International Journal of Scientific Research and Modern Technology (IJSRMT) ijsrmt.com
Volume 3, Issue 12, 2024
DOI: https://doi.org/10.38124/ijsrmt.v3i12.725

Integrated Magnetic and Chemical Tracers for Monitoring Subsurface Contaminant Transport in Hydrothermally Altered and Wastewater Impacted Coastal Environments

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Publication date 2024/12/28

Abstract

Coastal environments impacted by hydrothermal alteration and anthropogenic wastewater intrusion face complex challenges in monitoring subsurface contaminant transport due to dynamic redox gradients, fluid mixing, and heterogeneous sediment properties. This review explores the integrated application of magnetic and chemical tracers as a powerful approach to understanding the sources, movement, and transformation of contaminants such as heavy metals, nutrients, and pharmaceuticals in these systems. Magnetic tracers including magnetite and greigite serve as indicators of redox conditions and sedimentary processes, while chemical tracers such as rare earth elements, stable and radiogenic isotopes, major ions, and contaminants of emerging concern provide high resolution information on contaminant sources and biogeochemical behavior. The review examines tracer detection methods, transport mechanisms, and reactivity, emphasizing the complementary nature of magnetic and chemical signatures in delineating contaminant plumes. Through illustrative case studies, the utility of this integrated framework is demonstrated in diverse coastal contexts, including estuaries, wastewater impacted aquifers, and hydrothermally influenced sediments. The findings highlight the value of combining particulate and dissolved phase tracers for environmental forensics, remediation monitoring, and long term water quality assessment. The review concludes by identifying key research opportunities in tracer based environmental monitoring, including the development of portable detection tools, machine learning integration, and the establishment of standardized tracer libraries. This synthesis reinforces the importance of interdisciplinary approaches for managing contaminant transport in vulnerable coastal ecosystems.

***Keywords**: Magnetic Tracers, Chemical Tracers, Coastal Groundwater, Contaminant Transport, Magnetite, Greigite, Rare Earth Elements, Isotopes, Wastewater Monitoring.*

I. INTRODUCTION

Coastal environments represent dynamic and complex hydrological systems where land based inputs, oceanic forces, and subsurface processes interact in multifaceted ways. Among the most pressing concerns for these vulnerable zones is the contamination of groundwater and sediments from both natural geogenic sources and anthropogenic pollution. Two dominant drivers of such contamination are hydrothermal alteration in which geothermal fluids mobilize metals and alter geochemistry and wastewater intrusion, often characterized by elevated nutrient and pharmaceutical loads from domestic, industrial, and agricultural effluents (Fetter, 2018; Gosselin et al., 2007). The subsurface transport of these contaminants is difficult to monitor and predict due to hidden flow paths, heterogeneous permeability structures, and complex geochemical transformations. In response to this challenge, the scientific community has increasingly turned to the use of environmental tracers, particularly those integrating both magnetic and chemical properties, to track and understand contaminant movement across such dynamic coastal zones (Maher & Thompson, 1999; Liu et al., 2018).

Environmental tracers are substances either naturally occurring or introduced whose spatial and temporal behavior provides insights into hydrological or geochemical processes. In subsurface environments, magnetic tracers, such as magnetite (Fe_3O_4) and greigite (Fe_3S_4), are often linked to redox conditions and anthropogenic inputs, while chemical tracers, including major ions, isotopic ratios, and rare earth elements (REEs), reflect contaminant sources, transformation pathways, and mixing regimes (Verosub & Roberts, 1995; Aguilar Reyes et al., 2020). Integrating these two categories offers synergistic potential: magnetic minerals often act as proxies for particulate contamination and redox driven diagenesis, while chemical tracers provide fine grained evidence of solute behavior, contaminant sources, and reaction mechanisms (Zhu et al., 2016; Bonnière et al., 2024). The integrated use of both magnetic and chemical tracers is especially valuable in coastal aquifers and sediments, where pollution plumes often involve both solid phase contaminants (e.g., adsorbed heavy metals) and dissolved species (e.g., nitrates, pharmaceuticals) that follow different transport mechanisms.

In hydrothermally altered coastal settings, geothermal fluids rise through fractured bedrock or sediment columns, often carrying elevated concentrations of iron, manganese, silica, lithium, and heavy metals such as arsenic, copper, or lead (Ellis & Mahon, 1977; Giggenbach, 1992). These fluids can precipitate magnetite or sulfide minerals as they cool or interact with oxygenated waters, forming layers rich in authigenic magnetic minerals. In turn, these minerals can record the past presence and movement of geochemically significant fluids. Greigite, a ferrimagnetic iron sulfide, forms in reducing conditions often driven by sulfate reduction a process common in hydrothermal vents or organic rich sediments impacted by wastewater (Roberts, 1995; Rowan & Roberts, 2006). Thus, the presence and spatial distribution of magnetic phases in sediments can serve as historical markers for zones of past contaminant input or geochemical transformation (Maher & Possolo, 2013).

Conversely, wastewater impacted coastal environments are characterized by the introduction of anthropogenic compounds, including nutrients (e.g., nitrate, ammonium, phosphate), heavy metals (e.g., cadmium, zinc, chromium), and contaminants of emerging concern (e.g., pharmaceuticals, personal care products, artificial sweeteners) (Glassmeyer et al., 2005; Lapworth et al., 2012). These contaminants often infiltrate coastal aquifers via leaky septic systems, drainage canals, or treated effluent injection, posing risks to ecological health and potable water supplies. Chemical tracers such as gadolinium anomalies originating from medical contrast agents have emerged as powerful indicators of wastewater intrusion due to their stability and conservative behavior in groundwater (Kümmerer et al., 2000; Rabiet et al., 2009). Similarly, isotopic signatures of nitrate ($\delta^{15}N$ and $\delta^{18}O$) and boron ($\delta^{11}B$) are used to differentiate between wastewater, fertilizer, and natural sources of nitrogen pollution (Kendall et al., 2007; Vengosh et al., 2002). When these tracers are used in combination with magnetic measurements (e.g., magnetic susceptibility, remanent magnetization), they provide a dual parameter framework capable of mapping contaminant sources and zones of biogeochemical transformation.

One of the primary advantages of combining magnetic and chemical tracers lies in their complementary spatial and functional roles. Magnetic techniques such as measuring magnetic susceptibility or identifying mineral assemblages through isothermal remanent magnetization offer rapid, cost effective ways to screen large areas and infer contamination "hotspots" based on the accumulation of industrial or geogenic magnetic minerals (Liu et al., 2018; Zhu et al., 2016). These hotspots can then be examined in more detail using chemical tracers, which offer nuanced information about solute concentrations, contaminant ages, reaction pathways, and source attributions (Hunkeler et al., 2008). This integrated approach allows researchers and managers to move beyond single parameter assessments, improving their ability to design effective monitoring networks, prioritize remediation zones, and understand long term contaminant fate in complex coastal systems (EPA, 2024).

Furthermore, the transport behavior of magnetic versus chemical tracers in the subsurface differs in ways that provide complementary insights. Magnetic particles such as magnetite may be bound to sediments or transported as colloids, reflecting depositional and erosional processes, while dissolved chemical species are more directly linked to advective groundwater flow (Maher & Thompson, 1999; Aguilar Reyes et al., 2020). This means that magnetic tracers can reveal the physical sedimentary imprint of past contaminant events such as a historical spill or pulse flow while chemical tracers help track the ongoing migration of solutes and the biochemical processes that may attenuate or transform them. For example, nitrate may undergo denitrification, phosphate may adsorb to iron oxides, and heavy metals may co precipitate with sulfides processes that leave behind both geochemical and magnetic fingerprints (Verosub & Roberts, 1995; Maher & Possolo, 2013).

Given the mounting challenges of climate induced sea level rise, increasing urbanization of coastlines, and expanding geothermal exploration, there is a growing need for multidimensional tracer frameworks that can reliably monitor contaminant pathways and ecosystem risk in coastal environments. The integration of magnetic and chemical tracers provides such a framework, offering both rapid screening capacity and in depth chemical resolution. This review aims to synthesize recent advances in the application of integrated tracers to subsurface monitoring, with a focus on heavy metals, nutrients, and pharmaceutical contaminants. Specifically, we explore the properties, detection methods, and interpretative potential of key magnetic minerals (e.g., magnetite, greigite) and chemical tracers (e.g., REEs, isotopic ratios, pharmaceutical markers) in both hydrothermally altered and wastewater impacted settings. Through critical evaluation of case studies and methodological advances, this paper aims to identify best practices, knowledge gaps, and future directions for tracer based monitoring in coastal systems.

II. MAGNETIC TRACERS IN SUBSURFACE CONTAMINANT TRANSPORT

Environmental magnetism has emerged as a powerful approach for identifying and monitoring subsurface contamination, particularly in environments influenced by anthropogenic activity and geogenic alterations. Magnetic tracers, specifically ferrimagnetic minerals such as magnetite (Fe_3O_4) and greigite (Fe_3S_4), are sensitive to changes in redox conditions, sedimentation patterns, and industrial inputs (Maher & Thompson, 1999; Liu et al., 2012). In coastal systems impacted by hydrothermal fluids or wastewater discharges, these minerals can form authigenically or be introduced externally, often co transported with or linked to contaminant species such as heavy metals and sulfides. By mapping the spatial distribution, mineralogy, and magnetic properties of these phases, scientists can infer contaminant sources, transformation zones, and migration pathways (Zhu et al., 2016; Maher & Possolo, 2013).

➢ *Magnetite*

Magnetite is one of the most commonly studied magnetic minerals in environmental applications due to its strong ferrimagnetism, stability under a wide range of pH conditions, and ubiquitous presence in both natural and anthropogenically modified environments (Verosub & Roberts, 1995). In the context of subsurface contaminant transport, magnetite often functions as a proxy for pollution derived from industrial sources such as combustion, metallurgical processes, and vehicular emissions (Liu et al., 2018). It can also form in situ through oxidation of ferrous iron under oxidizing conditions or during hydrothermal alteration of iron bearing rocks.

The environmental significance of magnetite lies not only in its magnetic signal but also in its role as a carrier of trace metals. Numerous studies have demonstrated that magnetite rich sediments exhibit elevated concentrations of lead (Pb), cadmium (Cd), chromium (Cr), and zinc (Zn), particularly in industrial or wastewater impacted areas (Aguilar Reyes et al., 2020; Zhu et al., 2016). These metals can be physically adsorbed onto magnetite particle surfaces or chemically incorporated into its crystal lattice. This co association enables magnetite to serve as both a physical and chemical indicator of contamination.

In hydrothermally altered coastal zones, magnetite may form as a result of high temperature alteration of mafic minerals, releasing iron into circulating fluids that later precipitates as oxides upon mixing with cooler, oxygen rich groundwater. Such magnetite often has distinctive crystal morphologies and trace element signatures, which can help differentiate it from anthropogenic forms (Roberts, 2015). Additionally, biogenic magnetite produced by magnetotactic bacteria can form in microaerophilic zones at redox boundaries, further enriching the sediment's magnetic signature and offering clues about historical geochemical conditions (Maher et al., 2009).

➢ *Greigite*

Greigite is a ferrimagnetic iron sulfide (Fe_3S_4) that typically forms under reducing conditions, particularly in sulfate rich environments common to coastal sediments impacted by organic rich wastewater or hydrothermal discharges (Rowan & Roberts, 2006). As an intermediate phase in the transformation from mackinawite (FeS) to pyrite (FeS_2), greigite serves as an important marker of early diagenesis, reflecting microbial activity such as sulfate reduction and organic matter degradation (Roberts, 2015). Because these biogeochemical processes are commonly stimulated by wastewater inputs, greigite formation in sediments is often closely linked to anthropogenic nutrient loading and oxygen depletion (Glassmeyer et al., 2005).

Unlike magnetite, which can persist in a range of redox environments, greigite is more geochemically unstable and typically occurs within narrow redox windows. This makes it especially valuable for pinpointing transition zones in sediment columns where redox gradients are sharp, such as the interface between oxic seawater and anoxic porewaters in contaminated mudflats or estuaries. Moreover, greigite has been found to co precipitate with or sorb trace metals such as arsenic, copper, and nickel, thereby playing a role in the immobilization or remobilization of toxic species (Roberts, 1995; Liu et al., 2012).

In hydrothermal settings, greigite can also form due to the rapid mixing of metal rich reducing fluids with seawater, resulting in sulfide mineral precipitation. The presence of greigite in these contexts indicates highly localized reducing conditions, possibly at mixing interfaces or within microbial mats that thrive in thermally and chemically enriched environments (Rowan & Roberts, 2006). Because greigite frequently converts to more stable phases like pyrite or even magnetite upon diagenesis or oxidation, its detection in sediments suggests relatively recent or ongoing redox transformations a valuable insight in temporal studies of contaminant dynamics.

➢ *Detection Methods*

The identification and characterization of magnetite and greigite in environmental matrices rely on a suite of magnetic, mineralogical, and microscopic techniques. Among the most widely used methods are:

- Magnetic Susceptibility Measurements: This technique quantifies the ease with which a material becomes magnetized in an external field. Elevated values often correlate with higher concentrations of ferrimagnetic minerals like magnetite and greigite. It is commonly used for rapid field screening or core profiling (Maher & Thompson, 1999).
- Isothermal Remanent Magnetization (IRM) Acquisition: IRM curves are used to identify magnetic coercivity distributions and discriminate between different magnetic minerals. Magnetite typically shows

a low coercivity peak, while greigite has a broader, intermediate coercivity profile (Roberts, 2015).

- Thermomagnetic Analysis: This involves measuring the change in magnetization with temperature to identify Curie points. Magnetite has a Curie temperature of ~580 °C, whereas greigite loses magnetism around 330 °C. This helps distinguish between the two minerals in mixed samples (Rowan & Roberts, 2006).
- First Order Reversal Curve (FORC) Diagrams: These provide a detailed assessment of magnetic domain states and particle interactions, useful for identifying greigite's characteristic magnetic behavior in fine grained sediments (Lascu et al., 2015).
- X ray Diffraction (XRD): XRD is used to determine crystalline structures, confirming mineral identities. However, greigite's weak and overlapping peaks make this method most effective when coupled with other techniques (Roberts, 1995).
- Scanning Electron Microscopy (SEM) with Energy Dispersive X ray Spectroscopy (EDS): These techniques allow for imaging of particle morphology and determination of elemental composition. SEM can reveal spherical or framboidal forms indicative of greigite or combustion derived magnetite (Aguilar Reyes et al., 2020).
- Mössbauer Spectroscopy: Particularly useful for identifying oxidation states and iron coordination in magnetite and greigite, although it requires specialized equipment and is less commonly used in routine monitoring (Maher et al., 2009).
- Through the integration of these methods, researchers can assess not only the presence and abundance of magnetic minerals but also infer their origins (anthropogenic vs. natural), particle size distribution, and associated geochemical environments. The ability to link magnetic properties to specific contamination processes provides a powerful diagnostic tool in subsurface environmental studies. When combined with chemical analyses such as trace metal concentrations or isotopic profiling magnetic measurements enhance our understanding of both the physical and chemical evolution of contaminated coastal zones.

➢ *Chemical Tracers for Coastal Contaminant Monitoring*

Chemical tracers have long been used to investigate the sources, transport, and transformation of contaminants in hydrologically complex environments. In coastal zones, where subsurface contaminant movement is influenced by the interaction between freshwater, seawater, hydrothermal fluids, and anthropogenic discharges, chemical tracers provide indispensable insights into both natural geochemical processes and pollution signatures (Kendall et al., 2007; Vengosh et al., 2002). By analyzing the presence, concentration, and isotopic composition of selected chemicals including rare earth elements (REEs), isotopes, major ions, nutrients, and contaminants of emerging concern (CECs) researchers can identify contaminant sources, monitor plume migration, and assess natural attenuation processes (Lapworth et al., 2012; Bonnière et al., 2024).

- *Rare Earth Elements (REEs)*

The rare earth elements (REEs), encompassing the lanthanides plus yttrium, are increasingly recognized as effective geochemical tracers in both natural and contaminated groundwater systems. Due to their coherent chemical behavior, low natural background levels, and conservative mobility under specific conditions, REEs are particularly useful for assessing water rock interaction, geothermal mixing, and wastewater influence in coastal aquifers (Johannesson & Lyons, 1994; Kulaksız & Bau, 2011).

In hydrothermal environments, REE patterns often exhibit distinct fractionation signatures and positive or negative anomalies (especially in europium, cerium, and gadolinium) as a result of temperature driven redox and mineral interaction processes. For instance, europium (Eu) anomalies are commonly linked to high temperature water rock reactions where Eu^{2+} is preferentially mobilized under reducing conditions (Möller, 2002). These REE patterns serve as fingerprints to identify hydrothermal contributions in mixed groundwater regimes.

In wastewater impacted systems, anthropogenic gadolinium (Gd) has emerged as a robust indicator of contamination. The widespread use of Gd based contrast agents in magnetic resonance imaging (MRI), combined with the poor removal of these agents during conventional wastewater treatment, leads to elevated Gd concentrations in effluent and downstream water bodies (Bau & Dulski, 1996; Kümmerer et al., 2000). The anthropogenic Gd anomaly, typically calculated using PAAS normalized REE distributions, serves as a conservative and persistent marker of domestic sewage intrusion in both surface and groundwater (Rabiet et al., 2009).

Furthermore, REEs have been successfully applied to track plume movement through remediation systems, such as permeable reactive barriers (PRBs). Because they are present at ultra trace levels and behave conservatively in many aquifer systems, changes in REE concentrations and patterns can reveal subtle interactions between groundwater and barrier media, identifying zones of reactivity or flow bypass (EPA, 2024).

- *Isotopic Tracers*

Isotopic analysis plays a pivotal role in tracing contaminant origin, transport, and transformation in subsurface environments. Stable isotopes of light elements such as hydrogen (^{2}H), oxygen (^{18}O), nitrogen (^{15}N), sulfur (^{34}S), boron (^{11}B), and carbon (^{13}C) offer sensitive indicators of environmental processes, while radiogenic and metal isotopes (e.g., $^{87}Sr/^{86}Sr$, $^{206}Pb/^{207}Pb$, $\delta^{66}Zn$, $\delta^{65}Cu$) can aid in source attribution for specific pollutants (Kendall et al., 2007; Vengosh et al., 2002).

One of the most established isotopic applications in coastal groundwater is the use of $\delta^{15}N$ and $\delta^{18}O$ in nitrate to distinguish between wastewater derived nitrogen, fertilizer, and natural sources. Wastewater and manure typically show $\delta^{15}N$ values between +10‰ and +20‰ due to ammonia volatilization and microbial processing, while synthetic fertilizers tend to have lower $\delta^{15}N$ values (+0‰ to +5‰) (Aravena & Robertson, 1998). When coupled with $\delta^{11}B$, which is elevated in wastewater due to detergent and urine content, isotopic data can provide compelling evidence of sewage impact (Barth, 1998).

Similarly, strontium isotopes ($^{87}Sr/^{86}Sr$) are effective in tracing water rock interactions and identifying mixing between geologically distinct sources. Coastal aquifers receiving inputs from young volcanic rocks, seawater, and anthropogenic sources exhibit distinguishable strontium isotopic signatures, enabling deconvolution of complex hydrochemical regimes (Vengosh et al., 2002). Lead isotopes ($^{206}Pb/^{207}Pb$) can also differentiate natural lead from industrial or gasoline derived inputs, offering insights into metal contamination pathways (Chow & Earl, 1972).

Moreover, $\delta^{13}C$ and $\delta^{34}S$ isotopes help identify redox transformations. Enrichment in $\delta^{13}C$ of dissolved inorganic carbon may indicate microbial degradation of organic matter or methanogenesis, while $\delta^{34}S$ in sulfate reflects microbial sulfate reduction in wastewater impacted sediments (Krouse & Mayer, 1999). These transformations, in turn, affect contaminant mobility by altering pH, redox potential, and metal speciation.

- *Major Ions and Nutrient Salts*

Major ions such as sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and silica (SiO_2) are foundational to any groundwater assessment. In coastal systems, these ions are crucial for identifying seawater intrusion, hydrothermal mixing, and wastewater contamination (Fetter, 2018). For instance, elevated chloride and sodium levels, accompanied by conservative ratios, are indicative of marine water influence, while unusual concentrations of calcium or silica may suggest hydrothermal inputs (Giggenbach, 1992).

In wastewater plumes, nutrients such as nitrate (NO_3^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}) are key indicators of contamination. High nitrate concentrations are frequently associated with domestic or agricultural sources, but isotopic differentiation is often required to confirm their origin (Kendall et al., 2007). Ammonium, typically more mobile in reducing conditions, may signal anaerobic degradation of organic matter or septic system leakage. Phosphate, although strongly sorbed by iron and aluminum oxides, can be mobile in anoxic, reducing sediments and is frequently elevated near sewage outfalls (Venkatesan & Swaminathan, 2009).

Additionally, Cl/Br ratios can help distinguish between seawater and wastewater inputs, as typical seawater has a Cl/Br ratio of ~288, while wastewater may show significant deviation due to anthropogenic bromide use (Vengosh & Pankratov, 1998). Combined with trace element patterns and isotopic signatures, major ions help delineate plume boundaries and assess mixing relationships between multiple water sources.

- *Pharmaceuticals and Emerging Contaminants*

The rise of contaminants of emerging concern (CECs) including pharmaceuticals, personal care products, artificial sweeteners, and endocrine disrupting compounds has added a new dimension to tracer studies in wastewater impacted environments. These compounds are often highly specific to human activity, poorly removed during wastewater treatment, and detectable at ultra trace levels (Kolpin et al., 2002; Lapworth et al., 2012).

Among these, carbamazepine, diclofenac, sulfamethoxazole, and sucralose are widely used as wastewater tracers. Carbamazepine, an anti epileptic drug, is resistant to biodegradation and frequently detected in aquifers and streams downstream of sewage discharge points (Ternes et al., 2004). Sucralose, an artificial sweetener, passes through the human body and treatment plants largely unchanged and behaves conservatively in both surface water and groundwater systems, making it an excellent plume delineator (Buerge et al., 2009).

The presence of multiple pharmaceuticals in groundwater not only confirms wastewater intrusion but also provides insights into the attenuation capacity of aquifers. Compounds like caffeine and acetaminophen degrade relatively quickly and thus serve as short term indicators, whereas persistent compounds such as carbamazepine reflect long term contamination (Glassmeyer et al., 2005). Moreover, pharmaceuticals often co occur with nutrients and pathogens, reinforcing their role as multi indicator proxies for human wastewater impacts.

Detection of CECs requires advanced analytical methods, most commonly liquid chromatography tandem mass spectrometry (LC MS/MS), capable of identifying a wide range of compounds at ng/L concentrations. The integration of CEC monitoring with traditional tracers (e.g., isotopes and ions) enhances the resolution of plume mapping and source identification, particularly in mixed use or heavily urbanized coastal zones (Lapworth et al., 2012).

III. DISCUSSION

- *Tracer Transport Behavior and Geochemical Interactions*

Understanding the transport behavior and geochemical interactions of tracers is fundamental to accurately interpreting subsurface contaminant dynamics in coastal environments. The fate of both magnetic and chemical tracers is governed by complex interactions among hydrological flow regimes, redox conditions, sediment composition, and biogeochemical processes (Fetter, 2018; Hunkeler et al., 2008). In systems influenced by hydrothermal activity and wastewater intrusion, these interactions become even more critical due to the sharp chemical gradients and dynamic mixing zones present at interfaces between freshwater, seawater, and thermal fluids. This section explores the physicochemical behavior of tracers, their retention and mobility characteristics, and their reactivity within subsurface media.

- *Advection, Dispersion, and Mixing Dynamics*

Tracer transport in coastal aquifers is primarily driven by advection (movement with flowing groundwater) and dispersion (spreading due to heterogeneity and diffusion). These processes dictate the spatial extent and dilution of both conservative and reactive tracers. Chemical tracers such as chloride, bromide, gadolinium (from MRI agents), and sucralose behave conservatively, meaning they are not significantly adsorbed or transformed, making them reliable indicators of groundwater flow paths and mixing processes (Rabiet et al., 2009; Lapworth et al., 2012). In contrast, magnetic particles such as magnetite and greigite typically move with sediment rather than with water, acting as particulate tracers influenced more by sedimentation, erosion, and colloidal transport mechanisms than by groundwater velocity alone (Maher & Thompson, 1999).

In stratified coastal aquifers, vertical and lateral mixing of fresh groundwater with saline or hydrothermal fluids can create sharp chemical gradients. These mixing zones are often hot spots of geochemical reactivity, where conservative tracers may dilute while reactive tracers (e.g., nitrate, phosphate, heavy metals) undergo chemical transformations (Vengosh et al., 2002). Advection dominated flow transports dissolved solutes far from their sources, while magnetic mineral distribution often reflects historical deposition and localized transformations, enabling reconstruction of past contaminant loading events (Zhu et al., 2016).

- *Sorption, Retardation, and Colloidal Transport*

One of the most significant differences between tracers lies in their sorption behavior the tendency of compounds to bind to soil or sediment surfaces. Chemical tracers such as nitrate and chloride are typically weakly sorbed and thus have low retardation, allowing them to move with groundwater. In contrast, phosphate, heavy metals, and some pharmaceuticals are strongly sorbed and exhibit retarded transport, meaning they lag behind the advancing groundwater front (Barth, 1998; Venkatesan & Swaminathan, 2009).

Magnetite particles, particularly those in the nano and micro size range, may be transported via colloidal flow under favorable geochemical conditions. Colloids can remain suspended in groundwater, especially if they carry surface charges that prevent aggregation (Kretzschmar et al., 1999). However, their movement is sensitive to ionic strength, pH, and the presence of natural organic matter. For example, high salinity or calcium concentrations can cause colloid flocculation and deposition, limiting their mobility in seawater impacted zones (Ryan & Elimelech, 1996). This makes magnetic particles more suitable as site specific indicators rather than broad scale plume tracers.

Chemical tracers such as REEs and trace metals can also be transported in colloidal form or as dissolved complexes. The presence of organic ligands or chelating agents (e.g., Gd DTPA complexes in wastewater) enhances the solubility and mobility of certain metals, effectively transforming otherwise reactive tracers into conservative ones (Kümmerer et al., 2000). For example, anthropogenic gadolinium persists in the dissolved phase due to its stable complexation, making it a reliable tracer for treated effluent plumes even in saline environments (Bau & Dulski, 1996).

- *Redox Sensitivity and Biogeochemical Transformation*

Redox conditions exert a profound influence on tracer behavior and contaminant fate. In hydrothermally influenced systems and wastewater rich zones, redox gradients can shift rapidly, causing phase transitions, solubility changes, and mineral transformations. For instance, under reducing conditions, sulfate is converted to sulfide via microbial sulfate reduction, promoting the formation of greigite and pyrite and immobilizing associated metals like arsenic and lead (Roberts, 1995). These processes alter the geochemical environment and may lock contaminants into stable mineral matrices, reducing their mobility (Rowan & Roberts, 2006).

In contrast, oxidizing conditions favor the stability of magnetite and the mobility of certain oxyanions like nitrate and chromate. The transformation between magnetite and greigite is itself redox dependent: magnetite may dissolve under sulfidic conditions, while ferrous iron and sulfide may precipitate greigite under mildly reducing conditions (Maher et al., 2009). These shifts can create complex mineral assemblages within sediment profiles, encoding the history of contaminant plumes and redox fluctuations.

For isotopic tracers, redox sensitive processes leave diagnostic fractionation signatures. For example, denitrification under anoxic conditions enriches the residual nitrate in ^{15}N and ^{18}O, resulting in heavier isotopic ratios (Kendall et al., 2007). Similarly, sulfur isotope enrichment in sulfate ($\delta^{34}S$) can reflect sulfate reduction, while carbon isotopes ($\delta^{13}C$) can indicate organic matter degradation or methanogenesis (Krouse & Mayer, 1999). These isotopic shifts, when paired with chemical concentration gradients and mineralogical indicators (e.g., greigite presence), help validate contaminant attenuation pathways.

- *Co precipitation and Complexation*

Geochemical interactions involving co precipitation and complexation play significant roles in the fate of both contaminants and tracers. Co precipitation refers to the incorporation of contaminants into newly forming mineral phases. For example, heavy metals such as zinc, copper, and lead may co precipitate with iron oxides (e.g., magnetite, ferrihydrite) or sulfides (e.g., greigite, pyrite), leading to long term sequestration in sediments (Zhu et al., 2016). The formation of these mineral phases often occurs in zones where redox conditions shift or where contaminant laden groundwater mixes with geochemically distinct fluids.

Complexation, on the other hand, influences solubility and mobility. Organic ligands and anthropogenic chelators like EDTA or DTPA can stabilize metals in the aqueous phase, enhancing their transport. This behavior is particularly relevant for REEs and Gd based contrast agents, where strong complexation resists removal by sorption or precipitation (Bau & Dulski, 1996). Complexation can also reduce the effectiveness of reactive barriers or natural attenuation zones by keeping contaminants in mobile form.

In coastal settings with variable pH and salinity, complexation equilibria can shift dramatically. For instance, as groundwater rich in dissolved organic carbon mixes with saline water, changes in ionic strength may alter metal–ligand stability, triggering metal release or mineral precipitation (Vengosh et al., 2002). Understanding these interactions is critical when using chemical tracers to interpret contaminant transport, as apparent concentration changes may reflect speciation shifts rather than true dilution or dispersion.

IV. CASE STUDIES AND APPLICATIONS

The real world application of integrated magnetic and chemical tracers has advanced significantly over the past two decades, allowing researchers to track subsurface contaminant dynamics in diverse coastal settings. From hydrothermal environments and estuarine systems to wastewater impacted aquifers, field based studies illustrate the power of multi tracer approaches in identifying pollution sources, mapping contaminant plumes, and assessing attenuation or remediation effectiveness. This section reviews representative case studies where magnetic and chemical tracers have been employed synergistically to address key environmental challenges.

- *Mapping Heavy Metal Contamination Using Magnetite in Coastal Sediments (Qinhuangdao, China)*

Zhu et al. (2016) conducted a comprehensive study in the intertidal zone of Qinhuangdao, a coastal city in northeast China, to assess sediment contamination by trace metals. The research team integrated geochemical measurements (Pb, Zn, Cr, Ni, Cu) with magnetic susceptibility mapping to identify industrial and urban pollution hotspots. Results showed a strong spatial correlation between high magnetic susceptibility and elevated heavy metal concentrations, attributed to the co deposition of magnetite rich particles and metal bearing aerosols from industrial sources.

By analyzing core samples, the researchers also identified temporal trends in contamination, indicating recent pollution from port and municipal runoff. This case exemplifies how magnetic measurements can serve as rapid screening tools, guiding more resource intensive chemical analyses and supporting coastal sediment management and pollution control strategies.

- *Detecting Anthropogenic Gadolinium in Wastewater Impacted Aquifers (North Carolina, USA)*

Zabrecky et al. (2021) investigated the prevalence of anthropogenic gadolinium in surface and groundwater across the Triangle Region of North Carolina, USA. Gadolinium anomalies were found in streams and aquifers located downstream of major wastewater treatment plants, reflecting the discharge of Gd based MRI contrast agents into public waterways. Despite differences in hydrology and land use, the Gd signal was persistent over long distances (up to 30 km), demonstrating its utility as a conservative tracer of wastewater intrusion.

Moreover, Gd concentrations correlated with elevated levels of pharmaceuticals and nutrients, reinforcing its role as a proxy for emerging contaminant plumes. This study illustrates the value of rare earth element (REE) tracers in delineating diffuse wastewater impacts and highlights the need for improved wastewater monitoring and treatment technologies.

- *Characterizing Redox Transitions and Early Diagenesis via Greigite Detection (Pearl River Estuary, China)*

In a study of sediment dynamics in the Pearl River Estuary, a major outlet for urban and industrial effluents in southern China, researchers detected significant greigite formation in anoxic sediment layers (Wang et al., 2013). Greigite was identified using magnetic hysteresis, FORC diagrams, and X ray diffraction, and was spatially associated with acid volatile sulfide (AVS) zones and elevated dissolved phosphate concentrations. These findings indicated that microbial sulfate reduction driven by organic rich wastewater inputs was promoting greigite precipitation in early diagenetic zones.

The study confirmed that greigite could act as a diagnostic tracer for sediment anoxia and nutrient overloading, particularly in regions of intense eutrophication. Importantly, it also demonstrated that the presence of greigite could mark zones of metal immobilization, contributing to natural attenuation processes and informing long term sediment remediation planning.

- *Multi Tracer Evaluation of a Submarine Wastewater Discharge (Palermo, Italy)*

Bonnière et al. (2024) conducted an integrated tracer investigation of a submarine wastewater outfall near Palermo, Sicily. The study used a combination of chloride, boron, nitrate isotopes (δ^{15}N, δ^{18}O), gadolinium anomalies, and pharmaceuticals to track the movement and attenuation of contaminants discharged into a coastal aquifer and adjacent marine system. Elevated δ^{15}N values in groundwater indicated sewage derived nitrate, while Gd and sucralose provided conservative signals of effluent presence.

Notably, spatial variations in pharmaceutical concentrations revealed zones of natural attenuation, likely due to sorption and biodegradation in the sediment interface. The study demonstrated that combining conservative tracers (Cl^-, Gd, sucralose) with reactive ones (nitrate, pharmaceuticals) allows for a high resolution characterization of subsurface plume behavior, emphasizing the importance of tracer complementarity in wastewater monitoring.

- *Tracing Groundwater Flow Through a Permeable Reactive Barrier Using REEs (California, USA)*

The U.S. Environmental Protection Agency (EPA, 2024) implemented a field study to test the application of natural REE signatures as passive tracers in evaluating the performance of a permeable reactive barrier (PRB) installed to treat chlorinated solvent contamination in a coastal aquifer in California. By comparing REE concentrations and normalized patterns in upgradient, mid barrier, and downgradient wells, researchers identified zones where REEs were either retained by the barrier media or passed through unaltered.

In sections where REE patterns changed significantly, remediation reactions (e.g., sorption, mineral formation) were confirmed, while unaltered patterns indicated potential hydraulic bypass. This case study showcased REEs as a non invasive, low concentration tracer suite to validate engineered remediation performance, applicable to both organic and inorganic contaminants in coastal zones.

- *Assessing Historical Hydrothermal Inputs Using Magnetic Spherules (Red Sea)*

In offshore sediments from the Red Sea, Agarwal and Palayil (2022) recovered abundant magnetite and wüstite spherules, believed to originate from historical hydrothermal vent activity. These spherules, identified using scanning electron microscopy and magnetometry, served as direct indicators of metalliferous sedimentation linked to past submarine hydrothermal discharges.

The presence of these spherules, alongside elevated Fe and Mn concentrations, suggested that hydrothermal plumes had once influenced the coastal depositional environment, even though active venting was no longer occurring. This study illustrates the power of magnetic mineralogy to detect relict hydrothermal influence and highlights the potential for magnetic tracers to extend the temporal window of coastal geochemical investigations.

These case studies underscore the versatility and diagnostic power of integrated magnetic and chemical tracer systems. By combining rapid field screening tools (e.g., magnetic susceptibility) with precise chemical and isotopic analyses, researchers can obtain a multi dimensional understanding of contaminant pathways, source attribution, and geochemical transformation processes. This approach is particularly well suited to coastal settings where dynamic hydrology, variable redox conditions, and anthropogenic pressures complicate conventional monitoring.

As these examples demonstrate, successful application of tracer techniques hinges on a tailored selection of tracers including conservative solutes, redox sensitive isotopes, particulate bound minerals, and emerging contaminants matched to the specific environmental and hydrological context of the site. The synergy between magnetic and chemical tracers offers powerful insights for environmental forensics, plume management, and remediation planning.

V. CONCLUSION

The integration of magnetic and chemical tracers has emerged as a robust and multidimensional approach for monitoring subsurface contaminant transport in coastal environments impacted by hydrothermal alteration and anthropogenic wastewater inputs. These environments are inherently complex, characterized by fluctuating redox gradients, mixing of freshwater and saline waters, dynamic sedimentary processes, and diverse sources of pollution ranging from geogenic to urban effluents. As demonstrated throughout this review, the combined use of ferrimagnetic minerals such as magnetite and greigite and chemical tracers such as rare earth elements (REEs), stable and radiogenic isotopes, major ions, and emerging contaminants provides a complementary toolkit to assess both the solid phase and dissolved phase dynamics of contamination.

Magnetic tracers are particularly well suited for identifying zones of heavy metal accumulation, redox transitions, and historical depositional events. Magnetite serves as a proxy for industrial pollution and hydrothermal input, while greigite formation highlights zones of sulfate reduction and organic matter degradation, often associated with sewage contamination. These minerals record not only the presence of contaminants but also the prevailing geochemical conditions that control contaminant transformation and immobilization. When spatially mapped through magnetic susceptibility or coercivity measurements, they enable rapid screening of large areas and provide historical insights into contaminant fluxes and redox evolution.

On the other hand, chemical tracers offer high resolution, source specific diagnostics. REE patterns especially anthropogenic gadolinium have proven effective for tracing wastewater plumes, while isotopic ratios allow discrimination of contaminant origins and biogeochemical processes. Major ions and nutrient salts delineate mixing zones and salinity gradients, while pharmaceuticals and artificial sweeteners provide strong indicators of domestic sewage, with some acting as conservative tracers and others reflecting degradation pathways. These tracers are crucial for identifying the extent and persistence of contamination, informing both short and long term management strategies.

One of the most compelling arguments for integrating magnetic and chemical tracers lies in their complementary transport behaviors and reaction sensitivities. While chemical tracers are governed largely by advection, dispersion, sorption, and biodegradation, magnetic particles are transported via sedimentary or colloidal pathways, often preserving the fingerprint of depositional and diagenetic processes. This distinction allows researchers to reconstruct both the current dynamics and historical legacy of contamination, bridging the gap between hydrology and geochemistry.

Real world case studies further underscore the value of this integrated approach. From the mapping of heavy metal pollution in estuaries using magnetite, to the detection of wastewater derived gadolinium and pharmaceuticals in aquifers, to the identification of greigite as a marker of early diagenesis and redox transitions, the evidence is clear: combining tracers provides deeper insight than any single method alone.

As coastal environments continue to face pressures from urbanization, climate change, sea level rise, and increased geothermal exploitation, the demand for accurate, sensitive, and integrative monitoring tools will grow. Magnetic and chemical tracers, especially when employed together, offer a versatile, scalable, and scientifically rigorous means of understanding the fate and transport of subsurface contaminants in these fragile and valuable ecosystems.

Future research should focus on developing portable sensor technologies, machine learning tools for tracer data interpretation, and standardized tracer libraries for different contaminant sources and hydrogeological contexts. Emphasis should also be placed on longitudinal studies that link tracer signals with ecosystem responses and remediation outcomes. By advancing interdisciplinary frameworks that combine magnetism, geochemistry, hydrogeology, and environmental engineering, the field can enhance its capacity to safeguard water quality and ecosystem health in coastal regions around the world.

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