Adsorption behavior of organoarsenic compounds in soils

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The arsenic pollution is a world problem. Natural originated inorganic arsenic compounds are predominant cause of the water-related disease. In addition, anthropogenic originated organoarsenic compounds such as phenylarsonic acid (PAA) and diphenylarsinic acid (DPAA) are also pollution source. For example, DPAA polluted well water caused serious health problems in Kamisu, Japan. These phenyl arsenic compounds are considered as a decomposition product of chemical warfare agents produced during World Wars I and II, and even now such compounds still remain in the ground. Recently, adsorption and mobility of these aromatic arsenic compounds in agricultural soils have been investigated. However, their adsorption mechanisms on soil are still unknown. In general, the adsorption property of chemical compounds influences its migration process in natural environments such as soil-water system. Thus, it is important to understand the adsorption mechanism of the arsenic compounds to predict future fate of them in environment. Recently, we reported adsorption structures of PAA and DPAA on ferrihydrite obtained by X-ray absorption fine structure (XAFS) analysis and quantum chemical calculations [1]. In this study, we conducted As K-edge XAFS measurements for organoarsenic compounds adsorbed on soil, as well as adsorption experiments, to understand their adsorption behavior in soils. The results of EXAFS analysis suggest that all arsenic compounds in this study adsorbed on Fe or Al (oxyhydr)oxide in the soil mainly regardless of the organic functional groups. This fact indicates that the Fe/Al-(oxyhydr)oxides can control the mobility of organorarsenic compounds in the ground.

References:


Keywords: adsorption behavior, organoarsenic, XAFS, soil
Impact of Injecting Heated Water into Aquifer on Groundwater Quality

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In recent years, usage of geothermal heat energy, one of the renewable energy sources, draws attention in Japan. The geothermal heat can be used through heat pumps for building heating and cooling. A heat pump can extract heat energy either from the ground using underground heat exchangers or from pumped groundwater. While the former is referred to as a closed-type ground source heat pump (GSHP), the latter is known as an open-type ground source heat pump. The open-type GSHP systems also require either recharging heated or cooled groundwater into aquifers or discharging it into surface water systems. There are various advantages of using the open-type GSHP systems; energy efficiency is much higher than the closed-type GSHP systems. On the other hand, altering groundwater temperature may cause environmental impact such as elution of toxic elements from the aquifer or changes in microbial activities in the aquifer. However, such environmental impact caused by the open-type GSHP systems has been rarely studied and is generally poorly understood. To maintain its sustainable usage, more data on environmental impacts need to be collected from field experiments. The main objective of this study is, therefore, to investigate the impact of injecting heated water into the aquifer on groundwater temperature and its quality.

A field experiment was conducted from October 7 to December 2 in Fuchu campus of Tokyo University of Agriculture and Technology in 2014. Groundwater pumped from a pumping well was heated to 30 oC before it was injected to a confined aquifer at GL-50m from an injection well installed 10-m away from the pumping well at a rate of 20 L/min. The temperature of the ground below GL-10m is almost constant at 17 oC year-round at the experimental site. The heating load was therefore equivalent to 18.1 kW. Changes in temperature and element concentrations in groundwater were observed at two 50-m long observation wells installed at 1.4-m (O-1) and 5.3-m (O-5) away from the injection well. Temperature sensors were installed every 5 m at O-1 and O-5. Groundwater samples were collected from two aquifers; one at GL-40m (shallow) and another one at GL-50m (deep), from O-1 and O-5, every two or three days during the experiment. EC, pH, DO, ORP, and turbidity were measured immediately after samples were collected, while concentrations of sixteen trace elements and major ions were measured later using ICP-MS and IC, respectively.

Temperatures of the deep aquifer at O-1 and O-5 rose from 17 oC to 23 oC and 22 oC, respectively, while those of other depths remained almost unchanged or increased slightly, indicating that heated water was indeed directly injected to the deep aquifer. While pH, EC, and DO did not change, ORP showed a gradual decreasing trend in both aquifers. Turbidity was largely affected by injecting heated water as it increased to 60 NTU at the deep aquifer at O-1. That of the other aquifers stayed almost unchanged before, during, and after injecting heated water. As concentrations of elements might be affected not only by changes in temperature, but also by physical injection, it may be required to separate the impact of different processes. One of the approaches to do that is to take concentration ratios with an inert tracer. This is known as an internal standard method. As there was no artificial tracer added in this experiment, zinc, one of the more stable elements, was used as a tracer. Ratios to Zn concentration increased significantly during heating for some elements, such as Al.

From the field experiment, it was clearly shown that the turbidity of groundwater was strongly affected. As for trace elements and major ions, it was shown that injecting heated water might increase concentrations or concentration ratios for some elements, more careful data analysis needs to be done to clarify the mechanism of such effects.
Effects of particle size and thermal properties on thermal dispersion characteristics in porous media

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Understanding heat transport process in saturated porous media is essential, in regard to a widespread use of ground source heat pump systems and design of geologic repositories for high-level nuclear wastes. However, knowledge of thermal dispersion occurred due to advective heat flow is limited in the mechanisms of heat transport process. In this study, one-dimensional heat and solute transport experiments were conducted using glass beads with different size fractions, and stainless steel sphere with high thermal conductivity. Effects of particle size, thermal properties, and flow velocities on thermal dispersion characteristics and the difference between thermal and solute dispersion characteristics were discussed based on the column experiments. Glass beads with smaller size fraction showed smaller increase in thermal dispersion coefficient at higher flow velocity as compared to the one with larger size fraction. Flow velocity dependency on thermal dispersion coefficient was insignificant for stainless steel sphere, indicating thermal conduction dependent heat transport is dominant in the column due to higher thermal conductivity of the stainless steel.

Keywords: thermal dispersion, solute dispersion, thermal properties
Effects of temperature environment in dissolution and chemical forms of heavy metals of sediment in Arakawa lowland

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Global warming, heat island phenomenon in urban areas, and increased use of geothermal energy would affect the subsurface thermal, chemical, and biological environment. Change in subsurface temperature might affect dissolution and transport of chemical materials and the subsurface microbial activities. However, effects of temperature change on the subsurface environment including dissolution and chemical forms of heavy metals have not been fully clarified. In this study, effects of temperature on dissolution and chemical forms of heavy metals in sediment of Arakawa Lowland, Kanto district, Japan have been investigated by laboratory experiments.

Laboratory experiments to evaluate the relation between temperature and dissolution characteristics were conducted under three different temperature conditions (15\(^\circ\)C, 25\(^\circ\)C and 40\(^\circ\)C). Five chemical forms of heavy metals in residues from the dissolution experiment were also fractioned (Water soluble, Exchangeable, Bound to carbonates, Bound to iron and manganese oxides and Bound to organic matter) by the sequential extraction method. These experiments were conducted on sediment samples obtained from boring cores at around 17m, 31m, 39m and 44m depth (denoted as 17m-sample, 31m-sample, 39m-sample and 44m-sample, respectively).

Results showed that temperature conditions affected dissolution characteristics and chemical forms of heavy metals. Especially, boron in 17m-sample (marine sediment) and arsenic in 31m-sample (non-marine sediment) dissolved more at higher temperature and linear relations between temperature and dissolved concentration of these components were observed. Additionally, temperature condition also affected their chemical forms. Under 40\(^\circ\)C and 25\(^\circ\)C conditions, Bound to iron and manganese oxides and Exchangeable forms of boron in 17m-sample both decreased and Water-soluble boron increased compared to the 15\(^\circ\)C condition. Also under 40\(^\circ\)C and 25\(^\circ\)C conditions, Bound to iron and manganese oxides form of arsenic in 31m-sample decreased and Water-soluble and Exchangeable arsenic both increased compared to the 15\(^\circ\)C. These results imply that hardly-soluble forms of boron and arsenic might change to readily-soluble forms at higher temperature.

Keywords: subsurface temperature, dissolution characteristics, chemical forms, alluvial sediment
LOCALLY AVAILABLE SOILS AS LINER MATERIALS FOR DEVELOPING COUNTRIES: A COMPARISON WITH GEOSYNTHETIC CLAY LINER

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Solid waste management has become a major issue for the urban areas of developing countries. Due to rapid increase in urbanization coupled with the rise in community living standards the generation of municipal solid waste is highly accelerated in past few decades. At present most of the landfill practice in developing countries is open dumping without proper measures to mitigate the migration of contaminants to surrounding environment. It is the need of hour to construct engineering landfills with impermeable liners to avoid groundwater and surface water pollution. Most of the engineered landfills in developed countries are equipped with commercially available liner material known as Geosynthetic Clay Liner (GCL). GCLs are popular due to their extremely low hydraulic conductivity which is primarily due to the presence of a thin layer of bentonite. However, due to economic constraints, developing countries cannot afford engineered landfills equipped with such commercially available liners. In contrast, Locally Available Clayey Soils (LACs) are less expensive and can be used as bottom liners under the provision that they meet the recommended criteria for base liner. A detailed comparison between GCL and LAC with respect to both geotechnical and hydraulic performance can therefore provide the basis for using appropriate LACs as landfill liner material.

This study employed locally available soils obtained from Moragahakanda area of Sri Lanka (hereafter referred to as Soil M). Swell index, plasticity index and Hydraulic conductivity tests were carried out on Soil M and its mixtures with bentonite component of GCL. Soil-bentonite mixtures were prepared by mixing Soil M with 5% and 10% bentonite. Experimental Investigations were carried out using de-aerated water and 1M CaCl2 as hydrating liquids. The hydraulic conductivity tests were carried out on non-consolidated and pre-consolidated samples to investigate the effect of consolidation on hydraulic conductivity of candidate soils. Data on pure bentonite was used to examine the performance of Soil M and mixture soils compared to GCL. Results showed that the nature of hydrating liquid has an insignificant effect on swell Index and plasticity index of the candidate soils when compared to pure bentonite. Hydraulic conductivity was found to decrease with an increase in bentonite content when permeated with de-aerated water. However, the effect was found insignificant for CaCl2 permeation. An increase in consolidation pressure caused a decrease in hydraulic conductivity irrespective of permeating liquid and bentonite content. At very high consolidation pressure, all the candidate soils were found to exhibit much lower values of hydraulic conductivities than the maximum recommended value for base liners.

Keywords: Locally Available Soils, Geosynthetic Clay Liners, Soil-Bentonite Mixtures, Plasticity Index, Swell Index, Hydraulic Conductivity
Significant Improvement to Imaging Hydraulic Heterogeneity in Heterogeneous Geologic Media via Hydraulic Tomography

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Hydraulic parameters such as hydraulic conductivity (K) and specific storage (Ss) of geologic media are heterogeneous at multiple scales. A large number of techniques have been developed to deal with this heterogeneity, but little information is available on its performance in predicting groundwater flow and solute transport. In this presentation, I review the various heterogeneity mapping methods and introduce the concept of Hydraulic Tomography (HT). HT is a new approach to map the heterogeneity of the subsurface. It is analogous to geophysical tomography but different in a sense that the method relies on multiple pumping tests as sources of signals. These signals or drawdowns are detected in neighboring monitoring intervals. With a suitable inverse model, one can then estimate the three-dimensional spatial variability in K and Ss. One significant advantage of the approach is that it provides direct information on connectivity in hydraulic parameters, which is very important in contaminant transport problems. Research over the last decade has shown that this is a very robust technique and the estimated parameters are more reliable in predicting independently conducted pumping tests and tracer tests. I will introduce various synthetic, laboratory and field experimental results, compare HT against other heterogeneity mapping methods, and discuss future research directions.

Keywords: heterogeneity, contaminant transport, fractured rocks, stochastic hydrology, subsurface characterization, connectivity
Interactive effects of EC and pH on nitrous oxide emissions and denitrification

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Long-term fertilizer applications and saline water irrigation lead to the accumulation of salts and changes in soil pH. These changes may affect N2O emissions from soil. Interactive effects of EC and pH on N2O emissions were studied by using paddy soil in Ushimado, Okayama Prefecture, Japan. Closed incubation experiments were conducted in 100-mL glass bottles for 72 h at 25°C. Each bottle contained 5 g of air-dried soil and 25 mL of solution, which included KNO3 (10 mg NO3-N L−1) and NaCl (0 M, 0.005 M, 0.01 M, 0.05 M, 0.1 M, 0.2 M) for adjusting different electric conductivity (EC) levels under different pH: acid (HCl 0.005 M), neutral (no adjustment), and alkaline (NaHCO3 0.005 M). Nitrous oxide concentration in the headspace of the bottle was measured 3 h, 24 h, 48 h, and 72 h after incubation with gas chromatograph (GC-8A, Shimadzu, Kyoto, Japan). After gas collection, the solution was taken out for measuring pH, EC and concentrations of NH4+ and NO3−. Results indicated that pH was a significant factor controlling N2O emissions (P < 0.05). Nitrous oxide emissions were greater in higher EC treatments under the acid treatment. Nitrous oxide emissions peaked at 24 h of incubation and fell sharply afterwards due to further denitrification process. At 24 h, the highest N2O emissions was measured in 0.2 M NaCl (7.5 mg kg soil−1), followed by in 0.1 M, 0.05 M, 0.01 M, 0.005 M and 0 M treatments, which were 6.7, 5.1, 3.8, 2.0, and 1.2 mg N kg soil−1, respectively. Nitrous oxide reductase was sensitive to both high EC and low pH condition. In neutral and alkaline treatments, there was no significant effect of EC on N2O emissions during 72 h incubation (P > 0.05). The N2O emissions were 0 mg kg soil−1 at 3 h after incubation then ranged from 0.02 to 0.11 mg N kg soil−1. Ammonium concentration increased over the incubation periods. Higher EC promote NH4+ release. There was no significant difference in NO3− removal among treatments at different EC levels (P > 0.05). We conclude that low pH increased N2O emissions and higher EC under acid conditions promoted N2O emissions.

Keywords: Denitrification, EC, nitrous oxide, paddy soil, pH
Spatial prediction of soil water retention curves from particle size distribution data using Arya-Paris model

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Predicting soil water retention curves (SWRC) or their model parameters at any unsampled locations using a geostatistical spatial interpolation technique requires a number of high quality retention data. Obtaining SWRC is, however, generally tedious, time consuming, and sometime expensive. Therefore, pedotransfer functions (PTF), which allow one to predict soil hydraulic properties, such as SWRC, from easily measured soil properties, have been developed. One of the common PTF by Arya and Paris (AP) predicts water retention curves from particle size distributions (PSD) and dry bulk densities. In this study a geostatistical spatial interpolation technique was coupled with the AP model to predict water retention curves at given unsampled locations from PSD. There are two approaches available: (1) First, SWRC are predicted from PSD at given observed locations using the AP model. SWRC are then predicted at given unsampled locations through the geostatistical spatial interpolation technique from those predicted by the AP model. This approach is referred to as the PTF-first and Interpolation-later approach or the PI approach. (2) First, PSD and the bulk densities are predicted at given unsampled locations using the geostatistical spatial interpolation technique from observed PSD. Then, SWRC are predicted at the unsampled locations by the AP model from the interpolated PSD and bulk densities. This approach is then referred to as the Interpolation-first and PTF-later approach or the IP approach. Current study compares the performance of these two approaches to predict SWRC at any given unsampled location. Ordinary kriging (OK) one of the most commonly used geostatistical interpolation technique was used. The data used in this study were obtained from the Las Cruces trench site database, which contains water retention data for 448 soil samples. The dataset was then split into two sets, prediction and validation sets. This allows for the computation of prediction errors (mean absolute error or MAE and mean error or ME). The results show that performances of the PI and IP approaches were comparable, while the PI generally requires less workload as the number of kriging one needs to perform is much less for the PI compared to the IP. It was also shown that MAE were almost the same between the PI and the IP.