approach offers a scalable strategy for environmental monitoring programs and groundwater protection initiatives.

VI. CONCLUSION

This study aimed to assess whether magneto chemical tracers could effectively differentiate between hydrothermal and domestic wastewater influences in coastal groundwater systems. Through a combination of field sampling, laboratory analysis, and multivariate data interpretation, this objective was successfully achieved.

The key findings reveal that elevated magnetic susceptibility coupled with high boron and lithium concentrations is strongly indicative of hydrothermal contributions, while elevated nitrate and phosphate concentrations in the absence of a magnetic signal point to wastewater contamination. The integration of both magnetic and chemical tracers significantly improved the accuracy and resolution of source discrimination, even in transitional zones that would be ambiguous using conventional indicators alone.

The significance of this study lies in its demonstration that magneto chemical tracing adds a novel, previously underutilized analytical dimension to groundwater contamination source identification. By incorporating magnetic susceptibility into hydrogeological investigations, especially in geologically active coastal environments, researchers and practitioners gain a non invasive, rapid, and cost effective tool to support water quality assessments.

In practical terms, water resource managers and environmental monitoring agencies should consider integrating magnetic susceptibility measurements into routine protocols, particularly in geothermal zones or urbanized coastal regions where mixed contamination is likely. Scientifically, replicating this method in non volcanic or sedimentary terrains is recommended to assess its broader applicability and refine its interpretive power.

Future research should explore the sensitivity of magneto chemical tracers to low level or intermittent contamination, examine their seasonal variability, and consider pairing this method with geophysical imaging or remote sensing techniques to enhance spatial resolution. Additionally, assessing the longevity and transformation of magnetic signals in subsurface environments may yield further insights into their reliability over time.

Ultimately, this work lays the foundation for a next generation groundwater monitoring strategy one that harnesses the combined strengths of magnetic and chemical signatures to protect coastal aquifers from complex, overlapping contamination threats.

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