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Research Paper

Hydrological assessment using stable isotope fingerprinting technique in the Upper Chao Phraya river basin

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ABSTRACT

This study is focusing to assess the spatial and temporal distribution of rainfall using water stable isotope technique as well as the surface water-groundwater interactions for the aquifer systems in the Upper Chao Phraya river basin systems. Local precipitation, surface water, and groundwater along the main river courses and their tributaries are directly samples. Massive precipitation isotopic composition database from existing IAEA monitoring network (GNIB) along with local Bangkok precipitation isotopic signature are compared with precipitation from Chiang Mai province to better identify the rainfall isotopic compositions. In addition to the isotopic differentiation of precipitation in the area, its impacts on isotopic characteristics of surface water and groundwater are additionally explored. LMWLs (Local Meteoric Water Line) for local rainfall in Bangkok and Chiang Mai are generated with some seasonal variation due to rain out effect. Surface water is influenced by evaporation at some degree, revealing that rainfall may not be the primary source of surface water. Yom river's isotope values are far more D and ^{18}O-enriched compared to Ping's and Nan's, suggesting the mixing of groundwater with river water and/or the source of surface water may come from dry-period precipitation. Stable oxygen and hydrogen isotopes in groundwater fall on an evaporation line, and are thus indicative of the effects of high evaporation rates through the top surficial material. The isotopic similarity with the more depleted δD and δ^{18}O of groundwater samples suggests the potential mixing of groundwater with river water by different mixing processes (54% from river water and 46% from rainfall). The results show correlations in the isotope signature of shallow (< 50 m deep) and deeper aquifer (> 50 m deep) which may be associated with hydraulic connection and/or similar hydrogeological conditions. d-excess stable isotope analyses are beneficial to identify the relative contributions of the wet and dry seasonal sources to the groundwater recharge. The results indicate that groundwater sources are composed of ~ 71.4% wet seasonal sources and ~28.6% dry seasonal sources.

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1. Introduction

Environmental isotopes have now been regularly involved in geochemical, hydrological, and hydrogeological systems investigation for more than four decades, particularly beneficial for understanding groundwater and/or groundwater-surface water interaction systems. Most frequently used environmental isotopes include the heavy isotopes of the elements of the water molecules, hydrogen (^{2}H – also called deuterium, and ^{3}H – also called tritium), and oxygen (^{18}O). Applications of stable isotope ratios of hydrogen and oxygen in groundwater are based primarily upon isotopic variations in atmospheric precipitation, that is, in the input to the hydrogeological system under study.

Oxygen and hydrogen stable isotope maintain almost the same combination as of the meteoric water, implying that it contains the status of the initial formed meteoric water, and is a permanent natural tracer (Clark and Fritz, 1997). Stable isotopic compositions in groundwater are generally rarely affected by water-rock/soil ion exchange depth (McCarthy et al., 1992; Gat, 1996). The stable isotopic variations existing in groundwater might be the consequence of the concentration variation from inputs such as precipitation and surface water (Kendall and McDonnell, 1998) and therefore they can be employed as conservative groundwater tracers at aquifer-scale as long as there are no phase changes or fractionation along the flow-path.

Oxygen and hydrogen isotopes of water are widely used as tracers to understand processes such as precipitation, groundwater recharge, groundwater-surface water interactions, and basin hydrology (Gat, 1996; Vandenschrick et al., 2002; Deshpande et al., 2003; Gibson et al., 2005; Gammons et al., 2006). Groundwater and surface water display distinctive isotope signature in many areas as supported by previous research (Jacobson et al., 1991; Space et al., 1991; Acheampong and Hess, 2000), and therefore the isotopic signature of natural waters has often been used to define the system of mixed groundwater recharge areas among other recharge water sources and to characterize circulation paths and mixing or exchange processes between surface water and groundwater (Andreo et al., 2004; Payne and Yurtsever, 1974) by collecting the information of meteoric water and stable isotopes of oxygen and hydrogen in groundwater, in combination with the hydrogeological structure analyses and the groundwater flow in the study area. The combined study of oxygen and hydrogen isotopes in water sciences has been proven as a promising tool to exploring hydrological fluxes at a regional scale (Vandenschrick et al., 2002), including large-scaled precipitation, groundwater recharge, groundwater-surface water interactions, and basin hydrology (Gat, 1996; Clark and Fritz, 1997; Gibson et al., 2005; Sanford and Buapeng, 1996; Peng et al., 2002; Kuo and Wang, 2001; Mizota and Kusakabe, 1994; Blasch and Bryson, 2007; Heilweil et al., 2009; Yin et al., 2011; Singh et al., 2013). Unfortunately, stable isotope analyses of water have been conducted since the late 1990s (Sanford and Buapeng, 1996) in Thailand and are still considered very limited.

Recently, nation-wide drought stress situation due to exceptionally less rainfall in rainy season, prolonged dry season, and the expansion in agriculture and industry development has been threatening lives and Thailand's socio-economic status. The study area is the upper Chao Phraya basin located in a large central plain of Thailand with large irrigation serviced fields scattered all over the place, leading to individual private groundwater wells installation to compensate the frequent shortage of surface water. Groundwater table decline is spotted in some parts of the irrigated serviced fields due to uncontrolled severe pumping, leading to the critical current and future groundwater accessibility problems for the entire public water users in the system. The combined use of both surface water and groundwater to meet the total local water demand provides a solution to this insecure situation as known as conjunctive water management (Chun, 1964). Factors affecting the degree of interactions of surface water and groundwater include topography, underlying geology, subsurface hydraulic properties, temporal and spatial variation in precipitation, and local groundwater flow patterns (Cey et al., 1998). Determining the surface water-groundwater interactions and groundwater recharge sources is important for the effective management of groundwater resources, especially in drought threatening water resources management, and in the future conditions under climate uncertainties as well as determination of migration pathways for contaminants (i.e., contaminated shallow aquifer recharges deep groundwater). Although considering effective, the applications of stable isotope technique in water resources research in Thailand is still extremely rare. Additionally, strong evidences for recharge and surface water-groundwater interactions via stable isotopes analysis were not yet supplied in any related researches (Guo and Shen, 1995; Onodera et al., 2009; Saha et al., 2011) for Thailand case.

In this study, we investigated the temporal and spatial distribution of rainfall, surface water, and groundwater in the study area of Thailand from hydrogeological and stable isotopic perspectives using the stable isotope analysis of ^{18}O and ^{2}H as it can provide more reliable groundwater flow and pathway conceptual system.

Table 1. Groundwater storage and renewable water resources of the sub-basins (UNESCO).

Groundwater basin	Groundwater storage (million m^3)	Renewable water resources (million m^3)
Chiangmai-Lampoon	485	97
Lampang	295	59
Chiangrai-Prayao	212	42
Prae	160	32
Nan	200	40
Upper Chao Phraya	6,400	1,280
Lower Chao Phraya	6,470	1,294
Total	14,222	2,844

Stable isotopic signature of rainfall from Bangkok (Capital city of Thailand) existing monitoring network (GNIB; IAEA) starting from 1961 is compared with precipitation from Chiang Mai province station in the North of Thailand to better identify the local isotopic compositions of rainfall. In addition to the isotope signature distinction of precipitation in the area, the isotope characteristics of surface water and groundwater along the major rivers and irrigation canals in the upper Chao Phraya basin are also investigated. The results from this work provide useful information on hydrogeological processes such as the interactions of precipitation and surface water as well as groundwater entity (shallow vs. deep) in the study area with a view towards sustainable conjunctive use of surface water and groundwater.

2. Materials and methods

2.1 Study area

The upper Chao Phraya plain of Thailand shown in **Fig. 1** covers about 38,000 km^2 (approximately 180 km × 300 km) in 8 provinces with a population of 4 million people. The main landuse is 63% agriculture, out of which 21% is irrigated, and 24% is devoted for forestry. More than 90,000 groundwater wells exist in the region to serve as primary and secondary source of water supply.

Ping, Wang, Yom, and Nan Rivers are abundant in runoff and also high in sediment transport capacity. Most surface water is utilized for agricultural purposes in rainy season. Domestic and industrial water rely on water supply and groundwater. Agricultural sector also use groundwater in conjunction with surface water in dry period. To understand the use of water resources in this basin, the fundamental characteristics and recharge sources of the groundwater aquifer need to be analyzed.

2.2 Hydrogeological conditions of the study area

Chao Phraya river basin is divided by 5 major rivers that flow from North to South, forming a depositional flood plain geological unit with average elevation of 40-60 m above MSL. On the Eastern and Western sides are surrounded by mountains of volcanic rocks. The basin drains directly into the lower basin in the South, though the free discharge is partially obstructed by crystalline rocks. Annual average rainfall of 900-1,450 mm is reported in the study region. The wet season starts from April to September and accounted for 81% of the total precipitation. On the other hand, 19% of the total rainfall occurs in the dry season between October and March. Irrigation water is diverted from Nan River at Naresuan diversion dam. The groundwater aquifer forms the geological basis as a depositional flood plain from North to Southeast with mountains of volcanic rocks surrounded in the West. More than 3,000 groundwater wells are present in this area with several groups of active intensive groundwater extraction. The aquifer system was defined as two-layered aquifer with the thickness of the upper, semi-confining layer varying between 10-70 m and lower confining layer between 100-300 m based on the hydrostratigraphic concepts relying on the geological conditions of similar hydrogeologic properties and their confining boundaries.

Hydrogeologically, the Chao Phraya river basin is comprised of seven groundwater sub-basins: Chiangmai-Lampoon basin, Lampang basin, Payao basin, Prae basin, Nan basin, upper Chao Phraya basin, and lower Chao Phraya basin. Within these groundwater sub-basins, water is held in either confined or unconfined aquifers. Eight separate confined aquifers are located in the Upper Tertiary to Quaternary strata of the Bangkok area. Groundwater storage and renewable resources have been estimated for each groundwater sub-basin, as shown in **Table 1**.

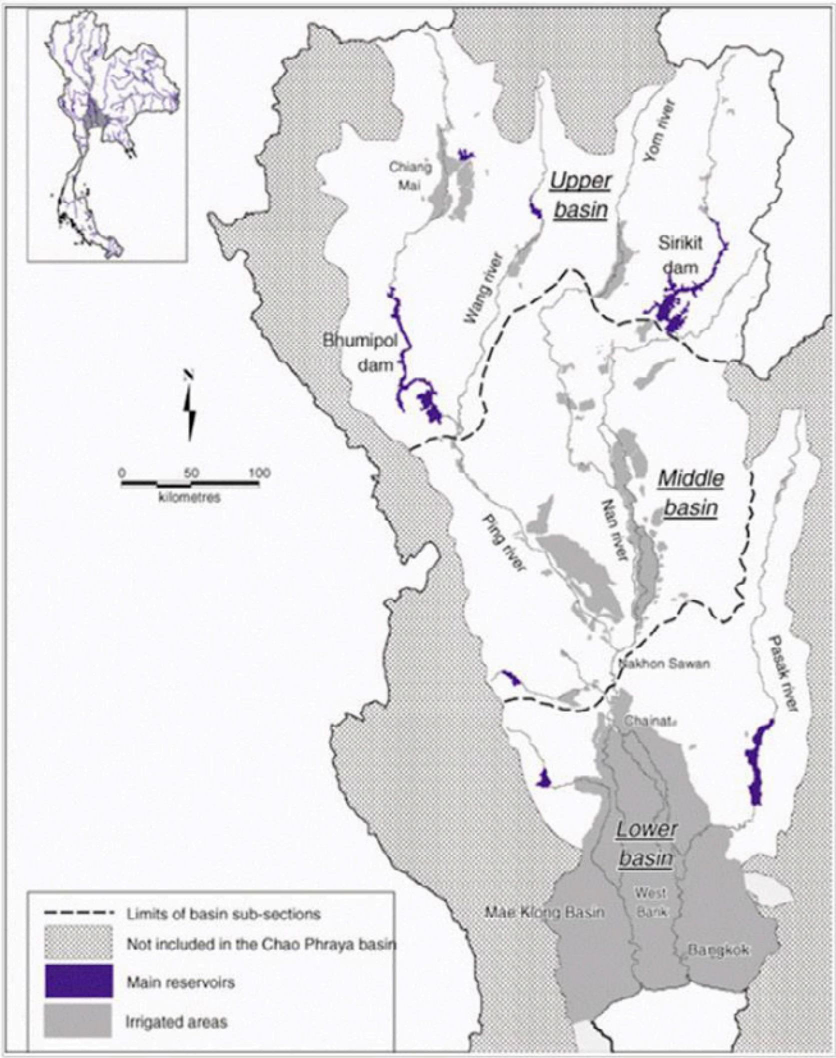

Fig. 1. Study area (upper Chao Phraya river basin).

2.3 Stable isotope sample collection

Precipitation, river water, and groundwater samples were collected for oxygen and hydrogen isotopic analyses from 2007-2008. Sampling was carried out in both wet and dry periods. Sampling procedures for precipitation were in accordance with IAEA guidelines (International Atomic Energy Agency 1983). The protocols are designed to minimize evaporation of the precipitation samples. **Fig. 2** shows 44 surface water and groundwater sampling locations distributed throughout the study area. Samples were collected using the following sampling bottles: 2×1-L glass bottles, 250-mL plastic container, and 2×60-mL glass bottles cooled with ice and stored in a dry place immediately after sampling.

Deeper groundwater is presumed to have a longer flow path and residence time compared with shallow groundwater, because it is buried in deeper confined aquifers. Seven surface water samples from local streams and irrigation canals, were collected along the flow path of surface water in the irrigation project. Stable oxygen isotopic compositions were analyzed using the CO_2-H_2O equilibration method (Epstein and Mayeda, 1953). The equilibrated CO_2 was measured using a VG SIRA 10 isotope ratio mass spectrometer. The hydrogen isotopic compositions were determined on a VG MM602D isotopic ratio mass spectrophotometer after was reduced to H_2 using zinc shots made by the Biogeochemical Laboratory of Indiana University (Coleman et al., 1982). All isotopic ratio resulted were reported as the d-notation (‰) relative to the international VSMOW (Vienna Standard Mean Ocean Water) standard, Physico-chemical parameters, electrical conductivity (EC), pH, total dissolved solids (TDS) and temperature were also measured at each sampling point. Major ion concentrations were analyzed using Ion Chromatography (Dionex) at the Department of Groundwater Resources, Thailand.

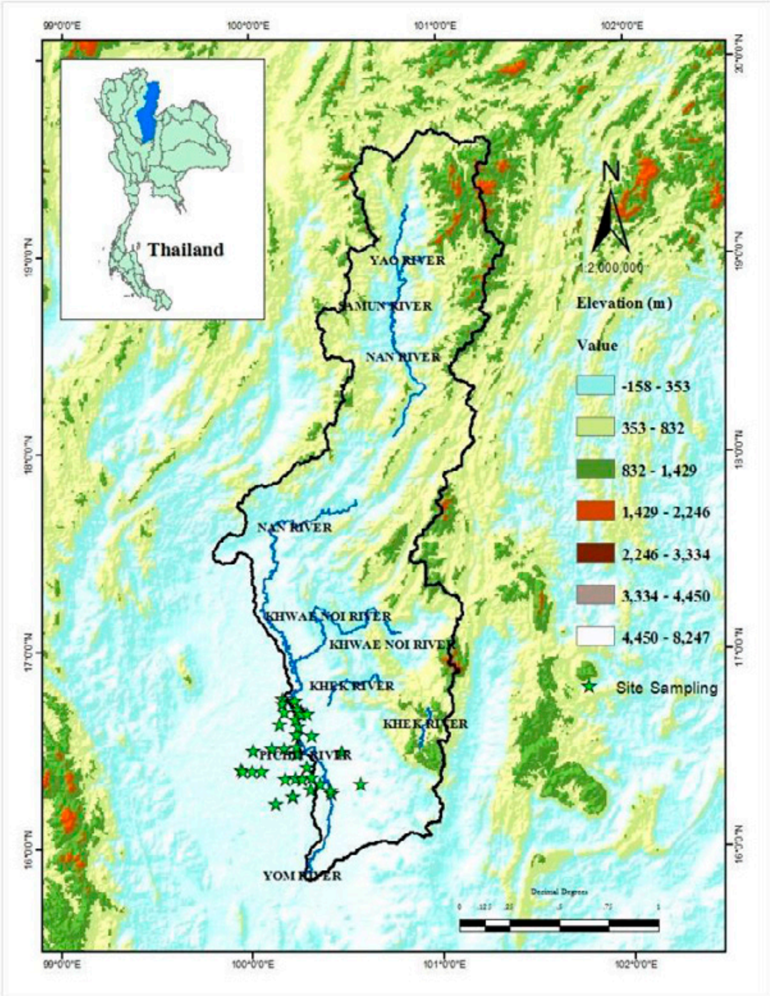

Fig. 2. Sampling sites.

2.4 Isotope analysis

We are using oxygen and hydrogen isotopes of water as tracers to understand hydrogeological processes in the study area based on the fractionation of $\delta^{18}O$ and δD driven by kinetic processes during evaporation and condensation (Dansgaard, 1964). The fractionation process is based on the equilibrium processes of the isotopes of evaporation and condensation and there is a specific relationship that governs the distributions of isotope values of oxygen and hydrogen in ocean and inland rainfall.

By employing oceans as the biggest reservoir of natural stable isotope, the measured values of stable isotopes in seawater are referred as standard values known as SMOW (Standard Mean Ocean Water). If *R* is the ratio of the heavy isotope to the light one, then the relative fractionation can be expressed (as deviation δ in per thousand parts) and shown in Eq. 1.

$$\delta = \frac{R_{sample} - R_o}{R_o} \times 1000\% \quad [1]$$

where R_{sample} is the isotope ratio in water sample and R_o is the isotope ratio in SMOW.
The mean weighted δD and $\delta^{18}O$ composition of water at each location was determined following Eq. 2:

$$R_{mw} = \frac{\sum_{i=1}^{n} P_i \delta X_i}{\sum_{i=1}^{n} P_i} \quad [2]$$

Craig (1961) generated a Global Meteoric Water Line (GMWL) by employing a linear regression method to analyze the oxygen and hydrogen isotopic composition insamples of precipitation, snow water, and river water from all over the world as expressed by Eq. 3:

$$\delta D = 8\delta^{18}O + 10 \quad [3]$$

Similar results by Dansgaard (1964) and Gat (1980), who later collected and analyzed samples globally, suggested a similar result as shown in Eq. 4:

$$\delta D = (8.17 \pm 0.08)\delta^{18}O + (10.56 \pm 0.64) \quad [4]$$

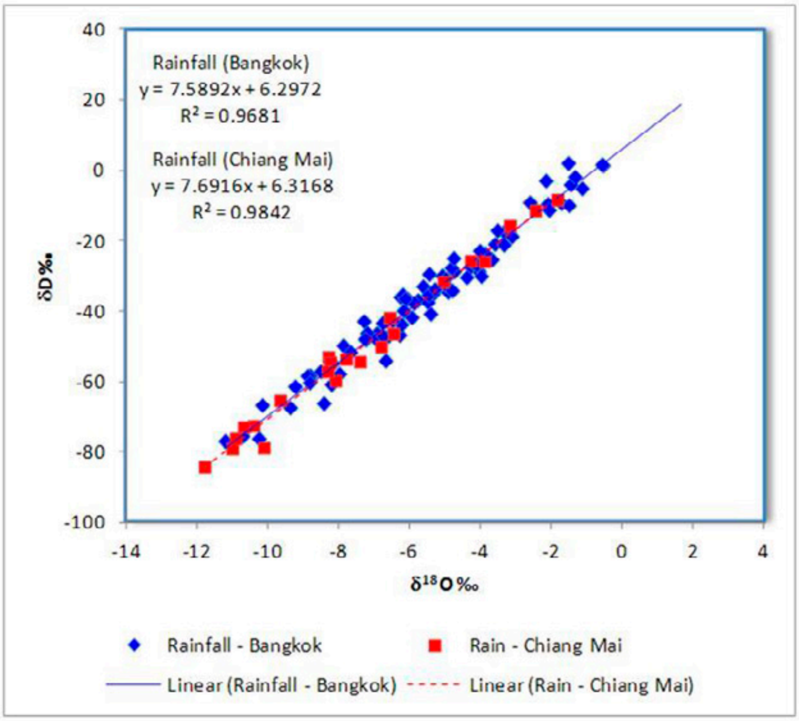

Fig. 3. Plots of δD vs. δ^{18}O for precipitation samples from Bangkok and Chiang Mai.

In the oxygen and hydrogen isotopes meteoric water line, the slope represents the ratio of the temperature relationship between δD and δ^{18}O when condensation occurs; while the value of the intercept is based on the evaporative conditions in the water source region. Most precipitation worldwide generally follows this trend. The intercept is also called "deuterium excess" or "d-excess" ($d = \delta D - 8\delta^{18}O$). The intercepts in most places around the world are about 10% based on GMWL regression line. In some areas that experience specific condensation and evaporation conditions (e.g., temperature and humidity) or have a unique terrain environment, however, deviate from GMWL with a different slope and intercept (called local meteoric water line) (Dansgaard, 1964; Darling and Armannsson, 1989). Interpretation of slope and intercept deviations from the meteoric water line is usually being caused by precipitation occurring during a warmer or colder climate than at present or by geochemical interactions occurring during underground passage. Slopes and intercepts are also location dependent due to distinctive rainfall evaporation characteristics or source evaporation conditions in various air mass sources. For example, North America: $\delta D = 7.95\delta^{18}O + 6.03$ (Dansgaard, 1964); Tropical Island area: $\delta D = 6.17\delta^{18}O + 3.97$ (Dansgaard, 1964); Japan: $\delta D = 8\delta^{18}O + 17.5$ (Sakai and Matsubaya, 1977). In general, if evaporation is faster, or if rainfall evaporation occurs, intercepts are higher. d-excess has become beneficial to identify the air mass source of meteoric water and todefine the seasonal recharge of groundwater (Deshpande et al., 2003; Gibson et al., 2005; Blasch and Bryson, 2007; Lee et al., 1999).

3. Results and discussion

3.1 Isotopic compositions of precipitation

In this study, the total of 22 precipitation samples collected from Chiang Mai province located in the upper Chao Phraya River basin were analyzed for their isotopic signatures of meteoric water. The δD of the precipitation ranged between -8.29 ‰ and -84.21 ‰ with a mean value of -50.79 ± 22.86 ‰. The δ^{18}O ranged between -1.84 **‰** and -11.79 **‰**, with a mean -7.42 ± 2.95 **‰**. The mean *d* was 6.32 **‰**. Linear regression analysis showed the LMWL of precipitation in Chiang Mai province to be $\delta D = 7.69\delta^{18}O + 6.32$ as shown in **Fig. 3**. The isotopic compositions database of water collected from the existing monitoring network (GNIB) also provides the stable isotopic signature of rainfall from Bangkok (Capital city of Thailand) as plotted in **Fig. 3**. The δD of the Bangkok precipitation was between 2.10 ‰ and -76.80 ‰ with a mean of -35.86 ± 18.75 ‰. The δ^{18}O ranged between 2.10 ‰ and -76.80 ‰, with a mean -35.86 ± 18.75 ‰. The mean d was 6.29 ‰. Linear regression analysis showed the LMWL of precipitation in Bangkok to be $\delta D = 7.59\delta^{18}O + 6.29$ as shown in **Fig.3.**

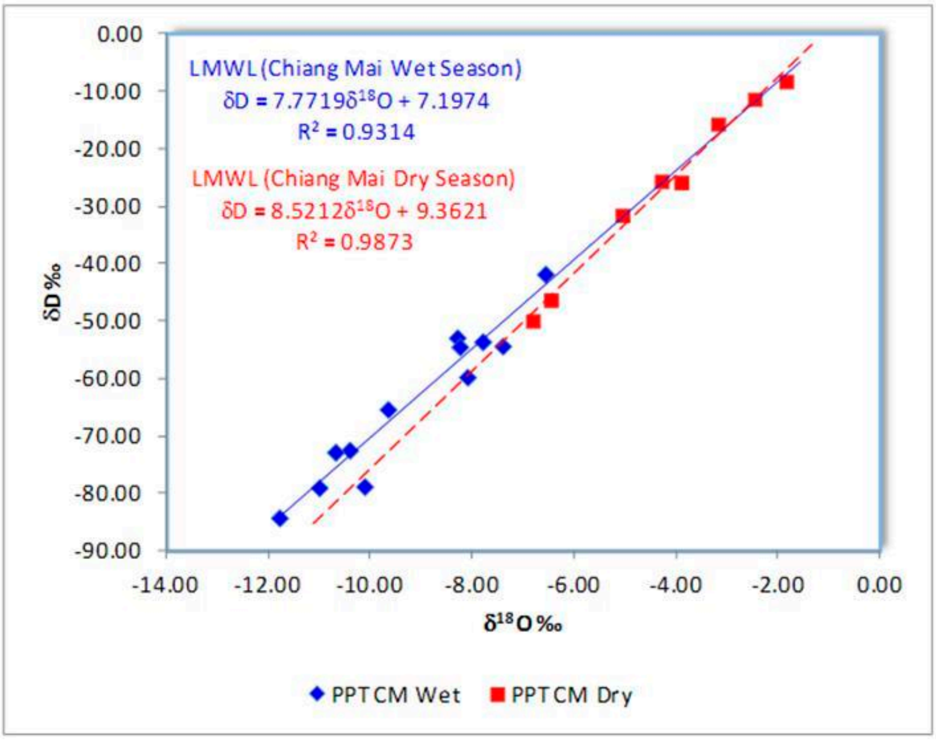

Fig. 4. Plots of δD vs. $\delta^{18}O$ for precipitation samples from Chiang Mai in wet and dry seasons.

Rainfall sample collection was done throughout the year to investigate any potential seasonal effects on isotope to describe seasonal effects on the local isotopic data: $\delta D = 7.770\delta^{18}O + 7.19$ for the wet season precipitation (June-October) and $\delta D = 8.52\delta^{18}O + 9.36$ for the dry season precipitation (November-May). Deviation of the slope and intercept of the wet season's regression line from GMWL of Craig (1961) was present. The wet season precipitation's intercept of 7.19 was found, while the intercept of 9.36 was claimed in dry season rainfall case. Those intercepts are lower than that of the GMWL of 10, perhaps due to the different air masses affecting the study area.

The more depleted hydrogen and oxygen isotopes compositions in the wet period than the dry seasons were revealed from this study based on the isotope signatures of precipitation in wet and dry seasons in Chiang Mai province located in the upper Chao Phraya River basin. This deviation of LMWL feature has been commonly observed in other regions (Yeh et al., 2011) and can be explained by the effects of temperature. For higher temperature, the hydrogen and oxygen isotope signatures may have been enriched in local precipitation. However, a tropical monsoon country like Thailand should be minimally affected by this temperature effect. Rainfall can also affect its own isotope compositions. The hydrogen and oxygen isotopes in precipitation are significantly depleted due to the raining out of heavy precipitation amounts over signature of the precipitation in Chiang Mai province of Thailand. Two LMWLs are plotted in **Fig. 4** to a relatively short time duration in seasons with heavier rainfall, known as the "rainfall amount effect" (Dansgaard, 1964). The temperature effect is normally pronounced in high-latitude continental regions, whereas the effect is pronounced in tropical regions (Yurtsever and Gat, 1981). Therefore, the signatures of hydrogen and oxygen isotopes in wet season can be explained by the mutual influence of rainfall amount and temperature, with the former have a stronger effect than the latter. Additionally, this finding suggests that the pre-monsoon rains (i.e., dry season) may originate from isotopically enriched local moisture sources (such as evaporated surface water bodies), whereas the monsoon rain clouds have travelled a greater distance and had multiple fractions before precipitation.

3.2 Isotopic compositions of surface water

Surface runoff, interflow, and groundwater (i.e., base flow) are the three major components of river water based on the traveling speed after rainfall. The arrival times for interflow and surface runoff can differ on the order of hours, so they both are considered coming from recent storms and should have similar isotopic compositions. Therefore, from stable isotope point of view, river water can be considered as being composed

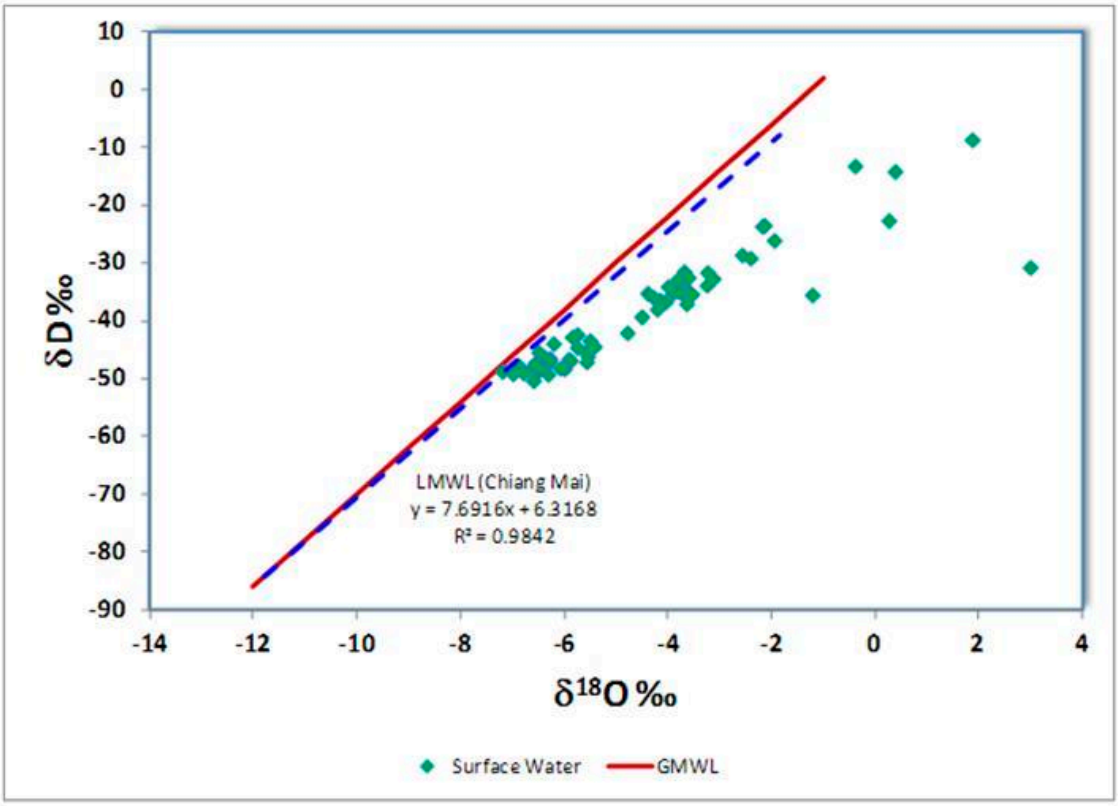

Fig. 5. Plots of δD vs. δ^{18}O for surface water samples in upper Chao Phraya river basin and LMWL (Chiang Mai province).

of groundwater and runoff, including surface runoff and interflow (Lu et al., 2006).

Sixty-eight surface water samples are collected and analyzed for isotope compositions. The δD of the surface water in the Upper Chao Phraya River basin ranged from -50.19‰ and -8.49‰, with a mean of -39.25‰ ± 9.62‰. The δ^{18}O ranged between -7.2‰ and 2.99 ‰, with a mean of -4.61‰ ± 2.19 ‰ as shown in **Fig. 5.** Regression line between δD and δ^{18}O of $\delta D = 4.020\delta^{18}O - 20.72$ was generated. All the river water samples plot below the LMWL **(Fig. 5).** The low slopes of LMWLs are commonly associated with low humidities and evaporation (Yurtsever and Gat, 1981). Surface water influenced by evaporation is offset to the right of the meteoric water line because of differences in how the two isotopes fractionate during evaporation (Clark and Fritz, 1997). It might be expected that some of the anomalously low slopes are caused by making linear regressions of small datasets (i.e., less than 6 samples) or ones where there is little seasonal variability (i.e., less than 1‰ range in δ^{18}O values and $r^2 < 0.8$). Hence, the low slope in this case is not artifacts of small datasets with limited variability, but is the characteristic of the river datasets themselves. The relatively smaller slope of 4.02 compared to that of GMWL (i.e., 8) and LMWL (i.e., 7.77 in wet period and 8.52 in dry season) therefore indicates that surface water in the study area is subjected to evaporation at some degree. This observation is attributed to evaporative enrichment of the heavier isotopes of both elements. Evaporation of surface water bodies causes an enrichment in the heavier isotopes of the residual water, resulting in slopes of the δD-δ^{18}O diagram in the range of 4 and 5.5 (Leibundgut et al., 2009). It remains unclear whether the evaporation occurs during rainfall, within the soil zone, or in the rivers. Further analyses of air mass isotopes in the study area may be required to better understanding the evaporation phenomenon. This finding, however, reveals that rainfall may not be the primary source of surface water. As a matter of fact, surface water may have come from upstream watersheds or lakes or from other big reservoirs or dams and it is worth for further exploration. Sirikit dam (in Utaradit province) is located upstream of the study area and a water sample was collected for further analysis. It is also possible that groundwater flow mainly contributes to the river water in the study area during the period of sample collection (March 2008). In many watersheds, it is commonly assumed that groundwater makes up the majority of stream flow during periods of baseflow known as "gaining stream". Stable isotopes of groundwater in the study area are further analyzed to evaluate potential dynamic interactions of surface water and groundwater. The results are later discussed in this work.

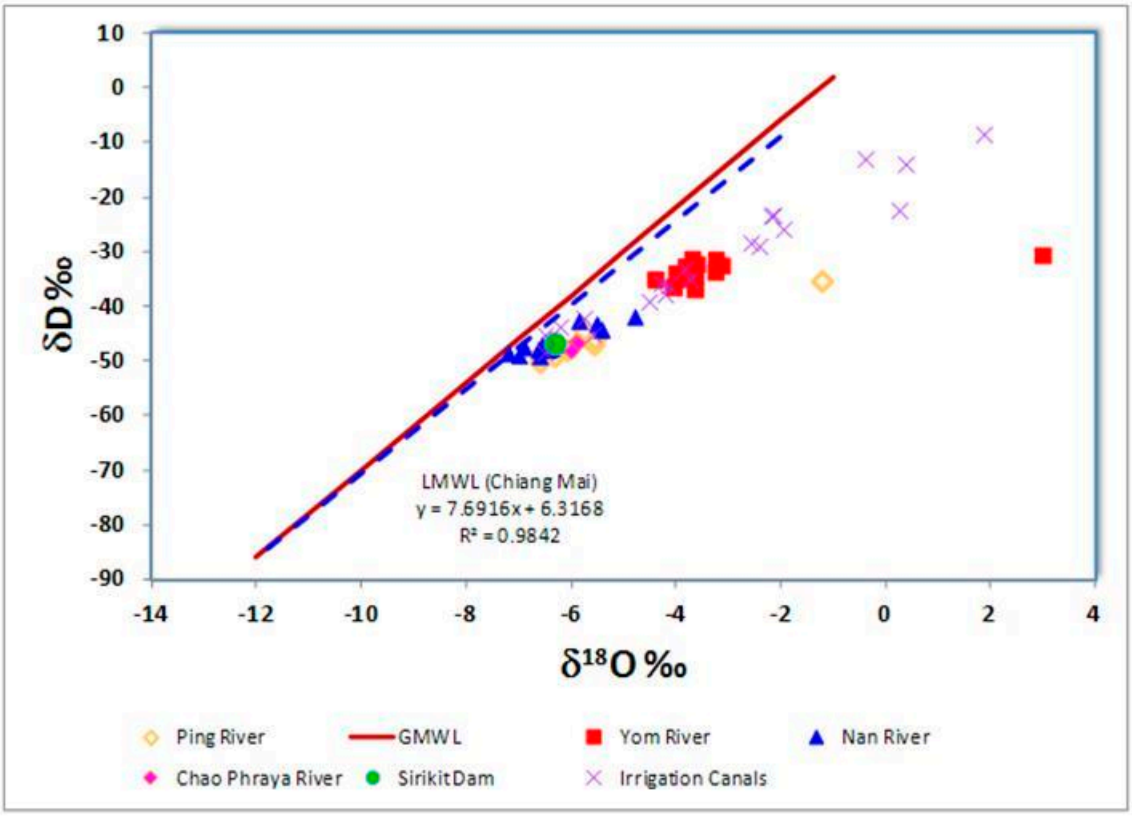

Fig. 6. Characterization of individual river δD vs. $\delta^{18}O$ compositions in Ping, Yom, and Nan rivers.

Further attempts to characterize surface water in the study area were made by generating LMWL for individual river in the upper Chao Phraya river basin. Isotopic compositions of water samples from Ping, Yom, and Nan rivers are separately plotted as shown in **Fig. 6**. Also plotted in the figure is the isotopic composition of surface water collected from smaller streams and irrigation canals in the study area. The $\delta^{18}O$ and δD values of surface water vary for each basin, especially for surface water samples collected from Yom river. The Ping and Nan water samples, with $\delta^{18}O$ values of –1.22 to –6.99, are more depleted than Yom river samples, with $\delta^{18}O$ of -3.13 to -4.39. Range of $\delta^{18}O$ and δD values from Ping and Nan rivers match the isotopic compositions of stored water in Sirikit dam (shown in **Fig. 6**) in Utaradit province in the Northern Thailand, which is generally referred to as D-enrich and ^{18}O-enrich because of evaporation. The isotopic signal values are far more enriched in heavy isotopes in Yom river basin (compared to those from Ping and Nan basins), revealing the mixing of groundwater into river water in this area or the origin of surface water may come from dry-period precipitation (previously shown in **Fig. 4**). One of the Yom river samples is much more enriched than the other river water samples (shown in the far right of **Fig. 6**).

3.3 Isotopic compositions of groundwater

Water in most rivers, generally, has 2 main components: (1) recent precipitation that has reached the river either by surface runoff, channel precipitation, or by rapid flow through the shallow subsurface flowpaths; and (2) groundwater. The relative contributions of these sources differ in each watershed or basin, and depend on the physical setting of the drainage basin (e.g., precipitation amount, seasonal variations in precipitation, temperature, potential evaporation, etc.), and also human activities (e.g., dams, reservoirs, irrigation usages, clearing for agriculture, channel re-structuring, etc.). The $\delta^{18}O$ and δD of rivers will also reflect how the relative amounts of precipitation and groundwater vary with time, and how the isotopic compositions of the sources themselves change over time. Seasonal variations are expected to be larger in streams where recent precipitation is the main source of flow, and smaller in streams where groundwater is the dominant source.

Stable isotopes of oxygen and hydrogen in groundwater, including spring water and well water, are investigated to gain insight into the groundwater characteristics in part of the upper Chao Phraya river basin of Thailand. The well water fall into 2 categories,

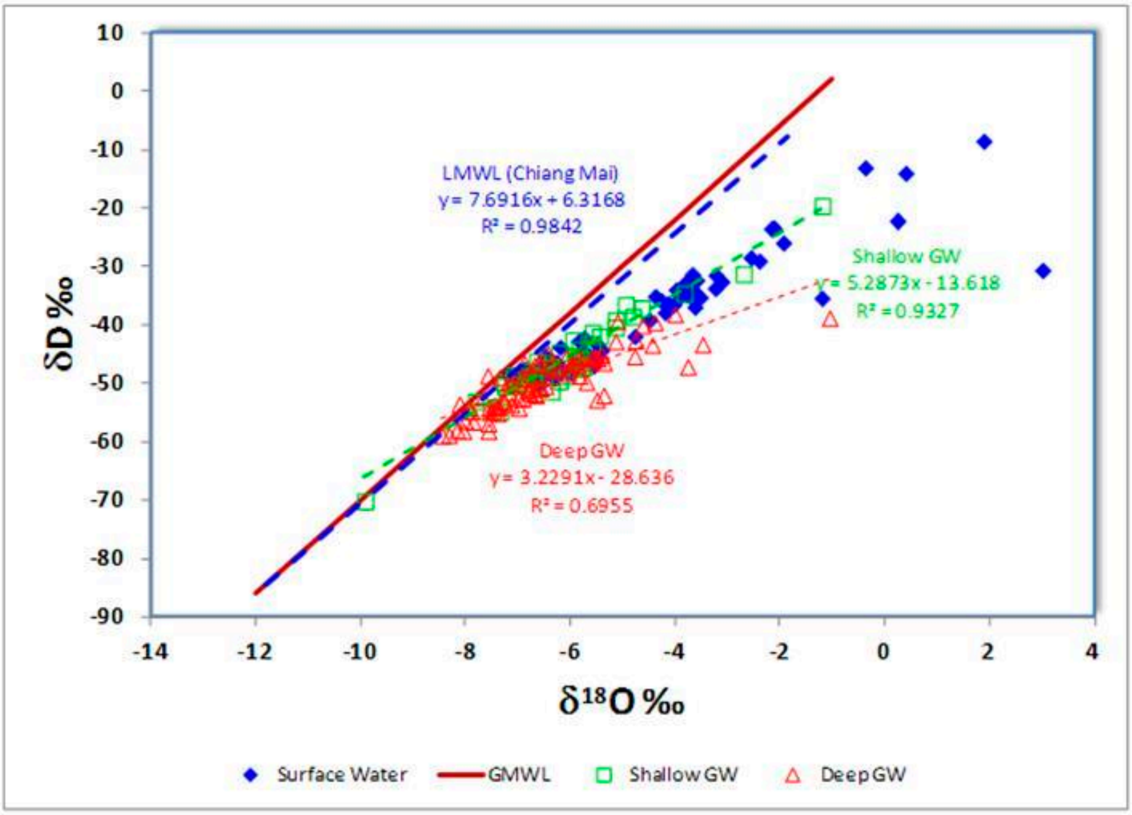

Fig. 7. Plot of δD vs. δ^{18}O for groundwater samples in upper Chao Phraya river basin and LMWL (Chiang Mai province).

i.e., water from shallow wells with depth < 50 m, and confined groundwater well of depth > 50 m). The isotopic compositions of groundwater are reported in **Fig. 7**.

The data in **Fig. 7** show that δD and δ^{18}O values of shallow groundwater range from -19.6 to -70.1 with a mean value of -46.68, and from -1.21 to -9.93 with a mean value of -6.14, respectively. Most of the groundwater samples plot slightly below the LMWL, and the linear fit for all groundwater samples ($\delta D = 4.020\delta^{18}O - 20.72$) has a lower slope than LMWL and GMWL. The groundwater data fall on an evaporation line with a lower slope and deuterium excess than the GMWL and LMWL, and is thus indicative of the effects of high evaporation rates attending high temperature and slow infiltration rates through the top surficial material.

Our groundwater data also are more depleted (i.e., less enriched) in D and ^{18}O than local precipitation collected from the same period during dry season. The more depleted isotope signature of local groundwater from our study suggests that the source of groundwater may not be from local precipitation. No groundwater samples collected from this study reflect the similar enrichment of δD and δ^{18}O isotopes like those observed from local rainfall in dry season. Rivers and streams samples are generally much more exposed to high effects of evaporation than groundwater in transit, and therefore are more isotopically enriched. However, our surface water samples collected from Ping and Nan rivers fall within the ranges of our groundwater δD and δ^{18}O values, with similar mean δ^{18}O values. The isotopic similarity with the more depleted δD and δ^{18}O isotopic compositions of our groundwater samples suggests the potential mixing of groundwater with river water. Consequently, groundwater in our study area appears to have been recharged primarily to (in the form of baseflow) or from rivers rather than simply from rainfall recharge. To be more specific, groundwater in the study area seems to be originated from Ping and Nan Rivers since surface water from Yom River expresses a distinctive enrichment in isotopic characteristics (compared to those of Ping and Nan Rivers'), and therefore could not contribute as a groundwater source.

The groundwater isotope data in this study also exhibits some slight seasonal variability. Groundwater isotopic compositions in wet season are slightly more enriched in D and ^{18}O; however, absolute differences between seasons are small (0.21‰ for δ^{18}O; 2.8‰ for δD). These differences can either result from a fraction of local seepage water with short residence times, or from uncertainties of groundwater sampling. Well screening depths are sometimes precisely unknown and therefore we expect some minor uncertainties when taking groundwater samples, i.e., water from same depths and taken with same flow rates during sampling. Although this study did not perform extensive monthly sampling and analysis of groundwater samples, the data used is much more representative of the character of groundwater in the entire basin since it includes data from both North and South, and the two major seasons (wet and dry seasons) of the year.

3.4 Mass balance analysis

In basin water budget studies, it is necessary to assess the proportion of the precipitation and river water that actually recharges our groundwater. Our basin groundwater can be recharged from rainfall over the basin and from Ping, Wang, Yom, and Nan river system tributaries draining from the North as shown in **Fig. 1**. The isotopic composition of groundwater equals the average weighted values of each recharge sources, such as from the annual composition of precipitation and river water in our case. Thus, deviations of groundwater isotopic ratio from that of precipitation are expected. As the basin size increases, the isotopic compositions of rivers are increasingly affected by subsequent alterations of the precipitation compositions by selective recharge and runoff, mixing with older groundwater and newer rain water, and by evaporation (Gat and Tzur, 1967; Fritz 1981; Gat, 1996). Local precipitation events are an important component of river water in the headwaters of large basins. For example, the average amount of new water in small forested watersheds during storms is about 40%, although during storms the percentage can be higher (Genereux and Hooper, 1998). In the lower reaches, local additions of precipitation generally can be of minor importance (Friedman et al., 1964; Salati et al., 1979), except during floods (Criss, 1999).

Groundwater is originated from infiltrated surface water and rainfall through recharging process. Therefore, by taking groundwater sources into consideration, its stable isotopic composition can be determined by oxygen and hydrogen isotopic compositions and recharge fractions of concerned sources. Using oxygen and hydrogen isotopic composition mass balance analysis, the groundwater recharge fractions of every recharge source can be evaluated in the study area. In this study, mixing between two distinct recharge sources (i.e., river water and precipitation) can be quantified by a simple linear algebraic equation:

$$C(V_A + V_B) = AV_A + BV_B \quad [5]$$

$$C = A\frac{V_A}{V_A+V_B} + B\frac{V_B}{V_A+V_B} = A(1-X) + BX \quad [6]$$

where A is the precipitation stable isotope value of the basin; B is the river water stable isotope value of the watershed; C is the groundwater stable isotope value of the basin; V_A is the amount of precipitation; V_B is the amount of river water; X is the recharge proportion of river water; and (1-X) is the recharge proportion of precipitation.

Based on the stable isotope analyses done in this study, the values of oxygen isotope of groundwater for the upper Chao Phraya River basin ranged from -1.84‰ to -11.79 ‰ with the mean value of -7.42 ‰. Seasonal effects can play an important role on the isotopic compositions of groundwater as the mean values of oxygen isotopic compositions of precipitation in dry and wet seasons for the upper Chao Phraya River Basin were -4.70 ‰ and -9.31 ‰, respectively. 27-yr historical rainfall data (data collected from 1979-2006) in the area suggested that the ratio of precipitation for dry and wet seasons was 0.19: 0.81. The weighted average $\delta^{18}O$ of precipitation was -8.43‰ in the upper Chao Phraya River basin. The values of oxygen isotopic compositions of river water for the dry and wet seasons were -6.07 ‰ and -3.01 ‰, respectively. The ratio of stream flow for the dry and wet seasons was 0.27: 0.73 from 1979-2006. The river water weighted average value for $\delta^{18}O$ was -3.84 ‰ in Ping and Nan Rivers.

The results show that 54% of the groundwater in the upper Chao Phraya River basin is derived from river water, and the other 46% is driven from the rainfall in the basin based on stable isotopic characteristics of the basin components. This finding reveals that groundwater in aquifer underneath the study area actually originates from 2 sources, i.e., the basin rainfall and river water, primarily due to the abundant precipitation in the wet season and a direct connection between river water and groundwater during the dry period. Using the mean d-value, the relative contributions of the wet and dry seasonal sources to the groundwater recharge can be calculated based on the following mass-balance equation:

$$d_{groundwater} = Xd_{wet\ season} + (1-X)d_{dry\ season} \quad [7]$$

where X and (1-X) are the fractions of wet and dry seasonal sources, respectively. Based on their d-values, the groundwater sources are composed of an average of approximately 71.4% wet seasonal sources and 28.6% dry seasonal sources.

4. Conclusions

The present study examines the temporal and spatial distribution of rainfall, surface water, and groundwater in the upper Chao Phraya river basin of Thailand by employing the stable isotope analysis of ^{18}O and ^{2}H. Stable isotopic composition of precipitation, river water, and groundwater is analyzed to generate an extensive isotope database for preliminarily assessing hydrologic characteristics of the basin. LMWLs of precipitation in Chiang Mai province and Bangkok are represented by $\delta D = 7.69\delta^{18}O + 6.32$ and $\delta D = 7.59\delta^{18}O + 6.29$, respectively. Seasonal variation of rainfall isotope signature in Chiang Mai province is demonstrated from non-identical LMWLs (i.e., $\delta D = 7.770\delta^{18}O + 7.19$ and $\delta D = 8.52\delta^{18}O + 9.36$ for the wet (June-October) and dry season precipitation (November-May), respectively). Rainfall can also affect its own isotope compositions. The hydrogen and oxygen isotopes in precipitation are significantly depleted due to the raining out of heavy precipitation amounts over a relatively short time duration in seasons with heavier rainfall, known as the "rainfall amount effect" (Dansgaard, 1964). The finding suggests that the pre-monsoon rains (i.e., dry season) may originate from isotopically enriched local moisture (such as evaporated surface water bodies), whereas the monsoon rain clouds have travelled a greater distance and had multiple fractions before precipitation.

Surface water (i.e., river water and water from irrigation canals). Rivers regression line between δD and $\delta^{18}O$ of $\delta D = 4.020\delta^{18}O - 20.72$ is generated, which is plotted below the LMWL. Surface water influenced by evaporation at some degree is offset to the right of the meteoric water line because of differences in how two isotopes fractionate during evaporation. This finding also reveals that rainfall may not be the primary source of surface water. As a matter of fact, surface water may have come from upstream watersheds or lakes or from other big reservoirs or dams and it is worth for further exploration. It is also possible that groundwater flow mainly contributes to the river water in the study area during the period of sample collection (i.e., March 2008). Individual isotope characteristics of water samples from Ping, Wang, Yom, and Nan show that Yom river water is D and ^{18}O-enriched due to evaporation. The isotopic signal values are far more enriched in heavy isotopes (compared to Ping and Nan water samples), revealing the mixing of groundwater into river water in this area or the origin of surface water may come from dry-period precipitation.

Stable oxygen and hydrogen isotopes in groundwater are investigated to gain insight into groundwater characteristics of the upper Chao Phraya river basin of Thailand. The groundwater data again fall on an evaporation line with a lower slope and deuterium excess ($\delta D = 4.020\delta^{18}O - 20.72$) than the GMWL and LMWL, and is thus indicative of the effects of high evaporation rates attending high temperature and slow infiltration rates through the top surficial material. Our surface water samples collected from Ping and Nan rivers fall within the ranges of our groundwater δD and $\delta^{18}O$ values, with similar mean $\delta^{18}O$ values. The isotopic similarity with the more depleted δD and $\delta^{18}O$ of groundwater samples suggests the potential mixing of groundwater with river water. Consequently, groundwater in our study area appears to have been recharged primarily to (in the form of baseflow) or from rivers rather than from simple local rainfall recharge. To be more specific, groundwater seems to be originated from Ping and Nan Rivers since surface water from Yom River expresses a distinctive enrichment in isotopic characteristics (compared to those of Ping and Nan Rivers'), and therefore could not contribute as the groundwater source.

Groundwater in the upper Chao Phraya river basin is affected by different mixing processes and also is contributed from river water and local precipitation sources as confirmed by stable isotope mass balance (54% from river water and 46% from rainfall in the basin). The results of stable isotope analyses show correlations in the isotope signature of shallow (i.e., < 50 m deep) and deeper aquifer (i.e., > 50 m deep) which may be associated with hydraulic connection and/or similar hydrogeological conditions. Water dating analyses (e.g., tritium dating, rubidium-strontium dating, and radiocarbon dating) are perhaps needed to distinguish the different mixing processes in more detail in aquifer of interest. *d*-excess stable isotope analyses are beneficial to identify the relative contributions or fractions of the wet and dry seasonal sources to the groundwater recharge. The stable isotope findings indicate that groundwater system in the study area is quite dynamic as its sources are temporally composed of an average of approximately 71.4% wet seasonal sources and 28.6% dry seasonal sources.

This work is one of the pioneer studies in applying the isotope fingerprinting technique to preliminarily assess the hydrologic characteristics in upper Chao-Phraya river basin of Thailand. Using oxygen and hydrogen isotopic compositions is demonstrated as a useful tool to investigate the spatial and temporal rainfall characteristics distribution and also gives valuable insights about the dynamic contributions for groundwater in the aquifer systems of interest. The results from this study also provide hydrological information on local precipitation, surface water, and groundwater in the study area. Possible linkages of surface water and groundwater resources are demonstrated spatially and temporally, which are substantially beneficial for a better conjunctive water management practice. With aids from detailed stable isotope and mass balance analyses along with other hydro-meteorological and hydro-geological data, simulation of fraction of groundwater baseflow in both wet and dry season is under taken using an advanced surface water-groundwater coupling model.

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