Diel redox changes of Rio Agrio, Argentina

Jackie Wrage
NDSU Geochemistry
December 11, 2014

Outline

- Background
- Introduction
- Study
- Results
- Conclusion
- Further Research

Where are we?

- Copahue Volcano
- Stratovolcano
- Active volcano:
  - Been erupting since 2012
  - Latest: 4th of July, 2014
- Name means “sulphur waters” in indigenous Mapuche

Study area

Rio Agrio river:

- Naturally acidic, starts at acid hot springs at the top of Copahue Volcano
- Owes acidity to influx of volatiles (SO_4, HCl, & HF)
- Enters Glacial Lake Caviahue
- Continues down to waterfall:

  Salto del Agrio
- Lower Rio Agrio

- *Increasing pH downstream*

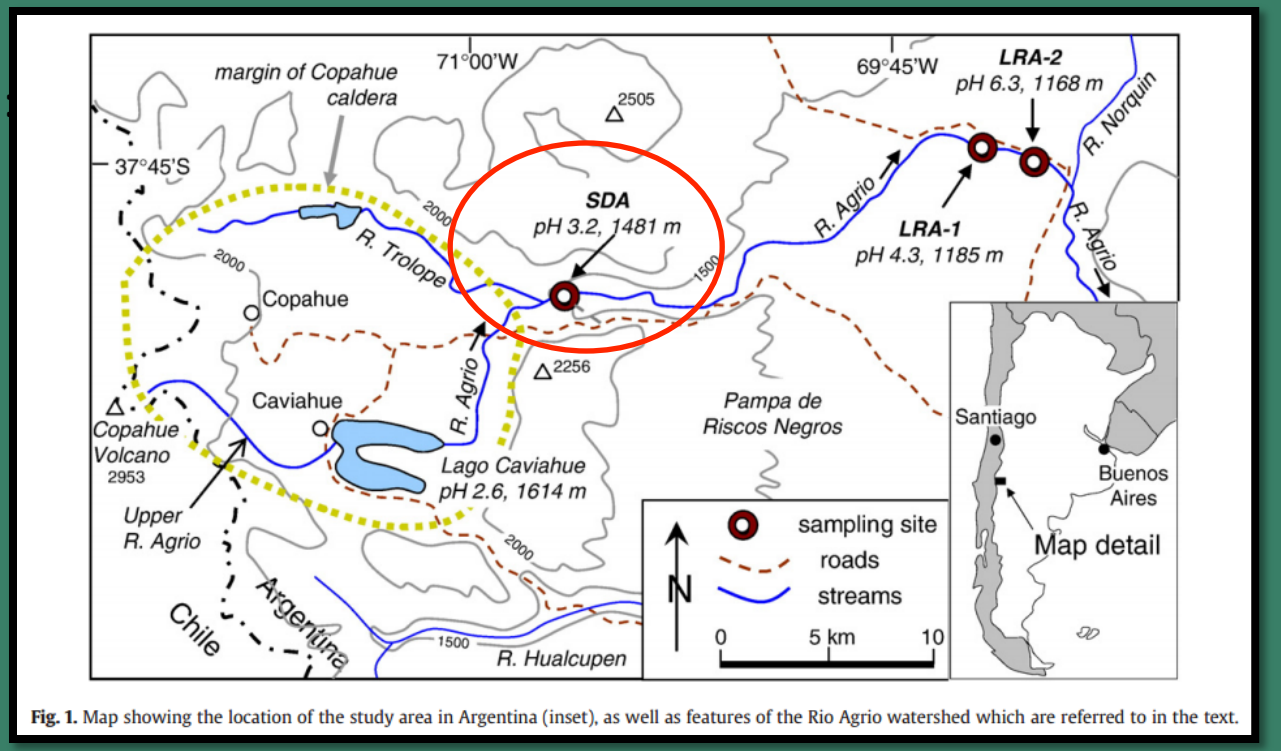


Fig. 1. Map showing the location of the study area in Argentina (inset), as well as features of the Rio Agrio watershed which are referred to in the text.

Diel redox changes of the Rio Agrio

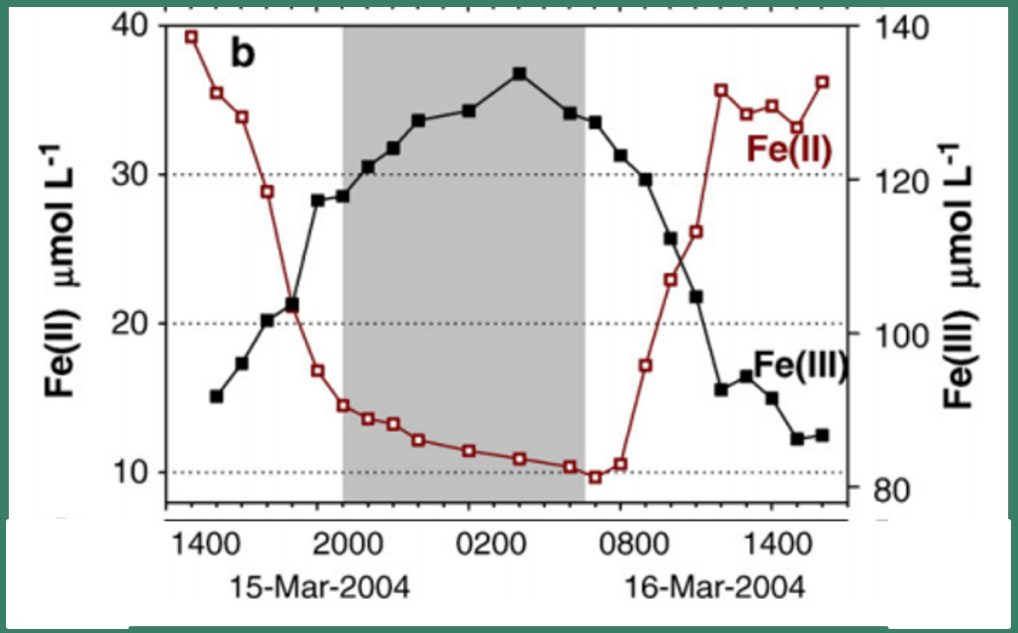
- Diel: Chemistry changes that occur within 24 hours (day to night differences)
- Redox: Chemical reactions in which atoms have their oxidation states changed

- I used data from Parker et al. (2008) at the sampling point of Salto del Agrio, a waterfall with pH of 3.2

Data

	pH	Temperature (°C)	Flow (m^3/s)	Al	Ca	Fe	Mg	Mn	Na	Si	P
Copahue source	1.5	80	NA	83,000	15,600	43,000	53,500	1140	>2200	4320	14
Lago Caviahue	2.6	15–26	–	810	550	470	1070	18	630	360	<3
SDA site	3.2	14.9	1.3	330	330	130	0490	9.0	370	360	<3
LRA-1	5.5	NA	NA	350	450	2.5	370	2.5	330	610	<3
LRA-2	6.3	15.4	0.50	13.0	580	1.4	450	2.4	350	360	<3

	Ba	Sr	K	Li	As	Zn	Cu	Cl	S	HCO_3^-	TDS
Copahue source	0.49	63.9	3000	160	76	87	0.063	NA	15000	NA	26,770
Lago Caviahue	0.11	1.9	120	1.6	0.45	0.46	0.079	NA	350	NA	602
SDA site	0.073	1.1	82	0.86	0.026	0.34	0.047	460	140	NA	254
LRA-1	0.080	1.4	89	0.60	<0.01	0.15	<0.016	NA	80	NA	145
LRA-2	0.066	1.6	105	0.43	<0.01	0.03	<0.016	281	86	31	134



Element analysis from Parker et al. (2008). Concentration in mmol.

Diel variations of total dissolved Fe^{2+} and Fe^{3+} (Parker et al. 2008)

The study

- Many studies done here, found that *concentration* and *speciation* of Fe changed from day to night

- *Why?*
- *Does this affect redox state of river?*

Why?

- Iron has 2 valence states: 3+ and 2+
  - Fe^{3+} is oxidized state (ferric)
  - Fe^{2+} is reduced state (ferrous)
- Studies have shown that in hyperacidic rivers (like Rio Agrio), **photoreduction** during the day causes the increase in Fe^{2+} and decrease in Fe^{3+}
- Photoreduction: A reduction reaction that takes place in the presence of light

$$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + H^+ + OH\cdot$$

This reaction occurs in the UV to near UV region of Electromagnetic Spectrum (200-450 nm) & is max with pH of 2-4

Summary of diel Fe speciation

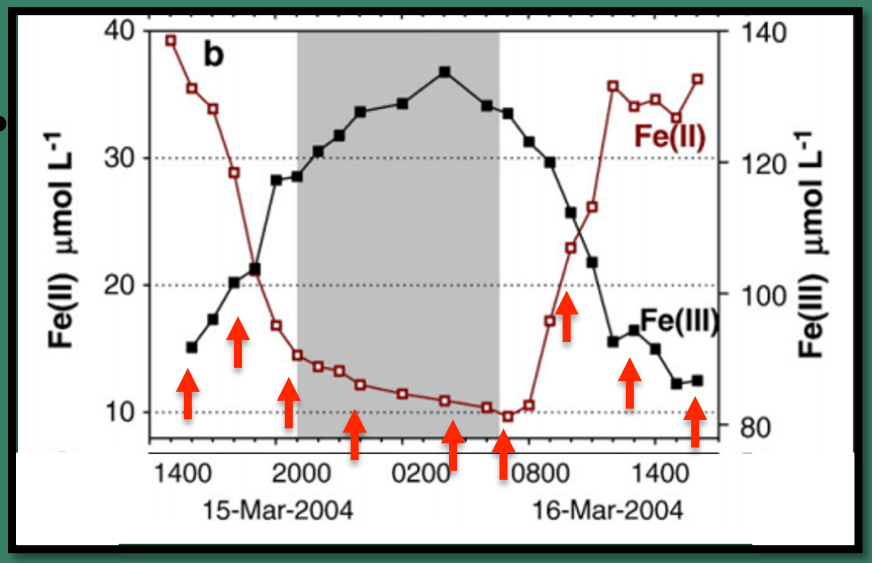
- Fe^{3+} increases at night – open to atmosphere, oxidizing environment

- Photoreduction during the day decreases Fe^{3+} and increases Fe^{2+}

Does this effect the redox state?

Using PHREEQ-C:

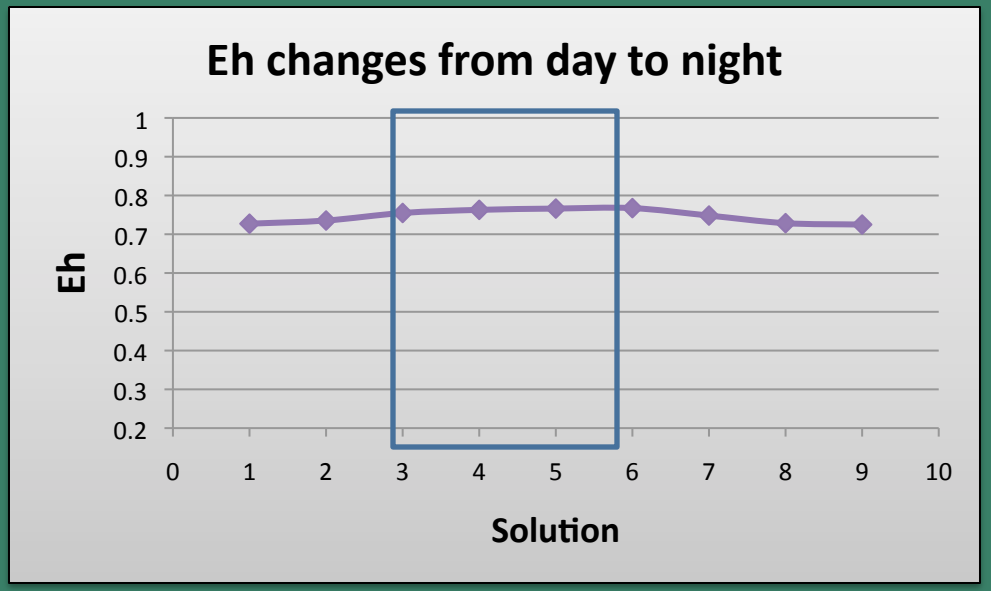
- I simulated photoreduction by changing the ratio of Fe species in the Salto del Agrio input file
- Used average element concentrations through 24
-




```
TITLE Solution 1-SDA
SOLUTION 1
    pH 3.2
    temp 14.9
    pe
    units mmol/L
    Al .33
    Ba .000073
    Ca .33
    Cl .46
    Cu .000047
    Fe(2) .035
    Fe(3) .09
    Li .00086
    Mg .49
    Mn .009
    K .082
    Si .36
    Na .37
    Sr .0011
    S .14
    Zn .00034
EQUILIBRIUM_PHASES 1
    O2(g) .66
    CO2(g) -3.52
END
```

Results

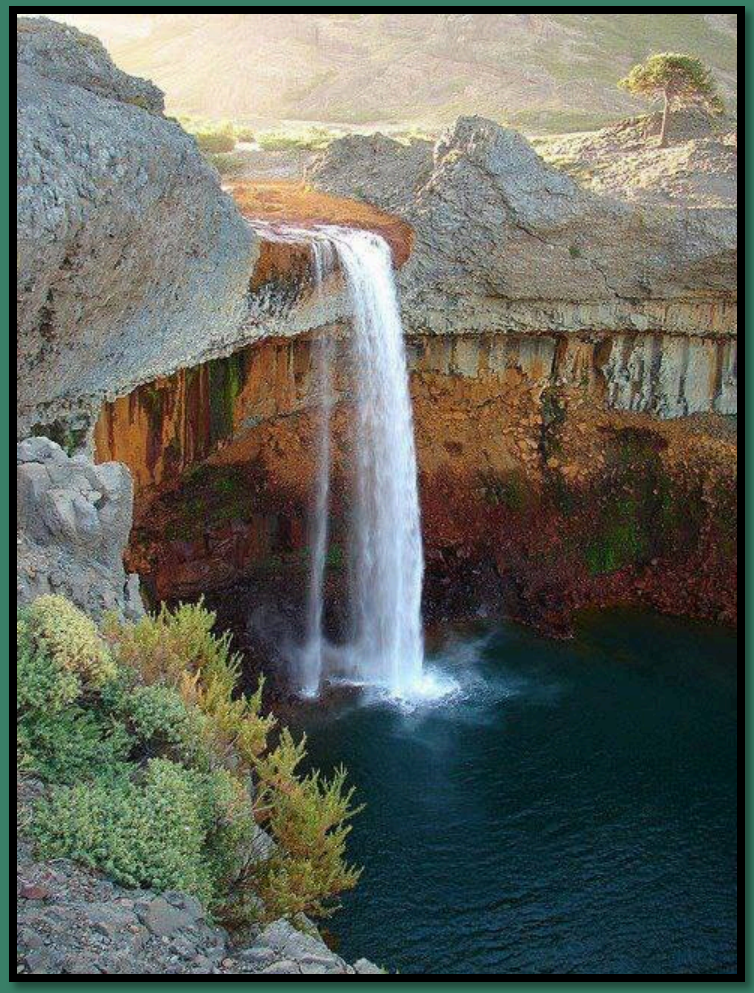
- Eh varied from 0.727 to 0.767
- Not a great difference
- *Increased slightly at night*
- Trend matched concentration of Fe^{3+} because it's the more oxidized species



Graph of diel Eh changes (Blue box represents nighttime values)

Conclusion

- Although the Fe speciation and concentration varied throughout the day, it did not effect the redox state of the entire river



Further Research

- Rio Agrio is a modern analog to the Martian environment and possibly early Earth
- Understanding interactions between organic & inorganic processes is important to astrobiology
- Fe-oxidizing bacteria are present in the Rio Agrio, studying their effect on the river chemistry can have important implications

References

Parker, S., Gammons, C., Pedrozo, F., and Wood, S. (2008) Diel changes in metal concentrations in a geogenically acidic river: Rio Agrio, Argentina. Jornal of Volcanology and Geothermal Research 178. 213-223.

Gammons, C., Nimick, D., Parker, S., Snyder, D., McCleskey, B., Amils, R., and Poulson, S. (2008) Photoreduction fuels biogeochemical cycling of iron in Spain's acid rivers. Chemical Geology 252. 202-213.


Questions?