Redox status of hot springs in Taiwan and earthquake precursors

陳文福
嘉南藥理科技大學
溫泉研究所
助理教授

Wen-fu Chen
Chianan University
Institute of Hot Spring Research
Assistant Professor

The basic question

- What is the better item (geochemical) for earthquake precursors?

The ideal situation

- Ions come from shallow aquifer: dissolved oxygen, nitrate, sulfate…. The oxidants
- Ions come from deeper aquifer: methane, sulfide, ammonium….. The reducers

In hot spring water

- The natural reducers that come from deeper aquifer will be a better earthquake precursor
- They carry information from fault zone of a deeper part

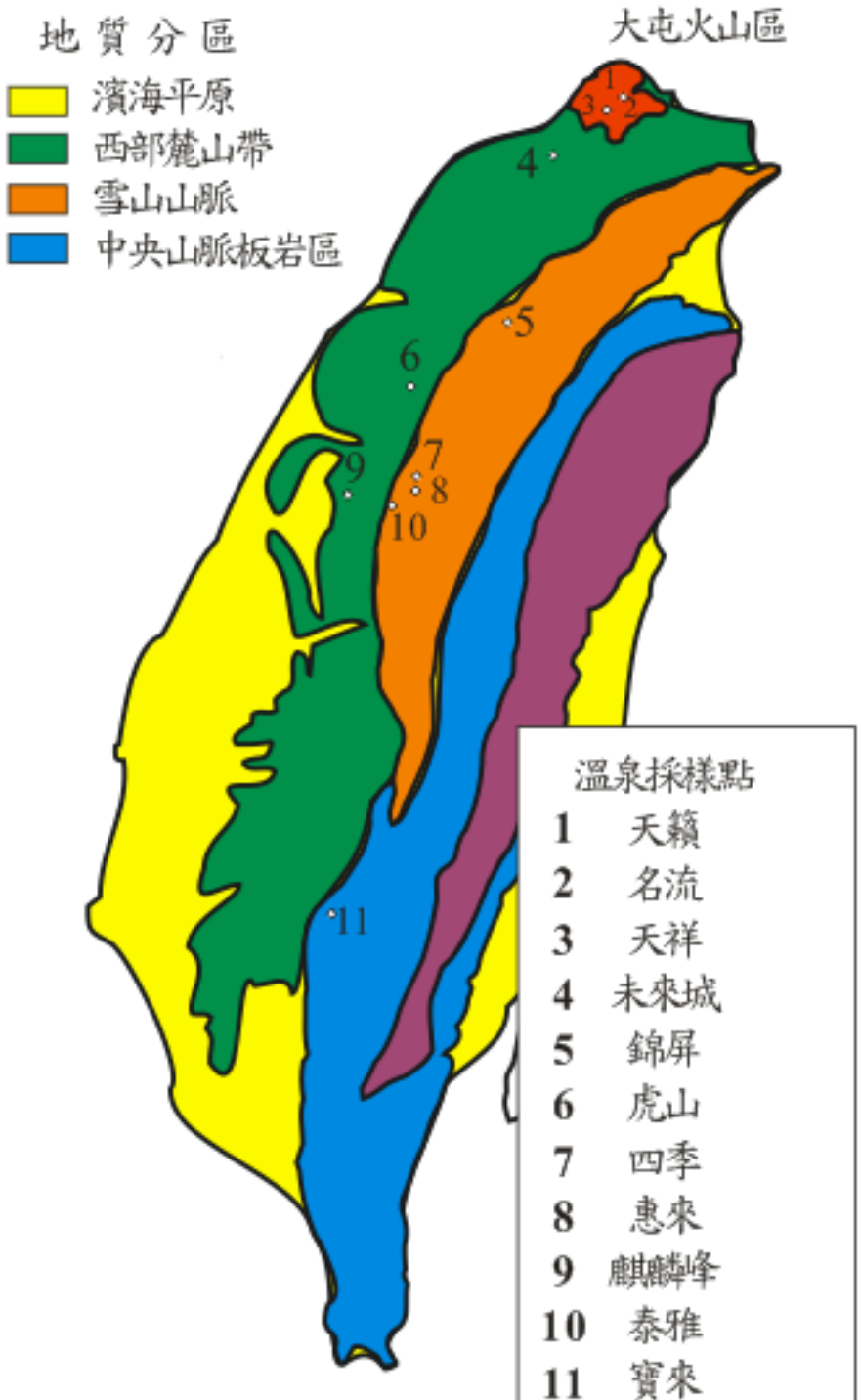
However

- Since the early scientific investigations by the Japanese scholars, hot springs of Taiwan have been studied for more than one hundred years.
- Although the basic of geology, occurrence, water temperature and chemistry of hot springs have been reported since the last century,
- however, the data of redox potential and important redox couples, e.g. sulfide and ammonium are quiet few.

The purpose of this study

- to explore the redox status of hot springs in Taiwan by measuring Eh in the field and to determine the concentrations of commonly found redox couples, i.e. O_2/H_2O, NO_3^-/NH_4^+, and HS^-/SO_4^{-2}.
- **To discuss the significances of redox couples for volcanological forecasting and earthquake precursors**

- A total of 11 hot springs located at 8 different areas from the north to the south of Taiwan were surveyed



- 3 sites are located in the Tatun Volcano Group
- 4 in the Western Foothill
- 3 in the Hsueshan Range
- 1 in the Central Range .

Locations of the sampled hot springs

Name	Location	Type	X (m)	Y (m)
Tien-Lai	Taipei Chingshan	Spring	309957	2787721
Elite	Taipei Chingshan	Spring	309997	2787598
Tien-Hsyang	Taipei Beitou	Spring	302612	2781544
Future Town	Taipei Linkou	WD* 1500m	286097	2774073
Jin-Pin	Hsinchu JienShin	WD 1000m	270331	2729598
Hu-Shan	Miaoli Taian	Spring	246763	2707343
Four Season	Taichung Kukuan	WD 80m	250127	2677939
Bali Nature SPA	Taichung Kukuan	WD 150m	250246	2677890
Kylin Peak	Taichung Dakun	WD 2000m	223027	2676166
Atayal	Nantou Pekangshi	WD 600m	243739	2663025
Baolai	Kaohsiung Baolai	Spring	220547	2554146

*WD: well depth

Values of temperature, electrical conductivity (EC), pH , dissolved oxygen (DO) and redox potential (Eh) measured in the field

Temperature (℃)	EC (μS/cm)	pH	DO (mg/L)	Eh (mV)
68.5 / 73.6	275 / 329	2.74 / 2.52	2.74 / 3.06	-145 / 95
80.0 / 56.0	286 / 503	2.49 / 2.60	2.81 / 2.55	-65 / 493
58.3 / 53.1	5840 / 4130	1.39 / 1.65	3.90 / 5.84	-23 / 382
47.6 /	18900 /	7.14 /	0.43 /	-216 /
41.3 / 41.8	813 / 809	8.55 / 8.42	2.53 / 1.52	-182 / -11
46.1 / 40.9	2340 / 2350	6.76 / 6.89	0.23 / 1.63	-277 / -236
57.7 / 54.1	490 / 496	7.72 / 7.81	0.44 / 0.54	-266 / -242
58.2 / 58.9	592 / 593	7.82 / 7.90	0.87 / 0.78	-245 / -231
30.1 / 65.4	1216 / 1005	8.00 / 8.62	1.10 / 3.82	-97 / -112
33.9 / 48.5	763 / 674	8.18 / 8.15	0.49 / 0.88	-55 / 27
59.0 / 50.0	2040 / 2030	6.95 / 7.00	0.32 / 2.45	-240 / 112

- The former values were measured in the source of outcrop or well head, the latter values were from the outlet of tank

- The measured Eh values at hot spring sources are all less than 0 mV, which indicates a reducing condition

Eh (mV)
-145 / 95
-65 / 493
-23 / 382
-216 /
-182 / -11
-277 / -236
-266 / -242
-245 / -231
-97 / -112
-55 / 27
-240 / 112

Hot springs of the Tatun Volcano Group

- The field-measured Eh values of the Tien-Lai, Elite and Tien-Hsyang hot springs are -145, -65 and -23 mV, respectively, which indicates a reducing environment.
- The concentrations of dissolved hydrogen sulfide in all the hot springs are larger than 5 mg/L, which suggest that hydrogen sulfide should be one of the important reducing agents in the water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- the concentrations of hydrogen sulfide from fumarolic gases of the Tatun Volcano Group are higher than sulfur dioxide, the ratios of H_2S/SO_2 range from 120 to 167, we suggest that hydrogen sulfide should be the dominant reducer

Ammonium concentrations

	EC*	Na^+	NH_4^+	K^+	Ca^{+2}
Tien-Lai	400	6.6	4.70	<0.1	9.8
Elite	388	7.3	1.10	3.8	8.9
Tien-Hsyang	8100	35.6	5.49	170	189
Future Town	19070	3620	54.8	179	592
Jin-Pin	775	176	<0.025	3.4	3.1
Hu-Shan	2270	480	5.24	13.1	26
Four Season	498	106	1.60	4.1	10.3
Bali Nature	594	131	2.47	4.6	8.2
Kylin Peak	1025	225	<0.025	28.8	17.7
Atayal	589	121	1.80	6.3	8.3
Baolai	1996	410	13.9	37.0	31.5

- Hot spring or groundwater with detectable concentration of ammonium (NH_4^+) also indicated a reducing condition.
- The measured Eh value of the Future Town hot spring is -216 mV and the concentration of ammonium is 54.8 mg/L, which is the highest value among the 11 hot springs we studied

- There are 9 of 11 hot spring samples that contain ammonium
- Thermodynamically, ammonium exists in the Eh range of -200 to -400 mV while pH is between 7.0 to 7.5 (Brookins 1988).

Ammonium were found

- in minerals of metamorphic and granitic rocks as quite systematic, suggesting that ammonium is one of the stable geochemical components in high temperature processes (Honma and Itihara 1981).

- A large percentage of hot springs that we investigated during the last years contain ammonium,
- e.g. Guanzihling 0.60, 關子嶺
- Lushan 6.8-18.9, 廬山
- Dongpu 2.41，東埔
- Jiaosi 5.70，礁溪
- Jhihben 16.6，知本　all in unit of mg/L

Volcanological Forecasting

- The concentration change of hydrogen sulfide and its derivative species is found to be a good indicator of changes in the fumarolic activity in volcanic area (Zimbelman et al. 2000, McGee et al. 2001, Symonds et al. 2001, Chiodini et al. 2002, Tassi et al. 2003).

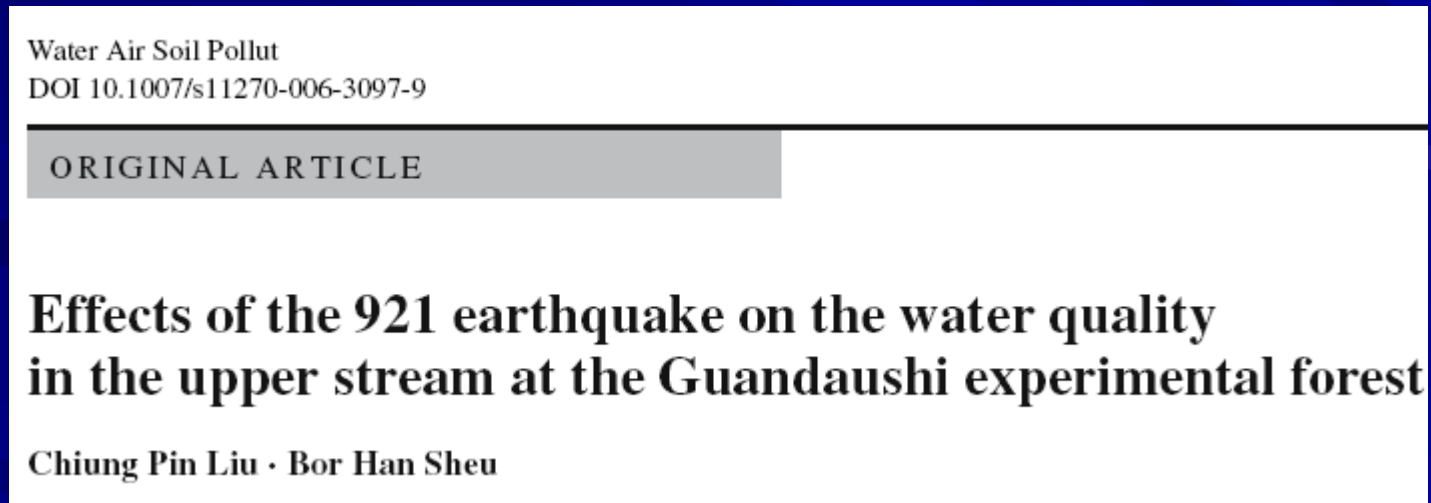
- Ammonium may be used as another useful indicator for geochemical surveillance of volcanic activity.
- A good correlation between vertical soil movements and change of ammonium had been observed (Valention and Stanzione 2004).

- Studies recommend that some of the geochemical items of hot springs, e.g. radon (Kuo et al. 2006, Yasuoka et al. 2006), chloride (Toutain et al. 1997, Toutain and Baubron 1999), calcium, sodium, sulfate, etc. (Biagi et al. 2001) would be capable of serving as earthquake precursors and fault activity indicators.
- However, case studies on ammonium and sulfide are rare.

Earthquake Precursors ?

Liu 2007

- ammonium concentrations in stream water from upper reaches of Guandaushi Creek in Nantou County increased by 20 to 40 times from August 1998 to September 1999 before the 921 Earthquake (7.3 magnitude).



Water Air Soil Pollut
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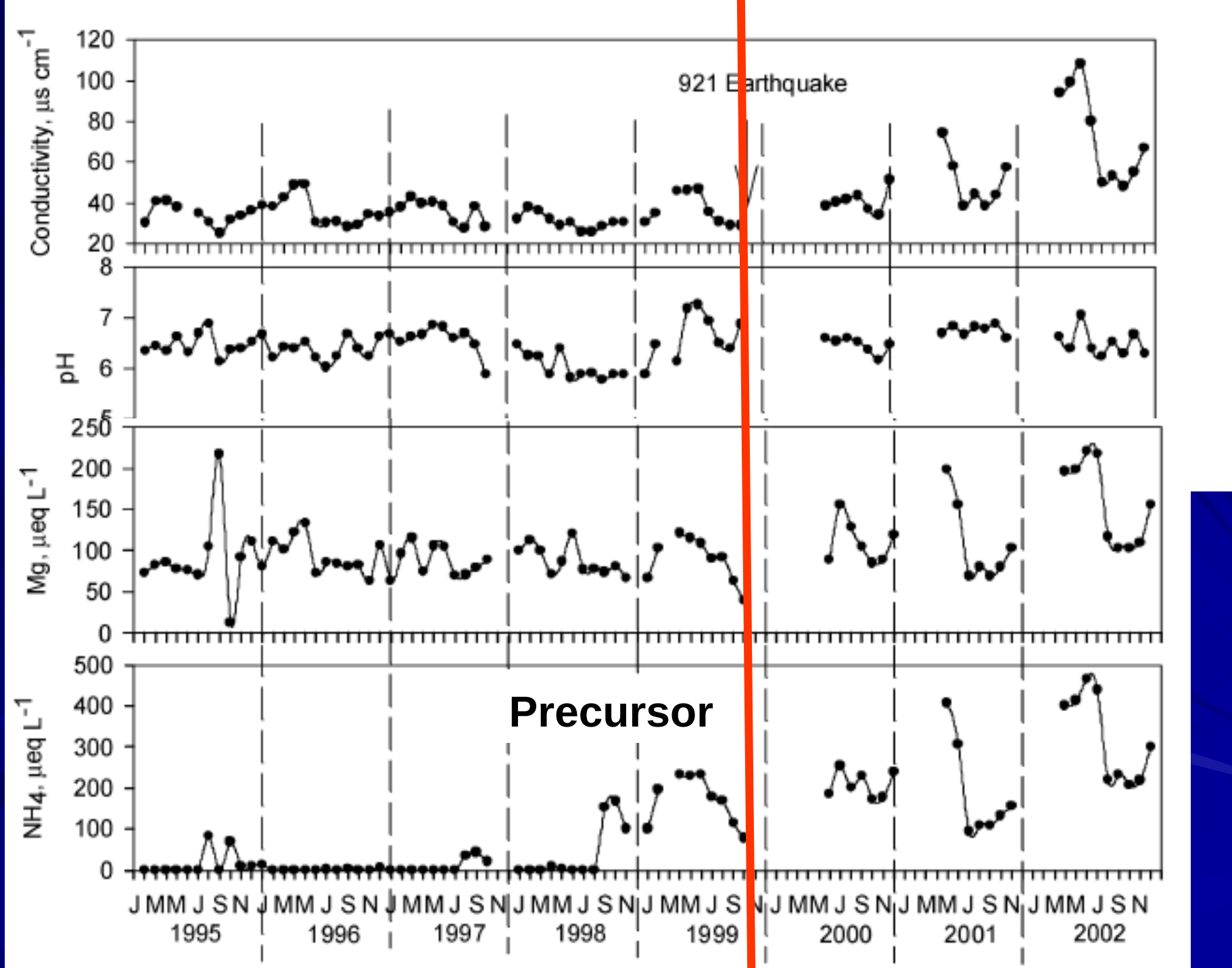
ORIGINAL ARTICLE

Effects of the 921 earthquake on the water quality in the upper stream at the Guandaushi experimental forest

Chiung Pin Liu · Bor Han Sheu


Conductivity, µs cm-1
120
100
80
60
40
20
921 Earthquake
pH
8
7
6
Mg, µeq L-1
250
200
150
100
50
0
NH4, µeq L-1
500
400
300
200
100
0
Precursor
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1995
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We suggest

- the ammonium may come from deeper anoxic aquifers and discharged to the Guandaushi Creek through an unknown fault zone.

- Hot springs circulated from deeper part of fault zone contain dissolved reducing agents of hydrogen sulfide and ammonium, which will be the ideal monitoring species for earthquake precursors

Thank you !