

## Study on the mechanism of soil and groundwater contamination by 1,4-Dioxane

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It is planned to implement the Environmental Quality Standard (EQS) for soil pollution of 1,4-Dioxane (DXA) in Japan soon. DXA ( $C_2H_8O_2$ ) has a density similar to that of water at room temperature and is a colorless and transparent liquid. It has a relatively low boiling point at 101°C, dissolves well in both water and oil, and belongs to the group of volatile organic compounds (VOC). Due to these characteristics DXA is a widely used solvent and was used in large amounts as stabilizer for 1,1,1-Trichloroethane (MC). It is assumed that DXA has a low affinity to adsorb on organic substances within the soil matrix, has a lower volatilization rate and is hence highly mobile. Therefore, it is likely that its soil and groundwater contamination mechanism is different compared to other VOC.

In this study, in order to understand the behavior characteristics of DXA in soil and groundwater, as well as soil and groundwater contamination mechanism, distribution experiments regarding DXA between solid-liquid phase and liquid-gas phase as well as three kinds of soil column experiments were conducted. Toyoura sand and organic soil were used for all experiments respectively. The results of these experiments about the behavior of DXA were compared to that of MC which often occurs together with DXA.

DXA was almost only present in pore water in the distribution experiments, and only a small amount adsorbed on soil particles or vaporizes into the gas phase. In case that MC was present as NAPL in water, the presence of MC phase did not affect the distribution of DXA.

Soil column experiments in order to understand the volatilization in unsaturated soil showed that DXA which vaporized from contaminated soil dissolves in soil water while spreading upwards through the soil gas, in case that DXA is present in the unsaturated soil. Therefore, the probability of DXA to spread until close to the soil surface through soil gas is low, and it was further shown the possibility that soil leachate values exceed the EQS for soil pollution in intermediate depths.

Further soil column experiments, in order to understand the infiltration properties during precipitation into the unsaturated soil, showed that DXA in the unsaturated zone will dissolve in infiltrating rain water and percolate with it; however, in case that rain water does not infiltrate into the unsaturated soil, the concentration of DXA remains high within the soil matrix. Hence it is likely that at places where rain water infiltration does not occur, such as under buildings, the concentration of DXA in the unsaturated soil remains high within the soil matrix and that DXA can be mobilized after demolition of buildings through infiltrating rain water until it reaches the aquifer where it may cause groundwater contamination.

In this research, DXA specific soil and groundwater contamination characteristics were examined by understanding the behavior characteristics of DXA in the unsaturated zone.

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Keywords: 1,4-Dioxane, soil and groundwater contamination, contamination mechanism, unsaturated soil, soil column experiment

## Hydrochemical and isotopic composition of groundwater in Douala, Cameroon: Effect of recharge and waste water on water contamination

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High water demand for domestic use in the Douala urban city with over 3 million inhabitants is met mainly by shallow groundwater through shallow wells, boreholes and springs in Pleistocene alluvium and Pliocene sand deposits. Chemical controls and recharge process of the groundwater have not been thoroughly investigated. Accordingly, this study examines the main controls on groundwater composition and spatial view of its contamination, timing of recharge and link between the recharge process and quality of the water. Conventional field measurements in January 2015 were followed by analysis of major ions and stable hydrogen and oxygen isotopes in 52 water samples. A significant range of EC values from 15 to 6890  $\mu\text{S}/\text{cm}$  in both surface water and the groundwater suggests various controls on the chemical composition of the water. Low pH values in the groundwater from 3.61 to 6.92 with an average value of 5.04 indicate an acidic aquifer. The water types were Na-Cl, Ca-Mg-SO<sub>4</sub>-Cl, Ca-Mg-HCO<sub>3</sub> and Na-HCO<sub>3</sub> with the Na-Cl water type being the most dominant in shallow open wells, boreholes and springs. Despite the nearness to the sea, only the River Wouri and few groundwater samples were strongly affected by salinization. Nitrate, which exceeded the WHO guide value of 50 mg/l in 22 % of the groundwater, poses a health problem, particularly infant methaemoglobinaemia. Mass ratios of Cl/Br in the groundwater ranged from 54 up to 3249 (with an average value of 652). The ratios scattered mostly along the mixing lines between dilute waters, septic-tank effluent and domestic sewage. The majority of samples especially the high NO<sub>3</sub><sup>-</sup> shallow open wells clustered around the septic-tank effluent end member. This cluster indicates that shallow groundwater in the urban city of Douala is highly contaminated by seepage from the numerous and widely distributed pit latrines. The stable isotopes in the groundwater indicated its meteoric origin and rapid infiltration after rainfall. Most groundwater samples plotted between precipitation in the months of April and August along the Douala meteoric line showing no isotopic signatures of the most depleted and heaviest September to October monsoon rains. The narrow plot suggests a timing of the main recharge between the April and August rains and no considerable variation in recharge conditions during the hydrological year. The  $\delta^{18}\text{O}$  values showed narrow ranges and overlaps in rivers (-3.10 to -2.13 ‰), springs (-3.09 to -2.90 ‰), shallow wells (-3.79 to -2.47 ‰), and boreholes (-3.53 to -2.88 ‰) with an even spatial distribution. These observations depict hydraulic connectivity, good water mixing and a homogeneous aquifer system mainly receiving local diffuse/direct uniform areal recharge from rainfall. The rapid and diffuse recharge through the permeable alluviums and sands favour the leaching of effluent from the pit latrines into the aquifer system; hence, the high NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> in shallow wells. Based on ionic relations, the groundwater chemistry is mainly controlled by silicate weathering, ion exchange and leaching of waste from pit toilets. Drilling of deep boreholes is highly recommended.

Keywords: groundwater chemistry, Cl/Br ratio, waste water contamination, environmental isotopes, diffuse groundwater recharge, Douala-Cameroon

## Ammonium and nitrate contamination source and dynamics in groundwater of Kathmandu Valley, Nepal

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Groundwater quality is a critical problem in the Kathmandu Valley, Nepal. The population of the city increased by 6 times in the last six decades and more than half of water demand depends on groundwater source. Microbial and nitrogen contamination causes loss of water resources, nevertheless, understanding of ammonia and nitrate source and contamination process in groundwater system. Objective of this study is to identify the source and contamination processes of the ammonium and nitrate in the groundwater.

Groundwater samples were collected from 32 shallow dug wells, 7 tube wells and 5 deep tube wells in September 2014 and August 2015. About 87% and 60% of groundwater exceeded WHO guideline values for ammonium and nitrate concentrations respectively. Nitrogen isotope values of ammonium suggest that natural soil production from lake sediments layer in the valley is main contamination sources for deep and shallow tube wells. In case of dug wells are contaminated by soil production with sewage nitrogen. And nitrogen and oxygen isotopes in nitrate suggest the sewage is main contamination sources of shallow dug wells and denitrification occurrence in shallow groundwater.

Ammonium nitrogen isotope values are shows less than 10%. On the other hand nitrate isotope values are above 10%, these differences of ammonium and nitrate-nitrogen isotope values are suggests the nitrate contamination sources are only sewage with out nitrification by ammonium originated from natural soil. The ammonium stored in groundwater body with out nitrification and denitrifications.

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Keywords: Kathmandu Valley, Groundwater, Nitrogen isotope in ammonia, Nitrogen and oxygen isotope in nitrate

## Temporal variation of contamination in perched water and groundwater at an open dumpsite in Sri Lanka

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*In Sri Lanka, solid waste management is mainly focused on waste collection and dump into open dumpsites. The leachate produced from these dumpsites often pollutes surface water and groundwater. Identification of temporal variation for leachate and groundwater quality is an important factor when installing leachate treatment systems, since water quality depends on many factors. In this study, an open dumpsite was selected from wet zone, Sri Lanka, and its perched water inside waste layer and groundwater quality were monitored for two years (March 2013 to March 2015). Perched water and groundwater samples were collected with one month interval and samples were analyzed for 14 parameters. Leachate pollution index (LPI) and piper diagrams were used to analyze the temporal variation of water quality. Overall and sub-indices of LPI were calculated to identify temporal variation of risk for groundwater contamination. Groundwater samples showed constant and low LPI values except for the initial stage of the monitoring and those constant values were similar to those for the control, a well located at out of the dumpsite. LPI indices calculated for perched water is higher than that of groundwater, but it gradually decreased with the time. There is no considerable different observed in perched water and groundwater with respect to the presence of heavy metals. Reduction of LPI exhibited the high dissolution of the pollutants over the time. No correlation was observed between LPI and amount of rainfall received over the time.*

Keywords: Open solids waste dumps, perched water, groundwater, contamination, leachate pollution index (LPI)

## V&V approach for the groundwater analysis

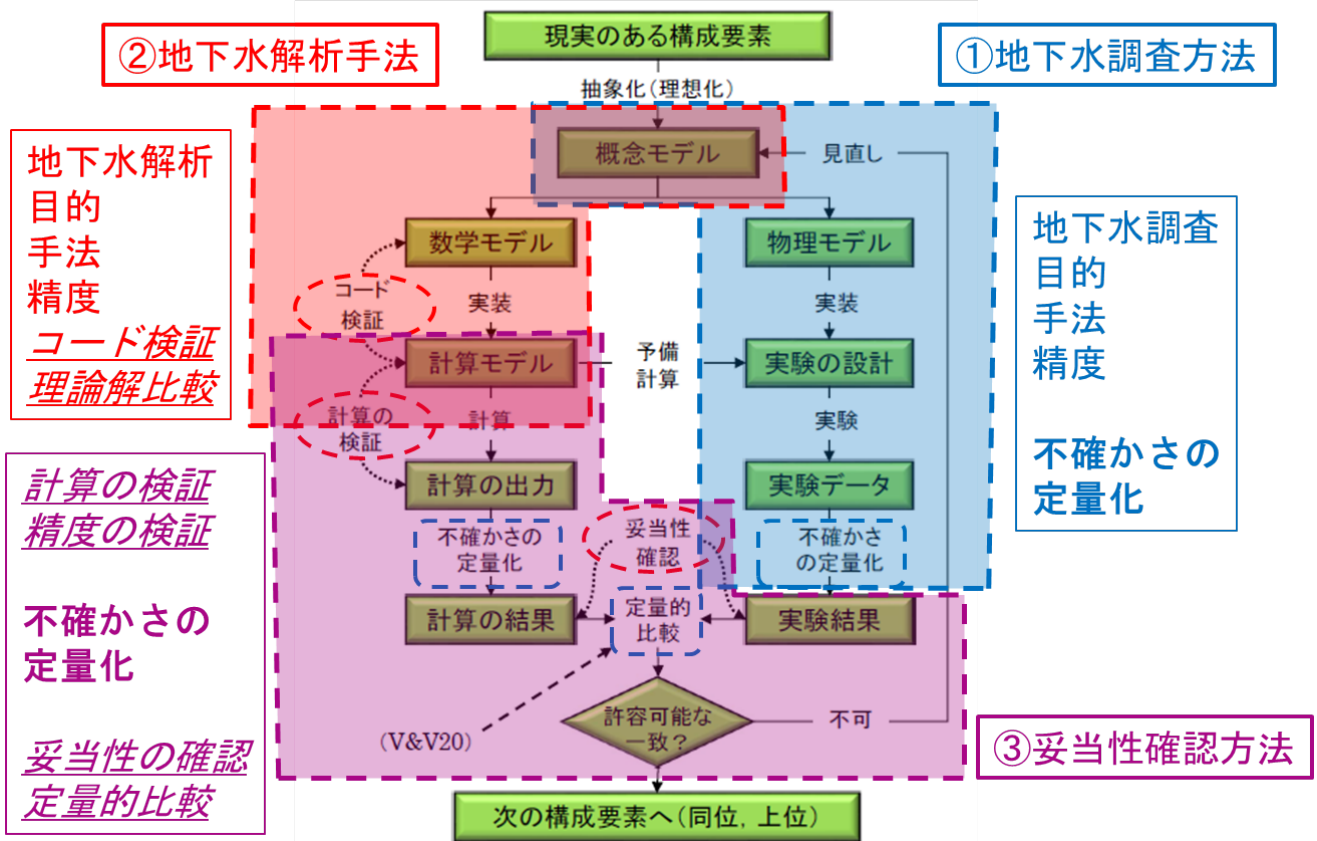
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In recent years, V&V (Verification and Validation) which supports the quality guarantee of numerical simulation is remarkably examined in a wide range of simulation fields, in addition to the quality guarantee in the ISO9001 series. There was not so much attention paid to V&V in view of groundwater flow analysis in the past. In the field of safety evaluation which is necessary for radioactive waste disposal, however, JSCE (Japan Society of Civil Engineers) has showed a series of procedures from creating numerical models to V&V for the purpose of groundwater flow analysis. In the related researches, there is a challenge which is using one of chemical characteristics for the prediction V&V of the age of groundwater, as well as traditional data like water level, pressure, and flow rate. There are also several researches about the evaluation method of heterogeneity and uncertainty. On the other hand, the basic law on the water cycle was enacted in 2014. It is estimated in the future that the necessity of groundwater flow analyses with V&V would rise up for the design and safety evaluation of underground facilities. In JAGH (Japanese Association of Groundwater Hydrology), a research group named as "the problem finding of V&V approach for groundwater analysis" started from 2015 in the investigation and research committee. The group is discussing which problems should be tackled for meeting social needs; collecting actual examples and experimental data for V&V of groundwater analysis code. In 2016, the group is planning to publish a book collecting code-verification samples and to give seminars concerning V&V.

Keywords: Groundwater flow analysis, Verification, Validation

ASME V&V10のフロー図と課題抽出にあたっての区分け



## Precise measurement of river cross-section using photogrammetry for discharge observation

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River discharge data can be calculated by multiplying river cross-section area and flow rate. As gaining precise river cross-section area is difficult, river discharge data often include some errors. Photogrammetry is a method to gain a precise shape of objects but it was hard for non-expert to master. Thank to the improved technology of digital photo, computer and computer software, we non-expert nowadays have chance to apply this technology to multiple fields. In this study, I used photogrammetry technology to acquire river cross-section data at Kosakuragawa River, foot of Mt. Tsukuba. The data matched with the data I gained with tape measure. By using photogrammetry, it is expected that we could gain much precise river cross-section data as we could gain continuous data of riverbed. When the light condition and water clarity is fine, we could apply this method and improve accuracy of discharge data.

Keywords: Photogrammetry, River cross-section, Discharge

## Discussion on application of observation wells for groundwater levels and land subsidence

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There have been occurred depletions of hydraulic potential in aquifers and land subsidence due to groundwater abstraction in many urban areas in Japan. Municipalities and the National Government have restricted the abstraction by laws and ordinances and have developed the network of observation wells for hydraulic potentials and land subsidence.

Recent years, in many urban areas, the monitoring of hydraulic potentials and land subsidence has been reduced because the hydraulic potentials and land subsidence have recovered and calmed by regulations. However, groundwater demand has increased again, especially after 2011 Great East Japan earthquake. In addition, the Basic Act on the Water Cycle decides that the municipalities have to monitor groundwater environment for conservation of water cycle. Therefore, the municipalities are forced to maintain the monitoring of observation wells and to manage appropriate groundwater development.

On the other hand, from the viewpoint of scientists and engineers who engage earth science, the observation wells are the "window" that can provide useful data of subsurface environment and are the important "tools" for appropriate understanding of unsteady groundwater environment system due to urbanization. In this presentation, application and issues of the observation wells will be discussed.

Keywords: observation wells for groundwater levels and land subsidence, application, groundwater issues, unsteady system, sustainable management



## Evaluation of subsurface warming in the Tokyo metropolitan area, Japan

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Three-dimensional subsurface temperature distribution and its long-term change were examined by repeated observations of temperature-depth profiles at monitoring wells from 2000 to 2015 and groundwater temperature monitoring from 2007 or 2012, to evaluate effects of regional groundwater flow and environmental changes due to urbanization on subsurface thermal environment in the Tokyo metropolitan area, Japan.

Subsurface warming has been found at shallow depths in the whole study area by our previous study (Miyakoshi et al., 2010). Especially, subsurface temperature beneath the city center was particularly high not only at shallow part but also deep part. In contrast, relatively low temperatures were found beneath the suburban area. Comparison result between past subsurface temperature data (2003 to 2005) and present subsurface temperature data (2013 to 2015) shows that subsurface warming is found at the shallow part in the last 9 to 10 years. Subsurface temperature increase in the city center is larger than the suburban area, and the temperature difference between both areas shows an increasing tendency. Additionally, subsurface warming in the present data was recognized deeper than the past data. This result suggests that distribution of subsurface warming is expanding toward the deeper part.

Moreover, results of subsurface temperature monitoring showed difference of subsurface warming tendency by area and depths. The difference suggests that subsurface warming was affected by not only surface warming but also many factors such as geological condition, groundwater flow and waste heat from subsurface structure. Results of this study suggest that mechanism of subsurface warming is able to be evaluated by combined analysis of geological condition, groundwater flow and subsurface temperature changes. This study was supported by JSPS KAKENHI Grant Number 25871190. This study was conducted as a part of Civil Engineering Center, T.M.G.- Akita Univ. - AIST Joint Research and Saitama Pref. -Akita Univ.- AIST Joint Research.

Keywords: subsurface temperature, groundwater flow, subsurface warming, groundwater environment, urbanization, Tokyo metropolitan area

On geochemical and isotopic characteristics of shallow urban groundwater in Shinagawa district, central Tokyo, Japan

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Water chemistry of shallow groundwater in the highly-populated Shinagawa district, central Tokyo, Japan, is discussed with special reference to its nitrate, sulfate and chloride concentrations. As a result of the water chemistry analysis, shallow groundwater proved to be characterized by a high nitrate, sulfate, and chloride concentrations. The enriched  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of nitrate and  $\delta^{34}\text{S}$  values of sulfate suggest leaking sewers is a potential source of nitrate and sulfate ions in shallow groundwater.

Keywords: Tokyo, megacity, shallow groundwater, groundwater pollution, isotope, hydrochemical process

## Studies on the groundwater environment in Choshi area (1)

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Groundwater contamination of nitrate nitrogen becomes a serious problem in the area which is active in agriculture and stockbreeding. Choshi area also suffers from the contamination problem because that area is also one of active areas of agriculture in Chiba prefecture. In order to grasp the situation of the nitrate nitrogen pollution on groundwater in Choshi area, the current research investigated the water qualities from 5 spots of the water wells and from 4 spots of spring in Choshi area from June 2014 to December 2015. Nitrate nitrogen concentration of 3 spots of spring water, which are extracted from the underside of a farmland, exceeded  $10 \text{ mg/L}^{-1}$  of the groundwater quality standard value (the maximum was  $30 \text{ mg/L}^{-1}$ ). On the other hand, in the well water from a spot near the TONE River, which is located far from a farmland, the nitrate nitrogen concentration was less than  $4 \text{ mg/L}^{-1}$ . This result suggested a possibility that some spring water was affected by nitrate nitrogen in leaching water from a farmland.

Keywords: ground water, nitrate nitrogen, water examination

## Modification of ammonium diffusion method for $\delta^{15}\text{N}$ analysis and application for contaminated groundwater in Nepal Kathmandu Valley

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The objectives of this study are to improve analysis methods of ammonia isotope and to apply for pollution source analysis of the environmental water sample. The target analysis is the groundwater of Nepal Kathmandu Valley. In this area, the dependence rate on groundwater is more than half of the total water demand, and there are many spots of exceed the ammonia standard value.

Ammonia isotope analysis of this study is a modification of the ammonia diffusion method of Holmes et al (1998). We succeeded in shortening the ammonium diffusion time from 14 days (original method) to 5 days. Ammonium concentrations were detected in the range of 2.0~17.1mg/L (n=9) and 1.8~15.3mg/L (n=6) from shallow dug well and shallow tube well, respectively.  $\delta^{15}\text{N-NH}_4$  was 2.1~23.3‰ (n=9) and 1.2~3.8‰ (n=6) from shallow dug well and shallow tube well, respectively. According to the previous studies, wastewater (human origin) has  $\delta^{15}\text{N-NH}_4=24\sim 40\%$  (Ambio, 2004) and lake sediment (natural origin) has  $\delta^{15}\text{N-NH}_4=-3.4\sim +2.1\%$  (Vreca&Muri, 2006). These results suggest that the main source of ammonium contamination is soil and mixture of soil and wastewater for shallow tube wells and dug wells, respectively.

Keywords: Nitrogen isotope in ammonia, Groundwater, Kathmandu Valley

## Evaluation of Different Groundwater Sampling Methods in the Investigation of Chlorinated Hydrocarbons in heterogeneous aquifers

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Geological heterogeneity affects the diffusion of chlorinated hydrocarbons between high and low permeability strata in groundwater plumes. Because of the concentration gradient, solutes in the low permeability zone will back-diffuse into the high permeability zone, leading to the phenomena of "tailing" and "rebound". However, these small but significant effects are often ignored, and the resulting mistaken mass transfer coefficient can cause erroneous assessments of the concentration distribution in low permeability zones. There are two parts to this study. One part is the correlation analysis of the concentrations obtained by the common sampling methods (micro-purge sampling and bailer sampling) for the chlorinated alkenes and chlorinated alkanes in 35 monitoring wells. The other part includes case studies to evaluate the use of three standard sampling methods (micro-purge sampling, bailer sampling and passive-diffusion bag sampling) for the analysis and comparison of heterogeneous aquifers.

Based on the results of three statistical hypothesis tests (t test, Z test and F test), there were no significant differences between bailer sampling and micro-purge sampling. The results thus show that both methods have a high correlation with regard to chlorinated alkenes and chlorinated alkanes ( $r=0.79\sim0.99$ ), with the differences between them likely to be due to variations in the location depth and degree of disturbance. The major flow mechanism during bailer sampling and micro-purge sampling is influenced by advection, and the water that is obtained with both methods is mainly from the high permeability zones. Therefore, the correlations between these two sampling methods with regard to the measured concentrations were high. If the geological heterogeneity is more complex, or the high and low permeability zones show complicated inter-bedding, then bailer sampling and micro-purge sampling will erroneously estimate the actual contamination conditions, especially for the pollutants that have diffused into the low permeability zone. Due to the flow mechanism of diffusion, passive-diffusion bag sampling can better reflect the distribution of contaminants in both high and low permeability zones. To ensure the validity of the data, the sampling bags should be in place for at least 14 days, and the necessary precautions taken to prevent interference during this period of time.

Based on hydrogeology and geological heterogeneity, this study suggests that it is necessary to adopt comprehensive strategies, such as a combination of simple well investigations, monitoring well investigations (to examine sandy aquifers, gravelly aquifers, distinct inter-bedding, and so on), deep monitoring well investigations (with the water level or sampling depth exceeding 40 meters) and investigation evaluations (or remediation evaluations). With the use of appropriate sampling methods and investigation techniques, it is possible to reduce the probability of erroneous estimations, and determine the distribution of actual contamination in both high and low permeability zones, as well as the possible pollutant sources.

Keywords: chlorinated hydrocarbons, Geological heterogeneity, diffusion, sampling methods, hypothesis testing