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**REMEDATION PLANNING OF 1,4-DIOXANE-CONTAMINATED  
GROUNDWATER BY USING NUMERICAL SIMULATION**

数値シミュレーションを用いた 1,4-ジオキサンによる  
地下水汚染の修復計画

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of  
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## ABSTRACT

Commonly used as a stabilizer for methyl chloroform, 1,4-dioxane is used extensively and directly in several industrial and commercial processes and in many consumer products. As a result of its widespread use, a large amount of 1,4-dioxane is released to the environment. Once 1,4-dioxane reaches the surface water or groundwater, it migrates as far the water flows because it is highly soluble and persistent in water ambient conditions. World Health Organization (WHO) classified 1,4-dioxane as Group 2B (possibly carcinogenic to human) and in late 2009 1,4-dioxane was added into Japan Environmental Quality Standards (EQS). Elevated 1,4-dioxane concentration has been detected at several contaminated sites in USA and illegal dumping and landfill sites in Japan.

At Kuwana illegal dumping site in Japan, where 30,000 m<sup>3</sup> of hazardous waste was illegally dumped between 1995 and 1996, groundwater was severely contaminated by Volatile Organic Compounds (VOCs), e.g., trichloroethylene and benzene. From 2002 to 2007, VOCs-contaminated groundwater was completely remedied by containing VOCs within the waste layer by implementing vertical slurry walls around the dumped waste, pumping contaminated groundwater inside and outside of walls for VOCs treatment (P&T), and flashing water into the waste layer by using treated water. However, high concentration of 1,4-dioxane was detected in both waste layer and groundwater, especially in deep aquifers inside and outside of the walls after 1,4-dioxane was newly added into EQS. This widely detection suggests that 1,4-dioxane cannot be contained by vertical walls and 1,4-dioxane migrates horizontally through the walls and vertically from the waste layer to the deep aquifer. The objective of remediation is to prevent 1,4-dioxane spreading out of the walls and to treat 1,4-dioxane in groundwater outside of walls within 10 years. For that reason, this study aims to propose a remediation plan for 1,4-dioxane-contaminated groundwater at Kuwana site. The most effective groundwater management tool “numerical simulation” was used to analyze remedial alternatives to achieve the remediation objective. Since the migration of 1,4-dioxane influenced by both vertical and horizontal flow, a 3-dimensional numerical simulation must be precisely developed to estimate the proper combination of amount of waste to be removed and the amount of groundwater to be pumped. Then, the developed numerical model was used to propose a proper remediation plan for Kuwana site considering future risk.

The unique properties of 1,4-dioxane cause its migration in groundwater to have limited

influences by sorption, biodegradation, and volatilization. Consequently, 1,4-dioxane migration strongly depends on groundwater flow. For that reason, hydraulic conductivities, the most uncertain parameters and critical to groundwater flow, should be precisely determined. In a conventional modeling approach, groundwater flow is estimated using hydraulic conductivities determined by least-square method in term of observed and calculated groundwater head (calibration), and then the estimated groundwater flow is used for predicting 1,4-dioxane distribution by convective dispersion analysis considering other parameters such as dispersivity, source location and concentration. Although other parameters are properly set, 1,4-dioxane distribution cannot be always precisely predicted because the calibrated groundwater flow model does not perfectly present the real groundwater flow. Thus, the calibrated groundwater flow should be verified to determine appropriate hydraulic conductivities considering 1,4-dioxane distribution. This study proposes a new approach with verification processes of groundwater flow estimation for precisely predicting 1,4-dioxane distribution in groundwater. In this approach, several acceptable sets of hydraulic conductivities in term of groundwater heads were determined by calibration and each set of hydraulic conductivities was verified to match between calculated and observed 1,4-dioxane concentrations. For the case of Kuwana site, five acceptable sets of hydraulic conductivities of the three aquifers were determined by the calibration using observed groundwater heads, and then verified to minimize the variance and average in the observed and calculated 1,4-dioxane concentration. Moreover, the shape comparison of 1,4-dioxane distribution in each aquifer was also carried out to obtain the best match with the observed field data. Because of adequate field data available at Kuwana site, the efficiency of a new approach comparing to the conventional one was confirmed. As a result, 1,4-dioxane distribution in groundwater was clarified by our approach more precisely than the conventional approach. Therefore, a new groundwater modeling approach that is practical for simulating 1,4-dioxane distribution was proposed by this study.

Afterwards, the above developed model was applied for the remediation planning for 1,4-dioxane-contaminated groundwater at Kuwana site considering waste removal and P&T. The amount of waste to be removed and the pumping locations and rates for P&T were determined by various scenario analysis considering both the depth of waste layer and 3-dimensional 1,4-dioxane distribution in each aquifer. Firstly, the pumping locations were determined based on the groundwater directions and current distribution of

1,4-dioxane in all aquifers, and then the proper combination of pumping rates were calculated so that the minimum average concentration outside of the walls was obtained. As a result, groundwater inside and outside of walls should be pumped with the rate of 50 m<sup>3</sup>/d and 10 m<sup>3</sup>/d respectively. Afterwards, by combining with the required pumping rates, four remediation plans with different amount of removed waste were considered for the analysis, plan (a): no waste is removed, plan (b): 1/2 of waste (highly 1,4-dioxane-concentrated waste) is removed, plan (c): 2/3 of waste (deeply distributed waste) is removed, and plan (d): all waste is removed. The average 1,4-dioxane concentration obtained from 78 monitoring wells outside of the walls in all aquifers was used to compare the effectiveness of each plan. Within 10 years of calculation period, we assumed that if the average 1,4-dioxane concentration of each aquifer lower than regulation limit in EQS of 0.05 mg/L, and then the remediation objective can be achieved. As a result, all three aquifers in plan (a) and (b) were not remedied. In plan (c), only the third aquifer was not remedied while all aquifers were remedied in plan (d). However, the removal of all the waste for treatment is not feasible because our cost analysis revealed that plan (d) is much more expensive than plan (c). Therefore, we tried to improve the remediation effectiveness of plan (c) considering the technical aspect. Plan (c) was found to be easily improved because the deep waste containing high concentration of 1,4-dioxane was already removed and the only remaining 1,4-dioxane in groundwater should be treated. By observing the concentration in 5 years after remediation, three pumping wells were found to be ineffective because 1,4-dioxane in their locations was already remedied so that they were switched to other locations where 1,4-dioxane was remaining high. As a result, groundwater in all aquifers in plan (c) could be remedied within 10 years. Therefore, this study proposes plan (c) as the most effective and economically feasible remediation plan. However, the remaining one-third of waste might contain 1,4-dioxane with high concentration and serve as the continuous source of 1,4-dioxane and spread out of the walls into the surrounding environment. In order to prevent this future risk, various scenarios with different pumping rates of pumping wells inside of walls were carried out. Accordingly, after the completion of remediation in the proposed plan (c), our simulation suggested that groundwater within the remaining waste must be pumped up for P&T at least 20 m<sup>3</sup>/d for preventing future risk.

In conclusion, this study proposed a new modeling approach that suitable and practical for predicting 1,4-dioxane distribution in groundwater. 1,4-Dioxane distribution in

groundwater can be predicted more precisely by using the proposed approach. Using the adequate available field data, the effectiveness of our new approach was confirmed. Subsequently, the developed model was used for proposing a feasible remediation plan for 1,4-dioxane-contaminated groundwater at Kuwana site. This study contributes the establishment of a new engineering method for the application of numerical simulation to remediation planning for groundwater at the site which is contaminated by newly regulated 1,4-dioxane.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

After the rapid economic growth in Japan in mid-20th century, environmental pollution has become a serious issue caused by industrial activities (Yoshiro, 1992). The problem of illegal dumping of industrial waste has been prolonged through decades because lack of landfill sites, price of waste management, and many mountainous area where illegal dumping can be easily carried out (Fujikura, 2011; Nakamura, 2007). As mentioned in (Ministry of Environment, 2010), the number of cases of illegal dumping of industrial waste increased from 1993 to 1998 reaching over 1000 cases annually. Recently, the solution of illegal dumping has become a major importance, since illegal dumping threatens the society's safety and security (Shoya et al., 2005; Ministry of Environment, 2005; Promentilla et al, 2006; Kawamoto and Urashima, 2006). The illegal dumping waste generally consists of toxic substances which cause the pollution to have different characteristic from typical environmental pollution (Kawamoto and Urashima, 2006). The restoration and recovery of illegal dumping sites to meet the conditions regulated by law or Environmental Quality Standards poses a variety of problems including not only the impacts on the surrounding environments but also major economic losses because it requires sophisticated technologies and long remediation period (Ministry of Environment, 2010; Shoya et al., 2005; Kawamoto and Urashima, 2006).

In many illegal dumping and landfill sites in Japan, groundwater and leachate water had been reported to contain significant level of 1,4-dioxane (Yasuhara, 1995; Nakasugi et al., 1999; Yasuhara et al, 1999; Ishii et al., 2001; Ishii et al., 2013). 1,4-Dioxane is an emerging contaminant which is widely used many industrial processes as a stabilizer in chlorinated solvents and also directly used in consumers products (Morh et al., 2010). 1,4-Dioxane is highly mobile and persistent in groundwater due to its properties so that it migrates as fast as groundwater flow (Liu et al., 2000; Mohr et al., 2010; Priddie and Jackson, 1991; Patterson et al., 1985; Zenker et al., 2003). The US EPA and International Agency for Research on Cancer classified 1,4-dioxane as Group 2B (possibly carcinogenic to human being) (World Health Organization , 2004). In late 2009, 1,4-dioxane was newly added into Japan Environmental Quality Standards. At this study area, Kuwana illegal

dumping site, elevated concentration of 1,4-dioxane was also detected in the surrounding groundwater. The residential area, public school, and river are located nearby the site. For that meaning, there is a high risk to human being and the surrounding environments by the spreading of 1,4-dioxane in groundwater. Therefore, remediation plan should be developed and implemented immediately to treat 1,4-dioxane in groundwater at the site and to prevent 1,4-dioxane from spreading further into the surrounding environment.

About 30,000 m<sup>3</sup> of contaminated waste was illegally dumped into Kuwana site between 1995 and 1996. Consequently, groundwater at Kuwana illegal dumping site was severely contaminated by Volatile Organic Compounds (VOCs) such as Dichloromethane (DCM) and Benzene. After the revelation of the site in 1997, site investigation and remedial countermeasures have been carried out. Pump-and-Treat (P&T) had been conducted from 2002 to 2007 after containment of all the waste by vertical slurry walls and treated water was used for water flushing on the waste layers. As a result, the surrounding groundwater was completely remedied. However, 1,4-dioxane was detected in the inside and outside of the walls even though the above countermeasures had been implemented. It is questionable that why the groundwater at upstream is also contaminated and how 1,4-dioxane move into the deep aquifer. Due to the complexity of hydrogeological conditions of the aquifer beneath the study area, we used one of the most powerful groundwater management tool “numerical simulation” to study clearly the groundwater and 1,4-dioxane phenomena at the site in order appropriately develop the remediation plan for the site.

However, since 1,4-dioxane is a newly regulated compound which was just added into Japan Environmental Quality Standards, it is a new challenging task in developing the appropriate remediation plan for such a contaminated site. Moreover, we have no experiences regarding the remediation of 1,4-dioxane-contaminated groundwater at illegal dumping sites. In addition due to the migration behavior of 1,4-dioxane in groundwater the conventional modeling approach for analyzing of VOCs transport could not be applicable for predicting 1,4-dioxane distribution. Therefore, in this study we proposed a new modeling approach which is practical and applicable for the prediction of 1,4-dioxane distribution in groundwater. Then, the developed model is used to develop the remediation plan 1,4-dioxane contaminated groundwater at Kuwana site which has complex hydrogeological conditions.

## 1.2 Research Objective

The main objective of this thesis is to develop an appropriate remediation plan of 1,4-dioxane-contaminated groundwater by using numerical simulation. Waste removal and P&T are considered as the remediation methods in this study because the waste contains 1,4-dioxane with high concentration and the previous remediation actions could not treat 1,4-dioxane within the waste layers. The amount of waste to be removed and the pumping plans for P&T will be determined through various scenarios analysis by numerical simulation. The remediation objective is to treat 1,4-dioxane-contaminated groundwater outside to the walls within 10 years and to prevent the 1,4-dioxane spreading throughout of the vertical slurry walls in case where the waste is remained.

According to the research background, even though VOCs was completely remedied, 1,4-dioxane is still remained in groundwater and distributes out of the walls in both upstream and downstream and into the deep aquifer. In order to develop the appropriate remediation plan, we need to clearly understand the groundwater flow and 1,4-dioxane migration behavior. There are many optimal modeling approaches for analysis of VOCs contaminant transport, but those approaches cannot be used for analysis of 1,4-dioxane transport which has the unique properties comparing to VOCs. For that reason, a more practical approach is needed to challenge with the problem of 1,4-dioxane transport analysis. Moreover, this study would help other sites contaminated especially by 1,4-dioxane.

## 1.3 Thesis Structure

This thesis is composed of five chapters which has the organization as shown in **Figure 1-1**. This section briefly describes the contents of each chapter and the relation between them. **Chapter 1** briefly describes the research background and research motivation regarding illegal dumping at the study area. Furthermore, the objective and the supporting methodology are presented. **Chapter 2** presents the site conditions and its remediation history. In addition, the review of related literature on 1,4-dioxane characteristics in groundwater and the general understanding of Verified Follow-Up (VF-UP) method. Lastly, the problems are clarified and defined for the study. In **Chapter 3**, a new approach is proposed for 1,4-dioxane-contaminated groundwater simulation especially for the Kuwana site which has complex hydrogeological conditions. Our new approach predicts

1,4-dioxane distribution in groundwater more precisely comparing to the conventional approach. The simulated 1,4-dioxane distribution will be used as the initial condition for prediction the remedial alternatives in the next chapter. The developed model was used for scenario analysis for selecting the appropriate remediation technologies for 1,4-dioxane groundwater remediation. **Chapter 4** uses the developed numerical simulation to develop the remediation planning considering waste removal combining with P&T. The amount of waste to be removed and pumping plans for P&T are defined by comparing the effectiveness of each remedial scenario. As a result, the most effective remedial alternative is selected and proposed for Kuwana site. Finally, the general conclusions of the current research are presented in **Chapter 5**.

# **Remediation Planning of 1,4-Dioxane-Contaminated Groundwater by Using Numerical Simulation**

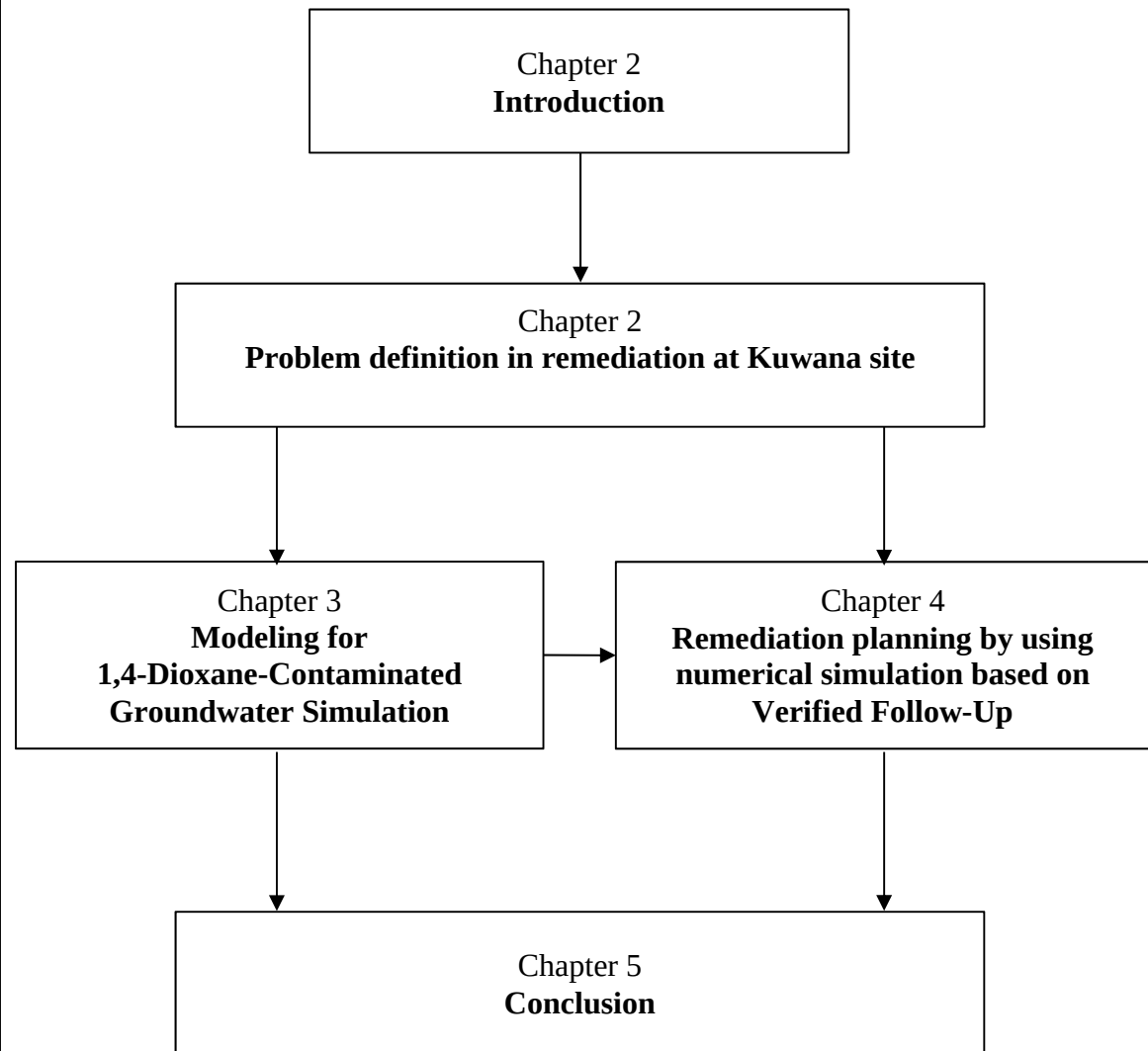


**Figure 1-1: Thesis Structure**

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## CHAPTER 2

### PROBLEM DEFINITION IN REMEDIATION AT KUWANA SITE

#### 2.1 Introduction

Groundwater numerical simulation has been widely used as a very invaluable tool for the proper management of the groundwater system, especially for accessing groundwater responses on the existing and the future activities (Liu et al., 2000; Becker et al., 2006; Matott, 2012; Zhen and Wang, 1999; Harvey et al., 1994; Bayer et al., 2005; Rizzo and Dougherty, 1996; Huang and Mayer, 1997). Groundwater model simulation has become a key to the success of an engineering implementation for groundwater management since the computer codes and computer capacity are extensively available which can provide the quick assessment of the future performance in groundwater management. However, the complexity of the groundwater system is always a challenging task in groundwater simulation especially for the site with complex hydrogeological features. In Japan, about three-quarter of land are cover by mountains and hills where most of the illegal dumping sites are carried. This study area, Kuwana illegal dumping site, locates in the hilly area which has steep slopes with complex hydrogeological features. For that reason, it requires the well understanding the field characteristics in order to perform the accurate groundwater simulation. Additionally, understanding the contaminant properties is also inevitable for predicting its distribution in groundwater.

Therefore, this chapter firstly describes the background and remediation history of Kuwana illegal dumping site, then followed by the fundamental understanding of 1,4-dioxane properties in groundwater. In addition, the schemes of Verified Follow Up approach considered in the remediation planning in this study will be reviewed. According to these descriptions and reviews, the problem in remediation of 1,4-dioxane in groundwater at Kuwana site could be defined and set up for this study.

#### 2.2 Site description and remediation history

Kuwana illegal dumping site is located in Kuwana city, Mie Prefecture, Japan (see **Figure 2-2a, 2-2b**). The dumped waste has approximately the area of 2,900 m<sup>2</sup> and the volume of about 30,000 m<sup>3</sup> with the maximum depth of 14.7 m (Ishii et al, 2001). The alternating sand and clay layers occur above the bedrock. The aquifer bed presents about 22 m below

the ground surface. In 2002, the vertical walls were constructed around the dumped waste and until the aquifer bed. Based on the hydrogeological data, the aquifer beneath this illegal dumping site is separated into three aquifers by confining clay layers. From the top to bottom, the first aquifer is denoted as unconfined aquifer while the second and the third aquifers are denoted relatively as semi-confined aquifers (**Figure 2-2c**). In general, the groundwater pressure is different among aquifers. In the first aquifer, the groundwater flow is generally influenced by the geographical gradient in which flow velocity is dominant. For the second aquifer, groundwater flow is in diverse directions because of the vertical flow from the first aquifer around the south walls area. On the other hand, the flow in the third aquifer is very slow and the groundwater flow is in reverse direction comparing to the first aquifer. For that reason, the main groundwater flow directions are different among aquifers (**Figure 2-2b**). The waste layers are located within the first and second aquifers.

This site was originally designed and operated as an inert-type landfill. According the Japanese regulation, the inert-type landfill is designed for receiving only the stable substances which could not cause any from environmental problem. Therefore, the waste limited to be landfilled in inert landfill site are plastics, rubber, metal, glass and ceramic, asphalt concert and inorganic solid matters (excluding shredded auto parts, printed circuit board, containers and packaging, lead battery electrodes, lead pipes and boards, cathode-ray tube, and plasterboards waste). Conversely, due to the poor control, hazardous wastes such as ash, sludge, and waste oil including hazardous materials were illegally dumped into this site between 1995 and 1996. Since then, groundwater around the site has been severely contaminated by the VOCs, e.g., chlorinated organic compounds and aromatics (Ishii et al, 2001). At that time, there was no waste treatment facility which can treat waste with high concentration of VOCs so that the construction of vertical slurry walls around the waste layers until bed rock and P&T were considered for treatment of VOCs within the waste layers and groundwater around the site (see **Figure 2-1**). These techniques were popular because they required low cost and easy implementation. On the other hand, other remedial techniques other than the above ones were also available, but those techniques are costly. From 2002 to 2007, VOCs-contaminated groundwater around the walls was completely remedied by containing of waste layers by vertical slurry walls and combining with P&T. The treated water was used for water flushing on the waste layers to keep waste layers saturated for maintaining the homogenous flow through the waste layers in order to wash out the VOCs within the whole waste layers.

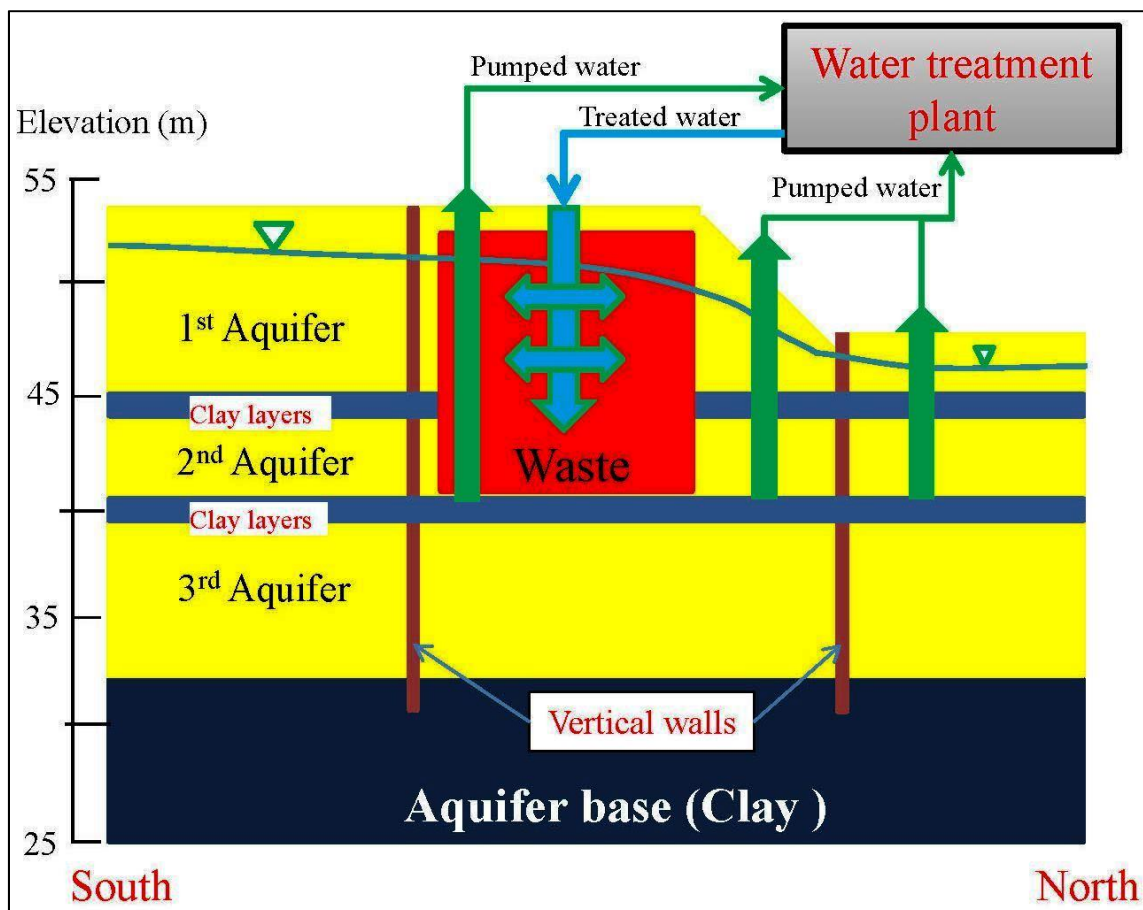


**Figure 2-1:** Illustration of previous remedial measures for VOCs

As a result, the VOCs-contaminated groundwater around the site was treated to a great extent and VOCs within waste layers were contained inside the walls. However, groundwater quality has been monitored after completion of remediation because the future risks might occur because the waste is still remained. Yet, after 1,4-dioxane was newly added into Japan Environmental Quality Standards in late 2009, 1,4-dioxane detected in groundwater inside and outside of walls with high concentration even though VOCs were already remedied. As shown in **Figure 2-2(b)** in which 1,4-dioxane distribution in each aquifer was obtained from the data measured Mie Prefecture in February 2011, the second and the third aquifers are contaminated by 1,4-dioxane. Actually, waste layers do not reach the third aquifer, but this aquifer is high contaminated by 1,4-dioxane as well. The phenomena is due to the groundwater flow interaction which transport 1,4-dioxane from the waste layers of the first and second aquifer in both side of vertical walls. Moreover, the implementation of water flushing, which create the highly different between water levels inside and outside of wall, also contribute to 1,4-dioxane spreading throughout the walls because the waste is the source of 1,4-dioxane.

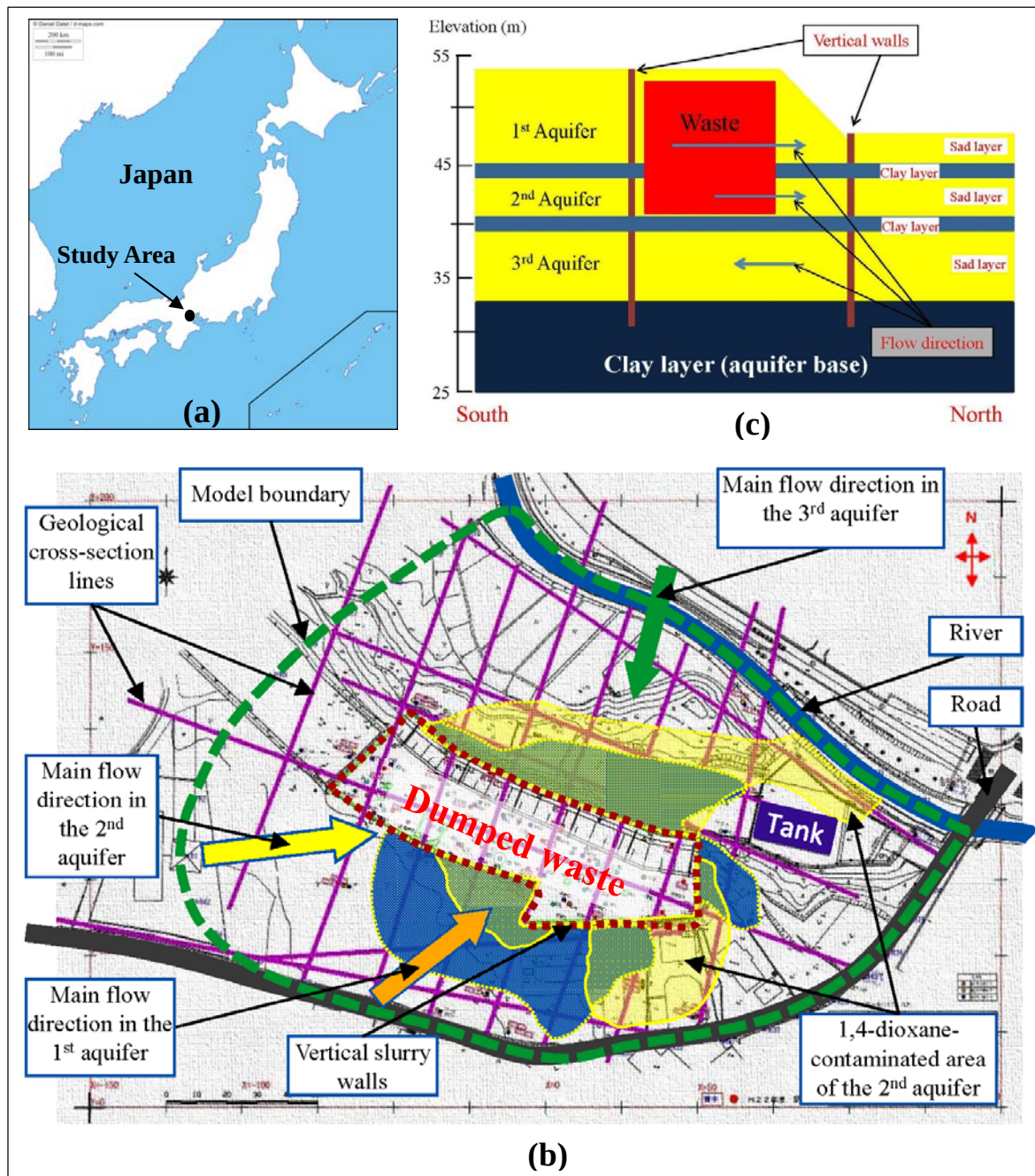


**Figure 2-2:** Location map (a), base map (b), and simplified section (c) of study area;

Source: (a) Map's link: [http://d-maps.com/carte.php?num\\_car=4472&lang=en](http://d-maps.com/carte.php?num_car=4472&lang=en) (Retrieved 2013),  
 (b) Modified from the Report of Mie Prefecture, 2011

### 2.3 1,4-Dioxane characteristics and occurrences

1,4-Dioxane is used as a stabilizer in chlorinated solvents (Morh et al., 2010). It is also used as a solvent for cellulose acetate, ethyl cellulose, benzyl cellulose, resins, oils, waxes, oil and spirit-soluble dyes (Budavari et al., 1996). Moreover, it is used as well as for electrical, agricultural and biochemical intermediates and for adhesives, sealants, cosmetics, pharmaceuticals, rubber chemicals and surface coatings (Anon., 1970). In Japan, 1,4-dioxane is used as a solvent and surface-treating agent for artificial leather and was formerly used as a stabilizer for trichloroethylene (WHO, 2004). The results of nationwide surveys in Japan show that the concentration of 1,4-dioxane in surface water, groundwater, coastal seawater, raw water for water supply, and in tap water sample from six cities in Kanagawa in 1995-1996 (Japan Ministry of the Environment, 1999, Abe, 1997, Magara et al., 1998, Abe, 1999, Abe, 1997).

**Table 2-1:** Selected physico-chemical properties of 1,4-dioxane, DCM, and Benzene

| Property                       | 1,4-Dioxane <sup>a)</sup>                      | DCM <sup>b)</sup>                                      | Benzene <sup>c)</sup>                                 |
|--------------------------------|------------------------------------------------|--------------------------------------------------------|-------------------------------------------------------|
| Physical state                 | Colorless, inflammable liquid                  | colorless liquid with penetrating                      | colorless, sweet odor, highly flammable               |
| Chemical formula               | C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>   | CH <sub>2</sub> Cl <sub>2</sub>                        | C <sub>6</sub> H <sub>6</sub>                         |
| Molecular weight               | 88.1                                           | 84.93                                                  | 78.11                                                 |
| Aqueous solubility             | dissolved                                      | 1.30×10 <sup>4</sup> mg/L at 25 °C                     | 1.79 g/L (15 °C)                                      |
| Density                        | 1.0329 g/mL                                    | 1.3266 g/mL at 20 °C                                   | 0.8787 g/mL at 15 °C                                  |
| Vapor pressure                 | 30 mmHg at 20 °C                               | 1.15×10 <sup>2</sup> mmHg at 25 °C                     | 75 mmHg at 20 °C                                      |
| Boiling point                  | 101.1 °C                                       | 40 °C                                                  | 80.1 °C                                               |
| Henry's law constant           | 4.88 ×10 <sup>-6</sup> atm m <sup>3</sup> /mol | 3.25×10 <sup>-3</sup> atm m <sup>3</sup> /mol at 25 °C | 5.5×10 <sup>-3</sup> atm m <sup>3</sup> /mol at 25 °C |
| Partition Coefficient, Log Kow | -0.27                                          | 1.25                                                   | 2.13                                                  |

a) Zenker et al., 2003,

b) U.S EPA, 2001,

c) ATSDR, 2007

Because of the its unique physical properties, listed in the **Table 2-1** below, 1,4-dioxane migrates in groundwater is strongly depending on groundwater because it is expected to be limited to biodegradation, adsorption, and volatilization (Zenker et al., 2003). Moreover, the physico-chemical properties of 1,4-dioxane were compared with those of Dichloromethane (DCM) (U.S EPA, 2001) and Benzene (ATSDR, 2007). Dichloromethane and Benzene are the compounds whose concentration levels are high in groundwater at Kuwana site comparing to that of other VOCs.

## **2.4 Verified Follow Up**

VF-UP is a new approach developed by (Furuichi, 2013) for remedial planning for groundwater-contaminated sites, considering expected and/or unexpected uncertain events in the future to complete remediation effectively (see **Figure 2-3**). The expected uncertain events should be considered as much as possible during the remediation planning. On the other hand, unexpected uncertain events, VF-UP provides intermediate review processes during remediation and post review processes after completion of remediation. The uncertain events might be cause by many uncertain factors which are categorized as technical and social uncertain factor. These uncertain factors which may occur in each planning phases will be described in detail in the next section.

During the intermediate review, the remediation plans are flexible for adaption of any improvements if the remediation does not progress or not be completed as planned. In that case, remediation objectives and plans might be changed, so that the additional or new remedial technologies can be applied after intermediate review process to improve the remediation efficiency or to adopt the uncertain event that may occur in order to meet the new objectives or plans that have been changed. Once the remediation is completed, and the site will be monitored to ensure whether the site is completely remedied, especially for the case where the contaminant source is still remained. In the meant time, post review involved with local residents needs to be conducted for risk commutation. Actually, risk communication with residents is necessary from the early phase of revelation of the site, however it is very important to conduct risk communication after completion of remediation to restore the confidence of the residents and get their acceptance of remediation completion.

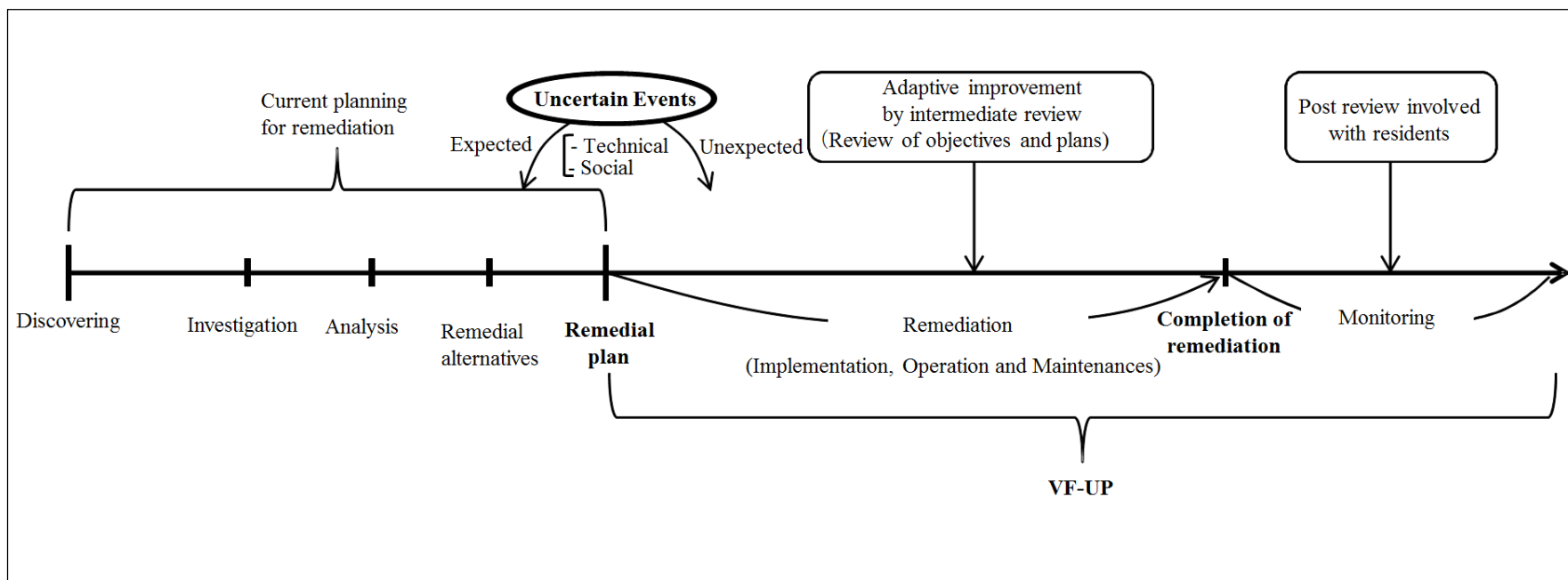


**Figure 2-3:** Remediation planning based on the concept of VF-UP

## **2.5 Problems in remediation planning for Kuwana site based on VF-UP**

### **2.5.1 Uncertain factors to be considered for remediation planning**

The expected and unexpected events caused by many factors categorized as technical and social uncertain factors. Remediation planning based on VF-UP requires planners to consider expected uncertain events as much as possible. Once the uncertain events occur in the future, during remediation or after completion of remediation, they may exert a significant influence on the progress of the remediation. In **Table 2-2**, the first column shows the process of remedial planning phase from site discovering to the completion of remediation and followed by the technical and social uncertain factors (Furuichi, 2013).

The uncertain events may happen due to technical uncertain factors that might happen at each phase from the site investigation to the completion of remediation. Once the contaminated site is discovered, field investigation is carried out for data collection for analysis. Generally, the number of data is limited and discrete over space and time, therefore, the analysis of hydrogeological condition, waste distribution, and contaminant distribution contains much uncertainty. Next, remedial alternatives and plans will be decided and implemented uncertainly. The selected technologies might be improper and not good enough for specific site condition and contaminants to be treated. Moreover, design and implementation of technologies might not be appropriate because the predicted hydrogeological condition, waste and contaminant distribution also contain uncertainty. In addition, operation and maintenance might not be well progress as planned because uncertain events may occur. Lastly, the completion of remediation might be judged in different ways from person to person which required the adequate knowledge and experiences. Besides, enough information must be required to be properly judged the completion of remediation.

For the uncertain events which are caused by the social uncertain factors, may occur at any time of the whole processes for remediation planning. There is no good communication in society structure and not enough disclosure for residents about the site information. The registration or law could be revised any time in which a new compound might be added into Environmental Quality Standards. Likewise, the remediation could be terminated due to the cuts in national subsidy. Furthermore, the new residents would complaint or protest against the contaminated site. Last but not least, the remediation is sometimes longer than

available funding period, so that the remediation might be left incomplete.

**Table 2-2:** Uncertain factors considered in remediation planning based on VF-UP

| Remediation planning phase                               | Technical uncertain factors | Social uncertain factors |
|----------------------------------------------------------|-----------------------------|--------------------------|
| Investigation and analysis after site discovering        | - Hydrogeological condition |                          |
|                                                          | - Waste distribution        | - Society structure      |
|                                                          | - Contaminant distribution  | - Not enough disclosure  |
| Remedial alternatives, remedial plans and implementation |                             | - Registration or law    |
|                                                          | - Selected technologies     | ▪ new standard           |
|                                                          | - Design and implementation | ▪ subsidy cut            |
|                                                          | - Operation and maintenance | - New residents          |
|                                                          |                             | - Funding                |
| Completion of remediation                                | How is “completion” judged? |                          |

### 2.5.2 Problem setting in this study

In order to more precisely develop remediation planning for 1,4-dioxane-contaminated groundwater at Kuwana illegal dumping site using numerical simulation, the significant level of 1,4-dioxane groundwater model is required because of the unique chemical properties of 1,4-dioxane and the complicity of Kuwana site condition. According to the unique properties of 1,4-dioxane mentioned above, 1,4-dioxane is expected to be very mobile and persistent in groundwater ambient condition because it migrates in groundwater without sorption, degradation, and volatilization. 1,4-Dioxane migration therefore strongly depends on groundwater flow. As described in the previous section, Kuwana illegal dumping site has very complex hydrogeological features. The groundwater flow directions are different between each aquifer and complicated because the site has three aquifers with interaction. Due to the above reasons, using the conventional approach in groundwater modeling is not enough sufficient for predicting 1,4-dioxane distribution at

Kuwana site because the optimum groundwater predicted by conventional approach is not always applicable to analyze 1,4-dioxane migration. Therefore, another new practical approach is needed to predict 1,4-dioxane distribution more rationally. Especially, the model will be important for analyzing the scenarios in remediation planning. Accordingly, the following two sequential problems were set in this study.

- (1) Modeling for 1,4-Dioxane-Contaminated Groundwater Simulation
- (2) Remediation planning by using the developed model based on VF-UP

These two problems will be addressed in detail in the following chapter 3 and chapter 4 respectively.

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## CHAPTER 3

### MODELING FOR 1,4-DIOXANE-CONTAMINATED GROUNDWATER SIMULATION

#### 3.1 Introduction

In many illegal dumping and landfill sites in Japan, groundwater and leachate water had been reported to contain significant level of 1,4-dioxane (Yasuhara, 1995; Nakasugi et al., 1999; Yasuhara et al., 1999; Ishii et al., 2001; Ishii et al., 2013). Because of its toxicity, 1,4-dioxane was newly added into Japan Environmental Quality Standards (Ministry of Environment, 2009). 1,4-Dioxane is expected to be very mobile and persistent in groundwater according to its chemical properties (Zenker et al., 2003). Henry's Law constant and aqueous solubility of 1,4-dioxane prove it to be limited to volatilization. 1,4-Dioxane has low adsorption into soils because of its low octanol-water partition coefficient. Furthermore, several field and laboratory studies have confirmed that retardation factor of 1,4-dioxane in subsurface is very limited (Zenker et al., 2003; Priddle et al., 1991; Liu et al., 2000). Likewise, numerous studies have been reported 1,4-dioxane is almost not biodegraded under ambient subsurface conditions (Mohr et al., 2010).

According to the above conditions, 1,4-dioxane migrates in groundwater is not significantly involved with volatilization, sorption, and biodegradation. Therefore, 1,4-dioxane migration in groundwater is strongly affected by groundwater flow. Hydraulic conductivities of aquifer materials are the most critical to groundwater flow (Spitz and Moreno, 1996). In addition, hydraulic conductivities obtained from field or laboratory tests normally are uncertain. Therefore, defining precise hydraulic conductivities for use in groundwater modeling is a great challenge in the field of groundwater studies.

In a conventional approach which is applicable for analysis of VOCs transport, hydraulic conductivities are inversely determined by groundwater flow model calibrations in which errors between calculated and observed heads are minimized (Spitz and Moren, 1996; Blessent et al., 2001; Franz and Rowe, 1993). Afterwards, groundwater flow model by using the determined hydraulic conductivities is used to predict contaminant concentration distribution considering the other factors such as source location, source concentration, and boundary conditions. However, even if the other parameters are precisely set, 1,4-dioxane distribution cannot be precisely predicted because the calibrated groundwater flow model

does not always properly represent the real conditions of groundwater flow at the field. For that reason, the calibrated groundwater flow should be reevaluated to define the most appropriate hydraulic conductivities that can represent the real groundwater flow and predict the 1,4-dioxane concentrations with minimal errors considering observed 1,4-dioxane concentration. In short, in case of analysis for VOCs, adsorption, volatilization, and biodegradation are the main factors influencing the concentration distribution in groundwater. However, in case analysis of 1,4-dioxane groundwater flow is the main influencing factor.

To deal with the above problems encountered when using the conventional approach, this study proposed a new approach for practically predicting 1,4-dioxane distribution in groundwater. In this new approach, several acceptable sets of hydraulic conductivities estimated by groundwater flow model calibration considering acceptable error in groundwater head are verified to achieve a better match between calculated and observed 1,4-dioxane concentrations. Our new approach was applied to a case study of an illegal dumping site in Japan where three aquifers have been contaminated by 1,4-dioxane for about 15 years. Groundwater flow models, by using various acceptable sets of hydraulic conductivities of the three aquifers, were verified to obtain a better prediction of 1,4-dioxane distribution considering the minimal mean error and root mean squared errors in 1,4-dioxane concentration and the distribution of 1,4-dioxane. The new approach was confirmed to be more effective in predicting 1,4-dioxane distribution in groundwater than the conventional approach in this case study.

*Be notified that the following contents, especially tables and figures were adopted and modified from Hem et al. 2013 which was accepted by the JSCE Journal of Environmental Systems and Engineering.*

### **3.2 Description of a new approach**

In a conventional approach (see **Figure 3-1a**), an optimal set of hydraulic conductivities ( $k_{cal}$ ) are determined so that the calculated groundwater heads ( $h_{cal}$ ) are consistent with the observed groundwater heads ( $h_{obs}$ ). Contaminant concentrations ( $c_{cal}$ ) are then estimated based on the groundwater flow by using an optimal set of  $k_{cal}$  so that  $c_{cal}$  are matched with observed concentrations ( $c_{obs}$ ). However, contaminant transfer is also affected by the other phenomena such as adsorption, degradation, and volatilization which

strongly depend on its chemical properties and soil quality in the field. Especially, in many cases of transport analysis of volatile organic compounds (VOCs) in which adsorption and biodegradability, chemical properties and soil quality significantly effect on the VOCs transport in groundwater. Therefore, in order to predict a long-term VOCs transport in groundwater, the degree of adsorption and rate of biodegradation in the field should be determined more precisely.

However, 1,4-dioxane has low adsorption on soils and low biodegradation according to its chemical properties. 1,4-Dioxane concentrations are therefore determined by mainly groundwater flow. For that reason, hydraulic conductivities which are crucial to groundwater flow must be precisely determined to be used for precisely predicting 1,4-dioxane distribution in groundwater. In our new approach (see **Figure 3-1b**), several acceptable sets of hydraulic conductivities, which are determined by calibration considering acceptable error in groundwater head, are used to estimate 1,4-dioxane distribution in groundwater. The several acceptable sets of hydraulic conductivities are further verified to define the better one in which a closer match between calculated and observed 1,4-dioxane concentrations is achieved. As a result, the precise groundwater flow and 1,4-dioxane distribution can be predicted by using the better set of hydraulic conductivities.

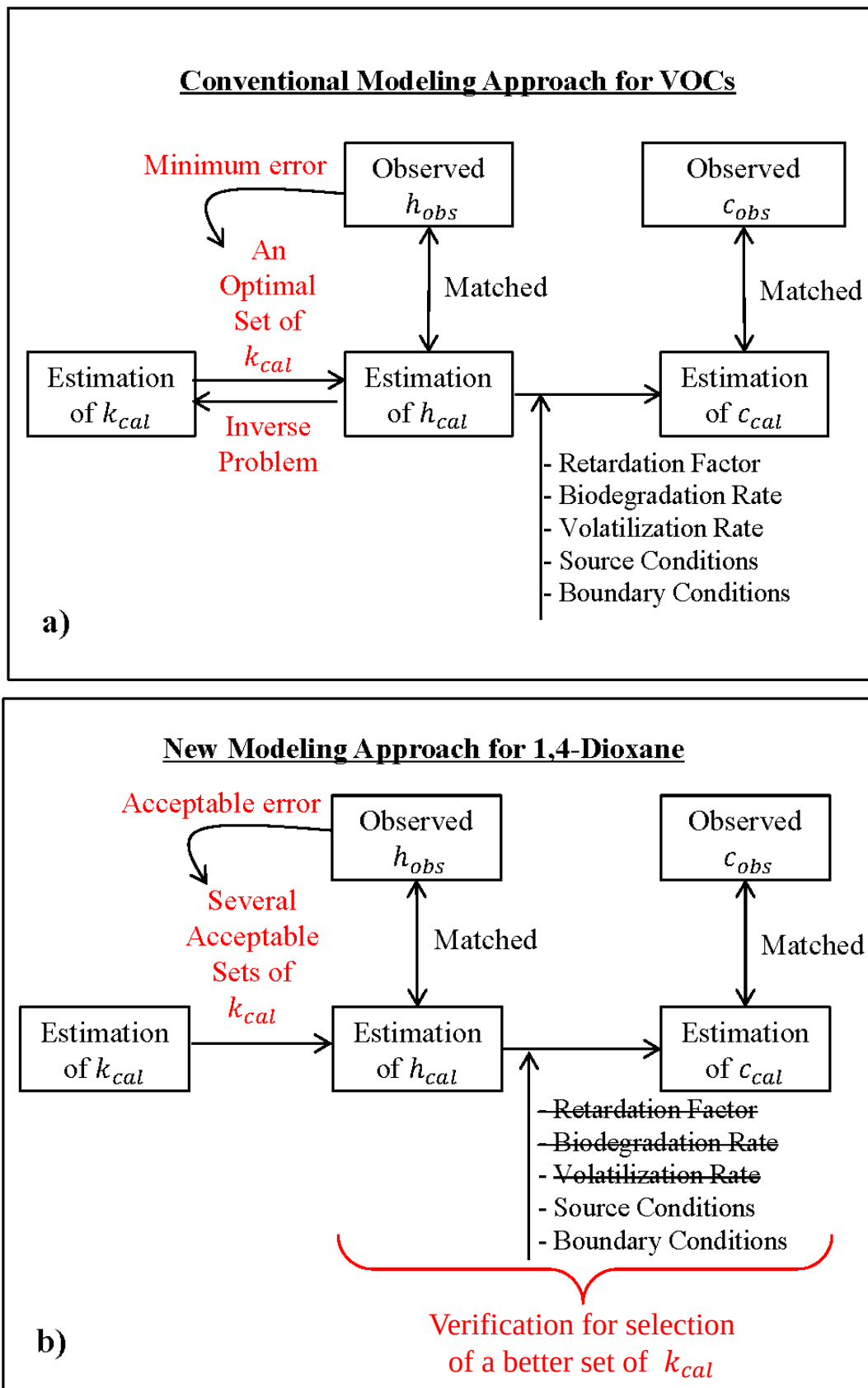


**Figure 3-1:** Conventional modeling approach (a) and new modeling approach (b)

### **3.3 Objectives of modeling and required field data in Kuwana site**

Since the hydrogeological condition is complex in which there are three aquifers with interaction, it is very difficult to develop a precise model. On the other hand, 1,4-dioxane migrates in groundwater as fast as groundwater flow and it is expected to be very limited to biodegradation, adsorption to the soils, and volatilization. Therefore, the appropriate groundwater model must be developed in order to predict 1,4-dioxane precisely. Fortunately, we have plenty amount of data which can be used to verified our model. For that reason, objective of model is to develop a new approach for modeling 1,4-dioxane at Kuwana which has complex hydrogeological condition.

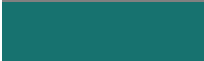
From the revelation of Kuwana site, several field investigations were carried out. Many boreholes were drilled within the waste layers as well as around the waste area. The data was measured and recorded by Mie Prefecture. There are many data available, especially groundwater level has been measured four times a week and once a month for 1,4-dioxane concentration. The data was accumulated at any condition such groundwater measured within dry or rainy season, with and without pumping. However, we cannot use all those data. We just selected some data required for modeling that can response to the objectives of modeling mentioned above.

For data used for modeling of groundwater flow and transport model for the condition without pumping was chosen based on the condition: for groundwater head measured within January 2011 was selected because from early 2010 groundwater pumping was stopped and groundwater table was observed to be stable. Groundwater data measured from the 24, 26, and 28 observation wells from the first, second, and third aquifer respectively were used to estimate the model boundary condition as well as to compare with the calculated results during flow model calibration processes. For 1,4-dioxane concentration data, it was selected from the average concentration from observation wells measured once a month from 19, 29, and 30 wells outside the vertical walls in the first, second, and third aquifer respectively from January to May 2011. The monthly average concentration data were used to compare with the results from each calibration in each aquifer.

The hydraulic conductivities were provided by Mie Prefecture in which each geological material has specific hydraulic conductivity value. Hydraulic conductivity values of most

materials were obtained by pumping test while that of some was obtained by estimation provided by Mie Prefecture (see Table). Based on the regulation, hydraulic conductivity of the slurry walls must be less than  $10^{-7}$  cm/s, and in term of safety we considered this value for the walls. However, hydraulic conductivities are considered as the main controlling factor for groundwater flow at this study area so that it must be thoroughly determined the proper value by conducting model calibration by using our new modeling approach.

**Table 3-1:** Hydraulic conductivity of aquifer materials,

| Aquifer material | Color                                                                               | $k_{obs}$ (cm/s)       | Source           |
|------------------|-------------------------------------------------------------------------------------|------------------------|------------------|
| Soil cover       |    | $1.0 \times 10^{-3}$   | Literature value |
| Clay             |    | $2.7 \times 10^{-7}$   | Pumping test     |
| Sand             |    | $4.7 \times 10^{-3}$   | Pumping test     |
| Clay             |    | $2.7 \times 10^{-7}$   | Pumping test     |
| Waste            |   | $1.0 \times 10^{-5}$   | Estimated        |
| Sand             |  | $6.3 \times 10^{-3}$   | Pumping test     |
| Clay             |  | $7.2 \times 10^{-8}$   | Pumping test     |
| Sand             |  | $6.3 \times 10^{-3}$   | Pumping test     |
| Gravel           |  | $3.1 \times 10^{-2}$   | Literature value |
| Clay (base)      |  | $3.4 \times 10^{-7}$   | Pumping test     |
| Wall             |  | $1.0 \times 10^{-7}$   | Estimated        |
| Tank             |  | $1.16 \times 10^{-10}$ | Estimated        |

### 3.4 Model development

#### 3.4.1 Governing equations

Basically, the development of any deterministic model for the groundwater flow and contaminant transport in groundwater flow system is a set of representative partial differential equations (Boba and Joshi, 1988). Equation (1) represents the net inflow into the volume that must be equal to the rate at which water is accumulating within the investigated volume (Zheng and Bennett, 2002).

$$k \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2} \right) + Q = 0 \quad (1)$$

where  $k$  is the hydraulic conductivity (m/s);  $h$  is the hydraulic head (m);  $Q$  is the local sources and sinks per unit volume (1/s);  $x, y, z$  is the space coordinate (m);  $t$  is time (s).

The transport model can be represented by the following advection-dispersion equation (Zheng and Bennett, 2002):

$$R \frac{\partial c}{\partial t} = -v_i \frac{\partial c}{\partial x_i} + \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial c}{\partial x_j} \right) - Q_s \quad (2)$$

where  $i, j$  are principal coordinate directions;  $c$  is the concentration (mg/L);  $Q_s$  is the concentration of solute of water that added from sources or sinks (mg/L.s).

$R = 1 + \frac{(1-n)\rho_s}{n} K_d$  is retardation factor of solute (dimensionless), where  $\rho_s$  is density of dry matrix material (kg/m<sup>3</sup>),  $n$  is total porosity (dimensionless),  $K_d$  is distribution coefficient (m<sup>3</sup>/kg).

And, three-dimensional dispersion coefficients for isotropic aquifer media  $D_{ij}$  are given in all coordinate directions as the following equations,

$$D_{xx} = \alpha_L \frac{v_x^2}{|V|} + \alpha_T \frac{v_y^2}{|V|} + \alpha_T \frac{v_z^2}{|V|} + D^*$$

$$D_{yy} = \alpha_L \frac{v_y^2}{|V|} + \alpha_T \frac{v_x^2}{|V|} + \alpha_T \frac{v_z^2}{|V|} + D^*$$

$$D_{zz} = \alpha_L \frac{v_z^2}{|V|} + \alpha_T \frac{v_x^2}{|V|} + \alpha_T \frac{v_y^2}{|V|} + D^*$$

$$D_{xy} = D_{yx} = (\alpha_L - \alpha_T) \frac{v_x v_y}{|V|}$$

$$D_{xz} = D_{zx} = (\alpha_L - \alpha_T) \frac{v_x v_z}{|V|}$$

$$D_{yz} = D_{zy} = (\alpha_L - \alpha_T) \frac{v_y v_z}{|V|}$$

where  $\alpha_L$  is longitudinal dispersivity (m),  $\alpha_T$  is transverse dispersivity (m),  $|V| =$

$\sqrt{v_i^2 + v_j^2}$  is magnitude of the velocity (m),  $D^*$  is the effective molecular diffusion coefficient (m<sup>2</sup>/s).

The parameters in the above equations are listed in the following table. The description of how these parameters were set will be described in the flow and transport calculation. And, generally, the effective molecular diffusion coefficient is negligible.

**Table 3-2:** Values of input parameters used in simulation

| Parameter | R (1,4-dioxane) | $\alpha_L$ | $\alpha_T$ | $D^*$ |
|-----------|-----------------|------------|------------|-------|
| Value     | 1.0             | 5.0        | 0.5        | 0.0   |

### 3.4.2 Spatial and temporal discretization

The model domain was considered regarding the available geological and hydrogeological data and covering the potential area of 1,4-dioxane distribution. The total area of the model domain is about 30,000 m<sup>2</sup> in which the upstream part is bordered by the road and the downstream part is bordered by the river (see **Figure 2-2b**). The discretization of model domain is preferably fine enough to obtain more accurate results. However, the finer mesh is always constrained by the computer capacity or required time for running the simulation, especially when contaminant transport simulation is performed. Gao (2011) evaluated the effect of vertical discretization in his transport models. His study results proved that the significant accurate results were obtained by increasing number of vertical discretization.

For this study, the discretized meshes size and vertical discretized number was considered from the sequential trial-and-error tests until the optimal error was achieved. As a result, the mesh size was equal to 6 m and vertical discretization was equal to 55 layers. Theoretically, if a smaller time step is set, the model can produces more accurate results, but it would result in excessive calculation time. In case of this model, the optimum time step was checked by varying the time step ranged from 0.5 to 15 days. As a result, the stable solutions with relatively less error were obtained for the time step ranged from 0.5 to 10 days.

### 3.4.3 Boundary and initial conditions

Generally, model boundaries are defined from the hydrological features adjacent to or within the model domain (Spitz and Morenó, 1996). However, since the natural hydrogeological features are in great distance away from this study area, boundary conditions were defined within the area where geological data are available. Along the model boundaries, it was assumed that there is no flux and water heads are constant. The entire model domain was assigned as the recharge boundary from rainfall.

Since early 2010, groundwater pumping was terminated. Accordingly, the groundwater levels returned to the stable condition. In this study, the average groundwater heads automatically recorded 8 times a month within January, 2011 were used for assigning boundary conditions. The annual rainfall data averaged from 2006 to 2010 will be input to the model (the detail explanation of this data use will be described later). The groundwater heads were measured from 24, 26, and 28 monitoring wells at the first, second, and third aquifers respectively. From all these measured heads, groundwater contours map of each aquifer is built by using Krigging method so that the head at the boundary of model can be predicted (see **Figure 3-2~3-4**). These extrapolated heads at the boundary were used as the constant-head boundary conditions for each aquifer for the flow model simulation. For the initial condition, since the flow model was run in the steady-state condition, the setting of the initial condition of the groundwater head is not necessary. In this model, the initial condition was set by default value in the model software itself.

For the transport model, the whole waste layers were considered as the contaminant source. The relative concentration of the contaminant source was fixed as 1 unit. In the ideal condition, the source might not be constant due to the decreasing of concentration washed by groundwater flow. However, considering the safety case, the source was considered as constant source over the calculation period. The boundary conditions of the groundwater flow from upstream and recharge from rainfall were fixed at a concentration equal to zero. The initial conditions for other geological materials were also assumed to be equal to zero.

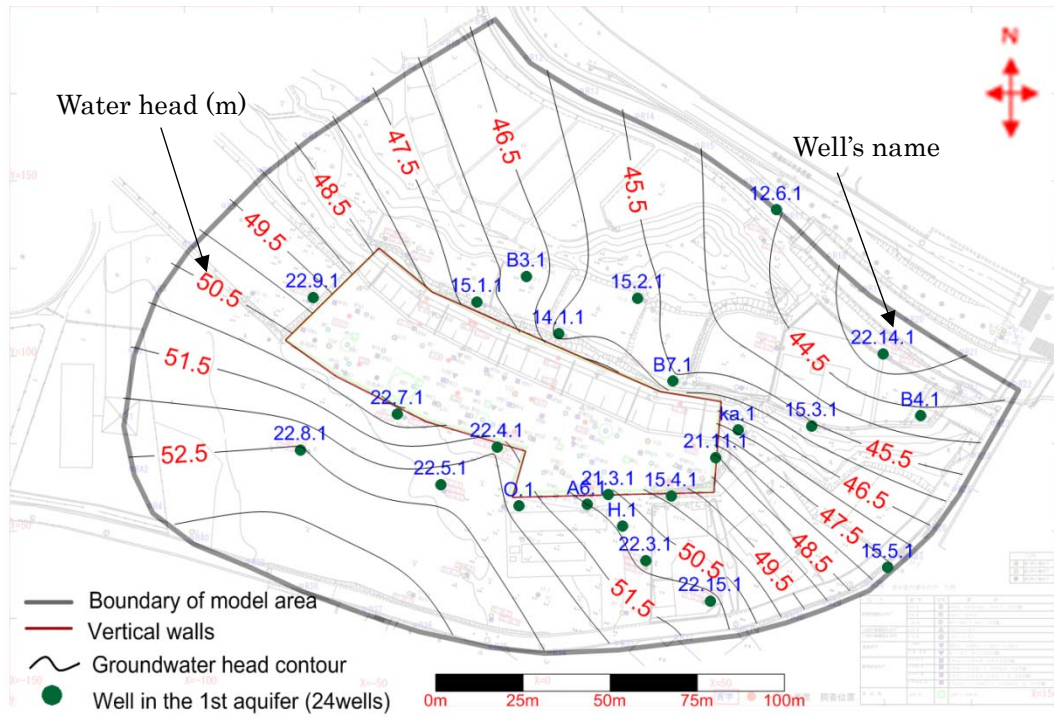


**Figure 3-2:** Observed groundwater contour map of the first aquifer

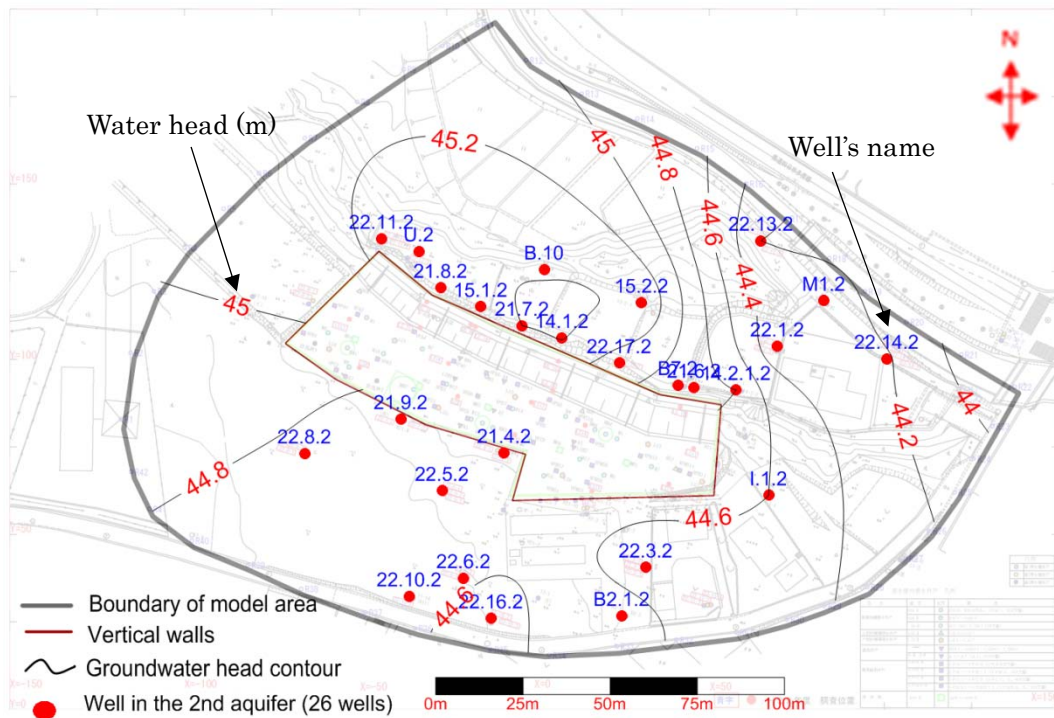
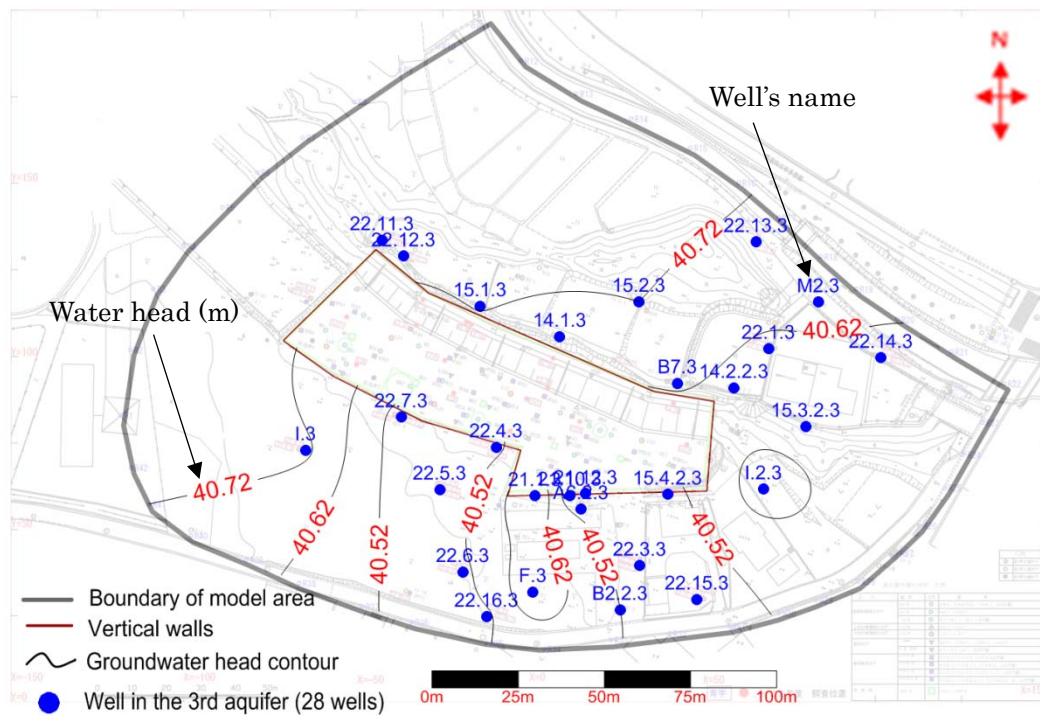


**Figure 3-3:** Observed groundwater contour map of the second aquifer



### 3.4.4 Solving method and used software

The application of finite element method to groundwater problem simulation was recently developed comparing the finite difference method. For the finite difference model, the heads throughout the domain are defined only at the nodal points themselves while the finite element model permits the application of variational or weighted residual principles. Finite element method is flexible for irregular boundaries of problem and, moreover, in solving coupled problems, such as contaminant transport, or in solving moving boundary problems, such as moving water table (Wang and Anderson, 1982).

For this model, numerical finite element methods based on the mixed Eulerian-Lagrangian approaches were used to solve the advection-dispersion equations. The Lagrangian methods are particularly suitable for solving advection term, while the Eulerian methods are more effective in dealing with dispersion term (Zheng and Bennett, 2002). In this paper, a three-dimensional numerical model was developed by using GeoModeler software for simulating the groundwater flow and 1,4-dioxane transport. GeoModeler is a numerical finite element-based software for modeling subsurface flow, solute transport, and heat transport processes which was recently developed by a Japanese company, GMLabo Inc. (<http://www.gmlabo.co.jp/>).

### 3.4.5 Geological model

Once the site was discovered, many boreholes were drilled inside and outside vertical walls from 1998 to 2010. Those wells were used for estimating the geometry of waste layers, geological stratigraphy, and groundwater heads and directions. Totally 92 boreholes were used to estimate the geological stratigraphy. 57 boreholes were drilled from 1999 to 2009 and 35 boreholes were drilled in 2010. All boreholes were integrated to make representative 14 geological cross-sections for building geological model, 8 sections for south-north direction and other 6 sections for west-east direction (see **Figure 3-5**).

In this research, we used all the above mentioned geological cross-sections for developing the geological model of the study area. The main geological materials are sand and intercalated clay layers. The waste layers locate within the first and second aquifers and it was covered by backfilled soil layer. The aquifer bed is formed by the thick clay layer. The three-dimensional geological model was built in model software using those 14 geological cross-sections through interpolation method. The GeoModeler software enabled the model developer to include the vertical walls with thickness of 0.55 m and depth varied from 18.5 m to 25 m depending on the depth from the ground surface and an underground tank with dimension of 13×7 m and 6.5 m of depth from ground surface. As a result, a three-dimensional geological model was developed. **Figure 3-6** shows the results of geological model viewed from the west-east (WE section) and south-north (SN section) directions with vertical exaggeration of 1.5. Location of WE and SN sections are shown in **Figure 3-5**. In addition, the top main clay layer which separates the first and second aquifers is not continuously distributed within the model area, especially at the inside of the walls. And, moreover, as shown in the **Figure 3-6**, a zone near the north-east corner part of the walls was zoomed in to show also another discontinuity of this clay layer. For the clay layer in between the second and third aquifers is continuously distributed within the model area. This might contribute to make the third aquifer isolated from the upper aquifers.

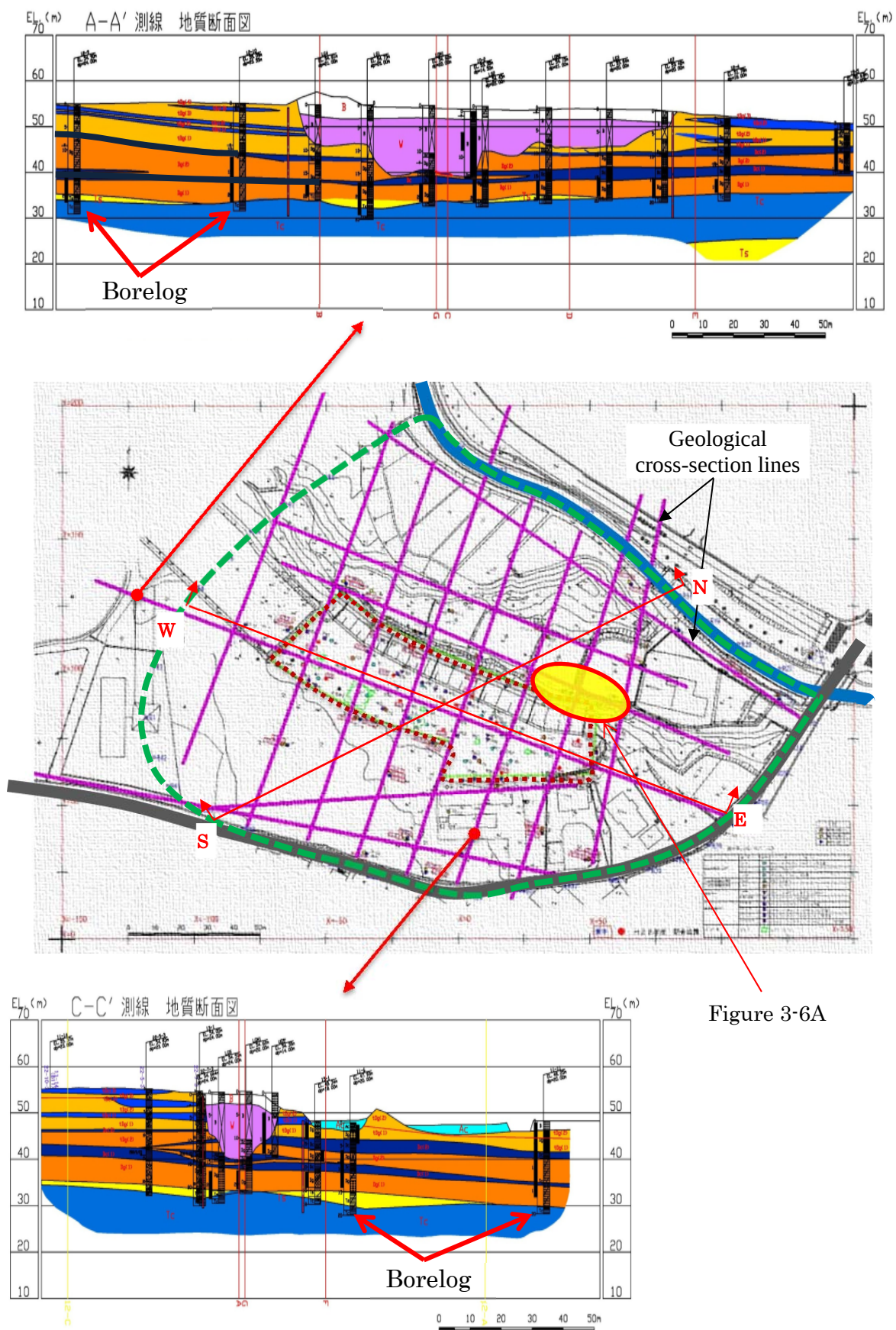


Figure 3-6A

Figure 3-5: Location map of input geological cross-section

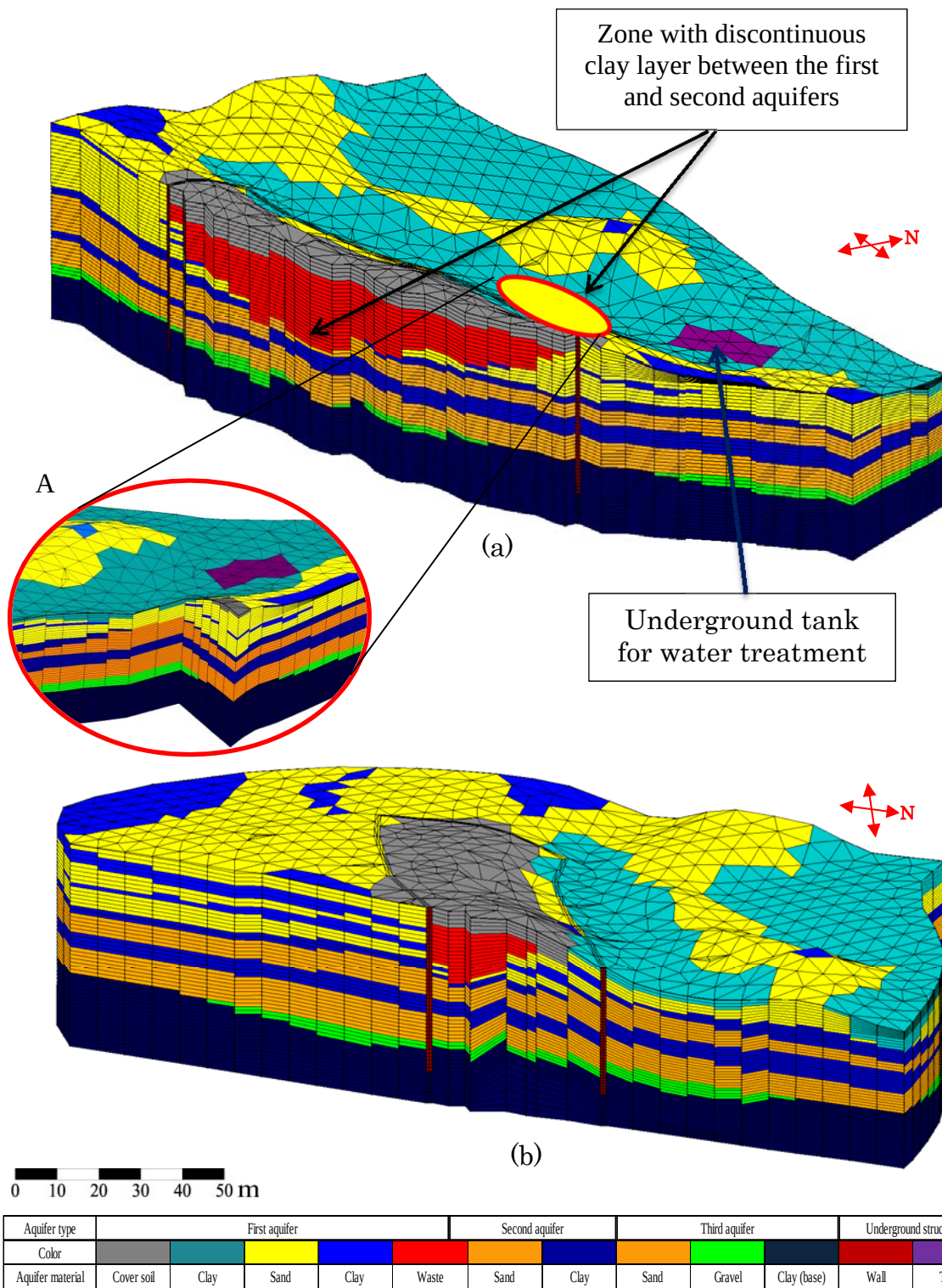


**Figure 3-6:** West-east (a) and south-north (b) geological cross-sections

### 3.5 Application of a new approach for model calibration

#### 3.5.1 Estimation of acceptable hydraulic conductivity sets by flow model

Generally, the model calibration is the process in which the model input parameters and boundary conditions are adjusted in order to provide the closer fit between simulated and measured hydraulic heads (Fitts, 2002). For this study, boundary conditions were assumed not to contain much uncertainty because it was defined by using adequate groundwater heads from a large number of monitoring wells.

Moreover, at some other study areas, rainfall was also considered as a major parameter which has much influence on groundwater flow (Lachaal et al., 2012; Barnett and Muller, 2008). However, at Kuwana site, groundwater flow model result was almost not changed even though the input rainfall data was increased to 2 or 3 times higher the average annual data obtained from 2006 to 2010 from a meteorological station nearby the Kuwana site (Japan Meteorological Agency, 2012). Accordingly, groundwater flow at Kuwana site is not much influenced by rainfall so that groundwater flow can be assumed to be mainly influenced by groundwater inflow from upstream which has seasonal fluctuation depend on rainfall. Therefore, only hydraulic conductivities of aquifer materials were taken into account for model calibration.

Based on the geological model, sand layers are dominant among other aquifer materials. Therefore, the hydraulic conductivities of the first ( $k_{S1}$ ), second ( $k_{S2}$ ), and third ( $k_{S3}$ ) sand layers were considered as the variables of the first, second, and third aquifers respectively in calibrations. The hydraulic conductivities were measured by Mie Prefecture in which  $k_{S1} = 4.7 \times 10^{-3}$  cm/s and  $k_{S2} = k_{S3} = 6.3 \times 10^{-3}$  cm/s. Besides, the hydraulic conductivities of the other materials were fixed at their given values as shown in **Table 3-1**. As described in the previous section, groundwater heads measured from 24, 26, and 28 monitoring wells from the first, second, and third aquifers were used to compare with the results of each aquifer respectively from all model calibrations.

To achieve the acceptable sets of  $k_{S1}$ ,  $k_{S2}$ , and  $k_{S3}$ , the  $k_{S1}$  was symmetrically fixed within plausible limit by multiplied and divided by 1, 5, 10, 50, and 100 and then  $k_{S2}$  and  $k_{S3}$  were automatically optimized on the basis of minimal error in groundwater head. This divided interval of  $k_{S1}$  will influence the result of 1,4-dioxane distribution. However, affect from the divided interval will be shown by the result of 1,4-dioxane in the next section. The

plausible limit was considered within the minimum and maximum values of sand material in literature values from  $2 \times 10^{-5}$  to  $6 \times 10^{-1}$  cm/s (Zheng and Bennett, 2002). The ending criteria of calibration process was considered when the minimum mean error ME(h) and root mean squared error RMSE(h) by comparing between calculated and observed groundwater heads obtained. Every calibration was performed to obtain the possible minimum error RMSE(h) between the calculated and observed groundwater head. As a result of calibration, 9 sets of hydraulic conductivities were obtained as listed in **Table 3-3**.

**Table 3-3:** Calibration results of hydraulic conductivities, in cm/s

| Calibration case |                       | Calibrated hydraulic conductivity |                       | Groundwater head error |         |
|------------------|-----------------------|-----------------------------------|-----------------------|------------------------|---------|
| Case             | $k_{s1}$              | $k_{s2}$                          | $k_{s3}$              | ME(h)                  | RMSE(h) |
| 1                | $4.75 \times 10^{-1}$ | $3.13 \times 10^{-1}$             | $9.46 \times 10^{-1}$ | 0.036                  | 0.474   |
| 2                | $2.37 \times 10^{-1}$ | $1.55 \times 10^{-1}$             | $4.14 \times 10^{-1}$ | 0.048                  | 0.473   |
| 3                | $4.75 \times 10^{-2}$ | $8.24 \times 10^{-2}$             | $2.75 \times 10^{-4}$ | 0.088                  | 0.393   |
| 4                | $2.37 \times 10^{-2}$ | $4.14 \times 10^{-2}$             | $2.81 \times 10^{-4}$ | 0.083                  | 0.391   |
| 5                | $4.75 \times 10^{-3}$ | $7.30 \times 10^{-3}$             | $3.31 \times 10^{-4}$ | 0.062                  | 0.384   |
| 6                | $9.49 \times 10^{-4}$ | $1.44 \times 10^{-3}$             | $2.31 \times 10^{-4}$ | -0.026                 | 0.391   |
| 7                | $4.75 \times 10^{-4}$ | $5.56 \times 10^{-4}$             | $1.00 \times 10^{-4}$ | -0.006                 | 0.398   |
| 8                | $9.49 \times 10^{-5}$ | $1.57 \times 10^{-4}$             | $3.52 \times 10^{-5}$ | -0.212                 | 0.721   |
| 9                | $4.75 \times 10^{-5}$ | $2.38 \times 10^{-5}$             | $3.77 \times 10^{-5}$ | -0.265                 | 1.023   |

The ME(h) and RMSE(h) were calculated by using the observation data from the total 78 monitoring wells shown in the **Figures 3-2~3-4**) based on the following formulas

Mean Error

$$ME(h) = \frac{1}{n} \sum_{m=1}^n (h_{cal} - h_{obs})_m$$

Root Mean Square Error

$$RMSE(h) = \sqrt{\frac{1}{n} \sum_{m=1}^n (h_{cal} - h_{obs})^2_m}$$

$h_{cal}$ : calculated head

$h_{obs}$ : observed head

$m$ : data identity

$n$  : number of data

Regarding the above described ranges of hydraulic conductivity of sand material, the result of  $k_{S3}$  of the case 1 was higher than the maximum limited value. Regarding the RMSE(h) values of those 9 cases, only case 3 to 7 have smaller error values of about 0.40 m. Therefore, only the sets of hydraulic conductivities in case 3 to case 7 are considered to be used for the analysis of 1,4-dioxane distribution. In a conventional approach, among these acceptable sets of hydraulic conductivities, a set in case 5 is considered as the better one because the RMSE(h) is the smallest among other cases. However, in our new approach, all these acceptable sets of hydraulic conductivities are used to estimated 1,4-dioxane distribution in groundwater and verified to find the closest match between the calculated and observed 1,4-dioxane concentrations and its distribution shapes.

### 3.5.2 Verification for selection of a better hydraulic conductivity set by transport model

As shown in geological cross sections, the whole waste layers were assumed to be the source of 1,4-dioxane. We assumed that 1,4-dioxane started to release from the source just after the finishing of illegal dumping in 1996, however the source concentration at that time was unknown. Fortunately, because of a large number of observed data of 1,4-dioxane was provided by Mie Prefecture so that we can assure the precise model calibrations. The 1,4-dioxane concentrations measurement were carried out once a month from 19, 29, and 30 wells outside the vertical walls in the first, second, and third aquifer respectively from January to May 2011. The monthly average concentration data were used to compare with the results from each calibration in each aquifer. The relative concentration was initially fixed as 1 for the source concentration, then using the acceptable sets of hydraulic conductivities to run 1,4-dioxane transport models. 1,4-Dioxane was assumed to be not retarded and not biodegraded in groundwater so that the retardation factor was set equal to 1.0. According to the scale of study area, the longitudinal and transverse dispersion coefficients obtained from the literature values were assumed to 5 and 0.5 m<sup>2</sup>/s

respectively (Schwartz and Zhange, 2003). The 1,4-dioxane transport model was run for 15 years, from 1996 to 2011 with the time step of 0.5 to 10 days. Actually the construction of vertical walls was completed in 2002, how in our calculation, we assumed that the vertical was included in the calculation since initial time of calculation in 1996. This assumption was considered due to the limitation of software application because the hydraulic conductivity could not be change during the calculation. On the other hand, another option can be also considered to assume that the initial time of calculation could be considered from the completion of 2002. However, to stand on the safety side, we consider the longer calculation time which is from 1996-2011. According to the result, there was not much difference in concentration between 1,4-dioxane distribution in 10 and 15 years of the above two options. For that meaning, our first assumption was reasonable and the calculation result was much fit to the measured data of 1,4-dioxane concentration.

As a result, the calculated concentrations of 1,4-dioxane were much higher than that values from field data at most of the wells. In order to minimize these errors (ME(c) and RMSE(c)), source concentration was decreased from gradually from 0.95 to 0.05 mg/L (**Figure 3-10**). The average error concentration index ME(c) and RMSE(c) corresponding to the result of each varied source concentration are calculated by using the total 78 observation 1,4-dioxane concentration data from the observation wells shown in **Figure 3-7 ~ 3-9**. We assumed that above ME(c) and RMSE(c) are the indicators for comparing the result of 1,4-dioxane transport analysis from each acceptable set of hydraulic conductivity. Additionally, the concentration distribution shapes of 0.05 mg/L of 1,4-dioxane distribution in each aquifer were also traced by mean of these 78 measured data. The 1,4-dioxane distribution resulted from each case of the acceptable set needs to be verified to match both criteria, error concentration and distribution shape in each aquifer. Even though, 1,4-dioxane concentration at some monitoring wells are measured to lower than detection limit of 0.005 mg/L, they are also contribute to trace the shape of 1,4-dioxane in each aquifer to be used to compare with that from the model results. Moreover, in term of environmental safety conservation in our prediction of 1,4-dioxane distribution, all the data with lower than detection limit should be also used for model calibration.

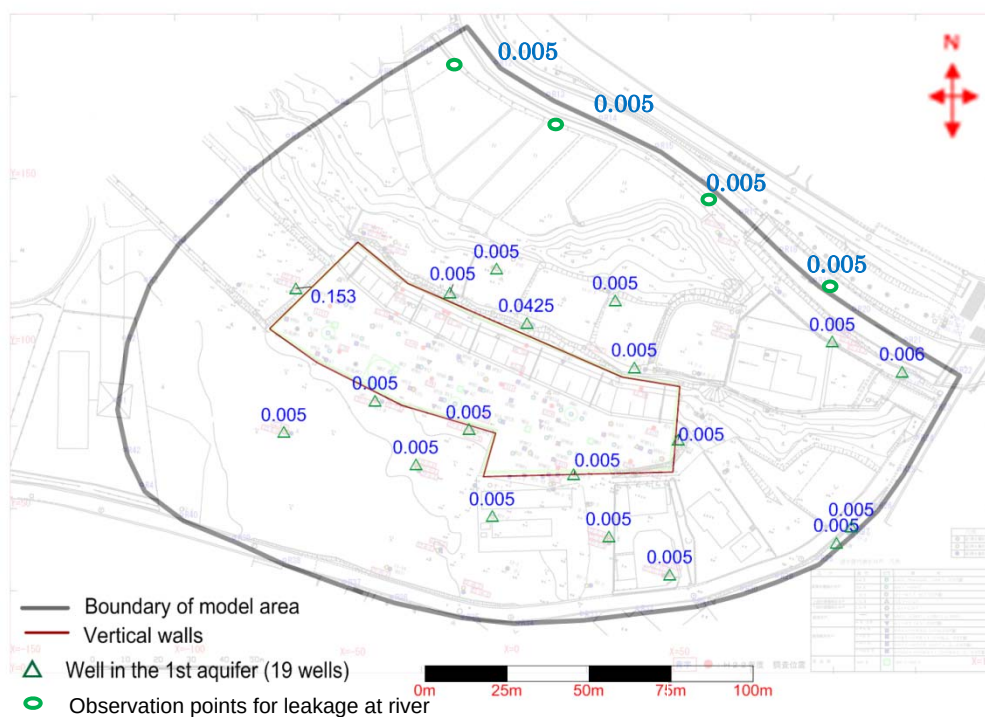


**Figure 3-7:** Observation 1,4-dioxane concentration of the first aquifer

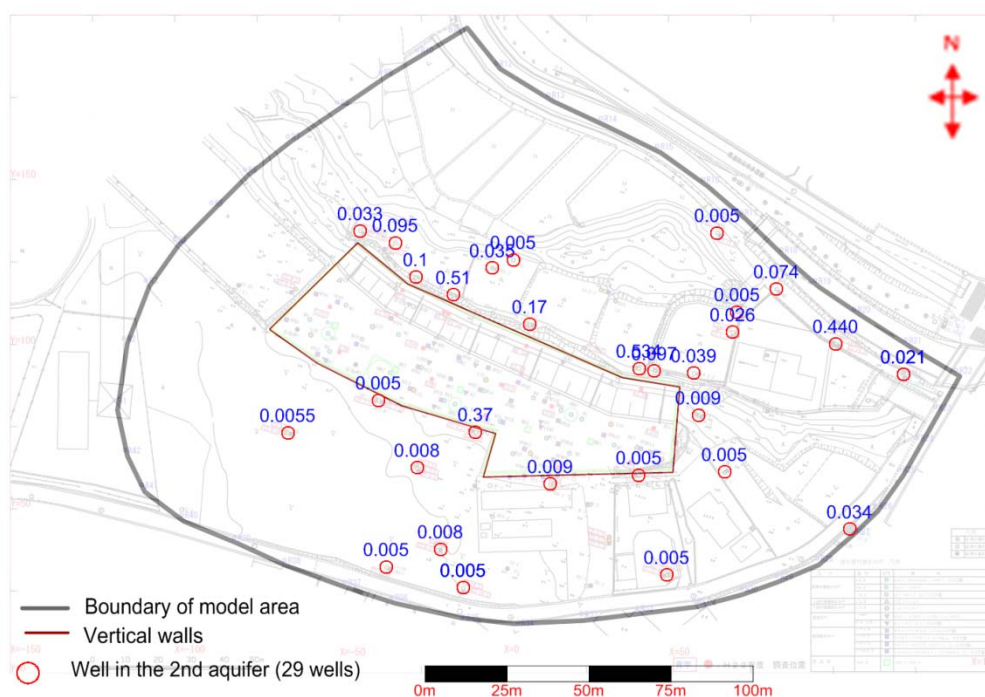


**Figure 3-8:** Observation 1,4-dioxane concentration of the second aquifer

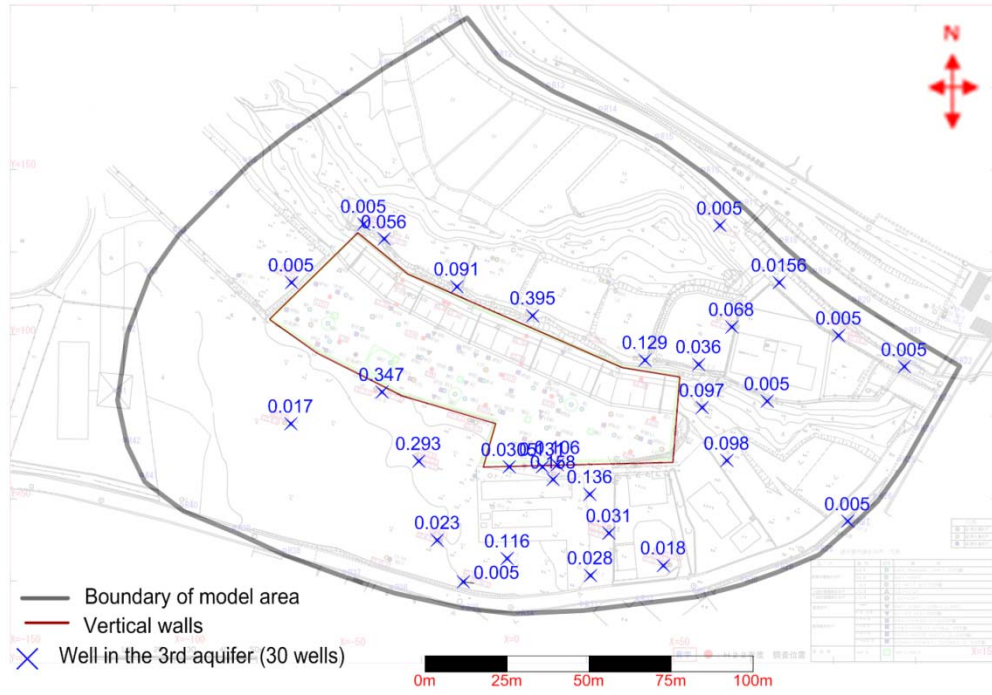


**Figure 3-9:** Observation 1,4-dioxane concentration of the third aquifer

And, the average error concentrations  $ME(c)$  and  $RMSE(c)$  are calculated based on the following formulas.

Mean Error

$$ME(c) = \frac{1}{n} \sum_{i=1}^n (c_{cal} - c_{obs})_m$$

Root Mean Square Error

$$RMSE(c) = \sqrt{\frac{1}{n} \sum_{i=1}^n (c_{cal} - c_{obs})^2_m}$$

$c_{cal}$ : calculated head  $c_{obs}$ : observed head

$m$ : data identity

$n$ : data number (78 wells)

In **Figure 3-10**, when the source concentration was decreased to 0.35 mg/L, ME(c) and RMSE(c) values are minimized. However, it is not easy to recognize that which set of hydraulic conductivity gave smaller error. Therefore, the ME and RMSE resulted from using all acceptable sets of hydraulic conductivity are compared in the **Figure 3-11**. Based on this result, the error concentration from one to another one set of hydraulic conductivity is very small different. Therefore, the divided interval of  $k_{SI}$  is rationally determined.

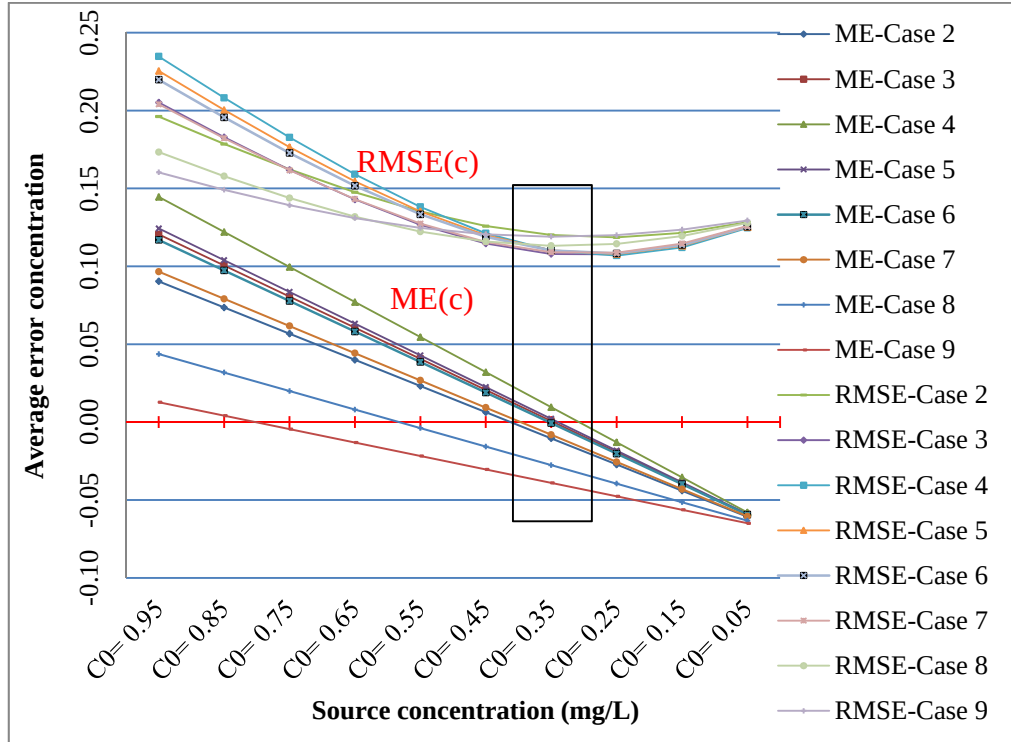


**Figure 3-10:** ME(c) and RMSE(c) of case 2 to 9 for source concentration ( $C_0$ ) from 0.95 to 0.05 mg/L

According to the ME(c) and RMSE(c) values, a better case might be the one among the case 3, 5, and 6. Therefore, a better case among these three cases cannot be defined by comparing only the concentration errors. In order to define the better case, the tendency of concentration distribution from these possible cases should be compared with that obtained from field data as shown in **Figure 2-2b**. As a result, the case 6 was further found to be the most considerable in which the tendency of 1,4-dioxane distribution in especially the second and third aquifers were consistent with those from the field data (see **Figure 3-12**). In contrast, as a result of case 3, 1,4-dioxane distribution is scattered widely within the model area in all three aquifers. Especially, 1,4-dioxane distribution in the second aquifer

as shown in **Figure 3-13**, 1,4-dioxane with high concentration tends to distribute northward until the north boundary which is much different from that shown in **Figure 2-2b**. Likewise, 1,4-dioxane distribution of case 5 (see **Figure 3-14**), which can be considered as the optimal case in conventional approach, is also widely distributed within the model area which is similar to that in case 3.

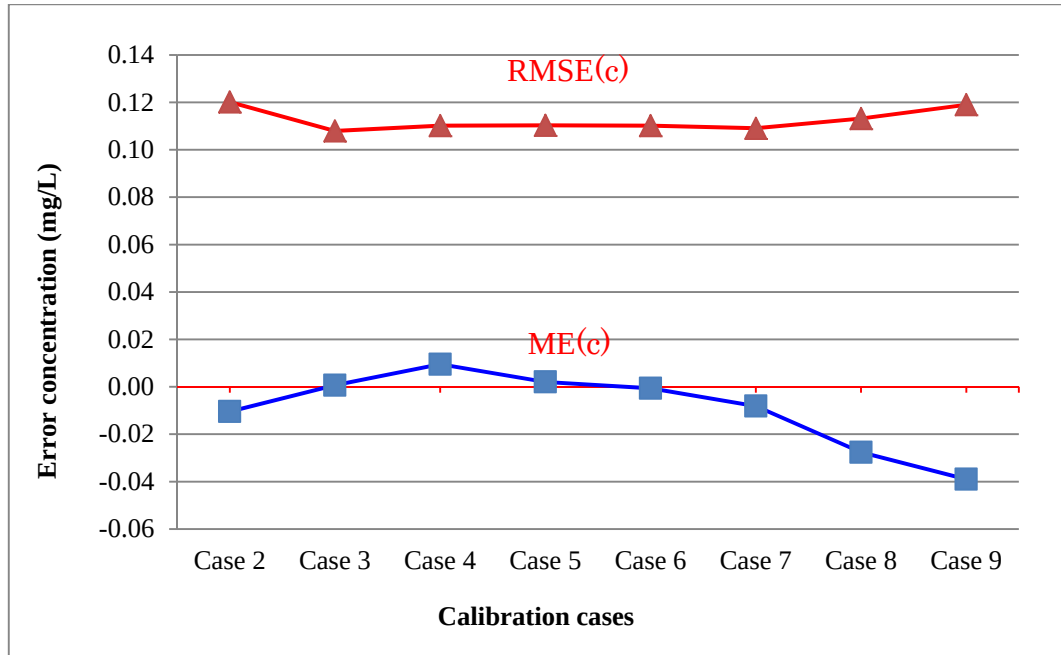


**Figure 3-11:** ME(c) and RMSE(c) of case 2 to 9 for the estimated  $C_0$  of 0.35 mg/L

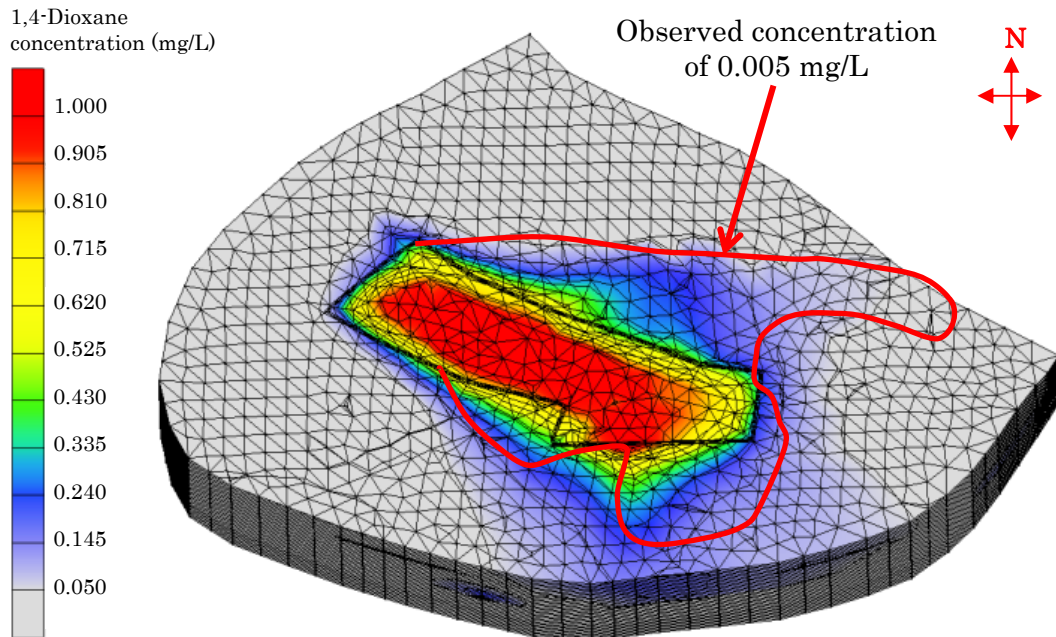


**Figure 3-12:** 1,4-Dioxane distribution in the 2<sup>nd</sup> aquifer in Case 6

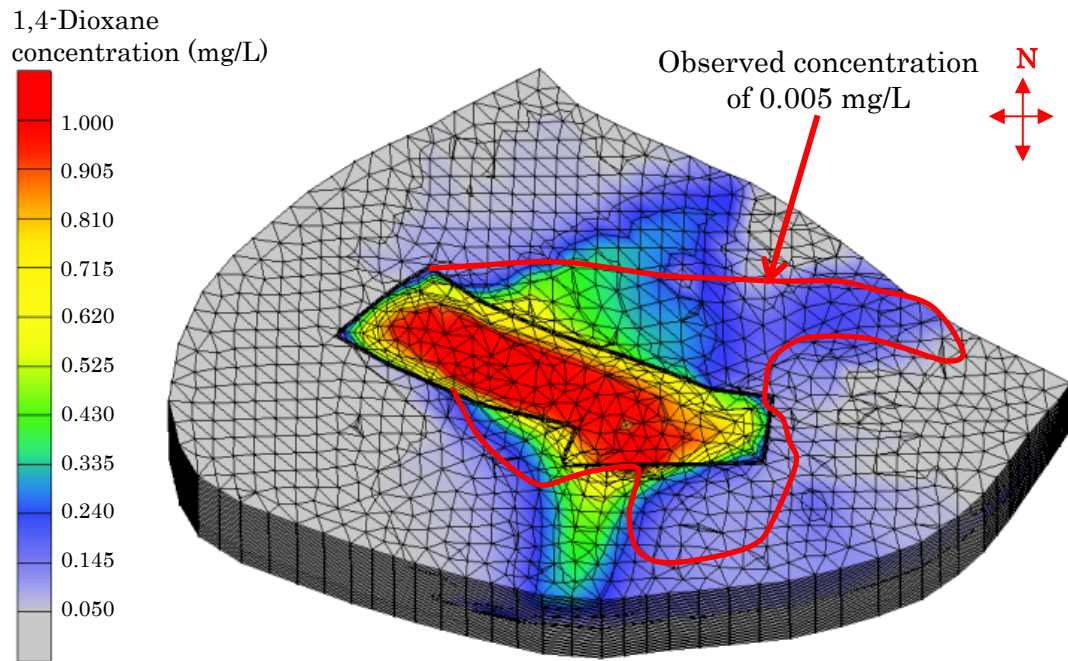


**Figure 3-13:** 1,4-Dioxane distribution of the 2<sup>nd</sup> aquifer of Case 3

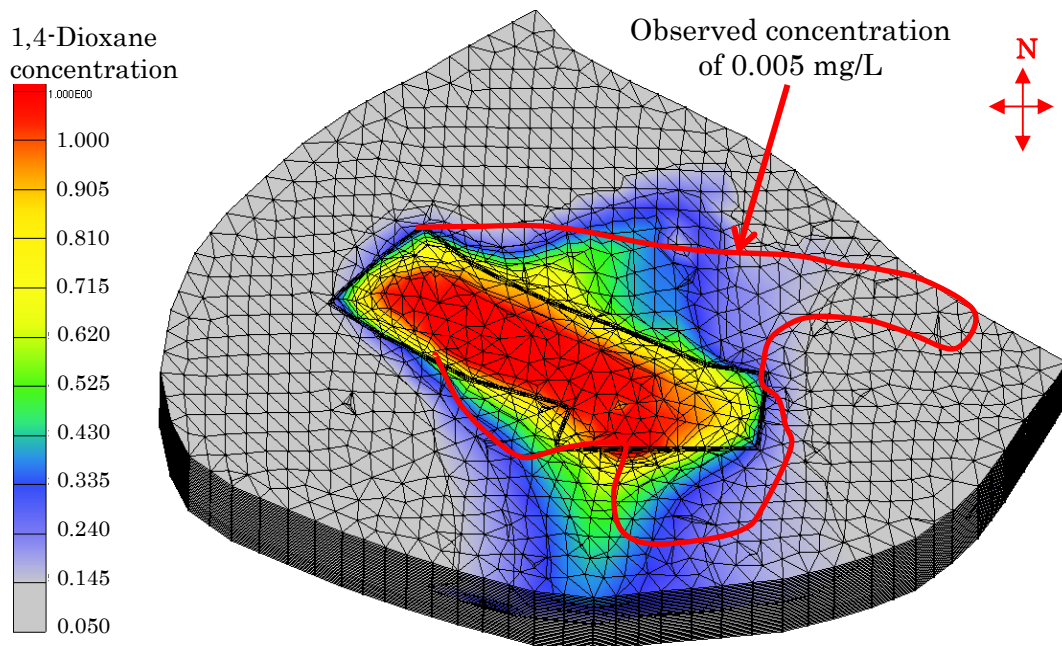
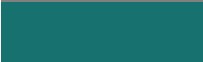
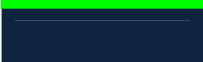
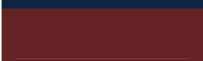


**Figure 3-14:** 1,4-Dioxane distribution of the 2<sup>nd</sup> aquifer of Case 5

Our new approach defined the better set of hydraulic conductivities in which the ME(c) and RMSE(c) are minimized to be smaller than those from which the hydraulic conductivities considered by a conventional approach (case 5), and it gave the most consistent of tendency of 1,4-dioxane distribution in aquifers. Groundwater flow and 1,4-dioxane distribution at the three aquifers were presented by using an calibrated set of hydraulic conductivity as shown in **Table 3-4**.

**Table 3-4:** The given and calibrated hydraulic conductivities, cm/s

| Aquifer material  | Color                                                                               | $k_{obs}$<br>(given data) | $k_{cal}$<br>(calibrated) |
|-------------------|-------------------------------------------------------------------------------------|---------------------------|---------------------------|
| Soil cover        |    | $1.0 \times 10^{-3}$      | -                         |
| Clay              |    | $2.7 \times 10^{-7}$      | -                         |
| Sand ( $k_{s1}$ ) |    | $4.7 \times 10^{-3}$      | $9.49 \times 10^{-4}$     |
| Clay              |    | $2.7 \times 10^{-7}$      | -                         |
| Waste             |   | $1.0 \times 10^{-5}$      | -                         |
| Sand ( $k_{s2}$ ) |  | $6.3 \times 10^{-3}$      | $1.44 \times 10^{-3}$     |
| Clay              |  | $7.2 \times 10^{-8}$      | -                         |
| Sand ( $k_{s3}$ ) |  | $6.3 \times 10^{-3}$      | $2.31 \times 10^{-4}$     |
| Gravel            |  | $3.1 \times 10^{-2}$      | -                         |
| Clay (base)       |  | $3.4 \times 10^{-7}$      | -                         |
| Wall              |  | $1.0 \times 10^{-7}$      | -                         |
| Tank              |  | $1.16 \times 10^{-10}$    | -                         |

### 3.5.3 Calibrated model

#### 3.5.3.1 Groundwater flow

The scatterplot of calculated against measured heads is illustrated in **Figure 3-15**. At most of the observation wells, the difference between calculated and observed groundwater heads was less than  $\pm 1$  m in the first and second aquifers. However, for that at observation wells of the third aquifer were found to be less than  $\pm 0.2$  m. Since the difference between observed and calculated groundwater head at each monitoring well of the third aquifer is small, the representative 28 points of monitoring wells seem to overlay on only one position in **Figure 3-15**.

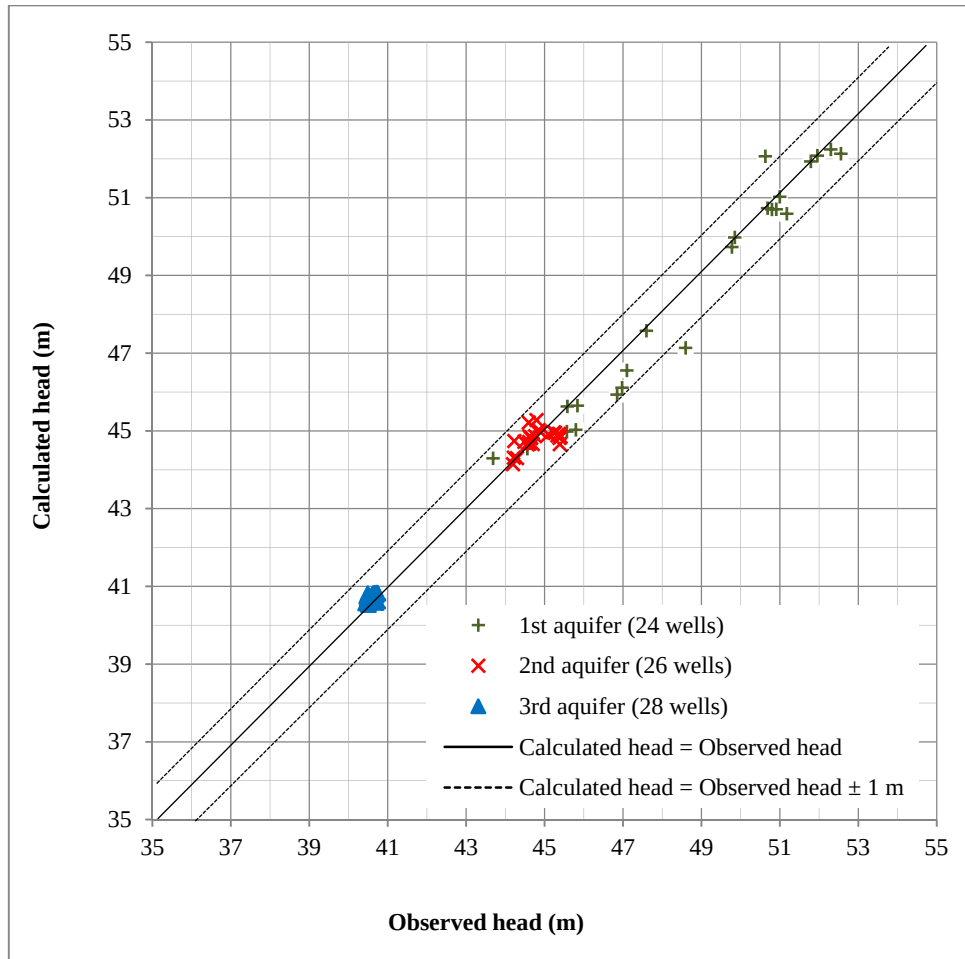


**Figure 3-15:** Comparison between calculated ( $h_{cal}$ ) and observed ( $h_{obs}$ ) heads

From flow model results, the calculated groundwater heads from the monitoring wells of each aquifer were exported and transformed into groundwater contour maps using Surfer software based on Kriging method. For the first aquifer (see **Figure 3-16**), the main groundwater flow directions from the simulated results were closely matched with the observed ones which were shown in **Figure 2-2b**. Among other aquifers, the groundwater flows in the first aquifer is dominant because it is unconfined aquifer with much different between water heads at the upstream and downstream of aquifer following the geographic slope. The different between the maximum and minimum head contours was 8 m.

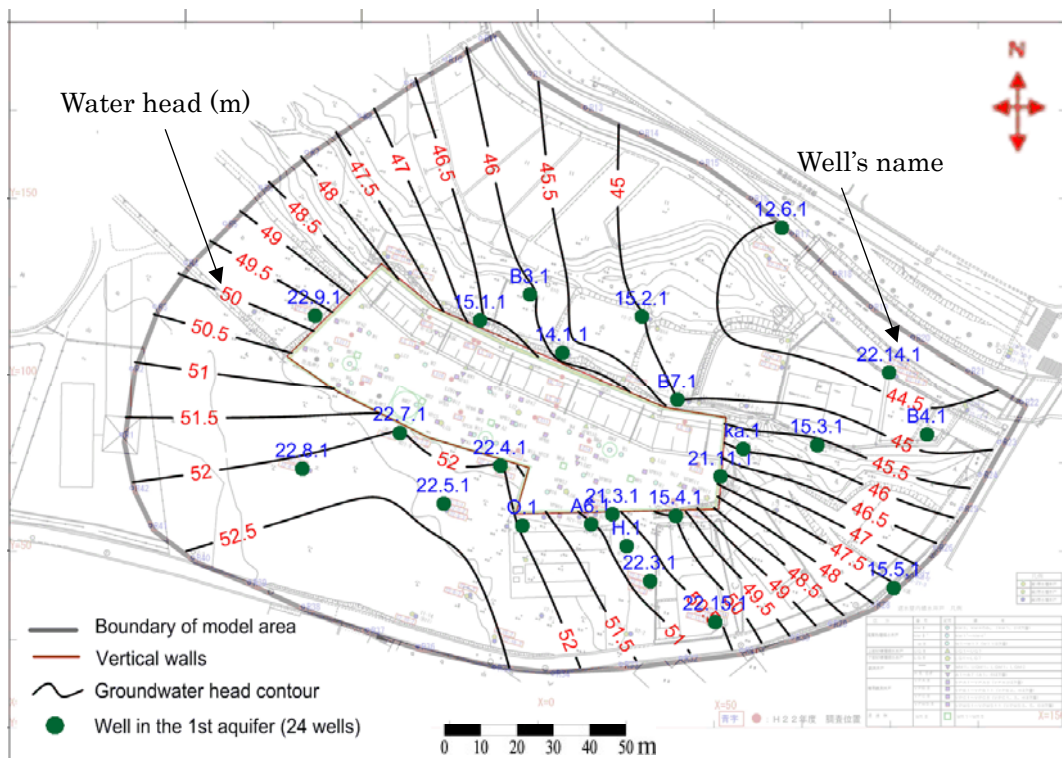


**Figure 3-16:** Groundwater head contour map of the first aquifer

For the second aquifer (see **Figure 3-17**), the groundwater flow is influenced by the vertical flow from the first aquifer forming a mount-shaped in around the Western part of vertical walls. This strong groundwater flow interaction because of the discontinuous clay layer which separates between the first and the second aquifer within the waste layer and also outside of walls which as shown in geological cross-section in **Figure 3-6**. In addition, the groundwater flow with a great velocity in the first aquifer is constrained by the vertical walls and waste layers where hydraulic conductivities are relatively small so that the

vertical flow from the first to second aquifers was presented. As a result, groundwater flows into two main directions to the north-west and south part of vertical walls. Based on the groundwater contours map shown in **Figure 3-17**, the total differences of groundwater heads in the second aquifer is about 1 m.

**Figure 3-17:** Groundwater head contour map of the second aquifer

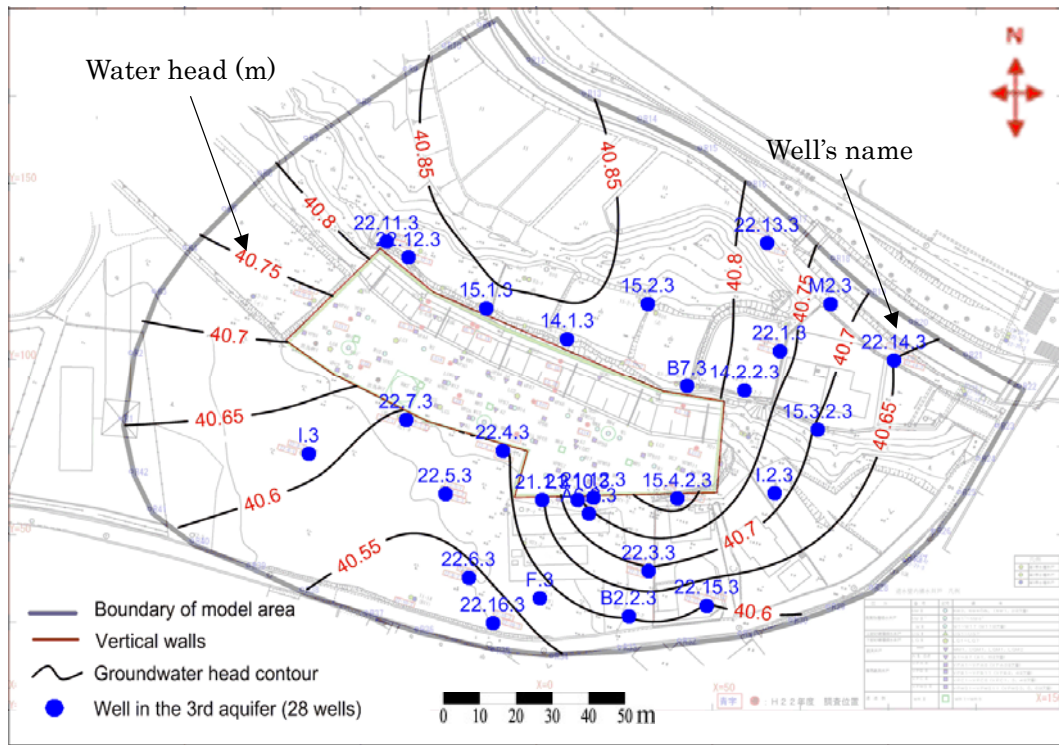


**Figure 3-18:** Groundwater head contour map of the third aquifer

### 3.5.3.2 1,4-Dioxane distribution

**Figure 3-19** shows the locations of 1,4-dioxane observation wells with the error concentrations ( $C_{cal}-C_{obs}$ ) at some wells in mg/L. Within the ranges of 5 times differences between calculated and observed concentrations were considered to be acceptable. In **Figure 3-19**, only wells with errors higher than acceptable ranges are shown with error values. For the other wells, only the locations are shown. In the first aquifer, 5 wells have high errors concentrations. All of these wells are located near vertical walls. In the second aquifer, 12 wells have errors concentrations outside the acceptable ranges. Most of these wells locate relatively close to the vertical walls.

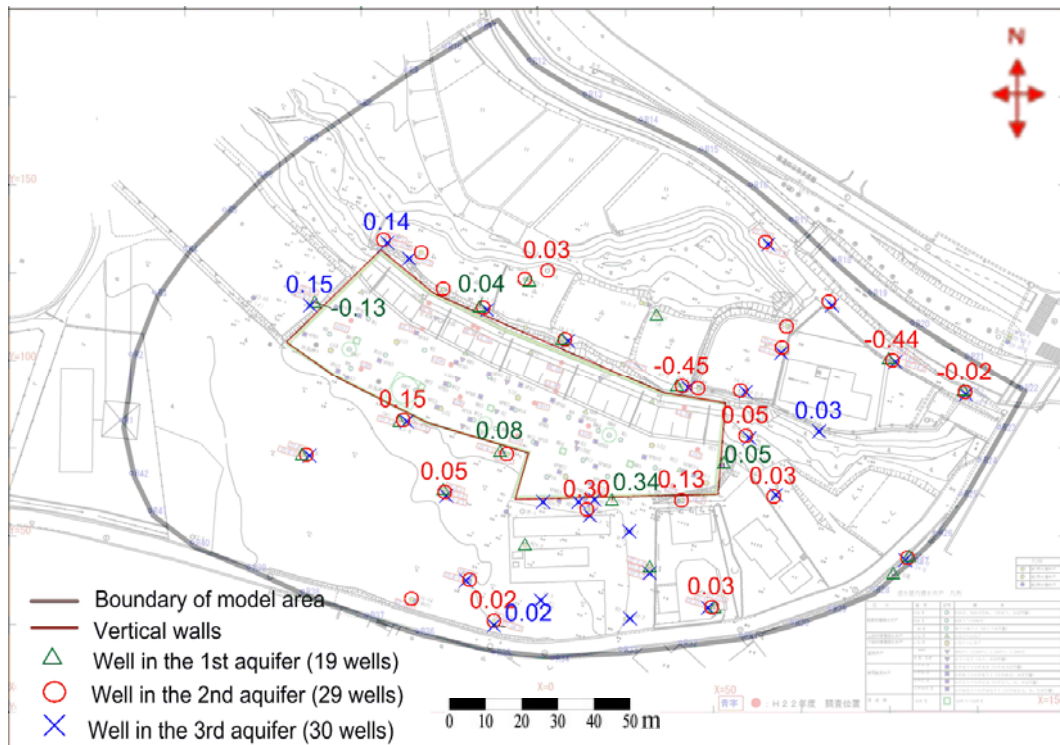


**Figure 3-19:** Locations of 1,4-dioxane observation wells in the 1st, 2nd, and 3rd aquifers

For the wells in the third aquifer, among 30 wells, only 4 wells have error concentrations higher than 5 times. Generally, in all aquifers, most of the wells which are located close to the walls have much error concentration. The homogeneity of aquifer materials and source conditions setting assumed in this model might be the major reasons that caused the distribution of these error concentrations. The comparison of the calculated and observed 1,4-dioxane concentration at all 78 monitoring wells were shown in the **Figure 3-20**. In **Figure 3-20**, many plots lined in the axis of  $c_{obs} = 0.005$  mg/L because the detection limit of 1,4-dioxane concentration is 0.005 mg/L.

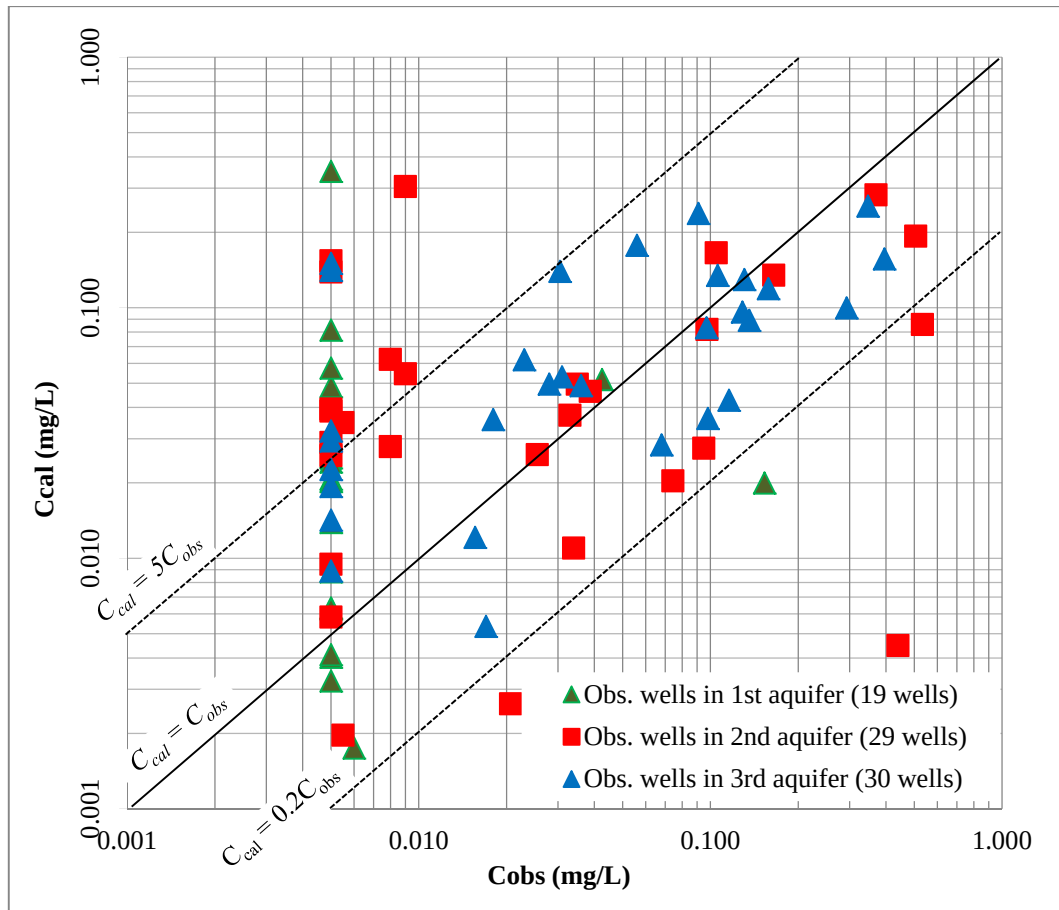


**Figure 3-20:** Comparison between calculated ( $c_{cal}$ ) and observed ( $c_{obs}$ ) concentration

**Figure 3-21 – 3-23** show the results of 1,4-dioxane distribution at 15-years period with concentrations higher than standards. Within the vertical discretization of 55 layers, the results of 1,4-dioxane distribution were viewed at the 10<sup>th</sup> layer for the first aquifer, at the 20<sup>th</sup> layer for the second aquifer, at the 34<sup>th</sup> layer for the third aquifer. The distribution shape of 1,4-dioxane of each aquifer is described and compared with field data measured in February, 2011 as shown in **Figure 2-2b**.

**Figure 3-21** shows that groundwater in the first aquifer is contaminated by 1,4-dioxane. In contrast, according to the field data, it is not contaminated. This phenomenon occurred maybe because of the source of 1,4-dioxane was set to be constant over calculation period. In reality, source should not be constant in space and time so that the waste layers and groundwater in the first aquifer might have been washed out because groundwater flow velocity in this aquifer is much higher than that of the other two aquifers.

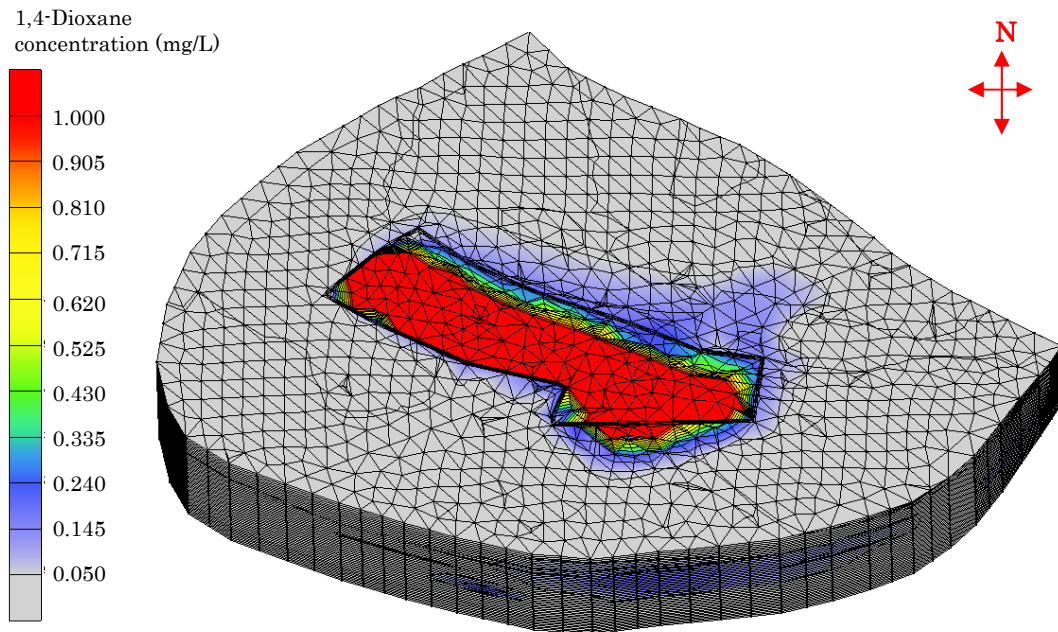


**Figure 3-21:** Simulation result of 1,4-dioxane distribution in the first aquifer

For the second aquifer (see **Figure 3-22**), 1,4-dioxane spreads in both upstream and downstream of aquifer because of the vertical flow from the first aquifer. 1,4-Dioxane seemed to spread further at south and north-west parts of the source with high concentration. The tendency of 1,4-dioxane distribution shapes are relatively coincident with the main groundwater flow directions which flow into two main direction into the north and south part of walls. It is also consistent when comparing with the distribution shapes given in **Figure 2-2b**.

For the third aquifer (see **Figure 3-23**), 1,4-dioxane migrates further in the south part of the source following the main groundwater flow direction until the south parts of the model boundary. However, the 1,4-dioxane concentration distribution in the third aquifer is slightly scattered with less concentration value comparing to those in the other two aquifers because the waste layers are not situated in this aquifer. It means that 1,4-dioxane migrates downward from the first and second aquifer and concentrated with high concentration within the walls, then disperses widely in this aquifer. The 1,4-dioxane distribution in this aquifer is much consistent with the given one.

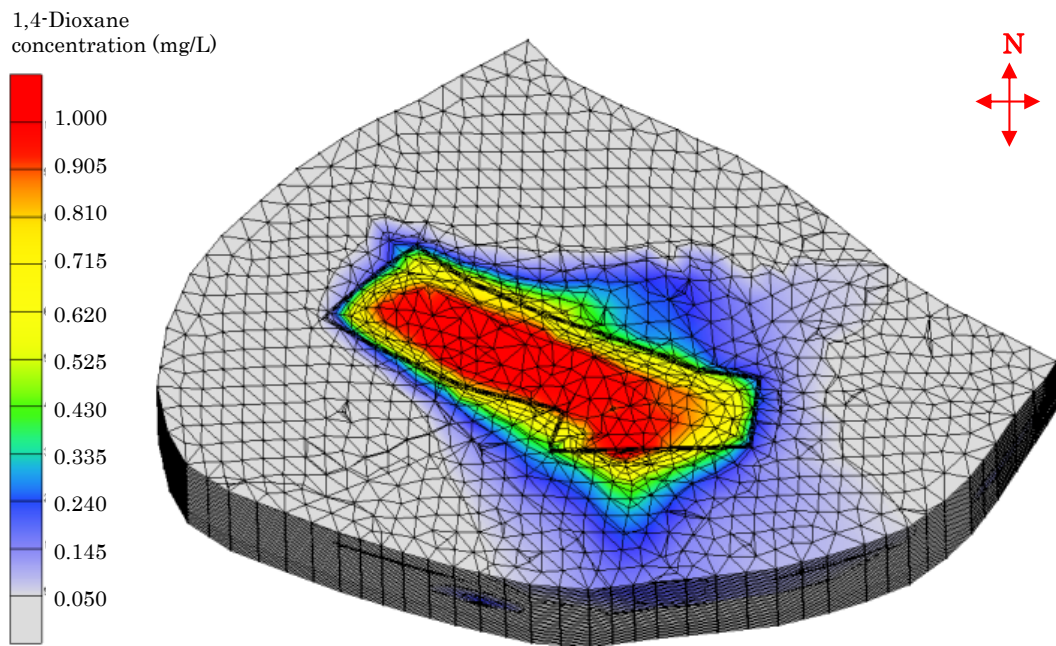


**Figure 3-22:** Simulation result of 1,4-dioxane distribution in the second aquifer

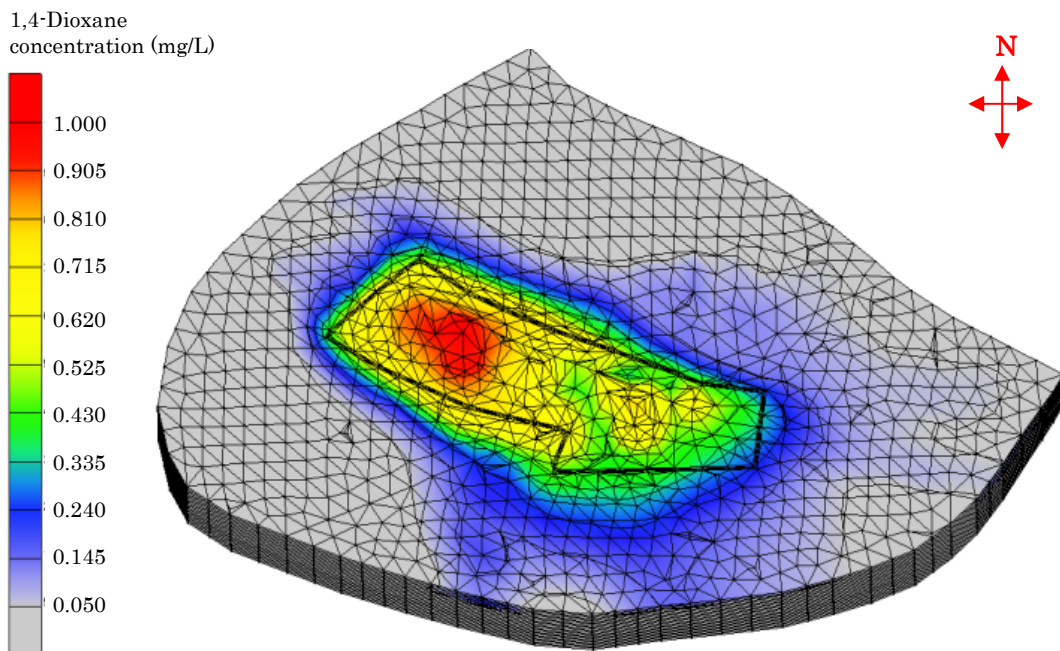


**Figure 3-23:** Simulation result of 1,4-dioxane distribution in the third aquifer

In addition, vertical 1,4-dioxane distribution at calculation time of 1, 5, 10, and 15 years are shown in **Figure 3-24** are used to described more detail the vertical distribution of 1,4-dioxane from the waste source into the deep aquifer due to the groundwater flow interaction. 1,4-Dioxane concentration spreads out of the wall since the first year of calculation starting from the second aquifer because the waste layer is closer to the wall at the left side of walls. The concentration of 1,4-dioxane is increasingly spreading out of the wall from the first to 10 years. However, from 10 to 15 years, the spreading concentration seems to be not much increased. In the second aquifer, 1,4-dioxane migrates across the walls into both sides of the vertical walls following the main flow directions. Simultaneously, high concentration of 1,4-dioxane move downwards from the first and second to the third aquifer within the walls, then it spreads out of the walls mainly into the south part of wall following the groundwater direction in the this aquifer. Moreover, 1,4-dioxane also migrate out of the walls at the bottom part of vertical walls. This phenomena suggests that depth of vertical is not deep enough to prevent the spreading of 1,4-dioxane out of that walls.

According to the mechanism of 1,4-dioxane migration, 1,4-dioxane spreading out of the walls since the early calculation time. It seems like the walls were not effective for containing to prevent 1,4-dioxane concentration from spreading out of the walls. We attempted to prove the effectiveness of the walls by conducting trial calculation for the case in which the hydraulic conductivity of the walls was increased to much higher than the set value for the above calculations. As the result, 1,4-dioxane concentration was found the move out of the wall widely until all model boundary with high concentration in all three aquifers. Therefore, the walls were proved to be effective to slow down the spreading 1,4-dioxane out of the walls.

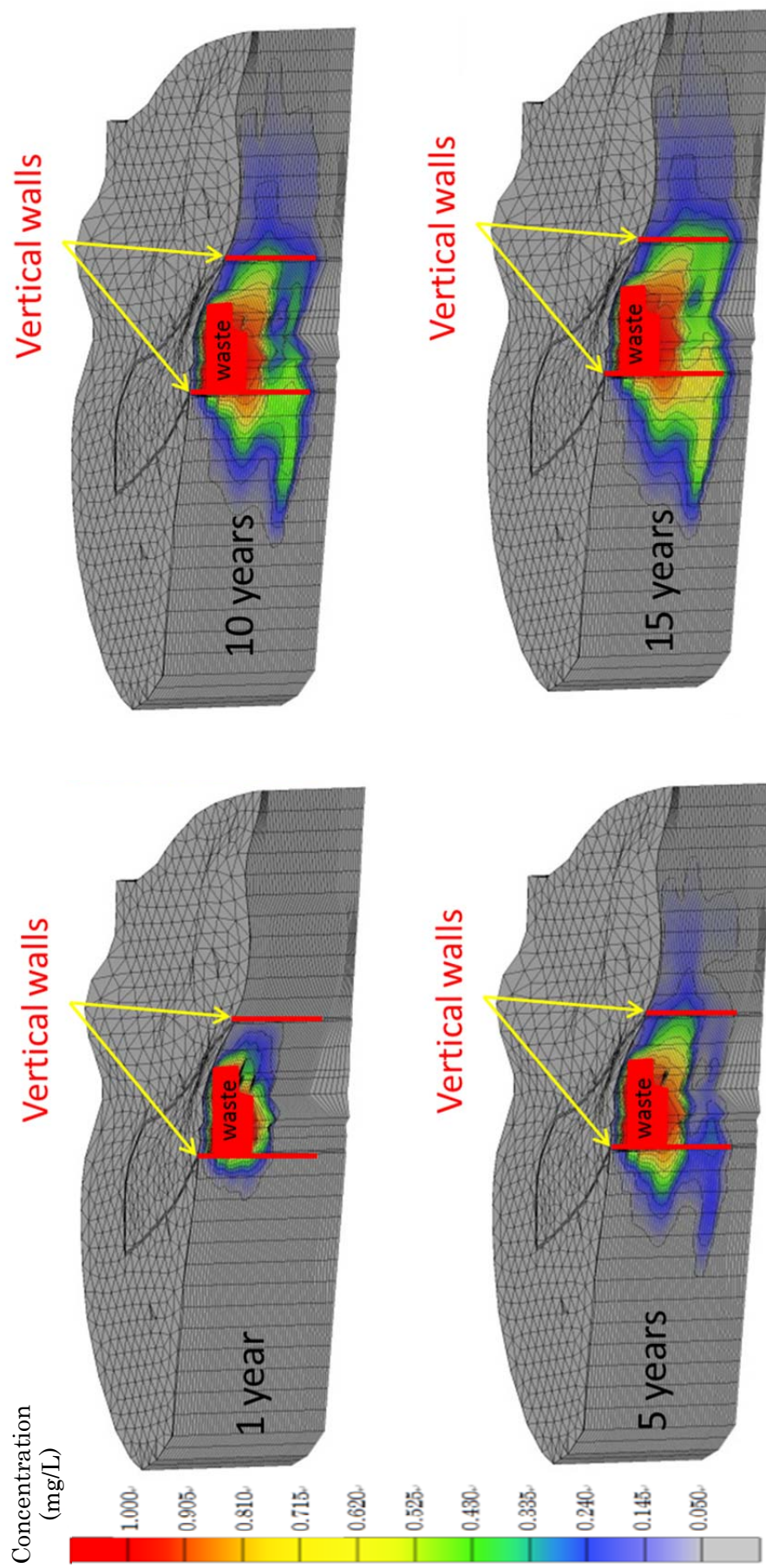


**Figure 3-24:** Vertical distribution of 1,4-dioxane concentration from 1 to 15 years  
(SN cross-section view)

### 3.6 Limitation of a new approach

Our new approach predicted the distribution of 1,4-dioxane at Kuwana site more precisely than the conventional approach by comparing both error concentration and tendency of 1,4-dioxane distribution of all the cases with that from the observed data shown in **Figure 3-12~3-14**. As mentioned above, e.g., the tendency of 1,4-dioxane concentration in the second aquifer in **Figure 3-12** (new approach) is much improved comparing to that in **Figure 3-14** (conventional approach). Yet, some of the wells contain much error, especially for that in the first and second aquifers as mentioned above. This is because of limitations in calculation assumptions and uncertainty in field investigation.

In many cases like this study, the constant source condition is usually used but it might be different from the real conditions. Our new approach cannot set the calculation conditions to reflect the real source condition. Moreover, geological conditions were assumed to be homogeneous over the model domain in which the distribution of hydraulic conductivity is the same at any points of the same geological material. These two major assumptions in the model cause 1,4-dioxane continuously and uniformly distributes over aquifers and moreover, the calculated concentrations at the wells beside the source are extremely high.

The uncertainty in field investigation was caused by discrete boring with limited numbers and measurement errors in 1,4-dioxane concentration. The numerical model based on convective-dispersion phenomenon using equations (1) and (2) might have limitations in comparison between calculated results and observed data.

For future works, the model needs to be improved by changing source conditions to reflect the real conditions, e.g., source concentration at each aquifer can set with different value. As one of attempt, 1,4-dioxane distribution was calculated especially by changing the source condition from constant to instant source. The result showed that 1,4-dioxane in the source and groundwater in the first aquifer was totally washed out while that of the second and third aquifers were partially remained. This tendency was similar to the current situation in the site. From this evidence, source conditions setting should be discussed to improve our model. Once the model is improved, it will be applied to analyze the effectiveness of remedial actions for 1,4-dioxane contaminated groundwater at Kuwana illegal dumping site by considering the required costs, time, and treated level.

Our new approach can be regarded as an effective modeling approach for the prediction of

1,4-dioxane distribution for not only Kuwana site, but also for other sites. Even though, this new approach should be applied to other sites to confirm its effectiveness.

### 3.7 Summary

Because of 1,4-dioxane migrates in groundwater without sorption, biodegradation, and volatilization according to its chemical properties, its migration strongly depends on groundwater flow. Hydraulic conductivities which are the most crucial parameters that influence groundwater flow should be precisely estimated.

In a conventional approach, only one set of hydraulic conductivities estimated by flow model calibration considering the observed groundwater heads is used to predict 1,4-dioxane distribution. However, 1,4-dioxane distribution is not precisely predicted by the calibrated groundwater model because there should be more precise groundwater flow in which another different set of hydraulic conductivities is used. The current study proposed a new approach to more precisely predict 1,4-dioxane in groundwater. In this approach, several acceptable sets of hydraulic conductivities in term of groundwater heads were used to predict 1,4-dioxane distribution and verified to match between the calculated and observed concentrations. Our new approach was compared with the conventional approach by a case study at Kuwana illegal dumping site in Japan where the three aquifers with complex hydrogeological features have been contaminated by 1,4-dioxane for about 15 years. The results showed that our approach could predict 1,4-dioxane distribution more precisely than the conventional approach. The mean error and root mean squared errors of estimated 1,4-dioxane concentrations were minimized and especially the distribution of 1,4-dioxane was found to be more consistent by applying our new approach.

By using a new modeling approach, groundwater flow and 1,4-dioxane mechanism were clarified. The discontinuity of clay layer in between the first and second aquifer especially within the vertical walls contributes to have strong vertical flow from the first aquifer into the second and third aquifers. Due to this vertical flow, 1,4-dioxane spread horizontally into both upstream and downstream of the second aquifer and also it migrates downwards into the third aquifer. Then, it migrates from the waste layer across the walls and through the bottom parts of walls so that the third aquifer is also contaminated by 1,4-dioxane even though there is no waste in this aquifer.

The proposed new approach can be regarded as an effective method which can entirely

improve groundwater model for precisely simulating groundwater flow and contaminant transport for not only Kuwana site, but also for other sites, especially for the sites where 1,4-dioxane or other similar contaminants are presented. However, the proposed approach should be applied to other sites to confirm its effectiveness.

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## CHAPTER 4

### REMEDICATION PLANNING BY USING NUMERICAL SIMULATION BASED ON VERIFIED FOLLOW-UP

#### 4.1 Introduction

The previous remediation measures have been applied for VOCs remediation at Kuwana site, however they could not be effective to complete 1,4-dioxane remediation because the waste contains elevated concentration of 1,4-dioxane. And due to the previous remediation actions, there was much different in groundwater between the inside and the outside of walls so that 1,4-dioxane can easily spread out of the walls into the surrounding environment, especially 1,4-dioxane is expected to migrate in groundwater faster than VOCs without biodegradation and adsorption to the soil according to its unique chemical properties (Liu et al., 2000; Mohr et al., 2010; Priddie and Jackson, 1991; Patterson et al., 1985; Zenker et al., 2003). Consequently, 1,4-dioxane might be more difficult to be contained by groundwater level control without waste removal. Regarding this problem, this study focused on developing remediation plans by using numerical simulation based on the concept of Verified Follow Up (VF-UP). VF-UP is a new approach developed by (Furuichi, 2013) for remedial planning for groundwater-contaminated sites, considering expected and/or unexpected uncertain events in the future to complete remediation effectively. Several studies have been conducted by applying the numerical simulation for groundwater contaminated site remediation focusing on mostly the elemental technique e.g., optimization of pumping rates, pumping locations, remediation time and costs (Liu et al., 2000; Becker et al., 2006; Matott, 2012; Zhen and Wang, 1999; Harvey et al., 1994; Bayer et al., 2005; Rizzo and Dougherty, 1996; Huang and Mayer, 1997). However, our study focused on the application of numerical simulation for whole remediation plans considering the element techniques. The element techniques can be flexible to be changed based on the whole condition of remediation at the site. Moreover, since VF-UP was newly developed, there is no study that proves its application to the real contaminated site, especially in remediation planning using numerical simulation.

In chapter 3, we developed a model to predict the 1,4-dioxane distribution in groundwater that can represent the groundwater flow and 1,4-dioxane distribution conditions after the previous remediation at the site. The existing numerical model for groundwater flow and

1,4-dioxane transport will be used for remediation planning in this study considering the same parameters and settings. However, the existing model were developed and calibrated for the groundwater condition without pumping. Therefore, the existing model will be recalibrated to correspond with pumping condition, because the observation groundwater heads and input boundary conditions must be different from condition without pumping.

The remedial objective in this study is to treat 1,4-dioxane in groundwater outside of vertical walls within 10 years which is limited to national subsidy and to prevent 1,4-dioxane from spreading throughout the walls to the surrounding environment. In this study, numerical simulation was applied to analyze the amount of waste to be removed and the pumping plans for treating 1,4-dioxane-contaminated groundwater at Kuwana illegal dumping site based on the concept of (VF-UP).

#### **4.2 Objective of Remediation in Kuwana Site Based on VF-UP**

Considering the above technical uncertain factors, there might be many uncertain events will occur at Kuwana illegal dumping site during the remediation and after completion of remediation because the site has complex hydrogeological features. There are three aquifers with interaction and groundwater flows in different directions. Moreover, the site has a steep slope so that groundwater control for 1,4-dioxane containment is difficult. Since the number of data is limited and discrete over space and time, prediction of groundwater flow and 1,4-dioxane distribution might involve much uncertainty which exert the remediation to progress slowly or remediation could not be completed within time as planned. Due to the above conditions, the uncertain events might occur during remediation and after completion of remediation. Therefore, in this study, two uncertain events were considered for remediation planning for Kuwana site:

- 1) Decreasing of remediation efficiency in P&T for 1,4-dioxane-contaminated groundwater out of the vertical wall.
- 2) Emitting of 1,4-dioxane through the vertical walls because the remaining waste might contain 1,4-dioxane with high concentration.

Waste removal and P&T were considered as remedial methods for 1,4-dioxane-contaminated groundwater at Kuwana illegal dumping site. The objective of numerical simulation for remediation planning based on the concept of VF-UP is to treat

1,4-dioxane outside of the walls within 10 years and to prevent the spreading of 1,4-dioxane within the walls in case where a part of waste is remained. Numerical simulation will play an important role for estimating the effectiveness of waste removal and P&T plans by considering the above mentioned expected uncertain events. During remediation, the performance of remediation was reviewed if any additional measures are needed for improving the effectiveness of remediation. However, if a portion of waste is remained, future risks of 1,4-dioxane spreading through the walls into the surrounding environment might occur. The future risks might occur after completion of remediation. For that reason, numerical simulation can be used to predict the possible occurrence of future risks so that the measures for against future can be considered beforehand.

#### **4.3 Development of remedial scenarios for numerical simulation**

Firstly, the location of pumping wells should be considered based on the distribution of 1,4-dioxane in groundwater as well as the groundwater directions in each aquifer. Pumping wells outside of the walls aimed to treat 1,4-dioxane outside the walls and the pumping wells inside to walls aimed to contain 1,4-dioxane within the vertical walls. For waste removal, we divided the waste into three partitions and we are going to start the removal of the waste from the left part of the vertical walls to the right part according to the current distribution of 1,4-dioxane and vertical deep waste distribution. As shown in **Figure 4-1**, the deep waste distribution and also the elevated concentration of 1,4-dioxane is concentrated within the waste at the left part of waste layers. Therefore, the scenarios for waste removal will start to remove one-third of waste from left to right so that we have four cases of different amount of waste to be removed, no waste removal, one-third of waste is removed, two-third of waste is removed and all the waste is removed. For the case of a portion of waste is removed, we assumed that an extra walls with the similar properties of existing walls is constructed to prevent the spreading of 1,4-dioxane from the remaining waste to the new backfill soil.

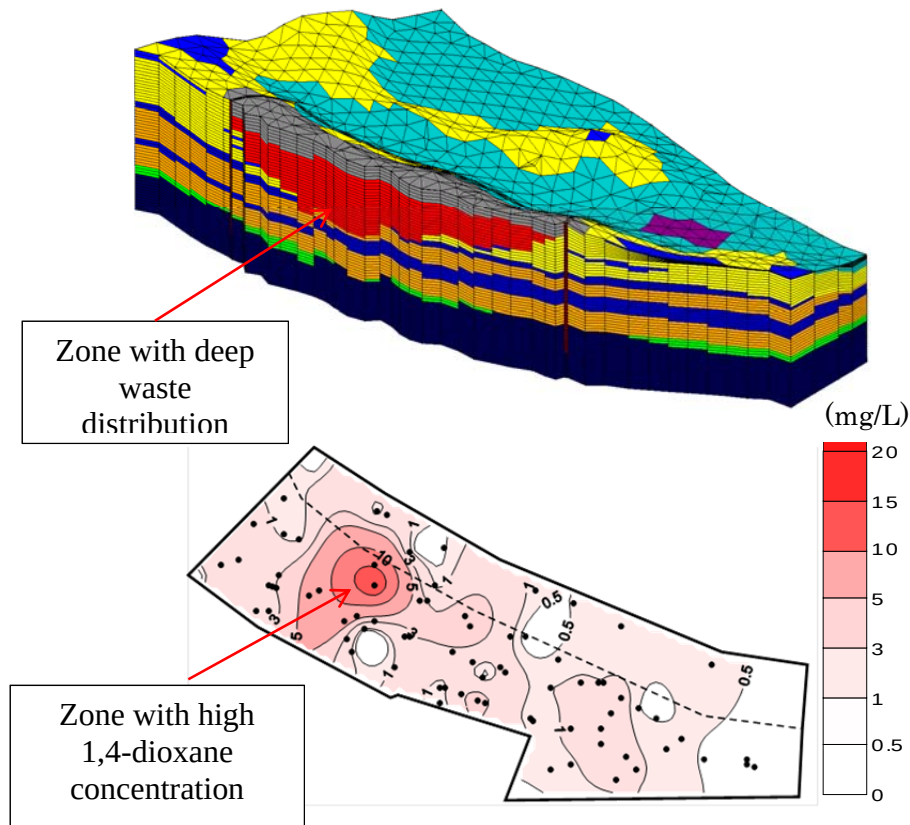


**Figure 4-1:** Waste and 1,4-dioxane concentration distribution

For pumping plan, the location of pumping wells are considered based on the distribution of 1,4-dioxane with pumping capacity of less than  $60 \text{ m}^3/\text{d}$  restricted to the capacity of water treatment facility at Kuwana site. Moreover, the remediation period must be less than 10 years limited to national subsidy. The location of this pumping plan is shown in the next section **Figure 4-3**.

Once the pumping wells inside (for containment) and outside of walls (for treatment groundwater outside the walls) are considered, numerical simulation will be conducted one by one scenario. Then compare the remaining concentration of 1,4-dioxane from the observation wells. The criteria for judgment of remediation efficiency is that the average concentration of 1,4-dioxane must less than  $0.05 \text{ mg/L}$  which is limited by the Japan Environmental Quality Standards.

For preventing future risk of 1,4-dioxane spreading throughout the walls to the surrounding groundwater, this study proposed the several scenarios for pumping plans which pump the groundwater from the remaining waste layers. The artificial monitoring points for observing the decreasing rate of 1,4-dioxane from each pumping plan are set north and

south parts of the walls.

The result of each concentration from those observation points will be plotted and compare to define the most optimal pumping rate that can minimize the spreading of 1,4-dioxane throughout the walls for the calculation period of 15 years.

#### **4.4 Modification of the 1,4-dioxane-contaminated groundwater model**

##### **4.4.1 Necessity of modification**

Our model was developed in the condition of which the groundwater observed during stationary condition without pumping. The hydraulic conductivities of geological materials of aquifers were determined precisely from the developed model using our new approach proposed. However, since the pump-and-treat remedial technology will adopted in this the remediation planning, we consider the pumping condition with pumping capacity up to 60 m<sup>3</sup>/d which is quite large amount that can influence the water levels at the model boundary. This is because the pumping locations are located closely to the boundary of study area. Moreover, groundwater in the third aquifer is quite limited because this layer has very limited groundwater inflow from the upstream. For that reason, the groundwater at the model boundary is obviously influenced by the pumping. To deal with this problem, the developed model requires to be modified through calibration using water level measured during pumping period. The calibration will be conducted by only changing the groundwater level at the boundaries of each aquifer so that the difference between observed and calculated groundwater heads is match to some extent.

##### **4.4.2 Model calibration for pumping condition**

It is never possible that one model can correspond to all the conditions on groundwater behavior (Barnett et al., 2012). For the case of Kuwana site, since the model domain is narrow, the pumping activities might influence the model boundary, e.g., the boundary might be lower than the condition without pumping. Therefore, the model calibrated using the data during the absence of pumping cannot be used to represent the groundwater behavior during pumping. For that reason, the existing model developed in the previous chapter requires to be calibrated for pumping condition. The available measured groundwater head data in the first, second, and third aquifers were obtained from 12, 12, and 14 monitoring wells respectively. These data were used for comparing within the

model result from each calibration. An error index, root mean square error RMSE(h) calculated by comparing the calculated and observed heads was used to compare the goodness-of-fit of each calibration result. Firstly, the existing model was run for the pumping condition by inputting all the above pumping data, case 0. As a result, the mean error of each aquifer ranged from  $\pm 0.5$ m so that the decreasing boundary will be done for calibration limited to 0.5 m. Normally, the boundary at the upstream (UB) is much influenced than that in the downstream (DB) of aquifer, therefore, the decreasing upstream boundary was prioritized for the calibration.

**Table 4-1:** Scenarios for model calibration and RMSE results (*adopted from Hem et al., 2013*)

| Calibration Case | Case 0 |    | Case 1 |    | Case 2 |    | Case 3       |    | Case 4 |    | Case 5 |    | Case 6 |    |
|------------------|--------|----|--------|----|--------|----|--------------|----|--------|----|--------|----|--------|----|
|                  | UB     | DB | UB     | DB | UB     | DB | UB           | DB | UB     | DB | UB     | DB | UB     | DB |
| First aquifer    | ×      | ×  | ✓      | ×  | ×      | ×  | ×            | ×  | ✓      | ×  | ✓      | ×  | ✓      | ✓  |
| Second aquifer   | ×      | ×  | ×      | ×  | ✓      | ×  | ×            | ×  | ✓      | ×  | ✓      | ×  | ✓      | ✓  |
| Third aquifer    | ×      | ×  | ×      | ×  | ×      | ×  | ✓            | ×  | ×      | ×  | ✓      | ×  | ✓      | ✓  |
| RMSE(h)          | 0.624  |    | 0.668  |    | 0.608  |    | <b>0.558</b> |    | 0.666  |    | 0.620  |    | 0.798  |    |

× Groundwater head boundary was not changed

✓ Groundwater head boundary was decreased 0.5 m from the original level

**Table 4-1** shows that case 3 gave the better minimum RMSE(h). In this case, only the upstream boundary of the third aquifer was decreased by 0.5 m while that of the first and second aquifers were kept the same as their original levels. The boundary of the third aquifer was influenced by the pumping because there was not enough water supplied from the boundary due to the low hydraulic conductivity and the aquifer thickness is thin. For the first and second aquifers, plenty of water was supplied from the boundary, especially from the upstream boundary. **Figure 4-2** shows the comparison between the calculated and observed head at monitoring wells in each aquifer. Additionally, groundwater flow

directions in each aquifer from case 3 were found to be consistent with those from the measured data during pumping. And, if there is no such calibration, groundwater flow direction of the third aquifer would be in reversion directions with these from measured data during pumping.

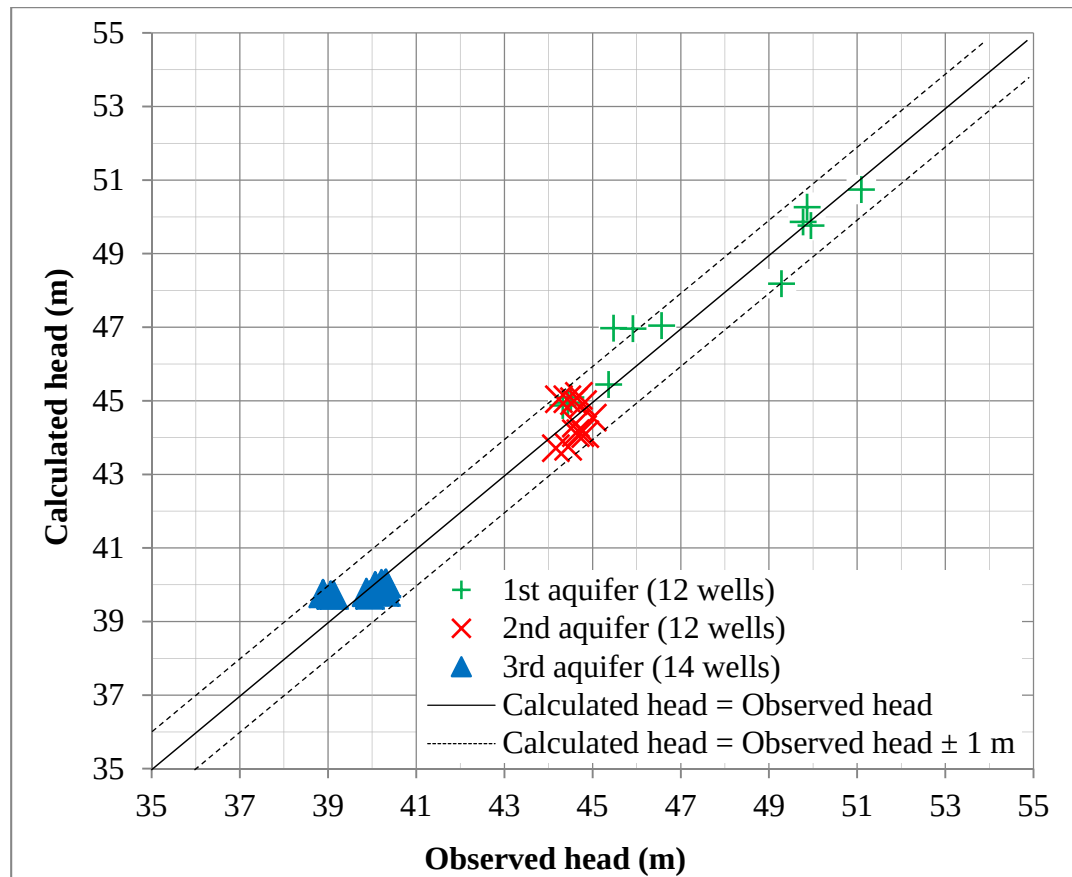


**Figure 4-2:** Comparison of calculated and observed head (*adopted from Hem et al., 2013*)

## 4.5 Scenario analysis by numerical simulation

### 4.5.1 Estimation of amount of waste to be removed and pumping plans

The required time will depend on several factors, which vary from site to site, e.g., it may take longer where the source has not been completely removed (U.S EPA, 2012). Since the national subsidy is limited, complete removal of waste from the site is impossible. This study has supposed four cases of waste removal with the same depth of about 15 m from ground surface, Plan (a) no removal of waste, Plan (b) one-third of waste is removed, Plan (c) two-third of waste is removed, and Plan (d) all of waste is removed. Based on the waste

and current 1,4-dioxane concentration distribution, the zone of waste to be removed is considered to start from eastern part of walls. For plan (c) and (d), extra wall which has similar property with the vertical slurry walls was consider (see **Figure 4-3**). In order to determine pumping well locations and rates, plan (c) is considered because it is the most considerable case based on the waste distribution and 1,4-dioxane concentration distribution. In case where a portion of waste is remained, the remaining waste is considered as the continuous source of 1,4-dioxane with relative concentration of 1 unit. The 1,4-dioxane concentration distribution calculated in the previous model was used as initial condition, however, 1,4-dioxane within the removed waste was excluded in calculation.

According to 1,4-dioxane distribution and deep waste distribution, locations of four pumping wells outside and two wells inside of walls were considered for plan (b). The wells inside the walls were used to pump groundwater from all aquifers, while the two wells outside the walls for only groundwater from the second and third aquifers. Therefore, 14 cases of simulation transport with different pumping plans were analyzed (see **Table 4-2**). The total pumping rates from each combination were limited by the capacity of treatment facilities of  $60 \text{ m}^3/\text{d}$ . As a result, the last pumping plan (P14) gives minimum average concentration outside of walls in each aquifer. Reviewing all the result from the 14 pumping plans, remediation is more effective when pumping rates of wells in waste layer increased, however, at least  $10 \text{ m}^3/\text{d}$  of water should be pumped to treat 1,4-dioxane outside of the walls.

From this result,  $50 \text{ m}^3/\text{d}$  is needed for pumping from the remaining waste layer and  $10 \text{ m}^3/\text{d}$  is needed for pumping from outside of walls for 1,4-dioxane remediation. The estimated pumping plan was used then to calculate the effectiveness of remediation of the rest three plans among the four proposed plans as shown in **Figure 4-3**.

**Table 4-2:** Scenarios of pumping rates among pumping plans

| Scenario of pumping rates | P1    | P2    | P3    | P4    | P5    | P6    | P7    | P8    | P9    | P10   | P11   | P12   | P13   | P14          |
|---------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------------|
| Inside of walls           | 15    |       |       |       |       |       |       |       |       |       |       |       |       |              |
| South of walls            | 5     | 10    | 15    | 20    | 5     | 10    | 15    | 20    | 5     | 10    | 15    | 5     | 10    | 5            |
| North of walls            | 5     | 10    | 15    | 20    | 5     | 10    | 15    | 20    | 5     | 10    | 15    | 5     | 10    | 5            |
| Total                     | 25    | 35    | 45    | 55    | 30    | 40    | 50    | 60    | 40    | 50    | 60    | 50    | 60    | 60           |
| First aquifer (19 wells)  | 0.037 | 0.036 | 0.034 | 0.033 | 0.035 | 0.032 | 0.031 | 0.030 | 0.031 | 0.030 | 0.029 | 0.029 | 0.029 | <b>0.029</b> |
| Seoond aquifer (29 wells) | 0.048 | 0.044 | 0.043 | 0.041 | 0.045 | 0.041 | 0.040 | 0.038 | 0.040 | 0.038 | 0.038 | 0.038 | 0.037 | <b>0.036</b> |
| Third aquifer (30 wells)  | 0.122 | 0.112 | 0.105 | 0.098 | 0.113 | 0.099 | 0.093 | 0.087 | 0.085 | 0.080 | 0.073 | 0.073 | 0.069 | <b>0.066</b> |
| All aquifers              | 0.069 | 0.064 | 0.061 | 0.057 | 0.064 | 0.058 | 0.055 | 0.052 | 0.052 | 0.049 | 0.047 | 0.047 | 0.045 | <b>0.044</b> |

Note: The location of observation wells were shown the **Figure 3-7 ~ 3-9** in previous chapter (adopted from Hem et al., 2013)

In plan (b), a portion of waste with highly concentrated of 1,4-dioxane is removed and it is denoted as a case of “1/2 of waste to be removed”. For the plan(c), all the portion of deep waste with high concentration is removed and it is denoted as a case of “2/3 of waste to be removed”. The volume of waste to be removed in these two plans is just an approximation of removing of deep waste with high concentration.

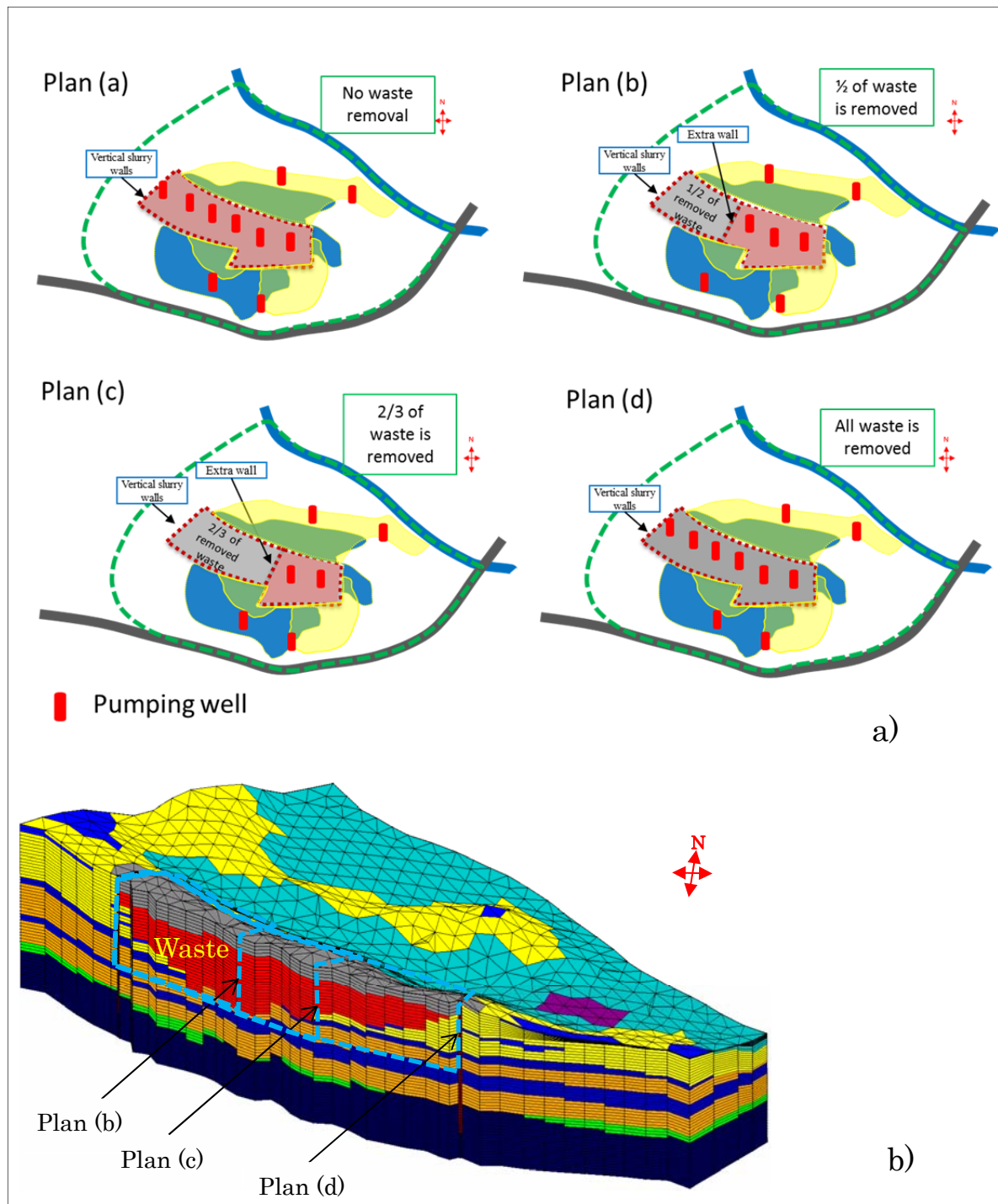


**Figure 4-3:** Plan view (a) and vertical view (b) of waste removal and pumping locations

Since the spatial distribution of waste is large, six and four pumping wells are required for plan (a) and (b) respectively. On the other hand, for plan (d), even all waste was removed, the remaining pumping capacity should focused on the treatment of 1,4-concentration of the third aquifer. Therefore, six pumping wells installed in only third aquifer. The average concentration observed at 19, 29 and 30 monitoring wells outside of the walls of the first, second, and third aquifer respectively is used to evaluate the effectiveness of each plan. As a result, the distributions of each plan are shown in the **Figure 4-4**.

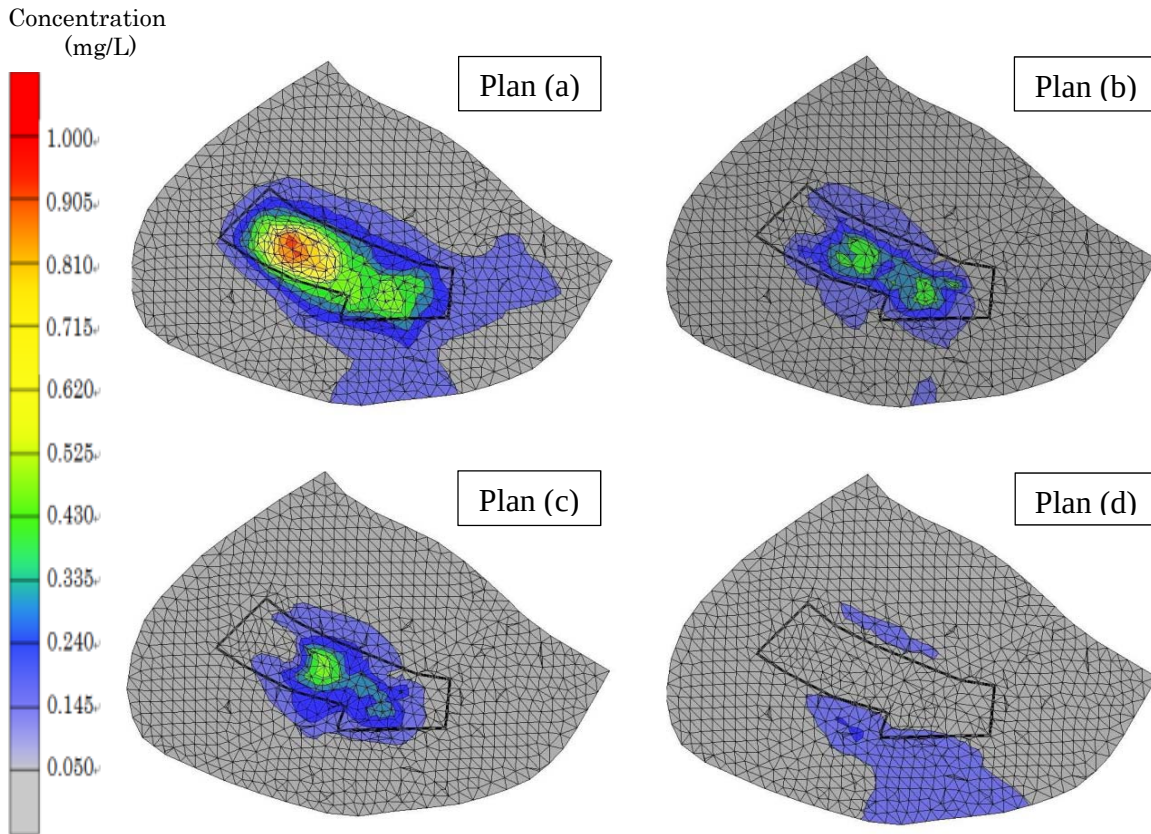


**Figure 4-4:** Result of 1,4-dioxane distribution of plan (a~d) at 10 years in third aquifer

Corresponding to the each plan, the results of remaining average concentrations measured from those observation wells are shown in **Figure 3-7 ~ 3-9** are plotted into the **Figure 4-5**. Groundwater outside of walls can be completely remedied to lower than standard limit only in plan (d). For plan (a) and (b), the groundwater outside of the walls could be remedied because the 1,4-dioxane remained high in all aquifers. In plan (c), groundwater of the first and second aquifers was completely remedied, but the third aquifer was still remaining high. Considering the cost analysis, the plan (d) is not feasible because it is very expensive to remove all the waste for treatment. Therefore, we considered to improve the

remediation effectiveness of plan (c) by considering technical aspect. Remediation effectiveness of plan (c) can be easily improved because the deep waste containing high concentration of 1,4-dioxane was already removed and the only remaining 1,4-dioxane in groundwater needs to be treated. Accordingly, we improved the effectiveness of remediation of plan (c) by checking the 1,4-dioxane concentration distribution at 5 years after starting remediation. As shown in **Figure 4-6**, three wells were found to be no longer effective so that we switched them into the zones where concentration was slowly decreased during remediation. In addition, groundwater outside of walls from only the third aquifer was pumped while a pumping well inside of walls was still kept to pump from the all aquifers.

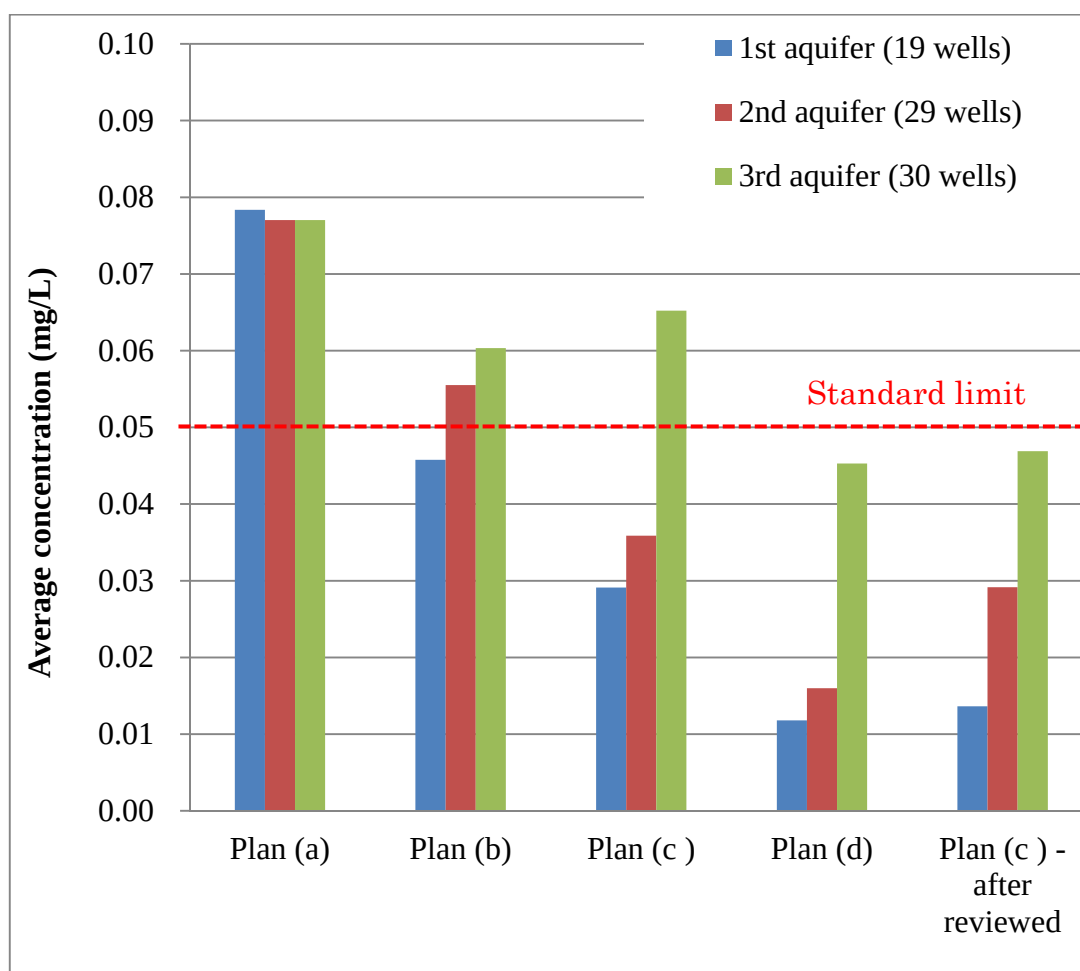


**Figure 4-5:** Figure 4-2: Average concentration in 10 years after remediation started  
(adopted from Hem et al., 2013)

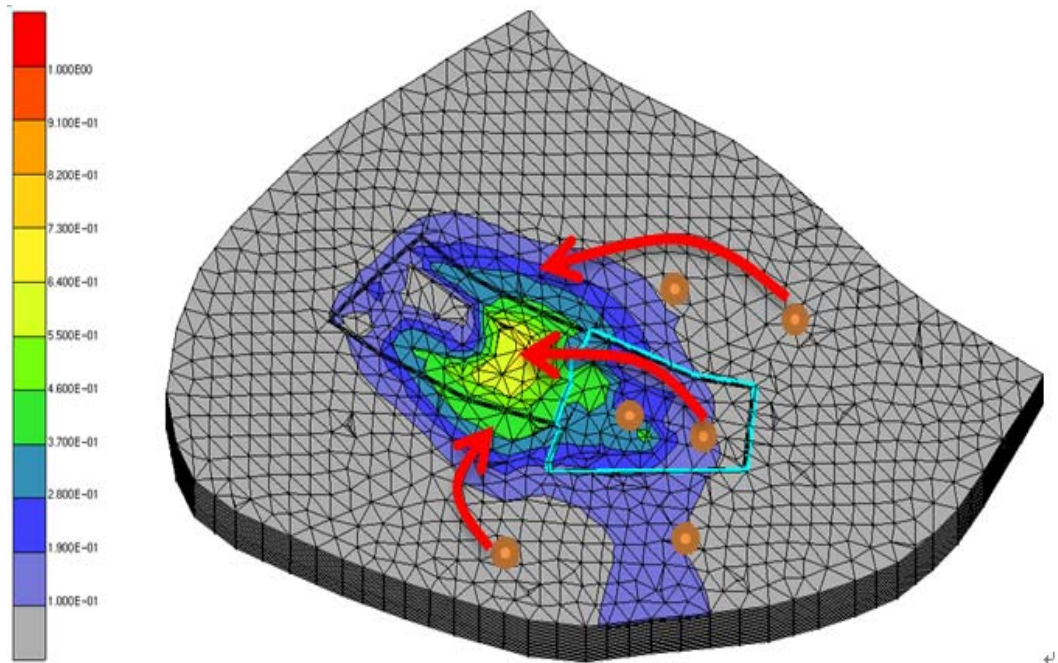


**Figure 4-6:** Changing locations of pumping wells at 5 years before

After the plan (c) was completely revised, simulation was rerun for another 10 years using the 5<sup>th</sup> year concentration of its result as initial concentration. As a result, **Figure 4-7** shows that 1,4-dioxane concentration especially in the third aquifer was decreased drastically from the first one year and gradually decreased to lower than standard limit in four to five years after improvement of plan (c). Therefore, in remediation planning, the revised plan (c) could be also proposed. As a result, the 1,4-dioxane concentration can be remedied within 10 years after changing pumping locations (see **Figure 4-8**). However, if revised plan (c) is applied for the site, when P&T will be shut down after completion of remediation, future risk of 1,4-dioxane spreading out of the walls might occur. Therefore, further study for future risk management should be further conducted.

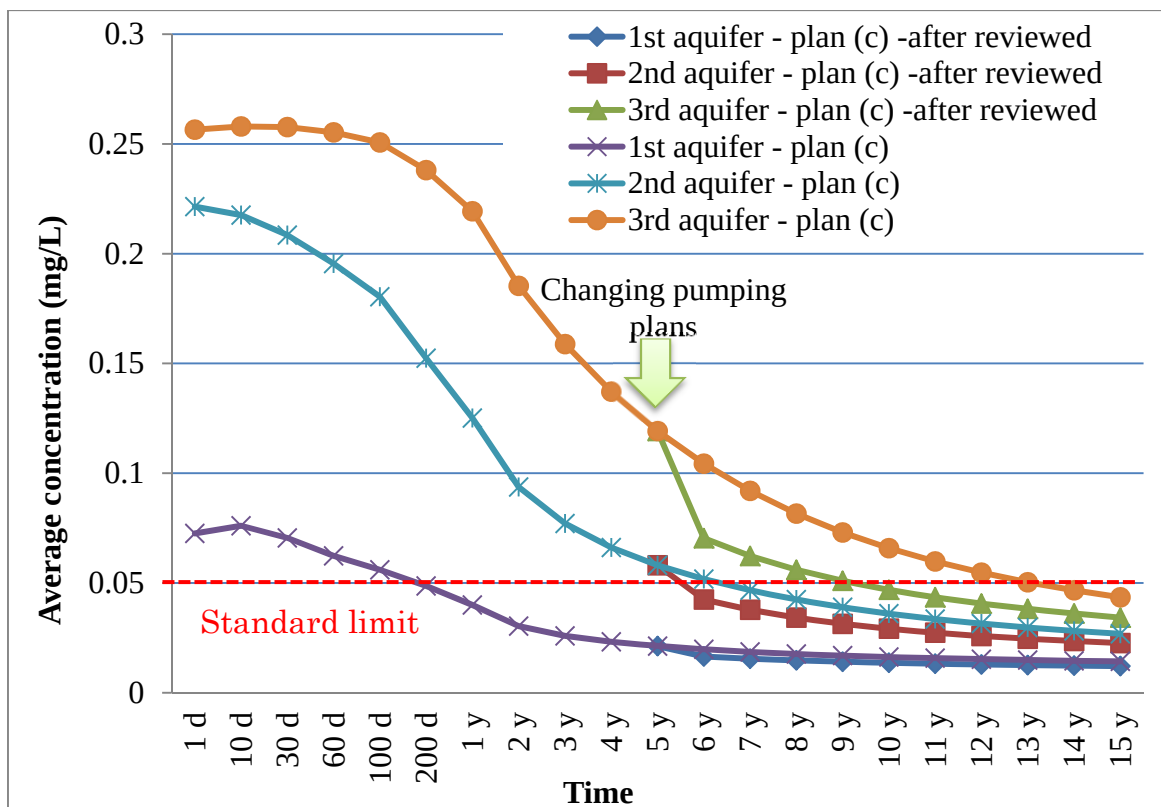


**Figure 4-7:** Decreasing average concentration in plan (c) from 1day to 15 years (*adopted from Hem et al., 2013*)

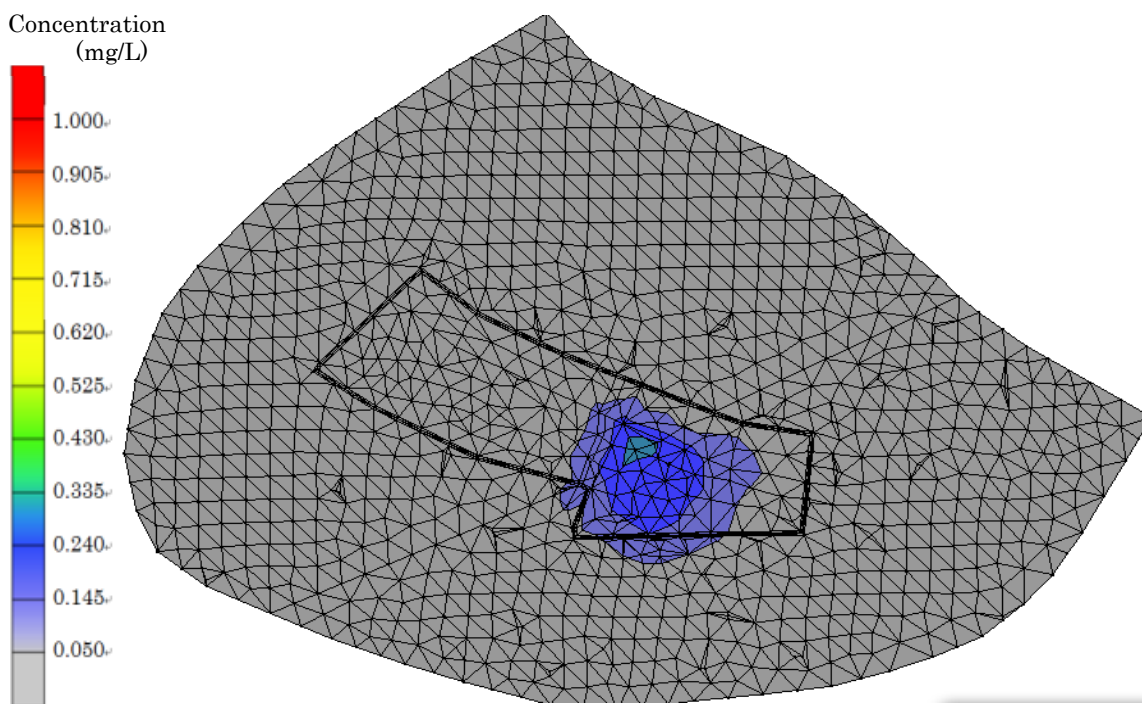


**Figure 4-8:** Result of 1,4-dioxane concentration distribution of Plan (c) at 10 years with changing locations of pumping wells

#### 4.5.2 Pumping plan for future risks management after completion of remediation

In order to predict the future risks that may occur after completion of remediation, we assumed that the remaining waste contain high 1,4-dioxane concentration. In this case, the whole remaining waste was assumed to contain 1,4-dioxane with relative concentration of 1 unit release constantly over calculation period for 15 years. As a result, if there is no pumping, 1,4-dioxane could spread out of the walls into the surrounding environment. For that reason, P&T is required. Using two pumping wells as similar as in plan (c), in which groundwater was pumped from the waste layer of all aquifers with pumping rates varied from 0 to 60 m<sup>3</sup>/d in order to observe the trench of decreasing rate of concentration until the minimum spreading concentration is achieved.

To observe the spreading concentration, 8 and 9 observation points were placed from the south and north walls respectively until the model boundary (see **Figure 4-9**). 1,4-Dioxane spreading was simulated for 15 years without pumping.

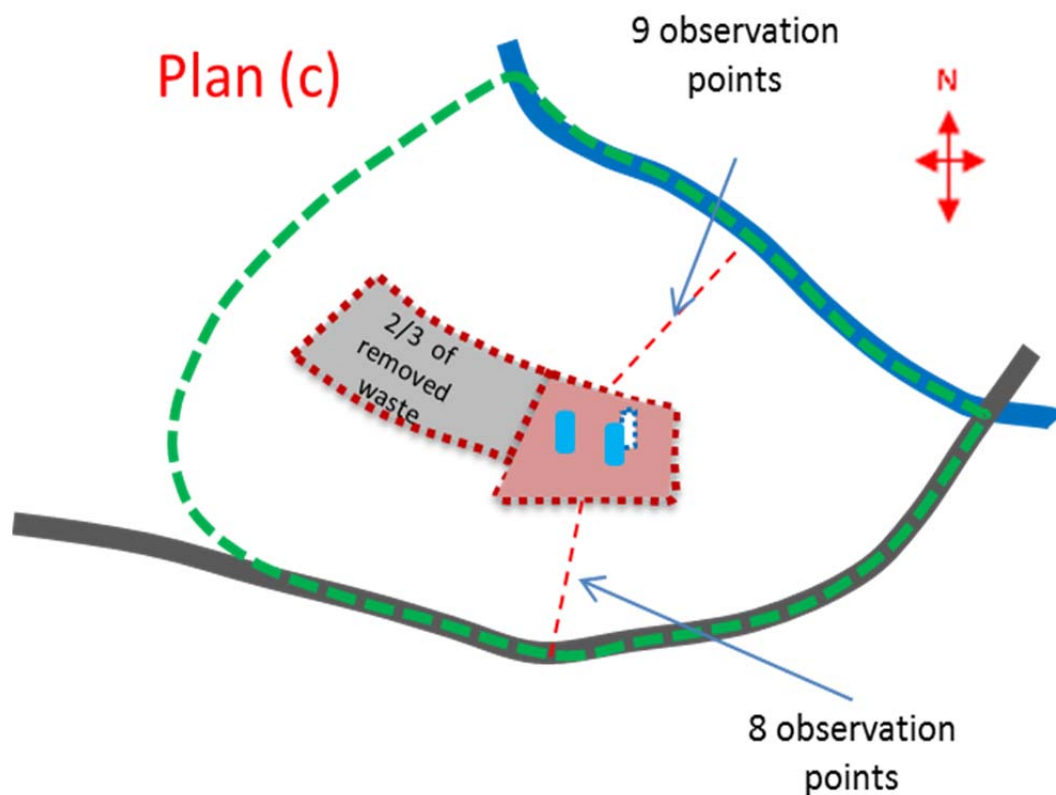


**Figure 4-9:** Location of observation points for average concentration spreading out of walls from each pumping rate for prevention of future risk

As a result, the average concentration of 1,4-dioxane from 17 observation points were plotted corresponding to the each pumping rate in **Figure 4-10**. In case of pumping rate reached 20 m<sup>3</sup>/d the average spreading concentration was minimized. If there no pumping for containment, 1,4-dioxane might spread out of the walls to the surrounding environment (see **Figure 4-11a**). Therefore, the required pumping rate for hydraulic containment to prevent future spreading of 1,4-dioxane into surrounding environment was determined as 20 m<sup>3</sup>/d. The distribution of 1,4-dioxane spreading out of the walls before and after applying the pumping plan of 20 m<sup>3</sup>/d is shown in **Figure 4-11**.

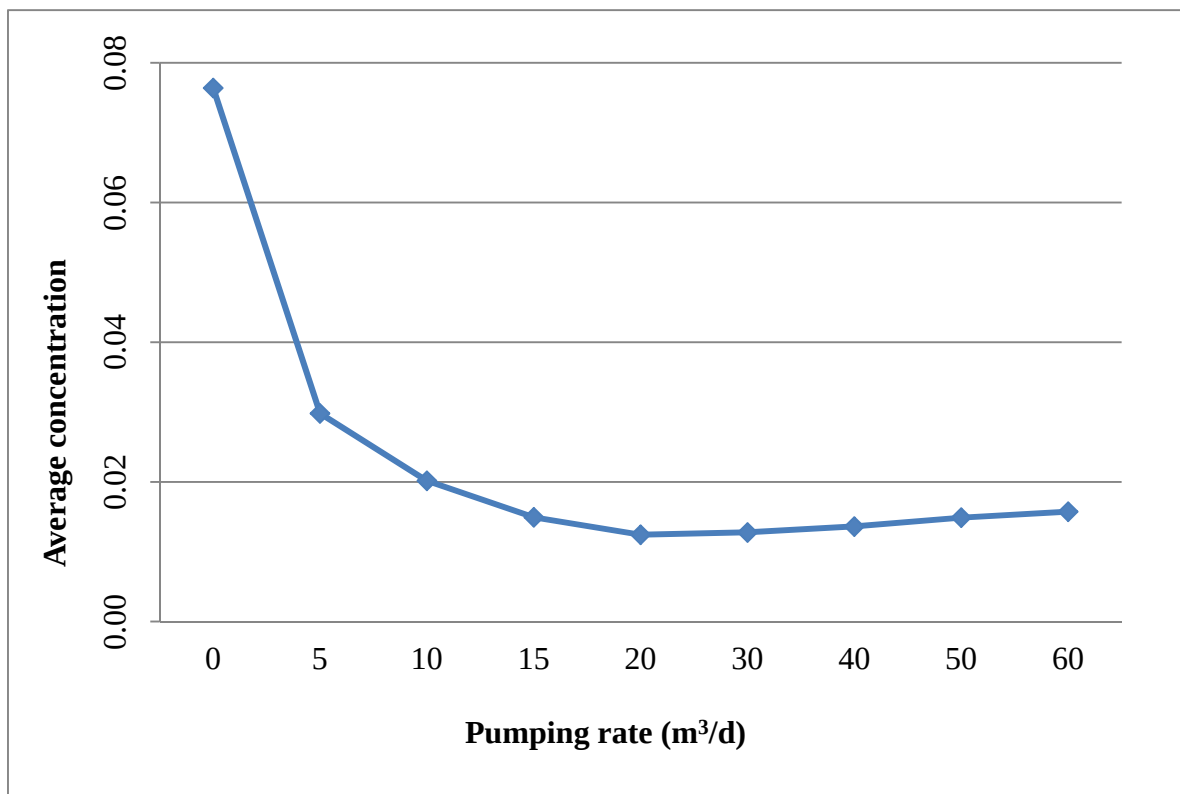


**Figure 4-10:** Average spreading 1,4-dioxane outside of walls in 15 year at each pumping rate (*adopted from Hem et al., 2013*)

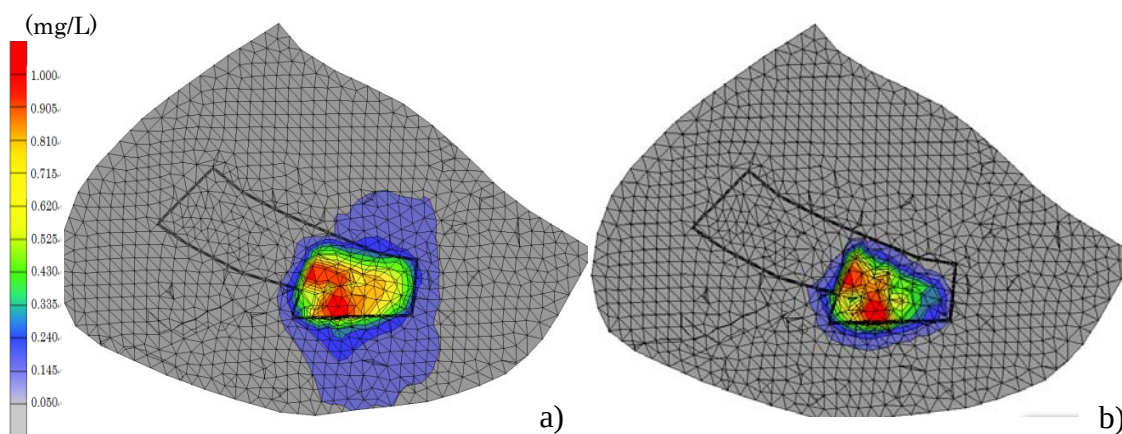


**Figure 4-11:** 1,4-Dioxane distribution in 15 year (a) without pumping and (b) with pumping of 20 m<sup>3</sup>/d

#### 4.6 Proposal of remediation planning for 1,4-dioxane-contaminated groundwater at Kuwana site

The most feasible remediation plan (c) among the other plans analyzed above is proposed for Kuwana site. Firstly, two-third of waste need to be removed and at the same time groundwater should be pumped up 50 m<sup>3</sup>/d and 10 m<sup>3</sup>/d from inside and outside of the walls respectively. Afterwards, at five years after starting the remediation, the effectiveness pumping wells must be reviewed to ensure whether or not additional new wells are needed or the pumping wells needs to be relocated. The revising of the pumping locations can be done by shutting down some pumping wells which have no more effect on the 1,4-dioxane remediation or the well at where 1,4-dioxane is already treated to some extent. After changing the location of pumping wells, the remediation plan (c) can implemented to remedy 1,4-dioxane outside of the walls and contain 1,4-dioxane from spreading out of the walls within the period of 10 years which is limited by national subsidy.

On the other hand, if the above plan (c) is implemented to the site, the future risk of 1,4-dioxane spreading out of the walls might occur after completion of remediation. This could happen because the remaining 1/3 of waste might contain high 1,4-dioxane concentration and serve as the continuous source of 1,4-dioxane. Therefore, this study proposed another addition alternative for preventing future risk of 1,4-dioxane spreading out of the walls by pumping groundwater from the remaining waste at least 20 m<sup>3</sup>/d.

#### 4.7 Summary

With regardless of national subsidy, the removal of all the waste can be considered so that 1,4-dioxane-contaminated groundwater inside and outside of the walls at Kuwana site could be completely treated by P&T within 10 years. However, since the national subsidy is limited, our study proposed a proper remediation plan to complete the remediation of 1,4-dioxane at Kuwana site in which at least two-third of waste should be removed and P&T should be carried out simultaneously. For P&T plan, two pumping wells were needed for pumping groundwater from the remaining waste with the total capacity of 50 m<sup>3</sup>/d. For remediation of 1,4-dioxane outside of walls, four pumping wells were required with the total capacity of 10 m<sup>3</sup>/d. However, to improve the effectiveness of remediation for the completion of remediation within 10 years, regarding the concept of VF-UP, pumping plan was changed at 5 years after remediation started. Furthermore, the future risks of spreading of 1,4-dioxane from the remaining waste through the walls into the environment was predicted by our numerical simulation by assuming that the remaining may contain 1,4-dioxane with high concentration. Therefore, the study suggested that groundwater within remaining waste must be pumped up at least 20 m<sup>3</sup>/d to keep containment of 1,4-dioxane within the remaining waste.

In conclusion, our numerical simulation was successfully applied to estimate the amount of waste to be removed and pumping a proper plan to achieve the objective of remediation planning for the real illegal dumping site based on the concept of Verified Follow Up.

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## **CHAPTER 5**

### **CONCLUSION**

This study proposes a new modeling approach that suitable for predicting 1,4-dioxane distribution. 1,4-Dioxane distribution in groundwater can be predicted more precisely by using our new modeling approach. Because of the adequate available field data, the effectiveness of our new approach was confirmed. Subsequently, the developed model was used for developing a remediation plan for 1,4-dioxane-contaminated groundwater at Kuwana site. The overall conclusion and contribution of in each chapter of this thesis is summarized as the following:

Chapter 1 briefly states the research background and research motivation regarding illegal dumping at the study area. Furthermore, the objective and the supporting methodology are presented. Lastly, the structure of thesis which indicates the description of each chapter and their relationship were presented.

Chapter 2 presents the site conditions and its remediation history. In addition, the review of related literature on 1,4-dioxane characteristics in groundwater and the general understanding of VF-UP method. Lastly, the problems are clarified and defined for the study. Additionally, this chapter defined clearly posed the problems for this research.

Chapter 3 successfully developed a model which is suitable for prediction of 1,4-dioxane precisely at Kuwana site which has complex hydrogeological conditions. Fortunately, at Kuwana site, a huge amount of field data is available so that it can be used to verify numerical simulation model. Therefore, a new approach is proposed for 1,4-dioxane-contaminated groundwater simulation especially for the Kuwana site. Our new approach predicts 1,4-dioxane distribution in groundwater more precisely comparing to the conventional approach. The simulated 1,4-dioxane distribution will be used as the initial condition for prediction the remedial alternatives for predicting remediation planning.

Chapter 4 uses the developed numerical simulation develops the remediation planning considering waste removal combining with P&T. The amount of waste to be removed and pumping plans for P&T are defined by comparing the effectiveness of each remedial scenario. As a result, this study proposes the most effective remediation plan in which at least two-third of waste should be removed by combining with P&T. However, the

remaining one-third of waste might contain 1,4-dioxane with high concentration and serve as the continuous source of 1,4-dioxane and spread out of the walls into the surrounding environment. In order to prevent the future risk of 1,4-dioxane spreading out of the walls from this remaining waste, scenarios by considering various pumping plans were analyzed. Our simulation suggested that groundwater within the remaining waste must be pumped up at least 20 m<sup>3</sup>/d.

In conclusion, this study contributes the establishment of a new engineering method for the application of numerical simulation to remediation planning for groundwater at the site which is contaminated by newly regulated 1,4-dioxane.