HEALTH RISK ASSESSMENT OF ARSENIC AND LEAD AND THEIR SPATIAL DISTRIBUTION IN GROUNDWATER AT BAN KHAI DISTRICT, RAYONG PROVINCE, THAILAND

BY

WIYADA NILKARNJANAKUL

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF
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ABSTRACT

Arsenic (As) and lead (Pb) contamination in groundwater is an important public health concern. This study is aimed at i) investigating As speciation and Pb levels between the dry season (March 2019) and the wet season (August 2019) and includes the spatial distribution in groundwater for the purpose of ii) determining the association between the two metals and the hydrochemical parameters. iii) The presence of heavy metals in the urine of 110 participants was evaluated by comparing those persons who had consumed groundwater from a well with As below 10 μg/L (L group) with those who had consumed water with levels above 10 μg/L (H group). Information from face-to-face interviewing was used to explain the factors relevant to iv) a health risk assessment of these participants. This assessment consisted of two methods, namely, a deterministic of the As species and a probabilistic of As and Pb.

The As level in the Ban Khai district area ranged from <0.300 to 183.00 μg/L, accounting for 22% of forty groundwater wells, which is above the guideline value of 10 μg/L set by the WHO. The predominant species showed a pentavalent form that had been influenced by oxidation conditions and pH level (6 to 8).

Meanwhile, the Pb concentration in the whole area was found to be below the WHO guideline of 10 µg/L. However, the spatial distribution of the two metals was not different in the two seasons. The As case can be explained by the effect of the groundwater flow that spent time mobilizing, while the Pb case can be described by its concentration and behavior. The primary sources of As and Pb may have originated from the weathering of minerals; while in some hot-spot wells, the presence of As might have been the result of anthropogenic activities in the nearby area.

Nearly 98% of the samples showed that the presence of Pb in the urine was within the normal level of 60 µg/gCr, as established by the National Institute of Occupational Safety and Health. While the As level in the urine ranged from 5.38 to 600.86 µg/L, the levels in approximately one-third of the samples exceeded the normal level of 50 µg/L that had been set by the National Health and Nutrition Examination Survey. The groundwater consumption from the well which had high levels of As was strongly related to the As levels in the urine of participants in the H group. Meanwhile, the socio-demographic factors of these residents had no association with differences in UAs levels between the L and H groups. The health risk assessment of As species showed that the area had the predominant forms of $HAsO_4^{-2}$ and $H_2AsO_4^-$, followed by H_3AsO_3, respectively. For probabilistic risks, drinking water was a major route for both non-cancer and cancer risks. The sensitivity analysis reported that As concentration had the highest impact on changes to the health risk value. Therefore, the local residents who had high UAs level should primarily monitor their health effects to protect against any long-term health consequences, especially cancer development. Meanwhile, an alternative source of water and an effective household treatment, in particular, was recommended, along with a specific method for decreasing As^{5+} levels prior to drinking.

Keywords: Groundwater contamination, As speciation, Health risk assessment, Bioindicator, Monte Carlo simulation

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Wiyada Nilkarnjanakul

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LIST OF ABBREVIATIONS

Symbols/Abbreviations	Terms
ADD	Average daily dose
AMSL	Above mean sea level
APHA	American Public Health Association
As	Arsenic
As^{3+}	Arsenite
As^{5+}	Arsenate
AT	Average time
BW	Body weight
Ca^{+2}	Calcium
Cl^{-}	Chloride
CO_3^{-}	Carbonate
CR	Cancer risk
DGR	Department of Groundwater Resources
DMR	Department of Mineral Resources
ED	Exposure duration
EF	Exposure frequency
ET	Exposure time
Fe	Iron
HCO_3^{-}	Bicarbonate
HI	Hazard index
HQ	Hazard quotient
IR	Intake rate
K^{+}	Potassium
Kg	Kilogram
km	Kilometers
km^2	Square kilometers

Symbols/Abbreviations	**Terms**
LADD	Lifetime average daily dose
m	Meters
Mg^{+2}	Magnesium
Mg	Milligram
mm	Millimeter
Na^{+}	Sodium
NHANES	National Health and Nutrition Examination Survey
NIOSH	National Institute of Occupational Safety and Health
NO_3^{-}	Nitrate
ORP	Oxidation reduction potential
RfD	Reference dose
SO_4^{2}	Sulfate
SA	Skin adsorption
SF	Slope factor
TCR	Total cancer risk
WHO	World Health Organization
UAs	Arsenic in urine
UPb	Lead in urine
USEPA	US Environmental Protection Agency
µg/L	Micrograms/Liter
µg/gCr	Micrograms/gram Creatinine

CHAPTER 1
INTRODUCTION

1.1 Problem Statement

Heavy metal contaminants, particularly arsenic (As) and lead (Pb), in the groundwater have been considered to be an important issue in several studies[1-5]. Man-made products make up one of the important uses of metals in activities such as industry, agriculture and mining, and these products are commonly used in daily life. Materials making up these products often consist of chemicals, especially, heavy metals, which are used in manufacturing processes. Improper waste management can release pollutants into the environment. Furthermore, these metals can be weathered out from the parent materials, in both rock and mineral forms[6]. Since heavy metals are hard to decompose and are stable in the environment, various factors, such as seasonal variations, hydrology and topography, influence their concentration and mobility[7]. Hence, environmental factors and transport are considered in order to understand their behavior and speciation in groundwater[5,8,9].

Ban Khai District is located in Rayong province, which is in the Eastern Economic-Corridor zone. The area is of great economic importance to Thailand, because of its rapid growth of industrial estates and communities. Furthermore, the land use of the agricultural areas consumes a higher proportion, as compared to the other sub-districts. One of the important water sources is groundwater, especially from the Rayong Basin area, which is an economically important groundwater source in Thailand. An increasing trend in water consumption may affect the groundwater levels and the interaction process of hydrochemicals in the area. A study conducted by the Department of Groundwater Resources (DGR)[10], reported that some areas had high concentrations of more than 10 μg/L of As and Pb when compared with the maximum value of heavy metals in groundwater used for drinking[11]. This finding was similar to a previous study by Ponsit[12], who found As concentrations in the range of 1.1 to 330.2 μg/L in some areas of the Ban Khai and Mueng districts, which are located in the Rayong

Basin. Although the background concentrations of As and Pb were low, the characteristics of geogenic rock, groundwater flow and human activities in the Ban Khai area may influence the mobility and accumulation phases of these metals. Therefore, groundwater use may probably result in adverse effects on human health.

The people who daily use As and Pb contaminated groundwater may experience any of various negative health effects. The signs and symptoms include such acute effects as fatigue, vertigo, abdominal pain and weight loss[13]. In the case of long-term exposure, they can experience health problems in the form of chronic diseases, such as neuropathy, birth defects, autism and cancer. Individual factors, such as the mechanisms of chemical toxicity, human behavior, related congenital diseases and dietary consumption, are associated with toxic responses[14-16]. Although the speciation can cause different toxic levels, the health risk assessment is commonly evaluated by using the total concentration. The risk value may be an overestimation, because only some of the species can cause a health impact[17]. For instance, the arsenite (As^{3+}) form has a greater toxic impact on health than arsenate (As^{5+}).

Understanding and insight in the toxicokinetics of the human body, the individual factors and their behaviors are going to be needed for further consideration before any additional information can be established as trustworthy. Moreover, a deterministic health risk is evaluated as a point estimate, while various studies have been carried out using the Monte Carlo simulation to predict health risks by using random variation[18,19]. Therefore, this study has been focused on i) determining the concentration of Pb and As speciation in groundwater and their distribution in Ban Khai District, Rayong Province, Thailand; ii) observing the association between concentrations of these heavy metals and hydrochemical parameters in groundwater; iii) investigating the relationship between As and Pb concentrations in urine as a factor affecting health; and iv) estimating health risk assessment including As speciation and probabilistic health risks from groundwater drinking and dermal exposure using the Monte Carlo simulation. The results are intended for use as information for the authorized officials in order to enable them to monitor and manage the water supply and the health-surveillance system for the purpose of protecting human health.

1.2 Study Objectives

General objectives

To study the spatial distribution of As speciation and Pb in groundwater and evaluate the bioindicator of local people including predicting their health risks in Ban Khai District, Rayong Province, Thailand

Specific objectives

1.2.1 To observe the concentrations of As speciation and Pb and their spatial distribution in groundwater between wet and dry seasons

1.2.2 To investigate the association between As speciation and Pb in groundwater and hydrochemical parameters such as pH, EC, DO, ORP, cations and anions

1.2.3 To determine the association between urinary As and urinary Pb and their factors affecting of residents in the area

1.2.4 To evaluate the potential health risk from groundwater exposure via oral and dermal absorption using two approaches: As speciation and the Monte Carlo simulation technique

1.3 Research Hypotheses

1.3.1 The seasonal variation was influenced by heavy metal concentrations in groundwater.

1.3.2 The hydrochemical parameters were affected by the As speciation and the concentration of Pb in groundwater.

1.3.3 The concentration of heavy metals in the urine depended on the heavy metal concentrations and the behaviors of consumers.

1.3.4 The health risk values were predominant in residents who used groundwater from the well with high heavy metal levels.

1.4 Definitions of Terms

1.4.1 "Heavy metals" refer to arsenic (As) and lead (Pb)

1.4.2 "Speciation" refers to total arsenic, arsenite (As^{3+}) and arsenate (As^{5+})

1.4.3 "Cations" refers to Ca^{2+}, Mg^{2+}, Na, K and Fe

1.4.4 "Anions" refers to HCO_3^-, SO_4^{2-}, NO_3^- and Cl^-

1.4.5 "Exposure assessment" refers to two pathways: i) oral exposure and ii) dermal exposure

1.5 Scope of study

1.5.1 The study area is located in Ban Khai District, Rayong Province, in the Eastern Region of Thailand. The groundwater wells, which were located within a 490 square-kilometer area of the Rayong basin, were purposively selected.

1.5.2 The factors affecting the heavy metals concentration in groundwater included topography, meteorology and hydrochemical parameters (pH, EC, DO, ORP, cations and anions).

1.5.3 The spatial distribution of heavy metals in groundwater was collected and investigated between the dry season (March 2019) and the wet season (August 2019).

1.5.4 Questionnaires and urine samples were collected in January of 2020 from the local residents as additional information to explain the factors affecting to health risk assessment.

1.5.5 Health risk assessments from groundwater consumption through drinking and dermal exposures were evaluated.

1.6 Expected outcomes

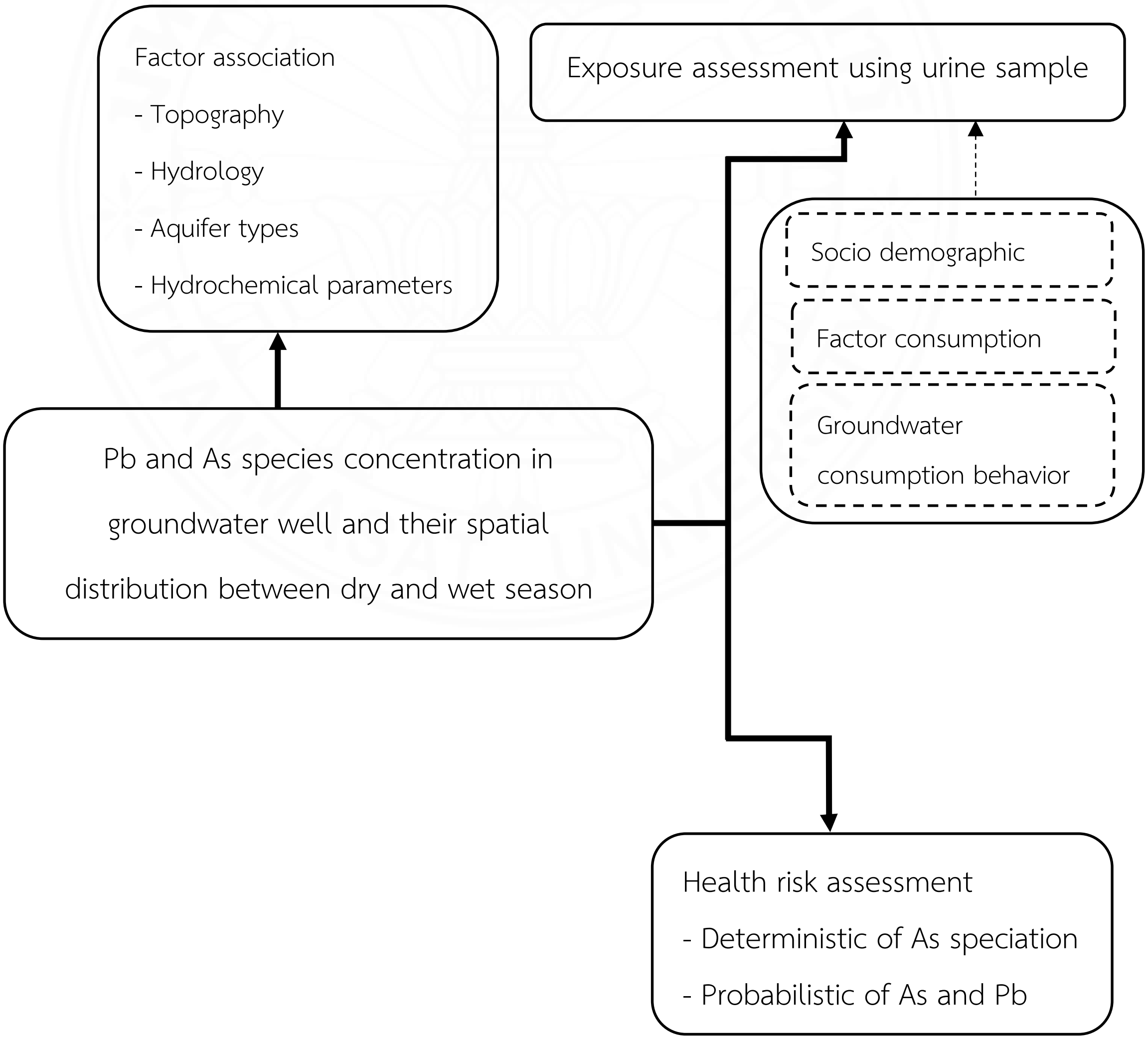
1.6.1 The information on heavy metals and their spatial distribution was collected in order to manage the water supply for residents in the area.

1.6.2 The association between heavy metals in groundwater and their hydrochemical parameters was established in order to select the appropriate treatment methods that would be needed to reduce their concentrations before drinking.

1.6.3 The presence of heavy metals in their urine was determined in order to understand the exposure from groundwater consumption and the relevant factors affecting such as socio-demographics, health information and groundwater-consumption behaviors.

1.6.4 The probabilistic health risks of these residents who consumed groundwater in the area were assessed in order to monitor the health risks of these people and manage the water supply in the area where they resided.

1.7 Conceptual framework



1.8 Limitations

1.8.1 This study was not focused on determining Pb speciation because of a lack of instrumental analysis.

1.8.2 Since the reference dose (RfD) and slope factor (SF) of As species were not established by a relevant organization, such as the US Environmental Protection Agency (USEPA) or the World Health Organization (WHO), the same values as of total As were used for both As species.

CHAPTER 2
LITERATURE REVIEW

2.1 Heavy metals

2.1.1 Arsenic (As)

I. Properties

Arsenic is an element with atomic number 33 on the periodic table. The symbol of arsenic is As. Its atomic weight and density are 74.922 g/mol^{-1} and 5.776 g/cm^3 at 273.15 Kelvin (K), respectively. At standard atmospheric pressure (atm), the boiling point of As is 887 K; it changes phase directly from a solid to a gas. At 28 atm, the melting point at temperature 1090 K can change As from a solid to a liquid phase. It is found naturally in the earth's crust. It can be classified into three groups such as arsine gas, organic and inorganic. The most common valences are the oxidation states of As, such states as metalloid arsenic (0 oxidation state), arsenite (3 oxidation state), arsenate (5 oxidation state) and arsine gas (-3 oxidation state).

II. Groundwater Sources of As

As can occur from the erosion of geogenic materials, including igneous, metamorphic and sedimentary rocks, since it is widely distributed in the Earth's crust. The As level in groundwater is generally approximately 1 μg/L. As compounds are present in general forms, such as arsenic acid (H_3AsO_4), arsenous acid (H_3AsO_3), arsenic trioxide (As_2O_3) and arsine (arsenic trihydride AsH_3). The reaction process in water can result in the dissolving of As compounds (solid phases), particularly sulfide realgar (As_4S_4), orpiment (As_2S_3) and arsenopyrite (FeAsS). Additionally, the characteristics of topographies, such as the plain area, lowland and alluvial sediments, are related to the levels of As that may be present[20].

On the other hand, there are man-made sources that can generate As in the environment along both direct and indirect pathways. Many countries, particularly in Asia, still observe As concentrations of 10 μg/L above the standard for drinking. High concentrations are commonly presented in areas located near anthropogenic sources. The industrial and agricultural activities are playing important roles in the contamination of groundwater, because the products and wastes contain these heavy metals[2,21]. Furthermore, large amounts of As in the soil and groundwater in the mining areas are reported by many researchers, while the concentrations that are present depend on the mineral types[22-25]. Combinations with other mineral ores, such as Pb and tin, are commonly a source of As. Some studies have shown that As in groundwater is usually found in colluvial sediments ranging from 1 to 5,000 µg/L because of disseminated sulfide ores in granite and alluvial in tin-mining areas[26,27]. The drainage and tailing pond are also contaminating the groundwater as surface runoff[28]. The major mineral component of arsenopyrite is a predominant source of As. Similarly, As contamination was found in Thailand near the areas where there was mining activity, including Nakhon Sri-Thammarat, Rayong, Saraburi, Pichit and Kanchanaburi Provinces[26,29].

III. Factor Affecting As Mobilization in Groundwater

a) Topography and meteorology

Geography and lithology are important factors affecting the concentration of As. Most As is commonly found in unconsolidated rocks and sediments, because it can be adsorbed by iron oxides under reduction conditions and leach into the aquifer[30,31]. However, the pollutant does not move immediately after being released from the source, because it was adsorbed by the sediment and other materials. Winkel et al.[20] found that the depth was correlated with As concentration, especially at a shallow depth, possibly because of the distance of mobilization from ground surface into the groundwater well. In addition, the seasonal variation can influence the As concentration[31,32].

b) As speciation

Inorganic As is predominant in groundwater. It is generally present in two forms, such as arsenite (As^{3+}) and arsenate (As^{5+}). In terms of geochemical processes in groundwater, these are important factors in the promotion of mobilization, as shown in Fig. 2.1. In the aqueous phase, the mobilization of As may occur as a result of desorption caused by competing interactions with dissolved components. Alternatively, it may take place as a consequence of host-material phase dissolution induced by organic-compound degradation at the microbial level. This activity takes place within the contaminant plume. Hydrochemical properties such as redox potential, pH and temperature, any complex ions that may be present, the grain size, components of the soil and sediments, and major ions all affect the mobilization and accumulation of As. For example, the oxidation condition of mineral sulfide is a cause of high As. This metal can leach and move into aquifer. The distribution of As in the liquid phase is related to the redox potential as an oxidation-reduction reaction in the aquifer. As^{3+} is predominant in a reduced condition; but when oxidized, it occurs as As^{5+} [31,33,34]. Adsorption with metal oxides, particularly Fe and Al oxides, can help limit its movement in water. At a near-neutral pH under aerobic conditions, arsenic is observed in co-precipitation with iron hydroxides[33]. On the other hand, a high phosphate (PO_4^-) decreases the ability of As adsorption with metal oxides, because PO_4^- is then replaced by As^{5+}. It results in the restriction of the adsorption area. The concentration of As in groundwater increased with higher concentrations of PO_4^-.

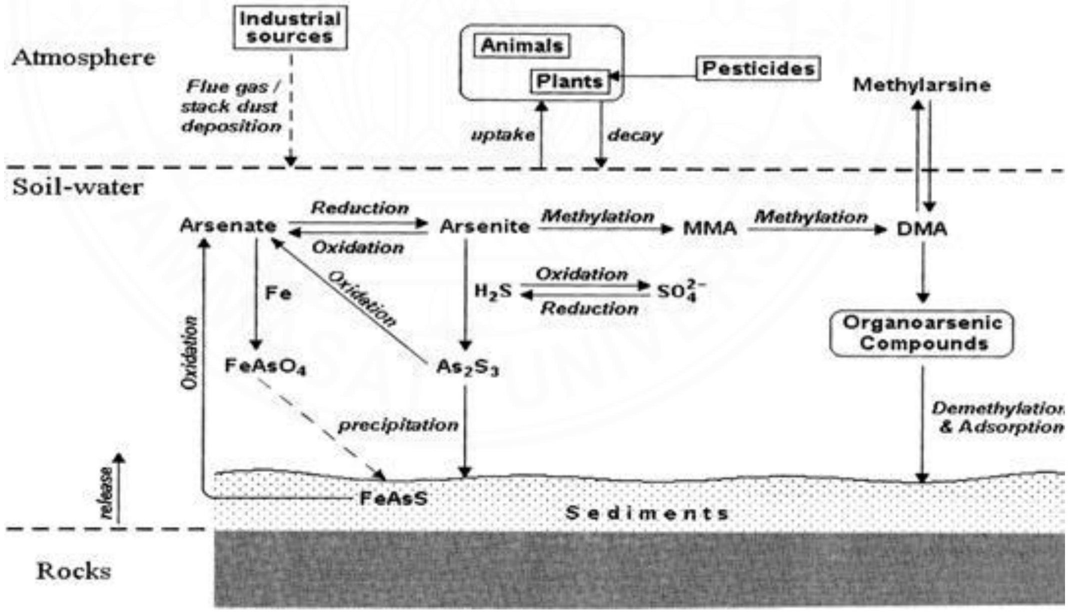


Figure 2.1 Reaction of arsenic in an aquifer[35]

c) Hydrochemical parameters

The pH value of groundwater, which ranges from 6.5 to 8.5, affects the transportation and desorption process by the oxidation-reduction potential (ORP)[15]. Several studies report that a high pH is associated with As-rich groundwater[26,36]. In the nature of As distribution, it has three reaction processes, namely, desorption at high pH under an oxidation process, desorption resulting from hydrochemical changes under a reduction process and mineral dissolution[9,37]. At a high pH and enrichment of $NaHCO_3$, As can degrade from sediment and has a high ability of mobilization in groundwater[36].

Meanwhile, the ORP can affect the mechanism and reaction process with chemicals and sediment, as well as the hydrology of the groundwater. The oxidized sulfide ore has a high ability to release inorganic As into the soil and water in the vicinity area[26,38]. Meanwhile, the weathering process of silicate and carbonate induces the desorption of As, which can then be released from the metal oxide in the sediment because of its condition of alkalinity. In addition, organic matter can leach more As at concentrated levels into the aquifer under reducing conditions, since organic compounds commonly consist of metal oxides, especially iron and sulfide minerals and pyrite. Meanwhile, the reduction condition is an important factor for As movement, particularly As^{3+} in groundwater.

Furthermore, cations and anions show a relationship with As mobilization. The dissolution of As from soluble iron oxyhydroxide can occur under an anaerobic environment because of the changing Fe-oxide structures[15,39]. High As^{3+} in groundwater is predominant as a species in an alluvial aquifer. A rich presence of As in groundwater results from a hydrochemical process, such as from high concentrations of Fe, NH^{4+} and PO_4^{3-} while low concentrations of SO_4^{2-} and NO^{3-} are found under a reducing condition.

IV. Health risk Assessments of As

Health risk assessments of As-contaminated groundwater are determined by the two pathways of oral and dermal exposures, and include the following biomarkers:

a) Oral route

Many studies have investigated risk assessment of As exposure in contamination areas throughout the world[14,32]. Phan et al.[15] compared the As contamination in groundwater among three types of community areas, namely, uncontaminated areas, moderately contaminated areas and extremely contaminated areas, which are located in the Mekong river basin. The potential health risk and the individual risks were characterized by two variables, one of which was the variable for the age group (children and adult) and the other for sex (male and female). Neither variable indicated an influence to risk value; the important factors, instead, were average daily dose and As in groundwater. In addition, Saha et al.[16] presented data showing that the ingestion rate and exposure duration had an association with health risk estimation. These findings corresponded to the results of a study conducted by Liang et al.[40], who demonstrated a high correlation between the As level in large contaminated areas and the risk value of residents. The people in the communities have shown both carcinogen and non-carcinogen effects. In addition, the shallow groundwater well was the first primary point in which a higher concentration was found than in a deep well, because this aquifer had a connection to a soil layer. Meanwhile, in a previous study, observations were made in the groundwater located in the intensity area of the chili fields of Ubon Ratchathani Province, Thailand. These results demonstrate that As concentration in the groundwater and in the urine of farmers were positively correlated with health risk values[41].

b) Dermal contact

There were a few studies that had conducted an assessment of health risk from skin exposure to As in groundwater. This pathway can lead to exposure by daily-life activities such as showering and hand washing. Households which use groundwater for domestic use had very low total cancer risk (<1%)[16].

c) Biomarkers

Various studies had investigated As concentrations in humans, such as in the urine, nails, and hair, which would be usable as biomarkers[42,43]. As was observed in hair samples, it ranged from 3 to 10 μg/g in persons who were exposed to As contamination in groundwater. These individuals had been afflicted with symptoms caused by ingesting shallow groundwater with rich contents of naturally occurring arsenic. The author concluded that the As concentration in hair and the ingestion rate have an association, but no correlation with age or sex[44]. Moreover, the level of inorganic As in scalp hair was relative to the daily intake by people and was affected by overdosing and long-term intakes of inorganic As[15]. In the case of urine, it was used as an indicator for finding As levels via the oral route. The urine samples were collected to determine indicators of exposure from subjects who had been using groundwater as a drinking water. The investigation of As in urinary samples from the children who had been drinking water from the well in agricultural areas was showed that there was a positive association between As levels and HI values[45]. Furthermore, other relevant factors included smoking, age, sex, occupation and food and beverage consumption[45-47].

V. Effects on Health from As Contamination in the Groundwater

The entry of As into the body has a relationship with the biologic state of the human body. Meanwhile, different As species represent different degrees of toxicity. The toxicity level depends, firstly, on whether the As is in an inorganic or organic form. Other influential factors of toxicity are its valence state, solubility, physical state and purity level. Also relevant to As toxicity are rates of absorption and elimination[48]. Inorganic As is normally more toxic than organic As. Also, a valence of III results in a higher toxicity level than a valence of V. The more rapidly absorbed forms of As have high levels of toxicity, while the forms that are most rapidly eliminated are generally less toxic. The biotransformation of inorganic As in the body consists of the following four steps[13]:

- **Absorption**

Generally, As concentration in the body can excrete about 70% of the ingested As from drinking water via the urine. A soluble trivalent arsenic compound, constituting almost all (≈ 95%) of the ingested As , is capable of being absorbed into the gastrointestinal (GI) tract. Trivalent As enters the body through a simple diffusion mechanism, while penta-valent As enters through cell membranes via an energy dependent transport system.

- **Distribution**

Following absorption into the GI tract, As becomes widely dispersed throughout the body by the blood circulatory system. Most of the body's tissues quickly dispose of the As, with the exceptions of the skin, hair, and nails, which tend to retain it. The remaining As in the human body often appears as signs in the skin, nails and hair, because these organs are high in keratin. The sulfhydryl group is the major of component in keratin; it can bind As and expose the effect of As in the body.

- **Metabolism**

As^{3+} and As^{5+} are in a water-soluble form. They have a rapid metabolism in the GI tract. Reduction of As^{5+} to As^{3+} occurs from the oxidative methylation of As^{3+}, chemically altering it with forms of mono-, di- or trimethylated products, producing methylated products by reaction with several enzymes. This process usually occurs in the blood and in the liver. However, trivalent methylated arsenicals have been observed in the urine and pose a carcinogen effect on people who suffering from contamination with inorganic As^{3+} rich groundwater[49].

- **Excretion**

Humans normally excrete a mixed combination of inorganic, monomethylated and dimethylated forms of As, although they do not normally dispose of any of the trimethylated forms of As. Organic As has a higher rate of elimination through the urine than inorganic As. The As excretion through the primary route of the urine is via the kidneys. There are also other, somewhat less significant, disposal routes of inorganic As. Such routes include fecal elimination, accumulation of the As in the hair and in the finger and toenails, and also through skin desquamation. Another such channel of elimination is through normal perspiration. Humans can excrete approximately 70% of inorganic As within a 48-hour period[50].

a) Signs and symptoms of acute exposure

Inorganic As has a direct toxicity to many systems of the human body. The GI tract and the epithelial cells contained within this tract are among the systems adversely affected by inorganic As. The As also adversely alters the systemic enzyme inhibition of the tract, leading to profound gastroenteritis and occasionally hemorrhaging, as well. These effects can be present within minutes to hours following ingestion.

b) Signs and symptoms of chronic exposure

Chronic oral consumption of As could lead to arsenicosis, which results in skin lesions and skin pigmentation, as well as bladder, kidney and, finally, lung cancers[24,51]. Furthermore, there may be insidious occurrences of neuropathy resulting in chronic toxicity in the absence of other apparent symptoms. In addition, there may be side effects that are observed with multi-organ and multi-system interactions, culminating in such disorders as diabetes, anemia and/or leukopenia.

VI. Health hazard information for inorganic As

a) Acute effects:

The symptoms of acute As toxicity were indicative of the effects of inorganic AS on the GI tract (nausea, vomiting) and on the central nervous-system [CNS] (headaches, weakness, delirium), and also on the cardiovascular system (hypotension, shock), as well[51,52].

b) Chronic effects:

Non-carcinogen effects from As exposure were found in many organ systems, such as the gastrointestinal, cardiovascular, urinary, hepatic, dermal, nervous, hematological, endocrine and reproductive systems. The RfD of oral and dermal for inorganic arsenic was 3×10^{-4} mg/kg-day, while 1.23×10^{-4} mg/kg-day was the threshold value for non-carcinogen effects[53,54]. The term “RfD” serves as an approximation of the day-to-day oral exposure of the human population to As. This term applies to certain sub groups which, while sensitive, are not likely to be at appreciable risk of deleterious non-cancer effects during their lifetimes.

c) Cancer Risk:

The Ingestion by humans of inorganic As has been correlated with elevated risks of non-melanoma skin cancer. Inorganic-As ingestion has also been correlated with elevated risks of cancers of the bladder, liver and/or lungs[48]. Inorganic As is classified in Group A as a human carcinogen. The EPA has calculated the SF of inorganic As to be about 1.5 per (mg/kg-day) via the oral route, and about 3.66 per (mg/kg-day) by dermal contact[53,54].

2.1.2 Lead (Pb)

I. Properties

The metallic element of lead, while very soft, is also quite dense and ductile. It offers high resistance to the passage of electrical currents. It normally occurs in lead compounds and may also be found in combination with other elements. The symbol of lead is Pb, which is from the Latin name Plumbum. Pb has an atomic number of 82, an atomic weight of 207.2 g/mol^{-1} and a density of 11.34 g/cm^{3}. The melting (or fusion) point of Pb is fairly low at 600.61° K, while its vaporization (or boiling) point is 2022° K. It is very stable and hard to decompose within the environment.

II. Sources of lead in groundwater

a) Natural source

Pb is distributed in low concentrations in sedimentary rocks and soils. It is usually found in the Earth's crust at a distribution of approximately 15-20 g/kg. The elemental state of Pb rarely ever occurs. Natural Pb enrichment occurs around base metal ores, which are shown to be in the +2 oxidation state. It often appears in the mineral galena (PbS) and in the oxidation products of lead sulfide ores, such as anglesite ($PbSO_4$) and cerussite ($PbCO_3$). Pb has two forms, organic and inorganic, which occur in the usual forms found in the environment. The differences in geological features could lead to a variety of Pb levels[55,56].

b) Anthropogenic sources

Normally, Pb occurs in natural sources, but man-made uses of Pb are the major cause of increased concentrations in the environment. It is used in in a large number of metallic products worldwide, especially by industries producing lead-based paints, batteries and electronic products, and also by the steel and petrochemical industries. High Pb concentrations in groundwater tube wells is presently near areas where such complications occur as untreated industrial outflow, sewage, domestic wastes, glasswork sites and agricultural runoff[57-59]. Moreover, improper management of mining areas where there is wastewater and chemical residues, which are a byproduct of their activity, has resulted in environmental contamination. A previous study case in Klity Creek, Thailand, Pusapukdepob et al.[29] demonstrated that discharge from tailing water to the creeks and streams is a cause of Pb contamination in the environment.

In addition, electronic waste-recycling areas, landfills and dumpsites can release Pb, which is component in their material composition, into the soil and groundwater. Elevated Pb concentrations have been reported in the soil and surrounding areas of landfills because of the waste composition of these aeras. Kiddee et al.[60] showed that Pb concentration had exceeded the Australian drinking water guideline values because of the releasing of leachate from the electronic waste-plant in the area. Similarly, the study of Wuana and Okieimen[25] showed that Pb in groundwater caused the water to become extremely contaminated around dumpsite areas. Recently, a study indicated that the Nonthaburi dumpsite has poor groundwater quality and is unsuitable for drinking (with contaminants ranging between 39-55 μg/L) as a result of the diffusion from leachate through soil and groundwater, respectively. Meanwhile, the expansion of the industrial zone and landfill areas is expected to result in a contamination by Pb in the groundwater of Rayong province. Furthermore, the change in the level of the groundwater has resulted in hazards from the hydrochemical properties[10].

III. The Pb-Mobilization Factor in Groundwater

Mobilization of heavy metals in groundwater can increase the potential of heavy metal distribution in the environment. The mineral compositions can influence the change of pH when released into water. For example, leaching of limestone, which is sedimentary rock, could lead to an increased pH, while sulfide minerals can decrease the pH. The binding form of Pb is an insoluble form. It is hard for it to move within the environment[22,61]. However, some factors can influence the releasing of Pb from a solid phase into the water. The effect of pH is the primary factor for the dissolving of Pb in groundwater or precipitation into an organic form. The soluble complex forms are usually present with chlorides, hydroxyls and organics. These forms increase mobility in the liquid phase. At an acidic condition, Pb speciation compounds of OH^-, Cl^-, CO_3^{2-}, SO_4^{2-} and HS^- are found. These species have the effect of releasing the metal from the substances into the water. With anelevated pH range extending to alkalinity, Pb is predominant in various forms in the hydroxo-species. such as $PbOH^+$, $Pb_3(OH)_4^{2-}$ and $Pb(OH)_2$ (aq), as shown in Fig. 2.2[62]. A pH above 6 prevents dissolution, so that the Pb compound is therefore in an insoluble form. Moreover, Pb^{2+} binding with sulfides and hydroxides from 3 to 6 and from 8.5 to 9 of pH, respectively, can cause the metal to assume an insoluble form, as shown in Fig. 2.3[63].

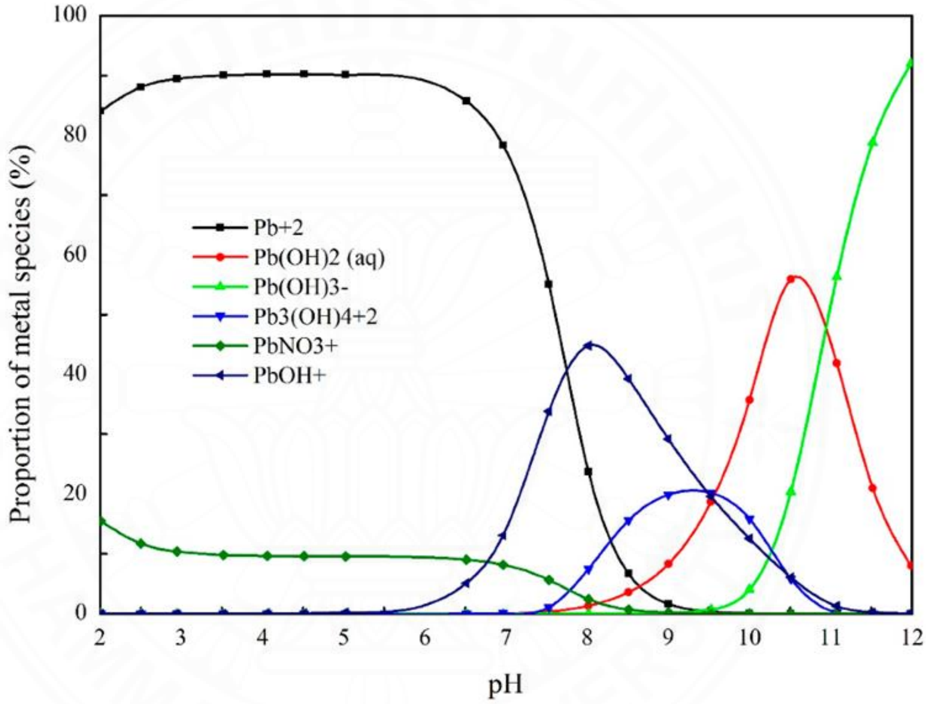


Figure 2.2 Effect of pH values on the aqueous speciation of lead in 0.01 M $NaNO_3$

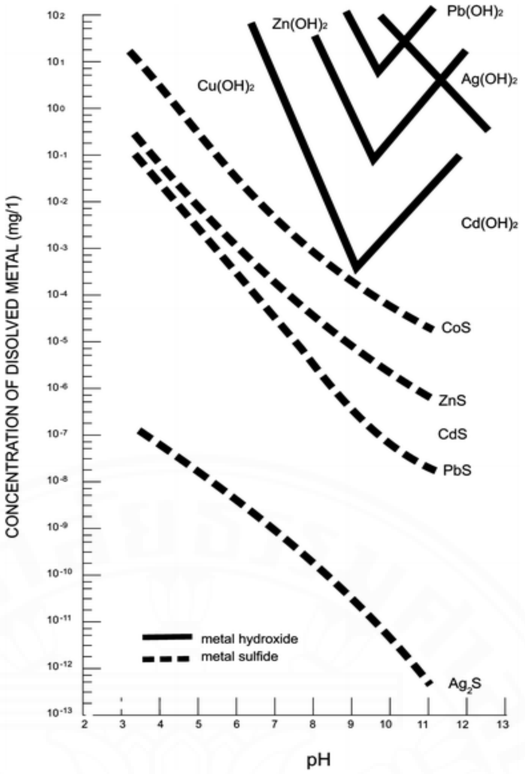


Figure 2.3 Solubility of metal hydroxides and sulfides as a function of pH

In the study of Jensen et al.[64], it was found that Pb is heavily concentrated in groundwater from the effect of leachate. It can cause the environment, such as in the soil and water, to assume an acidic condition. Therefore, organic matter might release Pb out into the environment. Dissolved lead concentrations are related to dissolved sulfates near acid-mine drainage areas. In addition, acid rain causes decreased water pH levels, since CO_2 and water react in the ambient air. Near landfill sites, leachate will usually cause the groundwater properties to assume a lower pH, while also affecting the organic solubles[22,65,66]. In the case of seawater, the major ions of the chlorides tend to combine with lead to form such compounds as $PbCl^+$. In contrast, at an increasing pH in water, Pb^{2+} is only minimally dissolved in organic matter, but is highly dissolved as a carbonate. This condition is strongly bound to the hydroxo-species form, such as $PbOH^+$. In the hydrochemical processes, these reactionshave less affect on the mobilization of Pb because of its stable form as a precipitate. The mobility has an indirect ORP. For example, if sulfur is present in an anaerobic environment, the lead can absorb it to form iron sulfide, and it is then presented as PbS, which has a immobilization form. Pb strongly adsorbs it to form hydrous ferric oxides (HFO). However, at low pH and Eh, the dissolved HFO can result in Pb being released into the environment, because it is then included with the element in its structure. Furthermore, seasonal variations, such as pre-monsoon and post-monsoon, impact metal concentration. Runoff from anthropogenic activities can result in the release of heavy metals, but only in a diluted form[58,67].

IV. Health risk assessments of Pb

a) Oral route

The health risk assessment studies of lead exposure via drinking groundwater were investigated around the globe. Thus far, there still remain a number of potential health hazards to the public from abandoned industrial Pb-processing sites, such as from mines operating from outdated standards or from lead smelters. Pollutants can be induced along two main routes: oral and dermal contact, and are likely to be found in people who drink the water daily. In terms of groundwater, Pb occurs in water through contamination from man-made activities, as well as from the weathering of rocks and minerals. Industrial activities, such as mining and tailing ponds, contribute to high Pb levels in the environment around the local areas. It may be released into the environment by translocation from place to place and enter the food chain. Many cases of groundwater contamination by anthropogenic sources pose high-risk health effects[5,65]. “Klithy Creek,” Thailand, is one of the case studies that can be used to demonstrate the relationship between lead contamination from the ore-dressing plants and the health effects on the residents in the area. The study of Zulfaris et al.[56] determined health risks from the drinking water in the special Capital region of Jakarta, Indonesia, which is located in the flat plains and slope areas. Contaminated Pb was founded in many groundwater wells. The RfD_{oral} for lead is 3.5×10^{-3} mg/kg-day[41].

b) Dermal exposure

Exposure to inorganic Pb compounds via skin contact results in a lower absorption rate than other routes. In contrast, organic Pb as a solvent form has a higher rate of absorption through a dermal route that depends on the fatty acid. It is normally found in cases of people who are exposed to fuel combustion more than groundwater contamination. Dermal contact from inorganic lead can cause a non-cancerous risk. The study involved only minimal investigation via this route because of the low or nearly non-effect it has on human health[16]. The RfD_{der} was 5.25×10^{-4} mg/kg-day[68].

c) Biomarker

For the determination of Pb accumulation in the human systems, the Pb samples are often collected from biological specimens, such as blood and urine. The presence of any acute effects is shown in nail, hair, blood and urine samples[69]. These biomarkers are used as a screening test in the workers or people who are exposed to lead and who suffer the intake of lead into their bodies within a short time[70-71]. The confounding factors, such as smoking habits, their occupations, their sex and age all affect the concentration levels of Pb in the urine Pb[72,73].

V. Health Effects from Lead Contamination in Groundwater

The principal routes of exposure and absorption of Pb in groundwater are through oral and dermal contact. The biological state of Pb in the body results from a number of different factors. Pb accumulates in the body over a person’s lifetime and is normally released from the body only very gradually[25].

- **Absorption**

Pb absorption depends on a variety of factors, including particulate size, route of exposure, health status and biokinetics. Pb is most frequently found in an inorganic form. While inorganic Pb is not metabolized in the liver, compounds of lead that are organic are nonetheless subject to being metabolized. Most of the organic form via the oral route is absorbed.

- **Distribution**

Inorganic Pb is absorbed in several organs, especially in the bones and soft tissues. The distribution in the bodies of adult and children is not different.

- **Metabolism**

The metabolism of inorganic Pb includes complex formation together with differences in the protein and non-protein ligands. Among the principle extracellular ligands are the albumen and nonprotein sulfhydryls. The delta-aminolevulinic acid dehydratase (ALAD) constitutes the principle intracellular ligands within the red blood cells. Pb also enters into complex formation with the proteins that are in the cell nucleus and in the cytosol.

- **Excretion**

Most of the Pb that enters the body is excreted in the urine and feces while the others, such as sweat, saliva, hair and nails, and breast milk are minor routes. Dermal exposure to lead nitrate or Pb acetate is excreted in the sweat and urine.

In case of Pb in the blood and bone, the Pb concentration depends on age, physiological state and other factors. When Pb gets into the body, it moves through the blood to the soft tissues, such as the brain, kidneys and lungs, and becomes distributed throughout the body. The half-life of Pb in adult human blood has been estimated at 28 days. The primary target organ of Pb accumulation is the bones and teeth in approximately 94% of adults and 73% of children. Therefore, cumulative Pb levels can be predicted in both groups, because the system spends a long-time removing Pb from the body.

VI. Groups Vulnerable to Pb Exposure

a) Children

The oral route is the primary exposure route for children. This age group is much more sensitive than adults because of differences in behavior and physiology. They have a greater risk from Pb exposure. Children, especially infants and young children, absorb Pb in the gut at around 5-to-10 times higher rates than adults. The efficiency of absorption in the GI is elevated, while the presence of elements, such as calcium, iron and zinc, is decreased. Pb absorbs these elements and inhibits the body growth of children. It can pose a potential effect on brain and nerve development (ASTDA, 2007b).

b) Pregnant women

The level of Pb may increase during pregnancy or lactation. Considerable health effects include low birth weight, risk to fetal development and neurological effects.

2.2 Health risk Assessment Methods

The scenario of health risk consists of four components, namely, the source of contamination, exposure pathways, routes of exposure and receptors. There are four steps in the process of risk assessment. These four steps are: (1) hazard identification, (2) exposure assessment, (3) dose-response assessment and (4) risk characterization. The process proceeds as follows:

Step 1: Hazard identification

This step examines chemical data for all contaminants detected at a site. The data, as observed, are related to concentration, spatial distribution and pathways along which toxicants in the environment move from the site to potential receptor points. Data includes historical background of the particular site, land-use characteristics, information pertinent to the area in question, contaminant levels in the air water and soil, sedimentation, particulars of the environment that could affect the chemical state and movement, populations that may be adversely affected and potentially affected biota.

Step 2: Toxicity assessment

This step defines toxicity as pertininet to the dose-response relationship for each chemical of concern. Output will consist of numerical constants to be used as independent variables in the risk-calculation equations. An uncertainty analysis then follows regarding these same numbers. The next task will be to explain how this uncertainty might possibly impact these risk estimates.

Step 3: Exposure assessment

This step is a quantitative risk assessment on state and transport. This assessment involves related sources (natural and anthropogenic sources), chemical reactions (mobility), transport mechanisms (groundwater flow), transformation mechanisms (biodegradation), exposure point (groundwater well), receptors (residential consumers of drinking water) and exposure routes (oral and dermal contact).

Step 4: Risk characterization

This step pertains to characteristics of risk from chemical exposure, which can be used to conclude probability of hazards and severity of hazards in the populations under study and to estimate risks by calculating quantitative estimates of both the non-carcinogenic and carcinogenic risks to receptors for all exposure scenarios. Risks are considered as follows, with explanations of each risk:

2.3 The Relevant Researches on Health risk Assessment

Evaluation of risk is one of the tools used to analyze health risk from the contaminated areas. There are various methodologies to determine risk assessment. Most of the studies use the equation to find a risk from chemical exposure, as shown in the topic of health risk assessment[48]. This method is needed to input the variation in the equation. The results of risk calculation come from the concentration of total chemicals, such as the total presence of arsenic. Moreover, software can generate the result of risk value in many cases. It can help the user to make decisions for management of risk in the area. However, these two methods are calculated by using total concentrations of the heavy metal. It means that some speciation that cannot affect human health is included in this value. Moreover, the precipitation form has no effect on potential health risk. Recently, the study of Zhang et al.[17] in China has been developing a novel methodology by adjusting the average daily intake and combination of the morphological simulation. This work compares risk assessment of total metal concentration, speciation and modified Cr^{6+} via oral route. The concentration and activity of metal species, which are used in equations, come from the “Visual MINTEQ Simulation” software. The results show that, for the modified average daily intake, there is higher risk accuracy than there is by using a total concentration. The level of metal species poses a potential risk. Some equivalence of the species is equal to zero, which may have no effect on humans.

Monte Carlo simulation

The Monte Carlo simulation is a technique for creating a predictive model. The process of analysis begins with a generator that selects a value for each variable within the relative values of the data set produced by the model and then producing a probability distribution for all possible values. The Monte Carlo simulation uses repeated random sampling to give a probability outcome as a multiple scenario. The probability is dependent on the variable that was input into the program at that point in time[74]. It has various tools for running the Monte Carlo models, such as @Risk software and Crystal Ball software. The Monte Carlo simulations have become an important technique for risk-assessment modeling worldwide. For cases of public health studies, the simulation model is applied to forecast and predict potential risk outcomes. There are important advantages for determining the values of such variables as concentration rate, body weight, skin-surface area, duration of exposure, exposure time and exposure frequency. Most of the studies focus on using of a range of values to track the results of different simulations[75]. The possible scenario from this technique is very useful, because it is simulated from the basis of one outcome and is compared with the associated obstacles to make the decision on risk management. In the study conducted by Deng et al.[76], 42 water samples were collected. The Monte Carlo simulation was employed to obtain a health risk assessment and to determine the water quality. The probability value from a simulation of 100,000 times supported the fact that that there is a high risk associated with the contaminated water source.

Many researchers revealed that a lack of complete knowledge, toxicological parameters and exposure parameters, especially the individual exceptions caused by the environment and a person's genetics and sex, can be a cause of uncertainty[19]. The point of estimation was a commonly occurring influence leading to an underestimated or overestimated health risk value. Therefore, random variation using the Monte Carlo technique was used to reduce the randomness and uncertainty of the prediction result[77,78].

2.4 Study area

2.4.1 Rayong Province

Rayong province is located in the Eastern Region of Thailand, with latitude and longitude of 12° 37' North and 101° 20' East, respectively. It shares a boundary with Chonburi Province to the West, North and East, and the Gulf of Thailand to the South. It has a coastal length of around 100 kilometers (km) on its southern boundary. Its area is approximately 3,552 square kilometers (km^2). Geographically, the topography of Rayong province consists of a plain alternating with highlands in a wave-like surface. The North and East of Rayong consist of a sloping surface area, while the South of Rayong extends into the Gulf of Thailand, which is lowland. The average elevation is approximately 1,035 meters (m) above sea level. It has two major rivers, the Rayong River (or, namely, the Khlong Yai), with a length of around 50 km. This river has a confluence with Klong Dok Krai and Khlong Nong Pla Lai. It starts from Khao Phanom Sat and Khao Gongsong. It flows through Pluak-Deang District, Ban Khai District and Muang Rayong District, respectively, with Pak Nam Subdistrict at the end of this river before reaching into the sea. The other river, the Prasae, has a critical line length of 25 km, which starts from the mountain range of Chanthaburi Province and flows into Khao Cha Mao District and Kleang, respectively. The end of the stream is Pak Nam Prasae Subdistrict, which flows into the sea.

The climate of Rayong Province is influenced by two types of monsoon. the northeast monsoon (from mid-October to February) and the southwest monsoon during the rainy season (from mid-May to October). The effect of the southwest monsoon is in the winds. The winds bring humidity and vapor from the sea, which then spread out into the Province. The weather in Rayong province subdivides into three seasons, as follows:

- Cool season (October to February), as influenced by northeast monsoon
- Summer season (February to May), as influenced by northeast monsoon
- Rainy season (May to October), as influenced by southwest monsoon

According to the statistical annual report for the period from 1981 to 2010, there are 113 rainy days, in which the mean annual rainfall is 1,401.3 mm. The rain is at its heaviest from September to October, with approximately 204 to 216 mm. of rainfall. The mean annual temperature is 28.2 degrees Celsius.

2.4.2 Ban Khai District

The study area is 480 km^2, and is located at latitude 12 46' 00" and longitude 101 18' 00". The area extends to many districts, including the South and the southastern Mueang District, the northeastern Wang Chan District, the northwestern Pluak Daeng District and the eastern Nikhom Phatthana District. The district includes seven sub-districts and is located in the Rayong Basin. The Basin has an area of 2,200 km^2, which contains the three Rayong subbasins of Ban Chang, Khlong Yai and Sumnaktorn subbasins, although this study area pertains only to the Khlong Yai subbasin. It consists mainly of rocks of two types, consolidated rocks and unconsolidated rocks and sediments. The first group, consolidated rocks, is found mostly in the areas of the high mountain ranges, mountains, hills and some beaches. This hydrogeologic unit in the Rayong Basin can be subclassified into three subunits, the silurian-devonian, the carboniferouspermian and the triassic. The second group, unconsolidated rocks and sediments, are present in the plain area and in the flood--plainand colluvial sediments. It subdivides into four units, the alluvial deposit, the colluvial deposit, the quaternary marine and continental deposits, and the quaternary marine sedimentary rocks (Fig. 2.4).

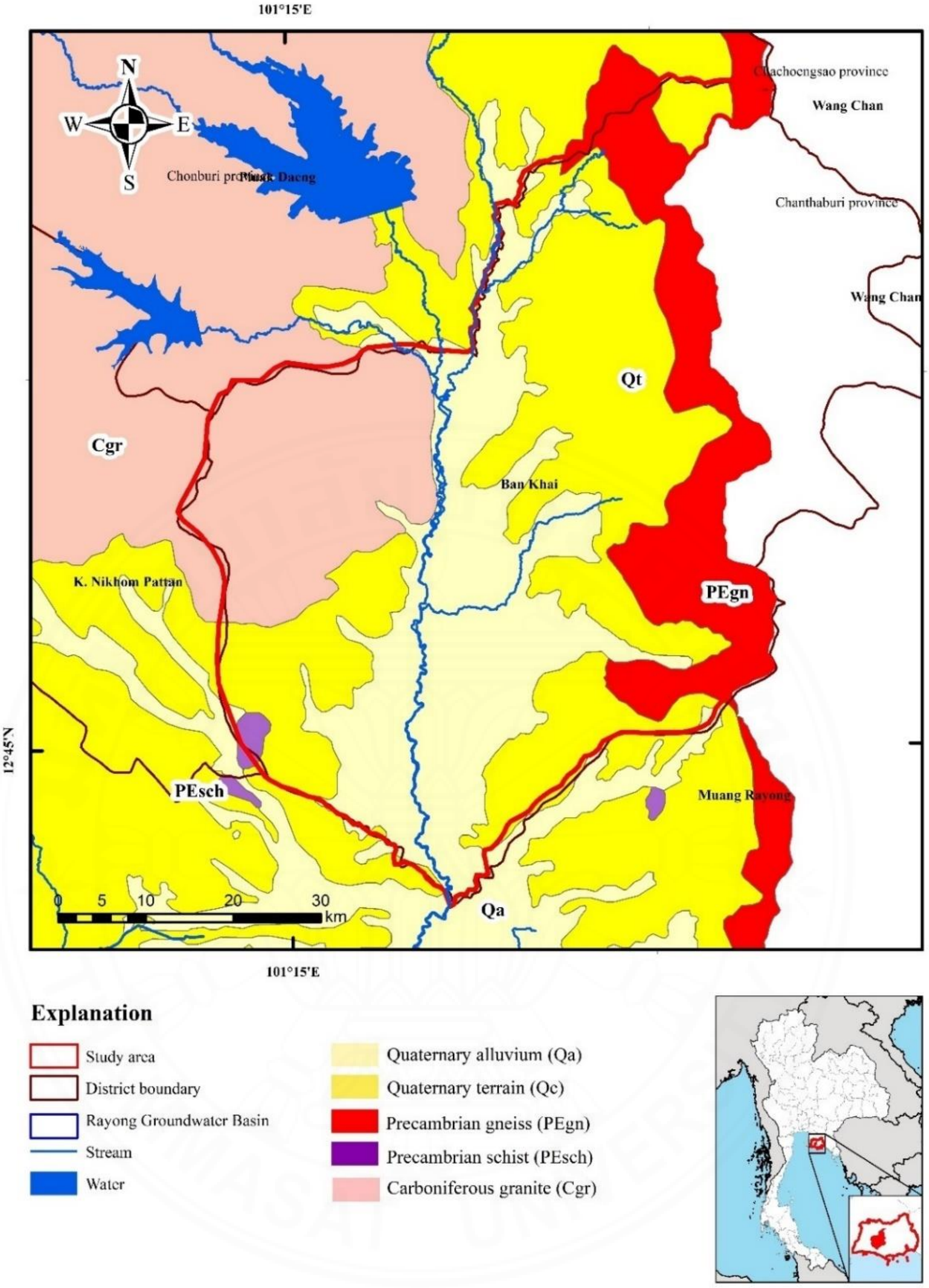


Figure 2.4 Geography of Ban Khai district

Most of the land use is agricultural and is used for rubber plantations, paddy fields and durian gardening. One landfill, which has been out of operation since 2015, is located in Nong Lalok Sub-district. Moreover, industrial zones and industries outside the estate, which are heavily involved with metals in such processes as sorting waste, metallic products and chemical-fertilizer manufacturing processes, are located in this district (Fig. 2.5).

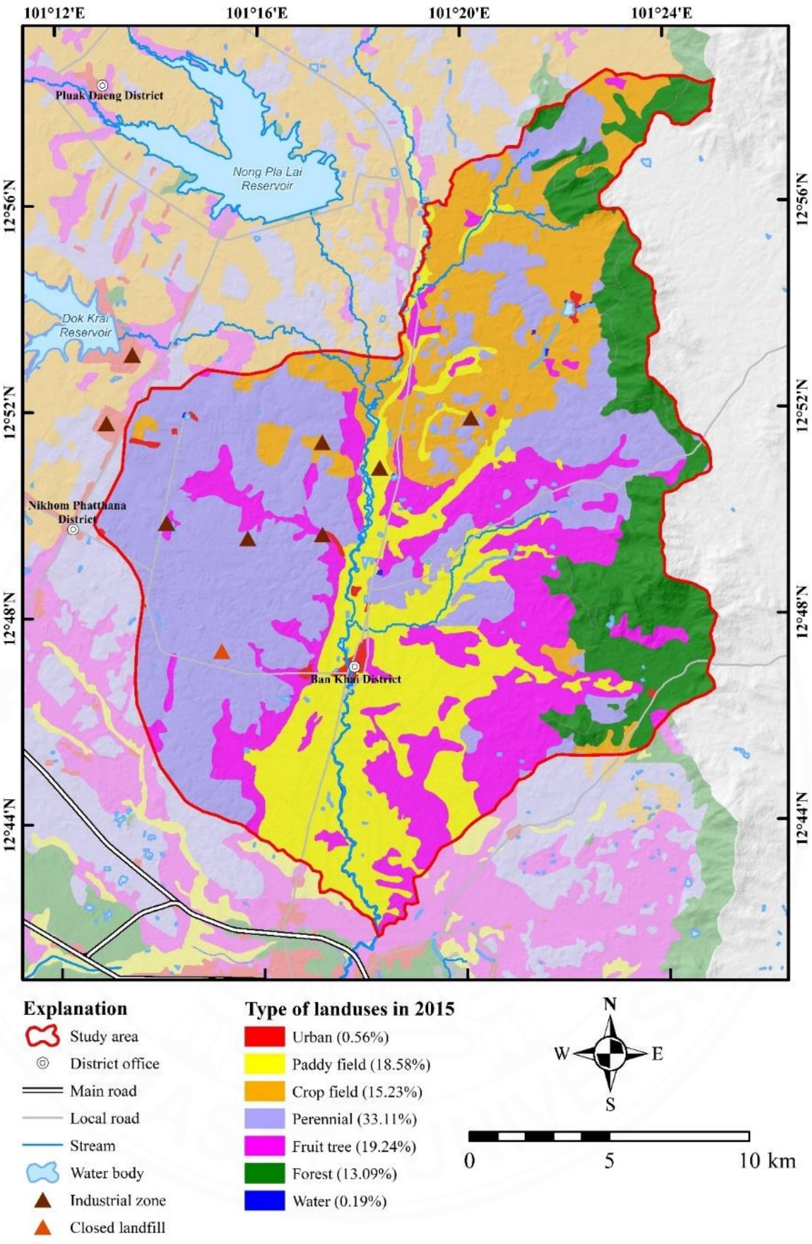


Figure 2.5. The landuses map of the study area

The background values of As and Pb in the Rayong Basin are <0.0028-0.0200 and ≤0.00007 mg/L, respectively. Most of the area in Ban Khai District consists of unsolidated rocks[79]. In the groundwater study in Rayong Province, the DGR[10] investigated the heavy metals in groundwater at such vulnerable areas as landfills, industrial areas, industrial waste disposal sites and petroleum stations. The results obtained show that As and Pb are at higher levels than allowed by the drinkingwater standard as set by the notification of the National Environment Committee, Issue 20 BE 2543 (2000). This notification had been written in accordance with the goal of supporting and maintaining compliance with the Quality of the National Environment Act BE 2535 (1992), which set standards of water quality in underground water sources. Similar results were also observed by Ponsit[12], who noted that the arsenic level in groundwater concentration ranged from 1.1 to 330.2 μg/L at 5.5 to 8 of pH in the Ban Khai area. Moreover, the speciation shows that As^{3+} is predominant in a reduction condition, while As^{5+} is in an oxidation condition. The well located in the recharge area is in this same condition, as a result of its exposure to oxygen.

CHAPTER 3
RESEARCH METHODOLOGY

3.1 The study Design

This study observed the concentrations of Pb and As speciation in groundwater wells in Ban Khai District, Rayong Province, Thailand. Furthermore, their distribution and the probabilistic health risk assessment from groundwater consumption were investigated. Meanwhile, the association of heavy metals in urine and their relevant factors were analyzed. A flowchart of this study is shown in Fig. 3.1.

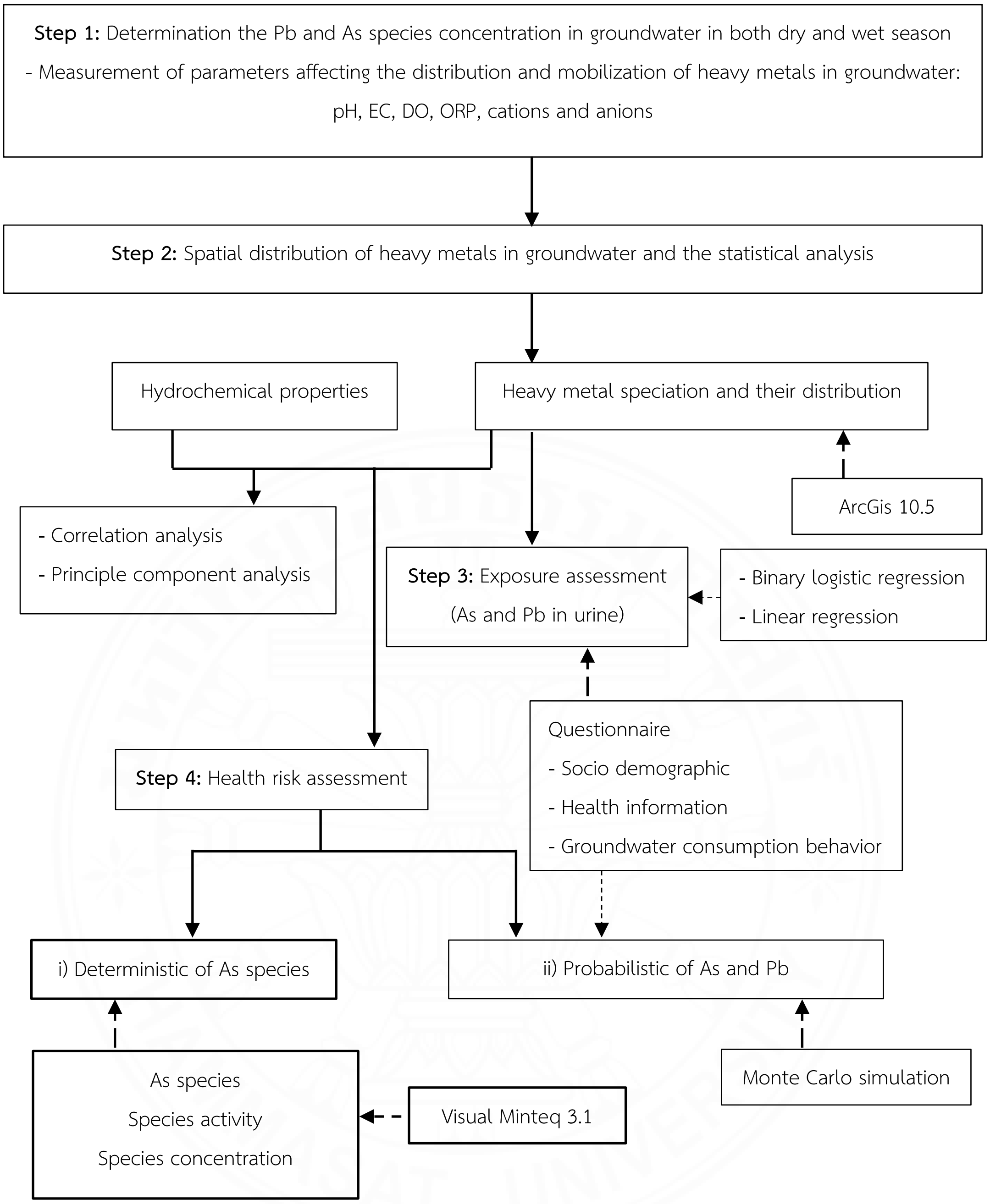


Figure 3.1 The study design

3.2 Groundwater Sampling and Analysis

There is a total of 164 groundwater wells in Ban Khai District under the control of the Rayong Basin[79]. In this study, 40 groundwater wells were purposively selected to cover the area. The study depended on accessibility to the wells during the months of March and August, 2019. These two months were understood as being representative of the dry and wet seasons, respectively. Altitude, latitude and longitude were measured at the sampling point by the Global Positioning System, ArcGis (Version 10.5). This GFS system was used to generate the spatial distribution of heavy metals in groundwater and urine by using an interpolation method. The method of choice for this purpose was the Inverse Distance Weighted method (IDW). The procedure for the groundwater sampling is shown in Fig. 3.2. The stagnant water in the groundwater wells was drained for 5 to 10 minutes before collecting a sample. After completing the flushing, the physio-chemical properties pH, EC, ORP and DO were measured immediately at the sampling point[80]. The Hach HQ30d was used to determine the pH, EC and DO values with intellical™ PHC 101 and ORP values by applying the intellical™ MTC101 methods.

Three polyethylene bottles were collected containing: i) anions (SO_4^{2-}, Cl^-, NO_3^- and HCO_3^-), ii) As, Pb and cations (Fe, Na^+, K^+, Ca^{2+}, Mg^{2+}) and iii) As^{3+}. All samples were filtrated through 0.45-µm nylon-syringe filters. Both ii) and iii) were adjusted to a pH of water of less than pH-2 with HNO_3^- to prevent metal precipitation. The As^{3+} was filtrated from the groundwater by using a disposal cartridge[81]. This cartridge can absorb only As^{5+}, but not As^{3+}, because of the selective nature of the aluminosilicate adsorbent. Hence, the As^{3+} was absolutely isolated from the As^{5+} in the bottle; HNO_3 was then added to the As^{3+}. These bottles were then labeled and stored below 4 °C for analysis[80].

The cation parameters were determined by the ICP-OES series Optima 2100DV and the PerkinElmer WinLab32TM software. The anion parameters NO_3^-, Cl^- and SO_4^{2-} were analyzed by ion chromatography, which uses the 4110D method, while the HCO_3^- was analyzed using the titration method 2320B[80]. For the heavy metals analysis (total As, As^{3+} and Pb), groundwater samples were analyzed by use of the GF-AAS (PerkinElmer AAnalyst

(600), while the As^{5+} concentration was calculated indirectly by the difference levels of total As and As^{3+}.

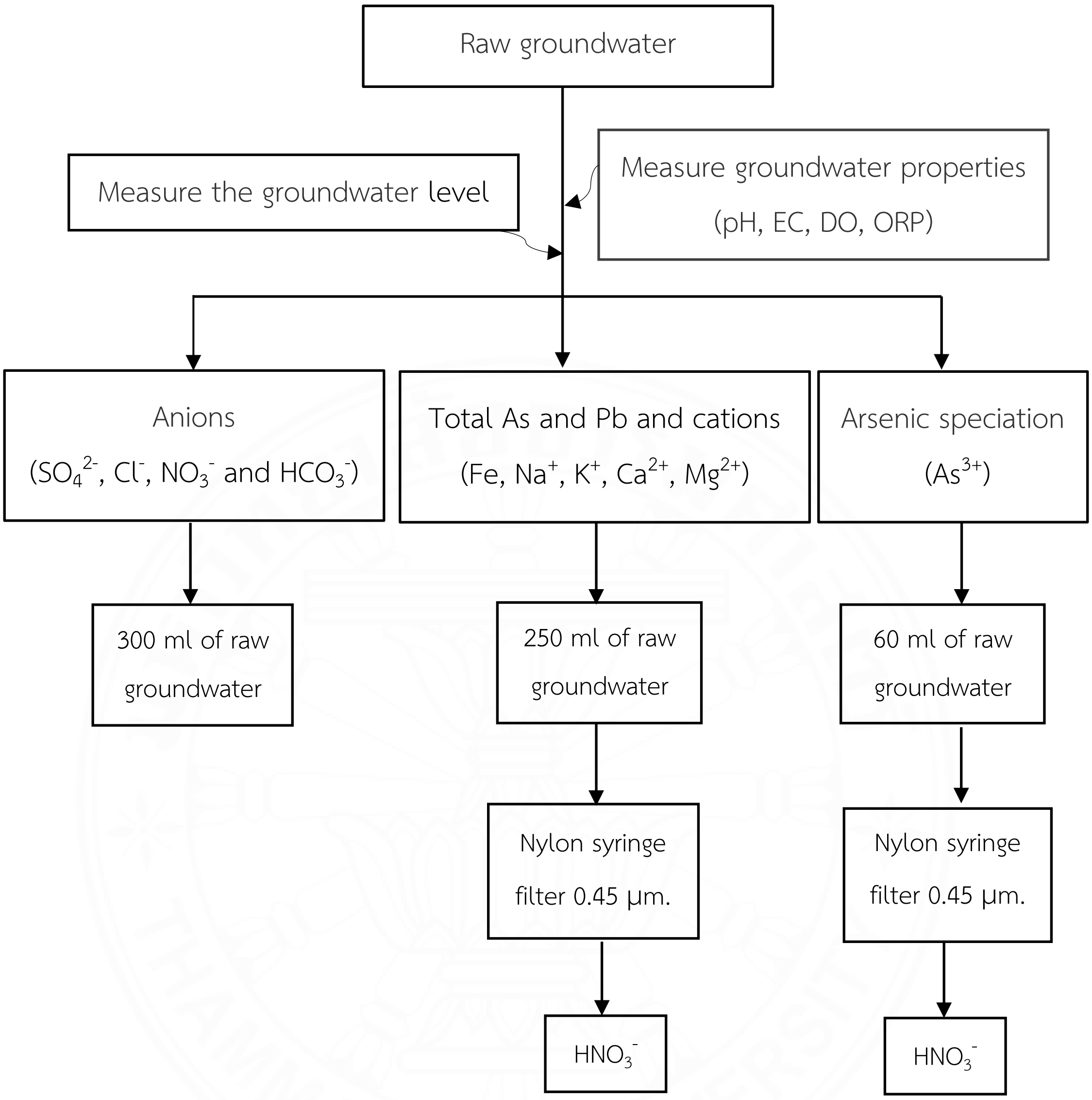


Figure 3.2 The procedure for groundwater collection

3.3 Questionnaire and Urine Analysis

3.3.1 Collection and sampling procedure

The questionnaire responses and urine samples were collected during January, 2020. The number of participants was selected as based on the stratified random-sampling method. The information received from the Rayong Provincial Statistical Office showed that Ban Khai had a population of 66,645 people in 2017, with a density of 137 persons per square kilometer. For the purpose of a sample-size calculation, the standard deviation (SD) of As in the urine found from the study of Wongsasuluk et al.[43] was used in the present study. Since this area was a rural area, most of the land uses were agricultural, and people were using groundwater for drinking and daily purposes. The formula of finite population mean was thus calculated by the following relation:

$$\mathrm{n} = \frac{\mathrm{N}\sigma^2 Z^2{}_{1-\frac{\alpha}{2}}}{d^2(\mathrm{N}-1) + \sigma^2 Z^2{}_{1-\frac{\alpha}{2}}}$$

Where

n = Number of sample size

N = Population size

σ = Standard deviation (0.14 based on Wongsasuluk et al.[43])

Z = Value from normal distribution associated with 99%
confidence level = 2.576

d = Margin of error (0.05 based on the research condition)

α = 0.01

- **The sample sizes**

$$\mathrm{n} = \frac{(66{,}645)(0.14^2)(2.576^2)}{0.14^2(66{,}645-1) + 0.14^2(2.576^2)}$$

According to the equation, at least 52 persons should be selected for the sample size. In this study, the participants were sub-classified into two groups, as follows: 55 persons of the L group, who consumed groundwater from the well containing As in the amount of < 10 μg/L; and 55 persons of the H group, who consumed groundwater from the well containing As in the amount of > 10 μg/L (using data from section 4.3.1). All participants were interviewed and urine samples were collected from them in order to evaluate the exposure assessment from their groundwater consumption and other relevant factors. The selection of the participants was based on these criteria, as follows:

- **Inclusion criteria**

i) A person who has accumulated a residence time of at least ten years in the Ban Khai area and has been using groundwater as drinking water and/or has maintained a daily consumption from a local well

ii) A person who is at least 18 years of age

iii) A person who has willingly agreed to participate in the project

- **Exclusion criteria**

i) A person who has been ingesting seafood, seaweed, instant noodles and/or canned food within 2 weeks of urine collection

ii) A person who wants to withdraw from the study during the period of data collection

iii) a person who has migrated from the living area of the study during the period of data collection

3.3.2 Urine analysis

The questionnaire was used in face-to-face interviews for the purpose of compiling: i) socio-demographic information; ii) health information; and iii) behavioral data pertaining to groundwater consumption (see Appendix A and B). The urine-collection protocol was explained and information was provided on the need for self-preparation prior to participation in this project. Urine samples of approximately 100 mL were collected during the first morning and stored frozen at -20 °C for analysis in a sterile polypropylene container. The analytical process followed the protocols for human biomonitoring methods[82]. All samples were diluted with 1:10 of HNO_3^- (v/v), while rhodium was used as an internal standard to prevent interference from the matrix effects. As and Pb in the urine were analyzed by the Special Lab Center Clinic of Thailand, using inductively coupled plasma-mass spectrometry (ICP-MS, PerkinElmer ELAN DRC-e). The presence of As in the urine (UAs) was expressed in units of µg/L, while the presence of Pb in the urine (UPb) was expressed in units of µg/g of creatinine (µg/gCr).

3.4 Quality Control

The electrometric instruments were calibrated with the standard solutions before determining the content of the samples in the study field. All sample containers were pre-cleaned with a 10% solution of HNO_3^- (v/v), rinsed with deionized water and air-dried before collecting the samples to prevent metal absorption from the polyethylene bottle surfaces. During the preparation and analytical process, an analytical-grade reagent was used in this study. For the heavy metals found during the groundwater analysis, R-square was 0.9990 of As and 0.9995 of Pb. The instrumental detection limits of GF-AAS were 0.3 of As and 0.4 µg/L of Pb, which were calculated by 3SD. The detection limit for the anions were 0.005 mg/L of Na, K and Fe; 0.001 mg/L of Ca^{2+}; and 0.05 mg/L of Mg^{2+}; and for the cations, the detection limit was 0.001 mg/L of SO_4^{2-} NO_3^- and Cl^-. In addition, the working performance standard was used to check at least one spike sample and reused after processing every 20 samples. The %recovery was within the range of 90-110%, of which 94% was As and 97% was Pb, while duplicated checkingoccurred at a rate of less than 10%.

The standard concentration ranged within 0-100 µg/L, with an R^2 of 0.9945. The instrument limit of detection (LOD) was 0.03 µg/L and the method limit of quantitation (LOQ) was 0.10 µg/L for As, while the LOD and LOQ of Pb were 0.10 µg/L and 0.50 µg/L, respectively. The analytical method was controlled fy use of the certified reference materials (Seronorm™ Trace Elements Urine L-2, Lot 1403081). For

As, the concentration was 222.04 µg/L, which was within the limits of 209.0 to 314.0 µg/L, while Pb was 85.32 µg/L, which was within the limits of 64.0 – 96.2 ug/L. The %recovery was within the range of 80 to 120% of the As and Pb. For the purpose of precise measurement observations, the %relative standard deviation (RSD) was analyzed 10 times, which included 1.0% at 25 µg/L, 1.7% at 50 µg/L and 0.1% at 100 µg/L, all of which were less than 10%. Spiked concentration was used after calibration, after every twenty samples and at the end of each analytical series in order to check and verify quality control.

3.5 Ethical Study

This study protocol, bearing the code of 053/2562, was approved by the Human Research-Ethics Committee of Thammasat University (Science), (HREC-TUSc). All participants were expected to give written informed consent and tocomplete questionnaires after the potential consequences and the urine-collection protocol were explained to them prior to enrollment. The Cronbach's alpha test was employed to assess the reliability and internal consistency of the questionnaire.

3.6 Statistical Analysis

The normal distribution was performed by the Kolmogorov-Smirnov (K-S test) normality test method before determining the statistical analysis. Mann-Whitney's U test was used to compare the median of heavy metals concentration between the dry and wet seasons, as well as their concentrations in groundwater and urine between the L group and the H group. Pearson's chi-squared was used to test the correlation of heavy metals concentration in urine between the participant group who consumed groundwater from the well with As < 10 µg/L (the L group) and the other group who consumed groundwater from the well with As > 10 µg/L (the H group). Spearman's rank correlation coefficient was determined to observe the correlation between the heavy metals and other hydrochemical parameters. In order to identify the probable sources, a principal-component analysis (PCA) was made. This analysis took place through the varimax rotation of Kaiser normalization[83]. The PCA loading was plotted in the form of clusters as a means of describing the spatial dimensions of the relevant factors. The interrelationship of the categorical data of the As in urine and relevant socio-demographic factors was illustrated through a binary logistic regression analysis, while the interaction of the As in urine and relevant factors was analyzed through a multiple linear regression. The extent of the exposure to As within the aqueous pathway of drinking, showering and agricultural activity was subject to a similar analysis. The statistical analysis was carried out by the SPSS software, PASW Statistic Base 18 for Windows. Meanwhile, the statistical significance was considered at a $p\text{-value} < 0.05$.

3.7 Health Risk Assessment

In this part, the health risk assessment was divided into two approaches, including a deterministic of the As species and a probabilistic of the As and Pb. Both approaches followed the four steps of health risk assessment. The first step, hazard identification, was to describe the potential health effects of heavy metals exposure. The second step was the toxicity assessment, which considered the relationship between metal concentrations and health effects. Meanwhile, the carcinogenic and non-carcinogenic effects that were observed to calculate health risks depended on each metal and route of exposure. Exposure assessment and risk characterization were then determined using both approaches, as follows:

3.7.1 Deterministic of As species

The As species was simulated using visual MINTEQ 3.1[84] by inputting the average values of the basic parameters of pH, ORP, temperature, As^{3+}, As^{5+}, Ca^{+2}, K^{+}, Mg^{+2}, Na^{+}, Cl^{-}, CO_3^{2-}, NO_3^{-} and SO_4^{2-} from the field investigation (see Appendix I). The output variable of As concentration and its activity were used to calculate the health risk assessment. The target metal (TM) for calculation was As. The calculated concentration of the As species in each groundwater well (C_j) was in units of μg/L, in which i is the number of target metals (i=1) and j is the number of metal species (from the output of Visual MINTEQ). The relative atomic mass (M) was 74.9216 g/mol. Meanwhile, the precipitation form was considered by using the weight calculated. The average daily doses through the oral and dermal pathways were then evaluated in accordance with Eqs. (3.1) to (3.4).

Step III): Exposure calculation

Oral exposure

1) Average daily dose of heavy metal (ADD): using the conservative equation[85]

$$\mathrm{ADD(mg/kg-day)} = \frac{\mathrm{C\ x\ IR\ \ x\ EF\ x\ ED\ }x\mathrm{CF_1}}{\mathrm{BW\ x\ AT}} \qquad \text{--- (3.1)}$$

2) Average daily dose of i speciation ($\mathrm{ADD_{i,j}}$)[17]

$$\mathrm{ADD_{i,j}(mg/kg-day)} = \frac{\mathrm{C_{i,j}\ x\ IR\ \ x\ EF\ x\ ED\ }x\mathrm{\ CF_1}}{\mathrm{BW\ x\ AT}} \qquad \text{--- (3.2)}$$

Where

C = Average concentration of heavy metal (μg/L)
$C_{i,j}$ = Average concentration of i speciation (μg/L)
IR = Ingestion rate (L/day)
EF = Exposure frequency (day/year)
ED = Exposure duration (year)
CF_1 = Conversion factor of unit
BW = Body weight (kg)
AT = Average time (day)

Dermal exposure

1) Average daily dose of heavy metal (ADD): using the conservative equation[85]

$$\mathrm{ADD\ (mg/kg-day)} = \frac{\mathrm{C\ x\ SA\ x\ F\ x\ PC\ x\ ET\ x\ EF\ x\ ED\ x\ CF_1 x\ CF_2}}{\mathrm{BW\ x\ AT}} \quad \text{--- (3.3)}$$

2) Average daily dose of i speciation ($ADD_{i,j}$)[17]

$$\mathrm{ADD_{i,j}(mg/kg-day)} = \frac{\mathrm{C_{i,j}\ x\ SA\ x\ F\ x\ K_p\ x\ ET\ x\ EF\ x\ ED\ x\ CF_1 x\ CF_2}}{\mathrm{BW\ x\ AT}} \quad \text{--- (3.4)}$$

Where

C = Average concentration of heavy metal (μg/L)

$C_{i,j}$ = Average concentration of i speciation (μg/L)

SA = Skin surface area (m^2)

F = Fraction of skin in contact with water (unit less)

K_p = Dermal permeability constant *(*unit less*)*

ET = Exposure time (h/day)

EF = Exposure frequency (day/year)

ED = Exposure duration (year)

CF_1 = Conversion factor of unit

CF_2 = Conversion factor of unit for water (L/cm^3)

BW = Body weight (kg)

AT = Average time (day)

Since some species exists in the form of precipitation in groundwater, weight value calculation of i speciation (W_i) was considering followed Eqs. (3.5) and (3.6)

$$\mathbf{r_i = \frac{A_i}{\sum A_i};\ \sum w_j = 1} \quad \text{--- (3.5)}$$

$$\mathrm{W_j} = \frac{\mathrm{c_j\ x\ r_i}}{\mathrm{\sum(M_i\ x\ r_i)}} \quad \text{--- (3.6)}$$

Where

C_j = Concentration of j speciation (mol/L) (Calculated by Visual MINTEQ modeling)

A_j = Activity of j speciation in As (Calculated by Visual MINTEQ modeling)

W_j = Weight value of j speciation in As

M_i = Relative atomic mass of As

r_j = Weight assignment of j speciation in As

Calculation of the heavy metal concentrations such as $C_{i,j}$ and C_j are calculated following Eq. (3.7).

$$c_{i,j} = \sum_{j} (1000\, \mathrm{x} C_j \mathrm{x} M_i \mathrm{x}\ n_j) \mathrm{x}\ W_j \qquad \text{--- (3.7)}$$

Where

$C_{i,j}$ = Concentration of total As speciation (μg/L)

n_j = The number of target metal from j speciation

Step IV) Risk characterization

The risk of As species could be characterized including non-cancer effect and carcinogenic effect that can calculated as presented Table. 3.1.

Table 3.1 Input parameters for risk characterization

Health risk assessment approach	**Risk characterization**	
	Non-carcinogen risk	**Carcinogen risk**
Conservative method	$HQ = \frac{ADD}{RfD}$	$CR = LADDxSF$
	$HI = \sum HQ$	$TCR = \sum CR$

Health risk assessment approach	Risk characterization	
	Non-carcinogen risk	Carcinogen risk
As speciation method	$\mathrm{HQ_{i,j}} = \frac{\mathrm{ADD}_{i,j}}{\mathrm{RfD}}$	$\mathrm{TCR_{i,j}} = \mathrm{LADD_{i,j}xSF}$
	$\mathrm{HI_{i,j}} = \sum \mathrm{HQ}_{i,j}$	$\mathrm{TCR_{i,j}} = \sum \mathrm{CR_{i,j}}$

Where:
HQ = Hazard quotient of heavy metals
$HQ_{i,j}$ = Hazard quotient of j speciation
HI = Total non-cancer risk of heavy metals
$HI_{i,j}$ = Total non-cancer risk of As speciation
CR = Cancer risk of As
$CR_{i,j}$ = Cancer risk of j speciation
$TCR_{i,j}$ = Total cancer risk of As speciation
SF = Slope factor of As
RfD = Reference dose of heavy metals

3.7.2 Probabilistic of As and Pb

In this approach, probabilistic health risk was carried out by use of the Monte Carlo model in Excel software using @RISK 8.2, Palisade Corporation (Student Version). The probabilistic distributions of each random variable were defined to determine corresponding mean and standard deviation by 5,000 repetitions. The interval estimation of risk values was presented as a numerical range within which an event might occur. Based on the simulation, the probability distribution of the exposure variables was assumed to take the form of log–normal and normal distributions (Table 3.2). Similar distributions were also carried out by various studies [86,87]. These distributions were inputted to predict the exposure and health risk assessment, while other parameters were fixed-point values. The health risk of As and Pb via drinking and dermal exposures are summarized in Table 3.2. The sensitivity analysis was conducted in order to evaluate the impact of the parameters and thereby identify the most influential parameters associated with health risks by use of Spearman’s correlation coefficient.

Table 3.2 The input parameters for a probabilistic health risk approach

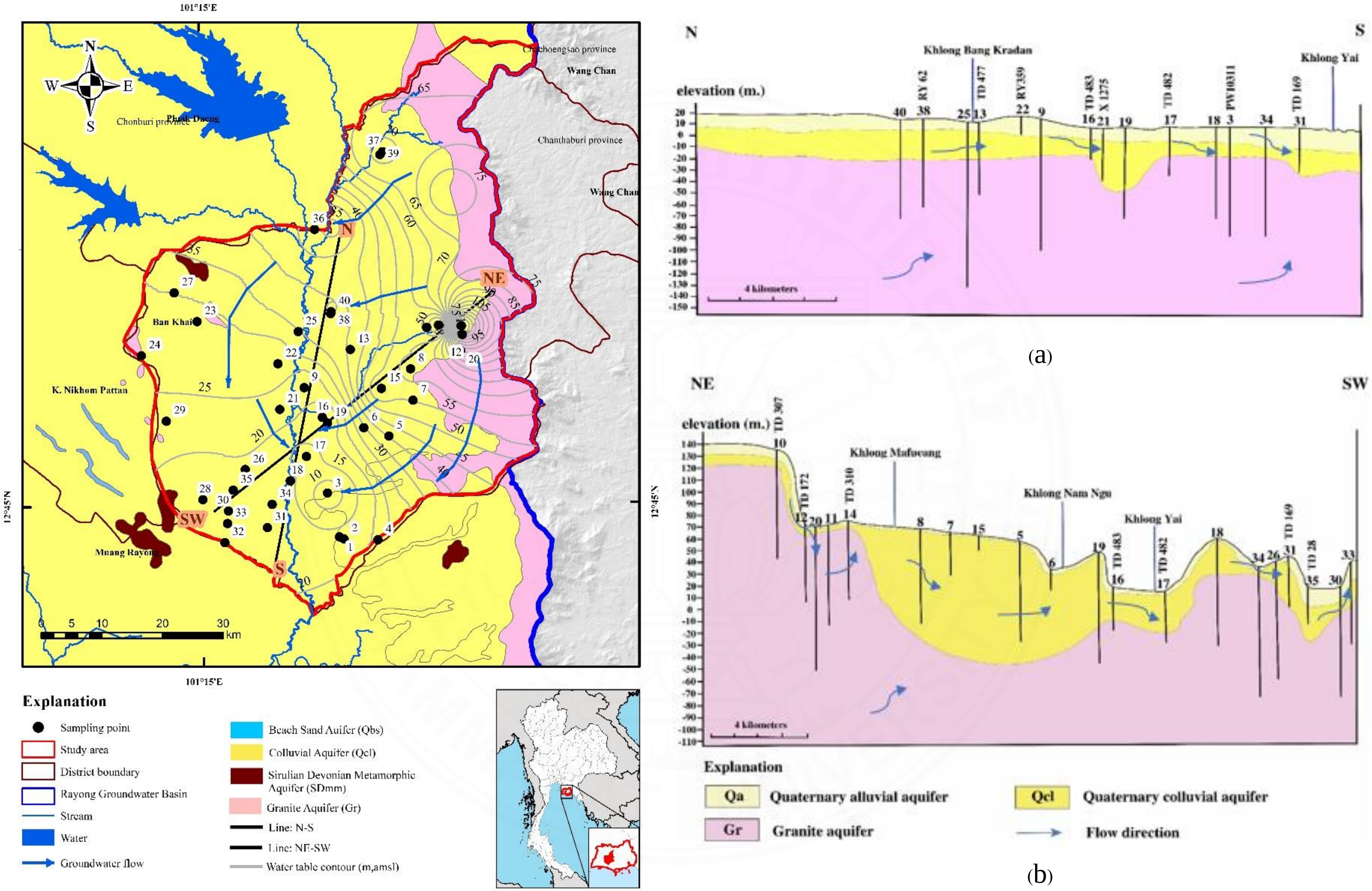
Parameters	Unit	Value	Probabilistic distribution	Reference
Heavy metal concentrations (C)	μg/L			
As concentration		16.13 ± 30.96	Log normal	This study
Pb concentration		0.67± 0.67	Log normal	This study
Ingestion rate (IR)	L/d	2.38 ± 0.72	Log normal	This study
Exposure frequency (EF)	d/y	365	Fixed value	USEPA, 1989
Exposure duration (ED)	y	19.15 ± 13.69 for drinking exposure	Log normal	This study
		20.88 ± 14.52 for showering exposure	Log normal	This study
		18.96 ± 14.42 for agricultural exposure	Log normal	This study
Conversion factor from μg to mg (CF_1)		0.001	Fixed value	
Unit conversion factor (CF_2)		0.001	Fixed value	
Skin surface area (SA)	cm^2	16,746.08 ± 1898.61	Normal	This study using USEPA, 1997
Fraction of the skin in contact with water (F)		0.925 for showering	Fixed value	Yu et al., 2010
		0.11 for hand exposure		
The dermal permeability constant (K_p)		0.001 for As	Fixed value	USEPA, 2004[85]
		0.0001 for Pb		
Body weight (BW)	kg	62.81 ± 12.62	Normal	This study
Average time (AT)	d	AT = ED in days for non-cancer risk	Fixed value	
		AT = Life time span; 76.5 y in days for cancer risk		Office of the National Economic and Social Development Council., 2019

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristics of the Groundwater Resource

Groundwater resources in the Ban Khai District, Rayong Province, involve two types of hydrologic units, those with consolidated aquifers and those with unconsolidated aquifers (Quaternary colluvial aquifer; Qcl aquifers). Consolidated aquifers (granite aquifer; Gr aquifer) consist of a permian-carboniferous meta-sediment aquifer, a silurian-devonian metamorphic aquifer, a precambrian metamorphic aquifer and a granitic aquifer. The other aquifier type comprises an alluvial aquifer, beach aquifer and colluvial aquifer. The 40 groundwater wells were sub-classified into two types, 13 wells of Qcl aquifers and 27 wells of Gr aquifer (Fig. 4.1). The depth of these wells ranged from 13 to 104 m in the Qcl aquifer (an average of 46 m) and from 36 to 150 m in the Gr aquifer (an average of 88 m). The groundwater levels ranged from 2.5 to 13.5 m and from 1.8 to 10.56 m from ground level during the dry and wet seasons, respectively. In this study, a total number of 80 groundwater samples were collected during the two seasons, including 40 samples for the dry and 40 for the wet seasons at the same sampling points.



(a)

(b)

Figure 4.1 Hydrogeological map with groundwater level and cross-section line in the study area of the Rayong Basin (a) N-S line and (b) NE-SW line[88]

4.2 Hydrochemical Properties

4.2.1 Physicochemical properties

The physicochemical properties are shown in Table 4.1. When considering the result as an overall yearly collection, the pH of the groundwater samples ranged from a slightly acidic pH of 5.25 to a slightly alkaline pH of 8.82. The median of pH values is shown to be near-neutral. However, 14 of the groundwater samples in the wet season and 19 of the dry-season samples were not within the pH range of the drinking water guideline[11]. The pH level was correlated with the values of EC and DO. A change in the pH value can affect the water condition by the influence of the ion reactions. Meanwhile, the EC was representative of the ions, including both anions and cations. Under a low pH condition, a decrease in the DO level was shown to occur by the redox reaction of water, which was caused by the electron transfer between hydrogen and oxygen. In the annual sample collection, most samples were predominantly in an oxidation state with a positive value. Higher amounts of oxygen may result from the influence of pressure by the pumping of well water. In contrast, some of the sampling points (Nos. 6, 7 and 15 at the well) had a more negative value of redox potential. These three wells were in the form of a hand-pump well, and their well depth ranged from 18 to 36 m from the surface. The water color showed a clear yellow shade of turbid sediment, while the other samples were clear and colorless. Similar results were found by Figura et al.[89], who explained the relationship of the microbial mechanism to the oxygen in the groundwater. Microbial respiration consuming oxygen, especially in the hyporheic zone, can cause a reduction in the amount of oxygen. Furthermore, these wells were located adjacent to the river, where its groundwater can interact with the river (Fig. 4.1). In addition, the pumping frequency also affected the factors associated with the oxidation-reduction states. Both the ORP and DO were important factors affecting the oxygen level in the groundwater. The oxidation condition presented a positive correlation with the DO value. In contrast, the reduction condition in the well resulted in a low DO value[90].

The statistical results obtained showed that the pH level was the only significant difference between the wet and dry seasons ($p\text{-value} < 0.05$). The range of pH value was 5.25 to 8.82 in the dry season and 5.37 to 8.55 in the wet season. Most of samples were weakly acidic and neutral in the dry and wet seasons, respectively. An increased pH value in the wet season may be caused by the effect of precipitation. The pH of the groundwater in the area showed a slightly acidic state that may possibly result from the effect of the rainwater. It could lead to a decrease in the pH level of the soils and the water. However, the effect on pH was dependent on the land uses in the area[79]. The results obtained corresponded to the study conducted by Ojekunle et al.[91], who stated that the emission of such gases as NO_3^-, CO_2 and SO_2 into the atmosphere in industrial areas was a common occurrence. These gasses can drop to the surface water, especially in the wet season. Meanwhile, the acid formation during the dry season can induce a decrease in the pH level after infiltration into the soil and groundwater.

Table 4.1 Hydrochemical parameters measured in the field during the dry and wet seasons

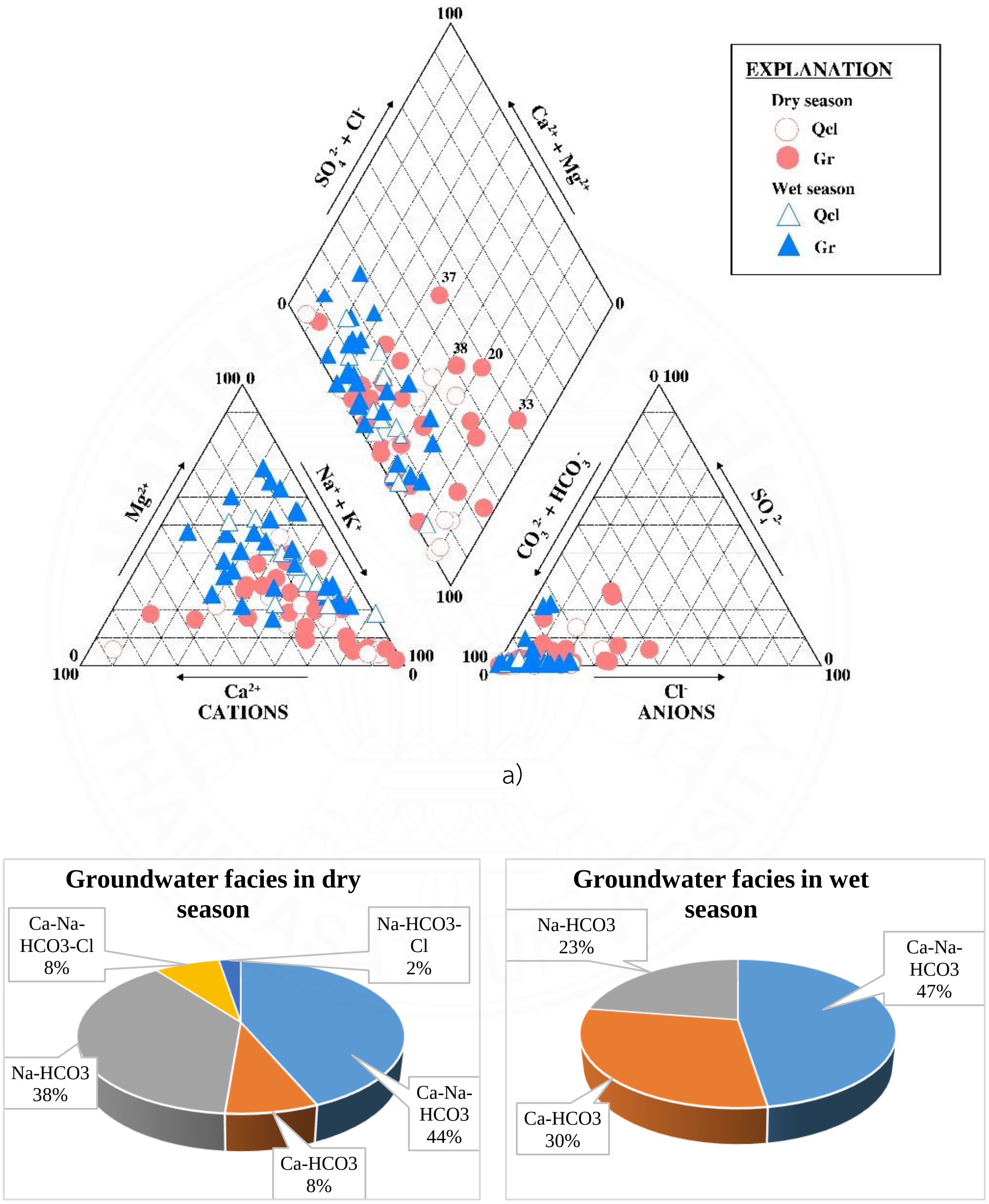
		pH	DO	EC	ORP	Ca^{2+}	Mg^{2+}	Na	K	Fe	SO_4^{2-}	NO_3^-	Cl^-	HCO_3^-
	unit	-	mg/L	µS/cm	mV	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Dry season (n = 39)	Mean	6.59	5.52	243.15	207.85	12.47	5.03	25.84	7.14	2.06	10.58	2.24	5.33	111.31
	Median	6.69	6.08	218.00	231.70	5.18	3.48	14.42	5.26	0.03	8.58	0.44	1.66	74.3
	SD	0.86	1.71	155.33	119.10	17.04	5.74	25.52	5.08	7.42	8.41	5.56	9.46	93.71
	Min	5.25	2.28	21.5	-140.1	0.19	0.15	2.08	1.36	0.01	0.48	<0.001	<0.001	4.72
	Max	8.82	7.82	553	383.9	77.55	34.53	96.07	20.81	43.47	33.7	28.30	40.60	339.0
Wet season (n = 40)	Mean	6.98	5.25	257.29	198.42	12.28	12.37	7.6	36.35	0.36	19.86	12.25	2.03	132.24
	Median	7.09	5.95	248.00	216.55	6.95	8.09	3.75	23.89	0.11	9.89	9.66	0.41	105.75
	SD	0.83	2.00	170.31	96.10	14.45	10.71	10.73	32.68	0.76	27.05	9.44	4.96	101.28
	Min	5.37	1.52	1.97	-128.70	<0.001	0.92	0.06	0.01	<0.005	0.23	0.58	<0.001	14.20
	Max	8.55	7.84	576.0	347.20	69.40	43.0	56.23	121.5	3.70	108.7	31.3	26.10	363.00
Average season (n = 79)	Mean	6.79	5.38	250.31	203.07	12.37	8.75	16.6	21.93	1.2	15.28	7.31	3.66	121.91
	Median	6.85	6.02	245.00	222.80	6.62	6.2	9.47	9.06	0.06	9.07	2.42	0.59	83.8
	SD	0.86	1.85	162.20	107.48	15.68	9.33	21.43	27.62	5.28	20.54	9.22	7.66	97.56
	Min	5.25	1.52	1.97	-140.1	<0.001	0.15	0.06	0. 01	<0.005	0.23	<0.001	<0.001	4.72
	Max	8.82	7.84	576.0	383.9	77.55	43.0	96.07	121.5	43.47	108.7	31.30	40.60	363.0
WHO guideline		6.5-8.5	-	-	-	-	-	-	-	0.5	200	50	250	-

4.2.2 Cation and anion properties

The charge-balance calculation was used to determine when to remove the samples that exceeded the acceptable error level of 10% (see Appendix D and E) [92,93]. The results of cation and anion concentrations collected in both seasons have been tabulated (Table 4.1). After calculating the charge-balance error, there were 39 remaining samples in the dry season, while 40 groundwater samples in the wet season were below 10%. The median level of HCO_3^- was found to be the highest as compared with the other ions, while Cl^- was the lowest in the groundwater. Almost all high concentrations of the cations and HCO_3^-, with the exception pf Fe, might occur from the decomposition of the parent materials[94]. Most of the parameters were within the acceptable level of the guideline value set by the WHO, except for the Fe content in some samples. Elevated Fe concentrations were present in the well of the Qcl aquifer, which may have been caused by the release of Fe mineral associated with the organic matter present in the shallow well. Although the concentration of NO_3^- was similar to the findings from the work of the DGR[79], which had surveyed the Rayong Province area, some samples showed high levels of NO_3^- as compared to the natural water sources (below 2 mg/L). In addition, chemical applications in agriculture might increase some of the nutrients needed for organic soil matter, which could be released into the groundwater system by reaction with environmental factors[95-97]. Furthermore, the biological oxidation of ammonia to a nitrite by the microbial process of nitrification was an important source of enhancing the NO_3^- level.

A comparison of the two seasons shows that most of the ions were at a predominant level in the wet season, except for Na^+ and Cl^-. Statistical results showed that the levels of Na^+, K^+, Mg^{2+}, SO_4^{2-} and NO_3^- were different in the two seasons (p-value < 0.05). These results were similar to the findings of a study conducted by Rao[98], who found that the ion concentration was mainly dependent on seasonal variations. The return flow from irrigated farm land was an important source of the increase in ions during the wet season[99]. On the basis of groundwater chemistry facies (Fig. 4.2), they can be sub-grouped into five types during the dry season, ordered in the following sequence: $Ca\text{-}Na\text{-}HCO_3$ > $Na\text{-}HCO_3$ > $Ca\text{-}HCO_3$ ≈ $Ca\text{-}Na\text{-}HCO_3\text{-}Cl$ > $Na\text{-}HCO_3\text{-}Cl$.

Meanwhile, during the wet season, they are classified into three types in the following sequence: Ca-Na-HCO_3 > Ca-HCO_3 > Na-HCO_3.



a)

b)

Figure 4.2 Hydrochemical components during the dry and wet seasons: a) Piper diagram and b) percentage of groundwater facies[88]

According to the plot of Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^-, the main source of ions was contributed by silicate weathering, while carbonate dissolution was a minor source, as shown in Fig. 4.3a[100]. Moreover, the study of Esteller et al.[101] and Rao[98] confirmed what is shown by this plot by using the reaction of the cation exchange between soil and aquifer, as follows in the equation below:

$$\text{Cations (silicates)} + H_2CO_3 = H_2SiO_4 + HCO_3^- + \text{cations} + \text{clays}$$

Under acidic conditions, the H_2CO_3 content may be rising and may have supported the chemical reaction, resulting in an elevated HCO_3^- level in the groundwater[102], as follows in the equation below:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

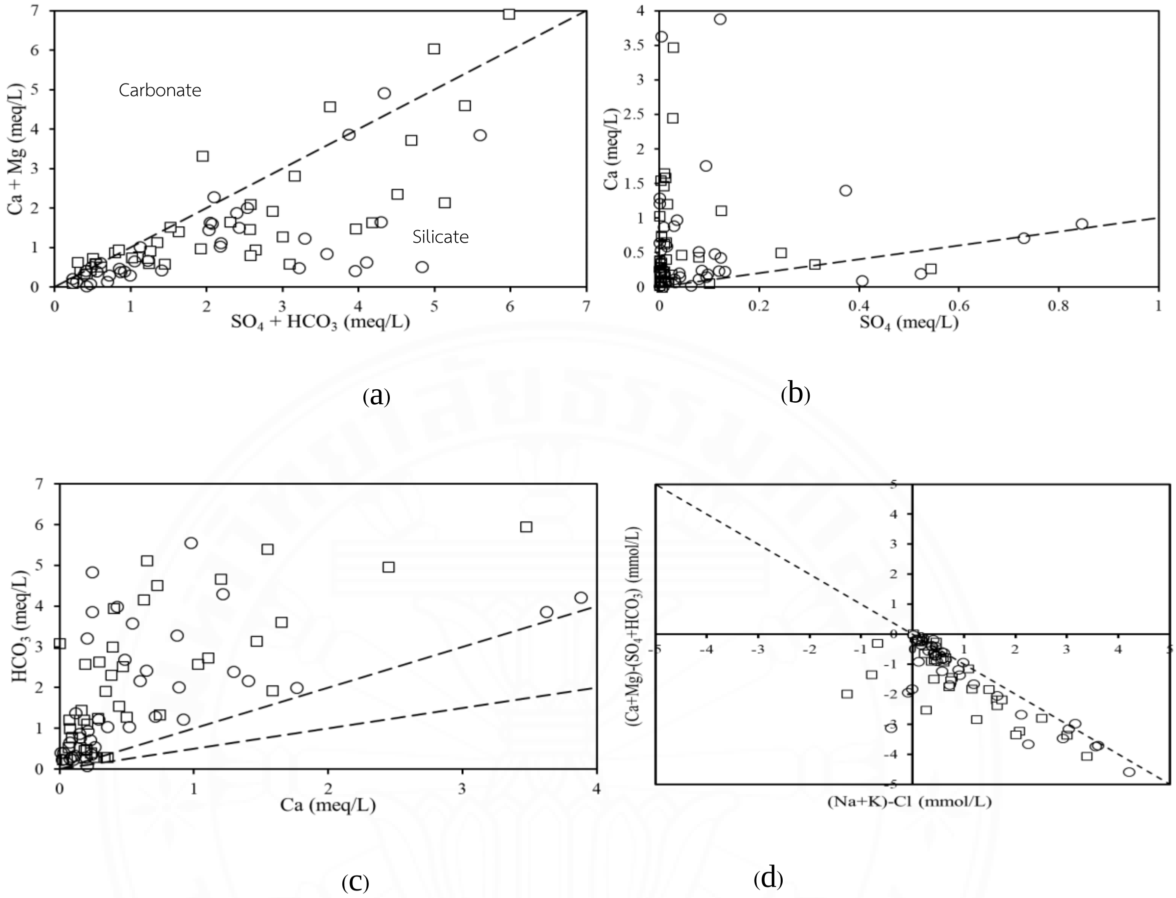
$$\text{(Calcite): } H_2CO_3 + CaCO_3 \longrightarrow Ca^{2+} + 2\,HCO_3^-$$

$$\text{(dolomite): } 2H_2CO_3 + CaMg(CO_3)_2 \longrightarrow Ca^{2+} + Mg^{2+} + 4\,HCO_3^-$$

This mechanism of Ca^{2+} and SO_4^{2-} can be explained by the mechanism of mineral dissolution, particularly dolomite and calcite, which are mostly founded in the adjacent area (Wang Chan District), as presented in Fig. 4.3c[94]. An increasing HCO_3^- concentration directly affects the pH level. Hence, it can influence the mobilization and speciation of heavy metals.

In terms of the minor groups of groundwater facies, the ion-replacement process, which was affected by the reversible reaction between Na-HCO_3 and Ca-HCO_3, can be explained[103,104]. The diagram of Ca^{2+}/HCO_3 could confirm this result (the ratio above 1), as presented in Fig. 4.3c[104-105]. This description corresponds to the findings of a study conducted by Wisitthammasri et al.[97], who illustrated the interrelationship of an ion-exchange reaction in both ions, as shown in Fig. 4.3d. Nevertheless, approximately 10% of the samples in the dry season were predominantly groups of Cl^-. The residence time and the aging of the groundwater were important factors affecting the hydrochemical composition[98]. Furthermore, the Na^+ and Cl^- were strongly related to the evaporite dissolution in the dry season resulting from the effect of the aqueous sediment interaction[106]. Moreover, the marine aerosol particles could have the effect of transmitting the Cl^-, as a result of the tropical monsoon[107,108].

For the Cl^- and SO_4^{2-} ions, the dominant facies were Na-HCO_3-Cl (well no. 37) and Ca-Na-HCO_3-Cl (well Nos. 20, 33 and 38), as shown in Fig. 4.2 and 4.2b. The presence of dominant ions may have been caused by the effluents discharged from the septic tankand some chemical input during the cultivation process[97,109]. In this study area, the groundwater might not have been affected by the seawater intrusion, because of a very low Cl^- level. Generally, the brackish water was found to have high Cl^- levels of around 500 to 1,000 mg/L[79]. This result agreed with certain published articles[110].



(a) (b)

(c) (d)

Figure 4.3 Scatter plot of (a) Ca +Mg vs SO_4 + HCO_3, (b) Ca vs SO_4, (c) HCO_3 vs Ca and (d) (Ca +Mg) + (SO_4 + HCO_3) vs (Na + K) - Cl during the dry season (circle) and wet season (rectangle), as compared to the theoretical dissolution curve (dashed line)[88]

4.3 Heavy Metals Distribution in the Groundwater and Their Factors Affecting

4.3.1 As concentration and spatial distribution

The result of the heavy metals presence in groundwater, as compared between the dry and wet seasons, is presented in Table 4.2. For the Qcl aquifers, the median level of As in the dry season was 9.952 μg/L, while in the wet season, this level was 4.859 μg/L. In the Gr aquifers, the median level of As during the dry season was 1.252 μg/L, while in the wet season, this level was 0.400 μg/L. The statistical analysis demonstrated that the two aquifer types were not significantly different in their As concentrations during the two seasons ($p\text{-value} > 0.05$). Nevertheless, the topography and environmental characteristic were also impacting the As concentration[111].

The Presence of As in groundwater may be a common occurrence resulting from the mineral dissolution and the influence of evaporation, particularly in an arid condition[26,112]. In addition, As caught within the organic matter or the clay minerals under natural evaporation could leach into the aquifer system because of the influence of microbial activity[9,59,113]. On the other hand, the dilution or lowered concentrations were most often caused by precipitation during the wet season[114]. When considering As speciation, it can be seen that As^{5+} was a dominant species, as compared to As^{3+}. The results obtained showed that concentrations of As and As^{5+} were different in the Qcl and Gr aquifers during the dry season ($p\text{-value} < 0.05$). A high As level was clearly observed in the Qcl aquifer. In addition to the characteristics of the geology, the other possible cause may have been the passage through the soil to the groundwater system.

The previously surveyed report noted that the area has a background As value ranging from less than 2.8 to 20 μg/L[79]. Approximately 78% of all wells were within this range, while the others had exceeded the guideline value set by the WHO (at well Nos. 1, 4, 6, 7, 17, 21, 22, 27 and 37). Moreover, this result was in line with the findings of Boonkaewwan et al.[110], who observed values ranging from 0.55 to 159.76 μg/L during the wet season. Meanwhile, most of the species were shown to contain

As^{3+} that may have been caused by the influence of hydrochemical values and environmental factors.

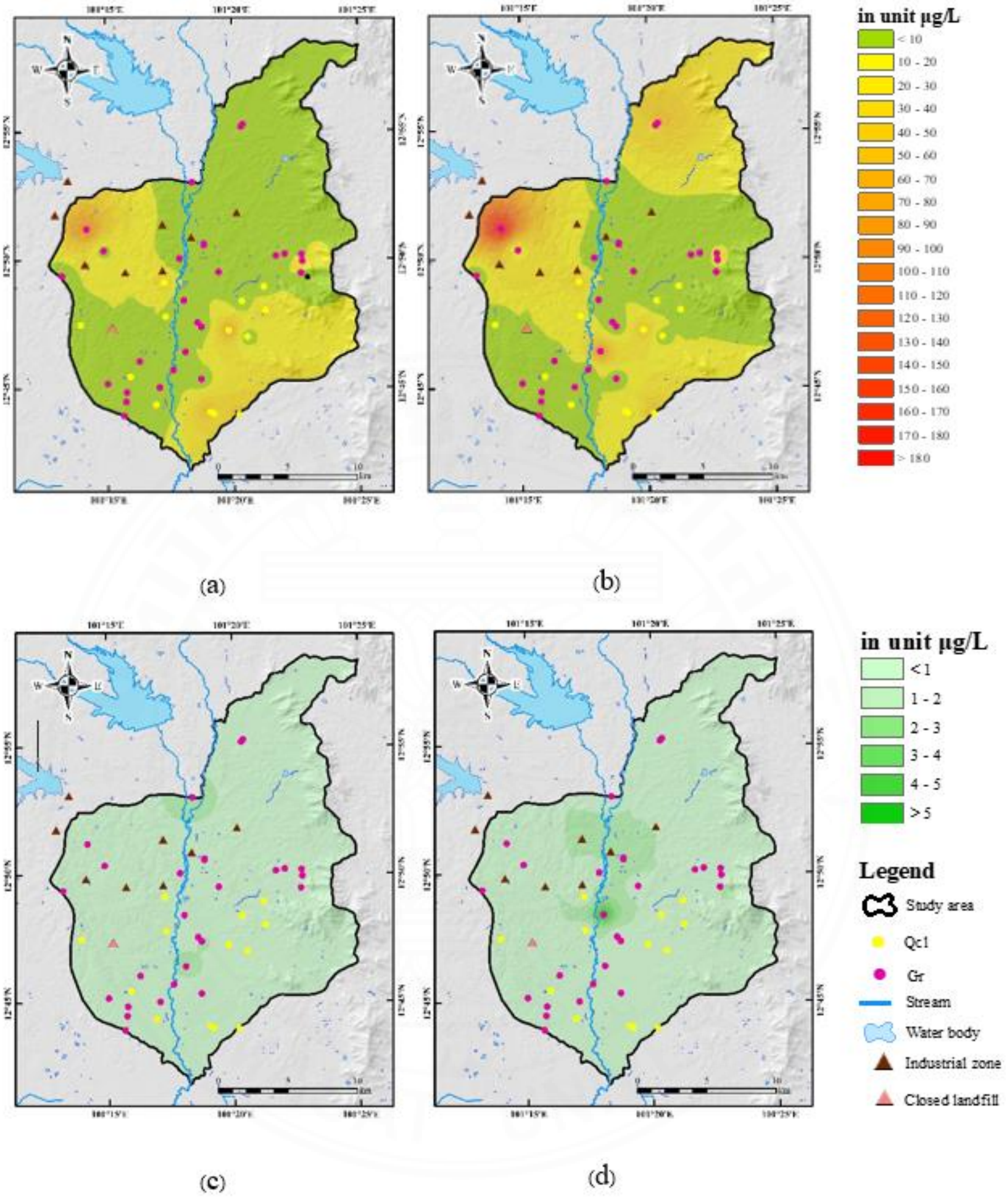
In Figs. 4.4a and 4.4b., the As distributions in the wet and dry seasons were compared. The high concentrations were shown as they occurred in the northwestern and the southeastern regions of the map. The different land-use types may be an important factor in the increase in concentration particularly, in the urbanized and agricultural areas (see Appendix C). The hot spot was observed at well no. 27 in both seasons. The highest As level was shown to occur during the wet season, which was as high as 183 μg/L. Furthermore, there are various sources that may have been the origin of the As contamination in the groundwater, including chemical input in the agricultural process, industrial activities and soil erosion[115-118]. According to the period of sample collection during the wet season, paddy cultivation usually starts in July. Several types of chemical inputs were used for rice farming, such as fertilizer, herbicides and insecticides[119]. Both precipitation and infiltration can affect the As distribution in the surrounding area. In addition, the levels of As were related to the direction of the groundwater flow. However, there was no difference in the As distribution during the dry and the wet seasons because of the low velocities of the groundwater flow. In addition to these factors, the topography, hydrochemical mechanisms and the hydrogeology also impacted the distribution[120].

Table 4.2 As and Pb concentrations in the groundwater wells during the dry and wet seasons (unit: µg/L)

Seasons	Groundwater types	Elements	Mean	Median	SD	Min	Max
Dry season (n = 40)	**Qcl (n = 13)**	As	20.768	9.952	26.202	0.366	73.260
		As^{3+}	9.037	1.127	18.173	BDL[a]	64.640
		As^{5+}	11.846	2.200	19.742	0.366	61.230
		Pb	0.443	BDL[b]	0.058	BDL[b]	0.539
	Gr (n = 27)	As	6.452	1.252	17.339	BDL[a]	88.260
		As^{3+}	1.383	BDL[a]	2.527	BDL[a]	10.570
		As^{5+}	5.247	0.684	15.398	0.012	77.690
		Pb	0.612	BDL[b]	0.380	BDL[b]	1.780
Wet season (n = 40)	Qcl (n = 13)	As	14.351	4.859	17.892	BDL[a]	50.780
		As^{3+}	3.772	BDL[a]	8.247	BDL[a]	29.590
		As^{5+}	10.765	3.088	15.396	BDL[a]	50.480
		Pb	0.482	BDL[b]	0.161	BDL[b]	0.862
	Gr (n = 27)	As	15.233	0.400	40.638	BDL[a]	183.000
		As^{3+}	3.735	BDL[a]	10.608	BDL[a]	40.910
		As^{5+}	11.731	0.400	34.304	BDL[a]	171.390
		Pb	0.774	BDL[b]	1.127	BDL[b]	5.737
Average year (n = 80)		As	13.025	1.333	28.670	BDL[a]	183.000
		As^{3+}	3.809	BDL[a]	10.303	BDL[a]	64.640
		As^{5+}	9.404	0.958	23.866	0.012	171.390
		Pb	0.618	BDL[b]	0.697	BDL[b]	5.737

Remarked: [a] : Concentration was below the detection limit (BDL) with less than 0.300 µg/L

[b] : Concentration was below the detection limit (BDL) with less than 0.400 µg/L



(a)

(b)

(c)

(d)

Figure 4.4 Spatial distribution of As concentration during (a) the dry season, (b) the wet season, Pb concentration in (c) the dry season and (d) the wet season[88]

4.3.2 Pb concentration and its spatial distribution

During the collection year, the Pb concentration in the groundwater samples ranged from <0.400 μg/L to 5.737 μg/L. Most of the samples did not exceed the WHO guideline value for drinking water of 10 μg/L. During both seasons, the median levels in the Qcl and Gr aquifers were below the detection limit. Although the maximum Pb concentration in the Gr aquifer in both seasons was clearly higher than in the Qcl aquifer, the statistical results showed no significant differences ($p\text{-value} > 0.05$). Generally, the Pb mostly originated from the parent material and accumulated in the organic matter. Nonetheless, the influence of environmental factors, such as low pH value and/or reduction conditions, can result in an increase in the solubility of Pb in the groundwater[121]. The result of this study provided a value similar to the background value, which was below 7 μg/L[79]. However, the issue of Pb contamination from household piping systems was a concern in many countries because of the corrosion problem[122-124]. At present, the households in this area are replacing lead pipes with pipes made from materials that do not react chemically in order to prevent the release of lead from their residential plumbing systems. Therefore, the Pb concentration was not significantly different among these samples ($p\text{-value} > 0.05$). Hence, Pb leaching from pipes was not the major source of lead in this study. Nevertheless, the extent of the problem could still be underestimated because of the Pb remaining in the old water in the groundwater wells.

According to Fig. 4.4d, some sampling points seem to be high in Pb levels than in the other wells, possibly because of human activity, particularly fertilizer input[125,126]. Moreover, the pumping might disturb the equilibrium of the hydrochemicals in the groundwater, resulting in the reaction condition. However, almost none of the wells in the Qcl and the Gr aquifers showed a different distribution in their wet and dry seasons, because the results were observed with very low Pb concentrations in those areas (Fig. 4.4c and 4.4d). Additionally, the behavior of this metal was commonly shown in a residual form[127]. In a manner similar to the pH level found in the present study, which ranged from near neutral to weak alkalinity, low mobility was predominant in the environment. Therefore, the mobilization of Pb usually needed a longer time period than the other elements under these same conditions[22]. For these reasons, annual monitoring of these wells was helpful in considering the Pb distribution when the area underwent land-uses changes.

4.3.3 Correlation between heavy metals and hydrochemical parameters

The correlation among the As speciation, Pb levels and hydrochemical levels is indicated in Table 4.3. The As level had a positive relationship with As^{5+} in both seasons. The dissolving of the chemical application composed of monosodium arsenate ($(NaCH_3HAsO_3)_3$), disodium arsenate ($(Na_2CH_3AsO_3)_3$), diethyl arsenic acid ($((CH_3)_2AsOCOH)$) and arsenic acid ((H_3AsO_4)) can result in enhancing the As and Na^+ levels in the soil and groundwater[116]. The effect of pH on the desorption of As was supported by increasing its concentration in the As^{5+} form within the alkaline water[114]. Moreover, the presence of HCO_3^- can promote the As and As^{5+} concentration[128]. In addition to the As species, the HCO_3^- also had a high association with the Na^+, K^+, Ca^{2+} and Mg^{2+} and pH levels, which can be originated by the silicate dissolution and cultivation process[129,130].

The strong positive factor of As mobilization was the pH value, which can be explained by the adsorption and desorption mechanism. For instance, a high As^{5+} adsorption was common under acidic water (pH = 4), while a low As^{5+} adsorption performance occurred on hydrous oxides under an elevated pH[131]. The mechanism of As reaction among its species was discussed in the study of Torres et al.[132]. Since the pH in the groundwater ranged from 6 to 8, it can support the As^{5+} form, allowing it to exist in the groundwater in a high proportion as compared to As^{3+}. Nevertheless, a correlation was not found between the pH level and As speciation during the wet season. Since dilution by rainwater can be interrupted, the influence of rainwater is subject to limitation. It was shown in the case of some wells that the redox reaction was positively associated with the As species, as shown in well Nos. 6 and 7. Although the pH levels in both groundwater wells were nearly neutral, the reduction was also strongly influenced, resulting predominantly in As^{3+}.

Bissen and Frimmel[133] reported that $Ca_3(AsO_4)_2$ and $CaHAsO_3$ are commonly founded in chemical fertilizers and pesticides. As based on this previous study, a dominant arsenite species was present, as well as a calcium composition. It can be implied that, because of the agricultural activity, one of the As^{3+} sources could dissolve into the soil and groundwater, respectively. The As^{5+} could then be changed by the environmental conditions, especially the oxidation condition. Furthermore, As^{3+} was related to Fe because of the dissolution of iron-rich minerals[134]. In addition to the As^{3+} source, the predominant species of arsenate was mainly generated from the replacement of alkaline mineral substances with plagioclase feldspars, such as K-feldspar ($K(AlSi_3O_8)$) to filatovite ($K[(Al,Zn)_2(As,Si)_2O_8]$). Therefore, the As^{5+} is commonly present as a result of the silicate dissolution[104,135].

When considering the properties of Pb, it can be seen that it has a negative correlation with HCO_3^- and pH between the dry and wet seasons. The behavior of this metal was stable within the range of pH that was found in this study and, similarly, in the study of Alloway[22]. Most of the Pb forms can be implied, like $PbCO_3$**,** which occurs in a strongly precipitated form in the aquifer system[136]. Meanwhile, the other parameters, namely, EC, Ca^{2+} and Fe, were also inversely correlated with Pb during the dry season. Under oxidizing conditions, Pb was caught with Fe and clay. On the other hand, Pb had a negative association with K^+, Mg^{2+} and Cl^- during the wet season. The chemical input during cultivation can be used to explain this association. As based on the information pertaining to this area, the wet season is a period for cultivation. Consequently, Pb can be accumulated in the soil because of its behavioral characteristics, while the other elements can be leached into the groundwater. In addition, the chemical compounds of Cl^- can be found in many agricultural products, including KCl, NaCl, $CaCl_2$ and $MgCl_2$. Likewise, the resulting ions were found to have high EC values[114]. Based on this result, the As species concentration should be considered, because its mobilization in the groundwater was promoted by this environmental condition.

Table 4.3 Correlation between heavy metals and hydrochemical parameters duing the dry season and the wet season[88]

Dry season																	
	pH	DO	EC	ORP	As	As^{3+}	As^{5+}	Pb	Ca^{2+}	Mg^{2+}	Na	K	Fe	Cl^{-}	NO_3^{-}	SO_4^{2-}	HCO_3^{-}
pH	1.000																
DO	**.326***	1.000															
EC	**.814****	-0.011	1.000														
ORP	-0.272	**.356***	-0.290	1.000													
As	**.393***	-0.020	**.411****	-0.038	1.000												
As^{3+}	0.273	-0.151	**.390***	-0.128	**.816****	1.000											
As^{5+}	**.489****	0.138	**.377***	0.067	**.876****	**.564****	1.000										
Pb	**-.407****	0.073	**-.365***	.528**	-0.041	-0.087	0.019	1.000									
Ca^{2+}	**.579****	-0.027	**.767****	-0.286	0.251	0.210	0.266	**-.437****	1.000								
Mg^{2+}	**.469****	0.069	**.566****	-0.130	**.358***	0.310	**.337***	-0.276	**.781****	1.000							
Na	**.790****	0.166	**.767****	-0.253	**.448****	**.330***	**.428****	-0.259	**.409****	**.344***	1.000						
K	0.210	0.002	0.165	-0.299	0.035	-0.103	0.060	-0.137	0.139	0.105	0.303	1.000					
Fe	0.050	**-.346***	0.206	**-.674****	-0.082	0.103	-0.277	**-.320***	0.216	0.063	-0.040	0.141	1.000				
Cl^{-}	-0.046	0.038	0.141	0.293	-0.083	-0.014	-0.204	0.170	0.151	0.064	0.073	-0.140	-0.065	1.000			
NO_3^{-}	0.048	0.269	-0.010	0.267	-0.028	-0.031	0.064	0.163	-0.009	-0.009	-0.031	0.214	-0.193	0.020	1.000		
SO_4^{2-}	-0.093	0.291	-0.001	**.412****	0.042	0.017	-0.038	0.173	0.045	0.142	0.035	0.074	-0.167	**.629****	0.124	1.000	
HCO_3^{-}	**.895****	0.047	**.888****	**-.391***	**.420****	0.298	**.508****	**-.364***	**.729****	**.540****	**.752****	0.258	0.134	-0.101	-0.042	-0.188	1.000

Wet season

	pH	DO	EC	ORP	As	As^{3+}	As^{5+}	Pb	Ca^{2+}	Mg^{2+}	Na	K	Fe	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-
pH	1.000																
DO	**.329***	1.000															
EC	**.705****	0.181	1.000														
ORP	0.010	**.466****	-0.092	1.000													
As	0.165	-0.190	0.173	-0.282	1.000												
As^{3+}	-0.082	-0.268	-0.029	-0.307	**.637****	1.000											
As^{5+}	0.181	-0.165	0.192	-0.256	**.996****	**.590****	1.000										
Pb	**-.463****	0.075	-0.282	0.077	-0.232	-0.174	-0.231	1.000									
Ca^{2+}	**.546****	0.053	**.586****	-0.234	0.262	**.354***	0.250	-0.307	1.000								
Mg^{2+}	**.740****	0.234	**.621****	-0.033	0.228	0.209	0.231	**-.405****	**.765****	1.000							
Na	**.443****	-0.183	**.474****	-0.219	**.447****	**.382***	**.440****	-0.173	**.523****	**.494****	1.000						
K	**.776****	0.075	**.690****	-0.172	**.354***	0.013	**.362***	**-.415****	**.415****	**.534****	**.530****	1.000					
Fe	-0.106	-0.188	0.038	**-.339***	**.398***	**.489****	**.381***	-0.099	0.238	0.067	**.458****	0.086	1.000				
Cl^-	**.518****	-0.008	**.497****	-0.173	0.240	**.381***	0.226	**-.334***	**.768****	**.731****	**.735****	**.432****	0.310	1.000			
NO_3^-	-0.051	-0.216	0.089	-0.224	0.200	**.323***	0.188	-0.189	0.184	0.118	0.126	0.082	0.134	0.259	1.000		
SO_4^{2-}	-0.032	0.169	0.080	-0.004	0.021	-0.068	0.033	0.285	0.197	0.179	-0.100	-0.046	-0.047	0.019	0.083	1.000	
HCO_3^-	**.834****	0.049	**.742****	-0.089	.405**	0.230	**.414****	**-.429****	**.709****	**.826****	**.692****	**.808****	0.185	**.686****	0.074	0.003	1.000

4.3.4 Principal component analysis (PCA)

The PCA indicated the correlation among the Pb and As speciation and hydrochemical parameters. The appropriateness of the data was checked by a Kaiser-Meyer-Olkin (KMO) and Barlett's sphericity test, and the appropriate number of factors was determined by the rotation method of varimax with a Kaiser Normalization, which was used to clarify the correlation among the involved factors. The cumulative value of the five factor components was 72.86 % of the total variance, which has eigenvalues above 1 (Fig. 4.5 and Table 4.4).

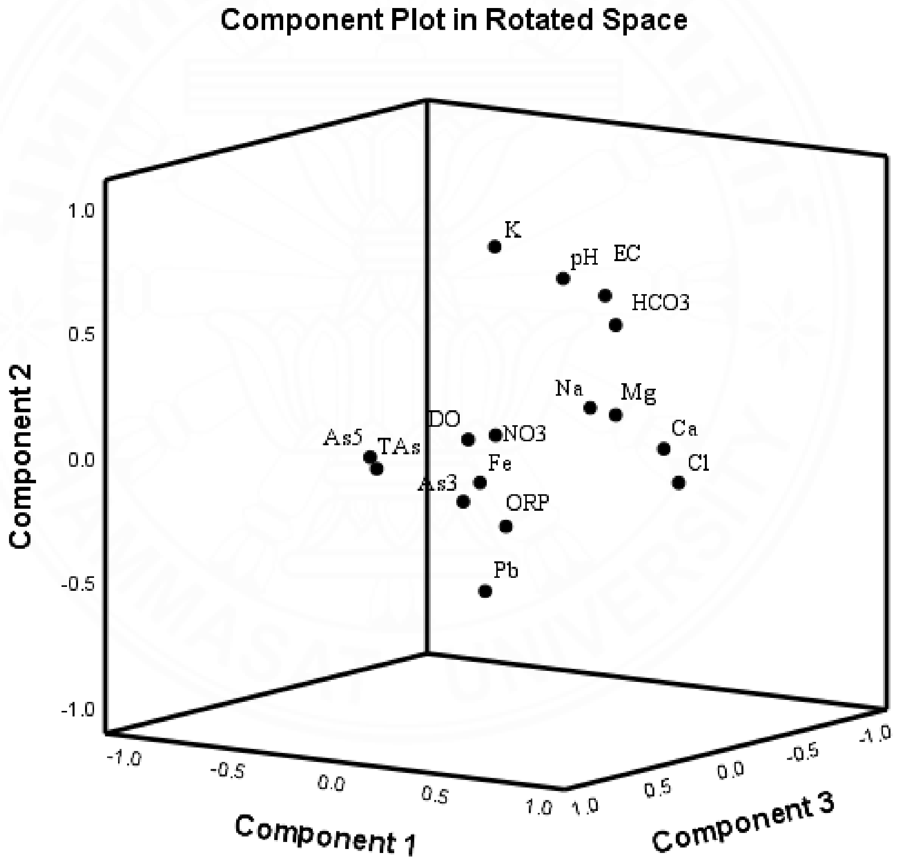


Figure 4.5 Plot of the principal component loading in the average year sample collection[88]

The first factor included pH, EC, Ca^{2+}, Mg^{2+}, Na^{+} and HCO_3^{-}. It could be interpreted that these parameters were related to the occurrence of the ion-exchange reaction in the aquifer[103,105]. The evapo-transpiration was a major phenomenon contributing the amounts of Na^+ and Cl^- that were especially prevalent during the dry season[106]. The geology in this area was characteristic of the S-type granites, which contained plagioclase feldspar minerals, including quartz, biotite, zircon, apatite, magnetite, K-feldspar (orthoclase), $CaAl_2Si_2O_8$ (anorthite) and $NaAlSi_3O_8$ (albite)[94,129]. Hence, from the dissolution of these types of minerals, there might be a source of HCO_3^- and Ca^{2+} [106,136]. In addition, the solubility of CO_2 in water was probably caused by an increase in the concentration of HCO_3^-. Moreover, pH was a potential factor in controlling the chemical reaction in the groundwater. The elevated pH could be increasing the As level, while the precipitation process of Pb was a common occurrence[132]. In addition to the natural source, anthropogenic activities could also be generating these metals[137].

Factors 2 and 3 were the representative transport mechanisms that were affected by the ORP in the aquifer system. Factor 2 was grouped with the reduction reaction and included the ORP, DO, As, As^{5+}, As^{3+} and Fe. In this condition, the As transformation was affected by groundwater bacteria. When the amount of oxygen was reduced, the As species could be transferred from As^{5+} to As^{3+} [110]. For example, the As^{3+} was the dominant species at well Nos. 6, 7 and 15, which were ar a negative ORP. In contrast, As^{5+} was predominant in the wells with a positive ORP[138,139]. The condition was correlated to the factor 3, which was predominated by As, As^{5+}, ORP and DO. Nevertheless, various influencing factors were still interrupting and changing the redox potential reaction[140].

Factor 4 was responsible for the presence of Ca^{2+}, Cl^- and K^+, which commonly originated from human activities, such as sewage discharges and cultivation. The effect of the rainfall is such that the rain can transfer the chemicals from the soil surface into the groundwater. However, all three ions were found in low concentrations that may have resulted from the impact of water mineralization[97].

Factor 5 consisted of Pb, NO_3^- and K^+. The chemical inputs in the cultivation were an important source, because they usually contained the essential nutrients for plant growth[22].

Table 4.4. Varimax-rotated principal-component analysis by Varimax with Kaiser Normalization

Parameters	Principal components				
	F_1	F_2	F_3	F_4	F_5
HCO_3^-	**0.920**	-0.205	-	-	.152
EC	**0.807**	-0.328	-0.137	-0.151	-
Mg	**0.753**	-	-	. 0295	-
pH	**0.744**	-0.376	-	-0.322	-
Ca	**0.674**	-	-0.146	**0.501**	-
Na	**0.660**	-	-	-	0.266
Pb	-0.419	-	0.126	0.286	**0.379**
As^{3+}	0.343	**0.838**	-	-	-
Fe	0.145	**0.667**	-0.362	**-**	0.139
As	0.440	**0.617**	**0.593**	-0.209	-
As^{5+}	0.399	**0.445**	**0.712**	-0.248	-
ORP	-0.179	**-0.453**	**0.645**	0.309	0.142
DO	-	**-0.463**	**0.566**	-	-
Cl	0.459	-0.118	-	**0.696**	-0.104
K	0.412	-0.286	-	**-0.467**	**-0.399**
NO_3	-	0.177	0.259	0.287	**-0.772**

Remark: Bold letter indicates high correlation in each component.

4.4 The Characteristics of the Participants

In this section of exposure assessment and health risk-assessment, the focus was on the 22 groundwater wells which people have been using for drinking, routine daily purposes and agricultural activity It was the As concentration in these wells that was used to sub-divide the participant groups, because the Pb was at a very low level in the groundwater sample, ranging from <0.400 μg/L to 3.1505 μg/L (Fig. 4.6). The 110 participants were equally classified into two groups. The L group was representative of the participants who were using groundwater from the well with a low As level (<10 μg/L), while the H group was the person who consumed groundwater from the well with a high As concentration (>10 μg/L).

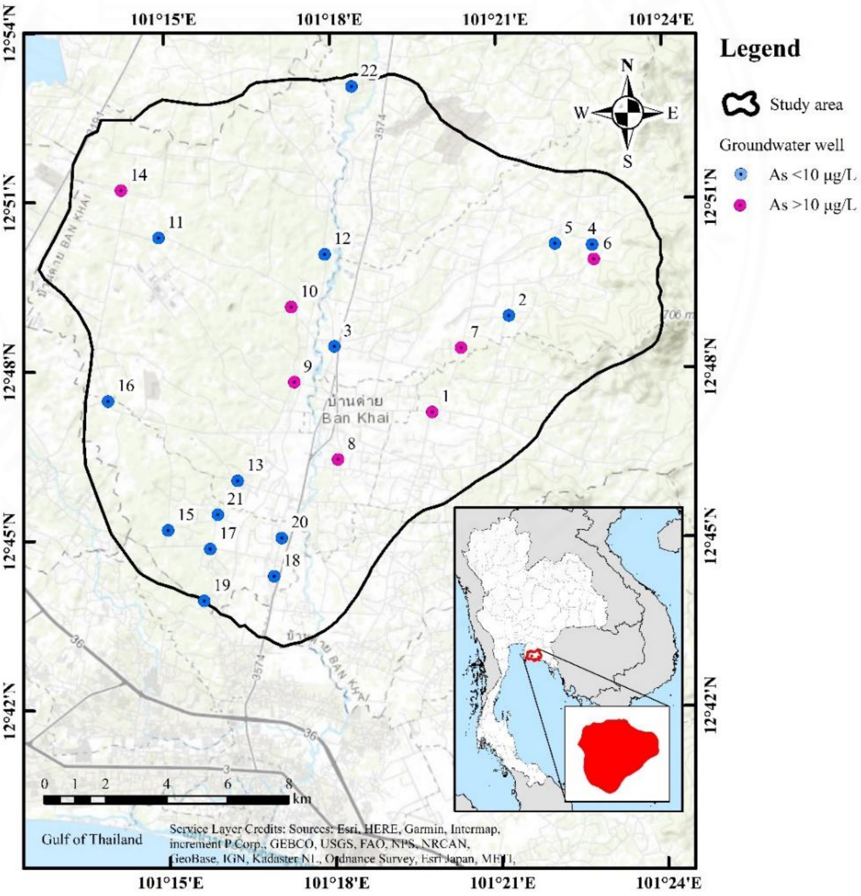


Figure 4.6 The 22 groundwater wells, focusing on exposure and health risk assessments

The overall characteristics of the 110 participants as determined by face-to-face interviewing are shown in Table 4.5. Ages of the participants were distributed within a range of 26 to 81 years, with a median age of 57.5 years; more than half were female. The number of household members ranged from 1 to 10 persons; they were found to be in various age groups. Large families were commonly found in rural areas, reflecting the cultural society of Thailand. The number of self-employed was somewhat higher, as compared to the agriculturists. According to the results obtained, the two groups were similar in their socio-demographics characteristics, including age, body-mass index (BMI), education and occupation. Meanwhile, the relevant symptoms during the six months before collecting the urine samples in the H group were found to be high, as compared to the L group.

Table 4.5 The sociodemographic characteristics, health information and groundwater consumption of local residents[141]

Characteristics	L group (n = 55)	H group (n = 55)	Total (n = 110)
Demographic information			
Sex			
Male	17 (31%)	14 (25%)	31 (28%)
Female	38 (69%)	41 (75%)	79 (72%)
Age (years old)			
Median (min-max)	56 (26-78)	58 (37-81)	57.5 (26-81)
BMI			
<18.5	2 (4%)	1 (2%)	3 (3%)
18.5-22.9	17 (31%)	19 (34%)	36 (33%)
>22.9	36 (65%)	35 (64%)	71 (64%)
Median (min-max)	24.69 (17.78-35.16)	23.62 (18.36-38.20)	24.25 (17.78-38.20)
Education			
Lower than the elementary	-	4 (7%)	4 (4%)
Elementary	31 (56%)	34 (62%)	65 (59%)
High school/ vocational certificate	21 (38%)	12 (22%)	33 (30%)
Diploma/High vocational certificate / Bachelor degree	3 (6%)	5 (9%)	8 (7%)
Occupation			
Government officer/State enterprises	1 (2%)	3 (6%)	4 (4%)
Agriculturist	22 (40%)	19 (34%)	41 (37%)
Self-employed	25 (45%)	23 (42%)	48 (44%)
Merchant	7 (13%)	10 (18%)	17 (15%)

Characteristics	L group (n = 55)	H group (n = 55)	Total (n = 110)
Family members (persons)	1-8	1-10	1-10
Health information			
The symptoms during six months ago			
Gastrointestinal system (Abdominal pain, Vomiting, Diarrhea, Anorexia)	30 (55%)	38 (69%)	68 (62%)
Cardiovascular system (Hypertension)	11 (20%)	24 (44%)	35 (32%)
Nervous system (Vertigo, Convulsions, Fatigue, Sleeplessness, Hallucinations)	39 (%71)	41 (75%)	70 (64%)
Urinary system (Bloody urine)	1 (2%)	2 (4%)	3 (3%)
Immune system (Arthritis)	27 (49%)	32 (58%)	59 (54%)
Alcohol consumption behavior			
No	38 (69%)	36 (65%)	74 (67%)
Yes	17 (31%)	19 (35%)	36 (33%)
Smoking behavior			
No	55 (100%)	51 (93%)	106 (96%)
Yes	-	4 (7%)	4 (4%)
Smoking status of family member			
Non-smoker	37 (67%)	33 (60%)	70 (64%)
Smoker	18 (33%)	22 (40%)	40 (36%)
Groundwater consumption			
Groundwater using purpose			
Drinking	50 (91%)	55 (100%)	105 (95%)
showering	51 (93%)	52 (95%)	103 (94%)

Characteristics	L group (n = 55)	H group (n = 55)	Total (n = 110)
Agricultural activity	39 (71%)	31 (56%)	70 (64%)
Household water treatment			
Treatment	20 (40%)	28 (51%)	48 (46%)
Non-treatment	30 (60%)	27 (49%)	57 (54%)

All of the participants used groundwater as their major source of drinking water (95%) and for showering purposes (94%), followed by agricultural activity (64%). Almost of these groundwater wells were treated by sand filtration, the aeration process and chlorination before distribution through the water pipelines. Meanwhile, 46% of household users have been using additional treatments, such as precipitation with alum and reverse osmosis before drinking. At present, Ban Khai District has undergone a slight change as a semi-urban society that could lead to a change in lifestyle, especially in the areas of occupation, land use and recreational activity. For instance, agriculture has long been a traditional occupation of the Thai people, while the number of self-employed people has been rapidly increasing because of the influence of economic development. Furthermore, their other water supplies might be exposed while they are working outside their homes.

4.5 Concentration of As in the Urine

4.5.1 Urinary As levels

As concentration in the urine of the participants was determined in both the L and H groups (Table 4.6). The As levels in the 110 urinary samples ranged from 5.38 µg/L to 600.86 µg/L, with a median value of 61.33 (Fig. 4.7). A comparison of the two groups shows that the As levels in the urine of the L and H groups ranged from 5.38 to 130.76 µg/L, and from 37.86 to 600.86 µg/L, respectively. The majority of the participants in the H group showed high cases of UAs, while their median As concentration was at quite a high level around two times as high when compared to the L groups. The results of As concentrations in urine show that approximately 98%

of the H group and 36 % of the L group exceeded the normal value of 50 µg/L, as set by the National Health and Nutrition Examination Survey (NHANES). A statistical analysis has revealed that the UAs level in both groups were significantly different (p-value < 0.001). It can be concluded that the person who ingests groundwater with a high As concentration (>10 µg/L) has a tendency to be found with a high UAs level.

Table 4.6 Urinary As level between the H group and the L group[141]

Well No.	Sample (n)	As level in groundwater (µg/L)	UAs (µg/L) Median (Min – Max)	
			H group	L group
1	1	56.01	130.86[a]	-
2	1	2.38	-	33.91[a]
3	1	0.52	-	33.93[a]
4	2	9.08	-	27.02[b] (22.87-31.16)
5	3	0.49	-	44.57 (22.53-44.69)
6	9	20.72	105.25 (52.23-178.34)	-
7	3	17.86	135.65 (56.14-145.32)	-
8	12	47.33	91.98 (59.46-139.82)	-
9	4	10.03	75.83 (53.46-135.02)	-
10	19	31.94	80.54 (37.86-350.06)	-
11	4	7.88	-	69.91 (61.75-111.75)
12	5	1.71	-	53.51 (42.39-80.30)
13	4	7.65	-	14.71 (9.32-73.09)
14	7	135.63	117.49 (51.96-600.76)	-
15	2	0.78	-	84.54[b] (38.31-130.76)
16	2	0.33	-	74.35[b] (42.02-106.68)
17	4	0.79	-	22.66 (19.75-38.96)
18	8	0.62	-	55.98 (16.46-113.77)
19	3	0.34	-	41.98 (5.74-87.4)
20	9	0.84	-	33.89 (5.38-121.91)
21	5	1.63	-	44.71 (11.25-121.77)
22	2	0.34	-	28.83[b] (23.02-34.63)
Overall median, Min-Max		2.04 (0.33-135.63)	90.09 (37.86-600.86)	41.98 (5.38-130.76)

Noted: [a] A value of the As concentration in the urine of one participant

[b] An average value of the As concentration in the urine of two participants

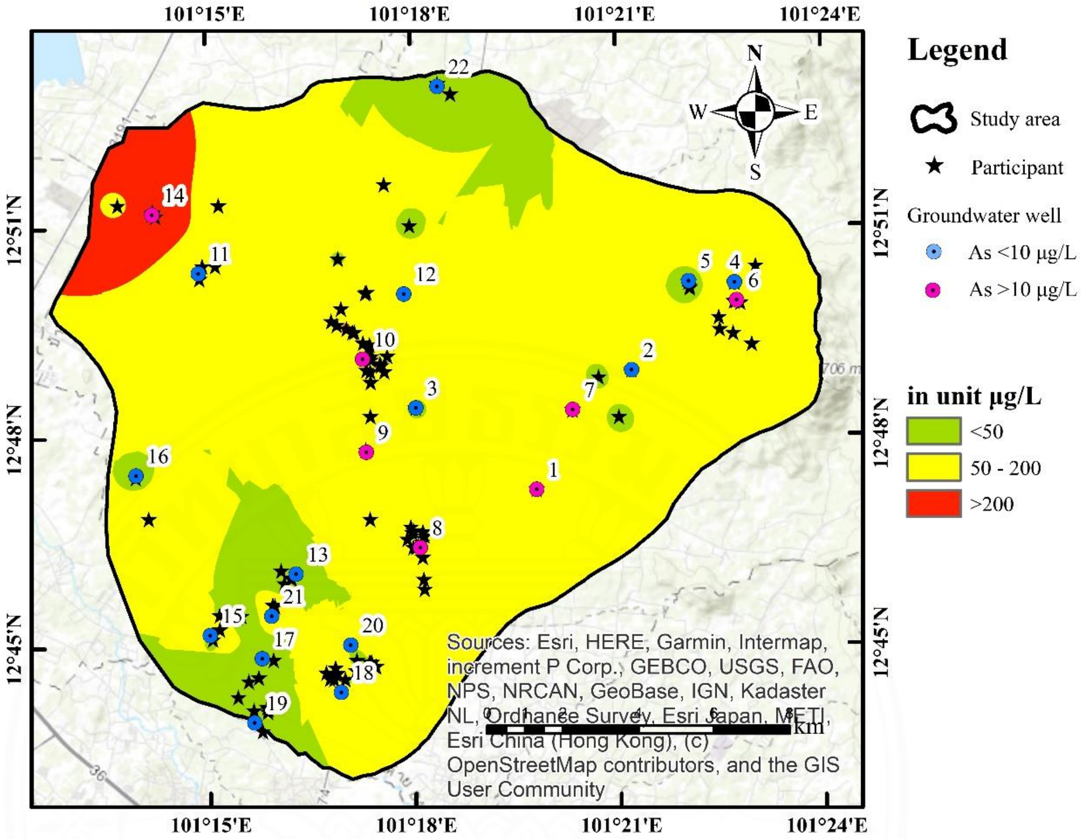


Figure 4.7 Urinary As concentrations of 110 residents[141]

The UAs levels of these participants were higher than those shown in the work of Wongsasuluk et al.[43], possibly because of the difference in the As concentrations in the groundwater well between the two areas. In addition, the Bureau of Occupational and Environmental Diseases (BOED)[142] reported that the As concentration in the groundwater of 21 provinces in the risk area of As contamination ranged from 0.001 to 92.6 µg/L in 2003. Meanwhile, the residents who were drinking the groundwater were found to have UAs levels ranging from 5 to 3,882 µg/L, accounting for 26% of the 2,791 residents with As levels between 36 and 70 µg/L[142]. Generally, the total As concentration in urine consisted of As compounds. A high toxicity was found with inorganic species that can be absorbed throughout the gastrointestinal tract. The human population was most often ingesting As from their diet, consisting, in particular, of rice, and from their drinking water[143]. The organic species, meanwhile, can be eliminated via urinary excretion[144-146]. However, many studies were concerned with the consumption of seafood and seaweed, resulting in excessive UAs concentration, especially in the forms of arsenobetaine and arsenocholine[147]. Therefore, this topic is an important issue requiring that all participants be informed and be prepared to control the content of other As sources. Nevertheless, some participants who had been ingesting groundwater with low As concentrations were still found to have high UAs levels of approximately 36%. Many researchers reported that cereals, traditional herbs, mollusks, crustacea and chocolate can be contributors to their UAs concentration levels[143,148-150].

Nonetheless, the As methylation capacity of the human genotype could be subject to various individual ethnic characteristics influencing the way in which the metabolism of As is being distributed, particularly in regard to the genotype of arsenite methyltransferase (AS3MT)[147,151,152]**.** Inorganic arsenic (iAs) is metabolized to MMA and DMA mediated by the AS3MT, which is related to the detoxification mechanism. A high level of (trivalent) iAs in the urine was detected in a person who is chronically exposed to iAs through the drinking water. The concentration was found to range from 10% to 20% of iAs (As^{3+} + As^{5+}), 10% to 15% of monomethylarsonic acid (MMA) and 60% to 75% of dimethylarsinic acid (DMA)[145,152,153]. Long-term accumulation in the tissues could be reflected in the development of skin lesions and skin cancer[154,155]. Therefore, the urine is an important biomarker to evaluate the association between As in the groundwater and human exposure.

4.5.2 Factors affecting urinary As

Since As concentration in the urine and groundwater was predominant, statistical analysis can be helpful in understanding the relationship between As concentration and its influencing factors, as follows:

i) Socio-demographic characteristics

The Pearson chi-square test revealed that all of the variables, including age, BMI, education, occupation, alcohol-consumption behavior, smoking status, smoking status of family members and household water treatment, had no correlation with the UAs levels between L and H group (Table 4.7). It can be explained that the sociodemographic characteristics of these residents were not influential to As concentration in the urine. Similarly, the household-treatment practices had no significant association with UAs level (p-value > 0.05). In this study area, residents may be consuming water from more than one source, since they work outside the home in such places as the cultivation areas and work places. Meanwhile, these residents can access the health center, data-information and both the health officer and relevant government officer. Therefore, these independent variables had a very low effect on the UAs levels.

Table 4.7 The relationship between urinary As and the socio-demographic factors between the H group and the L group[141]

Exposure or risk factor	As concentration in urine			
	<50 µg/L n (%)	>50 µg/L n (%)	cOR (95% CI)	p-value
Overall	35 (31.8)	75 (68.2)		
Age				
<60 years	21 (60.0)	42 (56.0)	ref	
>60 years	14 (40.0)	33 (44.0)	1.18 (0.52-2.66)	0.693
BMI				
Healthy weight (18.5-24.9)	24 (68.6)	50 (66.7)	ref	
Unhealthy weight (underweight/overweight/obese)	11 (31.4)	25 (33.3)	1.09 (0.46-2.58)	0.843
Education				
<Elementary	18 (51.4)	51 (68.0)	ref	
>Elementary	17 (48.6)	24 (32.0)	2.01 (0.88-4.56)	0.096
Occupation				
Government officer/State enterprises / Merchant/ Self-employed	19 (54.3)	51 (68.0)	ref	
Agriculturist	16 (45.7)	24 (32.0)	1.79 (0.79-4.08)	0.166

Exposure or risk factor	As concentration in urine			
	<50 μg/L n (%)	>50 μg/L n (%)	cOR (95% CI)	p-value
Alcohol consumption behavior				
No	21 (60.0)	40 (53.3)	ref	
Yes	14 (40.0)	35 (46.7)	1.31 (0.58-2.96)	0.513
Smoking status				
No	32 (91.4)	64 (85.3)	ref	
Yes	3 (8.6)	11 (14.7)	1.83 (0.48-7.04)	0.377
Smoking status of family member				
Non-smoker	23 (65.7)	47 (62.7)	ref	
Smoker	12 (34.3)	28 (37.3)	1.14 (0.49-2.65)	0.757
Household water treatment				
Treatment	0 (0.0)	4 (5.3)	ref	
Non treatment	35 (100)	71 (94.7)	1.40 (0.60-3.25)	0.433

p-value for Pearson chi square test

cOR: Crude odds ratio

ii) Exposure factors

The factors affecting the relationship between the UAs concentration and groundwater exposure, were analyzed by linear regression. The independent variables were considered to be representative of the different pathways: the amount of As in groundwater well (x_1), amount of drinking exposure (x_2), amount of showering exposure (x_3) and amount of agricultural exposure (x_4), which were calculated by using ET, EF, IR and ED (Table 4.8). The statistical results obtained demonstrate that both the drinking exposure and the As concentration were significantly correlated with UAs levels of these participants ($p\text{-value} < 0.05$). Similar studies have confirmed this result[62,155,157]. The model of the linear equation was $Y = 49.813 + 0.35\ (x_1) + 0.001\ (x_2)$. When considering the drinking exposure, it can be seen that all of the parameters which were used to calculate the amount of exposure were high when compared with dermal contact. It can result in an increase of the dose of ADD. The previous study indicated that Thai people commonly had high intake rates, since Thailand is located in a tropical region and is thus a country with a tropical climate[158]. This parameter was a major factor in supporting the significance of elevated UAs levels.

However, the dependent variable was not associated with the amount of dermal exposure from either showering or agricultural activities because of the exposure time and frequency[86]. It can be explained by real situations of case-by-case exposure. In the case if agricultural exposure, they were commonly using instruments like watering pots or hoses for drainage in the growing areas. Thus, the probability of direct skin contact was low. By contrast, exposure via showering was commonly found to occur two or three times per day, with only a short time period per event (10 min/time). Also, it was the contact time that affected the degree of actual skin absorption. Hence, it can be concluded that both activities were only minor pathways of As exposure in this case.

Table 4.8 Associated factors with urinary As concentration[141]

Independent variable	Univariate analysis			Multivariate analysis		
	B	95% CI	p-value	B	95% CI	p-value
As concentration in groundwater (x_1)	0.398	0.19 to 0.60	<0.001	0.35	0.15 to 0.56	0.001
Exposure via drinking water (x_2)	0.001	0.000 to 0.001	0.023	0.001	0.000 to 0.001	0.016
Exposure via showering (x_3)	-1.140×10^{-5}	0.000 to 0.000	0.338	-5.92×10^{-6}	<0.001 to <0.001	0.598
Exposure via agricultural activity (x_4)	-0.001	-0.002 to 0.000	0.086	-0.001	<0.001 to <0.001	0.167
Constant				49.813		

4.6 Concentration of Pb in the Urine

The median UPb level was 32.48 µg/gCr, ranging from 6.44 to 92.11 µg/gCr among all participants (Fig. 4.8). Almost all participants were below the normal value of Pb in the urine for a healthy adult, except for two persons whose UPb levels exceeded 60 µg/gCr[159]. Consequently, this element was not necessary for the classification of participant groups, since to do so would mean considering a factor that affected only a small number of people whose UPb levels were high (>60 µg/gCr). However, in the present study, higher UPb levels appeared approximately three times, as compared to certain other studies which observed the general population. The study of Sirivarasai and Kaorern[160] reported that people living near Bangkok and the Bangkok metropolitan area of Thailand, varying in age from 17 to 55 years old, were found to have UPb levels of 10.35±7.5 µg/gCr. The average UPb level of the people with no occupational exposure to heavy metals was 14.4 µg/gCr, and 42 µg/gCr for a 95th percentile of the population[161]. Inorganic lead was a major species to which humans suffered exposure. Most of its exposure is via the oral route, such as by food consumption and drinking, and is commonly eliminated in the urine (75-80%) and, to a lesser extent, in the feces[160].

Pb accumulated in the bones with a half-life of 5–20 years, while a small labile proportion was transferred to the blood with a half-life of 28 to 36 days, allowing plasma to enter into the tissue compartments. Some fractions were excreted via the urine and feces. Lead was not permanently absorbed in the bone but undergoes a slight resorption by the blood. Approximately 90% of blood lead could be present in the erythrocytes, while only at low levels in plasma[162]. There were occurrences of UPb from Pb in the plasma, which was filtrated in the glomeruli. Therefore, UPb levels are commonly related to a determination of its presence in the plasma, as well as to external exposure[163]. Erythrocyte lead of plasma and bone lead were correlated with UPb levels, which were representative of the bone's influence on plasma lead[164].

Some clinical studies investigated the relationship between UPb levels and several other factors, including age, sex, race/ethnicity, alcohol intake, education, income, smoking status, body weight, diabetes, hypertension, weak/failing kidney and cancer mortality[165-167]. This relationship corresponded to the findings of a study conducted by Goldwater et al.[168] and Sallsten et al.[169], who revealed that UPb has been employed as an indicator to assess the degree of exposure within the general population, especially environmental exposure. Although UPb could provide a valid and non-invasive alternative to BPb, its level might be subject to the influence of some individual biological factors and diurnal variation. In the case of a low UPb level, antioxidants such as vitamin C have been recommended to help decrease its concentration. The properties of this substance can play the role of a chelating agent which increases urinary lead excretion from the human body[170]. From the findings pertaining to Pb concentration in the groundwater and the UPb levels, it could be inferred that this element has a low health risk when absorbed via groundwater consumption at the present time.

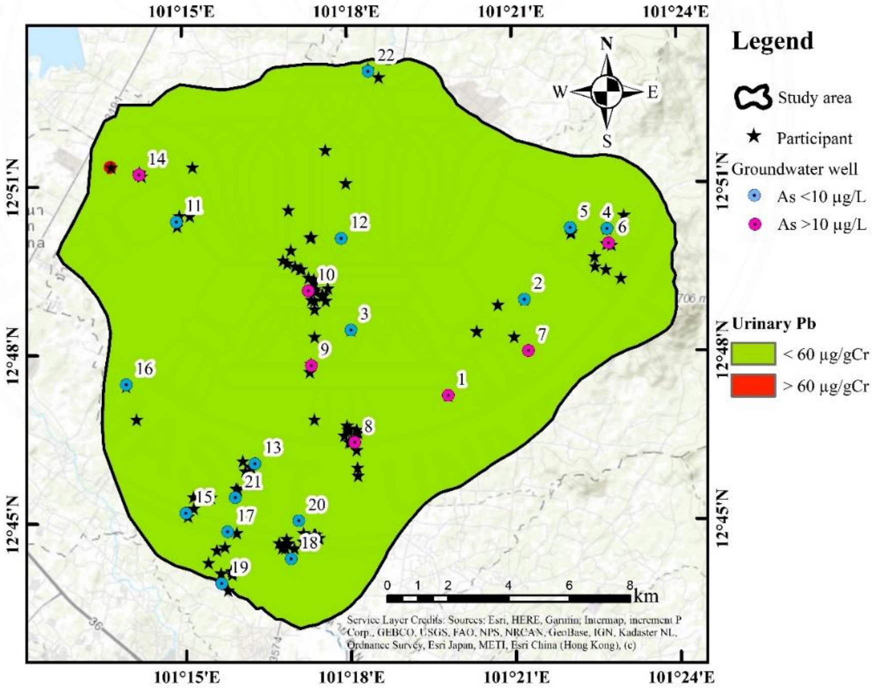


Figure 4.8 Urinary Pb concentration levels in 110 local residents

4.7 Human Health risk Assessment

This section has been separated into two parts, consisting of: i) deterministic health risk assessment by considering As speciation and ii) probabilistic health risk assessment by considering As and Pb concentrations.

4.7.1 Deterministic health risk assessment by considering As speciation

The Visual MINTEQ modeling generated seven aqueous As species: AsO_4^{-3}, $H_2AsO_3^-$, $H_2AsO_4^-$, H_3AsO_3, H_3AsO_4, $HAsO_3^{-2}$ and $HAsO_4^{-2}$ (Table 4.9). The distribution of the As species with mole percentage consists of two major components, AsO_4^{-3} (60.48% of $HAsO_4^{-2}$ and 39.52% of $H_2AsO_4^-$) and H_3AsO_3 (98.94% of H_3AsO_3 and 1.07% of $H_2AsO_3^-$). An approximately 76% mole concentration was existing with a pentavalent As species, and the remaining percentage was present in a trivalent state. The As dominant speciation showed a high activity of $HAsO_4^{-2}$, $H_2AsO_4^-$ (pentavalent As species) and an ascendant H_3AsO_3 (trivalent As species), respectively, while the concentration and activity levels of $HAsO_3^{-2}$ were very low in the groundwater sample. In this study, the prevailing As species that had been simulated from a model was strong with a real value derived from the field investigation.

Generally, the As species in the environment are found mostly with the arsenic acids ($HAsO_4^{-2}$, $H_2AsO_4^-$, H_3AsO_4) and arsenate ion or arsenate species (AsO_4^{-3}), as well as arsenious acids ($HAsO_3^{-2}$, $H_2AsO_3^-$, H_3AsO_3), arsenite, etc.[26]. Under the oxidation condition, the dominant As forms were demonstrated as $HAsO_4^{-2}$ and $H_2AsO_4^-$ in response to the results of this study[171]. Speciation is an important factor of the mobility and bioavailability in groundwater[172]. Low toxicity is presented when there is an elevated level of $HAsO_4^{-2}$ and decreased concentration of $H_2AsO_4^-$ and H_3AsO_4[173]. The electrical potential interactions were used to explain the reaction; it was the power of Visual MINTEQ that enabled this explanation. This software was recommended as a means of predicting As speciation by considering the redox reactions[174].

Table 4.9 The concentration and activity of As speciation by Visual MINTEQ modeling

As species		Concentration (mol/L)	Activity	Weight calculated	Concentration of As species (mg/L)
Pentavalence	AsO_4^{-3}	3.97E-12	1.77E-12	3.58E-10	5.85E-12
	$H_2AsO_4^-$	6.54E-08	6.18E-08	2.75E-01	4.49E-03
	H_3AsO_4	1.06E-12	1.06E-12	7.62E-11	1.24E-12
	$HAsO_4^{-2}$	1.00E-07	7.97E-08	5.43E-01	8.86E-03
Trivalence	$H_2AsO_3^-$	5.56E-10	5.25E-10	1.99E-05	3.25E-07
	H_3AsO_3	5.17E-08	5.17E-08	1.82E-01	2.97E-03
	$HAsO_3^{-2}$	8.13E-17	6.46E-17	3.57E-19	5.83E-21
		Total As species			1.63E-02

Table 4.10 Health risk assessment of As speciation

As species		Non cancer risk				Cancer risk			
		ADD_{ing}	ADD_{der}	HQ_{ing}	HQ_{der}	ADD_{ing}	ADD_{der}	CR_{ing}	CR_{der}
Pentavalence	AsO_4^{-3}	2.22E-13	6.09E-16	7.40E-10	2.03E-12	5.55E-14	1.64E-16	8.33E-14	2.46E-16
	$H_2AsO_4^-$	1.70E-04	4.68E-07	5.68E-01	1.56E-03	4.27E-05	1.26E-07	**6.40E-05**	1.89E-07
	H_3AsO_4	4.72E-14	1.30E-16	1.57E-10	4.32E-13	1.18E-14	3.50E-17	1.77E-14	5.25E-17
	$HAsO_4^{-2}$	3.36E-04	9.23E-07	**1.12E+00**	3.08E-03	8.42E-05	2.49E-07	**1.26E-04**	3.74E-07
Trivalence	$H_2AsO_3^-$	1.23E-08	3.38E-11	4.11E-05	1.13E-07	3.08E-09	9.12E-12	4.63E-09	1.37E-11
	H_3AsO_3	1.13E-04	3.09E-07	3.76E-01	1.03E-03	2.82E-05	8.34E-08	**4.23E-05**	1.25E-07
	$HAsO_3^{-2}$	2.21E-22	6.07E-25	7.37E-19	2.02E-21	5.54E-23	1.64E-25	8.30E-23	2.46E-25
Total As species (Visual MINTEQ)		6.19E-04	1.70E-06	2.06E+00	5.67E-03	1.55E-04	4.59E-07	2.33E-04	6.88E-07
Total As (Field investigation)		6.12E-04	1.68E-06	2.04E+00	5.60E-03	1.53E-04	4.53E-07	2.30E-04	6.80E-07

On the basis of these seven As species, their concentrations and activity were used to estimate the As species for a health risk assessment (Table 4.9). The ADD and characterization of risk from As exposure through drinking water and dermal contact are shown in Table 4.10. Using the methodology of health risk assessment, As speciation from the model was compared with the As concentration as a measured value (0.01613 mg/L). Meanwhile, the other input parameters used the same value in those methods. The result of the total As level from the model was just slightly higher than the total As value obtained from the field investigation, accounting for 1.18% (0.01632 mg/L). Approximately 1.20% of risk values such as the HI value and TCR value obtained by the Visual MINTEQ modeling program were at a high level as compared to the result from the field investigation. However, the error difference was less than 5%[17].

Although the direct calculation was convenient and not complicated, an As concentration calculated by modeling was recommended. Modeling was the preferred approach, because the As metal is present as a more complex species in the environment. Furthermore, the limitations of the instrument, the analytical techniques that would be involved, the time that would be needed and the total cost were also concerns that had to be considered. The modeling technique can be a helpful approach in assessing the As and its compounds for environmental-management and health risk assessment purposes, since there are soluble forms and a precipitation form of As that could have an effect on accuracy[173]. Zhang et al.[17] explained that the new method could establish the health risk value, since it mainly focuses on dissolving the inorganic As in groundwater. The precipitation form, on the other hand, was excluded because of its weight, which is a function of the metal’s concentration, activity and relative atomic mass. In addition to its mobilization, its toxicity was also revealed, following its characterization of risk. From this result, the pentavalent form of $HAsO_4^{-2}$ was established as a major species resulting in potential health risks, including both non-cancer risks and cancer risks. Meanwhile, $H_2AsO_4^-$ and H_3AsO_3 also had extremely high-risk values. The study of Li et al.[173] demonstrated that $H_2AsO_4^-$ was strongly toxic with a high bioavailability, as compared to the other pentavalent species. According to the results from a health risk estimation, the two methods differed slightly. Therefore, As species-concentration can used as an additional method that will be useful in selecting an effective treatment technique for reducing the health risks of the population.

4.7.2 Probabilistic health risk assessment by considering As and Pb concentrations

I) Non-carcinogenic risk

The health risk value distribution of As and Pb through the oral pathway was 3.31 ± 10.61, ranging from 2.80E-03 to 3.85E+02 and 7.65E-03 ± 8.60E-03 (As), and from 2.43E-04 to 1.25E-01 (Pb), respectively (Table 4.11). The 95th percentile of the HQ_{ing} level was 12.64 (ranging from 5.11E-03 to 3.85E+02) (Fig. 4.9), while the risk levels of the As and Pb by dermal exposure were 3.57E-02 ± 9.47E-02, ranging from 1.67E-04 to 3.09 (As); and 4.00E-05 ± 7.22E-05 , ranging from 5.48E-06 to 2.69E-03 (Pb), respectively. The 95th percentile of the HQ_{der} value was 1.17E-01 (ranging from 1.82E-04 to 3.09). According to the results obtained, groundwater drinking was the predominant pathway, resulting in a potential health risk in the area. The 95th percentile of the HI level was 12.67 (ranging from 1.39E-02 to 3.85E+02), which exceeded the safe value of 1. However, half of all simulation risk values were below the acceptable value.

Table 4.11 Variation range of HQ_{As} and HQ_{Pb} for both pathways and CR of As simulated through 5,000 iterations of the Monte Carlo Simulation

Parameter	5th Percentile	95th Percentile	5th Percentile	95th Percentile
Non-carcinogenic risk	HQ_{ing}		HQ_{der}	
As	6.79E-02	**1.26E+01**	2.25E-03	1.17E-01
Pb	1.13E-03	2.27E-02	3.99E-06	1.27E-04
Carcinogenic risk	CR_{ing}		CR_{der}	
As	**7.85E-06**	**9.48E-04**	3.20E-07	**1.99E-05**

Remarked: Bold lettering is representative of risk values that are above the safe level as proposed by the USEPA.

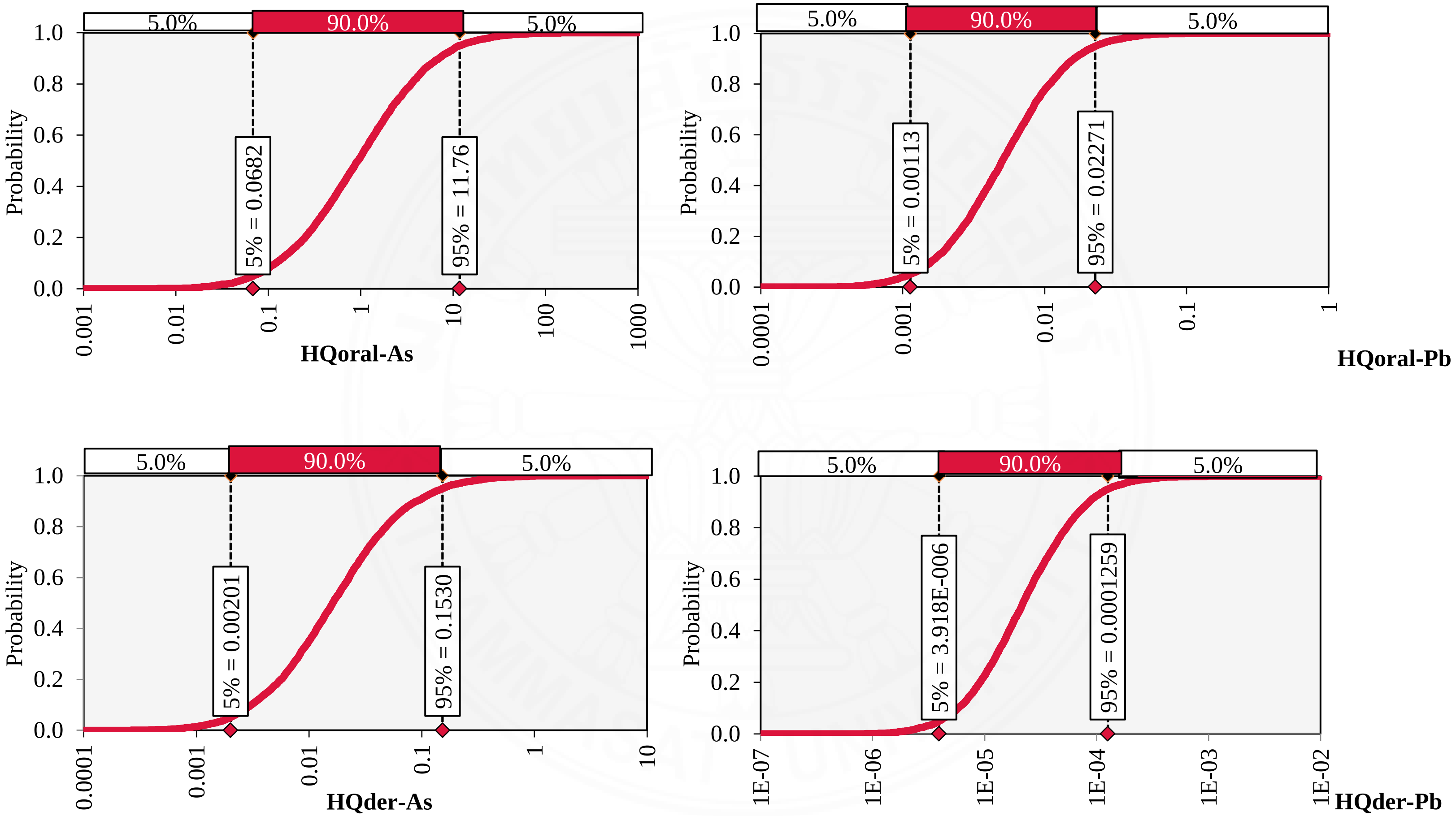


Figure 4.9 Probabilistic non-cancer risk level (HQ) reslting from the presence of As and Pb in groundwater via oral exposure and dermal exposure

II) Carcinogenic risk

The probabilistic risk value of the entry of As through oral exposure was 2.52E-04 ± 7.97E-04, ranging from 4.01E-07 to 3.29E-02 (Table 4.11). The 5th and 95th percentiles of the CR_{ing} were 7.85E-06 and 9.48E-04, respectively, which were both higher than the threshold level of 1E-06 (Fig.4.10). Meanwhile, the CR_{der} was 5.86E-06 ± 1.43E-05 (ranging from 2.54E-08 to 3.45E-04). It was determined from these results that the average risk level was mainly through the oral route, accounting for 43 times the risk of exposure via dermal contact. Since the CR_{ing} was at a high-risk potential, this pathway can result in a major increase of the TCR value. The average TCR value was 2.57E-04. The 95th percentile of the TCR value was 9.50E-04, while the highest risk level was 3.30E-02. Most of the random values were strongly influential in elevating the health risk value incurred by ingestion through oral pathways.

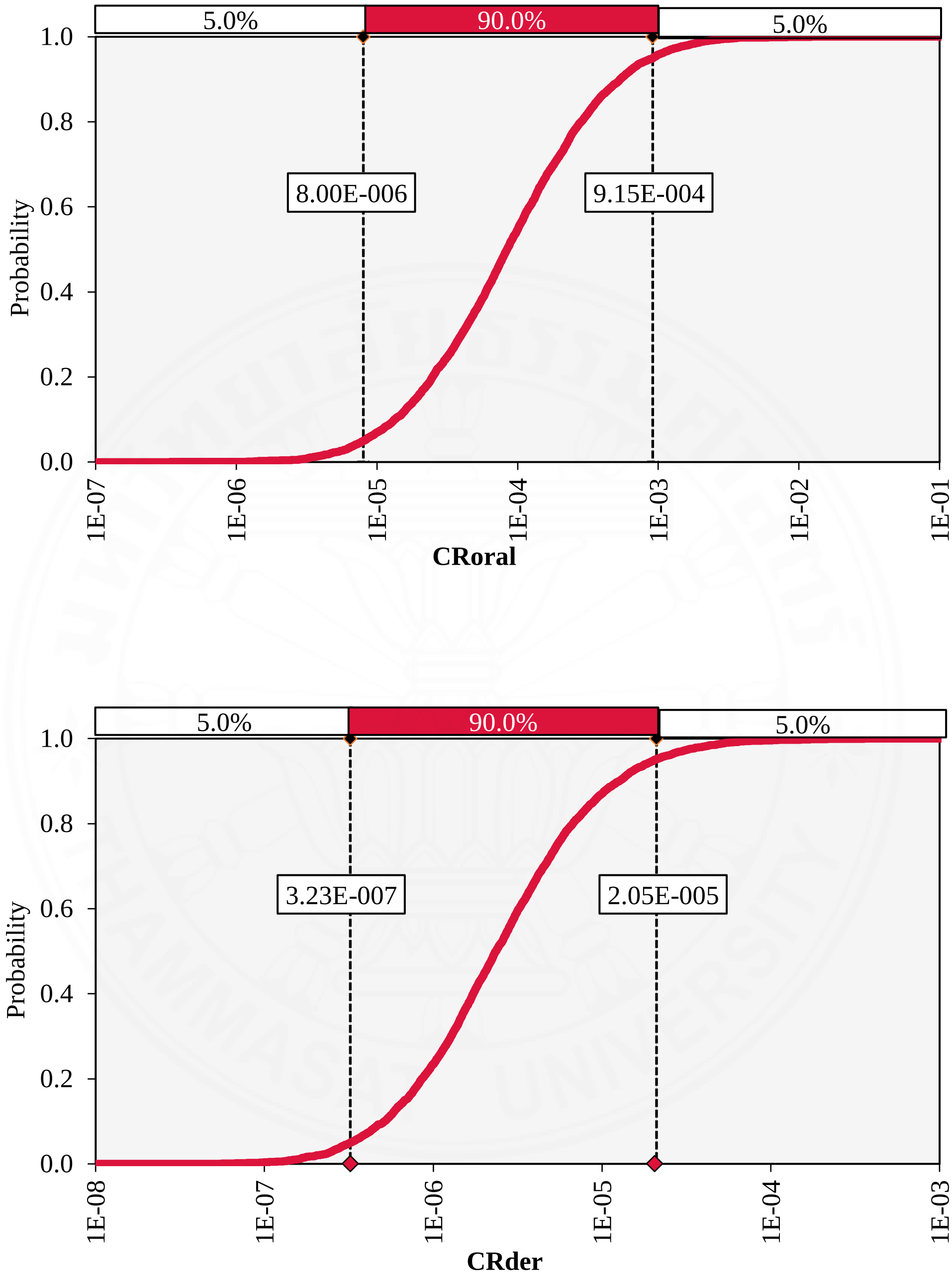


Figure 4.10 Probabilistic cancer risk level caused by As in groundwater via oral and dermal exposure

The As proved to be a major contributor to both non-carcinogenic risk and carcinogenic risk, since the average As in the groundwater appeared at a high concentration level (16.13 µg/L). Meanwhile, oral exposure was a major route, while skin contact was a minor route of exposure. Several studies have revealed risk values in the upper 95th percentiles that put the general population at a high potential of risk[86,87]. Epidemiological studies showed that chronic inorganic-As exposure through the drinking water is correlated with increased risk to the internal organs in the form of skin, bladder, kidney, liver and/or lung cancer[175]. Moreover, five years of As exposure in only small concentrations can cause hyperkeratosis in the form of pigmentation changes, skin lesions and hard patches on the palms and soles of the feet before finallydeveloping skin cancer[176]. In the past decades, As-contaminated groundwater from the effect of tin-mining activity in Ronpibul Sub-district, Nakhon Si Thammarat Province, Southern Thailand, was found, resulting in adverse health effects in the people of the area. Meanwhile, the movement of As to the adjacent areas can result in high As concentrations in the groundwater and a high risk value for those people who are drinking that water.

The potential risk through groundwater consumption was commonly affected by exposure factors, such as concentration and IR[43]. In addition to groundwater consumption, the accumulative risk associated with As could increase by the presence of algae, the consumption of rice, chocolate and Thai herbs, and occupations involving As in their activity[143,149,150]. Kaur et al.[177] revealed that the probabilistic approach was a good method and useful for estimating health risks and providing more information, as compared with deterministic calculation. However, these results were based on the available information and exposure scenario of these local residents. Therefore, the probabilistic health risk might change if people have their groundwater treated before drinking or by considering the other population groups. Consequently, chronic health effects caused by As-contaminated water could occur if the As concentration in the groundwater is not reduced.

III) Model Sensitivity Analysis of Risk Calculation

A probabilistic model was applied to estimate the health risk assessment, while the variance of risk value depended on the variability that occurred because of changes in the parameter variables. This study used @Risk software for sensitivity analysis by considering these parameters: C (As and Pb concentrations), IR, ED, ET, SA and BW, which were used for the assessment of risk via the oral and dermal pathways. The most influential impact factor on the health risk level can be explained by using the Spearman Rank correlation coefficient and by including HQ_{As} and HQ_{Pb} for the oral pathway, HQ_{As} and HQ_{Pb} for the dermal pathway and CR for both routes of exposure. The tornado plot indicates the percentage of sensitivity parameters, as shown in Fig. 4.11. In this condition, the greatest impact on the output variable was the As level, followed by ED and IR, respectively, in both non-carcinogenic risks and carcinogenic risks, while BW had an inverse impact on the model. A similar study confirmed this result[86]. It could explain why a high As concentration, long ED and high IR contributes to potential health risks. Meanwhile, many studies have reported that BW was inversely correlated to sensitivity[18,178,179]. Notably, a greater body weight tended to decrease sensitivity. Total body weight does not account for the magnitude of adipose tissue, muscle mass or lean body weight. The chemical binding with any of the tissues was widely distributed in the large body compartment, resulting in a low risk, as compared with the person who has only a small body weight. Therefore, the change of body weight can influence the tissue compartments and plasma protein binding[180].

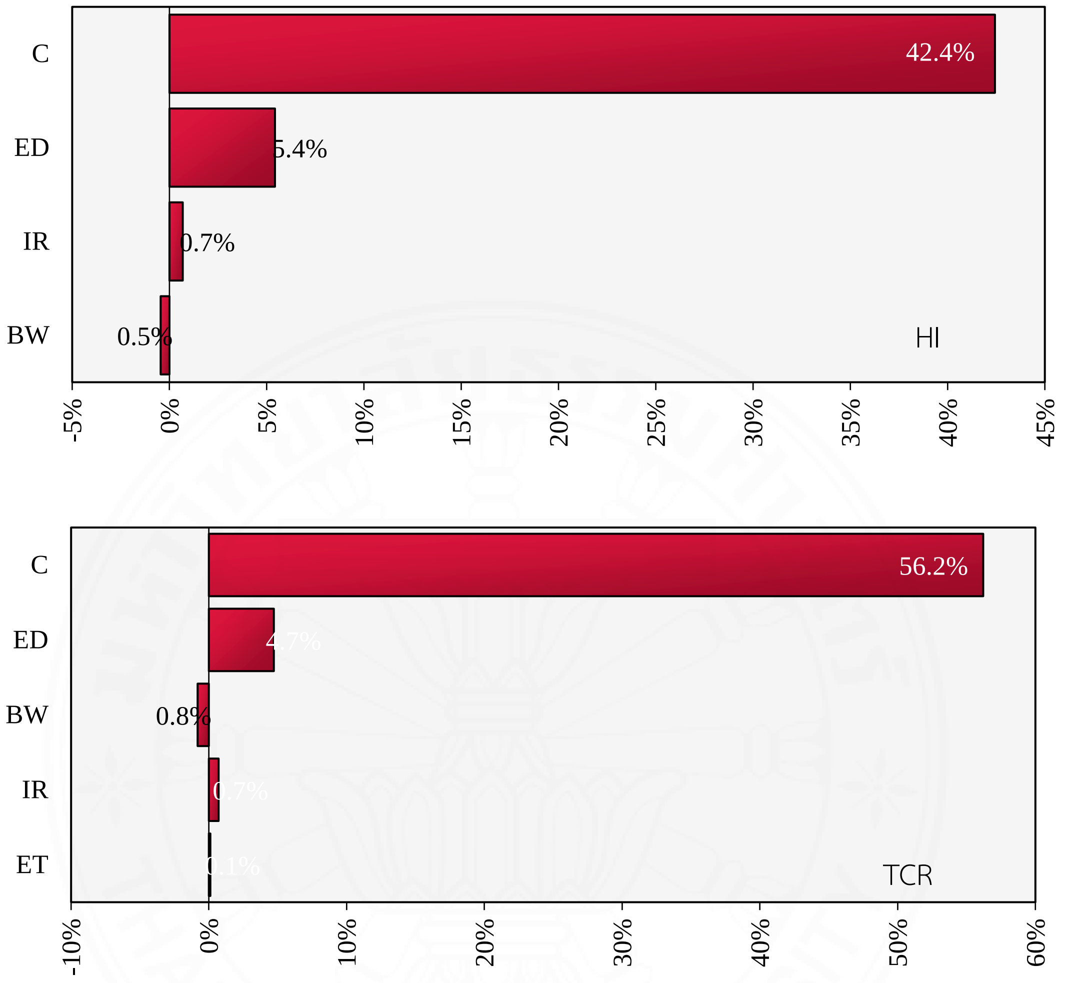


Figure 4.11 The contribution of the input parameters to the sensitivity of HI and TCR

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

This study investigated the As species and Pb concentrations and their spatial distribution in the groundwater of the Ban Khai District, Rayong Province, Thailand. From these results, the following conclusions may be drawn:

i) Heavy metals in the groundwater and their spatial distribution:

- As levels were above the WHO guideline of 10 µg/L for drinking water in approximately 22% of 80 samples, while the Pb levels in all samples was lower than the WHO guideline of 10 µg/L for drinking water.
- The major sources of As and Pb may originate from mineral weathering resulting from dissolution caused by silicate weathering. The highest As value (183 µg/L) may have affected the nearby industrial areas because of the influence of the groundwater flow.
- The As levels were different in the Qcl and Gr aquifers during the dry season. High As levels mainly existed in the form of As^{5+} in the Qcl aquifers. The results of multivariate statistics indicated that the oxidation condition and pH were the major factors controlling As speciation.
- The As distribution corresponded to the groundwater flow but did not differ between the dry and wet seasons. Meanwhile, there was a very low Pb content in the groundwater, and the contours for both seasons were similar.
- From the determination of the As species from the field investigation and calculation by use of Visual MINTEQ, it was shown that As^{5+} was the dominant speciation in the area.

The part of the health risk assessment pertaining to the effects of heavy metal contamination in the groundwater was determined two parts, including i) bioindicators for exposure assessment and ii) health risk assessment. This part of the assessment proceeded as follows:

i) Bioindicators in the form of UPb and UAs

- Approximately 98% of all UPb samples were within the normal NIOSH value of 60 µg/gCr for a healthy adult.
- In the case of UAs, the participants were sub-divided into two groups, an L group (people who consumed groundwater with As < 10 µg/L) and an H group (people who consumed groundwater with As > 10 µg/L). Most of the UAs samples from the H group exceeded the normal NHANES value of 50 µg/L.
- The participants in the H group had a positive correlation with their UAs levels. Otherwise, there were no socio-demographic factors correlated with the UAs levels in the L or H group. The As concentration-and-drinking exposure factors (IR, EF, ED and ET) had a major impact by increasing the UAs level while dermal contact was only a minor factor.

ii) Human health risk assessment

- The concentration of As speciation calculated by Visual MINTEQ modeling was ordered according to the following sequence: $HAsO_4^{-2} > H_2AsO_4^- > H_3AsO_3 > H_2AsO_3^- > AsO_4^{-3} > H_3AsO_4 > HAsO_3^{-2}$. The results of a deterministic health risk assessment of As from Visual MINTEQ and from the field of investigation were similar in value.
- The Monte Carlo approach indicated that the probabilistic estimated 95th percentile values of the HI and TCR values exceeded the safe levels of 1 and 10^{-6}, respectively.

- The As concentration was the predominant influential parameter for HI and TCR, but BW had a negative effect on human health risk.

5.2 Recommendations

Both the deterministic and probabilistic approaches were based on actual values taken from the questionnaire responses of the residents. The situation was controlled by the condition that had been set for the year in which data was collected on both the heavy metals concentration and the exposure parameters. The result of deterministic risk was an exact value and was shown as a point value, while the result of the probabilistic method was an estimation interval in which many scenarios were provided. In the case of health risk management, this scenario was useful and flexible, depending only on the limitation of the area. However, the predictive risk values can result in an overestimation. The exposure assessment is useful toward understanding the association between the source (As in the groundwater) and the receptors (users). The heavy metals in the urine were presented as a bioindicator of groundwater exposure. The results showed that a high As level in the groundwater wells was correlated with high levels of UAs. However, it cannot confirm that groundwater consumption was a source of As in the urine, because the people could be exposed to As from other sources encountered in daily life, such as in food, beverage and Thai herbs. However, there were still no chronically occurring signs from these participants, and there are none appearing at the present moment. Meanwhile, there were no cancer-death reports from Ban Khai District; there was no indication of death from such terminal conditions as chronic renal failure, or liver or lung cancer, anywhere in this area[181].

On the basis of this evidence, these recommendations are offered:

i) The relevant authorities should make available some alternative water supply and encourage the local residents to drink from more than one source, such as by drinking bottled water and water from water-vending machines. A program of this sort should be directed particularly toward those people who have been drinking water from wells with high As concentrations.

ii) In cases of unavoidable circumstances, effective treatment is needed in order to reduce the metals concentration. It will be necessary to consider the component factors and the oxidation-reduction potential, in particular. Meanwhile, the public health officers should be monitoring the health effects on the local residents, especially the multiple internal-organ cancers (liver, kidney, lung and bladder) and skin cancer. In addition to the participants in the H group, children are a particularly sensitive group. Their condition should be evaluated for exposure and a health risk assessment of their well-being should be made for further study.

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APPENDICES

APPENDIX A

Questionnaire in English version

Please fill ✓ in the square according to the true statements concerning yourself

Part I: Socio-Demographic information

1.1 General information

A. Address.. ....

B. Gender ☐ Male ☐ Female ☐ Others

C. Age .... years old

D. Weight .... Kilogram and Height .... Centimeter

E. How long have you lived in Ban Khai district, Rayong province?

.......years

F. Education ☐ Elementary ☐ High school

☐ Bachelor's or higher ☐ Any other (specified)...........

G. Occupational ☐ Student

☐ Government officer/State enterprises

☐ Agriculturist

☐ Local administration

☐ Employee

☐ Any other..........................

H. Number of family members .... persons

1.2 Personal health

1.2.1 Do you have the symptoms within these six months?

☐ Anorexia
☐ Diarrhea
☐ Convulsions
☐ Fatigue
☐ Hallucinations
☐ Vertigo
☐ Any other (specified)........
☐ Vomiting
☐ Bloody urine
☐ Hypertension
☐ Sleeplessness
☐ Arthritis
☐ Abdominal pain

1.2.2 Alcohol consumption

- Do you drink alcohol?
  ☐ Yes, ever (At present)
  ☐ Yes, ever (Stop drinking)
  ☐ No (skip to No. 1.2.3)
- Frequency☐ < 1 times/week ☐ 1-3 times/week ☐ > 3 times/week
- Duration time for drinking .... years

1.2.3 Do you smoke?

- Do you smoke cigarette?
  ☐ Yes, ever (At present)
  ☐ Yes, ever (Stop smoking)
  ☐ No (skip to No. 2.1)
- Frequency ☐ < 1 times/week ☐ 1-3 times/week ☐ > 3 times/week
- Duration time for smoking .... years
- Do the family members have smoking?
  ☐ Yes ☐ No

Part II: Water Consumption

2.1 Source of drinking water

A. The problem of water resources which you found in the area (You can choose more than one list.)

☐ Poor quality ☐ Lack of water supply for consumption and daily use

☐ Not enough of water supply ☐ Any other (specified).........

B. What is the source of water which you use for drinking (You can choose more than one list)?

☐ Groundwater supply

☐ Rain

☐ Bottled water

☐ Groundwater well

☐ Buying from the drinking water plant in the area

☐ Any other (specified).........

C. What is the activity, which you use from groundwater (You can choose more than one list?)

☐ Drinking/Cooking ☐ Bathing ☐ Washing some food ☐ Agricultural

☐ Any other (specified).......................................

2.2 Groundwater consumption

A. How to use the water from groundwater well?

☐ Directly from the well ☐ Storage in the container around .... months

B. What is the type of container which using for storage water?

☐ Stainless ☐ Aluminum ☐ Plastic ☐ Any other (specified)........

C. Do you use groundwater as a drinking water?

☐ Yes ☐ No

- How long of groundwater drinking............... Years
- Daily consumption .... Liters/day
- The volume of water which you use for cooking .... Liters/day
- Pretreatment before drinking or not?

☐ Yes, by boiling

☐ Yes, by adding choline

☐ Yes, by adding alum

☐ Yes, by other process (specified).........

☐ No

D. Do you use groundwater for showering?

☐ Yes ☐ No

Using for showering/washing

☐ Body ☐ Arm and hand ☐ leg and foot ☐ Face

- showering .... Times/day
- Exposure time ....Minutes/time
- showering ☐ Bath ☐ Shower ☐ Any other (specified).........
- Pretreatment before using or not?

☐ Yes, by boiling ☐ Yes, by adding choline

☐ Yes, by adding alum ☐ Yes, by other process (specified).........

☐ No

Duration time for groundwater showering .... Years

E. Do you use groundwater in agricultural activity?

☐ Yes ☐ No (End of question)

- Groundwater using ☐ Cultivation ☐ Farming ☐ Any other (specified).........
- What is the most of organ which has the opportunity to expose water during work?

☐ Body ☐ Arm and hand ☐ leg and foot ☐ Face

- Exposure time.............................. minutes/time
- Duration time for groundwater using for agricultural............... Years

_______________Thank you_______________

APPENDIX B

Questionnaire in Thai version

งานวิจัย การประเมินความเสี่ยงต่อสุขภาพจากสารหนูและตะกั่วและการกระจายตัวในน้ำบาดาล ในพื้นที่อำเภอบ้านค่าย จังหวัดระยอง ประเทศไทย

แบบสอบถามข้อมูลสำหรับผู้ใช้น้ำบาดาลเพื่อการอุปโภคบริโภค

คำชี้แจง แบบสอบถามนี้เป็นส่วนหนึ่งของงานวิจัย “การประเมินความเสี่ยงต่อสุขภาพจากสารหนูและตะกั่วและการกระจายตัวในน้ำบาดาล ในพื้นที่อำเภอบ้านค่าย จังหวัดระยอง ประเทศไทย”มีวัตถุประสงค์ เพื่อรวบรวมข้อมูลเพื่อใช้ประกอบการพิจารณาในการประเมินความเสี่ยงต่อสุขภาพจากการใช้น้ำบาดาล

แบบสอบถามนี้ ประกอบด้วยชุดคำถาม 2 ส่วน

ส่วนที่ 1 ข้อมูลทั่วไปของผู้ตอบแบบสอบถาม

1.1 ข้อมูลทั่วไป

1.2 ข้อมูลสุขภาพ

ส่วนที่ 2 ข้อมูลการใช้น้ำ

2.1 แหล่งน้ำดื่ม
2.2 ข้อมูลการใช้น้ำบาดาล

โดยขอให้เติมข้อความลงในช่องว่างหรือทำเครื่องหมาย ✓ ลงในช่องสี่เหลี่ยม ตามความคิดเห็นของท่าน และขอรับรองว่าคำตอบที่ได้จากแบบสอบถามนี้ถือเป็นความลับ การเผยแพร่ข้อมูลจะแสดงในรูปแบบ ข้อมูลสถิติเชิงภาพรวม ไม่เชื่อมโยงเป็นรายบุคคล

ส่วนที่ 1 ข้อมูลผู้ตอบแบบสอบถาม

1.1 ข้อมูลทั่วไป

ก. ที่อยู่.. ...

ข. เพศ ☐ ชาย ☐ หญิง ☐ ไม่ระบุ

ค. อายุ .... ปี

ง. น้ำหนัก .... กิโลกรัม ส่วนสูง .... เซนติเมตร

จ. ท่านอยู่อาศัยในพื้นที่อำเภอบ้านค่าย จังหวัดระยอง เป็นระยะเวลา .... ปี

ฉ. ระดับการศึกษาขั้นสูงสุด ☐ ประถมศึกษา ☐ มัธยมศึกษา

☐ ปริญญาตรีหรือสูงกว่า ☐ อื่นๆ ....

ช. อาชีพ ☐ นักเรียน/นักศึกษา ☐ ข้าราชการ/รัฐวิสาหกิจ ☐ เกษตรกร

☐ องค์กรปกครองส่วนท้องถิ่น ☐ รับจ้าง ☐ อื่นๆ ....

ซ. จำนวนสมาชิกในครัวเรือน (รวมผู้ตอบแบบสอบถามด้วย) .... คน

1.2 ข้อมูลสุขภาพ

1.2.1 <u>ในช่วงระยะเวลา 6 เดือน</u> ที่ผ่านมาท่านมีอาการใดบ้าง (ตอบได้มากกว่า 1 ข้อ)

● รู้สึกเบื่ออาหาร	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● รู้สึกคลื่นไส้อาเจียน	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● อาการท้องเสีย	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● ปัสสาวะมีเลือดปน	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● อาการชัก	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● ภาวะความดันโลหิตสูง	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● อาการอ่อนเพลีย เหนื่อยล้า	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี

● อาการนอนไม่หลับ	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● เห็นภาพหลอน	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● อาการข้ออักเสบ	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● อาการเวียนศีรษะบ้านหมุน	☐ มี นานๆครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● ปวดท้องภายในช่วงช่วงระยะเวลา 1 ชั่วโมงหลังรับประทานอาหาร	☐ มี นานๆ ครั้ง	☐ มีเป็นประจำ	☐ ไม่มี
● อื่นๆ (ระบุ)..			

1.2.2 การดื่มสุรา

- ท่านดื่มเครื่องดื่มที่มีส่วนผสมของแอลกอฮอล์ (เช่น เหล้า เบียร์ ไวน์) ใช่หรือไม่
  ☐ ใช่ ปัจจุบันยังดื่ม
  ☐ ใช่ เคยดื่ม (ปัจจุบันเลิกแล้ว)
  ☐ ไม่ใช่ (ข้ามไปข้อ 1.2.3)
- ความถี่ในการดื่มเครื่องดื่มที่มีส่วนผสมของแอลกอฮอล์
  ☐ <1 ครั้ง/สัปดาห์ ☐ 1-3 ครั้ง/สัปดาห์ ☐ มากกว่า 3 ครั้ง/สัปดาห์
- ระยะเวลาที่ท่านดื่มเครื่องดื่มที่มีส่วนผสมของแอลกอฮอล์ .... ปี

1.2.3 การสูบบุหรี่

- ท่านสูบบุหรี่ใช่ หรือไม่
  ☐ ใช่ ปัจจุบันยังสูบ
  ☐ ใช่ เคยสูบ (ปัจจุบันเลิกแล้ว)
  ☐ ไม่ใช่ (ข้ามไปข้อ 2.1)
- ความถี่ในการสูบบุหรี่
  ☐ <1 ครั้ง/สัปดาห์ ☐ 1-3 ครั้ง/สัปดาห์ ☐ มากกว่า 3 ครั้ง/สัปดาห์
- จำนวนบุหรี่ที่ท่านสูบ .... มวน/วัน หรือ.......มวน/สัปดาห์

- ระยะเวลาที่ท่านสูบบุหรี่ .... ปี
- สมาชิกในบ้านของท่านสูบบุหรี่ใช่ หรือไม่

  ☐ ใช่ ☐ ไม่ใช่

ส่วนที่ 2 ข้อมูลการใช้น้ำ

2.1 แหล่งน้ำดื่ม

ก. เหตุผลที่ท่านเลือกใช้น้ำบาดาลในการอุปโภคบริโภค (ตอบได้มากกว่า 1 ข้อ)

☐ น้ำไม่เพียงพอเพื่อการเกษตร

☐ หน่วยงานท้องถิ่นจัดไว้ให้โดยทำเป็นน้ำประปาหมู่บ้าน

☐ ขาดแคลนแหล่งน้ำเพื่อการอุปโภคบริโภค

☐คุณภาพจากแหล่งน้ำที่ใช้อยู่ไม่ได้มาตรฐาน

☐ อื่น ๆ(ระบุ)............................

ข. ท่านดื่มน้ำจากแหล่งใดบ้าง (ตอบได้มากกว่า 1 ข้อ)

☐ น้ำประปาหมู่บ้าน ☐ น้ำฝน ☐ น้ำดื่มบรรจุขวด ☐ น้ำบาดาล

☐ น้ำดื่มบรรจุถังที่ผลิตในเขตพื้นที่ ☐ น้ำตู้หยอดเหรียญ ☐ อื่น (ระบุ)..........

2.2 ข้อมูลการใช้น้ำบาดาล

ก. ท่านมีวิธีการนำน้ำบาดาลมาใช้อย่างไร

☐ ใช้โดยตรง

☐ กักเก็บไว้ก่อนนำมาใช้ โดยถังพักมีขนาดประมาณ..........ลิตร

☐ กักเก็บไว้ในถังพักเป็นระยะเวลา .... วัน ก่อนที่จะนำมาใช้

ข. ภาชนะที่ใช้รองรับหรือกักเก็บน้ำบาดาลเป็นวัสดุชนิดใด

☐ ถังสแตนเลส ☐ ถังอลูมิเนียม ☐ ถังพลาสติก ☐ โอ่งดินเผา

☐ โอ่งซีเมนต์ ☐ อื่น (ระบุ)..............................

ค. ท่านมีการดื่ม/กินน้ำบาดาลหรือไม่

☐ ดื่ม/กิน ☐ ไม่ดื่ม/ไม่กิน

- ระยะเวลาที่ใช้น้ำบาดาลในการดื่ม กิน .... ปี
- ปริมาณการดื่มน้ำต่อวัน .... ลิตร
- ปริมาณที่ใช้ในการทำอาหารต่อวัน (รวมถึงน้ำที่ใช้ในการล้างผัก/ภาชนะต่างๆที่ใช้ปรุงอาหารด้วย)........................ ลิตร
- ท่านมีการบำบัดน้ำก่อนนำมาดื่มกินหรือไม่

☐ มี โดยวิธีต้ม ☐ มี โดยวิธีเติมคลอรีน ☐ มี โดยวิธีกรอง

☐ มี โดยวิธีใส่สารส้ม ☐ มี โดยวิธีอื่นๆ (ระบุ)............. ☐ ไม่มี

ง. ท่านใช้น้ำบาดาลชำระร่างกายหรือไม่

☐ ใช้ ☐ ไม่ใช้

- การใช้น้ำเพื่อชำระร่างกาย

  ☐ ทั้งร่างกาย ☐บางอวัยวะ เช่น ใบหน้า/ แขนและมือ/ ขาและเท้า

- ท่านอาบน้ำวันละ .... ครั้ง
- ระยะเวลาที่อาบน้ำต่อครั้ง .... นาที
- วิธีการอาบน้ำ ☐ ตักขันอาบ ☐ ฝักบัว ☐ อื่นๆ(ระบุ).............
- ปริมาณน้ำที่ใช้ต่อครั้ง .... ลิตร
- ท่านมีการบำบัดน้ำก่อนนำมาใช้หรือไม่

  ☐ มี โดยวิธีต้ม ☐ มี โดยวิธีเติมคลอรีน ☐ มี โดยวิธีใส่สารส้ม

  ☐ มี โดยวิธีอื่นๆ (ระบุ)............. ☐ ไม่มี

- ระยะเวลาที่ใช้น้ำบาดาลในชำระร่างกาย .... ปี

จ. ท่านใช้น้ำบาดาลในการเพาะปลูก

☐ ใช้ ☐ ไม่ใช้ (ใช้น้ำจากแหล่งอื่น)

ขณะทำงานท่านมีโอกาส สัมผัสน้ำ /ร่างกายเปียก โดยส่วนใหญ่บริเวณใด

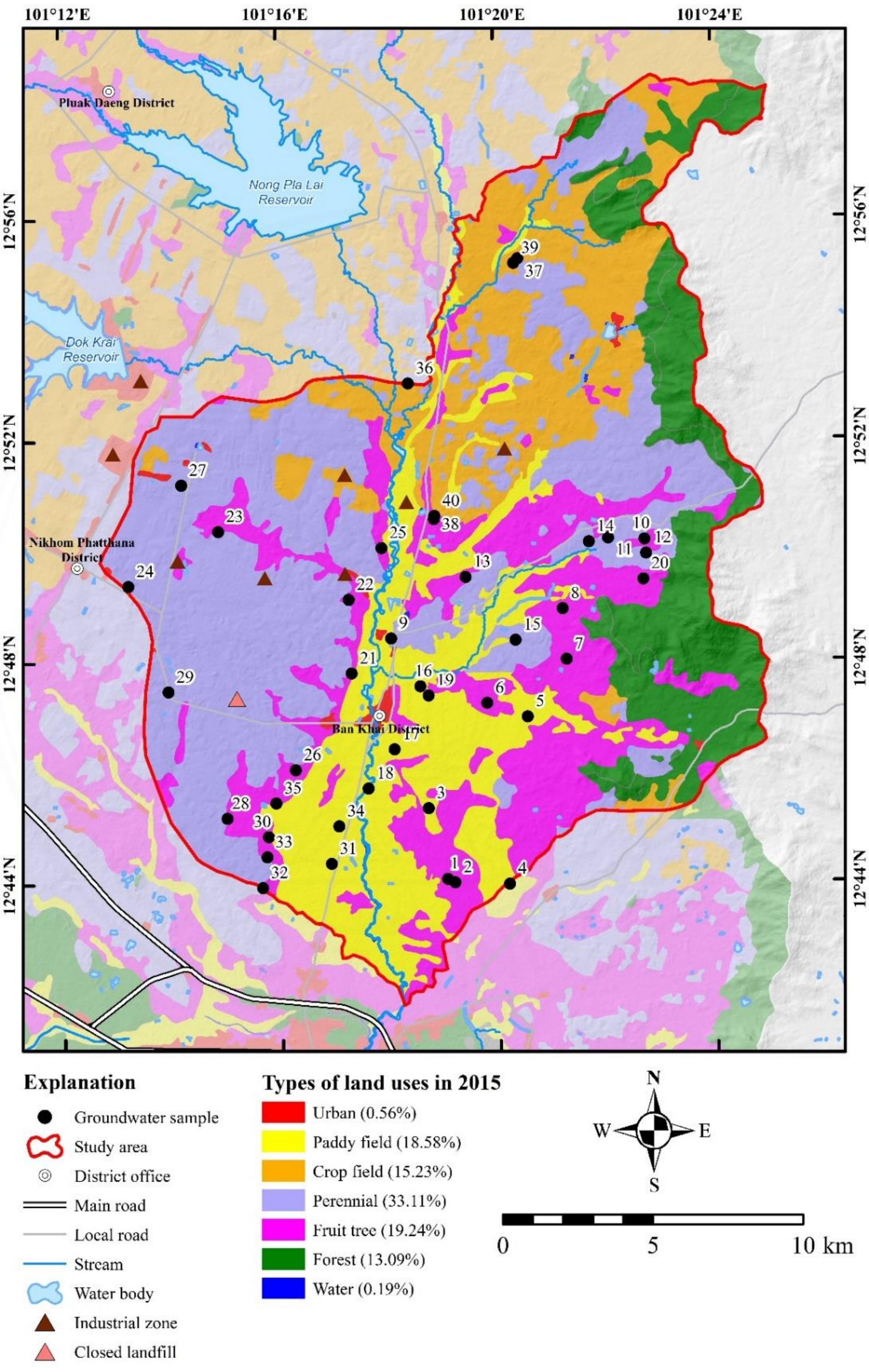
☐ ทั้งร่างกาย ☐แขนและมือ ☐ขาและเท้า ☐ ใบหน้า

- ระยะเวลาที่สัมผัสน้ำหรือเปียก ....นาที
- ระยะเวลาที่ใช้น้ำบาดาลในการทำการเกษตร.............ปี

*****************ขอบคุณค่ะ*****************

APPENDIX C

The land uses map of the study area with sampling points[88]



APPENDIX D

The charge balance calculation in dry season

Dry season (n = 39)

No	X	Y	Aquifer	Well depth (m)	Elevation (m, amsl)	Cations (mg/L)				Anions (mg/L)						Charge balance (%)
						Mg	Na	K	Fe	Cl-	NO_3^-	SO_4^{2-}	HCO_3^-	TDS	CO_3^{2-}	
1	751638	1408880	Qcl	22	50	34.53	47.07	13.95	0.16	5.48	<0.001	1.66	339.00	345.60	266.57	4.23
2	751882	1408764	Qcl	104	19	2.95	20.33	4.18	0.79	24.30	<0.001	6.29	43.70	165.12	59.58	-2.60
3	750994	1411235	Gr	98	52	1.07	2.08	1.36	0.02	0.48	<0.001	<0.001	14.20	13.76	134.39	-3.02
4	753699	1408721	Qcl	24	16	3.31	80.67	6.78	0.02	18.60	0.21	0.09	196.00	272.00	53.57	5.16
5	754289	1414295	Qcl	85	56	10.95	43.47	2.73	0.01	11.40	0.52	5.28	164.00	200.32	184.90	3.45
7	755583	1416215	Qcl	36	65	7.05	16.52	5.29	43.47	2.51	0.75	<0.001	146.00	280.96	191.41	4.96
8	755[redacted]	141[redacted]	Qcl	80	69	3.58	10.51	3.72	0.01	4.48	<0.001	0.12	63.70	65.92	187.16	1.23
9	749[redacted]	141[redacted]	Gr	128	25	0.15	5.631	12.96	0.03	4.71	<0.001	0.34	24.80	29.63	63.10	4.43
10	758170	1420222	Gr	92	136	3.48	5.85	2.64	0.21	8.58	1.19	3.78	20.10	44.86	354.26	3.89
11	756958	1420253	Gr	86	45	6.20	14.28	8.85	0.03	25.90	2.20	4.46	122.00	185.60	137.92	4.29
12	758226	1419750	Gr	67.5	71	7.25	33.24	2.86	0.04	21.50	<0.001	17.90	132.00	211.84	207.23	5.59
13	752217	1418938	Gr	73.5	49	10.32	17.33	4.13	0.40	5.07	<0.001	0.00	148.00	177.28	164.83	-4.24
14	756322	1420126	Gr	68	76	4.51	9.712	4.49	15.43	2.38	<0.001	<0.001	74.30	123.01	208.51	-3.38
15	753[redacted]	141[redacted]	Qcl	13	67	1.58	9.132	4.15	3.82	12.40	3.24	0.26	33.00	69.25	173.99	-3.17
16	750716	1415294	Gr	36	17	8.24	9.47	20.81	0.02	10.80	0.32	40.60	74.30	156.80	76.28	3.50
17	749860	1413196	Gr	42	14	2.88	12.49	4.84	0.01	9.07	0.40	4.51	47.20	65.28	46.80	-3.52
18	748992	1411888	Gr	92	60	1.01	24.31	8.98	0.02	25.00	0.12	1.89	57.80	105.86	154.12	-3.77
19	750988	1414991	Gr	94	48	0.71	14.09	6.42	0.01	6.10	0.13	1.50	40.10	46.85	122.90	2.52

Dry season (n = 39)																
No	X	Y	Aquifer	Well depth (m)	Elevation (m, amsl)	Cations (mg/L)				Anions (mg/L)						Charge balance (%)
						Mg	Na	K	Fe	Cl-	NO_3^-	SO_4^{2-}	HCO_3^-	TDS	CO_3^{2-}	
20	758598	1418600	Gr	122	28	2.43	13.45	4.77	0.01	12.00	0.79	19.50	18.90	79.04	79.95	-3.45
21	748430	1415718	Qcl	61.5	21	3.25	96.07	3.40	0.01	2.28	1.13	<0.001	295.00	353.92	65.82	-1.49
22	748328	1418173	Qcl	20	36	2.03	81.73	5.26	0.04	3.03	1.45	4.04	236.00	264.32	98.31	0.46
23	743983	1420430	Gr	37.5	10	12.48	14.42	3	0.01	25.40	1.55	5.80	257.00	316.80	76.17	5.01
24	740997	1418600	Gr	67	74	3.32	6.73	9.92	0.06	5.39	28.30	5.67	22.40	71.36	198.62	-1.70
25	749417	1419896	Gr	150	43	3.67	15.90	11.004	0.02	2.93	1.20	1.44	83.80	67.71	122.54	-3.73
26	746573	1412495	Gr	99	40	3.60	68.17	5.35	0.01	2.50	0.67	0.09	218.00	239.36	114.76	3.73
27	742754	1421976	Gr	39	47	6.01	12.16	7.88	0.01	6.03	17.50	3.78	63.70	100.80	142.12	5.10
28	744299	1410874	Gr	102	18	5.19	19.70	15.19	3.20	2.20	0.00	0.71	132.00	139.52	66.28	0.70
29	742334	1415087	Qcl	30	84	2.90	6.21	1.37	10.20	14.30	<0.001	0.17	236.00	274.56	221.91	-1.28
30	745675	1410265	Gr	90	16	4.31	39.75	16.22	0.21	1.28	0.76	0.39	200.00	225.28	57.68	0.59
31	747769	1409377	Qcl	42	44	2.36	86.2	9.06	0.63	15.00	0.11	5.87	243.00	296.32	119.67	0.72
32	745481	1408570	Gr	124	50	5.22	58.7	19.72	0.42	5.00	1.42	<0.001	262.00	278.40	146.39	2.69
33	745626	1409593	Gr	70	40	2.95	8.55	7.95	0.33	4.43	0.70	1.95	53.10	60.74	112.09	-4.04
34	748020	1410628	Gr	110	35	0.68	15.04	7.94	0.53	17.00	0.44	3.00	24.80	87.74	90.29	-1.11
35	745924	1411388	Qcl	30	17	8.80	35.07	15.57	0.02	33.70	7.48	35.00	79.10	216.32	78.59	4.00
36	750296	1425381	Gr	114	36	1.29	5.42	4.14	0.01	4.98	13.30	0.08	14.20	36.29	95.28	-3.92
37	753940	1429559	Gr	90	73	5.00	10.08	2.43	0.07	17.60	0.00	25.10	4.72	111.10	202.99	0.69
38	751161	1420866	Gr	84	35	1.37	10.27	2.51	0.01	16.20	0.22	4.61	17.70	61.31	93.12	-2.09
39	753940	1429559	Gr	100	69	8.93	19.66	3.71	0.01	13.70	0.00	1.38	123.00	179.20	209.10	2.89
40	751177	1420966	Gr	90	48	0.71	8.28	3.02	0.04	9.10	1.29	0.55	16.50	49.02	122.93	0.60

APPENDIX E

The charge balance calculation in wet season

Wet season (n = 40)

No	X	Y	Aquifer	Well depth (m)	Elevation (m, amsl)	Cations (mg/L)				Anions (mg/L)						Charge balance (%)
						Mg	Na	K	Fe	Cl-	NO_3^-	SO_4^{2-}	HCO_3^-	TDS	CO_3^{2-}	
1	751638	1408880	Qcl	22	50	36.57	56.23	7.70	0.21	108.70	9.11	0.10	329.00	357.12	274.92	-8.89
2	751882	1408764	Qcl	104	19	11.53	8.84	24.85	0.01	23.35	25.20	3.79	94.50	167.68	94.79	-5.47
3	750994	1411235	Gr	98	52	0.92	1.02	4.91	0.01	0.23	0.58	0.00	14.20	10.30	133.76	3.80
4	753699	1408721	Qcl	24	16	6.98	3.50	97.19	0.01	4.69	23.40	0.21	188.00	312.32	68.63	-5.45
5	754289	1414295	Qcl	85	56	7.71	4.16	67.89	1.56	10.34	13.40	0.11	161.00	198.40	171.62	-4.89
6	752[redacted]	141[redacted]	Qcl	36	33	6.84	1.98	21.41	0.35	6.36	18.60	0.001	67.30	1.26	110.56	-5.88
7	755583	1416215	Qcl	36	65	7.64	4.78	38.81	0.36	15.52	3.39	0.001	117.00	194.56	193.83	-5.13
8	755[redacted]	141[redacted]	Qcl	80	69	4.99	3.68	26.52	0.02	8.36	5.54	1.14	73.80	65.92	192.95	-4.22
9	749[redacted]	141[redacted]	Gr	128	25	2.96	0.06	6.84	0.01	0.24	5.24	0.00	28.50	28.22	74.64	4.33
10	758170	1420222	Gr	92	136	10.53	18.07	81.36	0.39	43.57	13.20	0.00	183.00	257.92	383.18	-3.69
11	756958	1420253	Gr	86	45	11.83	16.69	72.83	0.06	51.01	30.70	2.09	154.00	227.84	160.98	-5.50
12	758226	1419750	Gr	67.5	71	12.70	13.38	46.65	0.18	36.71	27.90	0.001	157.00	226.56	229.57	-2.60
13	752217	1418938	Gr	73.5	49	7.42	17.52	53.67	0.16	14.18	5.28	0.001	157.00	159.36	152.94	-1.99
14	756322	1420126	Gr	68	76	5.09	14.54	24.38	0.15	6.16	6.02	0.19	88.10	120.19	210.86	3.42
15	753[redacted]	141[redacted]	Qcl	13	67	6.29	0.67	9.90	0.02	5.77	15.50	0.39	29.80	67.46	193.30	5.01
16	750716	1415294	Gr	36	17	20.81	3.36	8.06	0.01	36.88	16.00	0.59	118.00	198.40	127.82	5.96
17	749860	1413196	Gr	42	14	4.71	3.96	22.13	3.70	3.57	19.80	0.20	81.60	136.32	54.32	3.14
18	748992	1411888	Gr	92	60	9.48	0.46	21.25	0.02	3.78	28.20	0.09	47.90	121.60	188.88	3.36
19	750988	1414991	Gr	94	48	6.34	0.32	5.74	0.04	1.45	6.92	0.13	32.40	10.56	145.99	4.75

Wet season (n = 40)

No	X	Y	Aquifer	Well depth (m)	Elevation (m, amsl)	Cations (mg/L)				Anions (mg/L)						Charge balance (%)
						Mg	Na	K	Fe	Cl-	NO_3^-	SO_4^{2-}	HCO_3^-	TDS	CO_3^{2-}	
20	758598	1418600	Gr	122	28	4.56	1.10	4.01	0.30	1.60	10.20	4.78	14.20	71.68	88.70	3.52
21	748430	1415718	Qcl	61.5	21	17.80	9.97	121.50	0.03	5.40	1.97	0.62	312.00	368.64	125.48	3.35
22	748328	1418173	Qcl	20	36	12.07	6.77	110.70	0.06	4.68	3.62	0.43	254.00	280.96	139.47	4.36
23	743983	1420430	Gr	37.5	10	43.00	13.87	42.19	0.26	105.00	31.30	1.25	303.00	350.72	201.30	-4.82
24	740997	1418600	Gr	67	74	8.14	1.64	4.61	0.08	5.35	5.85	26.10	18.10	72.32	218.39	2.09
25	749417	1419896	Gr	150	43	7.91	2.50	14.65	0.08	2.43	3.03	0.80	73.80	69.76	139.92	-5.12
26	746573	1412495	Gr	99	40	12.90	6.78	82.46	0.46	11.60	1.85	0.61	241.00	245.76	152.88	-5.36
27	742754	1421976	Gr	39	47	12.24	2.95	20.47	0.16	12.84	6.14	11.70	77.70	129.92	167.69	4.52
28	744299	1410874	Gr	102	18	15.23	4.64	23.40	0.01	13.82	1.93	0.001	141.00	158.08	107.44	-5.46
29	742334	1415087	Qcl	30	84	34.99	6.40	34.89	0.24	69.92	12.80	0.47	220.00	307.20	353.45	-0.71
30	745675	1410265	Gr	90	16	16.21	2.29	44.07	0.01	18.34	1.24	0.39	192.00	204.80	106.46	4.45
31	747769	1409377	Qcl	42	44	19.48	3.81	83.00	0.14	10.04	10.90	0.20	275.00	353.92	189.87	-3.46
32	745481	1408570	Gr	124	50	30.30	3.58	72.93	0.15	27.84	4.10	0.74	285.00	277.12	249.23	1.78
33	745626	1409593	Gr	70	40	8.03	1.45	10.19	0.06	3.41	4.94	0.87	60.90	69.76	132.94	-5.45
34	748020	1410628	Gr	110	35	5.19	0.34	17.80	0.06	0.63	24.30	0.50	32.40	73.60	108.76	5.04
35	745924	1411388	Qcl	30	17	9.81	2.96	67.67	0.01	13.46	20.50	5.93	167.00	238.72	82.72	2.85
36	750296	1425381	Gr	114	36	2.12	0.65	6.65	0.04	2.17	6.25	14.90	18.10	207.62	98.70	-4.27
37	753940	1429559	Gr	90	73	41.32	38.28	28.87	1.83	76.02	24.60	1.29	363.00	4.57	351.90	4.32
38	751161	1420866	Gr	84	35	3.36	1.74	7.06	0.23	8.78	15.10	0.19	18.10	91.52	101.26	5.69
39	753940	1429559	Gr	100	69	7.56	10.77	14.81	0.17	10.52	22.80	0.00	76.40	104.32	203.51	-4.38
40	751177	1420966	Gr	90	48	1.37	8.29	0.01	2.68	9.74	2.42	0.49	24.60	43.52	125.61	-1.82

APPENDIX F

List of 40 groundwater samples

No.	X	Y	Explanation
1	751638	1408880	หมู่ที่ 01 วัดสวนหลาว ตำบล หนองละลอก
2	751882	1408764	หมู่ที่ 04 บ้านตาขัน ตำบล ตาขัน
3	750994	1411235	หมู่ที่ 03 โรงเรียนวัดหนองคอกหมู 12903/1763-31 ตำบล ตาขัน
4	753699	1408721	หมู่ที่ 07 บ้านหนองตะแบก (วัดจุฬาเมธี) ตำบล ตาขัน
5	754289	1414295	หมู่ที่ 03 ศูนย์เด็กเล็กบ้านห้วงหิน (A78B02) ตำบล ชากบก
6	752[redacted]	141[redacted]	คุณสก[redacted] (บ่อส่วนตัว) ตำบล บ้านค่าย
7	755583	1416215	หมู่ที่ 06 บ้านหนองหว้า ตำบล ชากบก
8	755[redacted]	141[redacted]	หมู่ที่ 06 คุณสำ[redacted] (บ่อส่วนตัว) บ้านหนองหว้า ตำบล ชากบก
9	749[redacted]	141[redacted]	คุณเนี[redacted] (บ่อส่วนตัว) ตำบลบ้านค่าย
10	758170	1420222	หมู่ที่ 11 บ้านห้วยยาง ตำบล บางบุตร
11	756958	1420253	หมู่ที่ 04 อบต.บางบุตร (บ้านพะวอ) (A46B04) ตำบล บางบุตร
12	758226	1419750	หมู่ที่ 12 บ้านชากเล็ก ตำบล บางบุตร
13	752217	1418938	หมู่ที่ 01 โรงเรียนบ้านชากมะหาด ตำบล บางบุตร
14	756322	1420126	หมู่ที่ 04 บ้านอ่างชากไผ่ ตำบล บางบุตร
15	753[redacted]	141[redacted]	คุณนิ[redacted] (บ่อส่วนตัว) ตำบล ชากบก
16	750716	1415294	หมู่ที่ 02 บ้านคลองน้ำงู ตำบล บ้านค่าย
17	749860	1413196	หมู่ที่ 06 สวนสมเด็จพระเจ้าตากสินมหาราช ม.6 ตำบล บ้านค่าย
18	748992	1411888	หมู่ที่ 05 โรงเรียนวัดบ้านค่าย (A67B04) ตำบล บ้านค่าย
19	750988	1414991	หมู่ที่ 03 วัดกระบกขึ้นผึ้ง (บ่อ 1) (A81B01) ตำบล บ้านค่าย
20	758598	1418600	หมู่ที่ 04 วัดหนองกระบอก ตำบล หนองละลอก
21	748430	1415718	หมู่ที่ 02 บ้านกระโหม ตำบล หนองละลอก
22	748328	1418173	หมู่ที่ 01 วัดดอนจันทร์ (A56B02) ตำบล หนองละลอก
23	743983	1420430	หมู่ที่ 01 วัดสวนหลาว ตำบล หนองละลอก
24	740997	1418600	หมู่ที่ 10 โรงเรียนเทคนิคบ้านค่าย ตำบล หนองละลอก
25	749417	1419896	หมู่ที่ 07 ประปาบ้านตาสิทธิ์ (A75B04) ตำบล หนองละลอก
26	746573	1412495	หมู่ที่ 05 โรงเรียนบ้านตีนเนิน ตำบล หนองละลอก

No.	X	Y	Explanation
27	742754	1421976	หมู่ที่ 09 บ้านตัวอย่าง ตำบล หนองละลอก
28	744299	1410874	หมู่ที่ 04 บ้านปากป่า(บ่อ 1) (A58B03) ตำบล หนองตะพาน
29	742334	1415087	หมู่ที่ 06 บ้านคลองนฉางใต้ ตำบล หนองตะพาน
30	745675	1410265	หมู่ที่ 04 อบต.หนองตะพาน(บ่อ 1) (A38B03) ตำบล หนองตะพาน
31	747769	1409377	หมู่ที่ 01 บ้านเกาะ ตำบล หนองตะพาน
32	745481	1408570	หมู่ที่ 03 บ้านหนองตะพาน (A38B05) ตำบล หนองตะพาน
33	745626	1409593	หมู่ที่ 04 โรงเรียนบ้านหนองสะพาน ตำบล หนองตะพาน
34	748020	1410628	หมู่ที่ 02 บ้านน้ำโฉ่ (บ่อ 1) (A38B04) ตำบล หนองตะพาน
35	745924	1411388	หมู่ที่ 05 บ้านแหลมเหียง ตำบล หนองตะพาน
36	750296	1425381	หมู่ที่ 02 บ้านหนองปลาใหล (บ่อ 2) (A66B06) ตำบล หนองบัว
37	753940	1429559	หมู่ที่ 05 วัดป่าหวาย ตำบล หนองบัว
38	751161	1420866	หมู่ที่ 06 วัดประทุมมาวาส (A76B02) ตำบล หนองบัว
39	753940	1429559	หมู่ที่ 05 โรงเรียนวัดป่าหวาย ตำบล หนองบัว
40	751177	1420966	หมู่ที่ 06 โรงเรียนวัดประทุมมาวาส ตำบล หนองบัว

Noted: Black shading due to the personal data protection policy

APPENDIX G

List of 22 groundwater samples

No.	X	Y	As in groundwater (μg/L)	Explanation
1	752[redacted]	141[redacted]	56.01	คุณสก[redacted] (บ่อส่วนตัว) ตำบล บ้านค่าย
2	755[redacted]	141[redacted]	2.38	หมู่ที่ 06 คุณสำ[redacted] (บ่อส่วนตัว) บ้านหนองหว้า ตำบล ชากบก
3	749[redacted]	141[redacted]	0.52	คุณเนี[redacted] (บ่อส่วนตัว) ตำบล บ้านค่าย
4	758170	1420222	9.08	หมู่ที่ 11 บ้านห้วยยาง ตำบล บางบุตร
5	756958	1420253	0.49	หมู่ที่ 04 อบต.บางบุตร (บ้านพะวอ) (A46B04) ตำบล บางบุตร
6	758226	1419750	20.72	หมู่ที่ 12 บ้านชากเล็ก ตำบล บางบุตร
7	755583	1416215	17.86	หมู่ที่ 06 บ้านหนองหว้า ตำบล ชากบก
8	749860	1413196	47.33	หมู่ที่ 06 สวนสมเด็จพระเจ้าตากสินมหาราช ม.6 ตำบล บ้านค่าย
9	748430	1415718	10.03	หมู่ที่ 02 บ้านกระโหม ตำบล หนองละลอก
10	748328	1418173	31.94	หมู่ที่ 01 วัดดอนจันทร์ (A56B02) ตำบล หนองละลอก
11	743983	1420430	7.88	หมู่ที่ 01 วัดสวนหลาว ตำบล หนองละลอก
12	749417	1419896	1.71	หมู่ที่ 07 ประปาบ้านตาสิทธิ์ (A75B04) ตำบล หนองละลอก
13	746573	1412495	7.65	หมู่ที่ 05 โรงเรียนบ้านตีนเนิน ตำบล หนองละลอก
14	742754	1421976	135.63	หมู่ที่ 09 บ้านตัวอย่าง ตำบล หนองละลอก
15	744299	1410874	0.78	หมู่ที่ 04 บ้านปากป่า (บ่อ 1) (A58B03) ตำบล หนองตะพาน
16	742334	1415087	0.33	หมู่ที่ 06 บ้านคลองนฉางใต้ ตำบล หนองตะพาน
17	745675	1410265	0.79	หมู่ที่ 04 อบต.หนองตะพาน(บ่อ 1) (A38B03) ตำบล หนองตะพาน
18	747769	1409377	0.62	หมู่ที่ 01 บ้านเกาะ ตำบล หนองตะพาน
19	745481	1408570	0.34	หมู่ที่ 03 บ้านหนองตะพาน (A38B05) ตำบล หนองตะพาน
20	748020	1410628	0.84	หมู่ที่ 02 บ้านน้ำโฉ่ (บ่อ 1) (A38B04) ตำบล หนองตะพาน
21	745924	1411388	1.63	หมู่ที่ 05 บ้านแหลมเหียง ตำบล หนองตะพาน
22	750296	1425381	0.34	หมู่ที่ 02 บ้านหนองปลาไหล (บ่อ 2) (A66B06) ตำบล หนองบัว

Noted: Black shading due to the personal data protection policy

APPENDIX H

List of 110 participants

Well No.	Name	Sub-district	X	Y	UAs (µg/L)	UPb (µg/gCr)
1	นายสก[redacted]	บ้านค่าย	752[redacted]	141[redacted]	130.86	30.49
2	นายสำ[redacted]	ชากบก	755[redacted]	141[redacted]	33.91	30.57
3	นางสาวเนี[redacted]	บ้านค่าย	749[redacted]	141[redacted]	33.93	33.18
4	นายอนั[redacted]	หนองพะวา	754[redacted]	141[redacted]	31.16	25.93
4	นางปร[redacted]	หนองพะวา	758[redacted]	142[redacted]	22.87	26.41
5	นายหน[redacted]	หนองพะวา	756[redacted]	142[redacted]	44.57	30.55
5	นางสาวทัศ[redacted]	หนองพะวา	756[redacted]	142[redacted]	22.53	38.86
5	นางสาวธนิ[redacted]	หนองพะวา	756[redacted]	142[redacted]	44.69	23.45
6	นายเชี่[redacted]	ชากเล็ก	757[redacted]	141[redacted]	86.13	33.76
6	นางสาวชล[redacted]	ชากเล็ก	758[redacted]	141[redacted]	65.81	32.57
6	นางสาววา[redacted]	ชากเล็ก	758[redacted]	142[redacted]	178.34	44.59
6	นางกัญ[redacted]	ชากเล็ก	757[redacted]	141[redacted]	52.23	22.95
6	นางส้ม[redacted]	ชากเล็ก	758[redacted]	141[redacted]	105.25	59.11
6	นางวัน[redacted]	ชากเล็ก	758[redacted]	141[redacted]	114.96	33.87

Well No.	Name	Sub-district	X	Y	UAs (μg/L)	UPb (μg/gCr)
6	นางเจ[redacted]	ชากเล็ก	758[redacted]	141[redacted]	111.77	37.76
6	นางระ[redacted]	ชากเล็ก	758[redacted]	141[redacted]	76.95	32.79
6	นางทอ[redacted]	ชากเล็ก	758[redacted]	141[redacted]	154.35	54.52
7	นายนิ[redacted]	ชากบก	753[redacted]	141[redacted]	135.65	42.31
7	นางสัน[redacted]	ชากบก	753[redacted]	141[redacted]	56.14	49.82
7	นางวา[redacted]	ชากบก	755[redacted]	141[redacted]	145.32	32.51
8	นายสม[redacted]	บ้านค่าย	749[redacted]	141[redacted]	139.82	65.49
8	นางชุ[redacted]	บ้านค่าย	749[redacted]	141[redacted]	105.08	19.85
8	นางน้[redacted]	บ้านค่าย	749[redacted]	141[redacted]	72.18	15.32
8	นางรัช[redacted]	บ้านค่าย	749[redacted]	141[redacted]	72.51	24.82
8	นางอภิ[redacted]	บ้านค่าย	749[redacted]	141[redacted]	90.09	20.73
8	นางเพ็ญ[redacted]	บ้านค่าย	749[redacted]	141[redacted]	93.86	44.65
8	นางมา[redacted]	บ้านค่าย	749[redacted]	141[redacted]	106.4	17.68
8	นางจอ[redacted]	บ้านค่าย	749[redacted]	141[redacted]	60.79	20.96
8	นางสาวพร[redacted]	บ้านค่าย	749[redacted]	141[redacted]	118.66	33.33
8	นางบุญ[redacted]	บ้านค่าย	749[redacted]	141[redacted]	59.46	29.54
8	นางถน[redacted]	บ้านค่าย	749[redacted]	141[redacted]	118.46	37.89
8	นางพา[redacted]	บ้านค่าย	749[redacted]	141[redacted]	68.48	48.7

Well No.	Name	Sub-district	X	Y	UAs (µg/L)	UPb (µg/gCr)
9	นายพย[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	53.46	10.85
9	นางสม[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	57.57	33.71
9	นางเพี[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	94.08	18.81
9	นางสาวเจ[redacted]	หนองตะพาน	747[redacted]	140[redacted]	135.02	11.74
10	นายบุ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	55.52	12.76
10	นายส[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	58.33	55
10	นายคอ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	147.14	92.11
10	นายจัน[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	56.29	25.51
10	นายมน[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	108.85	40.9
10	นายปร[redacted]	คลองน้ำเย็น	747[redacted]	141[redacted]	85.4	11.76
10	นายสัง[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	80.54	35.09
10	นายไพ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	304.54	34.99
10	นางบั[redacted]	คลองน้ำเย็น	747[redacted]	141[redacted]	78.75	56.69
10	นางสาวคนึ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	213.17	38.5
10	นางสำ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	37.86	24.42
10	นางสาวไพ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	60.91	37.19
10	นางสาวจำ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	66.79	16.11
10	นางเร[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	84.82	20.19

Well No.	Name	Sub-district	X	Y	UAs (µg/L)	UPb (µg/gCr)
10	นางวา[redacted]	คลองน้ำเย็น	747[redacted]	141[redacted]	350.09	20.73
10	นางสาวสอ[redacted]	คลองน้ำเย็น	749[redacted]	141[redacted]	76.59	40.9
10	นางรุ่[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	58.75	17.86
10	นางมา[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	119.22	22.8
10	นางบุ[redacted]	คลองน้ำเย็น	748[redacted]	141[redacted]	87.41	17.13
11	นายสม[redacted]	คลองน้ำเย็น	744[redacted]	142[redacted]	72.92	18.41
11	นายเส[redacted]	คลองน้ำเย็น	744[redacted]	142[redacted]	111.75	16.56
11	นายรัช[redacted]	คลองน้ำเย็น	747[redacted]	141[redacted]	61.75	16.19
11	นางเพ[redacted]	คลองน้ำเย็น	744[redacted]	142[redacted]	66.89	39.79
12	นายสว[redacted]	ละหารไร่	748[redacted]	142[redacted]	53.51	50.09
12	นางไส[redacted]	ละหารไร่	748[redacted]	141[redacted]	62.55	34.21
12	นางนิ[redacted]	ละหารไร่	747[redacted]	142[redacted]	45.3	40
12	นางสา[redacted]	ละหารไร่	748[redacted]	141[redacted]	80.3	19.82
12	นางสม[redacted]	ละหารไร่	749[redacted]	142[redacted]	42.39	41.27
13	นายบุ[redacted]	บ้านตีนเนิน	746[redacted]	141[redacted]	9.32	34.82
13	นางสำ[redacted]	บ้านตีนเนิน	746[redacted]	141[redacted]	73.09	30.94
13	นางอน[redacted]	บ้านตีนเนิน	746[redacted]	141[redacted]	16.1	37.05
13	นางลำ[redacted]	บ้านตีนเนิน	746[redacted]	141[redacted]	13.32	28.08

Well No.	Name	Sub-district	X	Y	UAs (µg/L)	UPb (µg/gCr)
14	นายณั[redacted]	หมู่บ้านตัวอย่าง	742[redacted]	142[redacted]	600.76	34.79
14	นางกิ[redacted]	หมู่บ้านตัวอย่าง	742[redacted]	142[redacted]	583.14	59.76
14	นางสาวแส[redacted]	หมู่บ้านตัวอย่าง	744[redacted]	142[redacted]	51.96	23.65
14	นางบุ[redacted]	หมู่บ้านตัวอย่าง	742[redacted]	142[redacted]	54.72	40.6
14	นางกำ[redacted]	หมู่บ้านตัวอย่าง	742[redacted]	142[redacted]	117.49	22.19
14	นางบุ[redacted]	หมู่บ้านตัวอย่าง	742[redacted]	142[redacted]	95.67	31.58
14	นางพร[redacted]	หมู่บ้านตัวอย่าง	741[redacted]	142[redacted]	161.16	16.29
15	นางดว[redacted]	หนองตะพาน	744[redacted]	141[redacted]	38.31	11.58
15	นางอภิ[redacted]	หนองตะพาน	744[redacted]	141[redacted]	130.76	34.31
16	นางเห[redacted]	หนองตะพาน	742[redacted]	141[redacted]	42.02	59.76
16	นางสาวศิ[redacted]	หนองตะพาน	742[redacted]	141[redacted]	106.68	22.56
17	นายบู[redacted]	หนองตะพาน	745[redacted]	140[redacted]	19.75	6.44
17	นางฐิ[redacted]	หนองตะพาน	745[redacted]	141[redacted]	38.96	34.18
17	นางสง[redacted]	หนองตะพาน	745[redacted]	140[redacted]	21.16	14.32
17	นางกร[redacted]	หนองตะพาน	745[redacted]	140[redacted]	24.16	50.66
18	นายสม[redacted]	หนองตะพาน	747[redacted]	140[redacted]	16.46	13.16
18	นายไพ[redacted]	หนองตะพาน	747[redacted]	140[redacted]	57.87	34.84
18	นางสุว[redacted]	หนองตะพาน	747[redacted]	140[redacted]	30.12	27.45

Well No.	Name	Sub-district	X	Y	UAs (µg/L)	UPb (µg/gCr)
18	นางลั[redacted]	หนองตะพาน	748[redacted]	140[redacted]	53.56	7.16
18	นางโส[redacted]	หนองตะพาน	747[redacted]	140[redacted]	59.05	32.44
18	นางสุ[redacted]	หนองตะพาน	747[redacted]	140[redacted]	54.09	42.3
18	นางสาวสม[redacted]	หนองตะพาน	747[redacted]	140[redacted]	113.77	33.1
18	นางสุ[redacted]	หนองตะพาน	747[redacted]	140[redacted]	58.5	42.73
19	นายน[redacted]	หนองตะพาน	745[redacted]	140[redacted]	41.98	38.65
19	นางอ[redacted]	หนองตะพาน	745[redacted]	140[redacted]	5.74	43.9
19	นางวิ[redacted]	หนองตะพาน	745[redacted]	140[redacted]	87.4	20.65
20	นายส[redacted]	หนองตะพาน	745[redacted]	140[redacted]	29.8	21.42
20	นายอนุ[redacted]	หนองตะพาน	745[redacted]	140[redacted]	16.97	25.79
20	นางช[redacted]	หนองตะพาน	748[redacted]	141[redacted]	40.9	58.26
20	นางส[redacted]	หนองตะพาน	748[redacted]	141[redacted]	33.26	30.91
20	นางมา[redacted]	หนองตะพาน	747[redacted]	141[redacted]	41.93	21.79
20	นางอ[redacted]	หนองตะพาน	748[redacted]	141[redacted]	5.38	42.22
20	นางวิ[redacted]	หนองตะพาน	748[redacted]	141[redacted]	33.89	22.44
20	นางสม[redacted]	หนองตะพาน	748[redacted]	141[redacted]	121.91	39.17
20	นางสำ[redacted]	หนองตะพาน	748[redacted]	141[redacted]	100.83	22.77
21	นายสายช[redacted]	หนองตะพาน	745[redacted]	141[redacted]	11.25	19.56

Well No.	Name	Sub-district	X	Y	UAs (µg/L)	UPb (µg/gCr)
21	นางสาวอา[redacted]	หนองตะพาน	745[redacted]	141[redacted]	25.95	20.43
21	นางบุญ[redacted]	หนองตะพาน	744[redacted]	141[redacted]	44.71	40.69
21	นางสายส[redacted]	หนองตะพาน	745[redacted]	141[redacted]	51.06	48.25
21	นางขวั[redacted]	หนองตะพาน	746[redacted]	141[redacted]	121.77	26.93
22	นายธ[redacted]	หนองบัว	750[redacted]	142[redacted]	23.02	39.85
22	นายโย[redacted]	หนองบัว	750[redacted]	142[redacted]	34.63	47.14

Noted: Black shading due to the personal data protection policy

APPENDIX I

Input parameters for deterministic of As species (Visual MINTEQ software)

No.	pH	Temp	As^{3+}	As^{5+}	Ca^{+2}	Cl^{-}	CO_3^{2-}	Fe	K^{+}	Mg^{+2}	Na^{+}	NO_3^{-}	SO_4^{2-}	ORP
1	6.37	29.2	47.12	8.89	4.07	6.36	110.56	0.35	21.41	6.84	1.98	18.60	0.001	-46.70
2	6.43	29.2	0.300	2.39	5.34	6.42	190.06	0.015	15.12	4.29	7.10	5.54	0.63	237.40
3	5.49	30.2	0.300	0.522	1.94	2.48	68.87	0.02	9.90	1.56	2.85	5.24	0.17	176.80
4	6.82	33.35	1.19	7.90	5.06	26.08	368.72	0.3	42.00	7.01	11.96	7.20	1.89	160.75
5	6.85	30.65	0.37	0.267	22.32	38.46	149.45	0.045	40.84	9.02	15.49	16.45	3.28	243.90
6	7.24	32.7	0.621	20.24	24.32	29.105	218.4	0.11	24.76	9.98	23.31	27.90	8.95	220.55
7	6.96	29.8	15.218	2.64	16.34	9.015	192.62	21.92	22.05	7.35	10.65	2.07	0.001	-134.4
8	7.48	30.25	0.846	46.98	2.01	11.65	61.1	0.015	51.99	5.15	42.09	11.81	0.15	268.25
9	7.92	30.85	0.989	9.19	8.91	3.84	95.65	0.02	62.45	10.53	53.02	1.55	0.62	222.40
10	8.62	30.95	0.714	31.37	8.68	3.86	118.89	0.05	57.98	7.05	44.25	2.54	2.24	230.15
11	7.34	29.2	1.92	5.96	63.26	65.2	138.74	0.135	22.60	27.74	14.15	16.43	3.53	222.40
12	6.82	29.65	0.300	1.71	1.90	2.68	131.23	0.05	12.83	5.79	9.2	2.115	1.12	222.40
13	7.76	29.15	2.20	5.60	9.41	7.05	133.82	0.235	43.91	8.25	37.48	1.26	0.35	230.15
14	6.62	30.6	11.09	124.54	10.14	9.44	154.91	0.085	14.18	9.125	7.56	11.82	7.74	222.40
15	7.32	31.95	0.43	0.492	9.78	8.01	86.86	1.61	19.30	10.21	12.17	0.965	0.356	230.15

No.	pH	Temp	As^{3+}	As^{5+}	Ca^{+2}	Cl^{-}	CO$_3^{2-}$	Fe	K^{+}	Mg^{+2}	Na^{+}	NO$_3^{-}$	SO$_4^{2-}$	ORP
16	7.16	29.40	0.300	0.333	52.76	42.11	287.68	5.22	18.13	18.95	6.31	12.8	0.32	222.40
17	8.11	30.75	0.300	0.792	23.35	9.81	82.07	0.11	30.15	10.26	21.02	1.00	0.39	230.15
18	7.64	30.7	0.300	0.623	11.50	12.52	154.77	0.385	46.03	10.92	45.01	5.51	3.04	222.40
19	8.08	30.3	0.300	0.336	24.16	16.42	197.81	0.285	46.33	17.76	31.14	2.76	0.74	230.15
20	6.01	29.65	0.734	0.258	1.76	8.815	99.53	0.295	12.87	2.935	7.69	12.37	1.75	230.15
21	7.60	30.10	0.300	1.63	18.16	23.58	80.66	0.015	41.62	9.31	19.02	13.99	20.47	222.40
22	5.40	29.95	0.300	0.34	4.29	3.58	96.99	0.025	5.40	1.705	3.04	9.78	7.49	230.15
Average	7.09	30.39	3.92	12.41	14.97	15.75	146.33	1.42	30.08	9.17	19.38	8.62	2.96	195.20

BIOGRAPHY

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