Contaminated waters near Srebrenica: Mixing with PHREEQC

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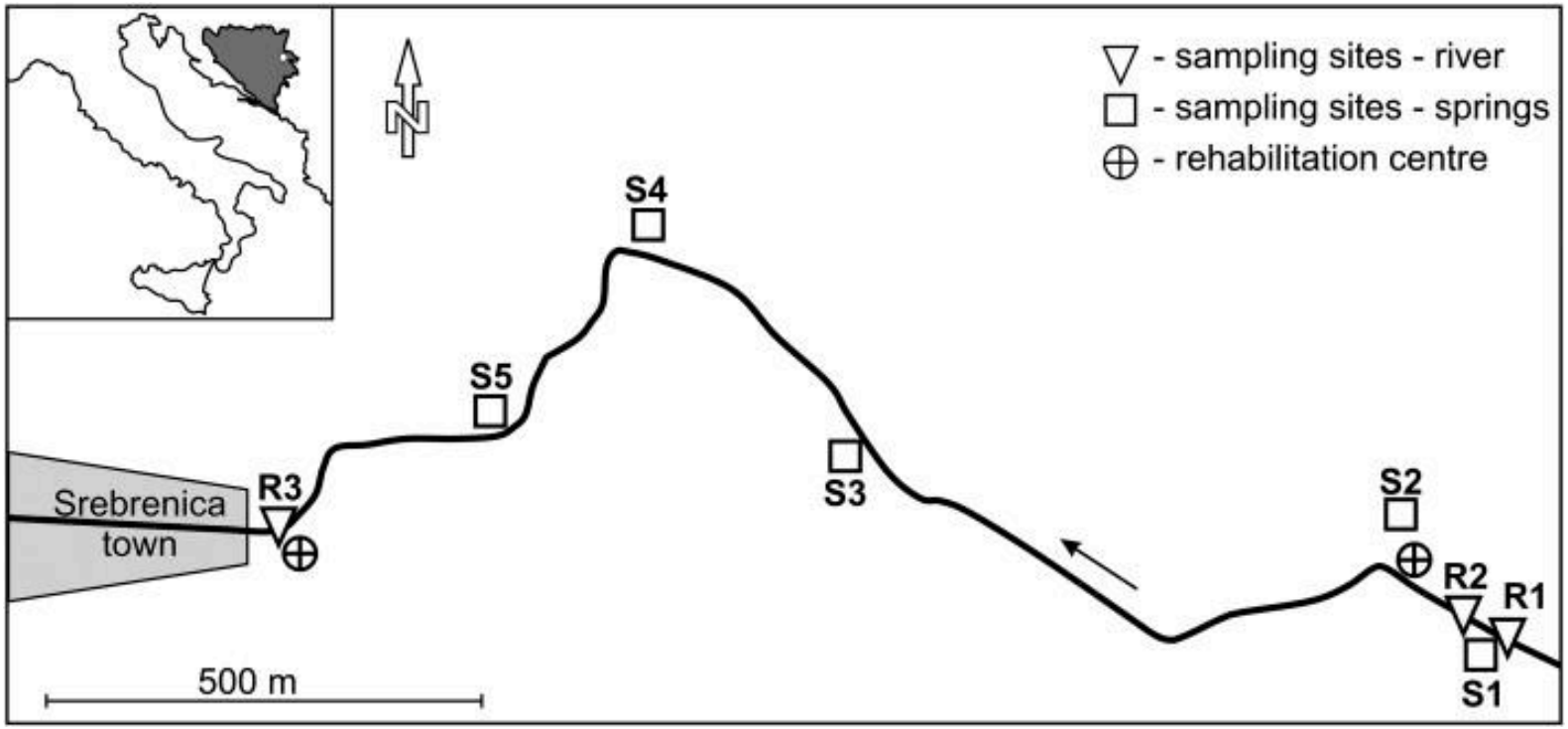
Outline

- Introduction
- Original Study
- Mixing
- My Modeling
- Conclusion

Introduction

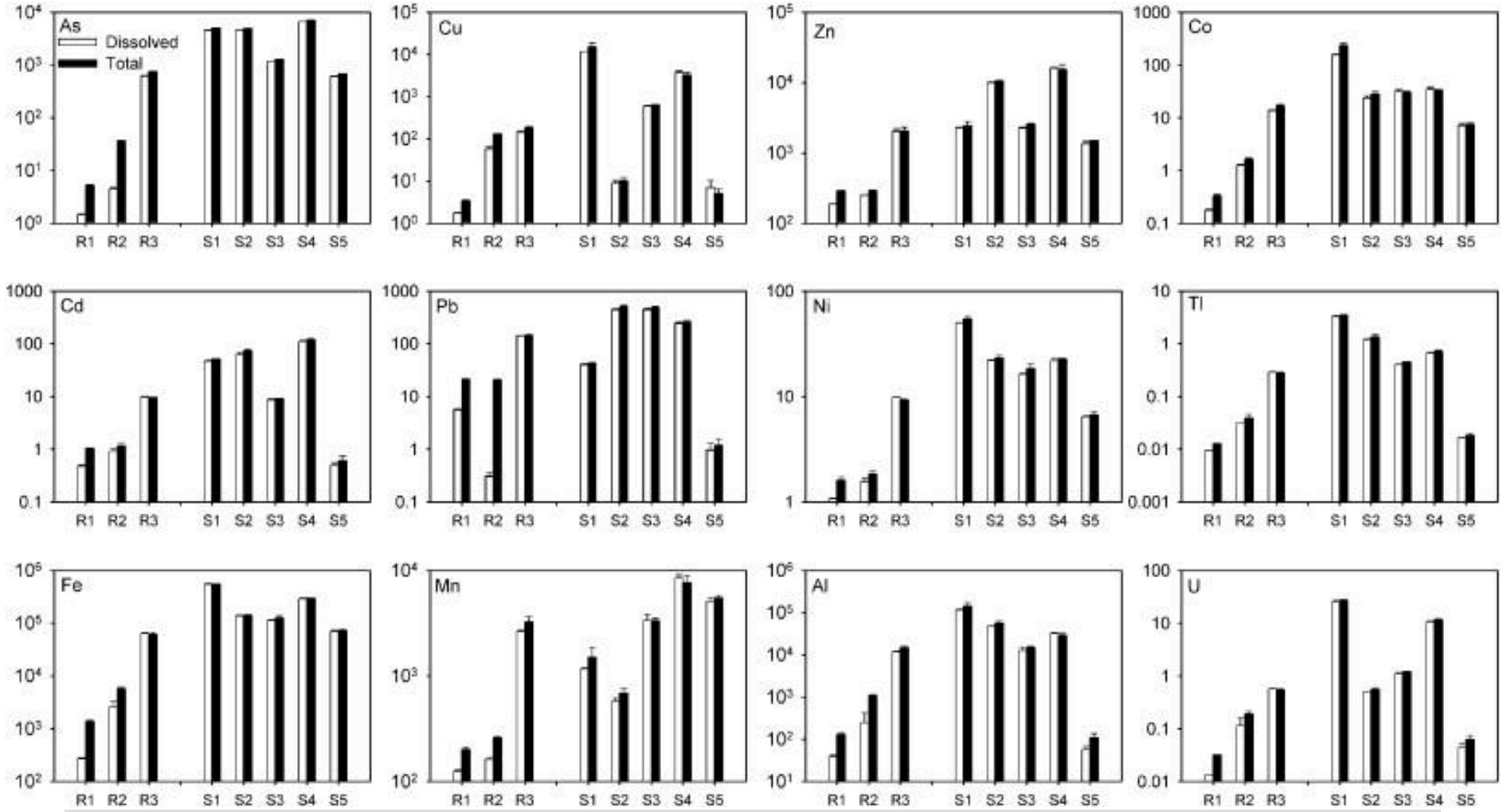
- Bijela Rijeka used for health-care purposes since 19th century
- River receives water from 5 acidic streams
- Final composition similar to acid mine drainage
- pH change from 7.3 to 3.4 over 1.5km

Location


- sampling sites - river
- sampling sites - springs
- rehabilitation centre
N
S4
S5
S3
S2
S1
R1
R2
R3
Srebrenica
town
500 m

Original Study

- Goal of original study was to 1) obtain a detailed chemical composition of the river and the springs 2) assess speciation
- 8 Samples taken - R(1-3) S(1-5)
- Samples taken during dry season (July 2009)


As
Dissolved
Total
Cu
Zn
Co
Cd
Pb
Ni
Tl
Fe
Mn
Al
U
R1 R2 R3 S1 S2 S3 S4 S5

Mixing

In this study, they didn't take discharge rate - they estimated them based on a basic mixing equation.

$$Q_{R1} \times [X]_{R1} + Q_{S1} \times [X]_{S1} = Q_{R2} \times [X]_{R2}$$

Q is discharge rate
[X] is concentration of a conservative element

Mixing

$$\mathbf{Q_{R1} \times [X]_{R1} + Q_{S1} \times [X]_{S1} = Q_{R2} \times [X]_{R2}}$$

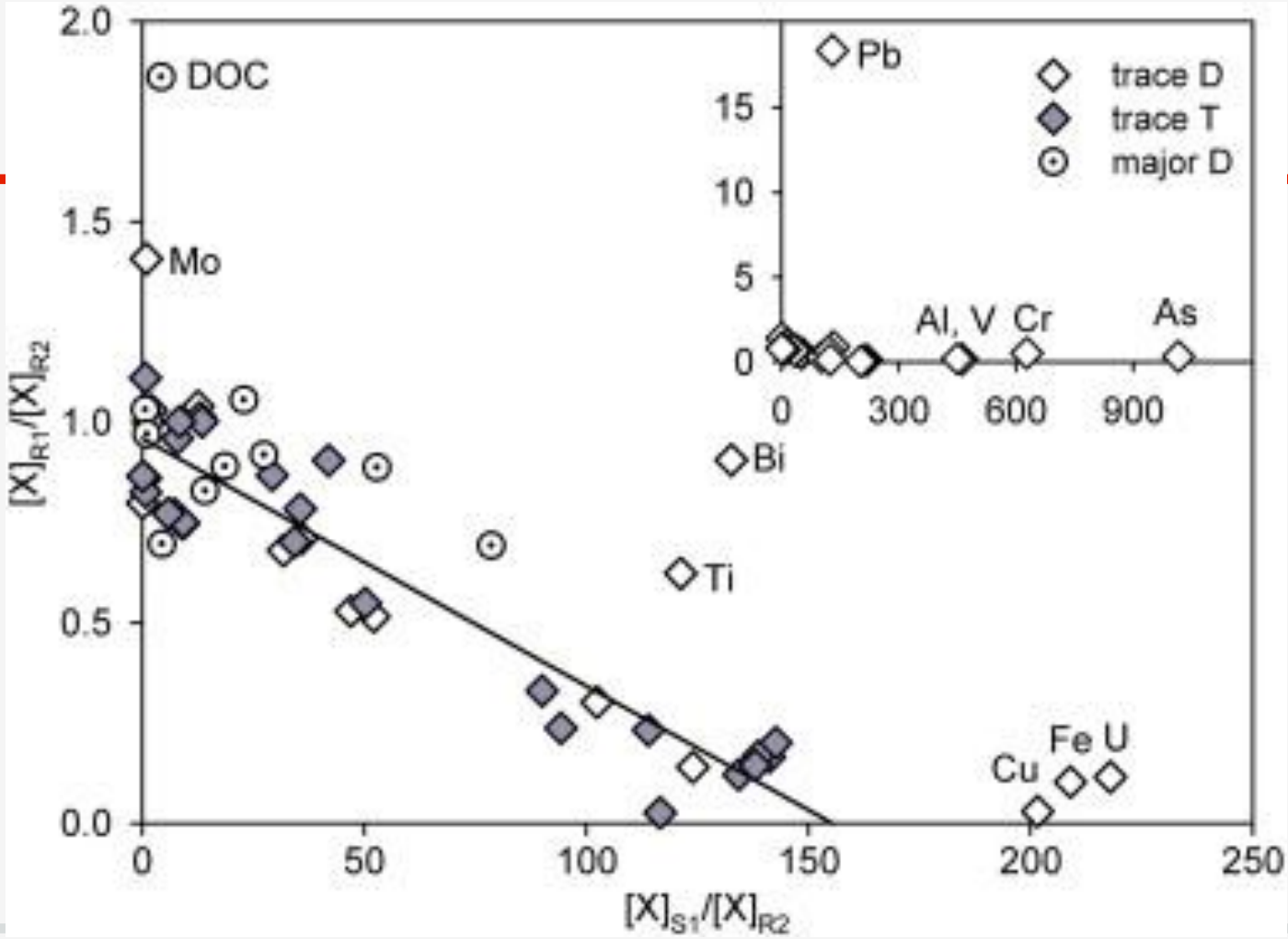
$$Q_{R1} \times [X]_{R1} = Q_{R1} \times [X]_{S1} - Q_{S1} \times [X]_{S2}$$

$$Q_{R1} \times [X]_{R1} = [X]_{R2} \times (Q_{R1} - ([X]_{S1}/[X]_{R2}))$$

$$[X]_{R1}/[X]_{R2} = (Q_{R2} - Q_{S1}\,[X]_{S1}/[X]_{R2})/Q_{R1}$$

$$[X]_{R1}/[X]_{R2} = -(Q_{S1}\,[X]_{S1}/[X]_{R2})/Q_{R1} + (Q_{R2}/Q_{R1})$$

$$\mathbf{[X]_{R1}/[X]_{R2} = -(Q_{S1}/Q_{R1}) \times ([X]_{S1}/[X]_{R2}) + (Q_{R2}/Q_{R1})}$$


2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
DOC
Mo
Ti
Bi
Pb
Al, V
Cr
As
Cu
Fe
U
15
10
5
0
300
600
900
trace D
trace T
major D
$[X]_{R1}/[X]_{R2}$
$[X]_{S1}/[X]_{R2}$

My Modeling

- Compare PHREEQC Mix Modeling to the equation the researchers used
- I used minteq.v4 database

Input File

```
TITLE Bijela Rijeka
SOLUTION 1
        pH 7.26
        temp 25
        units ug/L
        Ag      0.011
        Al      38.4
        As      1.47
        Ba      2.87
        Be      0.101
        Bi      0.002
        Cd      0.492
        Co      0.177
        Cr      0.030
        Cs      0.616
        Cu      1.74
        Fe      270
        Li      2.72
        Mn      125
        Mo      0.139
        Ni      1.06
        Pb      5.65
        Rb      1.55
        Sb      1.40
        Sr      53.2
        Ti      0.021
        Tl      0.010
        U       0.013
        V       0.040
        Zn      188
SAVE solution 1
```

```
TITLE Stream 1
SOLUTION 2
        pH 2.23
        temp 25
        units ug/L
        Ag      0.044
        Al      115000
        As      4530
        Ba      0.338
        Be      3.64
        Bi      0.279
        Cd      43.6
        Co      157
        Cr      35.6
        Cs      31.1
        Cu      11800
        Fe      549000
        Li      32.7
        Mn      1170
        Mo      0.088
        Ni      49.7
        Pb      39.8
        Rb      157
        Sb      18.0
        Sr      43.9
        Ti      4.08
        Tl      3.23
        U       25.2
        V       95.5
        Zn      2300
SAVE solution 2
```

```
TITLE R2
MIX 1
        1       165
        2       1
END
```

My Results - 159:1

Al(OH)3(am)	-2.42	8.38	10.80	Al(OH)3
Arsenolite	-52.04	-54.80	-2.76	As4O6
As2O5	-23.79	-17.08	6.71	As2O5
CoFe2O4	11.51	7.98	-3.53	CoFe2O4
Cupricferrite	3.78	9.76	5.99	CuFe2O4
Cuprite	-11.72	-13.13	-1.41	Cu2O
Cuprousferrite	5.85	-3.07	-8.92	CuFeO2
Diaspore	1.50	8.38	6.87	AlOOH
Fe(OH)2	-9.07	4.50	13.56	Fe(OH)2
Ferrihydrite	0.30	3.49	3.19	Fe(OH)3
Gibbsite	0.09	8.38	8.29	Al(OH)3
Goethite	3.00	3.49	0.49	FeOOH
Hematite	8.41	6.99	-1.42	Fe2O3
Lepidocrocite	2.12	3.49	1.37	FeOOH
Maghemite	0.60	6.99	6.39	Fe2O3
Magnetite	8.08	11.49	3.40	Fe3O4
SbO2	0.58	-27.24	-27.82	SbO2

- Modeled R2 pH value of 4.367 compared to measured pH 6.71
- I predicted that Arsenic would precipitate - it is extremely undersaturated.
- Iron & Copper supersaturations match up with precipitation event
- Ferrihydrite discussed in the study as a main precipitate, not even supersaturated in this - perhaps due to lack of modeling with DOC

My Results - 160:1

Al(OH)3(am)	-2.42	8.38	10.80	Al(OH)3
Arsenolite	-52.06	-54.82	-2.76	As4O6
As2O5	-23.80	-17.09	6.71	As2O5
CoFe2O4	11.52	7.99	-3.53	CoFe2O4
Cupricferrite	3.79	9.77	5.99	CuFe2O4
Cuprite	-11.72	-13.12	-1.41	Cu2O
Cuprousferrite	5.85	-3.06	-8.92	CuFeO2
Diaspore	1.51	8.38	6.87	AlOOH
Fe(OH)2	-9.06	4.50	13.56	Fe(OH)2
Ferrihydrite	0.31	3.50	3.19	Fe(OH)3
Gibbsite	0.09	8.38	8.29	Al(OH)3
Goethite	3.01	3.50	0.49	FeOOH
Hematite	8.41	7.00	-1.42	Fe2O3
Lepidocrocite	2.13	3.50	1.37	FeOOH
Maghemite	0.61	7.00	6.39	Fe2O3
Magnetite	8.09	11.50	3.40	Fe3O4
SbO2	0.58	-27.25	-27.82	SbO2

- Modeled R2 pH value of 4.37 compared to measured pH 6.71

My Results 161:1

Al(OH)3(am)	-2.41	8.39	10.80	Al(OH)3
Arsenolite	-52.09	-54.85	-2.76	As4O6
As2O5	-23.81	-17.10	6.71	As2O5
CoFe2O4	11.53	8.00	-3.53	CoFe2O4
Cupricferrite	3.80	9.78	5.99	CuFe2O4
Cuprite	-11.71	-13.12	-1.41	Cu2O
Cuprousferrite	5.86	-3.06	-8.92	CuFeO2
Diaspore	1.51	8.39	6.87	AlOOH
Fe(OH)2	-9.06	4.50	13.56	Fe(OH)2
Ferrihydrite	0.31	3.50	3.19	Fe(OH)3
Gibbsite	0.10	8.39	8.29	Al(OH)3
Goethite	3.01	3.50	0.49	FeOOH
Hematite	8.42	7.00	-1.42	Fe2O3
Lepidocrocite	2.13	3.50	1.37	FeOOH
Maghemite	0.62	7.00	6.39	Fe2O3
Magnetite	8.10	11.51	3.40	Fe3O4
SbO2	0.57	-27.25	-27.82	SbO2

- Modeled R2 pH value of 4.372 compared to measured pH 6.71

Conclusion

- Phreeqc mixing shows copper/iron precipitating, not much else
- pH change is too drastic based on these models

Questions?

References

Lenoble, V., Omanović, D., Garnier, C., Mounier, S., Đonlagić, Le Poupon, C., and Pižeta, I., 2012. Distribution and chemical speciation of arsenic and heavy metals in highly contaminated waters used for health care purposes (Srebrenica, Bosnia and Herzegovina). Science of the Total Environment 443 (2013) 420-428.