

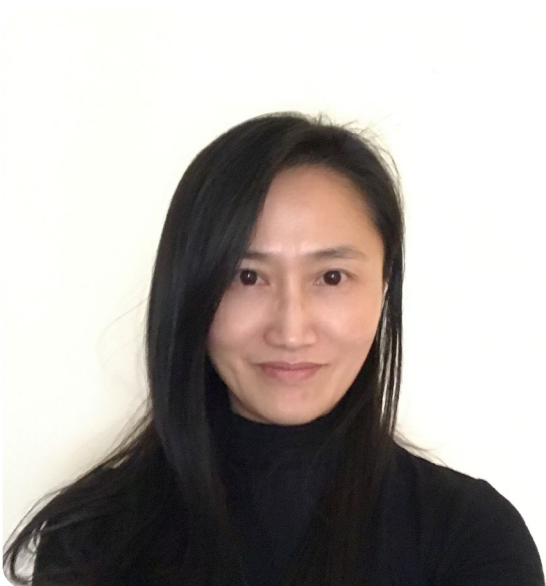


Agenda Item: DOH Review of Groundwater Plume

DOH Evaluation and
Interpretation of Groundwater Contamination
and Chemistry

FTAC - April 9, 2026





- Melissa Thaw, PhD, Red Hill Environmental Coordinator, Office of Environmental Quality Control
- Robert Whittier, M.S., Geologist, Environmental Management Division, Safe Drinking Water Branch
- Dan Burnell, PhD – DOH - TetraTech
- Jie Xu, PhD – DOH - TetraTech



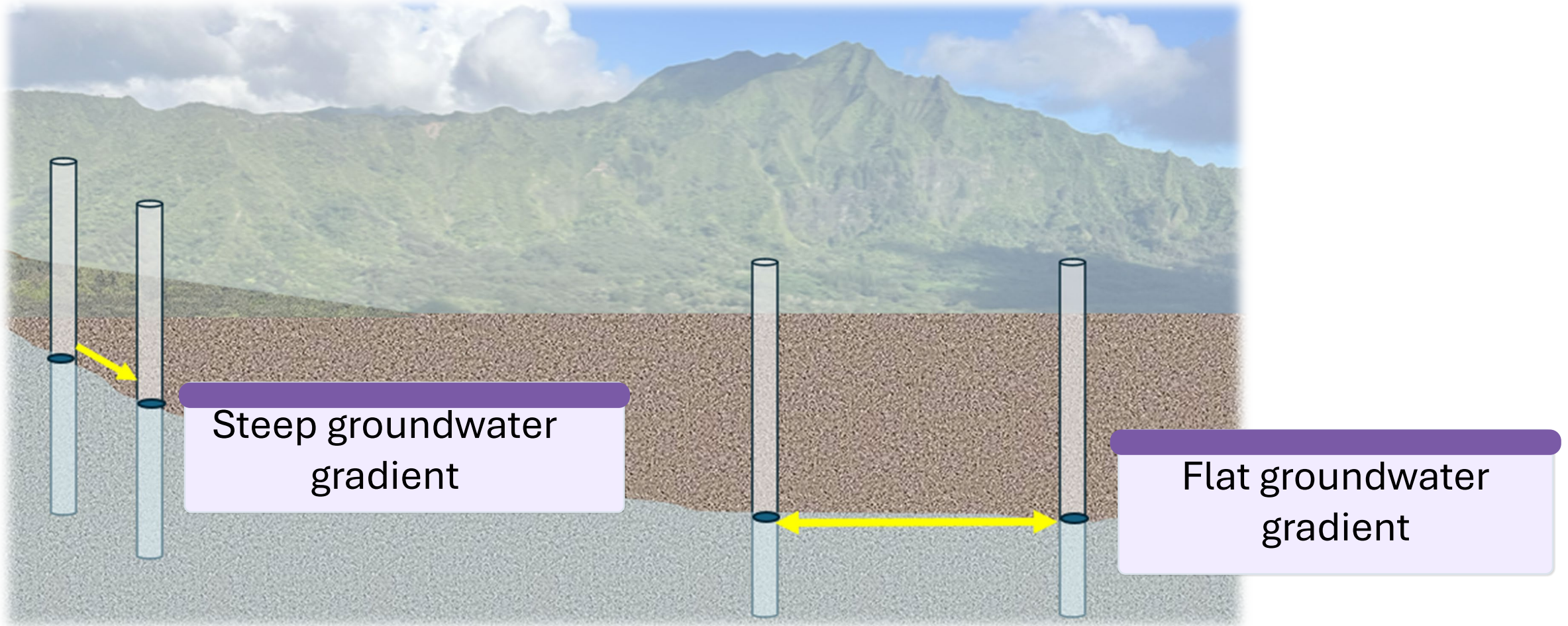
Overview of Presentation

1. Background: groundwater and geology
2. Q: what can water chemistry data tell us?
3. Data & Methods
4. Results & Preliminary Findings



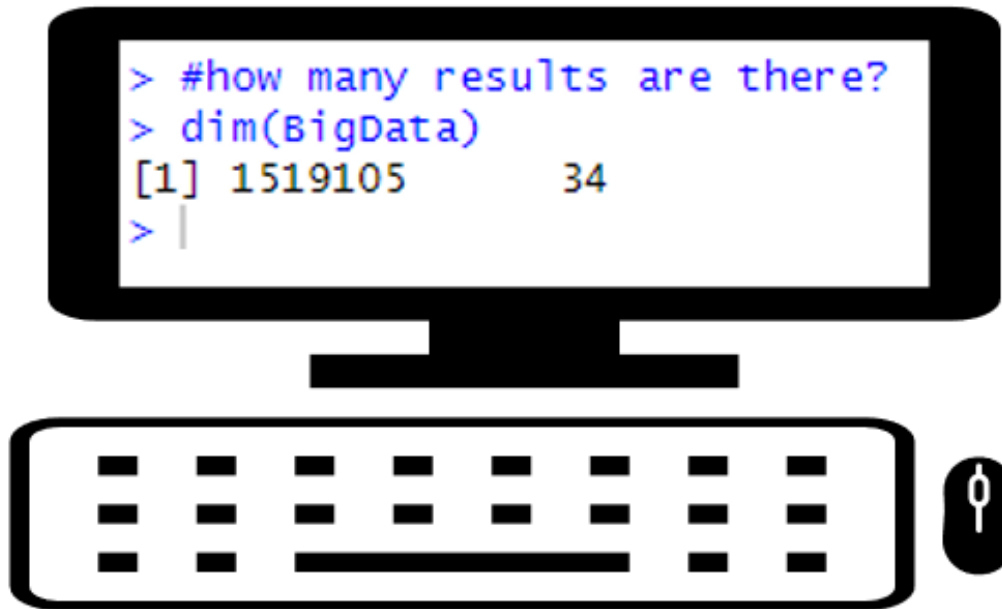
```
> #how many results are there?
> dim(BigData)
[1] 1519105      34
>
```

Regionally flow is mauka to makai, but the Red Hill site has a relatively flat groundwater gradient.

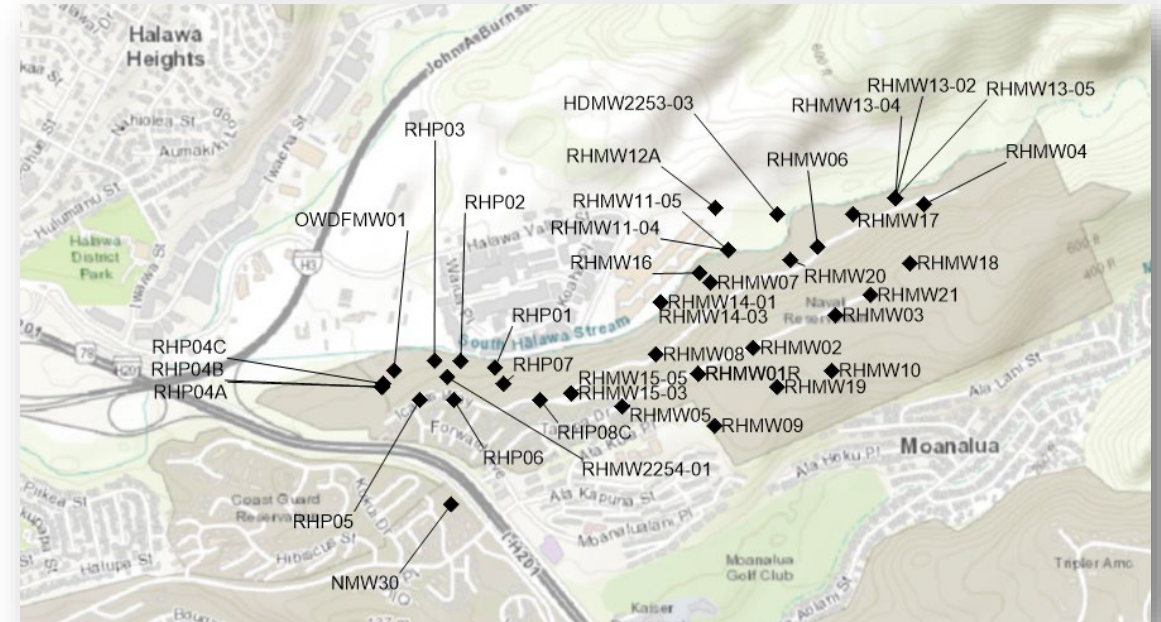




Red Hill geology is complex and heterogeneous



Groundwater data: a “zillion” results



Red Hill groundwater wells

We used data from 44 groundwater wells.

Groundwater data used for this assessment / “zillion” parameters

General chemistry

- Conservative tracers
- Fuel breakdown indicators



Fuel contamination



General Chemistry:

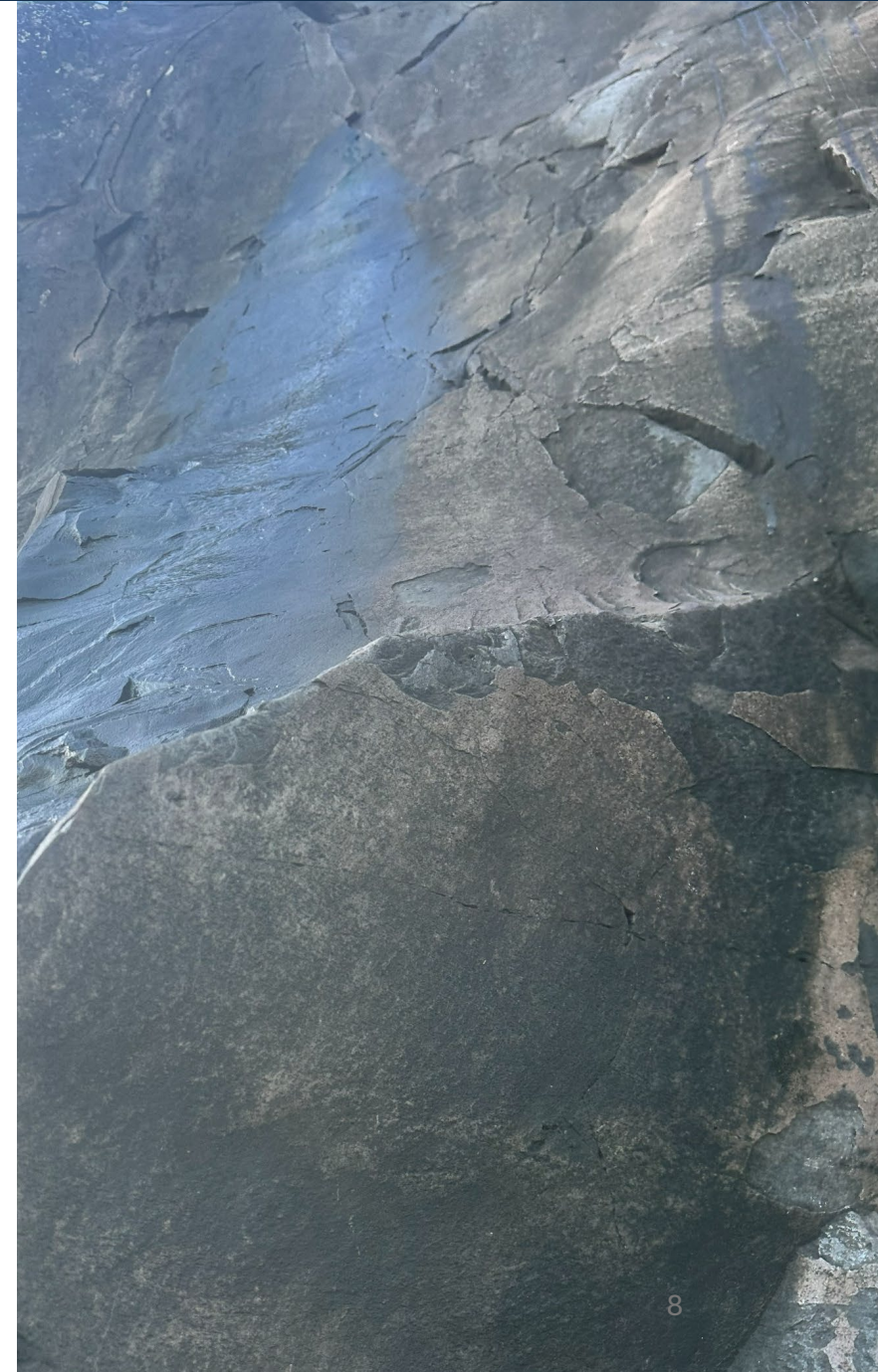
- oxidation–reduction potential (ORP)
- pH
- alkalinity
- chloride
- nitrate + nitrite ($\text{NO}_3^- + \text{NO}_2^-$)
- silica (SiO_2)
- ionic ratios: SO_4/Cl , Na/Cl , and Ca/Mg

Contamination:

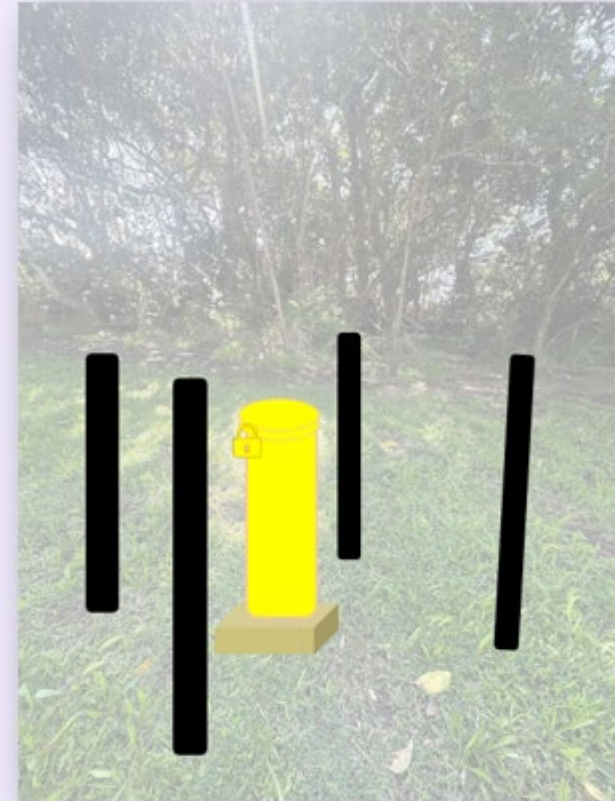
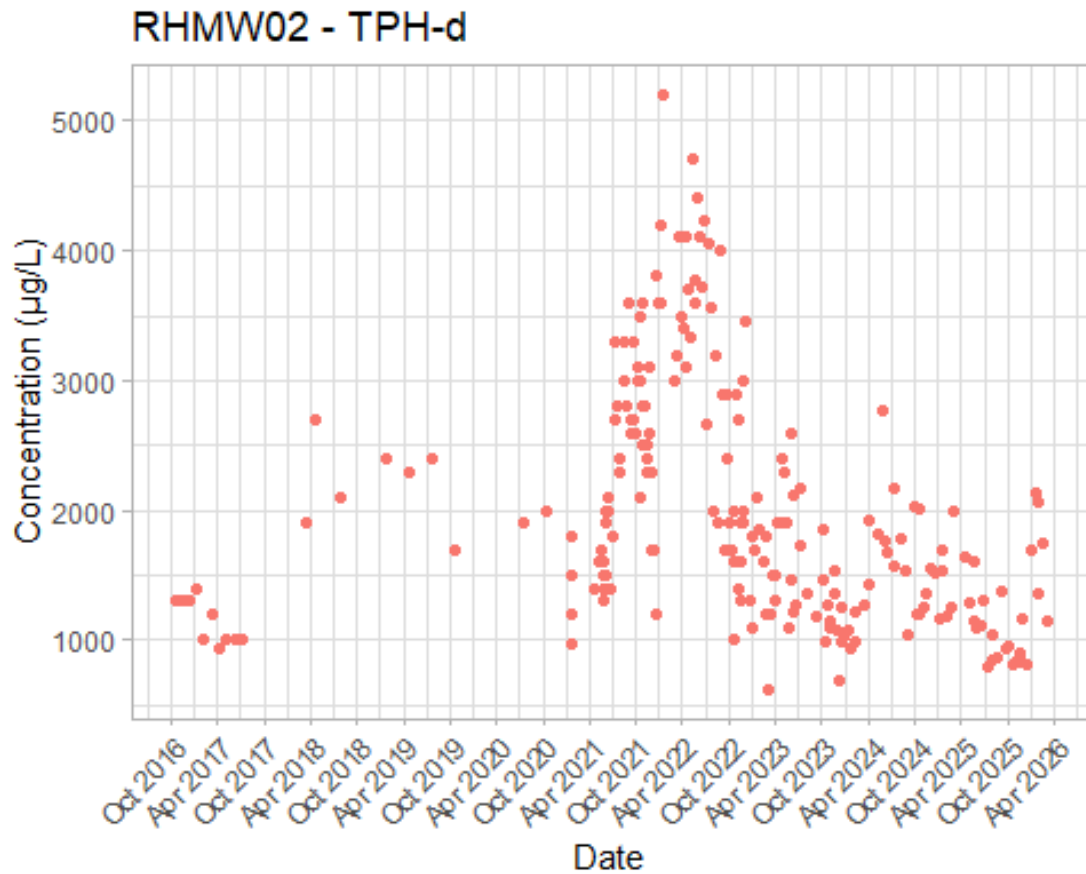
- TPH-d
- TPH-o

Driving question

What does the groundwater chemistry tell us about the contamination, water flow, mixing and other processes?



Example time series ... 1/many



Conceptual depiction of a groundwater well.

Groundwater Chemistry Near Red Hill

The study used multiple chemical clues, PCA, and HCA to help distinguish background, transition, and plume-related groundwater in the complex basalt aquifer.

44 monitored locations

9 indicators

2022–2024

Geochemical Parameter	Unit	Sample Size	Mean	Standard deviation	Min	Max
pH	-	2,926	7.53	0.66	6.4	10.2
ORP	mV	2,926	129.23	102.67	-181	264.2
Alkalinity	mg/L	539	103.68	46.78	53	270
Chloride (log)	log (mg/L)	542	1.95	0.37	1.5	3.1
Nitrate+Nitrite	mg/L	603	0.77	1.03	0	5.5
Silica	mg/L	72	53.85	16.06	13.7	98
SO4/Cl ratio	-	548	0.30	0.22	0.12	1.09
Na/Cl ratio	-	47	0.76	0.35	0.28	2.29
Ca/Mg ratio	-	47	0.97	0.23	0.48	1.69

How the study was performed

Instead of relying on one number, the study combined many water-quality clues.

- 1 Measure water chemistry**
 Field measurements, major ions, nutrients, and simple ratios.
- 2 Look for pair-wise chemical parameter links**
 A correlation matrix shows which measured indicators move together.
- 3 Find the main patterns**
 PCA compresses many signals into a few big patterns (gradients).
- 4 Group similar wells**
 HCA sorts wells into similar chemistry neighborhoods.

Why this matters: In a heterogeneous basalt aquifer, biodegradation, redox change, mixing, and rock-water interaction can all happen at once. That makes “one-parameter” explanations incomplete.

Chemical parameters provide clues about water condition and geochemical processes

Each measurement says something different. Together they create a chemical fingerprint.

Water condition

- **pH** = how acidic or basic the water is
- **ORP** = whether conditions are more oxygen-rich or oxygen-poor

Buffering (resistance to changes in pH) and Mixing (water blending together)

- **Alkalinity** = water's ability to buffer acids and is an indicator of natural attenuation
- **Chloride** = conservative (non-reactive) salt tracer that helps track mixing

Recharge and rock reaction

- **Nitrate + nitrite** = clues about natural attenuation and anthropogenic influences
- **Silica** = interaction between groundwater and basalt

Ratio clues

- Na/Cl
- SO₄/Cl
- Ca/Mg

Why those ratios matter

Evaporation from ocean is a source of our water with characteristics ion composition

Na/Cl: helps flag water-rock interaction (ion exchange).

SO₄/Cl: helps reflect sulfur cycling from processes such as natural attenuation.

Ca/Mg: helps distinguish between weathering of basalt and limestone.

Geochemical Parameter

pH
ORP
Alkalinity
Chloride (log)
Nitrate+Nitrite
Silica
SO ₄ /Cl ratio
Na/Cl ratio
Ca/Mg ratio

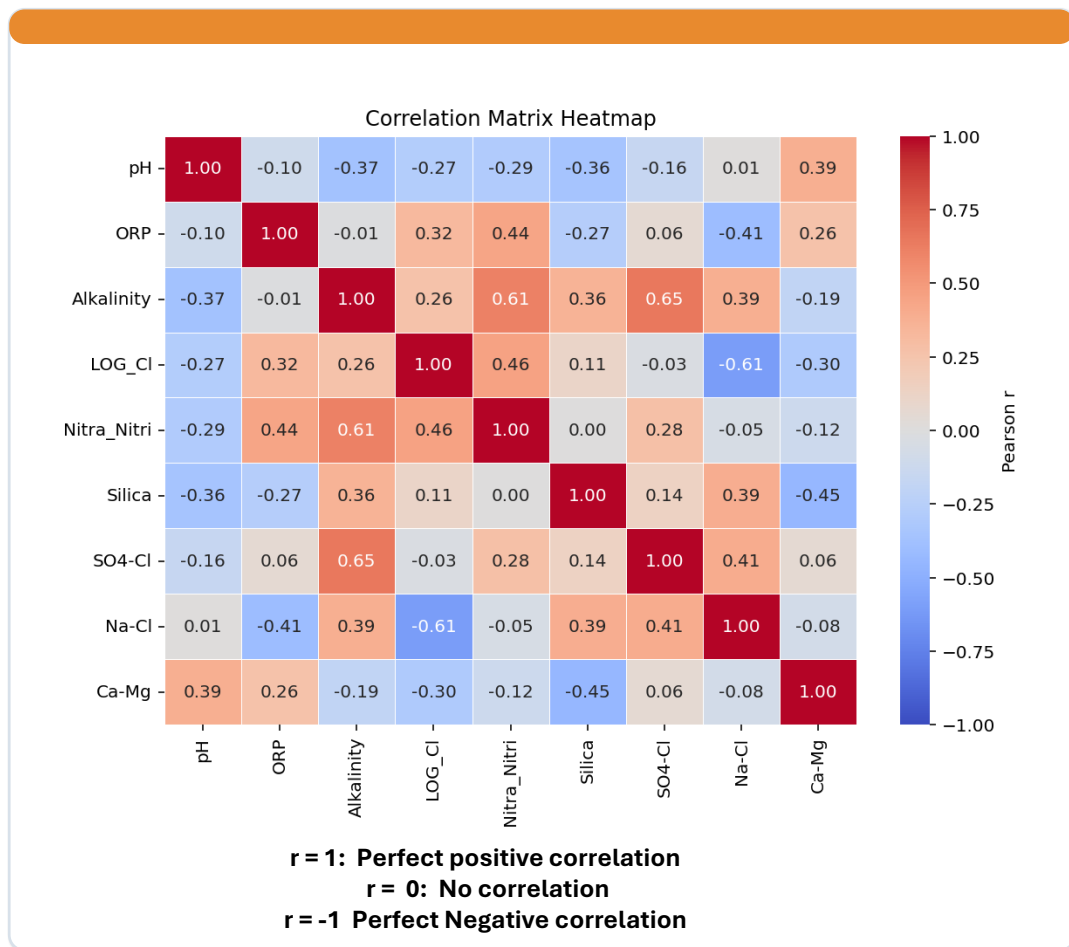
Big message

No single parameter is enough on its own. These measurements respond to overlapping processes, so the strongest interpretation comes from using them together.

Taken together, these indicator parameters help track recharge, biodegradation, redox change, mixing, and mineral reaction processes in the aquifer.

Correlation matrix: a useful first look, but only pair-wise (2 parameters at a time)

Matrix shows which pairs of measurements tend to move in same direction (positive correlation) or move in opposite directions (negative correlation)



What it showed

- Alkalinity rose with nitrate ($r = 0.61$) + nitrite and with SO_4/Cl ($r = 0.65$ ~ **positive correlation**).
- Chloride rose with nitrate + nitrite ($r = 0.46$ ~ **positive correlation**).
- Na/Cl moved in the opposite direction from chloride ($r = -0.61$ ~ **negative correlation**).

What that means

The water chemistry is likely shaped by linked buffering, salinity, oxygenated versus anoxic conditions (redox), exchange between dissolved minerals (ion exchange), and mineral reactions — not by one simple process.

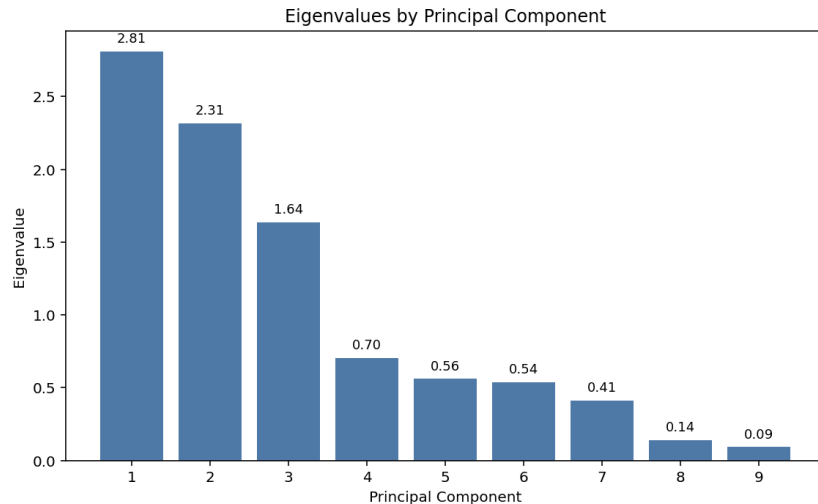
Key limitation of pair-wise correlation

It only compares two variables at a time and mainly captures linear relationships. That makes it hard to untangle several overlapping processes or clearly sort wells into water types.

That is why PCA and HCA are useful next: they use the full chemical fingerprint, not just one pair at a time.

PCA indicates 3 main patterns in the chemistry

Principal component analysis (PCA) combines all 9 geochemical indicators at once.



≈ 73%

of the overall variation was captured by the first three components.

PC1 = buffering + recharge / biogeochemistry

This pattern captured changes linked to alkalinity, nutrients, and buffering as groundwater evolves.

PC2 = redox + salinity / ion exchange

This pattern separated more reaction-dominated water from more oxidized and chloride-rich water.

PC3 = mineral balance + weathering

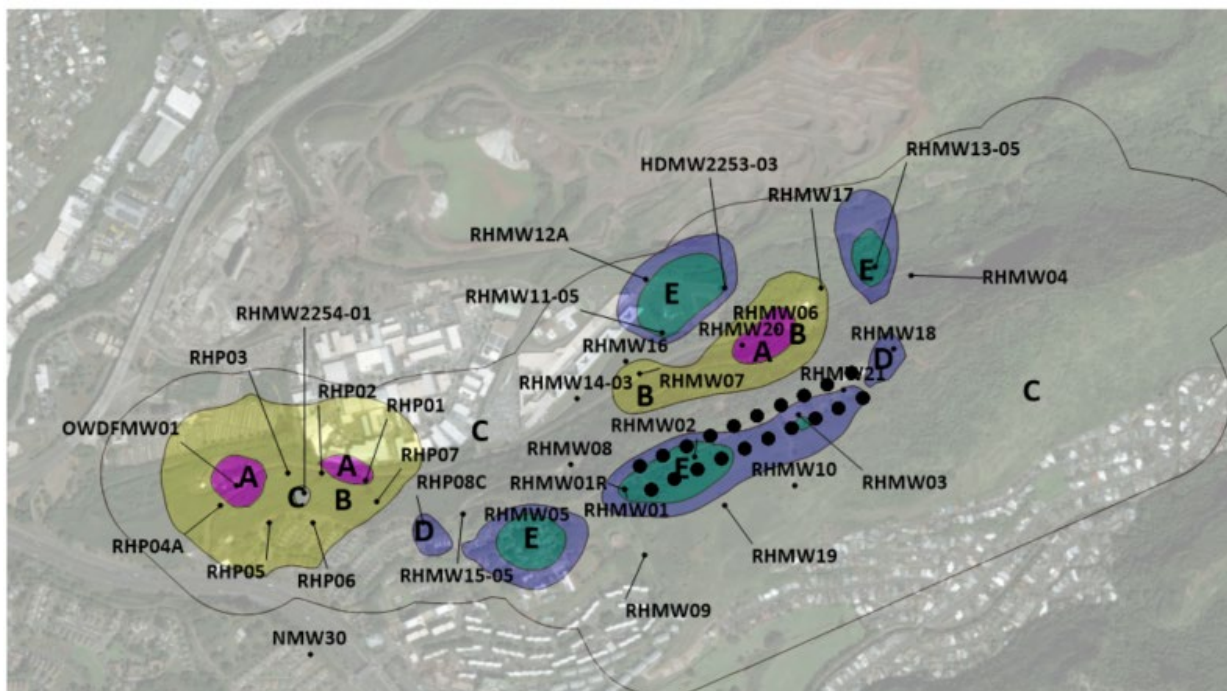
This pattern reflected differences between carbonate-type buffering and silicate weathering in basalt.

Why PCA adds more information?

It uses all variables together and turns overlapping signals into a few major patterns.

HCA grouped wells into similar chemistry neighborhoods

Mapping (kriging) of HCA groups indicates zones of similar geochemical parameter fingerprints.



HCA-based chemistry domains across the site

What the groups may mean

- **A-B:** more recharge-influenced or less altered water
- **C:** broad transition / mixing zone
- **D-E:** more plume-related or source-related chemistry

Why HCA adds more information

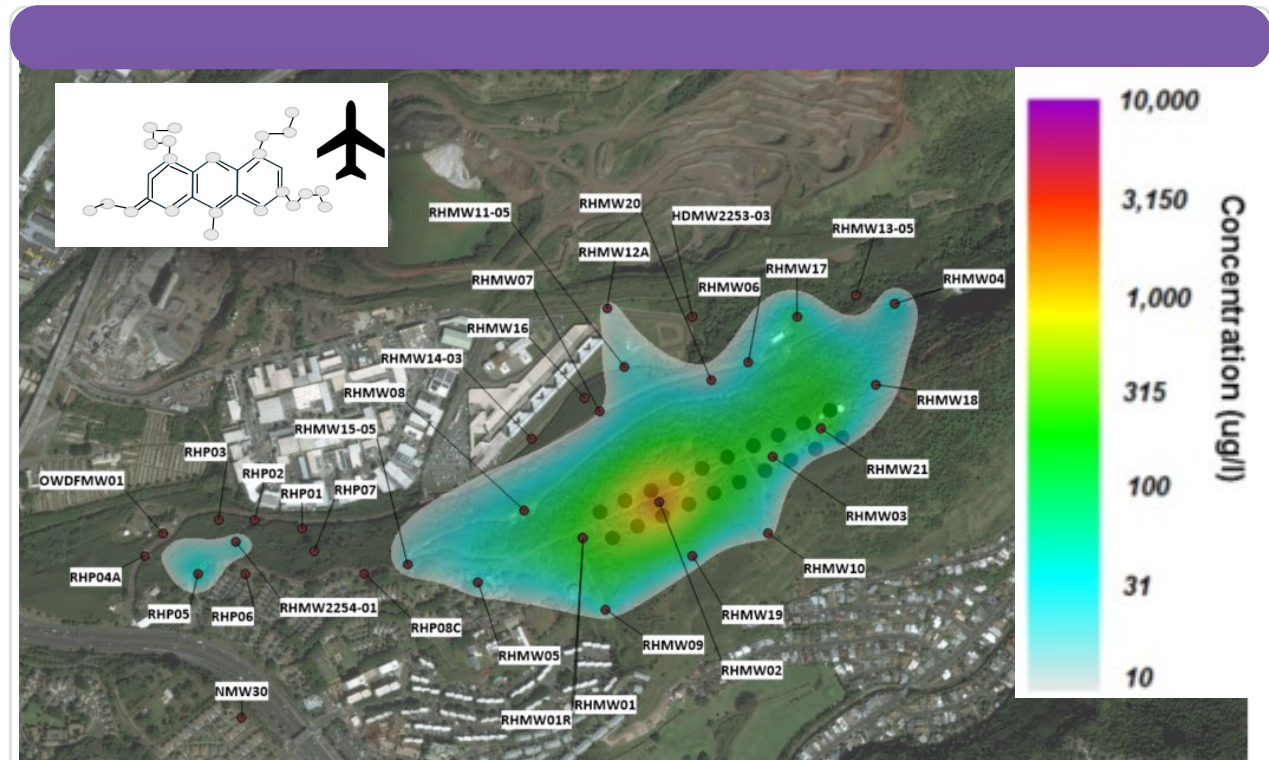
Instead of describing relationships between variables, HCA groups wells by their whole chemistry fingerprint. That makes distinct water types easier to see.

Interpretation

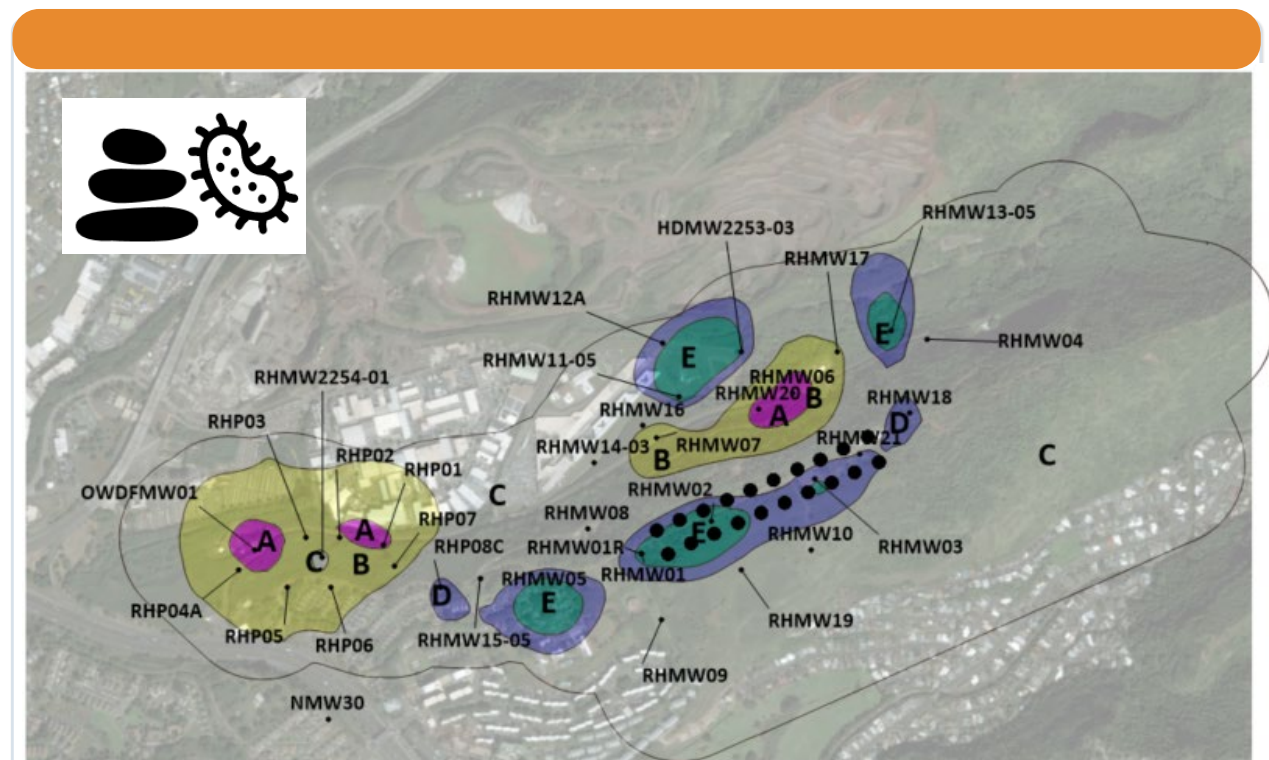
Indicates similarity with TPH plume maps, but the geochemical response extended more broadly through the shallow groundwater system.

Pair-wise correlation is a good starting point, but PCA and HCA provide a picture because they analyze many variables at the same time from different perspectives.

Mapping clusters adds to spatial understanding by building on plume maps



Plume map represents average TPH-d from Jan. 2022 through Sept. 2024 * not current conditions



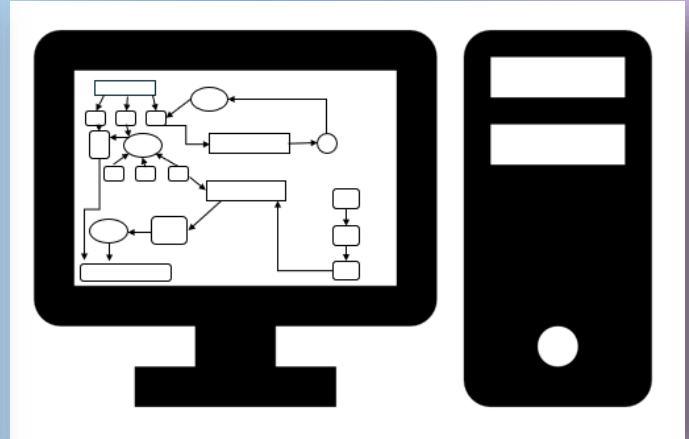
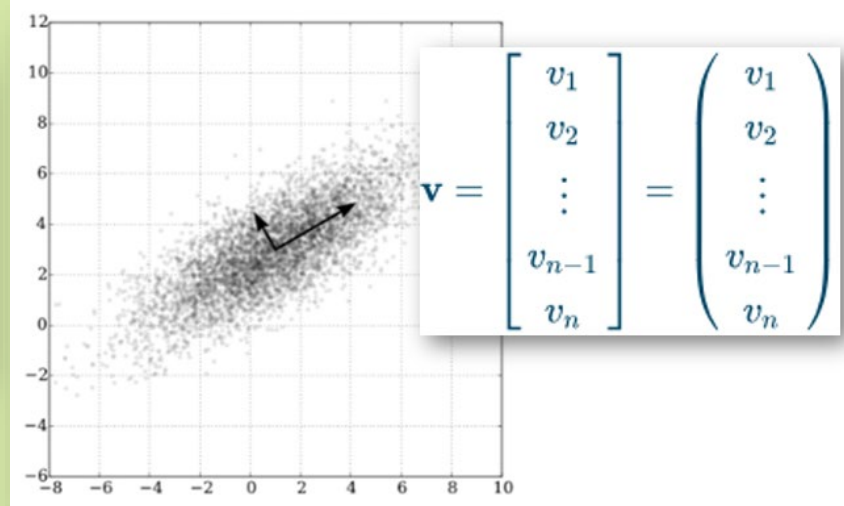
Cluster map results from general chemistry data Jan. 2022 - Sept. 2024

Findings

- We selected chemical indicators to help identify and understand patterns due to flow and mixing as well as fuel degradation processes.
- PCA showed us the dominant processes that control the groundwater chemistry.
- HCA showed us spatially the distinct chemical zones that are related to contaminant zones.
- Biodegradation is reducing concentrations at the site.

Complementary approaches

“We are always on the verge of making new discoveries... science is a continuous process of correcting and refining our understanding.”— Stephen Hawking



Tracer
Studies

Field
Observations

Chemistry
Statistical
Analyses

Groundwater
Flow Models