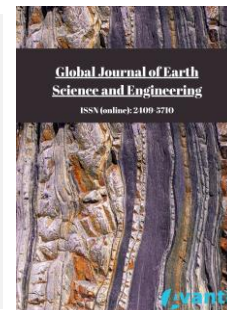








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# Forensic Hydrochemistry for Environmental Crime Investigation: A PRISMA-Based Systematic Review of Isotopic and Geochemical Fingerprinting Techniques

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## ABSTRACT

Forensic hydrochemistry applies chemical and isotopic analysis to water systems, providing powerful tools for investigating environmental crimes such as illegal dumping, groundwater pollution, and oil spills. This review systematically examined seventy-five (75) articles following PRISMA guidelines, highlighting techniques such as stable isotope analysis, compound-specific isotope analysis (CSIA), geochemical fingerprinting, and advanced mass spectrometry. Results show isotopic tracers effectively differentiate natural from anthropogenic sources, though CSIA offers direct evidence of contaminant degradation, strengthening legal accountability. Geochemical and hydrocarbon fingerprinting further support source attribution, though challenges persist due to overlapping isotopic ranges, high analytical costs, and baseline data gaps. Emerging approaches, such as LC-HRMS for persistent pollutants, expand forensic applications. Overall, forensic hydrochemistry advances environmental justice by enabling reliable pollution attribution, improving litigation outcomes, and contributing to sustainable water resources management.

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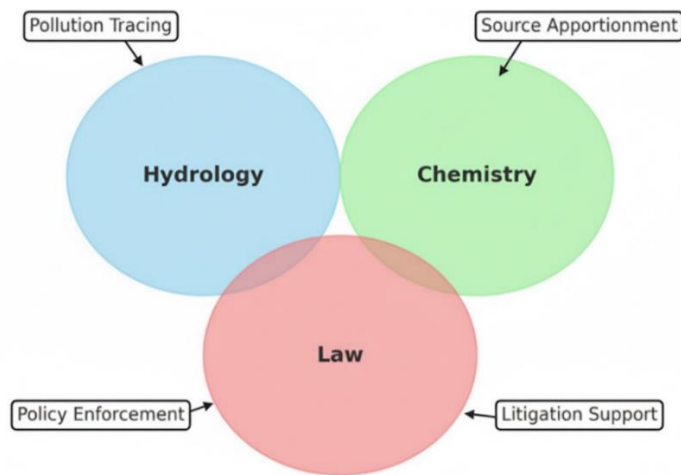
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## 1. Introduction

Water, as the most essential natural resource, carries a wealth of chemical and isotopic data that mirrors its interaction with the surrounding environment [1, 2]. Beyond its social and ecological importance, water can serve as a silent witness in the investigation of environmental crimes, e.g., illegal dumping of industrial effluents, groundwater pollution, oil spills, and transboundary pollution. Forensic hydrochemistry-an evolving sub-discipline at the interface of hydrology, chemistry, and law- leverages advanced analytical techniques to decode these chemical signatures [3, 4]. Tracing contaminants, identifying pollution sources, and establishing cause-and-effect relationships offer crucial evidence that strengthens environmental litigation and policy enforcement.

The rationale for this review lies in the increasing frequency and complexity of water-related crimes in both developed and developing regions. Conventional environmental monitoring often fails to meet the evidentiary standards needed in court, leaving many cases unresolved [5, 6]. Forensic hydrology bridges this gap by applying rigorous scientific methods, e.g., isotope ratio analysis, trace metals profiling, and geochemical fingerprinting, thereby enhancing both attribution accuracy and legal defensibility. Additionally, with the rise of emerging pollutants- including pharmaceuticals, microplastics, and persistent organic contaminants- the need for reliable forensic techniques is greater than ever [7, 8]. Hence, by exploring these principles, methodologies, and applications of forensic hydrochemistry, this review aims to highlight its transformative role in safeguarding water resources, protecting public health, and holding polluters accountable. Lastly, strengthening this field contributes not only to environmental justice but also to the wider pursuit of sustainability and responsible resource management. Fig. (1) shows a schematic Venn-style diagram illustrating the interdisciplinary nature of forensic hydrochemistry at the interface of hydrology, chemistry, and law. Applications include pollution tracing, source attribution, litigation support, and policy enforcement.



**Figure 1:** Conceptual framework of forensic hydrochemistry.

## 2. Method

### 2.1. Literature Review

This review was performed following the Preferred Reporting Items for Systematic Reviews and Meta-Analysis (PRISMA) guidelines to ensure transparency, reproducibility, and methodological rigour [9, 10]. A systematic literature search was performed across multiple academic databases, including WoS, Scopus, PubMed, and Google Scholar. Search terms combined key concepts related to forensic hydrochemistry, isotopic fingerprinting, groundwater pollution, and environmental forensics. Boolean operators (AND/OR) were used to refine the queries, for instance: ("forensic hydrochemistry" OR "environmental forensics" OR "water forensics") AND ("stable isotopes" OR "CSIA" OR "trace elements") [4, 11]. The initial search covered publications from 1995 to 2025 to capture both foundational and recent advances. Reference lists of relevant articles and review papers were further screened to identify additional eligible studies.

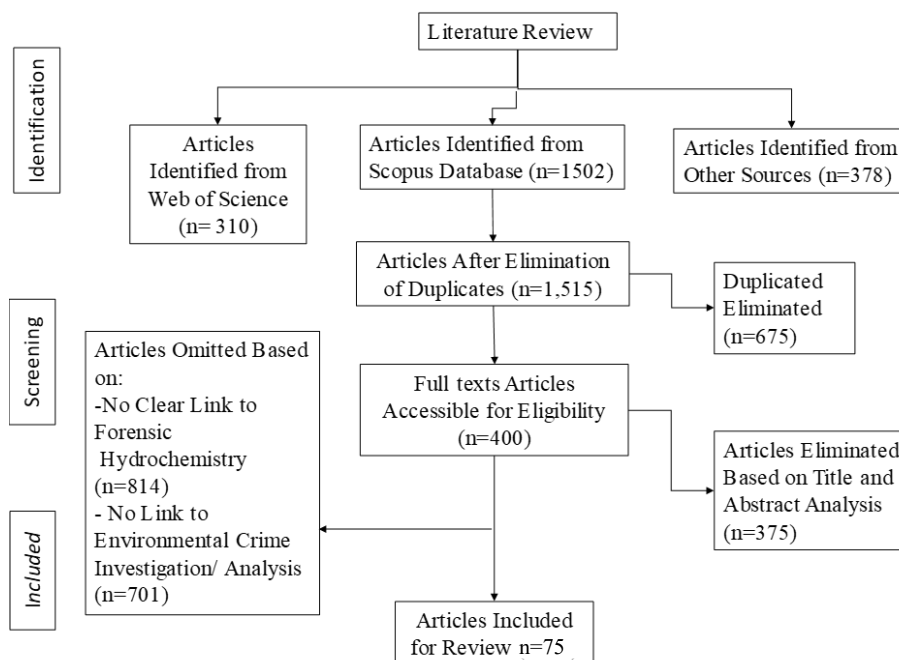
## 2.2. Inclusion and Extraction Criteria

Studies were included if they: (i) applied hydrochemical, isotopic, or geochemical techniques for forensic purposes in surface water, groundwater, or environmental pollution contexts [4]; (ii) reported empirical results or case studies relevant to pollution attribution, sources apportionment, or legal disputes [12, 13]; and (iii) were published in peer-reviewed journals. Both field investigations and laboratory-based tracer studies were considered. Exclusion criteria were applied to studies that: (i) lacked clear forensic relevance, focusing purely on hydrogeology without peer review [14, 15]; or (iii) were written in languages other than English. To ensure scientific rigour, only studies with clearly defined methodology and measurable outcomes were retained.

## 2.3. Systematic Search Strategy and Methodology

### 2.3.1. Study Selection and Data Extraction

A systematic review is based on the transparency and reproducibility of the search strategy in order to achieve the integrity of this kind of review. In this research, the identification stage was encoded to extract a broad amount of literature in multi-disciplinary databases to make sure that the overlap point between hydrogeochemical study and forensic detectives was not missed. This search was done in November 2025 and included all records available till that date. Three major sources were used: the Web of Science Core Collection, the Scopus database, and Other Sources, which comprised grey literature, Google Scholar and tracking of key review articles backwards. This complex methodology was necessary since forensic hydrochemistry usually occupies the outer margins of conventional environmental science and criminal justice databases, and a wide net has to be thrown at the outset (Fig. 2).



**Figure 2:** PRISMA flow diagram.

The search terms were customised to the syntax type of each site. In the case of Web of Science, the search query was as follows: TS=("forensic hydrochemistry" OR "environmental forensic" OR "water chemistry investigation") AND TS=("environmental crime" OR pollution source tracking" OR illegal dumping). This search query led to the discovery of 310 records. In the case of Scopus (where the volume of literature was the greatest, 1,502 records), the string was changed to TITLE-ABS-KEY (hydrogeochemical and forensic analysis or isotopic tracing) and (contamination and criminal investigation or legal evidence). In addition, 378 references were determined by alternative means, with most of the references targeting government reports and technical forensic manuals. Such joint efforts led to an original pool of 2,190 raw records.

The shift to the screening process was initiated with the help of an effective deduplication process. Since Scopus and Web of Science have a certain overlap, it was possible to distinguish 675 duplicates and eliminate them, thus getting 1,515 unique records to screen the title and abstract. Two reviewers carried out this stage and reduced selection bias since it was done independently. The logic of strict hierarchical exclusion ruled the screening process. The first step that was taken involved the removal of 375 papers based on their titles and abstract alone, since they were either purely geological without any forensic usage or duplication and thus had not been swept out by the initial software. This reduced the number of articles to 400 full-text articles, which were identified to be retrieved and evaluated in terms of eligibility in a detailed manner.

The stage of eligibility is the most vital optimisation of the PRISMA flow [16, 17]. Among the 400 articles that were measured in their entirety, many of them were weeded out, as they did not fit the thematic criteria of the review. In particular, 814 cases of omission were identified, when articles did not demonstrate any clear connection with forensic hydrochemistry (e.g. they have talked about the general water quality without the methodology through which one can find out the source of the particular water or the legal proofs). In addition, 701 articles were omitted as they did not directly relate to the investigation or analysis of environmental crime, and they usually focused on the natural geogenic contamination. It should be noted that there were also articles that fit in several exclusion criteria, yet were grouped according to their principal cause of rejection. This was done by a stringent winnowing process that left only the most pertinent and quality evidence.

Finally, 75 articles were used in the end review following the systematic elimination of non-pertinent studies. These studies are the state of the art in applying chemical signatures in water to resolve environmental crimes. The screening performance demonstrated that there is a definite tendency in the field, as the overall scope of hydrochemistry is huge; a particular application to forensic investigation is a niche and needs a specific isotopic and molecular tracking. Recording all the stages of this flow, starting with the original 2,190 records, all the way to the final 75, this search strategy gives a clear audit trail that will give credence to the findings of the review and make it possible to update it later as the field of forensic hydrochemistry develops.

### **2.3.2. Assessment of Quality of Inclusion Studies**

In order to ascertain that the methodology is reliable, the assessment of the quality of the incorporated studies was done through a simplified approach based on the general systematic review practice, with modifications according to PRISMA guidelines. All the studies were assessed based on five criteria: (i) clarity of sampling design, (ii) suitability of methods of data analysis, (iii) transparency of description of methodology, (iv) strength of data interpretation to identify source, and (v) recognition of limitations of the study. The qualitative score of the studies was high, moderate or low methodological. The majority of the studies were of moderate to high quality, especially those studies that utilised multi-isotope or more sophisticated geochemical methods, with fewer high-quality studies having no detailed sampling protocols or fully developed uncertainty analysis. These tests were used in the interpretation and synthesis of findings.

## **3. Results**

A total of 75 studies were reviewed (Table 1), covering diverse isotopic and chemical forensic techniques applied to water, sediments, and hydrocarbons. Stable isotopes ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $\delta^{11}\text{B}$ , Sr isotopes) were widely used to trace groundwater recharge, nitrate sources, and wastewater infiltration. For example, Campbell, Kendall [18] and Kaown, Shouakar-Stash [19] showed that nitrogen and oxygen isotopes could differentiate between septic, fertiliser, and sewage nitrate inputs, while Widory, Petelet-Giraud [20] and Sankoh, Derkyi [21] revealed the utility of multi-isotope fingerprints for urban wastewater pollution. Strontium isotopes [22] and multi-isotope frameworks [23, 24] proved effective in distinguishing natural versus anthropogenic salinity and mining-derived inputs. Compound-specific isotope analysis (CSIA) emerged as a central forensic tool. Studies including [25-27] established CSIA's value in proving in-situ Biodegradation of hydrocarbon and fuel sources and distinguishing degradation from dilution in groundwater plumes. Recent reviews [28-30] have considered CSIA workflows, QA/QC protocols, and theoretical bases, enhancing its robustness in environmental litigation.

**Table 1: Literature summary.**

S. No.	Technique / Matrix	Study Type	Study Location /Region	Sample/ Study Focus	Major Findings	Forensic Relevance	Limitations/ Remarks	Ref.
1	Stable isotopes ( $\delta^{18}\text{O}$ , $\delta^2\text{H}$ ) / groundwater	Field case study	Canada	Groundwater recharge tracing	Isotopes identified recharge sources and evaporation effects.	Supports hydrological source identification.	Climatic variability affects signatures.	[37]
2	Nitrate isotopes ( $\delta^{15}\text{N}$ , $\delta^{18}\text{O}$ ) / groundwater	Field case study	USA	Agricultural groundwater contamination	Distinguished fertiliser and sewage nitrate sources.	Identifies anthropogenic nitrate pollution.	Source overlap is possible.	[38]
3	CSIA / chlorinated solvents	Lab-based analytical study	USA	Chlorinated solvent contamination	Isotope fractionation revealed contaminant degradation.	Tracks contaminant transformation.	Requires high-precision instrumentation.	[39]
4	Hydrocarbon fingerprinting / marine oil	Field case study	Gulf of Mexico	Marine oil spill investigation	Chemical signatures identified spill sources.	Supports environmental litigation.	Weathering alters composition.	[40]
5	Major ion hydrochemistry/ groundwater	Field case study	India	Groundwater contamination assessment	Hydrochemical facies identified water-rock interactions.	Helps identify pollution pathways.	Limited source specificity.	[41]
6	Sr isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) / groundwater	Field case study	Belgium	Groundwater origin studies	Sr isotopes distinguished geological ion sources.	Separates geogenic and anthropogenic inputs.	Requires a geological baseline.	[42]
7	Dual isotope analysis/nitrate	Field case study	USA	Nitrate pollution tracing	Isotopes indicated agricultural runoff dominance.	Improves pollution attribution.	Temporal variability.	[38]
8	Trace metal fingerprinting/ wastewater	Field case study	USA	Industrial wastewater discharge	Metal ratios linked pollution to industries.	Supports regulatory enforcement.	Background geochemical variation.	[43]
9	Multivariate statistics/ groundwater	Field case study	Spain	Groundwater quality assessment	PCA revealed pollution sources.	Useful screening tool.	Large datasets are required.	[44]
10	Stable carbon isotopes ( $\delta^{13}\text{C}$ )	Field case study	Germany	Carbonate dissolution processes	Identified carbon sources in groundwater.	Separates natural vs anthropogenic carbon.	Biological processes complicate signals	[45]
11	Noble gas isotopes	Field case study	Italy	Groundwater age dating	Determined groundwater residence time.	Reconstructs contamination history.	Expensive instrumentation.	[46]
12	Rare earth elements/ groundwater	Field case study	USA	Geochemical fingerprinting	REE patterns linked chemistry to lithology.	Identifies geological sources.	Requires ICP-MS.	[47]
13	Hydrochemical facies analysis	Field case study	Nigeria	Aquifer characterization	Piper diagrams revealed dominant water types.	Supports contamination pathway analysis.	Qualitative interpretation.	[48]
14	CSIA / chlorinated solvents	Field case study	USA	Industrial contamination plumes	Identified multiple contaminant sources.	Determines liability.	High analytical cost.	[49]
15	Sulfur isotopes ( $\delta^{34}\text{S}$ )	Field case study	Germany	Sulfate contamination tracing	Distinguished gypsum dissolution from industrial sources.	Useful in mining pollution cases.	Isotopic overlap is possible.	[50]
16	Oxygen isotopes in phosphate	Lab-based analytical study	UK	Phosphorus pollution tracing	Identified anthropogenic phosphate sources.	Supports eutrophication studies.	The method is still developing.	[51]
17	Geochemical fingerprinting/ river	Field case study	China	River pollution assessment	Chemical signatures linked pollutants to industrial discharge.	Supports source identification.	Extensive sampling required	[52]
18	Mixing models	Lab-based modelling study	USA	Watershed contamination	Estimated proportional pollution sources.	Quantifies pollutant inputs.	End-member uncertainty.	[53]

Table 1 (contd....)

S. No.	Technique / Matrix	Study Type	Study Location /Region	Sample/ Study Focus	Major Findings	Forensic Relevance	Limitations/ Remarks	Ref.
19	Hydrochemical modelling	Lab-based modelling study	Global	Groundwater contamination transport	Modelled pollutant migration.	Supports forensic reconstruction.	Model uncertainty.	[54]
20	Stable isotopes ( $\delta^{18}O$ , $\delta^2H$ )	Field case study	Australia	Surface water origin studies	Identified evaporation and recharge sources.	Water provenance studies.	Seasonal variability.	[55]
21	Lead isotopes	Field case study	France	Heavy metal contamination	Identified industrial lead sources.	Environmental forensic evidence.	Complex isotopic mixing.	[56]
22	Mercury isotope analysis	Field case study	USA	Mercury contamination tracing	Isotopes revealed emission sources.	Pollution attribution.	Analytical complexity.	[57]
23	Hydrochemistry + isotopes	Field case study	China	Groundwater contamination	Combined methods improved source discrimination.	Strengthens forensic evidence.	Requires a multi-method approach.	[58]
24	Isotope hydrology	Field case study	South Africa	Groundwater flow studies	Identified recharge zones.	Supports contamination pathway tracing.	Baseline data required.	[59]
25	Organic contaminant fingerprinting	Field case study	USA	Petroleum hydrocarbon contamination	Linked contamination to refinery sources.	Environmental litigation support.	Weathering alters markers.	[60]
26	Environmental DNA / water	Lab-based	Denmark	Microbial contamination detection	Detected pollution sources	Emerging forensic tool	Method evolving	[61]
27	Nitrate isotope analysis	Field	Canada	Urban groundwater contamination	Identified sewage leakage	Infrastructure management	Seasonal variation	[62]
28	Radon tracing	Field	Australia	Groundwater-surface interaction	Identified discharge zones	Pollution transport tracing	Short half-life	[63]
29	Hydrochemical statistics	Field	Japan	Aquifer pollution	Cluster analysis grouped contamination	Environmental monitoring	Data quality dependence	[64]
30	Isotope mixing models	Lab	USA	River nutrient pollution	Estimated agricultural contribution	Watershed management	Model assumptions	[65]
31	Geochemical fingerprinting/ mine drainage	Field case study	United Kingdom	Mine drainage contamination	Metal ratios identified mining pollution sources.	Supports legal attribution of mining pollution.	Geological background noise.	[66]
32	Strontium isotope analysis/ groundwater	Field case study	Global	Water provenance studies	Sr isotopes identified mixing of aquifer sources.	Useful for hydrological forensic investigations.	Requires detailed geological data.	[67]
33	Isotope fractionation analysis/ contaminants	Lab-based analytical study	Germany	Biodegradation studies	Isotope fractionation identified microbial degradation pathways.	Tracks natural attenuation processes.	Complex interpretation.	[68]
34	Chromium isotopes/ groundwater	Field case study	United States	Industrial chromium contamination	Isotopes distinguished natural vs industrial chromium sources.	Supports remediation and pollution attribution.	Limited baseline data.	[69]
35	Hydrochemistry + GIS mapping	Field case study	Sudan	Pollution hotspot mapping	Spatial analysis identified contamination hotspots.	Supports environmental monitoring and management.	High sampling density required.	[70]
36	CSIA / BTEX compounds	Field case study	Germany	BTEX contamination in groundwater	Isotopic shifts indicated biodegradation processes.	Tracks remediation effectiveness.	High analytical cost.	[71]
37	Groundwater age tracers (CFCs)	Field case study	United States	Contamination timing studies	Age dating revealed the timing of contamination.	Supports environmental litigation.	Atmospheric variability.	[72]
38	Hydrogen isotopes/ water	Field case study	Global	Water origin identification	Isotopes distinguished meteoric and evaporated water.	Supports hydrological tracing.	Seasonal variability.	[73]

Table 1 (contd....)

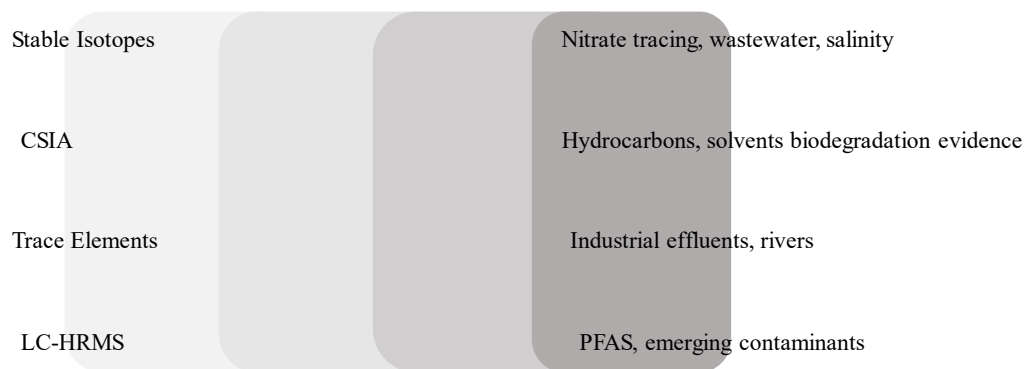
S. No.	Technique / Matrix	Study Type	Study Location /Region	Sample/ Study Focus	Major Findings	Forensic Relevance	Limitations/ Remarks	Ref.
39	Hydrochemical ratios/groundwater	Field case study	Netherlands	Saltwater intrusion studies	Ion ratios indicated seawater mixing.	Identifies contamination processes.	Requires baseline hydrochemistry.	[74]
40	Nitrogen isotope tracing / rivers	Field case study	United States	River eutrophication studies	Isotopes identified sewage-derived nutrients.	Supports water quality management.	Isotope overlap.	[75]
41	Trace element fingerprinting/runoff	Field case study	United States	Urban runoff contamination	Metal signatures linked pollution to traffic emissions.	Supports urban pollution investigations.	Complex source mixtures.	[76]
42	Sulfur isotopes/ mine drainage	Field case study	United States	Acid mine drainage studies	Isotopes identified sulfide oxidation processes.	Supports mining environmental regulation.	Isotopic variability.	[77]
43	Hydrochemical evolution modelling	Lab-based modelling study	Netherlands	Groundwater chemistry studies	Modelled geochemical evolution of groundwater.	Supports contamination pathway interpretation.	Model uncertainty.	[78]
44	Rare earth element analysis/ groundwater	Field case study	United States	Aquifer geochemistry	REE patterns indicated lithological control.	Supports geochemical fingerprinting.	Advanced instrumentation required.	[79]
45	Stable isotope hydrology/river basins	Field case study	Global	River basin hydrology	Isotopes identified precipitation sources.	Supports basin-scale hydrological investigations.	Temporal variability.	[80]
46	Isotopic analysis of dissolved inorganic carbon	Field case study	Canada	Carbon cycling in groundwater	Isotopes identified carbon sources.	Supports groundwater contamination assessment.	Biogeochemical complexity.	[81]
47	Environmental tracer techniques/ groundwater	Field case study	Australia	Groundwater flow investigation	Multiple tracers identified recharge zones.	Supports contamination transport studies.	Tracer availability.	[82]
48	Hydrochemical fingerprinting/ water chemistry	Field case study	United Kingdom	Industrial pollution studies	Chemical signatures linked pollutants to factories.	Supports regulatory enforcement.	Requires baseline monitoring.	[83]
49	Integrated isotopes + hydrochemistry	Field case study	China	Groundwater contamination	The combined approach improved source attribution.	Strengthens forensic evidence.	Complex data interpretation.	[84]
50	Multi-tracer hydrochemical analysis	Field case study	United States	Watershed pollution tracing	Multiple tracers identified dominant pollution sources.	Supports environmental forensic investigations.	High sampling requirements.	[38]
51	Stable isotopes ( $\delta^{15}\text{N}$ , $\delta^{18}\text{O}$ ) / nitrate	Field case study	United States	Urban nitrate contamination	Isotopes distinguished nitrate sources.	Supports pollution attribution.	Overlapping sources.	[18]
52	Multi-parameter chemical fingerprinting	Lab-based analytical study	United States	Contaminant plume fingerprinting	Fingerprints differentiated plumes from the background.	Environmental forensic investigations.	Depends on source samples.	[85]
53	CSIA ( $\delta^{13}\text{C}$ ) / chlorinated solvents	Field case study	United States	PCE/TCE biodegradation	CSIA proved in situ degradation.	Supports liability determination.	High analytical cost.	[25]
54	CSIA (C, H) + hydrocarbon indices	Field case study	Pakistan	Diesel spill attribution	CSIA distinguished diesel sources.	Fuel spill and theft attribution.	Overlap among fuels.	[26]
55	CSIA / organic pollutants	Review article	Global	Applications of CSIA	CSIA is useful for source and transformation analysis.	Benchmark forensic methodology.	Mixed-source issues.	[29]
56	CSIA theory/isotope fractionation	Review article	Global	CSIA conceptual framework	Provides a theoretical basis for isotope forensics.	Supports the interpretation of isotope evidence.	Complex fractionation.	[28]
57	LC-HRMS / PFAS analysis	Lab-based analytical study	Europe	PFAS contamination	Non-targeted PFAS improved source identification.	Supports PFAS regulation and litigation.	PFAS mixture complexity.	[35]

Table 1 (contd....)

S. No.	Technique / Matrix	Study Type	Study Location /Region	Sample/ Study Focus	Major Findings	Forensic Relevance	Limitations/ Remarks	Ref.
58	Geochemical fingerprinting/ sediments	Field case study	United States	River metal contamination	Fingerprints identified industrial and sewage inputs.	Assigns responsibility for pollution.	Sediment transport effects.	[31]
59	Stable isotopes (B, N, O)	Field case study	Sierra Leone	Wastewater tracing	Isotopes tracked wastewater infiltration.	Supports effluent contamination investigations.	Baseline data required.	[21]
60	CSIA / PACs in groundwater	Field case study	Canada	Petroleum contamination	CSIA distinguished diesel-derived PACs.	Oil spill forensic investigations.	Weathering alters isotopes.	[86]
61	CSIA / chlorinated benzenes	Field case study	Germany	Aquifer contamination	CSIA demonstrated natural attenuation.	Supports plume assessment.	Field heterogeneity.	[87]
62	Integrated hydrochemistry + isotopes + statistics	Field case study	China	Landfill contamination	Integrated methods delineated contaminant pathways.	Clarifies complex contamination cases.	Requires multidisciplinary expertise.	[36]
63	Trace element fingerprinting/rivers	Field case study	South Korea	Nakdong River pollution	Trace elements mapped anthropogenic sources.	Identifies pollution inputs.	High sampling density required.	[32]
64	CSIA protocols / contaminated sites	Review article	Global	CSIA workflow guidance	Provided QA/QC guidance for CSIA.	Improves forensic workflow reliability.	Standardisation needed.	[30]
65	Multi-isotope (S-O, O-H) + trace metals	Field case study	South Korea	Mining contamination	Isotopes separated mining vs natural sources.	Mining pollution attribution	Mixing complicates signals.	[23]
66	Hydrocarbon fingerprinting/soil & groundwater	Field case study	United States	Oil spill investigation	Hydrocarbon markers differentiated sources.	Petroleum contamination investigations.	Weathering effects.	[34]
67	Stable isotopes ( $\delta^{18}\text{O}$ , $\delta^2\text{H}$ , $\delta^3\text{H}$ )	Field case study	United States	Groundwater recharge study	Isotopes identified recharge and mixing.	Supports water rights and contamination disputes.	Requires isotopic baseline.	[88]
68	Strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ )	Field case study	Israel	Salinity and water-rock interaction	Sr isotopes traced salinisation processes.	Forensic tool for groundwater salinity.	Geological variability.	[22]
69	Multi-isotope ( $\delta^{11}\text{B}$ , $\delta^{15}\text{N}$ , $\delta^{18}\text{O}$ )	Field case study	France	Wastewater infiltration	Combined isotopes resolved wastewater sources.	Supports legal attribution.	Complex mixing effects.	[20]
70	CSIA hydrocarbons/ groundwater	Field case study	Germany	Hydrocarbon plume degradation	CSIA distinguished degradation from dilution.	Supports contamination liability assessment.	Technically demanding.	[27]
71	Trace elements + isotopes/ oilfield brines	Field case study	Mexico	Produced water contamination	Elemental ratios tracked produced water.	Oilfield contamination forensics.	Requires baseline characterisation.	[33]
72	Isotopic + hydrochemical tracers	Field case study	Italy	Groundwater contamination	Combined tracers identified anthropogenic impacts.	Supports contamination liability cases.	Overlapping isotopic signals.	[89]
73	Multiple isotopes (S, O, Sr)	Field case study	Japan	Mining and industrial contamination	Isotopes distinguish mining from natural sources.	Supports environmental litigation.	Long-term monitoring is required.	[24]
74	Stable isotope geochemistry / environmental samples	Review article	Global	Review of isotope theory and applications in environmental systems	Stable isotope systematics explain geochemical processes controlling water chemistry and contaminant tracing.	Provides a theoretical framework supporting forensic hydrochemistry applications and isotope-based source attribution.	Conceptual review does not present site-specific case studies.	[90]
75	Stable isotopes ( $\delta^{15}\text{N}$ , $\delta^{18}\text{O}$ ) / groundwater nitrate	Field case study	South Korea	Identifying agricultural vs. sewage nitrate sources in groundwater	Dual nitrate isotopes distinguished nitrate derived from fertilisers and sewage inputs.	Enables forensic identification of nitrate pollution sources in groundwater systems.	Overlapping isotopic ranges between sources may complicate interpretation.	[19]

Complementary approaches include geochemical fingerprinting [31, 32], trace element ratios [33], and hydrocarbon markers [34], which helped identify pollutant plumes, industrial effluents, and petroleum sources. Evolving liquid chromatography- high-resolution techniques such as LC-HRMS for PFAS [35] expanded forensic capabilities to persistent pollutants. Integrated studies [36] combining hydrochemistry, statistics, and isotopes provided a clear delineation of pollutant pathways in complex systems. Overall, isotopic and chemical fingerprinting techniques significantly advanced environmental forensics by enabling source attribution, evidence of degradation, and legal accountability.

Overall, chemical and isotopic fingerprinting techniques significantly advanced environmental forensics by allowing source attribution, evidence of degradation, and legal accountability. Limitations remain in the form of overlapping isotopic ranges, baseline data requirements, and cost-intensive analyses, highlighting the need for multi-tracer and multidisciplinary techniques. Fig. (3) shows an overview of major forensic techniques and their applications. Stable isotopes are used for nitrate tracing, wastewater attribution, and salinity studies. Compound-specific isotope analysis (CSIA) addresses hydrocarbons, solvents, and biodegradation evidence. Trace elements identify industrial effluents and riverine inputs, whereas LC-HRMS extends forensic capacity to PFAS and evolving pollutants.



**Figure 3:** Summary of isotopic and geochemical forensic techniques.

## 4. Discussion

### 4.1. Isotopic Techniques for Source Attribution

Stable isotope techniques were among the most widely used forensic tools across the reviewed studies. Nitrogen and oxygen isotopes ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ) effectively distinguished nitrate derived from agricultural fertilisers, septic tanks, and sewage [18, 19]. However, overlapping isotopic ranges often limited precision, needing baseline characterisation of local sources. Boron isotopes ( $\delta^{11}\text{B}$ ) offered additional discriminatory power for wastewater tracing, with Sankoh, Derkyi [21] and Widory, Petelet-Giraud [20] illustrating how multi-isotope frameworks ( $\delta^{11}\text{B}$ ,  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ) resolved urban wastewater infiltration into aquifers. Strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) were also pertinent for apportioning salinity and water-rock interactions [22], particularly in arid and mining-influenced basins. Multi-isotope studies [23, 24] showed that combining sulphur, strontium and oxygen offered robust attribution of mining and industrial pollutants. These findings underscore isotopic fingerprints as critical forensic markers for differentiating natural background processes from human inputs.

#### 4.1.1. Evidence-Based Support for Legal Accountability and Litigation Outcomes

The capacity of forensic hydrochemistry to strengthen legal accountability is fundamentally tied to its ability to meet rigorous evidentiary standards, such as the Daubert or Frye standards, by providing objective, reproducible data. While conventional monitoring may indicate the presence of a pollutant, isotopic and geochemical fingerprinting offer the "silent witness" necessary for source attribution in environmental crime cases. Explicit case-study evidence from the reviewed literature demonstrates that these techniques move beyond general observation to provide scientifically defensible evidence in litigation.

#### **4.1.2. Compound-Specific Isotope Analysis (CSIA) and Liability**

In cases of groundwater pollution involving chlorinated solvents or petroleum hydrocarbons, Compound-Specific Isotope Analysis (CSIA) has proven indispensable for determining liability. Unlike concentration-based data, which can be affected by simple dilution, CSIA tracks the isotopic fractionation that occurs during microbial degradation. Studies have established CSIA's value in proving in-situ biodegradation, allowing investigators to distinguish between active remediation (natural attenuation) and the simple physical migration of a contaminant plume. This distinction is critical in court for assigning long-term environmental liability and financial responsibility for cleanup. For instance, CSIA sulfur in chlorinated solvents like PCE and TCE has been used as a benchmark methodology for proving degradation, which directly informs the legal determination of how long a pollutant has been present in an aquifer.

#### **4.1.3. Multi-Isotope Frameworks in Mining and Salinity Disputes**

Furthermore, multi-isotope frameworks have significantly improved litigation outcomes in complex industrial and mining disputes. The integration of sulfur, oxygen, and strontium isotopes has successfully distinguished acid mine drainage (AMD) from natural geogenic sulfate in volcanic and sedimentary aquifers. Research by Hosono, Hossain [24] suggests that combining these tracers offers a robust attribution of mining and industrial pollutants, even in regions with high geological background noise. This level of precision enables the precise assignment of responsibility to specific mining operations, transforming what was once speculative "geological variability" into court-admissible forensic evidence. Similarly, Vengosh, Spivack [22] utilised strontium isotope ratios to apportion salinity sources in coastal aquifers, successfully distinguishing between seawater intrusion and the dissolution of evaporitic minerals—a finding with significant implications for water-rights litigation.

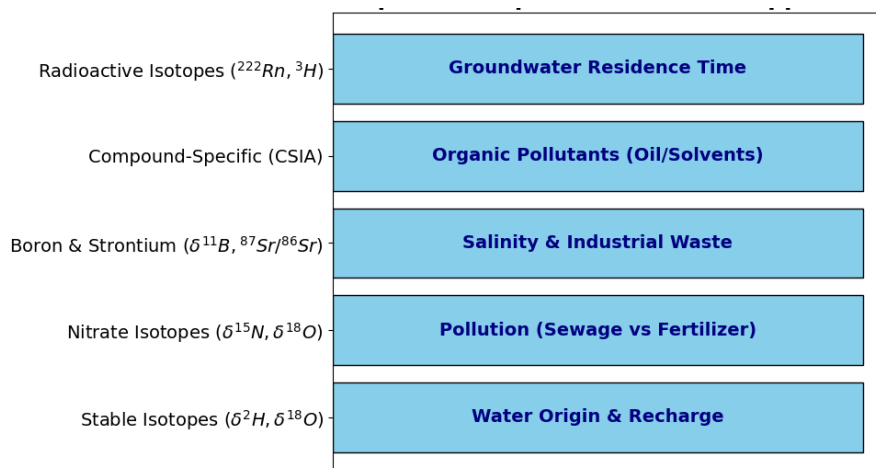
#### **4.1.4. Resolving Urban and Agricultural Conflicts**

In urban settings, the legal defensibility of forensic hydrochemistry is highlighted by the use of dual-isotope plots combined with boron. Case studies by Widory, Petelet-Giraud [20] and Sankoh, Derkyi [91] show that boron serves as a unique tracer for detergents, which are ubiquitous in domestic wastewater but absent in agricultural runoff. This allows forensic investigators to resolve disputes between municipal sewer authorities and agricultural entities by providing a clear isotopic map of pollutant origins. By identifying "fingerprint" regions for specific sources like manure or fertilisers, these dual-isotope plots provide the scientifically defensible evidence required for source attribution in environmental crime cases.

#### **4.1.5. Emerging Pollutants and High-Resolution Forensics**

As environmental crimes evolve to include "forever chemicals" and pharmaceuticals, the field is expanding into high-resolution mass spectrometry (LC-HRMS). Work by Charbonnet, Rodowa [92] on PFAS (per- and polyfluoroalkyl substances) has demonstrated that non-targeted screening can identify specific chemical markers linked to individual manufacturers or industrial processes. This level of granularity is essential for modern litigation, where multiple potential polluters may be located in the same catchment area. By bridging the gap between conventional monitoring and advanced chemical signatures, forensic hydrochemistry transforms subjective observations into objective data, thereby improving litigation outcomes and contributing to the wider pursuit of sustainability and responsible resource management.

Fig. (4) shows a dual isotope plot that differentiates nitrate pollution sources by mapping  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  ratios. Specific sources, like manure or fertilisers, occupy unique "fingerprint" regions. This allows forensic investigators to distinguish human waste from agricultural runoff, providing scientifically defensible evidence for source attribution in environmental crime cases. The use of stable isotope techniques has become one of the most effective analytical methods used in forensic hydrochemistry due to the fact that it gives natural tracers that would be used to resolve various sources of contamination in intricate hydrological systems [4, 93]. In contrast to the traditional chemical analyses in which the concentrations of pollutants are the main results, isotopic signatures present the data about the origin and the change of substances in the environmental matrices [71, 94]. This has seen isotopic methods take centre stage in the environmental forensic examinations, in which it is important to establish the source of contamination that caused the issue to hold the involved parties accountable, as well as ensure that the environmental dumping issue is relieved.



**Figure 4:** Isotopic techniques and forensic applications.

Analysis of nitrogen and oxygen isotopes in nitrate ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) is one of the most commonly used isotopic instruments in hydrochemical studies. These isotopes have been very useful in separating nitrates that are formed through agricultural fertilisers, sewage effluent, atmospheric deposition and soil organic nitrogen [95, 96]. Evidence on the use of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  as an indicator of the origin of nitrates in alpine watershed systems was established by Campbell, Kendall [18] that showed that atmospheric deposition and soil nitrification processes could contribute to the overall pattern of nitrates. Their research demonstrated that using the technique of isotopic analysis might distinguish between natural and anthropogenic components of nitrogen cycling in the framework of groundwater.

Based on this study, Kaown, Koh [97] used dual isotope methods to determine several sources of nitrate pollution in groundwater systems, and were able to separate nitrogen produced by fertilisers and sewage as well as by septic tanks. The results underscore the significance of the isotopic prints in the anthropogenic pollution tracing in agricultural and urban settings.

Although effective, nitrogen and oxygen isotopes have some cases in which they overlap with other isotopic backgrounds of different sources of nitrates, and this may complicate the interpretation [96, 98]. As an example, manure and sewage-derived nitrate usually have similar  $\delta^{15}\text{N}$  value, so it is hard to conclude what exactly causes the contamination using only two isotopes. To overcome this shortcoming, multi-isotope techniques are being more extensively used, which involve combining other isotopic tracers. Widory *et al.* have shown that the addition of boron isotopes ( $\delta^{11}\text{B}$ ) together with  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  has a great influence on the ability to differentiate the source of the wastewater in the groundwater system. Boron isotopes were used in their study as a special tracer of detergents, which are frequently present in domestic wastewater, and this facilitated the capacity to differentiate urban sewage pollution and agricultural nitrogen runoff [99]. On the same note, the literature emphasised the role of multi-isotope frameworks in investigating groundwater pollution in developing nations, whereby baseline hydrochemical information are frequent limitation [91, 100]. These analyses indicated that the more isotopic tracers used, the more evidence they have on attributing sources and also give more credibility to forensic interpretations.

In addition to the study of nitrogen and boron isotopes, the ratios of strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) have also been widely used in forensic hydrochemistry [67]. Isotopes of strontium are highly advantageous, as their ratios are highly sensitive to the geological composition of materials forming the aquifers and thus, they give information on the interaction between water and rocks and geochemical evolution. Likewise, the use of strontium isotopes was reported to determine the source of salinity in the groundwater sources of coastal aquifers in Israel [22]. Their study indicated that the salinity was not only caused by the intrusion of the seawater but also affected by the dissolution of the evaporitic minerals in the aquifer system. This was a remarkable discovery in that the isotopic methods were capable of distinguishing between the natural geologic processes and human impacts on the chemistry of groundwater.

Multi-isotope methods with sulphur, oxygen, and hydrogen isotopes have also been applied in tracking industrial pollution, mining effects, and wastewater release, in addition to the strontium isotopes. Hosono, Hossain [24] examined the hydrobiogeochemical evolution in Japanese volcanic aquifers with the help of numerous isotopic tracers and was able to prove that groundwater chemistry might be affected by both natural geochemical processes and anthropogenic activities. In their research, the authors highlighted the role of combining isotopic data with hydrochemical measurements in seeking to effectively elucidate the origin of contaminants in complicated geological environments.

The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are also important stable water isotopes that are critical in forensic hydrology, especially in determining sources of recharge and hydrological chains [101]. Thus, isotopes in water can give information about atmospheric processes, evaporation and recharge mechanisms of groundwater. These isotopes assist in the determination of the origin of the contaminants, whether they are formed locally through precipitation or in the river or the imported water. This kind of information can be of great significance in a case of environmental litigation, where it is possible to determine the source of the polluted water, hence making it the source of contamination.

The other important usage of isotopic methods is in determining mining-related pollution. In the mining industry, it is common to use the multiple sulfur isotope ( $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ , and  $\delta^{36}\text{S}$ ) to differentiate between sulphate in natural geologic formations and sulphate produced by oxidation of sulphide minerals in the mining process [77]. Multi-isotope systems, which incorporate sulphur, oxygen and strontium isotopes, have found applications that have been especially useful in the determination of acid mine drainage and other mining-related pollutants [84]. These isotopic features give distinctive geochemical prints which can directly attribute pollution episodes to given mining activities.

Isotopic techniques are not limited to their significant benefits. A significant limitation is the fact that one needs a great deal of background information to develop natural isotopic curves in a particular area. In the absence of sufficient baseline data, it is hard to explain the difference between natural variability and anthropogenic inputs. Likewise, isotopic studies may involve complex equipment like isotope ratio mass spectrometry (IRMS), which is both costly and technologically challenging [45]. These can be a constraint in the popularisation of the isotopic methods in developing nations where there is a lack of analytical facilities.

Nonetheless, these limitations are being overcome by some improvements in analytical technology and statistical modelling. The most recent approach to enhancing the classification of pollutant sources is the proposed machine learning methods that are integrated with isotopic datasets. The study by Samborska-Goik and Wassenaar [3] showed that sophisticated data analytics could be used to improve the interpretation of the isotopic data sets to find subtle patterns in the environmental data that would have otherwise been missed. These innovations are a significant move in enhancing the precision and the availability of the isotopic forensic techniques.

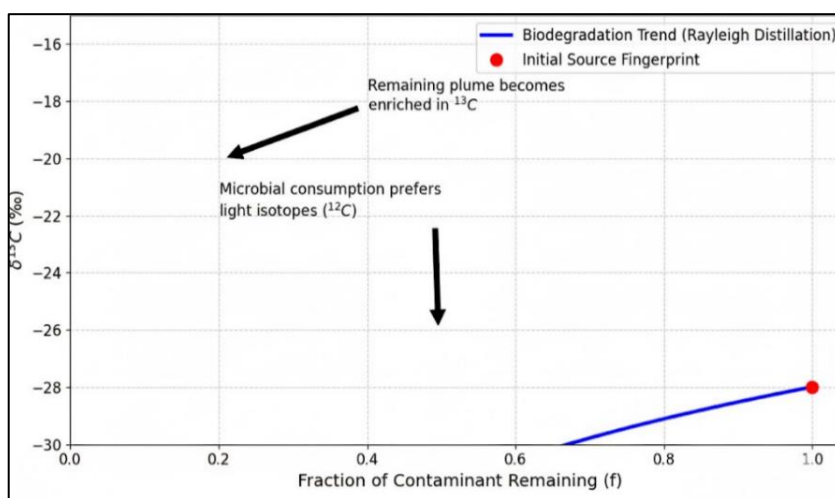
On the whole, the isotopic methods are still a part of forensic hydrochemistry since they are credible and scientifically justifiable methods of determining the sources of contamination. Their capacity to differentiate between natural and human-made pollution makes them very essential in environmental monitoring, enforcement of regulations and legal investigations. Following the growing complexity of contaminating the environment as a result of urbanisation, industrialisation, and climate change, the field of using isotopic tracers in environmental forensics will continue to grow.

## 4.2. CSIA and Biodegradation Evidence

Compound-specific isotope analysis (CSIA) emerged as a robust forensic method to establish not just pollutant origin but also transformation processes. Mundle, Johnson [25] showed that CSIA of chlorinated solvents offered definitive proof of in-situ Biodegradation, which is essential for liability and remediation decisions. In the same vein, Meckenstock, Morasch [27] revealed that CSIA could separate the degradation process from dilution effects in hydrocarbon plumes-an essential distinction for legal disputes. Muhammad, Frew [26] further extended CSIA to diesel attribution, integrating statistical and isotopic tools to discriminate between multiple diesel sources in spill

or theft investigations. However, CSIA applications remain technically demanding and costly and weathering effects can obfuscate interpretation [86]. Even so, the method's ability to offer direct evidence of degradation represents a major advancement for Environmental forensics.

One of the best methodology developments in the field of environmental forensics is Compound-specific isotope analysis (CSIA). In contrast to bulk isotope analysis, which quantifies the isotopic signatures of pools of chemicals in a complex mixture, CSIA can determine the amounts of individual compounds in a complex mixture of contaminants [71, 102]. This enables the scientists to trace the source, transformation, and degradation route of a certain pollutant in the environment. Consequently, CSIA is now a critical method to examine contamination of hydrocarbons, chlorinated solvents, pesticides and other organic pollutants. Fig. (5) shows a graph illustrating Compound-Specific Isotope Analysis (CSIA) as proof of biodegradation. As microbes consume a contaminant (moving left on the x-axis), they preferentially use light isotopes, causing the remaining plume to become enriched in heavy  $^{13}\text{C}$ . This distinct isotopic trend provides scientific evidence of active degradation versus dilution.



**Figure 5:** Conceptual CSIA evidence for biodegradation.

Fig. (5) illustrates a conceptual framework for environmental forensic investigations. It shows how the integration of multiple tracers (isotopes and chemical markers), statistical analysis, and site data transitions from a pollutant plume into actionable forensic evidence, ultimately informing regulatory investigation and environmental policy.

The possibility to separate between the process of contaminants degradation and a simple process of dilution is one of the main benefits of CSIA. Declining pollutant concentrations in most incidences of groundwater contamination can be taken as signs of natural attenuation. Nonetheless, the reduction in concentration on its own does not always imply biodegradation since the contaminants can be diluted by mixing or dispersion by groundwater. CSIA overcomes this weakness by considering the isotopic fractionation taking place in the course of chemical reactions [71, 103]. As the microorganisms break down organic contaminants, the lighter isotopes are used at a higher rate and a detectable difference in isotopic composition is therefore observed. This documentary enrichment offers a first-hand testament that the biodegradation is in the process of taking place.

Schmidt, Zwank [71] were also among the earliest scientists to establish the usefulness of stable isotope fractionation analysis in the biodegradation of contaminated aquatic environments. They demonstrated that the use of isotopic enrichment of hydrocarbon compounds in carbon and hydrogen isotopes would allow the quantitative demonstration of microbial degradation taking place. Notably, the authors highlighted that isotopic fractionation patterns were applicable in order to differentiate between biodegradation and non-reactive processes like dilution or sorption.

The continued evolution of CSIA methodology has made it possible to do finer studies on the sources of contaminants. Indicatively, Mundle, Johnson [25] used CSIA on chlorinated solvents in groundwater and proved

that isotopic signatures could indicate the presence of in-situ biodegradation when remediation efforts were being performed. Their results offered a good indication that micro-processes were actively modifying contaminants within the subsurface environment, thus embracing natural attenuation approaches in managing the environment. On the same note, binti Muhammad [104] applied CSIA in the forensic study of diesel contamination. With the combination of using isotopic analysis and statistical modelling methods, the researchers could differentiate between various sources of diesel in spill and theft studies [25, 49, 103]. This method proved the ability of CSIA to solve complicated contamination cases in cases of mixtures of various sources of petroleum products.

Besides the hydrocarbon pollution, CSIA has been used on pesticides, pharmaceuticals and new organic pollutants. Schürner, Maier [105] carried out experimental research of isotopic fractionation of pesticides and pharmaceuticals in aquifer models. Their study showed that the compound-specific isotope signatures could be involved in the tracing of the degradation paths of these contaminants, giving great information on their environmental behaviour and persistence.

Although CSIA has great potential, it is linked with a number of challenges. One of the weaknesses relates to the effect of environmental weathering conditions, including evaporation, photodegradation, and sorption processes, which may occasionally modify the isotopic profiles and make them hard to interpret [106, 107]. Likewise, the methodology needs advanced analytical instrumentation and specific skills that might limit its use in off-the-shelf environmental surveillance programs. The other problem is in the interpretation of isotopic data in complicated environmental systems where several processes can take place at a time [68, 106, 107]. As an example, biodegradation, dilution, volatilisation, and chemical transformation can all have a role in the contaminant levels and isotopic patterns. The main problem of CSIA is that researchers now combine it with additional methods of analysis, including hydrochemical analysis, molecular biology instrumentation and statistical modelling [71, 106].

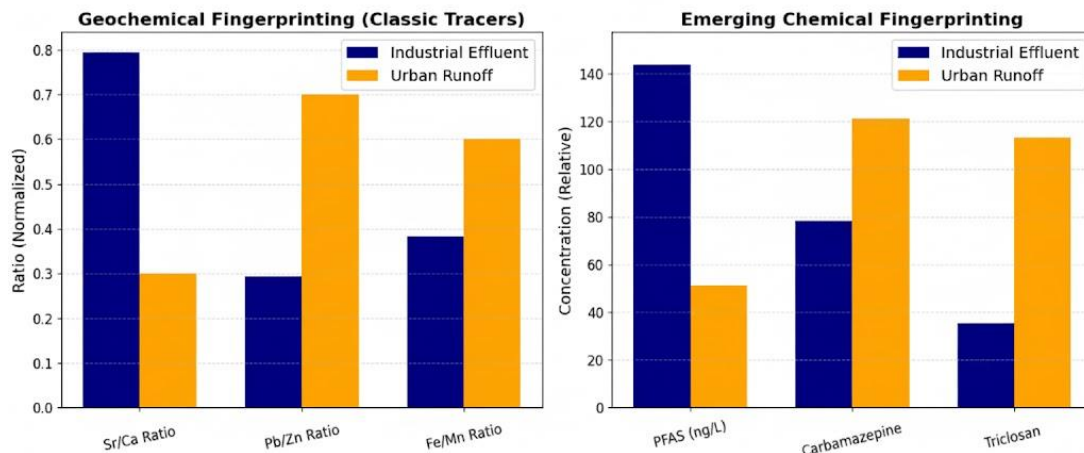
The current reviews published by Won, Eun-Ji [29] and Jonás, García-Rincón [30] highlight the significance of standardised CSIA workflow and quality control measures to guarantee the reliability of the results [108]. Such studies indicate that stringent methodological models should be used, comprising, but not limited to, calibration standards, isotope mass balance calculations, and error analysis. The issue of standardisation is especially significant in the forensic setting, where the outcomes of the analysis can be retained as evidence in the court of law.

Nevertheless, CSIA is still among the most potent methods that can be used in environmental forensic investigations. The fact that it can give first-hand evidence of degradation of the contaminants makes it invaluable in litigation situations where there is a need to ascertain the blame that led to the occurrence [102, 109]. In addition, CSIA also provides a better remediation strategy by establishing whether there are effective natural processes for reducing the concentration of contaminants in the groundwater systems. CSIA is likely to be used even more as the products of analytical technologies develop. The sensitivity and efficiency of compound-specific isotopic measurements are likely to be enhanced by such innovations as high-resolution mass spectrometry and automated isotope analysis [71, 103]. These innovations will increase the capability of forensic hydrochemistry in handling a more complex environmental contamination scenario.

### **4.3. Geochemical and Emerging Chemical Fingerprinting**

Beyond isotopes, geochemical fingerprinting using trace metals and hydrocarbon markers played a key role in pollution attribution. Miller, Mackin [31] and Jung, Jeong [32] used trace element fingerprints in rivers successfully to differentiate industrial and sewage contributions, although sediment transport processes sometimes blurred signals. Hydrocarbon fingerprinting [34] and petroleum markers have been used for oil spill investigations, though their reliability might decline due to weathering and environmental alteration. More recently, Charbonnet, Rodowa [35] introduced LC-HRMS for PFAS investigations, combining targeted and non-targeted analysis to trace complex mixtures of persistent pollutants. This represents an important expansion of forensic chemistry into emerging pollutants with considerable regulatory implications. Alongside the isotopic techniques, trace element and organic molecular fingerprinting techniques are now also a vital element of environmental forensic studies (Fig. 6).

Geochemical fingerprinting has the basis of the idea that various pollution sources have unique chemical signatures which are useful in tracking the contaminants to their source. Such chemical traces can be trace-metals, rare earths, distributions of hydrocarbons and other molecular tracing [40, 76, 104].



**Figure 6:** Comparative analysis of geochemical ratios and emerging chemical markers for source attribution.

The use of trace element analysis to differentiate between industrial, municipal, and natural sources of contamination in the aquatic systems has been very prevalent. Indicatively, Miller, Jerry [31] established that trace metal fingerprints had the capacity to distinguish the industrial effluent input and the municipal wastewater input into the river systems [46, 62, 63, 75, 83]. The researchers determined the major sources of contamination and measured their effects on the environment by examining the relative content of the metals, which included lead, zinc, copper, and cadmium. On the same line, the trace elements fingerprinting technique was used to test pollution in urban rivers affected by various anthropogenic activities [42, 76, 104, 110]. Their examination showed that there were unique geochemical indications of industrial discharge, urban run-off, and sewage effluent. The findings revealed the significance of the trace element analysis as a measure to determine sources of pollution within many urbanised settings where the presence of more than one contaminant can be common.

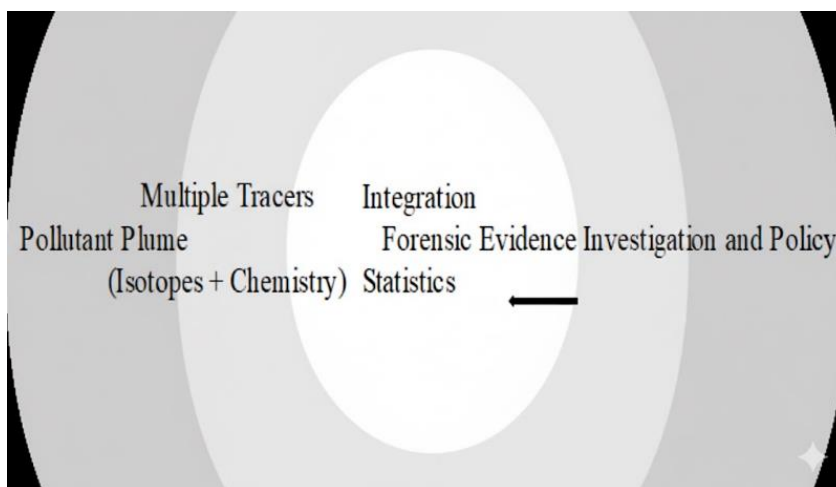
Geochemical fingerprinting is also used in investigating oil spills and petroleum contamination. Hydrocarbon fingerprint methods involve the analysis of the distribution of certain compounds of petroleum, including polycyclic aromatic hydrocarbons (PAH) and biomarkers, to determine the source of spilt oil. Such methods have extensively served in environmental forensics to know whether the oil pollutant is tanker spillage, pipeline leakage, or natural leakage [40, 76, 104]. Hydrocarbon fingerprinting may, however, be complex with the influences of the weathering of the environment, which changes the chemical composition of the products of petroleum with time [104]. Evaporation, oxidation and the degradation by microbes may alter the proportion of hydrocarbon substances, and it becomes harder to trace the true source of contamination. Nonetheless, these problems have been overcome through the adoption of advanced analytical procedures and statistical modelling methods that have enhanced the accuracy of the hydrocarbon fingerprinting methods.

Recent developments in the field of analytical chemistry have characterised the field of environmental forensic studies to include new contaminants such as perfluoroalkyl and polyfluoroalkyl substances (PFAS), pharmaceuticals, and personal care products [40, 43, 49, 104, 108]. Thus, the application of liquid chromatography-high resolution mass spectrometry (LC-HRMS) in conducting the forensic examination of PFAS contamination was proposed. The methodology consisted of the focused study of the established PFAS chemicals and the non-target screening strategies that could reveal the presence of new pollutants. This combined method of analysis is one of the greatest improvements in the science of environmental forensics since it provides the researcher with the ability to identify complex formulations of new contaminants that might not otherwise be known through the traditional method of analysis. With the growing regulatory interest in PFAS and other recalcitrant contaminants, the methods will become more significant in future environmental studies.

The other emerging opportunity is the application of rare earths as geochemical tracers (REEs). REEs are characterised by typical distribution patterns which may either represent geological sources, industrial emissions or human-made inputs. Johannesson, Tang [79]; Johannesson, Telfeyan [47] found that REE signatures in organic-rich waters have the potential to offer useful information on geochemical processes and transport of pollutants in waters. These factors, hence, provide supplementary devices in separating natural background situations from human pollution. In general, geochemical fingerprinting methods complement the isotopic ones by providing more evidence on the attribution of the pollutant's origin. By applying both of them, it is possible to have a more in-depth insight into the contamination processes and enhance the credibility of forensic interpretations.

#### 4.4. Integrated and Multidisciplinary Solutions in Forensic Hydrochemistry

Several studies emphasised the value of integrating isotopes, hydrochemistry, and statistical approaches to tackle complex contamination scenarios. Zhou, Xiong [36] showed that combined methods were critical for distinguishing landfill leachate from sewer-derived pollutants in urban systems, providing clarity in cases where single-tracer approaches fell short. Reviews by Schürner, Maier [28], Won, Yun [29], and Jonás, Evangelos Gatsios [30] underscored the need for standardised CSIA workflows, QA/QC procedures, and theoretical frameworks to ensure reproducibility and reliability in forensic investigations. Together, these results reveal that no single technique is universally sufficient; rather, multi-tracer and multidisciplinary strategies are essential for robust attribution, particularly where overlapping isotopic signals or complex mixing processes occur. Fig. (7) shows a workflow diagram showing the integration of isotopic, hydrochemical, and statistical tools in environmental forensic investigations. The processes move from pollutant plume identification, through multi-tracer analysis and integration to the production of defensible forensic evidence for litigation and policy action. The scenarios of environmental contamination are usually very complicated, with a variety of sources of pollutants, various modes of transport, and evolving biogeochemical processes. When this happens, it might be the case that based on a single style of analysis, one can arrive at ambiguous or inconclusive results. There is, therefore, a growing focus on the need to utilise integrated and multidisciplinary methods which integrate various lines of evidence into a form of sound pollutant source attribution. The combination of the isotopic analysis, hydrochemical parameters and multivariate statistical techniques is one example of such integration [41, 84].



**Figure 7:** Integrated forensic hydrochemistry approach.

This method can be effective in identifying the sources of contamination of landfill leachate and sewer-derived pollution in urban groundwater systems. The researchers could discard the overlapping signals of the contaminants and define the primary sources of the pollution by combining the isotopic tracers with the statistical results of the hydrochemical measurements. On the same note, an environmental forensic approach was used together with multivariate statistical models to unfold intricate pollution cases with numerous industrial and mining emitters [43, 111]. These analyses revealed that statistical methods like principal component analysis (PCA) and cluster analysis may be utilised to reveal patterns in big environmental data and may assist in interpreting isotopic and geochemical signatures.

The integrated methodologies are especially useful when the isotopic signals coincide or when the chemical fingerprints can be changed because of environmental factors. As an example, the conjunction of isotopic tracers with the microbial analysis may lead to information regarding the biodegradation pathways and contaminant transformation processes. These interdisciplinary studies enable the researcher to correlate the chemical alterations with those of biological processes, resulting in the enhancement of the environmental forensic interpretations.

Schürner, Maier [105]; Won, Yun [108] and Hughes and Jonas [112] also highlight in their recent reviews that it is important to build standardized analytical frameworks in integrated forensic investigations. These papers point to the necessity of strict quality assurance, quality control measures, standardised sampling requirements and reproducible workflows in analysis. To make sure that forensic hydrochemical evidence can be scientifically well-grounded, it is necessary to establish such standards and guarantee the legal admissibility of such evidence.

The other significant feature of multidisciplinary methods is the combination of hydrological modelling and forensic chemical studies [113, 114]. The ability to simulate groundwater flow, contaminant transport and mixing within an aquifer system can be done by hydrological models. With the isotopic and geochemical data, these models can be used to determine the occurrences of contamination and the most probable sources of the pollutants. The development of integrated forensic methodologies is also being facilitated by the success of data science and machine learning. Machine learning algorithms are able to process huge datasets of the environment and determine trends which would otherwise be hard to recognise with the help of conventional statistical techniques [115, 116]. These methods can be used to enhance the predictive abilities of environmental forensic inquiries and enhance the classification of sources of pollutants.

From a regulatory and legal point of view Integrated forensic hydrochemistry creates firmer evidence of litigation and policy decision-making in the environment. Through the integration of two or more independent lines of evidence, investigators will be in a position to come up with stronger and justifiable conclusions concerning the source and effects of environmental contamination. This interdisciplinary model thus enhances the role of science in environmental legislation and regulation. Altogether, integrated forensic hydrochemistry is the future of investigations of environmental contamination. Isotopic, chemical, statistical and modelling techniques can be used together to source attribution in complex environmental systems to provide more accurate, reliable results. With the current development of analytical technologies, the combination of a variety of scientific methods will become more significant in ensuring environmental justice and protecting water resources.

## 5. Conclusion

Forensic hydrochemistry has evolved as a transformative field, bridging science, law, and environmental protection. By applying isotopic geochemical and compound-specific analytical techniques, it enables accurate source attribution of contaminants, provides evidence of degradation processes, and strengthens legal accountability in environmental crime investigations. The reviewed studies underscore its effectiveness in tracing nitrate, hydrocarbons, metals, and emerging pollutants, e.g., PFAS, while also emphasising limitations such as overlapping isotopic ranges, baseline data needs, and high analytical costs. Importantly, integrated multi-tracer and multidisciplinary approaches offer the most robust results, especially in complex pollution scenarios. As water-related crimes and emerging contaminants increase, advancing standardisation, affordability, and data accessibility will be essential. Lastly, forensic hydrochemistry not only supports environmental justice but also contributes to safeguarding water resources and ensuring sustainability for future generations.

## Conflict of Interest

The authors declare that there are no competing interests associated with this manuscript.

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## Author Contribution

S.U.W: Conceptualization, methodology design, systematic search, data synthesis, writing – original draft, manuscript revision.

N.B.A: Methodology supervision, analytical oversight, interpretation of isotopic and geochemical data.

I.U.K: Data extraction, validation, cross-checking, contribution to Results and Discussion.

S.I: PRISMA methodology refinement, literature matrix organization, critical manuscript revisions.

A.B.U: Conceptual framework support, review of hydrochemical and forensic components, editing, proofreading, final manuscript harmonization.

## References

- [1] Bañuelos JL, Borguet E, Brown Jr GE, Cygan RT, DeYoreo JJ, Dove PM, *et al.* Oxide- and silicate-water interfaces and their roles in technology and the environment. *Chem Rev.* 2023; 123(10): 6413-544. <https://doi.org/10.1021/acs.chemrev.2c00130>
- [2] Claude C, Miche H, Gassier G, Cherigui F, Dutour Y. Hydrogeochemical and isotopic approach to groundwater management in a Mediterranean city dependent on external water supply (Aix-en-Provence, SE France). *Water.* 2025; 17(11): 1634. <https://doi.org/10.3390/w17111634>
- [3] Samborska-Goik K, Wassenaar LI. Reimagining the Kendall plot: using  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate and advanced machine learning to improve N pollutant source classification. *Isotopes Environ Health Stud.* 2025;61(3):310-35. Available from: <https://doi.org/10.1080/10256016.2025.2467863>
- [4] Brčeski I, Vaseashta A. Environmental forensic tools for water resources. In: *Water Safety, Security and Sustainability: Threat Detection and Mitigation.* Springer; 2021. p. 333-70. [https://doi.org/10.1007/978-3-030-76008-3\\_15](https://doi.org/10.1007/978-3-030-76008-3_15)
- [5] Thorén H, Soininen N, Kotamäki N. Scientific models in legal judgements: the relationship between law and environmental science as problem-feeding. *Environ Sci Policy.* 2021; 124: 478-84. <https://doi.org/10.1016/j.envsci.2021.07.018>
- [6] He X. Judicialisation for environmental public interest protection in China: the faces of court in different forms of environmental litigation. *J Energy Nat Res Law.* 2025; 43(2): 179-202. <https://doi.org/10.1080/02646811.2024.2365070>
- [7] Kumar A, Kumar A, Seema K, Kumari K. Detection and remediation techniques for emerging contaminants. In: *Emerging Contaminants in Water and Wastewater: Sources and Substances.* Springer; 2025. p. 223-53. [https://doi.org/10.1007/978-3-031-82579-8\\_10](https://doi.org/10.1007/978-3-031-82579-8_10)
- [8] Talreja N, Hegde C, Kumar EM, Chavali M. Emerging environmental contaminants: sources, consequences and future challenges. In: *Green Technologies for Industrial Contaminants.* 2025. p. 119-49. <https://doi.org/10.1002/9781394159390.ch5>
- [9] O'Dea RE, Lagisz M, Jennions MD, Koricheva J, Noble DW, Parker TH, *et al.* Preferred reporting items for systematic reviews and meta-analyses in ecology and evolutionary biology: a PRISMA extension. *Biol Rev.* 2021; 96(5): 1695-722. <https://doi.org/10.1111/brv.12721>
- [10] Parums DV. Review articles, systematic reviews, meta-analysis, and the updated preferred reporting items for systematic reviews and meta-analyses (PRISMA) 2020 guidelines. *Med Sci Monit.* 2021; 27: e934475-1. <https://doi.org/10.12659/MSM.934475>
- [11] Lourenço MdSTA, Di Maggio RM, Germinario C, Grifa C, Izzo F, Langella A, *et al.* Discovering halite traces on a victim's clothing through a forensic geoscience analytical approach: a suspicious case in Italy. *Forensic Sci.* 2024; 4(3): 396-408. <https://doi.org/10.3390/forensicsci4030024>
- [12] Achathuparambil Gopalakrishnan B, Varghese GK, Pivato A, Lega M. Pollution crime scenario reconstruction for effective environmental redress. *Environ Forensics.* 2025; 26(2): 276-91. <https://doi.org/10.1080/15275922.2024.2431313>
- [13] Baragaño D, Ratié G, Sierra C, Chrastrný V, Komárek M, Gallego J. Multiple pollution sources unravelled by environmental forensics techniques and multivariate statistics. *J Hazard Mater.* 2022; 424: 127413. <https://doi.org/10.1016/j.jhazmat.2021.127413>
- [14] Frankham GJ, Ogden R, Baker BW, Ewart KM, Johnson RN, Kuiper I, *et al.* Standards in wildlife forensic science, with a focus on non-human DNA analysis. *Anim Genet.* 2025; 56(2): e70005. <https://doi.org/10.1111/age.70005>
- [15] Clément P, Schlage WK, Hoeng J. Recent advances in the development of portable technologies and commercial products to detect  $\Delta^9$ -tetrahydrocannabinol in biofluids: a systematic review. *J Cannabis Res.* 2024; 6(1): 9. <https://doi.org/10.1186/s42238-024-00216-0>
- [16] Rethlefsen ML, Page MJ. PRISMA 2020 and PRISMA-S: common questions on tracking records and the flow diagram. *J Med Libr Assoc.* 2022; 110(2): 253. <https://doi.org/10.5195/jmla.2022.1449>

- [17] Trifu A, Smîdu E, Badea DO, Bulboacă E, Haralambie V. Applying the PRISMA method for obtaining systematic reviews of occupational safety issues in literature search. *MATEC Web Conf.* 2022; EDP Sciences. <https://doi.org/10.1051/mateconf/202235400052>
- [18] Campbell DH, Kendall C, Chang CC, Silva SR, Tonnessen KA. Pathways for nitrate release from an alpine watershed: determination using  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ . *Water Resour Res.* 2002; 38(5): 10-1--9. <https://doi.org/10.1029/2002WR001578>
- [19] Kaown D, Shouakar-Stash O, Yang J, Hyun Y, Lee K-K. Identification of multiple sources of groundwater contamination by dual isotopes. *Groundwater.* 2014; 52(6): 875-85. <https://doi.org/10.1111/gwat.12130>
- [20] Widory D, Petelet-Giraud E, Brenot A, Bronders J, Tirez K, Boeckx P. Improving the management of nitrate pollution in water by the use of isotope monitoring: the  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\delta^{11}\text{B}$  triptych. *Isotopes Environ Health Stud.* 2013; 49(1): 29-47. <https://doi.org/10.1080/10256016.2012.666540>
- [21] Sankoh AA, Derkyi NS, Frazer-Williams RAD, Laar C, Kamara I. A review on the application of isotopic techniques to trace groundwater pollution sources within developing countries. *Water.* 2022; 14(1): 35. <https://doi.org/10.3390/w14010035>
- [22] Vengosh A, Spivack AJ, Artzi Y, Ayalon A. Geochemical and boron, strontium, and oxygen isotopic constraints on the origin of the salinity in groundwater from the Mediterranean coast of Israel. *Water Resour Res.* 1999; 35(6): 1877-94. <https://doi.org/10.1029/1999WR900024>
- [23] Kim D-M, Kwon O-H, Oh YS, Lee J-S. Interpreting complex geochemistry of groundwater in a coastal paddy field near a mine using isotopic signatures of sulfate and water. *Environ Geochem Health.* 2021; 43(10): 4105-22. <https://doi.org/10.1007/s10653-021-00869-3>
- [24] Hosono T, Hossain S, Shimada J. Hydrobiogeochemical evolution along the regional groundwater flow systems in volcanic aquifers in Kumamoto, Japan. *Environ Earth Sci.* 2020; 79(18): 410. <https://doi.org/10.1007/s12665-020-09155-4>
- [25] Mundle SO, Johnson T, Lacrampe-Couloume G, Pérez-de-Mora A, Duhamel M, Edwards EA, *et al.* Monitoring biodegradation of ethene and bioremediation of chlorinated ethenes at a contaminated site using compound-specific isotope analysis (CSIA). *Environ Sci Technol.* 2012; 46(3): 1731-8. <https://doi.org/10.1021/es202792x>
- [26] Muhammad SA, Frew RD, Hayman AR. Compound-specific isotope analysis of diesel fuels in a forensic investigation. *Front Chem.* 2015; 3: 1-10. <https://doi.org/10.3389/fchem.2015.00012>
- [27] Meckenstock RU, Morasch B, Griebler C, Richnow HH. Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated aquifers. *J Contam Hydrol.* 2004; 75(3): 215-55. <https://doi.org/10.1016/j.jconhyd.2004.06.003>
- [28] Schürner HKV, Maier MP, Eckert D, Brejcha R, Neumann C-C, Stumpp C, *et al.* Compound-specific stable isotope fractionation of pesticides and pharmaceuticals in a mesoscale aquifer model. *Environ Sci Technol.* 2016; 50(11): 5729-39. <https://doi.org/10.1021/acs.est.5b03828>
- [29] Won E-J, Yun H-Y, Lee D-H, Shin K-H. Application of compound-specific isotope analysis in environmental forensic and strategic management avenue for pesticide residues. *Molecules.* 2021; 26(15): 4412. <https://doi.org/10.3390/molecules26154412>
- [30] Jonás G-R, Evangelos Gatsios RJL, Estella AARNE. Advances in the characterisation and remediation of sites contaminated with petroleum hydrocarbons. In: *Environmental Contamination Remediation and Management.* 2023. p. 1-675.
- [31] Miller JR, Mackin G, Orbock Miller SM. Geochemical fingerprinting. In: Miller JR, Mackin G, Orbock Miller SM, Eds. *Application of Geochemical Tracers to Fluvial Sediment.* Cham: Springer Int Publ; 2015. p. 11-51. [https://doi.org/10.1007/978-3-319-13221-1\\_2](https://doi.org/10.1007/978-3-319-13221-1_2)
- [32] Jung M-J, Jeong Y-J, Shin W-J, Cheong AC-s. Isotopic distribution of bioavailable Sr, Nd, and Pb in Chungcheongbuk-do Province, Korea. *J Anal Sci Technol.* 2024; 15(1): 46. <https://doi.org/10.1186/s40543-024-00460-2>
- [33] Birkle P, García BM, Milland Padrón CM, Eglington BM. Origin and evolution of formation water at the Jujo-Tecominoacán oil reservoir, Gulf of Mexico. Part 2: isotopic and field-production evidence for fluid connectivity. *Appl Geochem.* 2009; 24(4): 555-73. <https://doi.org/10.1016/j.apgeochem.2008.12.010>
- [34] Morrison RD. Critical review of environmental forensic techniques: part II. *Environ Forensics.* 2000; 1(4): 175-95. <https://doi.org/10.1006/enfo.2000.0018>
- [35] Charbonnet JA, Rodowa AE, Joseph NT, Guelfo JL, Field JA, Jones GD, *et al.* Environmental source tracking of per- and polyfluoroalkyl substances within a forensic context: current and future techniques. *Environ Sci Technol.* 2021; 55(11): 7237-45. <https://doi.org/10.1021/acs.est.0c08506>
- [36] Zhou S, Xiong H, Song X, He Z, Peng Q, Guo X, *et al.* Spatial prediction of groundwater nitrate by explainable machine learning models and remote sensing indicators under conditions of imbalanced datasets. *Geocarto Int.* 2025; 40(1): 2557953. <https://doi.org/10.1080/10106049.2025.2557953>
- [37] Cane G, Clark ID. Tracing groundwater recharge in an agricultural watershed with isotopes. *Groundwater.* 1999; 37(1): 133-9. <https://doi.org/10.1111/j.1745-6584.1999.tb00966.x>
- [38] Kendall C, Elliott EM, Wankel SD. Tracing anthropogenic inputs of nitrogen to ecosystems. In: *Stable Isotopes in Ecology and Environmental Science.* 2007. p. 375-449. <https://doi.org/10.1002/9780470691854.ch12>
- [39] Slater GF. Constraining the fate of chlorinated ethenes in groundwater systems using stable carbon compound-specific isotope analysis. 2001.
- [40] Wang Z, Stout SA, Fingas M. Forensic fingerprinting of biomarkers for oil spill characterization and source identification. *Environ Forensics.* 2006; 7(2): 105-46. <https://doi.org/10.1080/15275920600667104>
- [41] Ravikumar P, Venkatesharaju K, Somashekar R. Major ion chemistry and hydrochemical studies of groundwater of Bangalore South Taluk, India. *Environ Monit Assess.* 2010; 163(1): 643-53. <https://doi.org/10.1007/s10661-009-0865-1>

- [42] Brems D, Ganio M, Degryse P. The Sr-Nd isotopic fingerprint of sand raw materials. In: *Glass Making in the Greco-Roman World: Studies in Archaeological Sciences*. 2014; 4: 31-67.
- [43] Morrison RD, Murphy BL. *Environmental forensics: contaminant specific guide*. Elsevier; 2010.
- [44] Helena B, Pardo R, Vega M, Barrado E, Fernandez JM, Fernandez L. Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga River, Spain) by principal component analysis. *Water Res*. 2000; 34(3): 807-16. [https://doi.org/10.1016/S0043-1354\(99\)00225-0](https://doi.org/10.1016/S0043-1354(99)00225-0)
- [45] Moers M, Jones D, Eakin P, Fallick A, Griffiths H, Larter S. Carbohydrate diagenesis in hypersaline environments: application of GC-IRMS to the stable isotope analysis of derivatized saccharides from surficial and buried sediments. *Org Geochem*. 1993; 20(7): 927-33. [https://doi.org/10.1016/0146-6380\(93\)90104-j](https://doi.org/10.1016/0146-6380(93)90104-j)
- [46] Zappala J, Bailey K, Mueller P, O'Connor T, Purtschert R. Rapid processing of 85Kr/Kr ratios using atom trap trace analysis. *Water Resour Res*. 2017; 53(3): 2553-8. <https://doi.org/10.1002/2016WR020082>
- [47] Johannesson KH, Telfeyan K, Chevis DA, Rosenheim BE, Leybourne MI. Rare earth elements in stromatolites-1: evidence that modern terrestrial stromatolites fractionate rare earth elements during incorporation from ambient waters. In: *Evolution of Archean Crust and Early Life*. Springer; 2013. p. 385-411. [https://doi.org/10.1007/978-94-007-7615-9\\_14](https://doi.org/10.1007/978-94-007-7615-9_14)
- [48] Olobaniyi S, Owoyemi F. Characterization by factor analysis of the chemical facies of groundwater in the deltaic plain sands aquifer of Warri, western Niger delta, Nigeria. 2006.
- [49] Rebele LM, Jeffrey AW, editors. The use of compound specific isotope analysis (CSIA) for discerning sources of trichloroethylene (TCE) and perchloroethylene (PCE) within a commingled groundwater plume in California, USA. In: *Environmental Forensics: Proceedings of the 2013 INEF Conference*. Royal Soc Chem; 2014. <https://doi.org/10.1039/9781782628347-00136>
- [50] Mayer B, Fritz P, Prietzel J, Krouse H. The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. *Appl Geochem*. 1995; 10(2): 161-73. [https://doi.org/10.1016/0883-2927\(94\)00054-A](https://doi.org/10.1016/0883-2927(94)00054-A)
- [51] Jackson-Blake LA, Dunn SM, Helliwell R, Skeffington R, Stutter M, Wade AJ. How well can we model stream phosphorus concentrations in agricultural catchments? *Environ Model Softw*. 2015; 64: 31-46. <https://doi.org/10.1016/j.envsoft.2014.11.002>
- [52] Yang Z, Li C, Chen H, Shan X, Chen J, Zhang J, *et al.* Source-oriented ecological and resistome risks associated with geochemical enrichment of heavy metals in river sediments. *Chemosphere*. 2023; 336: 139119. <https://doi.org/10.1016/j.chemosphere.2023.139119>
- [53] Phillips DL, Gregg JW. Source partitioning using stable isotopes: coping with too many sources. *Oecologia*. 2003; 136(2): 261-9. <https://doi.org/10.1007/s00442-003-1218-3>
- [54] Parkhurst DL, Appelo C. Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *US Geol Surv*; 2013. Report No.: 2328-7055. <https://doi.org/10.3133/tm6A43>
- [55] Gat JR, Airey PL. Stable water isotopes in the atmosphere/biosphere/lithosphere interface: scaling-up from the local to continental scale, under humid and dry conditions. *Glob Planet Change*. 2006; 51(1-2): 25-33. <https://doi.org/10.1016/j.gloplacha.2005.12.004>
- [56] Monna F, Lancelot J, Croudace IW, Cundy AB, Lewis JT. Pb isotopic composition of airborne particulate material from France and the southern United Kingdom: implications for Pb pollution sources in urban areas. *Environ Sci Technol*. 1997; 31(8): 2277-86. <https://doi.org/10.1021/es960870+>
- [57] Blum JD, Sherman LS, Johnson MW. Mercury isotopes in earth and environmental sciences. *Annu Rev Earth Planet Sci*. 2014; 42: 249-69. <https://doi.org/10.1146/annurev-earth-050212-124107>
- [58] Zhang Z, Liu F, Chen S, Zhang J, Jiang W, Ning H, *et al.* Strontium isotope and multi-tracer insights into groundwater mixing and fluoride mobilization in the Luanhe River Delta, Northern China. *Appl Geochem*. 2025; 2025: 106567. <https://doi.org/10.1016/j.apgeochem.2025.106567>
- [59] Verhagen B. Isotope hydrology and its impact in the developing world. *J Radioanal Nucl Chem*. 2003; 257(1): 17-26. <https://doi.org/10.1023/A:1024724705499>
- [60] Peters KE, Walters CC, Moldovan JM. *The biomarker guide*. Cambridge: Cambridge Univ Press; 2005. <https://doi.org/10.1017/CBO9781107326040>
- [61] Thomsen PF, Sigsgaard EE. Environmental DNA metabarcoding of wild flowers reveals diverse communities of terrestrial arthropods. *Ecol Evol*. 2019; 9(4): 1665-79. <https://doi.org/10.1002/ece3.4809>
- [62] Aravena R, Robertson WD. Use of multiple isotope tracers to evaluate denitrification in groundwater: study of nitrate from a large-flux septic system plume. *Groundwater*. 1998; 36(6): 975-82. <https://doi.org/10.1111/j.1745-6584.1998.tb02104.x>
- [63] Burnett W. Radon as a tracer of submarine groundwater discharge. In: *Nuclear and Isotopic Techniques for the Characterization of Submarine Groundwater Discharge in Coastal Zones: Results of a coordinated research project 2001-2006*. 2008. p. 93-104.
- [64] Shrestha S, Kazama F. Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji River Basin, Japan. *Environ Model Softw*. 2007; 22(4): 464-75. <https://doi.org/10.1016/j.envsoft.2006.02.001>
- [65] Phillips DL, Inger R, Bearhop S, Jackson AL, Moore JW, Parnell AC, *et al.* Best practices for use of stable isotope mixing models in food-web studies. *Can J Zool*. 2014; 92(10): 823-35. <https://doi.org/10.1139/cjz-2014-0127>
- [66] Younger PL, Banwart SA, Hedin RS. Mine water hydrology. In: *Mine Water: Hydrology, Pollution, Remediation*. Springer; 2002. p. 127-270. [https://doi.org/10.1007/978-94-010-0610-1\\_3](https://doi.org/10.1007/978-94-010-0610-1_3)

- [67] Bentley RA. Strontium isotopes from the earth to the archaeological skeleton: a review. *J Archaeol Method Theory*. 2006; 13(3): 135-87. <https://doi.org/10.1007/s10816-006-9009-x>
- [68] Elsner M, Zwank L, Hunkeler D, Schwarzenbach RP. A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. *Environ Sci Technol*. 2005; 39(18): 6896-916. <https://doi.org/10.1021/es0504587>
- [69] Ellis AS, Johnson TM, Bullen TD. Chromium isotopes and the fate of hexavalent chromium in the environment. *Science*. 2002; 295(5562): 2060-2. <https://doi.org/10.1126/science.1068368>
- [70] Babiker IS, Mohamed MAA, Hiyama T. Assessing groundwater quality using GIS. *Water Resour Manag*. 2007; 21(4): 699-715. <https://doi.org/10.1007/s11269-006-9059-6>
- [71] Schmidt TC, Zwank L, Elsner M, Berg M, Meckenstock RU, Haderlein SB. Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Anal Bioanal Chem*. 2004; 378(2): 283-300. <https://doi.org/10.1007/s00216-003-2350-y>
- [72] Busenberg E, Plummer LN. Dating young groundwater with sulfur hexafluoride: natural and anthropogenic sources of sulfur hexafluoride. *Water Resour Res*. 2000; 36(10): 3011-30. <https://doi.org/10.1029/2000WR900151>
- [73] Craig H. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science*. 1961; 133(3467): 1833-4. <https://doi.org/10.1126/science.133.3467.1833>
- [74] Appelo CAJ, Postma D. *Geochemistry, groundwater and pollution*. 2nd ed. Rotterdam: Balkema; 2005. <https://doi.org/10.1201/9781439833544>
- [75] Kendall C, Caldwell EA. Chapter 2 - fundamentals of isotope geochemistry. In: Kendall C, McDonnell JJ, editors. *Isotope Tracers in Catchment Hydrology*. Amsterdam: Elsevier; 1998. p. 51-86. <https://doi.org/10.1016/B978-0-444-81546-0.50009-4>
- [76] Davis CM, Fox JF. Sediment fingerprinting: review of the method and future improvements for allocating nonpoint source pollution. *J Environ Eng*. 2009; 135(7): 490-504. [https://doi.org/10.1061/\(ASCE\)0733-9372\(2009\)135:7\(490\)](https://doi.org/10.1061/(ASCE)0733-9372(2009)135:7(490))
- [77] Seal RR. Sulfur isotope geochemistry of sulfide minerals. *Rev Mineral Geochem*. 2006; 61(1): 633-77. <https://doi.org/10.2138/rmg.2006.61.12>
- [78] Postma D, Kjølter C, Sogaard Andersen M, Condesso de Melo M, Gaus I. Geochemical modelling of processes controlling baseline compositions of groundwater. In: Edmunds WM, Shand P, Eds., *Natural Groundwater Quality*. USA: Blackwell Publishing, Ltd.; 2008 pp.71-90. <https://doi.org/10.1002/9781444300345.ch4>
- [79] Johannesson KH, Tang J, Daniels JM, Bounds WJ, Burdige DJ. Rare earth element concentrations and speciation in organic-rich blackwaters of the Great Dismal Swamp, Virginia, USA. *Chem Geol*. 2004; 209(3-4): 271-94. <https://doi.org/10.1016/j.chemgeo.2004.06.012>
- [80] Gat JR, Gonfiantini R. Stable isotope hydrology: deuterium and oxygen-18 in the water cycle. IAEA Tech Rep Ser. 1981; 210: 337.
- [81] Clark ID, Fritz P. *Environmental isotopes in hydrogeology*. CRC Press; 2013. <https://doi.org/10.1201/9781482242911>
- [82] Cook P, Plummer L, Busenberg E, Solomon D, Han L. Effects and processes that can modify apparent CFC age. In: *Chlorofluorocarbons in hydrology: A guidebook*. Vienna: International Atomic Energy Agency; 2006, p. 31-58.
- [83] Edmunds W. Contribution of isotopic and nuclear tracers to study of groundwaters. In: Aggarwal PK, Gat JR, Froehlich KFO, Eds. *Isotopes in the Water Cycle*. Dordrecht: Springer; 2005, p. 171-92. <https://doi.org/10.1007/1-4020-3023-1>
- [84] Li X, Tang C, Cao Y, Li D. A multiple isotope (H, O, N, C and S) approach to elucidate the hydrochemical evolution of shallow groundwater in a rapidly urbanized area of the Pearl River Delta, China. *Sci Total Environ*. 2020; 724: 137930. <https://doi.org/10.1016/j.scitotenv.2020.137930>
- [85] Plumb RH. Fingerprint analysis of contaminant data: A forensic tool for evaluating environmental contamination. Las Vegas (NV): U.S. Environmental Protection Agency; 2004. Report No.: EPA/600/5-04/054. Available from: <https://www.epa.gov/sites/default/files/2015-06/documents/plumb2004.pdf>
- [86] Ahad JME, Martel R, Calderhead AI. Isotope forensics of polycyclic aromatic compounds (PACs) in a contaminated shallow aquifer. *Chemosphere*. 2023; 342: 140169. <https://doi.org/10.1016/j.chemosphere.2023.140169>
- [87] De Vera J, Chen W, Phillips E, Gilevska T, Morgan SA, Norcross S, *et al.* Compound-specific isotope analysis (CSIA) evaluation of degradation of chlorinated benzenes (CBs) and benzene in a contaminated aquifer. *J Contam Hydrol*. 2022; 250: 104051. <https://doi.org/10.1016/j.jconhyd.2022.104051>
- [88] Oster H, Sonntag C, Münnich KO. Groundwater age dating with chlorofluorocarbons. *Water Resour Res*. 1996; 32(10): 2989-3001. <https://doi.org/10.1029/96WR01775>
- [89] Barbieri M, Nigro A, Petitta M. Groundwater mixing in the discharge area of San Vittorino Plain (Central Italy): geochemical characterization and implication for drinking uses. *Environ Earth Sci*. 2017; 76(11): 393. <https://doi.org/10.1007/s12665-017-6719-1>
- [90] Hoefs J. Variations of stable isotope ratios in nature. In: Hoefs J, Ed. *Stable Isotope Geochemistry*. Berlin, Heidelberg: Springer; 2009. p. 93-227.
- [91] Sankoh AA, Derkyi NSA, Frazer-Williams RA, Laar C, Kamara I. A review on the application of isotopic techniques to trace groundwater pollution sources within developing countries. *Water*. 2021; 14(1): 35. <https://doi.org/10.3390/w14010035>
- [92] Charbonnet JA, Rodowa AE, Joseph NT, Guelfo JL, Field JA, Jones GD, *et al.* Environmental source tracking of per-and polyfluoroalkyl substances within a forensic context: current and future techniques. *Environ Sci Technol*. 2021; 55(11): 7237-45. <https://doi.org/10.1021/acs.est.0c08506>

- [93] Philp RP. The emergence of stable isotopes in environmental and forensic geochemistry studies: a review. *Environ Chem Lett.* 2007; 5(2): 57-66. <https://doi.org/10.1007/s10311-006-0081-y>
- [94] Négrel P, Blessing M, Millot R, Petelet-Giraud E, Innocent C. Isotopic methods give clues about the origins of trace metals and organic pollutants in the environment. *TrAC Trends Anal Chem.* 2012; 38: 143-53. <https://doi.org/10.1016/j.trac.2012.03.017>
- [95] Xu S, Kang P, Sun Y. A stable isotope approach and its application for identifying nitrate source and transformation process in water. *Environ Sci Pollut Res.* 2016; 23(2): 1133-48. <https://doi.org/10.1007/s11356-015-5309-6>
- [96] Zhang Y, Shi P, Song J, Li Q. Application of nitrogen and oxygen isotopes for source and fate identification of nitrate pollution in surface water: a review. *Appl Sci.* 2018; 9(1): 18. <https://doi.org/10.3390/app9010018>
- [97] Kaown D, Koh D-C, Mayer B, Lee K-K. Identification of nitrate and sulfate sources in groundwater using dual stable isotope approaches for an agricultural area with different land use (Chuncheon, mid-eastern Korea). *Agric Ecosyst Environ.* 2009; 132(3-4): 223-31. <https://doi.org/10.1016/j.agee.2009.04.004>
- [98] Koszelnik P, Gruca-Rokosz R. Determination of nitrate isotopic signature in waters of different sources by analysing the nitrogen and oxygen isotopic ratio. *Environ Sci Process Impacts.* 2013; 15(4): 751-9. <https://doi.org/10.1039/c3em30920g>
- [99] Guoinseau D, Louvat P, Paris G, Chen J-B, Chetelat B, Rocher V, *et al.* Are boron isotopes a reliable tracer of anthropogenic inputs to rivers over time? *Sci Total Environ.* 2018; 626: 1057-68. <https://doi.org/10.1016/j.scitotenv.2018.01.159>
- [100] Zhao W, Yang D, Sun Q, Gan Y, Bai L, Li S, *et al.* Combining multi-isotope technology, hydrochemical information, and MixSIAR model to identify and quantify nitrate sources of groundwater and surface water in a multi-land use region. *Environ Sci Pollut Res.* 2023; 30(33): 80070-84. <https://doi.org/10.1007/s11356-023-27720-9>
- [101] Blasch KW, Bryson JR. Distinguishing sources of ground water recharge by using  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ . *Groundwater.* 2007; 45(3): 294-308. <https://doi.org/10.1111/j.1745-6584.2006.00289.x>
- [102] Hofstetter TB, Bakkour R, Buchner D, Eisenmann H, Fischer A, Gehre M, *et al.* Perspectives of compound-specific isotope analysis of organic contaminants for assessing environmental fate and managing chemical pollution. *Nature Water.* 2024; 2(1): 14-30. <https://doi.org/10.1038/s44221-023-00176-4>
- [103] Xiong J, Li G, An T. New advance in the application of compound-specific isotope analysis (CSIA) in identifying sources, transformation mechanisms and metabolism of brominated organic compounds. *Crit Rev Environ Sci Technol.* 2022; 52(22): 3973-96. <https://doi.org/10.1080/10643389.2021.1993053>
- [104] Muhammad SA. CSIA of petroleum hydrocarbons: forensic fingerprinting and oil spill characterisation. University of Otago; 2012.
- [105] Schürner HKV, Maier MP, Eckert D, Brejcha R, Neumann C-C, Stump C, *et al.* Compound-specific stable isotope fractionation of pesticides and pharmaceuticals in a mesoscale aquifer model. *Environ Sci Technol.* 2016; 50(11): 5729-39. <https://doi.org/10.1021/acs.est.5b03828>
- [106] Elsner M, Imfeld G. Compound-specific isotope analysis (CSIA) of micropollutants in the environment-current developments and future challenges. *Curr Opin Biotechnol.* 2016; 41: 60-72. <https://doi.org/10.1016/j.copbio.2016.04.014>
- [107] Smith JD, Adam R, Maarif S. How social movements use religious creativity to address environmental crises in Indonesian local communities. *Glob Environ Change.* 2024; 84: 102772. <https://doi.org/10.1016/j.gloenvcha.2023.102772>
- [108] Won E-J, Yun H-Y, Lee D-H, Shin K-H. Application of compound-specific isotope analysis in environmental forensic and strategic management avenue for pesticide residues. *Molecules.* 2021; 26(15): 4412. <https://doi.org/10.3390/molecules26154412>
- [109] Zhang X, Yi L, Li R. Identification of dense nonaqueous phase liquid sources in groundwater: a review of isotope technique. *Environ Sci Pollut Res.* 2024; 31(40): 52688-706. <https://doi.org/10.1007/s11356-024-34427-y>
- [110] da Silva Jr FMR. Brazil: "the continent" that does not look at its ground. *Environ Toxicol Chem.* 2020; 39(10): 1859-60. <https://doi.org/10.1002/etc.4829>
- [111] Siddique MAB, Islam ARMT, Hossain MS, Khan R, Akbor MA, Hasanuzzaman M, *et al.* Multivariate statistics and entropy theory for irrigation water quality and entropy-weighted index development in a subtropical urban river, Bangladesh. *Environ Sci Pollut Res.* 2022; 29(6): 8577-96. <https://doi.org/10.1007/s11356-021-16343-7>
- [112] Hughes JA, Jonas M. Time and crime: which cold-case investigations should be reheated? *Crim Justice Ethics.* 2015; 34(1): 18-41. <https://doi.org/10.1080/0731129X.2015.1025505>
- [113] Lischeid G, Balla D, Dannowski R, Dietrich O, Kalettka T, Merz C, *et al.* Forensic hydrology: what function tells about structure in complex settings. *Environ Earth Sci.* 2017; 76(1): 40. <https://doi.org/10.1007/s12665-016-6351-5>
- [114] Gutierrez-Lopez A. Methodological guide to forensic hydrology. *Water.* 2022; 14(23): 3863. <https://doi.org/10.3390/w14233863>
- [115] Alsharif MH, Kelechi AH, Yahya K, Chaudhry SA. Machine learning algorithms for smart data analysis in internet of things environment: taxonomies and research trends. *Symmetry.* 2020; 12(1): 88. <https://doi.org/10.3390/sym12010088>
- [116] Sarker IH. Machine learning: algorithms, real-world applications and research directions. *SN Comput Sci.* 2021; 2(3): 1-21. <https://doi.org/10.1007/s42979-021-00592-x>