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SUSTAINABLE DEVELOPMENT OF WATER RESOURCES, WATER SUPPLY AND ENVIRONMENTAL SANITATION

Application of Nanofiltration Processes to Fluoride Removal From Groundwaters in the Chiang Mai Basin

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The highly concentrated fluoride in groundwater has been observed in the confined aquifers of the alluvial sediments in the Chiang Mai Basin. Nanofiltration process was applied to the control of fluoride exposure to the local residents, who have suffered from serious dental and osteal fluorosis.

The membrane plants used polyamide nanofilters, which were found to have different fluoride removal rates depending on pH of feed waters. Although fluoride removal rates were high at neutral to basic pH, calcium carbonate scale on the membrane surface was estimated to be the major problem in membrane fouling. Optimum combination of pretreatment in the membrane plant was evaluated through the investigation on the groundwater quality and the operational conditions.

Introduction

NEARLY a half of the world's population use groundwater sources for drinking water and for other uses (IRC, 1998). It was reported on the World Water Day in 1998 that almost 80 percent of the world's rural population depends on groundwater as a sole source of safe drinking water. Natural occurrence of arsenic and fluoride caused by soil desorption or rock weathering is widely known as a common problem of groundwater use throughout the world. Fluoride is a common element in groundwater, but high concentration of fluoride in drinking water has generated health problems in Asian and African countries. The United Nations Environmental Programme (UNEP, 2002) estimated that the total number of people at risk of fluorosis would be tens of millions even by a modest estimation. The United Nations Children's Fund (UNICEF) highlighted the problems of fluoride in the rift valley areas in Africa, in India and in China. Ingestion of excess fluoride led to severe fluorosis mostly through drinking water. Fluoride affects teeth and bones, as well as many organs in human body and disrupts human body's critical biological functions. World Health Organization (WHO, 2004) suggested an adverse effect on tooth enamel at fluoride concentration in drinking water to be between 0.9 and 1.2 mg/L, and the risk of skeletal fluorosis will increase with total fluoride intakes above 6mg/day. Fluoride exposure through drinking water is associated with the temperature because people living in high temperature areas consume more drinking water than those living in cold climate. The Food and Drug Administration (FDA, 2003) in the United States stipulated fluoride concentration in bottled water based

on the annual average of maximum daily air temperatures at the location where the bottled water is consumed. Health hazards of fluoride are more frequent and severe in the tropical region than in the cold region. WHO (2004) suggested that coagulation, activated alumina and membrane filtration might eliminate fluoride from groundwater. However, coagulation and adsorption treatment technologies are not effective to eliminate fluoride below the WHO guideline value of 1.5 mg/L. Hence rain water harvesting and developing alternative water sources are the only choice to get clean and safe water in some regions.

The Chiang Mai Basin is located in northern Thailand. The Ring River runs through the basin to separate Lamphun Province and Chiang Mai Province. Both surface and ground water resources, mainly in the alluvial flat, are relatively abundant in this basin. However, according to Asnachida (1992), the surface water has been contaminated by pesticides and pathogenic bacteria, while the water demand has expanded with the growth of population and industries. Hydrogeological investigations of the Chiang Mai Basin were initially conducted by the Department of Mineral Resource in 1964 to help developing groundwater resources. Since then groundwater in the entire Chiang Mai Basin has been extensively exploited. Due to low awareness of the risks of fluoride, many local people were exposed to fluoride in groundwater, which caused serious endemic fluorosis. When the health effect of fluoride was made public, local and central governments prompted small-scale membrane filtration plants as community water systems (Matsui *et al.*, 2004). These membrane plants are owned and operated by

public water utilities or private sector. Although the groundwater quality varies from place to place, those membrane plants consisted of the same pre-treatment process and membrane module specifications. In our preliminary study on 9 constructed membrane plants, one plant pulled out of operation because of an unsatisfactory water quality in the treated water. In general, fluoride in groundwater tends to co-exist with calcium and bicarbonate. Membrane filtration processes require an appropriate pre-treatment to reduce these components in order to prevent calcium carbonate scaling on the membrane surface. Polyamide composite membranes are the most popular nanofiltration membranes, which carry negative electric charge on the surface in aqueous phase. The membrane plants in Lamphun also use polyamide membranes. The charge effect of nanofiltration membranes plays an important role in the separation of ions in the solution; hence it is possible to reject ions at relatively low pressure than the pressure with a reverse osmosis. Tay *et al.* (2002) developed an aqueous model on the effects of pH on ionization of membranes charged groups, which determined the membrane surface charge. Choi *et al.* (2001) indicated rejection of anionic monovalent ions such as fluoride was effected by the surface charge. Matsui *et al.* (2006) demonstrated that the fluoride rejection by the polyamide composite membrane is closely related with surface charge density. It was shown that at weakly acidic pH, the membrane surface approached to neutral charge, and fluoride removal rate decreased.

This paper focuses on the groundwater quality analysis to elucidate enrichment of fluoride within groundwater, and the evaluation of both membrane and pretreatment processes for the fluoride removal. Efficiency of pretreatment proc-

esses was evaluated based on iron, manganese, dissolved organic carbon and calcium removal. Water samples were taken from groundwater, as well as each process of the membrane plants.

Materials and Methods

Site Description

The study area was on the left bank of the Ping River in the Chiang Mai Basin, where the fluoride concentrations in groundwater are high according to the reports of the local governments and Department of Mineral Resources (2000).

The groundwater samples were collected from a total of 133 existing wells as shown in Figure 1. The site selection took into consideration of well depth, access road and population distribution. In this study, groundwater of unconfined aquifer and infiltrated water (shallow and dug wells) were excluded from sampling to avoid the effects of dilution by the Ping River and by other tributaries. Many of the residents live on the flood plain at an altitude of less than 280m above the mean sea level (MSL). There are also densely populated areas in the alluvial plain of 280~330 m above MSL, where they are dependent on groundwater in confined aquifer of 100~200 m in depth. Groundwater resources in the Quaternary sediments of the plains provide waters for domestic use, irrigation and other usage. The membrane plants are located in this area. The hilly terrace at 330~400 m above MSL has scattered population. Water samples were collected at orchards where groundwater was pumped up from the confined aquifer at a depth of 80~150 m. There are old terraces or the young terraces colluvial sediments from the late Tertiary Period.

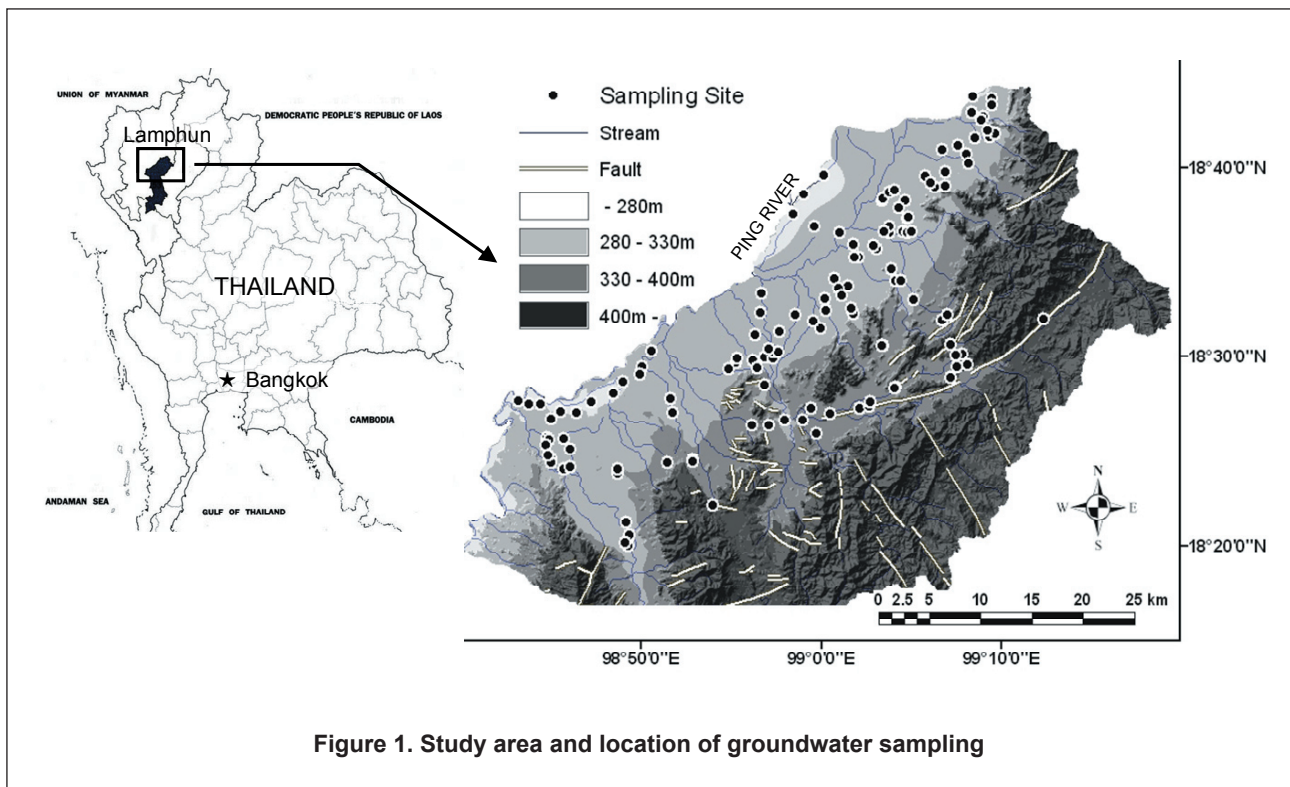


Figure 1. Study area and location of groundwater sampling

Laterite outcrops were frequently observed in the hilly terrace. Alluvial plains, terrace and mountainous area more than 330m above MSL formed several faults along the valleys. Some water samples included the groundwater of the fissure waters in the faults or crush of bedrock.

Water Quality Analysis

The water quality parameters analyzed on the spot were temperature, pH, electric conductivity (EC) and oxidation-reduction potential. Ferrous iron (Fe²⁺) and ammonium ion (NH₄⁺) were analysed with a portable spectrophotometer (Hach, DR-890). Alkalinity was measured by sulfuric acid titration to the end point of pH 4.5 using methyl orange indicator. The oxidation-reduction potential (ORP) values were converted into the electron activities pe. The bicarbonate concentration was calculated from alkalinity and pH. The samples for the analysis of cationic ions (Na⁺, Mg²⁺, K⁺, Ca²⁺, T-Fe, T-Mn) were filtrated through 0.22 μm cellulose acetate membranes and then into plastic bottles and were acidified to pH below 2 by the nitric acid (1%v/v). Groundwater samples for the anionic ions (F⁻, Cl⁻, Br⁻, NO₃⁻, NO₂⁻, PO₄³⁻, SO₄²⁻) and silicate (SiO₂) analyses were handled with the same procedure as the cation samples except for acidification. These water samples were brought back to the University of Tokyo and subsequently underwent through the laboratory measurements. Inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 3000, Perkin Elmer) was used to determine the cationic ions and SiO₂ concentrations. Anionic ions were analyzed by Ion chromatography (IC, 761 Contact IC, Metrohm Ion Analysis). Geographical, geological and land use data were obtained from Geo-Infomatics and Space Technology Centre, Northern Region (2004) at Chiang Mai University, and were processed by ArcGIS (ver.9.0). The water quality data were calculated for chemical species and solution equilibrium for each element with WATEQ4F (USGS, 2001).

Membrane Plant Overview

All of the eight membrane plants investigated in this study had the same treatment process though their production capacities varied. The schematic flow diagram of the typical membrane plant is illustrated in Figure 2. Groundwater was

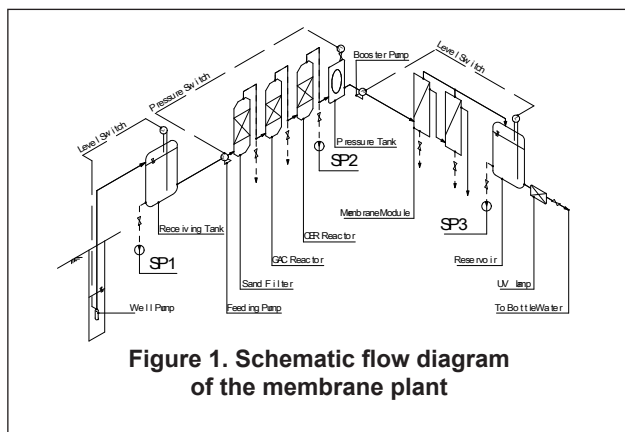


Figure 1. Schematic flow diagram of the membrane plant

pumped up to the Receiving Tank, which is connected to the pretreatment vessels and further to nanofiltration membranes conducted through the pre-treatment facilities. The pre-treatment process consisted of a sand filtration tank (Sand Filter) for iron and manganese removal was followed by a granular activated carbon adsorption tank (GAC Reactor) for DOC removal and then to the ion exchange reactor filled with strong acid cation exchange resin (CER Reactor) for Ca²⁺ removal. The groundwater pump, feeding pump to the pre-treatment and booster pump to the membrane module are controlled by the level switch in the receiving tank, the pressure switch in the pressure tank and level switch in the reservoir, respectively. Samples for water quality analysis were taken at 3 points, i.e., SP1~SP3, as indicated in the Figure 2. Raw water quality, pre-treated water quality and membrane permeate quality were estimated from analytical results of SP1, SP2 and SP3, respectively. The specifications and operational conditions for the membrane plants are summarized in Table1.

Results and Discussion

Fluoride distribution and raw water quality of the membrane plants

8 membrane plants, denoted as A~H, are shown in Figure 3. Fluoride distribution determined by analysis of 133 groundwater samples is also shown in Figure 3. The Ministry of Public Health in Thailand sets the fluoride standard for drinking water as 0.7mg/L (tolerable 1.0mg/L). The WHO's guideline value for drinking water is 1.5mg/L. Fluoride concentrations are classified into 3 levels: namely, low level of less than 0.7mg/L, moderate level of 0.7 to 1.5mg/L and high level of more than 1.5mg/L. As a result, 47 out of 133 wells were classified to be high-level fluoride contamination where the highest reached 16.1mg/L. Highly contaminated fluoride wells distinguishably clustered in the plains where aquifers consisted of alluvial deposits.

Table 1. Capacity of the membrane plants and their specifications

Run	Water Product Rate	Note	Specification and operational condition
Public Plant	1~5 (m ³ /day)	Delivery to 150~200 households Supplied by bottle 1L or 20L capacity	Polyamide composite NaCl retention 99.4% @ 2000mg/L, 1MPa, pH7~8 Module diameter: 4 or 8 inches Operational pressure:
Private Plant	~50 Peak: 100 (m ³ /day)	Seasonal fluctuating demand and the production Supplied by bottle 1L or 20L capacity	0.8~1.5 Mpa Permeate flux: 1m ³ /m ² /day Recovery less than 30% per one bank module, 40~50% per two banks Anti-scalant: citric acid for calcium carbonate scaling, sodium hydrosulfite for iron fouling

There are percentile (5, 50, 95%) values for all 133 groundwater samples, 86 samples of low to moderate fluoride and 47 samples of high fluoride are shown in Table 2, with raw water quality of the 8 membrane plants (A~H).

Groundwater in Lamphun had high water temperature above 25 °C and low DOC concentration of less than 1.5 mg/L, which has no correlation with fluoride concentrations. High level fluoride was contained in groundwater with neutral to weak alkaline pH, higher EC and alkalinity, and lower calcium concentrations than groundwater with low and moderate fluoride level. High T-Fe and T-Mn concentrations were detected in the groundwater of laterite outcrops on the terrace, while these concentrations were low in the alluvial plains where high fluoride was contained. Raw water of plant B, C, D, F, H contained high levels of fluoride and plant A, E, G had low to moderate fluoride levels, which indicated that plant A, E, G were not necessary to be constructed.

Identification of the high fluoride area

As in the cases of fluoride contamination in semi-arid region, Jacks *et al.* (2005) and Travi *et al.* (2001) exemplified that the contamination proceeding in groundwater was associated with rock weathering and evapotranspiration in India and Ethiopia respectively. Carrillo-Rivera *et al.* (2002) and Kundu *et al.* (2001) reported that fluoride in groundwater had derived from the intrusion of fluoride rich geothermal water. Kim *et al.* (2005) investigated the high fluoride occurrence along the faults bisecting granite terrains and suggested fluoride concentration of groundwater was enriched by the interaction with granitic rocks. Groundwater of Lamphun had a distinct location, where fluoride in groundwater was enriched in aquifers of alluvial plains. Mild temperature and rainfall of the Monsoon Asia are another characteristics of the groundwater in Lumphun.

Figure 4 shows the fluoride concentrations of Lamphun groundwater related with the metals of the alkaline earth ions ($\text{Ca}^{2+} + \text{Mg}^{2+}$) and with alkali metal ions ($\text{Na}^+ + \text{K}^+$).

Fluoride had a positive correlation with ($\text{Na}^+ + \text{K}^+$) and a negative correlation with ($\text{Ca}^{2+} + \text{Mg}^{2+}$). According to the literature (Asnachida, 1992), clay minerals with high cationic exchange capacity were scattered in the Ping River Basin including the studied alluvial plains. Groundwater, the one dominated by Na^+ , estimated to be originated from the cationic exchange reactions. There aqueous Ca^{2+} have been replaced by specific Na^+ from one of these clay minerals.

As a result of eliminating Ca^{2+} ions in the groundwater, fluoride ions were concentrated in the aqueous condition that prevented a calcium fluorite (CaF_2) from precipitation. Saturation Index (*SI*) of the groundwater for CaF_2 is shown in Figure 5. The *SI* value was calculated by logarithm of the value derived from product between fluoride and Ca^{2+} concentrations in groundwater divided by the solubility product. Temperature and pH of each sample, as shown by the ranges in Table 2, were used to calculate *SI* value. In theory, *SI* value indicates sub-saturation to be in negative, saturation to be in zero and super saturation to be in positive. Practically, saturation was estimated by *SI* value within the range from -0.37 to +0.37 ($-0.37 < SI < +0.37$), considering an ambiguity of the thermodynamic constant.

As shown in Figure 5, CaF_2 was saturated by more than 5 mg/L of fluoride concentration in groundwater, and the fluoride concentrations were controlled with Ca^{2+} concentration. It was deduced that the cationic exchange reaction replaced Ca^{2+} by Na^+ should dominate the fluoride solubility in the groundwater.

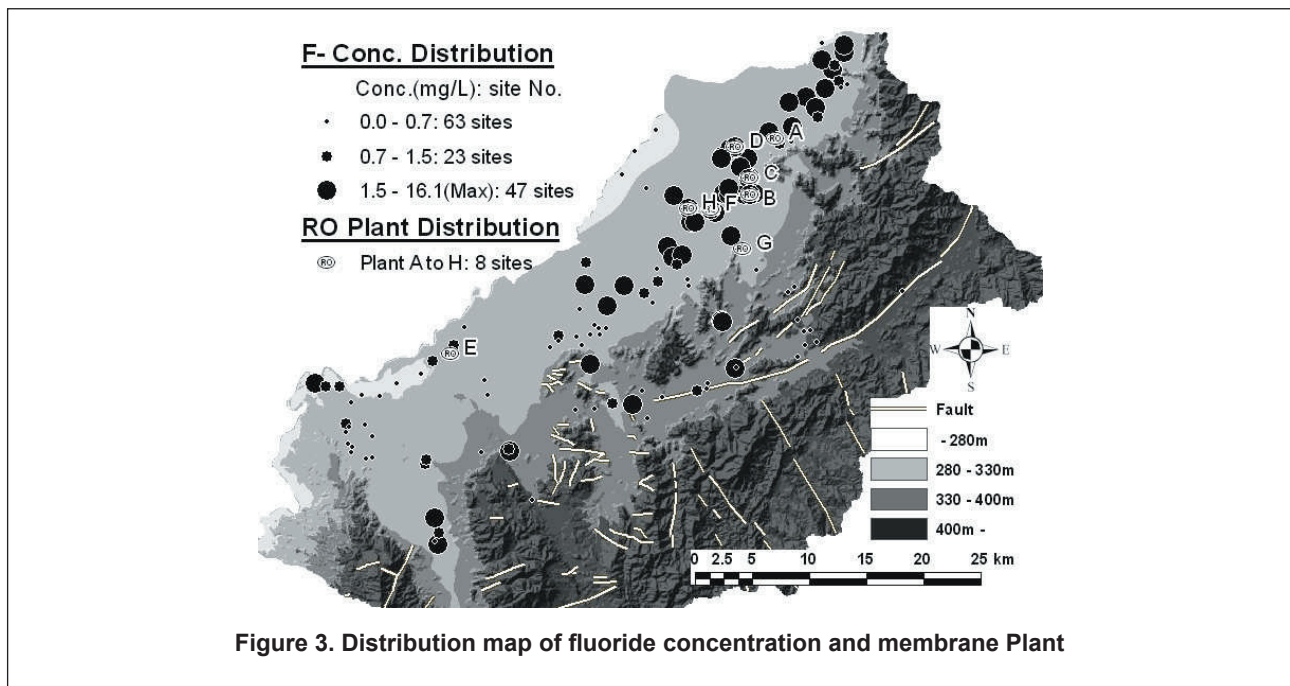


Figure 3. Distribution map of fluoride concentration and membrane Plant

Water property of high fluoride groundwater

The groundwater with high fluoride tended to contain high alkalinity dominated with HCO_3^- . Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are the major carbonate minerals, but they do not yield SiO_2 . According to the literature (Hounslow, 1995), the weathering of carbonate minerals dominates groundwater property if the ratio HCO_3^- (mM) to SiO_2 (mM) concentrations in the groundwater ($\text{HCO}_3^-/\text{SiO}_2$) is above 10. If the ratio is less than 5, the weathering of silicate minerals should be a dominant process. The $\text{HCO}_3^-/\text{SiO}_2$ is shown in Figure 6. as a function of Fluoride concentration. 87% of groundwater with high fluoride concentration were higher than 10 in $\text{HCO}_3^-/\text{SiO}_2$.

CaCO_3 saturation indices of the groundwater were calculated and the SI distribution map is shown in Figure 7.

All membrane plants except Plant A belonged to saturation area as CaCO_3 . Groundwater saturated with CaCO_3 was mainly distributed in the alluvial plains that reached 74 sampling sites out of 133. Additionally, the groundwater of 38 sampling sites, which all included CaCO_3 saturation sites, were saturated with $\text{CaMg}(\text{CO}_3)_2$. All groundwater including membrane plants contained low SO_4^{2-} (median 4.8mg/L) concentration that were not saturated with calcium sulfate (CaSO_4)

Table 2. Water quality of Lamphun groundwater samples and membrane plants (A-H) in raw water

	Temp °C	pH	EC mS/m	Alkalinity	Ca-Hardness	DOC	T-Fe	T-Mn mg/L	SiO_2	F ⁻
				mg/L as CaCO_3						
All ground waters of 133 wells (percentile)										
5%	25.6	6.0	16.2	78	12.9	0.10	ND	ND	14.2	0.1
50%	28.2	7.0	53.9	275	82.2	0.35	0.10	0.10	23.7	0.7
95%	30.6	8.0	102.9	429	297.4	1.48	5.40	1.80	58.1	11.2
Low to moderate fluoride ground waters of 86 wells (percentile)										
5%	25.6	5.8	13.2	56	16.4	0.09	ND	ND	14.1	0.1
50%	27.9	6.9	43.0	215	105.1	0.39	0.20	0.19	25.8	0.4
95%	30.1	7.4	96.3	424	316	1.20	6.22	2.50	60.6	1.3
High fluoride ground waters of 47 wells (percentile)										
5%	25.6	6.7	41.7	240	12.7	0.12	ND	ND	14.9	1.6
50%	28.7	7.5	63.6	325	49.4	0.31	ND	ND	20.4	4.7
95%	31.1	8.1	109	430	160	1.77	0.47	0.37	53.5	12.6
Raw water quality of membrane plants (A ~ H)										
A	28.3	6.7	33.9	150	61.7	1.11	0.22	0.13	27.4	1.3
B	27.4	7.7	97.7	420	95.6	0.48	0.10	ND	17.4	3.6
C	30.0	7.3	72.5	350	26.2	0.32	0.14	0.13	20.0	11.0
D	30.0	7.3	64.1	330	23.5	0.10	0.12	0.10	17.8	7.6
E	30.1	6.9	64.1	370	200	0.25	1.30	0.11	21.7	0.7
F	28.6	8.0	77.5	390	11.7	0.12	0.13	ND	16.0	13.4
G	25.5	7.0	45.6	220	106.4	0.29	0.40	0.18	51.9	0.8
H	31.1	8.2	64.9	350	23.5	0.19	0.11	0.08	16.2	6.5
ND: Not Detectable (less than detection limit 0.01mg/L)										

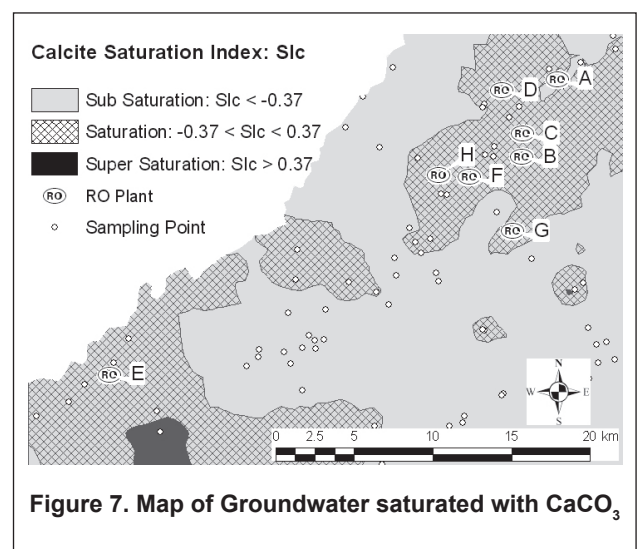
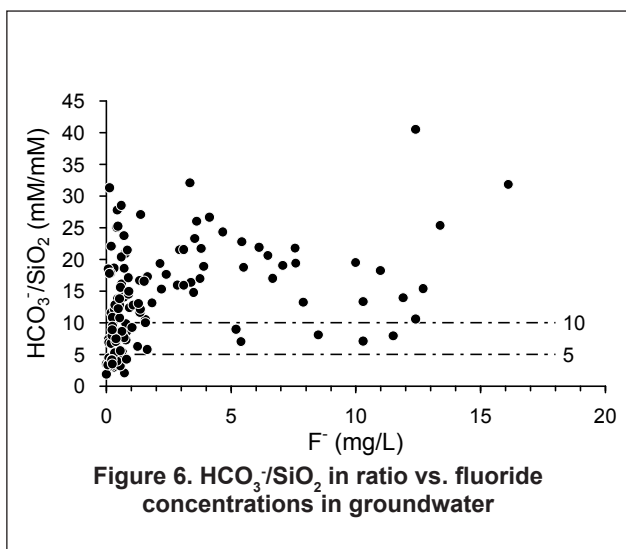
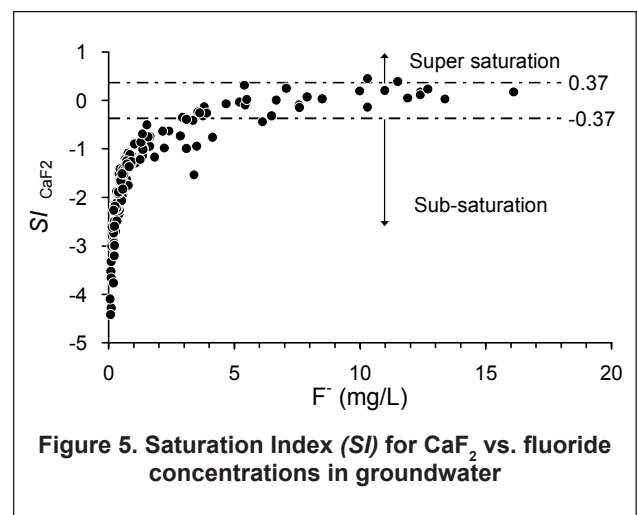
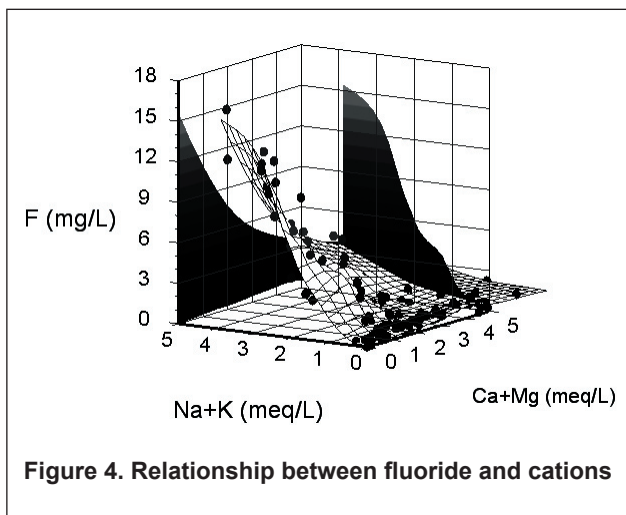
Membrane plant assessment

Samples of raw water (SP1), pre-treated water (SP2) and membrane filtered water (SP3) were taken and determined for T-Fe and T-Mn, DOC, SiO₂ and fluoride concentrations as shown in Figure 8 as (a), (b), (c) and (d), respectively.

T-Fe and T-Mn in Plants C, E, F and H were eliminated by the pre-treatment below the detection limit of 0.01mg/L. At Plants E and H, raw water was pre-chlorinated to oxidize iron and manganese. Additionally in Plant E, a small amount of sodium hydrosulfite was intermittently injected to the pre-treated water to prevent iron scale. However, the effectiveness of the anti-scalant was not clear from this investigation. Plants C and F did not apply the pre-chlorination, but the iron and manganese removal unit had enough capacity and was frequently washed. On the other hand, Plants A and B had T-Fe in the pre-treated water, and Plant D and G contained T-Fe and T-Mn in the pre-treated water. Plants A, B and D did not properly wash the iron and manganese removal unit. Plant G did not have pre-chlorination, though the raw water contained relatively high 0.4mg/L of T-Fe and 0.18mg/L of T-Mn. Additionally, the capacity of iron and manganese

removal unit was too small to treat the raw water at that flow rate. A trace of iron and manganese should be adsorbed on a membrane surface. The membrane fouling caused by iron and manganese enables the binding to membrane through an interaction with co-existing organic substances.

The median DOC in raw water of all the membrane plants was as low as 0.35mg/L, though GAC reactor was installed to remove DOC. Plant A, B and D used 1% citric acid as anti-scalant. However, the injection rate, which was equivalent to 1mg/L of DOC, was too small to reduce pH. The citric acid dosage rate was not effective to control carbonate scale. In general, more than half an amount of DOC is humic substances. Elimelech *et al.* (2002) suggested that waters saturated with calcium sulfate promoted calcium sulfate scale formation with the co-existing humic substances. Groundwater in Lamphun was not saturated with the calcium sulfate because of low SO₄²⁻ content. Even with the maximum ionic strength of the membrane plants, raw water contained 0.012mM SO₄²⁻ in Plant B, which was not high concerning adsorption of natural organic substances on the membrane.



SiO₂ was not removed by the pre-treatment process except Plant G which employed both anion and cation exchange resins in the pretreatment. The solubility of SiO₂ is 100~120mg/L at pH7 and 25°. The median temperature of Lamphun groundwater was as high as 28.2° and high fluoride area had relatively low SiO₂ as 20.4mg/L. All the membrane plants (A~H) were operated with recovery lower than 50%. Under these circumstances, membrane fouling with SiO₂ would not be a critical factor.

Fluoride was not removed by the pre-treatment process excluding Plant G. As mentioned before, anion exchange resin installed in the pretreatment contributed to the elimination of fluoride in Plant G. All plants performed high fluoride rejection in the membrane treatment process. At neutral to weakly basic pH, polyamide membrane are able to reject fluoride effectively. Lamphun groundwater with high fluoride was weakly alkaline with median pH of 7.5, which was favorable condition for fluoride removal.

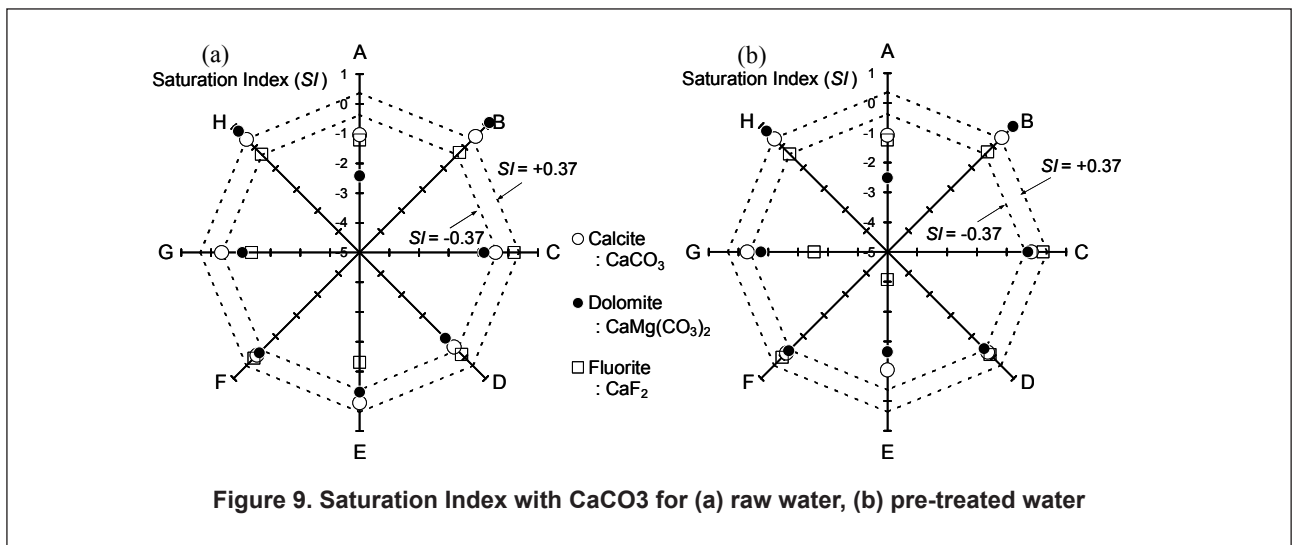
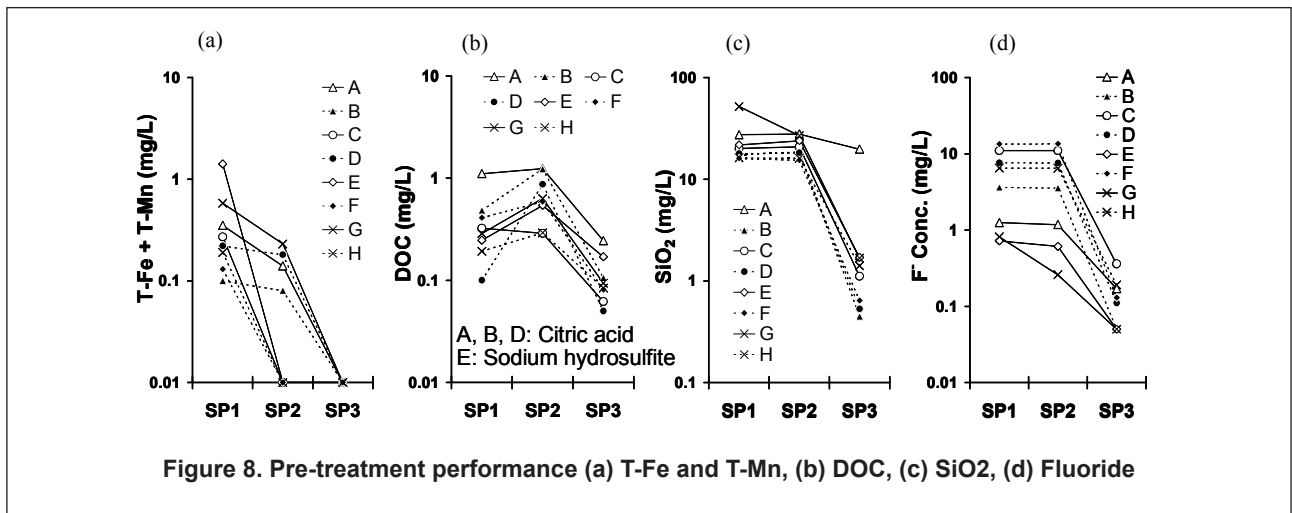
Ca²⁺ removal by the pretreatment is important to prevent calcium carbonate fouling on membranes. However, only Plant E exchanged Ca²⁺ effectively with Na⁺. Pre-treated

waters in other plants contained almost the same Ca²⁺ concentrations as raw waters. Saturation Index (SI) for the calcium minerals (calcite, dolomite and fluorite) were calculated based on the water properties of (a) raw water and (b) pre-treated water (Figure 9). Calcite-saturated raw water in Plant E was brought down to sub-saturated in pre-treated water by the pretreatment. All other plants except for E showed little difference in SI values between raw waters and pre-treated waters.

Conclusion

Fluoride concentrations of Lamphun groundwater were controlled by Ca²⁺ concentrations. In the alluvial plain, quality of the groundwater was dominated by HCO₃⁻ through weathering of carbonate minerals. As a result, the groundwater of 74 sites out of 133 and 7 membrane plants out of 8 were saturated with Calcium carbonate.

The studied 8 membrane plants were equipped with almost the same pre-treatment process and membrane modules in similar specifications. Considering the raw water quality of membrane plants and operational condition with low



recovery, DOC and SiO₂ would not cause membrane fouling. Hence, the GAC pretreatment to reduce DOC was not mandatory. T-Fe and T-Mn were retained in pre-treated water at 4 membrane plants. Ca²⁺ removed by the cation exchange reactor did not function at 7 membrane plants where the cation exchange resin was not replaced or regenerated properly. High fluoride contained groundwater presented alkaline pH which was favorable to reject fluoride by polyamide membrane. However, it was suggested that alkaline groundwater may cause membrane fouling due to calcium carbonate precipitation.

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