

Concentration and Potential Mobility of Trace Metals in Surface Sediment of the North Pacific Ocean By BCR Sequential

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Metals can accumulated in sediment, sludge and soil may therefore pose an environmental problem concerning possible metal transfer from sediment to the aquatic system and including them in the food chain. European Community Bureau of Reference (BCR)sequential methods commonly used to trace metals in the sediment or soil samples and can be provide information about bio-availability, mobility or toxicity which are basically depend on the chemical bonding between metals and solid phases of the samples.

Geochemical fractionation of Cadmium (Cd), Lead (Pb), Cobalt (Co), Zinc (Zn), Iron (Fe) and Manganese (Mn) in sediment of the North Pacific Ocean were determined using four-stages of modified BCR sequential extraction methods combination with ICP-MS. Also the contamination factors and risk assessment code effects on surface sediment samples are discussed.

The mean contents of the trace metals in surface sediment of the North Pacific Ocean were: Cd: 0.00; Pb: 13.94; Mn: 2732.94; Fe: 29795.10; Co: 22.16; and Zn:76.75 $\mu\text{g.g}^{-1}$, allowing to arrange the trace metals concentration from higher to lower were in the following order: Fe > Mn > Zn > Co > Pb > Cd. Pb was distributed in three fractions (acid soluble, reducible, and residual). Mn and Co were found in a group with mainly reducible fraction, while Fe and Zn were mainly in residual fraction. The high contamination factor was obtained for Mn and Co in the sediment samples, while the lowest was found for Fe. The result showed non risk for Fe, Co, Pb and Cd, while low risk is indicated for Mn and Zn at all stations.

Keywords: trace metals, BCR sequential extraction, North Pacific Ocean

Leaching Properties of Naturally Occurring Heavy Metals from the Soils around Abandoned Metal Mines

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The major threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, chromium, arsenic, as well as selenium, fluorine and boron. The effects of such heavy metals on human health have been extensively studied and officially reviewed by international organizations such as the WHO and heavy metal pollutions have been regulated by national environmental standards and/or laws such as the Soil Contamination Countermeasures Act in Japan.

Leaching of naturally occurring heavy metals from the soils around abandoned metal mines into surrounding water systems, either groundwater or surface water systems, is one of the major pathways of exposure. Therefore, understanding the leaching properties of toxic heavy metals from naturally polluted soils is of fundamental importance for managing abandoned metal mines, excavated rocks discharged from tunneling and/or selecting a pertinent countermeasure against pollution when it is necessary.

In this study, soil samples taken from the surroundings of abandoned metal mines in Tochigi, Miyagi, Yamagata, Akita and Iwate prefectures in Kanto and Tohoku regions were collected and analyzed. The samples contained multiple heavy metals such as lead, arsenic and chromium. Standard leaching test and sequential leaching test considering different forms of contaminants, such as trivalent and pentavalent arsenics, and trivalent and hexavalent chromiums, together with X-ray Fluorescence Analysis (XRF), X-ray diffraction analysis (XRD) and Cation Exchange Capacity (CEC) tests were performed. This presentation illustrates the details of the above experimental study, discusses the relationships among leaching properties, and chemical and mineral compositions, indicates the difficulties associated with remediation of naturally polluted sites, and emphasizes the importance of risk-based countermeasures against naturally occurring heavy metals.

Keywords: Naturally occurring, Heavy metals, Leaching properties, Mineral composition, Bulk concentration

Self-potential inversion for the estimation of hydraulic conductivity in the presence of unsaturated zone

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Self-potential (SP) is the electrical potential naturally generated in and on the earth. The positive electrical charge in the diffuse layer of the electrical double layer is conveyed by the groundwater flow. The electrical potential is generated when the groundwater flow through the porous medium. This electrical potential directly reflects on the Darcy velocity in the porous material, and therefore the hydraulic conductivity can be estimated from the SP data. The hydraulic conductivity has non-linear characteristics as functions of the water saturation, and so does SP. These features suggest that the effect of the unsaturated zone should be considered for much quantitative analysis of SP. However, the dependency of the SP on the water saturation makes the development of inversion difficult. We solved this problem with the adjoint state method for the calculation of the sensitivity matrix that could save the calculation time. The characteristic of water saturation in SP based on Van-Genuchten model is adapted to our inversion. We applied our inversion to a synthetic SP profile to test the performance of our inversion scheme to compare the results with and without the consideration to unsaturated zone. When the effects of the unsaturated zone are not considered, the value of estimated hydraulic conductivity is underestimated. On the other hands, more accurate image could be derived from the inversion with the consideration to the unsaturated zone. Therefore, our inversion technique would allow us to obtain the accurate hydraulic conductivity structure from SP data at the ground surface, although the SP is affected by the distribution of saturation.

Keywords: Self potential, Inversion, Hydraulic conductivity, Unsaturated zone

Root Water Uptake and Soil Water Storage in a Karst Savanna on the Edwards Plateau, Texas, USA

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Woody plants, especially Ashe juniper (*Juniperus ashei*) and honey mesquite (*Prosopis glandulosa*), are encroaching into a karst savanna on the Edwards Plateau in central Texas. However, their impact on hydrology is unclear because of high variability in soil depth and uncertainties about shallow and deep root contributions to water uptake in rocky soil overlying bedrock or other substrates that limit water storage capacity and root growth, and create high spatial variability in plant available water. This complex below-ground structure, while not uncommon, has not been adequately characterized by most hydrological models. We evaluated root water uptake and water storage in the karst of the Edwards Plateau, at a typical savanna site with ~50% woody cover, mainly Ashe juniper (*Juniperus ashei*) and honey mesquite (*Prosopis glandulosa*). Water content profiles to a depth of 1.6 m were measured by neutron thermalization and time domain reflectometry at 36 locations in a 25-by-25 m grid (5 m node spacing). Bulk density profiles were measured by gamma densitometry. Temporal changes in water storage were compared with eddy covariance measurements of evapotranspiration (ET) to evaluate relative amounts of ET originating from root water uptake at various depths. Water storage capacity in the measurement grid ranged from 185 to 401 mm, and coupled with heterogeneous distribution of trees created high spatial variability in root water uptake. Water uptake was higher beneath trees than beneath grass, in part because tree roots were able to extract water from regions of the root zone with high rock density. On average, 81% of the water uptake occurred from the upper 1 m of the profile with the greatest uptake occurring at depths of 0.4 to 0.8 m. An estimated 10% of the uptake occurred from below the maximum measurement depth of 1.6 m. While this result confirms the hypothesis that trees on rocky substrates take up water from greater depths compared to similar ecosystems on soil, it also refutes the view that trees in karst regions have greater access to groundwater.

Keywords: Root water uptake, Karst, Evapotranspiration, Spatial variability

Estimation of Water Flux in Andisol with a Penta-Needle Heat Pulse Probe

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The potential for using heat pulse probes for estimating soil water flux as well as soil thermal properties has received more attention this past decade. Although many studies were carried out to validate water flux estimation using heat pulse probes in sandy soils, few studies were reported for other soils. The purpose of this study was to estimate water fluxes in an aggregated Andisol using a heat pulse probe, and investigate the applicability with hydrodynamic dispersion in a soil.

The Penta-needle heat pulse probe, which has a central heater needle surrounded by two pairs of orthogonally arranged thermistors, was used to estimate two directional water flux. Steady-state saturated water flow and unit-gradient unsaturated water flow experiments were conducted in Mie Andisol. To achieve saturated conditions, the Andisol was packed in the column with a bulk density of 0.85 g/cm³ and afterward it was saturated by applying water from column bottom. A glass filter was located at the bottom of the column. CaCl₂ solutions were applied from the top of the column at fixed rates using a peristaltic pump, and outflows from the bottom were measured by a scale. The flow rates were decreased stepwise from fast (around 350 cm/day) to slow rates (around 5 cm/day). Using faster flow steps, steady state saturated water flows were developed. Steady state conditions for unit-gradient - unsaturated water flow were developed by controlling suction at the column bottom, in which water contents were uniform and water flowed by gravity. At each flow steps, heat pulse measurements were conducted, and the influent solution concentrations were changed to obtain breakthrough curves (BTCs) by measuring soil electrical conductivities with four-probe salinity sensors. Water fluxes were estimated by applying an analytical solution to temperature rise data. Dispersivities were determined by applying the convection-dispersion equation to BTCs. Each experiment, including packing soil and water flow testing, were repeated a few times.

In saturated conditions, water fluxes estimated by the heat pulse probe agreed well with independently measured water fluxes in one experiment and underestimations were found in two cases. For unsaturated conditions, estimated water fluxes agreed well with actual fluxes even in the experiment with disagreement in saturated conditions. The flux estimation errors were compared with dispersivities which can be interpreted as the scale of water flow spreading from mean displacement position. Large estimation errors were found for experiments with large dispersivities ($\lambda > 1.5$ cm), while errors were relatively small for conditions with smaller dispersivities both in saturated and unsaturated water flows. Generally, dispersivity values in aggregated Andisol is larger in saturated condition than in unsaturated condition. The experimental results in this study indicates that the applicability of heat pulse probe to aggregated soils potentially results in better water flux estimation in unsaturated conditions.

Keywords: soil water flux, heat pulse probe, Andisol, dispersivity

Geostatistical Interpolation of Thermal Properties of Boring Core Samples

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Ground source heat pump systems (GSHP) that use ground or groundwater as a heat source can achieve much higher coefficient of performance (COP) than conventional air source heat pump systems. Although use of GSHP systems has been rapidly increasing worldwide, environmental impacts by GSHP systems have not been fully investigated. To rigorously assess GSHP impact on the subsurface environment, instead of relying on "effective" properties, ground thermal properties including thermal conductivity and heat capacity need to be accurately characterized.

A geostatistical least-square interpolation method, known as kriging, has been used to characterize the spatial distribution of soil (or ground) physical (both hydrological and thermal) properties in one, two, and three dimensional domains. Kriging can estimate not only the values of an attribute at un-sampled locations accounting for spatial correlations between variables but also their uncertainties in terms of an error variance. Ordinary kriging (OK) which estimates unknown value as a linear combination of neighboring observations is one of the most commonly used kriging estimators. A secondary variable which is spatially cross-correlated with the primary variable can be used to reduce the estimation variance for the primary variable. Such method is known as cokriging. Ordinary cokriging (OCK) is one of the most commonly used cokriging estimator. The objective of this study was to compare OK and OCK in terms of estimating soil thermal properties along 50-m boreholes through the cross validation. Water content and sand content, which are relatively easy to measure, were used as the secondary attributes in cokriging.

In this study, undisturbed boring core samples were collected from two 50-m long boreholes at the campus of Tokyo University of Agriculture and Technology in Tokyo. Volumetric heat capacity (HC), thermal conductivity (TC), gravimetric water content (WC) and volumetric sand content (SC) were measured every 10-20 cm along the cores. The impact of sampling intensity on prediction errors were investigated by drawing random subsets of increasing size and using them to predict thermal properties at the remaining locations (jackknife approach). Then, subsets of N data were selected randomly or randomly per 10-m depth from the entire data set. For both sampling approaches, 50 different random subsets were selected to account for sampling fluctuations. Thermal properties at the remaining locations were then predicted.

This study showed that increasing the size of the subset leads to smaller mean absolute error. It was also found that kriging with random subsets per every 10-m depth yields lower mean absolute error than that with random subsets. Prediction errors by OCK were smaller than those by OK when the sampling intensity was the same.

Keywords: thermal conductivity, kriging, cokriging, sampling intensity, prediction error

Evaluation of Tangential Model Parameters with Respect to Various Soil Types

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Usage of Tangential model (Kohgo, 1995) for Soil Water Retention Curves (SWRCs) fitting requires knowing its parameters which are the numerical values of the coordinates of 3 tree points that are selected on the SWRC obtained from an experiment. Performing such an operation might be time consuming and may also lead to errors in the parameter estimation. This study aims to estimate these parameters and investigate possible relations between the parameters and some basic soil properties. SWRCs data and their corresponding hydraulic and physical properties were taken from the Unsaturated Soil Hydraulic Properties Database (UNSODA). The selected data consisted of 458 soils; among them: sand, sandy loams, loamy sands, sandy clay loams, silty loams, silty clay loams and silty clays. These SWRCs were fitted to Tangential model using nonlinear regression analysis with solver, the in-built Microsoft Excel tool. The iteration procedure, in solver, was the Generalized Reduced Gradient method. Results showed that the model performed well. The sum of the squared residuals (SSR) varied between 0.00011 and 0.2114 for sand and sandy soils, while it ranged between 0.021 and 0.00017 for all the others. Highest SSR values were noted with coarse sandy soils while the lower SSR values were noted with materials of finer structure. This suggests that this model is more adapted to fine structured soils. An attempt is being made in order to predict the Tangential model parameters, through multiple linear regression analysis, by using the soil bulk density values, saturated volumetric water content and the soil grain size distribution data.

Keywords: soil water retention curves, simulation, UNSODA, parametric model, fitting