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Fluoride: A naturally-occurring health hazard in drinking-water resources of Northern Thailand

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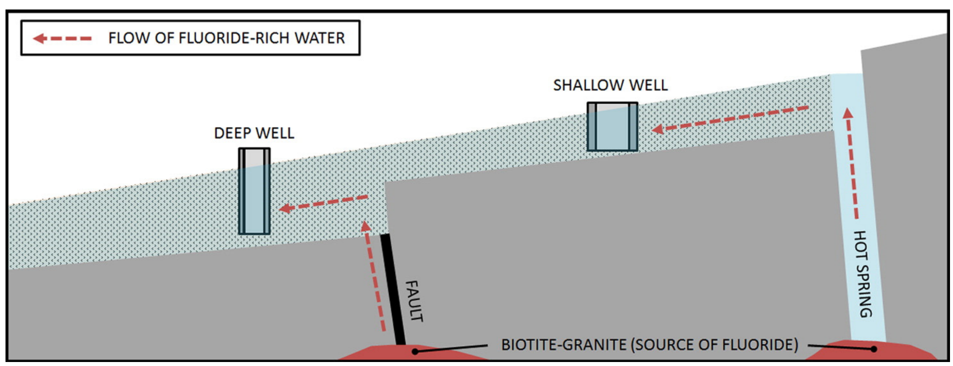
HIGHLIGHTS

- Two unconnected high-fluoride anomalous zones in Northern Thailand were mapped.
- Biotite-granite is identified as the source of fluoride in water resources.
- Natural and anthropogenic processes control the transport of high-fluoride water.
- The risk of fluorosis in Northern Thailand still persists.

GRAPHICAL ABSTRACT



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ABSTRACT

In Northern Thailand, incidences of fluorosis resulting from the consumption of high-fluoride drinking-water have been documented. In this study, we mapped the high-fluoride endemic areas and described the relevant transport processes of fluoride in enriched waters in the provinces of Chiang Mai and Lamphun. Over one thousand surface and sub-surface water samples including a total of 995 collected from shallow (depth: ≤30 m) and deep (>30 m) wells were analysed from two unconnected high-fluoride endemic areas. At the Chiang Mai site, 31% of the shallow wells contained hazardous levels (≥1.5 mg/L) of fluoride, compared with the 18% observed in the deep wells. However, at the Lamphun site, more deep wells (35%) contained water with at least 1.5 mg/L fluoride compared with the shallow wells (7%). At the Chiang Mai site, the high-fluoride waters originate from a nearby geothermal field. Fluoride-rich geothermal waters are distributed across the area following natural hydrological pathways of surface and sub-surface water flow. At the Lamphun site, a well-defined, curvilinear high-fluoride anomalous zone, resembling that of the nearby conspicuous Mae Tha Fault, was identified. This similarity provides evidence of the existence of an unmapped, blind fault as well as its likely association to a geogenic source (biotite-granite) of fluoride related to the faulted zone. Excessive abstraction of ground water resources may also have affected the distribution and concentration of fluoride at both sites. The distribution of these high-fluoride waters is influenced by a myriad of complex natural and anthropogenic processes which thus created a challenge for the management of water resources for safe consumption in affected areas. The notion of clean and safe drinking water can be found in deeper aquifers is not necessarily true. Groundwater at any depth should always be tested before the construction of wells.

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1. Introduction

Most cases of drinking-water resource degradation are in direct association with the contamination of water as a result of anthropogenic activities, for example pesticides and fertilisers from agriculture, tailings from mining operations, effluents from industrial processes, chemical spills, etc. (Gilbert, 2012; Meybeck and Helmer, 1989; Meybeck, 2002; Vitousek et al., 1997; Vorosmarty et al., 2010). While contaminants of anthropogenic origin will likely continue to be a major cause of the impairment of drinking-water resources, naturally-occurring drinking-water hazards, although less commonly reported, do exist — and they play a substantial part in the threat to public health and the livelihoods of millions around the world each year. One such example is the highly-publicised accidental mass poisoning from the drilling of wells into groundwater containing naturally-occurring arsenic in Bangladesh (Acharyya et al., 1999; Ahmad et al., 1997; Dhar et al., 1997). Between 35 million and 77 million people are at-risk to drinking arsenic-contaminated water (Smith et al., 2000). Another important naturally-occurring drinking water hazard is fluoride, which is the main focus of this study.

The element fluorine is the lightest member of the halogen group and is the most electronegative. As such, it is the most reactive of all elements (Brindha and Elango, 2011). Fluorine does not occur in the environment naturally in its elemental state but rather as the negatively charged fluoride ion, F^-, because of its high tendency to react and combine with other elements forming strong electronegative bonds and producing ionic compounds (Ayoob and Gupta, 2006). Fluoride is therefore mostly retained in minerals and rocks in the lithosphere. Fluoride has an ionic radius very similar to that of a hydroxide ion (OH^-) and substitutes readily in hydroxyl positions in late-formed minerals of igneous rocks (Edmunds and Smedley, 2005). It is widely dispersed, making up 0.06–0.09% of the composition of the earth's crust. Fluoride concentrations in freshwater bodies such as rivers and lakes are generally less than 0.5 mg/L, while fluoride content of seawater is higher at approximately 1.0 mg/L. In groundwater, however, significantly higher concentrations of fluoride can occur, especially in areas where fluorine is found in great abundance in local subterranean minerals and rocks (Fawell et al., 2006).

In small amounts, fluoride is beneficial for oral health because it reduces the ability of plaque bacteria to produce acid that damages teeth. Fluoride also improves the chemical structure of the enamel by making it more resistant to acid attack that causes tooth decay (Ayoob and Gupta, 2006). For these reasons, fluoride is added to toothpaste; in some countries, to drinking water (Edmunds and Smedley, 2005). However, prolonged exposure to high doses of fluoride is detrimental because of the risk of fluorosis. The most common symptom of dental fluorosis is mottling, and ultimately, destruction of teeth. With exposure to high concentrations for prolonged periods, fluoride may accumulate in bones, leading to crippling skeletal fluorosis. Once developed, the symptoms of fluorosis are irreversible (Ayoob and Gupta, 2006).

Exposure to fluoride occurs mainly through inhalation or ingestion (Fawell et al., 2006). In areas where solid fuel burning is prevalent for cooking or heating, the concentration of fluoride in the indoor atmosphere can be elevated due to the combustion of coal with high fluoride content, leading to increased exposure through the respiratory route. In China alone, almost 1.5 million cases of dental fluorosis and an estimated 18 million cases of reported skeletal fluorosis were related to fluoride emissions from the burning of coal (Ando et al., 2001; Hou, 1997; Li and Cao, 1994). Worldwide, however, the inadvertent consumption of the colourless, tasteless and odourless fluoride in drinking water is the single largest contributor to daily fluoride intake (Murray, 1986).

Globally, an estimated 200 million people are exposed to high concentrations of naturally-occurring fluoride that exceeds the World Health Organisation's (WHO) guideline value of 1.50 mg/L for drinking water (Ayoob and Gupta, 2006; Fawell et al., 2006). Fluorosis is endemic in at least 25 countries on almost every continent including Asia, Africa, Europe, North and South America (Fawell et al., 2006). For instance, in the Hetao Plain of Inner Mongolia, China, approximately 6 million people are at risk to fluorosis from drinking high-fluoride water. Nearly 2 million of this total has shown signs of dental fluorosis; nearly a quarter of a million are suffering from skeletal fluorosis (Guo et al., 2012; He et al., 2013). In India, where 90% of the rural population rely on groundwater as drinking water sources, more than 60 million people in more than half of the states in the country are at risk to high levels of fluoride exposure (Gupta et al., 2005; Kundu et al., 2009; Viswanathan et al., 2009).

Incidences of fluorosis have also been documented in other countries, including Thailand. One of the earliest reports in Thailand was a nationwide nutrition survey carried out by the United States Inter-Departmental Committee on Nutrition for National Defence in the 1960's (Leatherwood et al., 1965). Cases of dental fluorosis were found in every region of the country, but it was most prevalent in Northern Thailand (61% of 3614 people surveyed). Further, the fluoride concentrations in drinking water and urine samples of local people in the northern region were also found to be the highest compared to the other regions (Leatherwood et al., 1965). Despite the prevalence and severity of the problem, subsequent scientific studies and reports pertaining to fluorosis have been rare. In one, Ratanasthien (1991) reported severe cases of fluorotoxicosis involving osteosclerosis (or abnormal calcification on various parts of bones) associated with the drinking of fluoride-contaminated groundwater in Chiang Mai Province of Northern Thailand. Also in Chiang Mai Province, Namkaew and Wiwatanadate (2012) found links between lower back pains – a common symptom of acute fluorosis – and the consumption of high-fluoride groundwater in elderly villagers. In another Chiang Mai-based study, McGrady et al. (2012) estimated a three-fold increase of dental fluorosis prevalence (to at least 37%) for subjects ingesting water with fluoride concentrations of 0.90 mg/L or more. Incidences of fluorosis have also been documented in several other provinces in Northern Thailand. In Chiang Rai Province, Noppakun et al. (2000) attributed the mottling of enamel in primary school children to the consumption of drinking waters contaminated with fluoride-enriched waters from nearby hot springs. In Lampang, the prevalence of dental fluorosis among children at the age of 12 was 10% in 1995 (Vuttipitayamongkol, 2000). In Lamphun, Takeda and Takizawa (2008) reported significantly elevated levels of fluoride (up to 4.9 mg/L) in urine samples of school children living in a village supplied with high-fluoride water, compared to the maximum of 0.94 mg/L fluoride in the urine of children utilising low-fluoride water from another village.

Despite the awareness of the potential risk of fluoride contamination in drinking water for half a century, fluorosis still represents a serious and widespread health problem particularly to some rural communities of Northern Thailand. Oddly, studies that identify the extent of high-fluoride areas, the origin, and the transport of fluoride in water sources – all aspects that are crucial for drinking-water resource management and public health safety – are limited. Further, the lack of scientific reporting and public dissemination of health and safety information threatens the ability to manage drinking water resources safely in at-risk areas. For example, the construction of many drinking water wells in locations with high levels of fluoride may have occurred in the past, and may still be occurring now. Our motivation is to contribute to local rural water management in the region by (1) mapping the extent of two high-fluoride endemic areas; and (2) describing the relevant transport processes of fluoride from source to sink.

2. Study area

The study area is located on the eastern part of the Ping River Basin, which is situated between the Khun Tan Mountain range to the east and the Ping River to the west (Fig. 1). The site extends from Chiang Mai

Province in the north to Lamphun Province in the south. In Chiang Mai, the study was carried out predominantly in the districts of Doi Saket, San Kamphaeng, and Mae On. In Lamphun, the capital district of the province (*Amphoe Mueang* Lamphun), the districts of Ban Thi and Pa Sang were covered.

2.1. Climate

Annual rainfall in the area ranges from 800 mm in the lowlands (~350 m a.s.l) to 1500 mm in the highlands (~1800 m a.s.l.) with seasonal rainfall between May and October accounting for over 90% of the annual total (Lim et al., 2012; Margane and Tatong, 1999; Wood and Ziegler, 2008). Temperature is typically lowest, 3.7 to 17.2 °C, between the months of November and February based on meteorological records from 1967 to 2001 (Uppasit, 2004). Historical records from the same period show that highest temperatures of the year usually occur in the months of February to April in the range of 32.1 to 41.4 °C (Uppasit, 2004).

2.2. Geology

The Ping River Basin is generally regarded as an inter-montane pull-apart basin formed under an extensional tectonic regime between the Late Cretaceous and the Early Tertiary periods following the collision of the Indian with the Eurasian plate (Asnachinda, 1997; Margane and Tatong, 1999). The structural framework of the basin is governed by N–S trending extensional faults that are related to the movement of NW–SE and NNE–SSW trending strike-slip faults which have been active since the Oligocene (Asnachinda, 1997).

Lithologically, the basin can be divided into two parts: (1) the well-indurated rocks from the Paleozoic to the Mesozoic eras; and (2) the poorly-indurated rocks of the Tertiary and Quaternary periods (Wattananikorn et al., 1995; Fig. 2). Sedimentary Paleozoic and metamorphic Cretaceous (Khorat Group) rocks underlie the basin as well as the western and eastern mountain ranges (Wattananikorn et al., 1995). Of importance to this study is the intrusion of the Late Triassic/Earliest Jurassic granitic rocks of the eastern marginal belt of plutons – the Khuntan Batholith of biotite-granite – in the Palaeozoic rocks on the eastern part of the basin (Yokart et al., 2003). Biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$) is a known source of fluoride in the environment (Chae et al., 2006). Fluoride can be transferred from these granitic rocks to groundwater through dissolution (Chae et al., 2007; Nordstrom et al., 1989). Above the sedimentary Palaeozoic and metamorphic Cretaceous rocks is the Tertiary sequence of which the oldest unit is the Mae Sod Formation of the Mio-Pliocene (Wattananikorn et al., 1995).

2.3. Hydrogeology

Unconsolidated Quaternary alluvium deposits are important aquifers and lie unconformed over older rock formations, covering most of the Ping River Basin (Wattananikorn et al., 1995). The Quaternary deposits that are of relevance to the study area can be categorised into two geomorphological units: (i) flood plain alluvial deposits; and (ii)

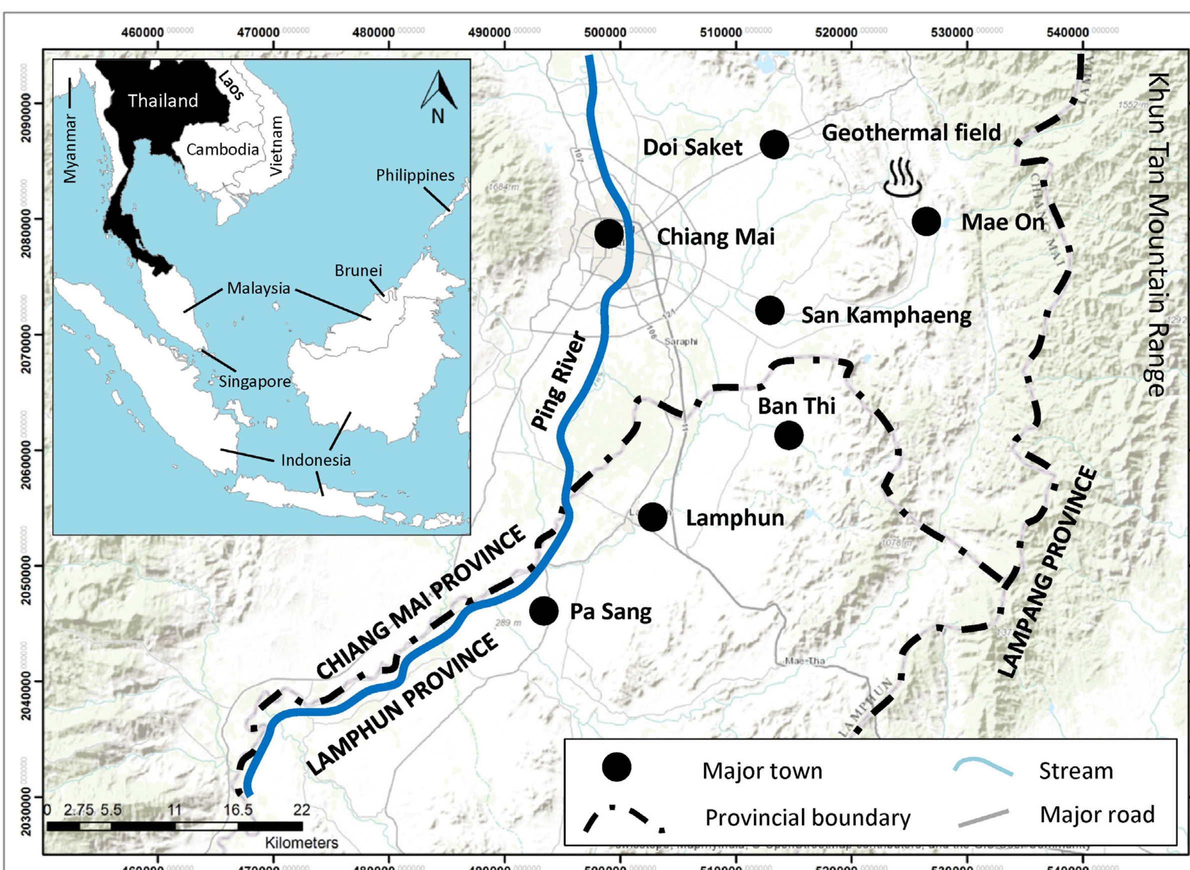

Fig. 1. Location map of the study site in the Ping River Basin. Inset: Thailand and its neighbouring countries of Southeast Asia.

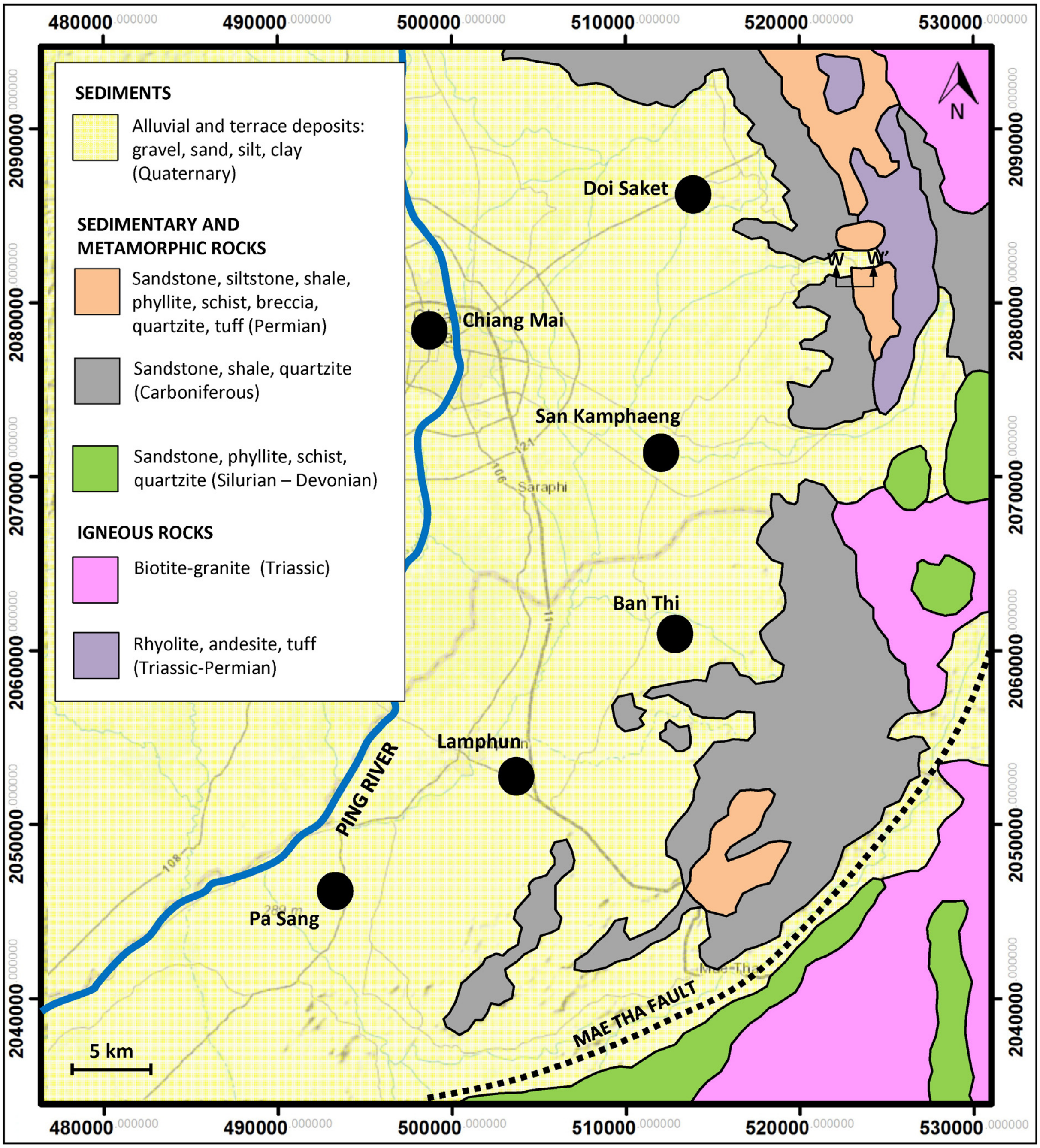

Fig. 2. Geological map of the study site (after Department of Mineral Resources, 1995). Section W–W′ is detailed in Fig. 7.

low-terrace colluvial deposits. Holocene alluvial deposits are restricted to the floodplains and meander belts of the Ping River that cover the central part of the basin. The formation is composed mostly of well-sorted sand and gravel overlain by a few metres of clay. This area has the highest groundwater exploitation potential in the basin with well yields greater than 20 m^3/h (Intrasutra, 1983). The Middle-Upper Pleistocene low colluvial terraces flank the central alluvial plain. These formations are composed of thick beds of fine sediments including kaolinite with intercalating sand and gravel lenses (Intrasutra, 1983). These low permeability layers of fine materials function as aquitards to restrict the flow and mixing of groundwater from one aquifer to another (Suvagondha and Jitapunkul, 1982). At the low-terrace colluvial deposits, well yields vary in the range of 12 to 60 m^3/h (Intrasutra, 1983).

2.4. Geothermal source

A section of the north-eastern part of the study site falls within a geothermal field. The 12-ha geothermal field, which has more than 70 natural hot springs (Singharajwarapan et al., 2012), has been studied for its geothermal energy production potential (Barr et al., 1979; Chuaviroj, 1988; Praserdvigai, 1986; Ramingwong et al., 1978;). Geothermal waters from these springs are known to have high levels of fluoride – for example a concentration as high as 42 mg/L has been recorded (Ratanasthien et al., 1987).

2.5. Human activities

Agriculture is very important to the livelihood of the local communities of Chiang Mai and Lamphun. Approximately 34.5% of the population in both provinces are involved in the agricultural sector (Thomas, 2005). An estimated 11% and 18% of the total land areas are used for agricultural activities in the provinces of Chiang Mai and Lamphun, respectively (Thomas, 2005). Besides surface water sources like rivers and canals, farmers also pump groundwater for irrigation. Additionally, the groundwater is also extracted for use by the industrial sector. Anuwongcharoen (1989) reported that the Lamphun Industrial Estate, located to the east of the Lamphun Province's capital district, heavily exploits the local groundwater resources for industrial activities.

3. Methods

Water samples from private and community (village or town) wells from Chiang Mai Province were collected between May 2013 and December 2013. Sampling in Lamphun Province was carried out from January 2014 to April 2014. A total of 175 and 301 samples were collected from deep and shallow wells in Chiang Mai, respectively. At the Lamphun study site, 301 and 218 samples were collected from deep and shallow wells respectively. Due to the proximity of the geothermal field (where waters from hot springs are known to contain high levels of fluoride), we also collected samples from surface waters (e.g. streams, rivers) to investigate the influence of these high-fluoride geothermal waters on the local surface water geochemistry in the Chiang Mai study area. In addition, water samples were also collected directly from the hot springs. A total of 121 surface water samples as well as 6 geothermal water samples were collected.

Water samples from wells with depths of 30 m or less (typically hand-dug wells or borewells from private residences) are categorised as shallow wells. Water samples from wells with depths greater than 30 m (typically community borewells that supply water village-wide) are designated as deep wells. Water samples from hand-dug wells were collected using a 2-L bucket lowered from the top of the well with a rope. Water samples from borewells were collected directly from taps. The depths of hand-dug wells were obtained by lowering a weighted measuring tape to the base of wells; borewells depths were obtained by interviewing the owners (for private wells) or the caretakers of village water supply systems (for community wells). Samples sent for laboratory analyses were stored in distilled water-rinsed, 250-mL polyethylene bottles and stored in the dark at approximately 4 °C.

Specific electrical conductivity and pH of water samples were determined on site using a handheld multi-parameter probe (YSI 556 MPS, Yellow Springs, OH, USA). Concentrations of fluoride from water samples were first determined on site by colorimetry (SPADNS method, upper limit: 2.00 mg/L F^-) with a portable spectrophotometer (Hach® DR2800™, Loveland, CO, USA). Prior to processing, raw samples were filtered through a 0.45-µm nylon-membrane to remove suspended particles that may interfere with the colorimetry determination. Samples with fluoride concentrations of at least 2 mg/L (upper detection limit for SPADNS), as well as all samples from deep wells, were (re)analysed for fluoride in the GEOLAB at the Department of Geography, National University of Singapore, using a high-pressure ion chromatography system (Dionex™ ICS-5000, Thermo Scientific™, Sunnyvale, CA, USA). Concentrations of major groundwater cations and anions including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} from a subset of well water samples were also determined by ion chromatography.

To understand the spatial variation of fluoride concentration in water sources, sampling sites with the corresponding fluoride concentrations (represented with different colours for various concentration groups) were mapped using a geographic information system (GIS) software, ArcGIS (Esri, Redlands, CA, USA). The range (minimum and maximum concentration), median, mean and standard deviation of the measured parameters were calculated and tabulated. Regression analysis was performed to determine the correlation between fluoride and the other water quality parameters.

4. Results

4.1. Spatial distribution of fluoride

4.1.1. Chiang Mai Province

As expected, water samples collected from the geothermal springs contained the highest concentrations of fluoride ($n = 6$; mean = 17.03 mg/L; range: 12.30–19.89 mg/L). A total of 121 surface water samples were collected. Surface water samples with the highest fluoride concentrations were found in streams close to the geothermal field to the northeast of the site (Fig. 3). The maximum fluoride concentration recorded in surface water was 18.84 mg/L where the sample was collected from a stream draining the geothermal field. The concentrations of fluoride in surface water gradually decreased away from geothermal field in the south-westerly direction following the flow of the local stream system.

A total of 175 and 301 water samples were collected from deep and shallow wells, respectively. Approximately 18% of the water samples from deep wells contained fluoride with concentrations greater than 1.50 mg/L, the guideline value recommended by the WHO for safe (long-term) drinking-water consumption (WHO, 2011; Fig. 4). More shallow wells contained unsafe levels of fluoride than deep wells (Fig. 5). Approximately 31% of these water samples were found to contain fluoride exceeding the WHO guideline threshold. Comparison of fluoride concentrations in water from paired deep and shallow wells of the same locality (collected no more than 50 m from each other) demonstrated that the shallow wells in this area have a relatively higher susceptibility to high-fluoride water intrusion (Fig. 6A). In 61% of the pairs, shallow wells had higher concentrations of fluoride than deep wells.

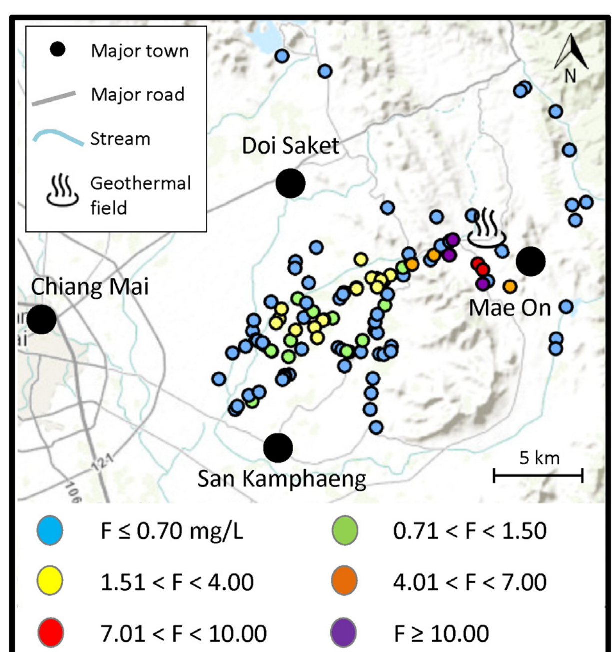

Fig. 3. Sampling locations of surface waters and corresponding fluoride concentrations in Chiang Mai Province.

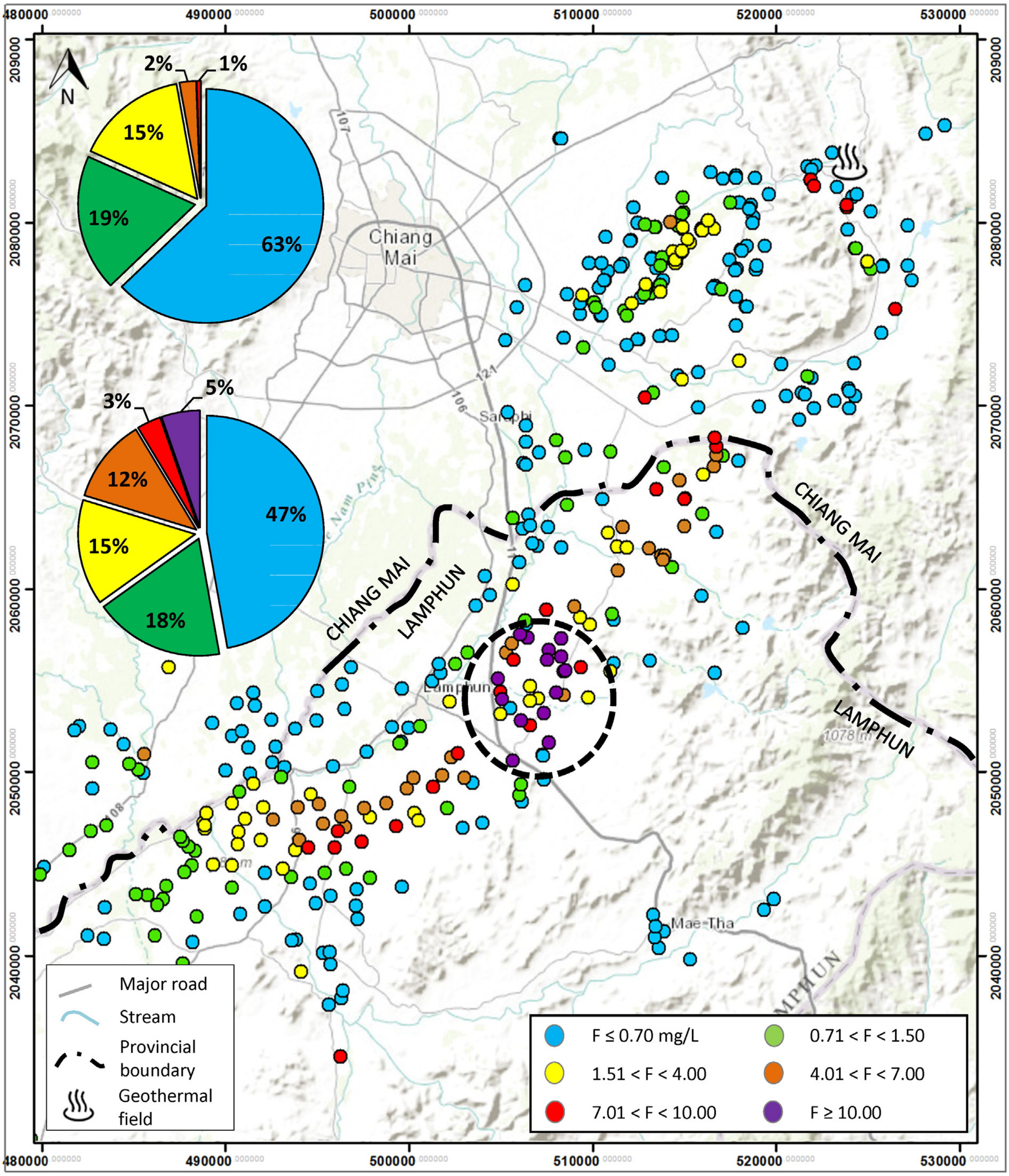

Fig. 4. Locations of sampled deep wells and corresponding fluoride concentration ranges. Pie charts show statistical summary of fluoride concentration ranges in deep wells at study sites in Chiang Mai (top) and Lamphun (bottom), respectively. Black dotted circle: 'Hot spot' in high-fluoride anomalous zone.

The spatial patterns of fluoride distribution in deep and shallow wells revealed a linear-shaped, high-fluoride ($F^- > 1.50$ mg/L) anomalous zone within the study area, similar to that as observed in the surface waters (Figs. 4 and 5). This zone extends from the geothermal fields in the northeast to the edge of San Kamphaeng town centre in the southwest of the Chiang Mai study site.

We did not find any relationships between the concentrations of fluoride and either the physicochemical water quality parameters (pH and specific electrical conductivity) or the major ions (Na^+, K^+, Mg^{2+} and Ca^{2+}) of the water samples from shallow and deep wells (Table 1).

4.1.2. Lamphun Province

A total of 301 water samples were collected from deep wells at the Lamphun study site. Approximately 35% of these water samples had concentrations of fluoride greater than the recommended WHO drinking-water quality threshold value of 1.50 mg/L (Fig. 4). Up to 5% from these samples had fluoride concentrations of more than 10.00 mg/L. The highest recorded value was 14.12 mg/L. Of the 218 shallow well water samples collected, only 7% had concentrations greater than the recommended WHO drinking-water quality threshold (Fig. 5). Concentrations of fluoride in water samples from shallow wells were

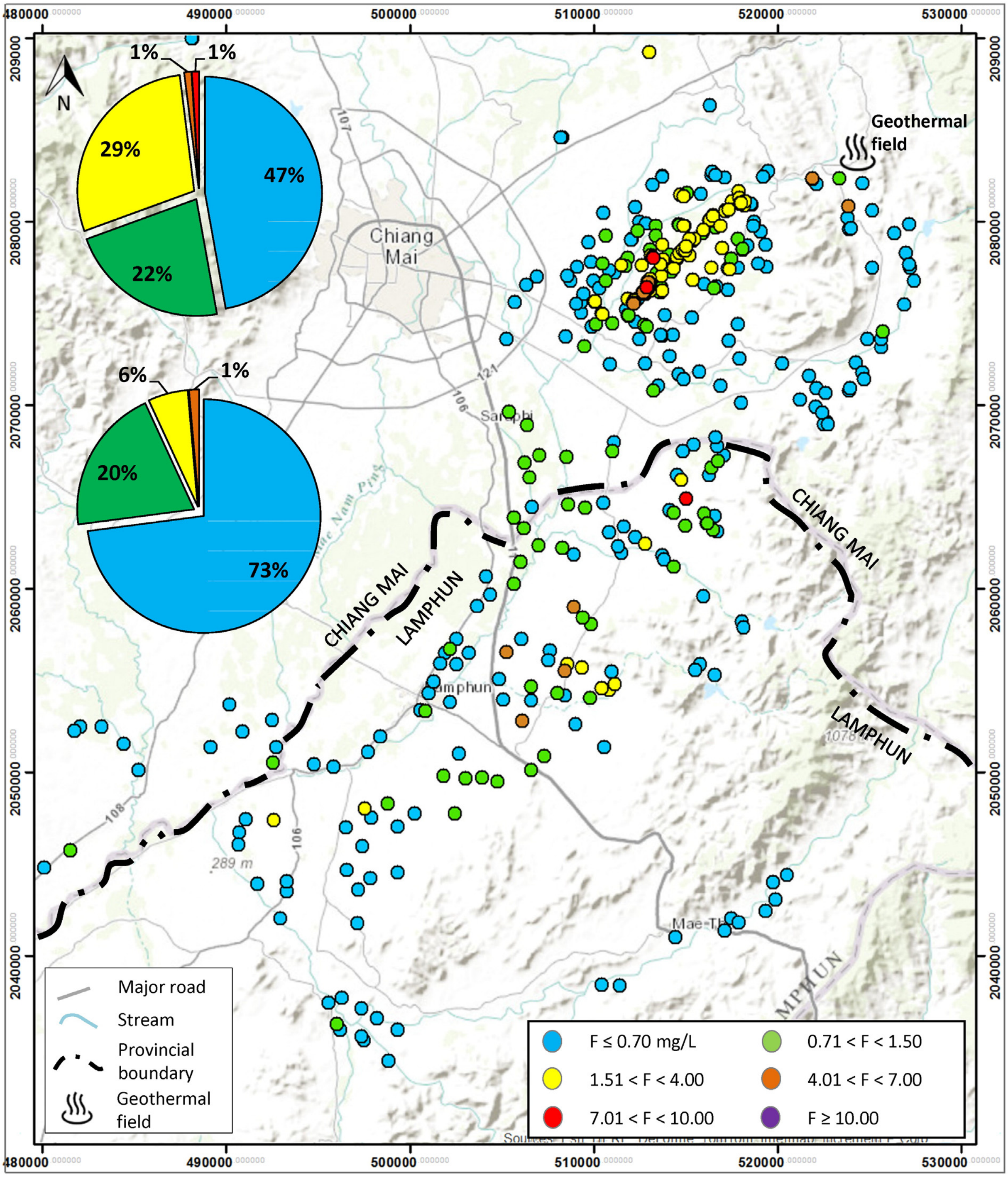

Fig. 5. Locations of sampled shallow wells and corresponding fluoride concentration ranges. Pie charts show statistical summary of fluoride concentration ranges in shallow wells at study sites in Chiang Mai (top) and Lamphun (bottom), respectively.

generally lower; the highest recorded value was 5.63 mg/L. Comparison of fluoride concentrations in the water samples from paired deep and shallow well samples (collected no more than 50 m from each other) showed that deep wells were more influenced by high-fluoride waters than the shallow wells — a result in contrast with that at the Chiang Mai site (Fig. 6B). All deep wells contained higher levels of fluoride than the shallow wells.

A well-defined, curvilinear high-fluoride anomalous zone can be identified on the map showing fluoride concentrations in sampled deep wells (Fig. 4). This zone trends in the northeast-southwest direction, with an eastward arc extending from the villages in the northeast of Ban Thi District to the east of Pa Sang town centre. A 'hot spot' of the high-fluoride zone occurs immediately east of the Lamphun town centre (demarcated with a black dotted circle in Fig. 4). Concentrations of fluoride in many deep wells within this hot-spot are in excess of 10 mg/L. Fluoride concentrations in deep wells appear to decrease gradually along this arcuate zone with distance away from the hot spot. In contrast, concentrations of fluoride decrease sharply in deep

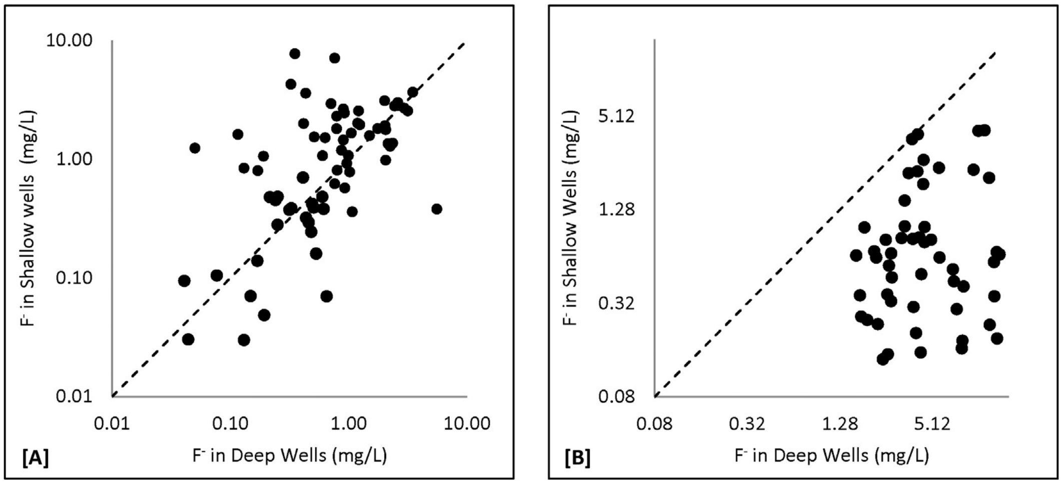

Fig. 6. Comparisons of fluoride concentrations between shallow and deep wells at the high-fluoride anomalous zones in Chiang Mai [A] and Lamphun [B]. All data represent paired samples. The dotted line indicates the 1:1 line. Values falling below this line indicate the fluoride concentrations from the deep well samples are greater than the shallow well samples.

groundwater at areas immediately to the east and west of the high-fluoride anomalous zone.

Only a limited number of shallow-well samples (15/218) contained high concentrations of fluoride with concentrations of more than 1.50 mg/L (Fig. 5). These wells were found sporadically within the curvilinear high-fluoride anomalous zone from Ban Thi District in the northeast to Pa Sang District in the southwest. The concentrations of fluoride in water samples from these shallow wells ranged from 1.81 to 5.63 mg/L.

In a comparison of fluoride concentrations with physicochemical parameters of water (pH, specific electrical conductivity) and important groundwater ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}), only Na^+ in the deep wells was correlated with fluoride (coefficient of determination, $R^2 = 0.70$) (Table 2).

5. Discussion

5.1. Source and transport of fluoride

5.1.1. Chiang Mai Province

The gradual decrease of fluoride concentration from the northeast to the southwest, as depicted in Fig. 3, suggests that the geothermal field is a common origin of fluoride at the study site. Fluoride-enriched geothermal waters are discharged from the hot springs in the area and transported across the study site, creating the linear zone of high-fluoride. Other researchers (e.g., Ratanasthien and Ramingwong, 1982; Ratanasthien et al., 1987; Ratanasthien, 1991) have also reported that the elevated groundwater fluoride levels were due to the intrusion of geothermal waters, but they did not explain the transport processes.

Evidence suggests that the fluoride-enriched waters from the hot springs are a result of deep-circulating, locally-derived and low-fluoride meteoric water that originates from a higher altitude (Praserdvigai, 1986; Ramingwong et al., 1978). This water percolates into deep granitic geothermal reservoirs formed within a complex, high-faulted graben structure where it is heated to 180–200 °C, as estimated by Na–K–Ca geothermometer (Praserdvigai, 1986; Ramingwong et al., 1978; Wood and Singharajwarapan, 2014). The descending water not only encounters a heat source, it also acquires chemical constituents, including fluoride, from the surrounding biotite-bearing plutons (Fig. 7). Fluoride is transferred from rock into water via the dissolution from biotite, which contains fluorine at the OH^- sites of the octahedral sheet (Chae et al., 2007; Nordstrom et al., 1989).

To elaborate this water–rock/mineral interaction, we refer to the work by Chae et al. (2006) who performed laboratory experiments on batch dissolution of granite and biotite at room temperature (25 °C). They found that, for granite, concentrations of fluoride in water doubled in approximately 500 h, while dissolution of biotite resulted in a 100% increase of fluoride in less than 200 h. Additionally, dissolution of fluorine-bearing minerals in rocks was enhanced with increasing temperature or residence time (Chae et al., 2007; Kim and Jeong, 2005; Nordstrom et al., 1989; Saxena and Ahmed, 2003). These findings support our belief that heating in the deep granitic reservoirs at the study site facilitates the release of fluoride.

Chuaviroj (1988) described the presence of a second reservoir that also may yield geothermal fluids. This reservoir is made up of faults, fractures and zones of lateral continuity in sedimentary rocks situated above the primary granitic reservoir. This secondary reservoir likely channels geothermal waters laterally across the study site (Fig. 8). A detailed record of the faults and fractures in these sedimentary rocks were

Table 1
Statistical summary of water quality parameters from deep and shallow wells at the Chiang Mai study area.

Parameter	Deep well samples						Shallow well samples					
	n	Min.	Max.	Median	Mean	S.D.	n	Min.	Max.	Median	Mean	S.D.
pH	175	4	9.85	7.06	7.04	0.78	301	4.45	9.24	7.12	7.11	0.69
SEC (μS/cm)	175	18	3900	488	527	438	301	30	4413	743	887	662
F^- (mg/L)	175	0.01	9.60	0.48	0.92	1.28	301	0.01	8.48	0.75	1.16	1.17
Na^+ (mg/L)	62	0.20	578.14	38.45	52.28	80.98	93	0.20	668.90	38.51	65.36	100.71
K^+ (mg/L)	62	0.20	9.68	0.51	1.52	1.88	93	0.20	210.10	0.95	17.47	43.62
Mg^{2+} (mg/L)	62	1.16	238.30	27.62	33.37	32.68	93	0.20	106.15	31.44	36.12	22.92
Ca^{2+} (mg/L)	62	0.30	138.80	33.20	37.10	25.72	93	0.30	139.70	47.53	52.19	31.87

Note: SEC — specific electrical conductivity; S.D. — standard deviation; Cl^- and SO_4^{2-} were not measured for this site.

Table 2
Statistical summary of water quality parameters from deep and shallow wells at the Lamphun study area.

Parameter	Deep well samples						Shallow well samples					
	n	Min.	Max.	Median	Mean	S.D.	n	Min.	Max.	Median	Mean	S.D.
pH	301	4.81	10.89	7.99	7.93	0.59	218	5.95	9.82	8.02	7.92	0.59
SEC (μS/cm)	301	36	1440	471	480	214	218	43	2854	556	647	463
F^- (mg/L)	301	0.01	14.12	0.76	2.21	3.17	218	0.01	5.63	0.44	0.65	0.76
Na^+ (mg/L)	275	2.16	214.15	55.24	66.90	50.35	108	3.43	688.96	59.05	98.67	123.30
K^+ (mg/L)	275	0.61	33.64	4.24	5.86	4.80	108	0.22	178.87	9.59	20.93	33.15
Mg^{2+} (mg/L)	275	0.20	55.23	11.02	13.20	9.03	108	0.86	58.70	14.64	17.74	12.61
Ca^{2+} (mg/L)	275	1.22	151.00	35.98	41.96	28.76	108	5.20	170.95	48.65	51.92	28.17
Cl^- (mg/L)	275	0.33	177.24	5.89	13.71	21.11	108	0.69	727.01	20.70	51.41	96.34
SO_4^{2-} (mg/L)	275	0.02	4231.00	4.03	26.12	255.05	108	0.02	252.72	25.41	39.28	47.74

Note: SEC — specific electrical conductivity; S.D. — standard deviation.

not available to us and therefore, we were unable to elaborate more pertaining to this secondary reservoir and its association with the high-fluoride zone at the Chiang Mai site.

Lateral flow of geothermal water also occurs in the alluvial and terrace deposits that overlay these sedimentary rocks as described above. In this layer, the flow direction of geothermal fluids follows the local groundwater flow pattern and therefore results in the intrusion of fluoride-enriched waters, especially in shallow wells down-gradient of the hot springs (Fig. 8).

To understand how the hydrological controls of the shallow aquifers affect fluoride distribution, we compared the zone of high-fluoride to a piezometric contour map of the Ping River Basin based on the work of Intrasutra (1983) (Fig. 9). The study area is located in the northernmost section of the basin where excessive pumping of groundwater for irrigation, an anthropogenic process, has lowered the water table (Intrasutra, 1983). The extent of the high-fluoride endemic areas aligns with the hydrogeological gradient of the groundwater. Fluoride is transported from the source (the geothermal field) where the piezometric head is the highest to the end of the high-fluoride anomalous zone where the piezometric head is the lowest. The shallow wells we sampled with the highest levels of fluoride ($F^- > 4$ mg/L) were located at the end of the zone where the piezometric head was lowest. This finding of an accumulation of fluoride in an area where the water table is lowest is based on three groundwater surveys conducted between 1981 and 1982. As we were unable to acquire more survey data, there is some uncertainty in this interpretation.

To further explain the spatial distribution of fluoride at the site, we recognise that geothermal fluid flows upward through narrow fissures, emerging at the surface as hot springs (Fig. 8). Above ground, fluoride-enriched fluids move across the study area in the south-westerly direction, according to the flow of the local streams which aligns with the linear zone of high-fluoride as observed. The general flow direction of these streams is similar to the groundwater flow direction. The gradual decrease in concentrations of fluoride with increased distance from the geothermal field is probably the result of dilution as stream water originating from the fluoride source (geothermal field) mixes with other surface waters with low fluoride concentrations. Some artificial enhancement of surface water may take place following the extraction of fluoride-rich groundwater for irrigation, discarding of fluoride-rich wastewater from reverse osmosis filtration facilities, and diversion within the extensive canal system in the area.

5.1.2. Lamphun Province

In contrast with the study site at Chiang Mai Province, the deeper wells of the study site at Lamphun Province had higher levels of fluoride than shallow wells. At this site, different factors control the transport

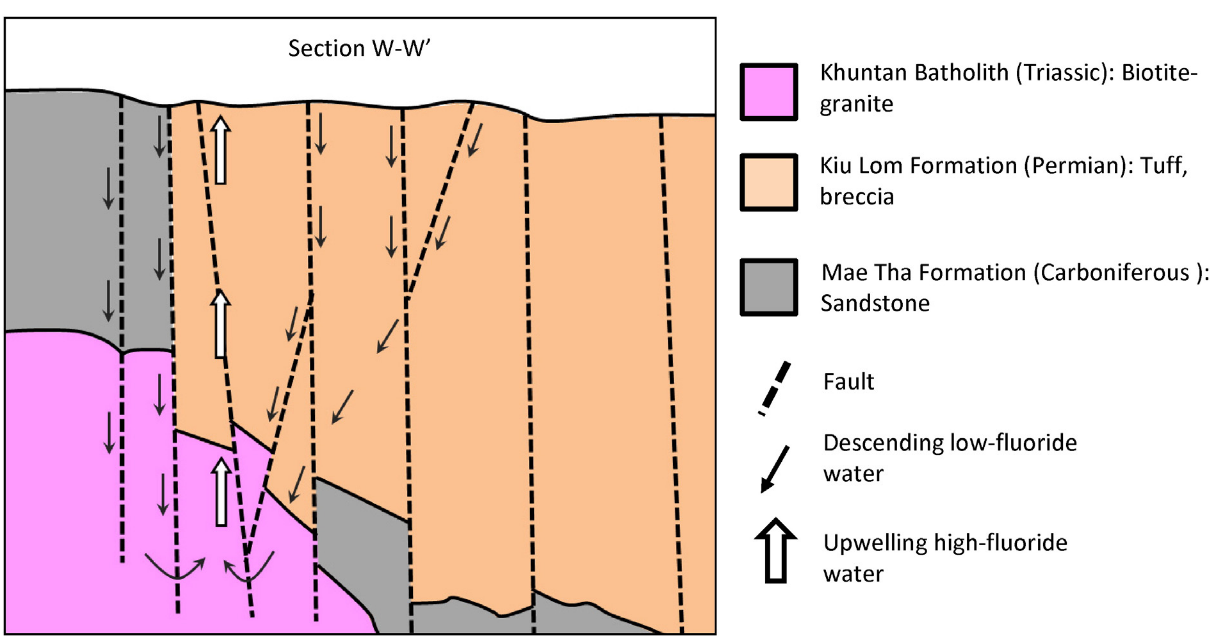

Fig. 7. Model cross-section of geologic stratigraphy (after Praserdvigai, 1986) at the geothermal field and the genesis of high-fluoride geothermal water — Section W–W′ from Fig. 2.

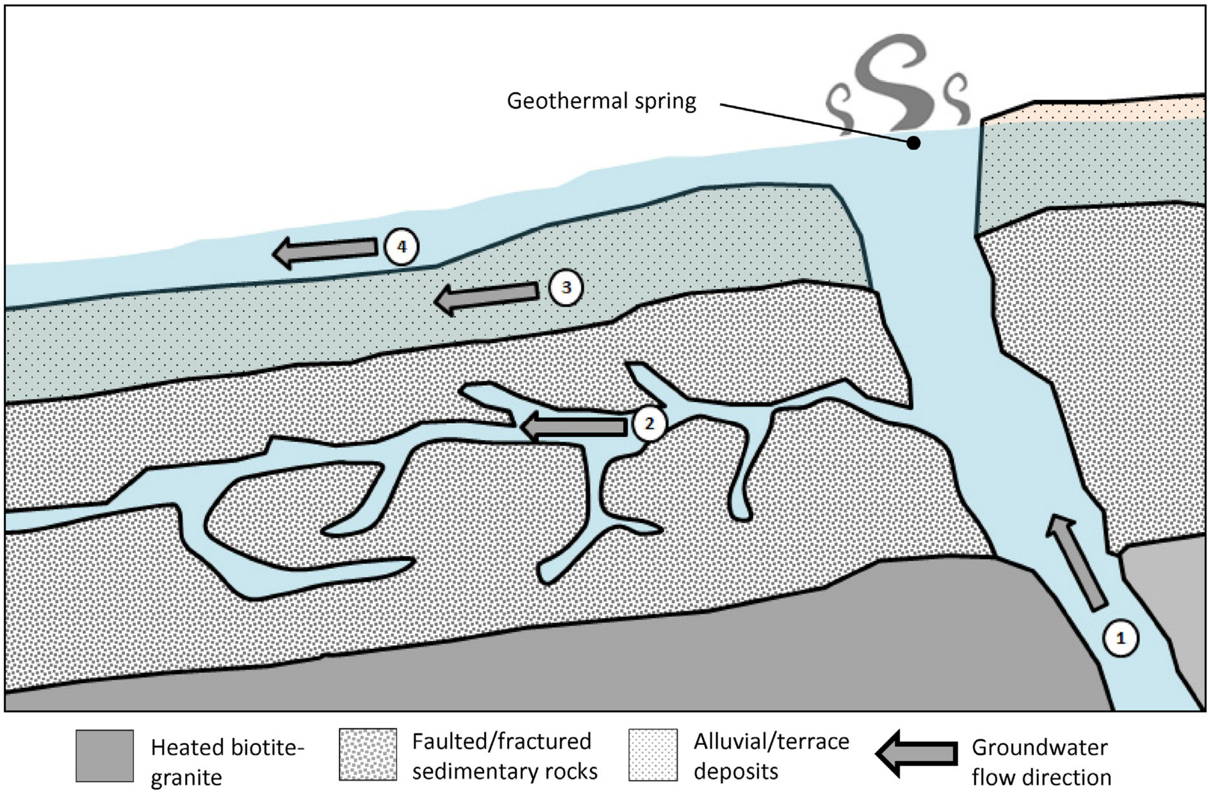

Fig. 8. Model longitudinal section of the Chiang Mai study area showing the multiple modes of the transport of fluoride-enriched geothermal waters from the source. [1] Upwelling of geothermal fluids with high concentration of fluoride acquired from the dissolution of biotite in the primary, heated granitic-reservoirs made up of high angular faults. [2] Secondary reservoirs formed by faulting and fracturing in the sedimentary rocks facilitate deep lateral transport. [3] Lateral transport through highly-permeable alluvial and terrace deposits following the groundwater flow direction. [4] Geothermal waters emerge to the surface and distributed across the study area by local streams and rivers.

and distribution of fluoride in the groundwater. Shallow wells with high fluoride content generally coincide with the areas where the highest concentrations of fluoride are also found in deep groundwater, implying a connection between the two. This connection may be mixing of normally low-fluoride shallow groundwater during deep groundwater abstraction of deep fluoride-enriched water. Suvagondha and Jitapunkul (1982) noted a layer of impermeable clay at an average depth of 60 m between two principal aquifers in the study area. This impermeable layer is an aquitard that prevents the mixing of groundwater between the two aquifers. However, the construction of deep wells potentially breaches the aquitard, creating a portal allowing the intrusion of deep, fluoride-enriched groundwater into the shallow aquifer. In addition, fluoride from deep sources may also enter the shallow groundwater system via the screens of borewells (Fig. 10).

The curvilinear and eastward-trending, convex zone of high-fluoride concentrations in deep wells aligns (in direction and shape) with the conspicuous Mae Tha fault to the east of the Ping River Basin, as well as other minor faults in the area (Department of Mineral Resources, 1995; Fig. 9). This alignment supports the existence of a previously unmapped, blind fault buried beneath the basin fill, as well as its likely association with a geogenic source of fluoride related to the faulted zone. A gravity survey of the Ping River Basin by Wattananikorn et al. (1995) supports the existence of this fault. The gravity anomaly map showed a belt of steep-to-moderate gravity gradients, reflecting boundary fault zones, on the east side of the basin near the eastern mountain range (Wattananikorn et al., 1995). The location of this 'inferred' fault coincides with the high-fluoride zone found in this study (Fig. 11).

Kim and Jeong (2005) concluded a similar fault-fluoride association in the south-eastern part of the Korean peninsula where 10% of the surveyed public water supply wells contain fluoride exceeding the safe drinking water limit of 1.50 mg/L. They described two environmental processes that have contributed to the occurrence of high-fluoride distributed along major faults: (i) the weathering (dissolution) of fluoride-bearing rocks in faults; and (ii) the upward flowing of deep fluoride-enriched groundwater along the fault zone. We believe both of these processes are crucial in the genesis and transport of fluoride-enriched waters in the geothermal field at the Chiang Mai site. The same processes are therefore probably applicable to the Lamphun site, with the fluoride-bearing biotite-granite intrusion in the Palaeozoic rocks as the plausible source.

An alternative explanation of the occurrence of the high fluoride levels in Lamphun is that Ca^{2+} ions are removed from the groundwater by replacing Na^{+} ions from clay minerals with high cationic exchange capacities, thereby preventing the precipitation of the highly insoluble calcium fluorite (CaF_2), resulting in the accumulation of F^{-} in the groundwater (Asnachinda, 1992). While this process is plausible, it is unlikely to be the dominant control because it can neither account for the discernible differences of fluoride concentrations between deep (high fluoride) and shallow (low fluoride) groundwater, nor the curvilinear shape of the high-fluoride anomalous zone. Moreover, we did not find a relationship between Ca^{2+} and F^{-} from the water samples of both deep and shallow wells.

We did, however, observed a positive correlation between Na^{+} and F^{-} in water samples from the deep wells at the study area in Lamphun. The source of the Na^{+} may originate from the granitic rocks from which the F^{-} was derived. Chae et al. (2006) demonstrated in their batch granite dissolution experiments a simultaneous increase of Na^{+} and F^{-} concentrations due to the progressive dissolution of granite.

Finally, it is plausible that the occurrence of the fluoride 'hot spot' in Lamphun may be caused by a similar human-influenced hydrogeological factor that influenced the extent of the high-fluoride anomalous zone at the Chiang Mai site. In addition to the extraction

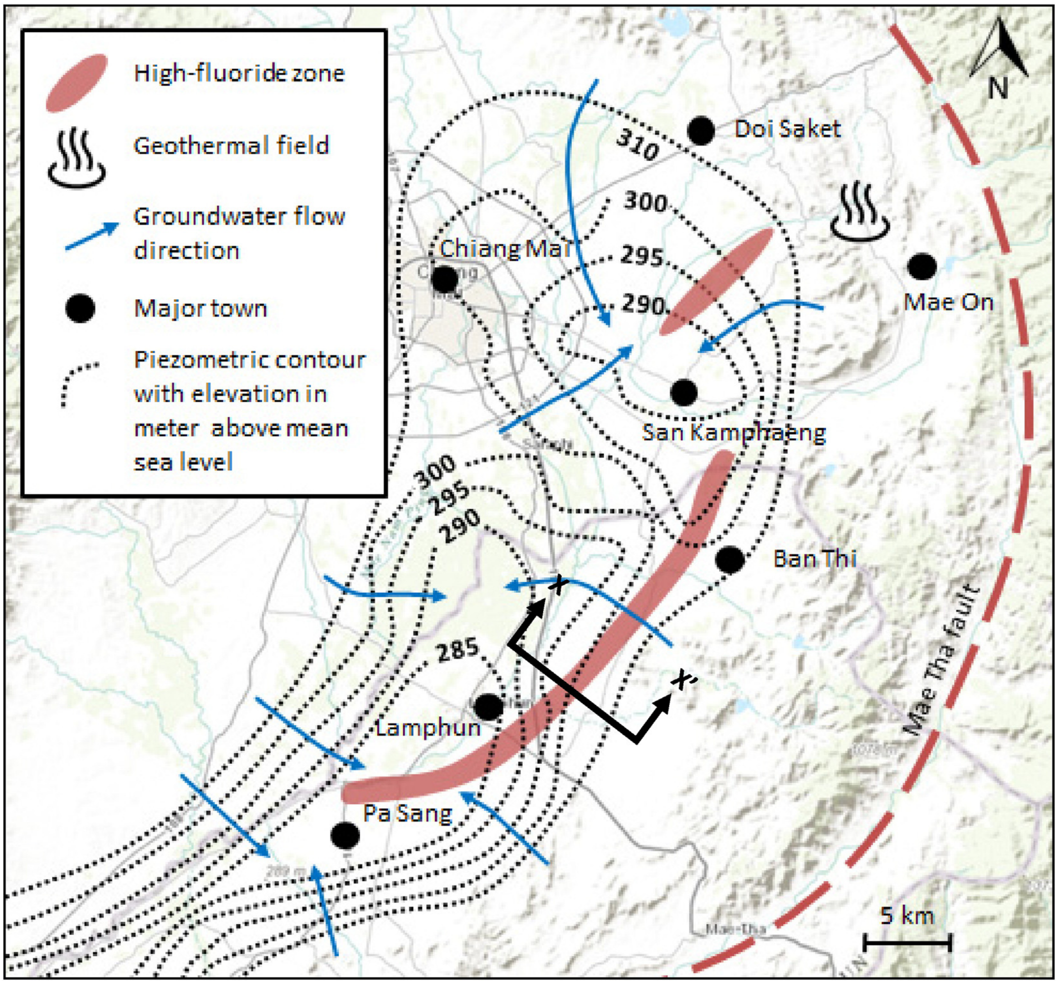

Fig. 9. Piezometric contour map (after Intrasutra, 1983) showing groundwater flow in the Ping River Basin and the high-fluoride anomalous zones in Chiang Mai and Lamphun. The Mae Tha fault which has a similar alignment with the high-fluoride anomalous zone of Lamphun is also shown. Section X–X′ is detailed in Fig. 10.

for agriculture, a part of the hotspot also coincided with the Lamphun Industrial Estate where heavy extraction of groundwater also occurs (Anuwongcharoen, 1989). The extraction of groundwater may have also changed the hydraulic gradient of local groundwater thereby creating a local depression in the groundwater level at the hotspot where fluoride can potentially accumulate (Fig. 10). Unfortunately, we do not have current survey data of the piezometric surface to verify this assertion.

5.2. Risk of fluorosis

In recent years, many rural villagers have been informed of the risks of fluorosis from drinking high-fluoride water through health education programmes in schools for children, as well as other outreach programmes conducted by government health workers. Most villagers have responded by using bottled water instead of water piped from village water supplies (but also in response to unclean water from other sources such as pathogens from faecal sources and agrochemicals such as pesticides). Yet, the risk of fluorosis persists. Takeda and Takizawa (2008) found that many of the subjects from their study in the Lamphun Province still had high levels of fluoride in their urine despite drinking fluoride-free bottled water. They attributed this to the ingestion of rice cooked with high-fluoride water in the local piped-water supply. In many parts of Thailand, including Northern Thailand, glutinous rice or 'sticky rice' (*Oryza sativa var. gluotinosa*) is the main staple food. During preparation, this rice is washed several times and then soaked in water overnight before steamed. In laboratory experiments, Takeda and Takizawa (2008) demonstrated that fluoride content in rice was proportional to the concentration of fluoride in water used for soaking, as well as the duration of the soaking.

Traditionally, the rice fields in Northern Thailand were rain-fed, and therefore, harvest in the past was only once per year. More recently, farmers have used groundwater for irrigation to produce a second growing season. We observed an abundance of irrigation wells in rice fields and farms in the high-fluoride anomalous zones in both Chiang Mai and Lamphun. We assume, based on laboratory experiments, the use of high-fluoride water for irrigation contributes to an increase in fluoride intake in the area. In one example, Jha et al. (2013) conducted a pot culture experiment to evaluate the bioaccumulation of fluoride in rice using irrigation water with different levels of fluoride concentration. Fluoride content in rice grains increased by 41%, 59% and 96% when irrigated with water containing fluoride concentrations of 2, 4 and 8 mg/L, respectively, in comparison with rice irrigated with fluoride-free water.

5.3. Drinking-water management implications

Numerous low-pressure, reverse osmosis (RO) membrane filtration water treatment plants have been built in Thailand to provide clean drinking water. These plants are either operated by the communities

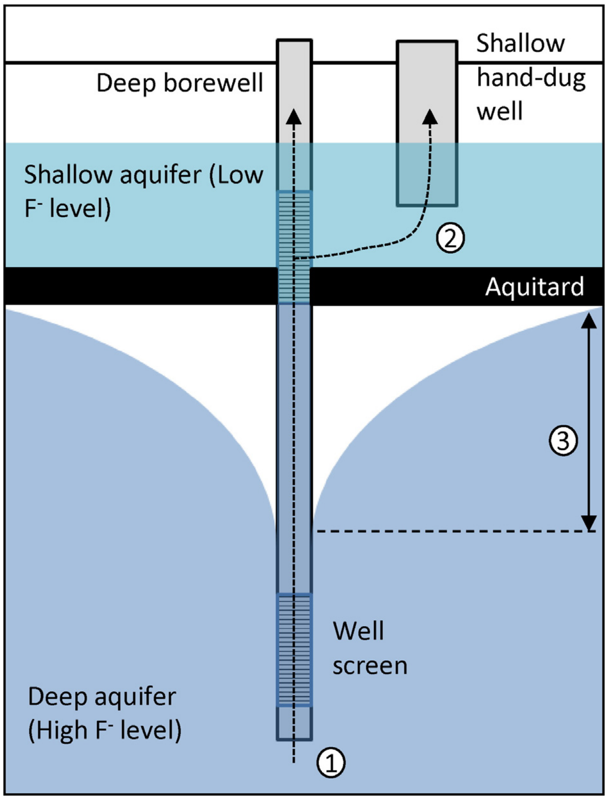

Fig. 10. Cross sectional profile of the Quaternary alluvium deposits at the Lamphun site. [1] Abstraction of high-fluoride water by deep wells. [2] Intrusion of high-fluoride water from deep to shallow aquifer. [3] Well drawdown: intensive groundwater extraction may have caused a depression in water table, thus creating the high-fluoride hotspot as observed at the Lamphun site.

themselves or by private companies. The community-managed public plants produce between 1 to 5 m^3 of drinking-water per day, while the private plants typically produce up to 50 m^3 per day (Matsui et al., 2006). Reverse osmosis membrane filtration is often preferred over other treatments because of its ease of operation and relatively lower cost of drinking-water production. More importantly, especially for the sites in this study, this method of drinking-water treatment is

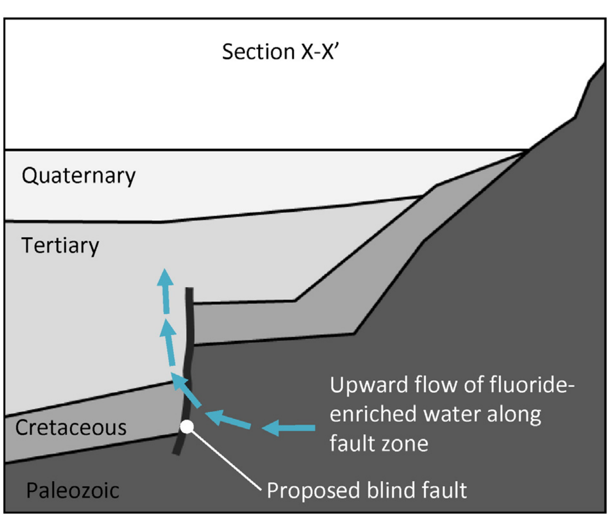

Fig. 11. Stratigraphic section of the Ping River Basin at the high-fluoride anomalous zone in Lamphun — Section X–X′ from Fig. 8 (after Wattananikorn et al., 1995).

attractive because it efficiently removes fluoride, even when present in high concentrations.

There are however flaws with the applicability of RO membrane filtration for drinking-water production. In their study in Lamphun Province, Matsui et al. (2006) noted that despite investments made for the construction of these drinking-water treatment facilities, one of the nine plants studied was in not operation due to the poor and unfavourable quality of the local raw water for treatment. In particular, the polyamide composite membranes used in RO membrane filtration process were prone to fouling from calcium carbonate ($CaCO_3$) precipitation that occurs in the raw alkaline groundwater at their study site.

The average water recovery rate for these plants is approximately 40% (Matsui et al., 2006); therefore, less than half of the groundwater abstracted is converted into drinking water that can be consumed safely. The remainder is wastewater. The inefficiency of this process is somewhat unsustainable in terms of local water resource management, particularly if water is extracted from confined aquifers where recharge rate is low. Monitoring wells have already shown significant lowering of groundwater of up to 1.0–1.5 m per year (Intrasutra, 1983; Margane and Tatong, 1999), indicating the recharge rate is much lower than the rate of groundwater abstraction for a variety of agricultural, industrial, and domestic purposes.

As the chemical characteristics of the reject-brine from RO filtration reflect the feed water source (Squire, 2000), as much as 6 L of wastewater, highly enriched in fluoride, is generated for every 4 L of potable water produced. There are multiple options for the proper disposal of the reject-brine, including direct discharge to sewer systems, deep-well injection, and evaporation ponds (Ahmed et al., 2001; Squire et al., 1996; Squire, 2000). However, none of these options are currently available to the rural communities we visited. The wastewater is typically released on-site untreated. Developing safe waste-management infrastructure is costly and requires technical expertise for operation and maintenance — luxuries many rural communities do not possess. While impacts of the disposal of reject-brine water directly into the environment (e.g. streams, groundwater) is not known, it contributes to the (re)distribution of fluoride-rich water throughout the study area. In doing so, it likely increases the concentrations of fluoride, potentially to hazardous levels, in some water bodies that otherwise might be safe drinking-water resources.

6. Conclusison

Our analysis of more than a thousand surface and sub-surface water sources shows that high levels of fluoride in confined areas of Chiang Mai and Lamphun are not solely functions of distance from a nearby geothermal field. Multiple modes of transport of sub-surface and surface water, as well as water interaction with geological features, create/maintain these anomalous zones. In addition, anthropogenic activities influence the distribution of fluoride in surface waters in the area.

This complexity in fluoride genesis and transport creates a challenge for managing water resources for safe consumption in affected areas. As we have demonstrated, water at different depths may have different, unpredictable levels of fluoride. The simple assumption that deep water is safer than shallow water is not valid. This is demonstrated in this study where we found that more shallow wells in the Chiang Mai zone had higher concentrations of fluoride than deep wells; the opposite relationship was found in the Lamphun zone. Regardless of location, groundwater at any depth should always be tested before the construction of wells to provide water for domestic use.

Existing wells abstracting from high-fluoride aquifers need not be abandoned if the water is otherwise uncontaminated. Reverse osmosis filtration is a viable treatment to remove fluoride but it is expensive to install/maintain and it generates substantial wastewater that requires proper disposal. A simple solution to managing fluoride-rich water for domestic use is dilution with water of low fluoride concentration.

Dilution could be achieved by mixing fluoride-rich water with groundwater abstracted from depths with low fluoride levels — although constant monitoring would be needed to ensure the mixture remained below the recognised risk threshold.

Finally, because the risks of fluorosis still exists in communities in zones of high-fluoride, particularly in areas where insufficient resources hinder the ability to obtain sufficiently treated water for drinking and food preparation, continuing (re)education is needed to inform community members of the risk of long-term consumption of fluoride in local water resources.

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