Groundwater around Lake Sevan: Insights from hydrochemical and isotope analyses

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Motivation

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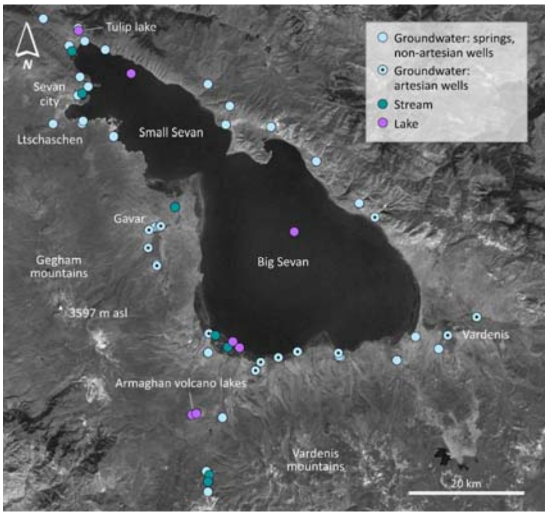
- Extension of current groundwater monitoring and literature data
- Ultimate goal: updated concept for groundwater monitoring

Fieldwork



- Two short field campaigns (Oct 2022, May 2023)
- Joint fieldwork with local monitoring experts, Harutyun Yeremyan & Gegham Muradyan
- Focus on South and South-West, due to political situation; few samples East of lake
- Total of 75 samples:
  - 45 groundwater samples: artesian and non-artesian wells, springs
  - 9 stream samples
  - 21 lake samples: Small Sevan, Big Sevan (Martin Schultze, Karsten Rinke), smaller lakes in the area

Fieldwork

- Field parameters in flow-through cell (Temperature, pH value, Electrical Conductivity, O_2)
- Alkalinity test (mini photometer) and nitrate test strips (rough estimate)
- Sampling using analyte-specific bottles and preservation techniques
- Radon (^{222}Rn) survey


Field parameter kit


Artesian "Vardenik" well


Nitrate test strip

Hydrochemistry: Piper plots

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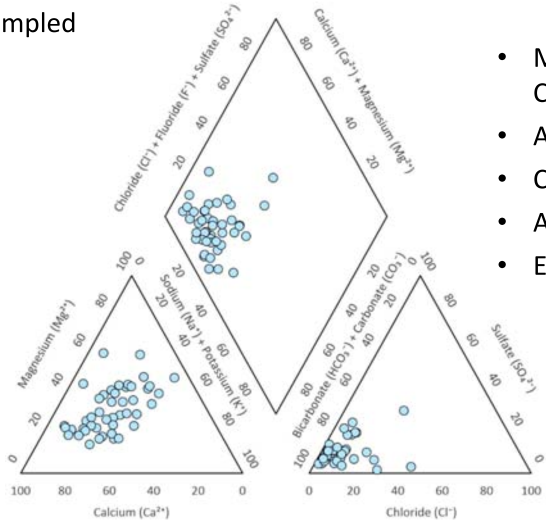
Piper plot for sampled groundwater



- Most ions analyzed via Ion Chromatography (except bicarbonate)
- Acceptable Charge Balance Errors
- Cations: strong variability
- Anions: bicarbonate dominates
- EC: rather variable (80 – 5200 µS/cm)

Freshest waters: springs

Saltiest waters: (some) artesian wells

Hydrochemistry: Piper plots

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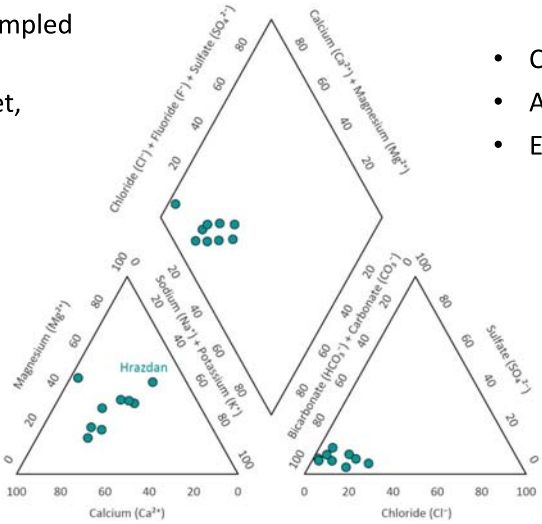
Piper plot for sampled streams

Argichi, Dzknaget, Hrazdan, Lichk, Tzaghkants, etc.



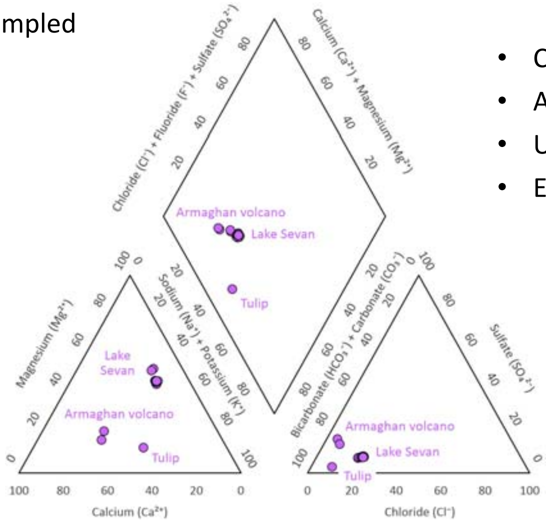
- Cations: significant variability
- Anions: bicarbonate dominates clearly
- EC: variable (60 – 770 µS/cm)

Small mountain creeks

Hrazdan river (at lake outlet)

Hydrochemistry: Piper plots

Piper plot for sampled lakes



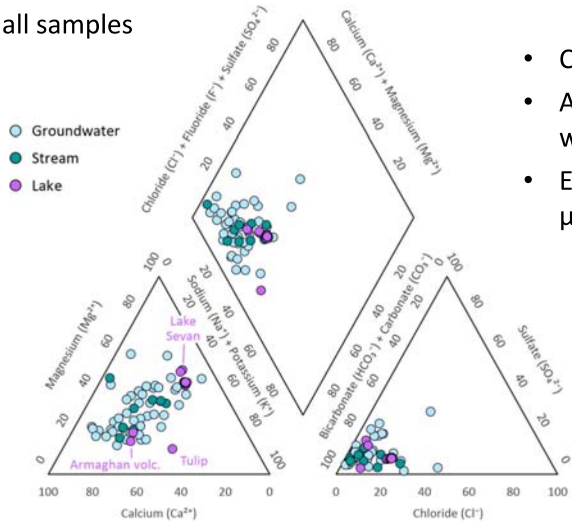
- Cations: strong variability
- Anions: bicarbonate dominates
- Unique hydrochemical fingerprints
- EC: variable (50 – 790 µS/cm)

Armaghan volcano

Lake Sevan (evaporation effect)

Hydrochemistry: Piper plots

Piper plot for all samples



- Cations: overall strong variability
- Anions: bicarbonate dominates in all water types
- EC: overall very variable (50 – 5200 µS/cm)

Hydrochemistry: Spatial patterns

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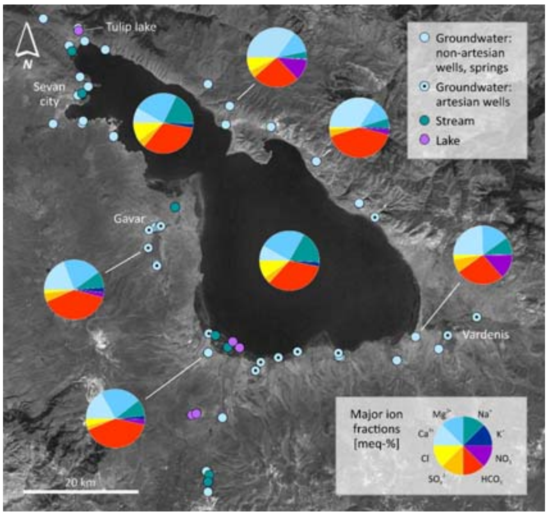

- Groundwater in West and South: Calcium and magnesium often balanced (geology dominated by volcanics, e.g. andesite)
- Groundwater in East: Calcium dominates over magnesium (geology includes limestones)
- Lake Sevan:
  - Magnesium dominates over calcium
  - Calcium probably precipitated
  - Rel. large fractions of sodium and chloride (evaporative concentration)
- Common: bicarbonate is most important anion
- Partly significant nitrate fractions

Hydrochemistry: Nitrogen species

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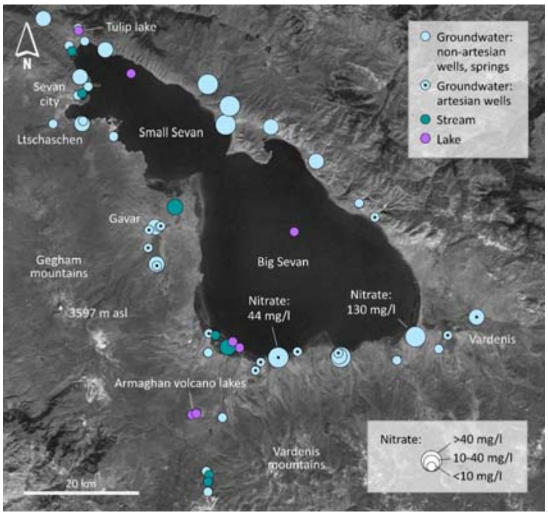
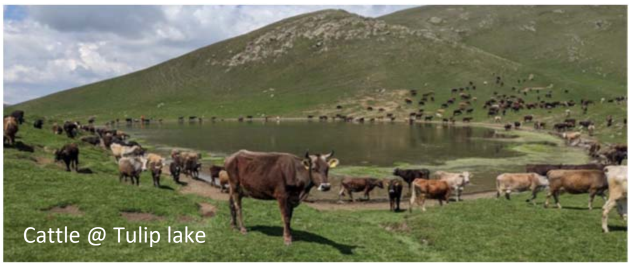
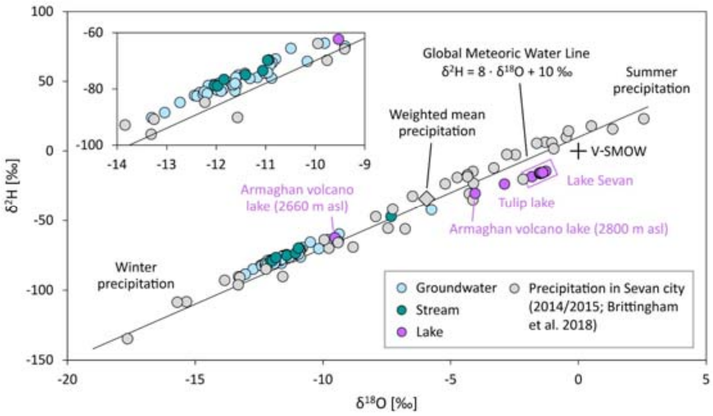


- Nitrate elevated in some springs and non-artesian wells (up to 130 mg/l); partly agricultural wells, cattle manure in vicinity
- Some artesian wells concerned (up to 44 mg/l)
- Ammonium partly elevated in fish farm waters, streams, and lakes


Cattle @ Tulip lake

Stable isotopes (water)

Dual isotope plot: δ^2H vs. $\delta^{18}O$

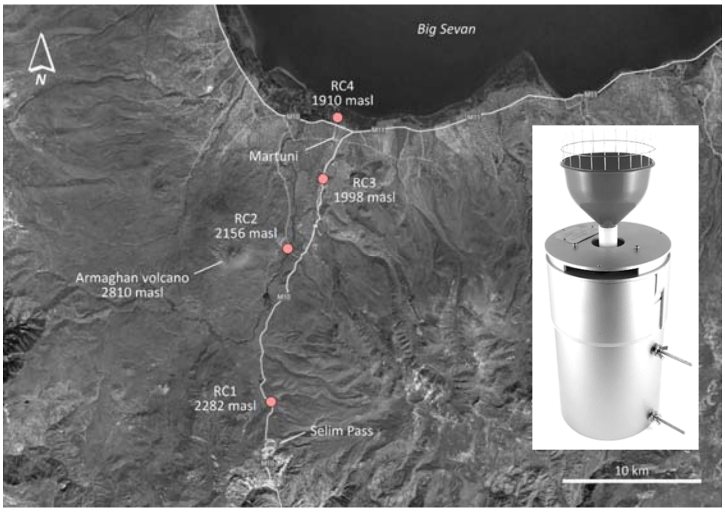


- δ^2H & $\delta^{18}O$ "fingerprint"
- Precipitation data needed for comparison (here: Sevan city)
- Samples plot near "Global Meteoric Water Line"
- Lakes show evaporation effect (shift to the right)
- Groundwaters and streams show limited scatter (compared to prec.)
- …but are more depleted compared to weighted mean precipitation
- → seasonal recharge bias (snowmelt)
- → elevation effect (to be studied!)

Stable isotopes (water)

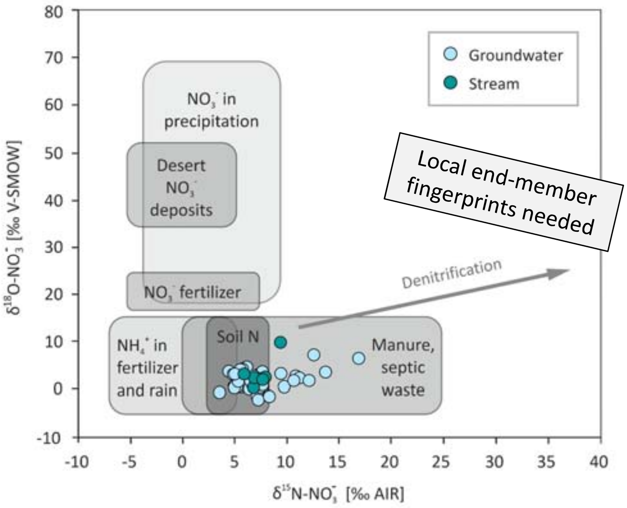
Constraining elevation effect (→ mean recharge elevation) requires local data:

- Cumulative, evaporation-free precipitation collectors by Palmex
- Installation along elevation gradient in Aug 2023 (1910 – 2283 masl)
- Monthly sampling intended
- Higher elevations challenging, especially in winter



Stable isotopes (nitrate)

- Some elevated nitrate concentrations; even detectable in artesian wells
- $\delta^{15}N$ & $\delta^{18}O$: isotopic fingerprint of nitrate
- Some samples plot in „Manure“ field, many also in „Soil N“ field (overlap)
- Ongoing: cross-check with signature of collected fertilizer and manure samples



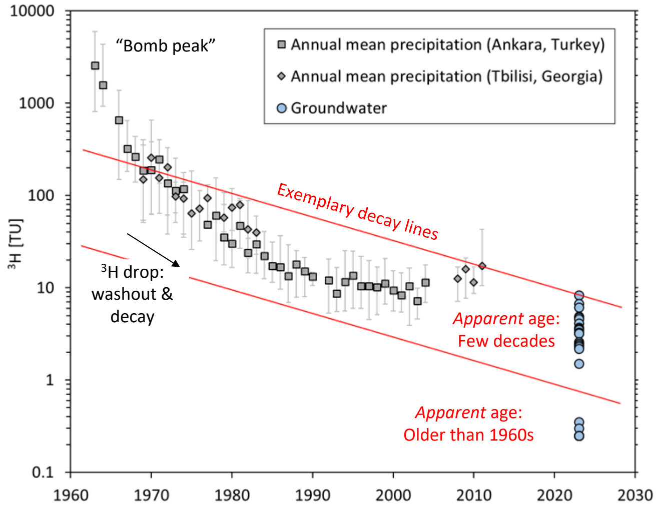
Tritium

- Tritium (^3H) has a half-life of 12.3 years
- Natural occurrence in atmosphere and water cycle, but large emissions during thermo-nuclear bomb tests (especially 1960s)
- Detectable ^3H in groundwater indicates recent recharge (after 1960), so useful tool
- ^3H in groundwaters: <0.5 – 8.3 TU (Tritium Units)
- Elevated nitrate/ammonium concentrations partly coincide with ^3H
- Even some artesian wells show ^3H
- → vulnerability indicator!

https://www.norsar.no/in-focus/75th-anniversary-of-the-first-atomic-bomb

Tritium

- Simplified, rough estimation of "*apparent* ages"
- Comparison with ^3H in precipitation of IAEA monitoring stations in the region (Ankara, Tblisi)
- Some groundwaters (<1 TU) were apparently recharged before 1960s
- Most ^3H values suggest apparent ages of a few decades (agricultural activity during this time → nitrate)



Radon (^{222}Rn) in lake water

- ^{222}Rn is a noble gas → it behaves chemically inert
- ^{222}Rn can easily be detected on-site
- ^{222}Rn is permanently produced in any aquifer matrix (decay of ^{226}Ra) and thus a naturally occurring component of groundwater (GW)
- There is no ^{222}Rn production in surface waters → strong gradient
- ^{222}Rn shows a short half-life of only about 3.8 days

→ **^{222}Rn presence in surface waters indicates groundwater discharge**

- Groundwater discharge can be localized based on ^{222}Rn distribution patterns in surface waters
- Groundwater discharge can be quantified based on a modelled ^{222}Rn mass balance
- For quantification of the results, a groundwater "end-member" is required

Radon (^{222}Rn) in lake water

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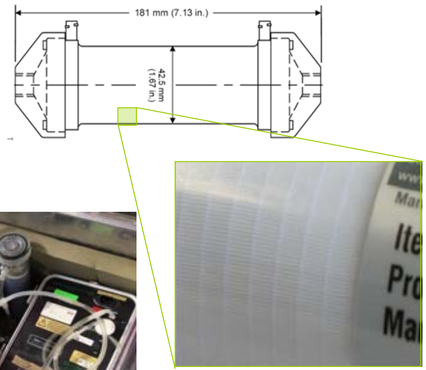
Activities

Lake survey



End-member survey

Radon (^{222}Rn) in lake water

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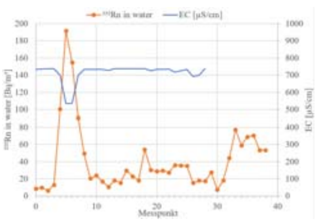
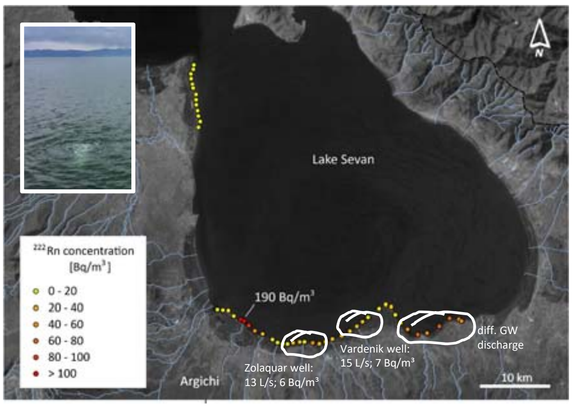
Results





Based on ^{222}Rn patterns mapped in the lake (close to shore, GW discharge was detected along the southern shoreline

Radon (^{222}Rn) in lake water

Conclusions

The survey resulted in a set of radon baseline data, representative for both groundwater and lake water, that will help evaluating the results of future surveys.

Surface water background: 5 ± 3 Bq/m³
Groundwater end-member: 21 ± 3.3 kBq/m³) → The radon potential of the aquifer as well as its spatial variability allow using radon as indicator for groundwater discharge.

The survey revealed groundwater discharge into the lake along the southern shoreline, which is in general of diffuse nature, but can at certain locations be intensified by on-shore or off-shore producing artesian wells.

The on-site activities gave the opportunity to practically introduce the approach (including all related potential challenges of fieldwork) to the Armenian colleagues, namely to Mr. Harutyun Yeremyan.

Summary

- EC values somewhat variable, but most waters are fresh
- Most groundwaters and streams fresher than Lake Sevan (latter affected by evaporative concentration)
- Major ion signature in groundwater governed by geology and residence time
- Lake Sevan shows different major ion patterns: less calcium due to precipitation; chloride and sodium enriched due to evaporation
- Nitrate (and/or ammonium) partly elevated, occasionally even in artesian wells
- δ^2H & $\delta^{18}O$ suggest seasonal recharge bias (snowmelt season) and elevation effect
- ^3H data indicate variable apparent ages, often a few decades