Continuous isotopic Water Sampling Cavity Ring-Down Spectroscopy (CWS-CRDS) for real-time measurements of water isotopes

*David Kim-Hak[1]

1. Picarro, Inc.

Stable isotopes of water (d^{2}H, d^{18}O) are unique tracers of many hydrological processes including evaporation, precipitation, reservoir mixing and residence time. Historically, discrete water samples have been collected and analyzed via either Isotope Ratio Mass Spectrometry, or more recently laser-based spectroscopic methods, such as Cavity Ring-Down Spectroscopy (CRDS). However, the analysis of discrete samples precludes the ability to construct high resolution water isotopes data sets through time and space. Previously, research groups have developed laboratory-built diffusive samplers for extracting water vapor from liquid [1,2] and then analyzed that vapor via CRDS instruments, whose continuous flow design and high frequency measurement interval (< 1 Hz) makes them uniquely suited to real-time, high throughput measurements. Here we present details of the first commercially-available and field-deployable Continuous isotopic Water Sampler (CiWS) coupled to a Picarro L2130-*i* for isotopic water analysis. The CiWS device utilizes an expanded polytetrafluouroethylene (ePTFE) membrane to extract water vapor into a dry air stream. The resultant water vapor is analyzed by a Picarro L2130-*i* for d^{2}H and d^{18}O. An automated software program provides user-specified time-averaged data and switches between four ports to enable easy calibration. Tight temperature and flow rate control regulates fractionation across the membrane. In-lab testing demonstrates that the system can achieve a raw precision (1s of 3 minute average) better than 0.05/0.15 ‰(d^{18}O/d^{2}H), respectively, and a reproducibility of 0.15/0.5 ‰(d^{18}O/d^{2}H) over seven days, even under variable ambient air and water temperature conditions.

Keywords: cavity ring-down spectroscopy, water stable isotope

Seasonal variation of ^{17}O-excess of precipitation in East Asian Monsoon region, Okinawa, Japan

*Yuina Uechi[1], Ryu Uemura[1]

1. University of the Ryukyus

A high-precision analysis of the δ^{17}O of water has provided a promising new tracer ^{17}O-excess (Barkan and Luz, 2005). The changes in ^{17}O-excess is caused by molecular diffusion process during evaporation, which is basically similar to d-excess ($= \delta D - 8 \times \delta^{18}O$). In fact, a positive correlation between ^{17}O-excess and d-excess of water vapor was observed in the ocean (Uemura et al., 2010). However, much lower correlations were found in Antarctica (Landais et al., 2008; Touzeau et al., 2016) and in the United States (Li et al., 2012), probably because of kinetic fractionations. Here, we measured the isotopic composition in precipitation on Okinawa jima (Japan) to reveal seasonal ^{17}O-excess variation in East Asian monsoon region. Precipitation samples were collected every week over 2 years in Okinawa, Japan. The δ^{18}O, δ^{17}O and δD of water were measured using a cavity ring-down spectroscopy (L2140-i, Picarro). The ^{17}O-excess in precipitation shows lower values in summer and higher values in winter. The seasonal variation is similar to that of d-excess, which was interpreted as changes in relative humidity in the moisture source ocean (Uemura et al., 2012). The results suggest that the precipitation in Okinawa is mainly controlled by isotope fractionation during the evaporation in the ocean.

Keywords: 17O-excess, the triple isotopic composition, precipitation

Alternative to toxic substance for water sample preservation to measure stable carbon isotopic composition of DIC: preliminary result

*Hiroshi A Takahashi[1], Hiroko Hanada[1]

1. Geological Survey of Japan, AIST

Carbon isotopic composition of dissolved inorganic carbon (DIC) of natural waters plays an important role in understanding of the carbon behaviors in the fields of oceanography and hydrology. It is indisputable that the isotopic change after sampling to measurement should be prevented. The employment of a toxic substance, e.g., mercuric chloride ($HgCl_2$) or sodium azide (NaN_3), to suppress biological (microbial) activities has established as a means of analyzing seawater samples. However, we cannot use the toxic substance without permission in the field campaign. Moreover, the use of toxic substance causes high ecological risks, e.g., human or organisms heaths. It requires the cost and time for disposal of wastewater. We suggested the possibility of salt (NaCl) to inhibit microbial activities at the Goldschmidt Conference 2016. The additional examinations using salt was carried out. As the result, salt cannot be used for low DIC concentration samples to measure carbon isotopes. The carbon isotopic ratios of those samples were shown slightly lower values than those of salt-free ones. However, the carbon isotopic ratio change is negligible in high DIC concentration samples by salt addition. DIC concentration was measured lower for the salt added samples, especially high DIC concentration samples. These changes may be caused by solubility change of gas species.

Kuo (1998) utilized benzalkonium chloride (BAC: cationic surfactant) as a less hazardous alternative to $HgCl_2$ for drinking water analysis. Gloël et al. (2015) represented that BAC could be an effective tool for short-term preservation of seawater samples, but is ineligible for sample storage over weeks to months. However, we consider that BAC has a potential for sample sterilization for DIC analysis, because BAC permeates the cytoplasmic membrane causing cell death. We examined the effect of BAC for carbon isotopic analysis of DIC samples, in order to establish procedure without using the toxic substance. Water samples were preserved into 10mL or 30mL glass vials after dissolving sugar, and BAC was added to half of those vials.

The preliminary results by groundwater, pond water and river water suggested that the BAC could be used to sample sterilization for carbon isotopic analysis of groundwater samples. DIC concentration was increased and carbon isotopic ratio was decreased during 4 weeks preservation for the no sterilized samples (BAC-free), but they were shown to be constant for the sterilized ones (BAC added). For the next step, we will examine the effectiveness of BAC to inhibit microbial activities in water using other natural water samples.

Gloël, J., Robinson, C., Tilstone, G. H., Tarran, G. and Kaiser, J. (2015) Technical note: Could benzalkonium chloride be a suitable alternative to mercuric chloride for preservation of seawater samples? *Ocean Sci.* **11**, 947-952.

Kuo, C. Y. (1998) Improved application of ion chromatographic determination of carboxylic acids in ozonated drinking water. *J Chromatogr A.* **804**, 265-272.

Keywords: DIC, carbon isotope, benzalkonium chloride

Estimation of DIC escape from a mangrove forest in Ishigaki Island inferred from using stable carbon isotopic analysise.

*Miyuki Kondo[1], Hiroshi A Takahashi[2], Shinpei Yoshitake[3], Mitsutoshi Tomotsune[4], Kazutoshi Kinjo[5], Toshiyuki Ohtsuka[3]

1. National Institute for Environmental Studies, 2. National Institute of Advanced Industrial Science and Technology, 3. Gifu University, 4. Kobe University, 5. University of the Ryukyus

It have been considered that mangroves forests have a largest carbon reservoir in terrestrial ecosystem and most carbon-rich tropical forests and substantial amount of carbon sink. However, the majority of the mangrove net primary production remains unaccounted for by current carbon budgets. Previous observation of mangrove carbon budgets has neglected the exchange of both ecosystem gross primary production and respiration. In addition, neglecting the escape of DIC derived from heterotrophic respiration leads to an overestimation of ecosystem net productivity estimates based on eddy covariance techniques. Here, we measured DIC concentrations and carbon isotopes over complete tidal and diel cycles in the mangrove tidal creek in Ishigaki island, SW Japan. The DIC escape calculated from the mangrove forest was computed using isotopic mass balance model. DIC concentrations and carbon isotopic values showed consistent tidal variation in August, with DIC ranging from 2017 to 3061 μmol/L, and 0.37 to 10.33 ‰, respectively. The carbon isotopic values were lower than expected for the mixing of the river water and seawater DIC during low tide, due to the ^{13}C-depleted DIC inputs from the mangroves. An isotopeic mass balance model was used to determine the DIC concentration derived from mangrove in the estuarine waters. The contribution to DIC escape from the mangrove in estuarine water was risen sharply in tandem with low tide ranging from 55 to 836 μmol C/L.

Keywords: Carbon cycle, Mangrove forest, DIC, 13C

Preliminary study of volatile flux from magma of Aso volcano through shallow groundwater layer, Kumamoto Prefecture, Southwest Japan

*Masaaki Takahashi[1], Kohei Kazahaya[1], Tsutomu Sato[1], Hiroshi A Takahashi[1], Akinobu Miyakoshi [1], Yuki Tosaki[1], Noritoshi Morikawa[1], Akihiko Inamura[1], Jun Daimaru[1], Hiroko Handa[1], Atsuko Nakama[1], Hinako Shimizu[1], Hisako Takeuchi[1]

1. The National Institute of Advanced Industrial Science and Technology

Volatile flux of magma of Aso volcano through shallow ground water layer is preliminary studied by groundwater and river (Shirakawa, Kurokawa and Midorikawa) surveys in Aso caldera and adjacent areas. Flow rates of S and Cl of Kurokawa river (Ofuchi Bridge, Aso-dani, Akamizu) are 53.7ton/day and 25ton/day, and of Shirakawa river (Myoken Bridge, Nango-dani, Kain) are 12.3ton/day and 5.4ton/day, respectively.
It is necessary to understand volatile flux of magma of Aso volcano through shallow groundwater layer considering the amount of sulfur and chlorine supplied from rainfall or strata, or the influence of hot spring water (deep groundwater) to shallow groundwater layer.

This study was supported by the Secretariat of the Nuclear Regulation Authority, Japan.

Keywords: Aso caldera, groundwater and river survey, volatile flux of magma, hydrogen and oxygen isotopic ratio

Runoff processes of volcano springs in the northeast foot of Mt. Ontake

*Kazuyoshi Asai[1]

1. Geo-Science Laboratory

Hydrological observation and sampling of the spring were carried out at the northeast foot of Ontake volcano. Stable isotope ratio and concentration of transient tracer (CFCs, SF_6) were measured in Geo-science laboratory. Based on the results, we discuss the runoff-processes of the springs with short residence time less than 10 years.

Keywords: Volcano springs, Mt. Ontake, Runoff-processes

Comparison of stable water isotopes between lake bottom springs and groundwater around Lake Kawaguchi at the northern foot of Mount Fuji

*Shinya Yamamoto[1], Takashi Nakamura[2], Yukihiko Serisawa[3]

1. Mount Fuji Research Institute, Yamanashi Prefectural Government, 2. Interdisciplinary Graduate School, Research Center for River Basin Environment, University of Yamanashi, 3. Faculty of Education, University of Yamanashi

In Lake Kawaguchi, we previously reported the existence of lake bottom springs at the depth of 8 meters in the east of the Unoshima Island. Lower water isotope values around the springs indicate groundwater inflows from the surrounding mountains, however, the detailed source area of the springs was not determined due to the mixing with lake waters. In this study, we directly obtained spring water by scuba diving, and compared its water isotope ratios with those in groundwater around the lake collected at the same period. Water isotope values of the springs were higher than those in groundwater from the southern side of the lake, and showed more close values to groundwater from the northern side of the lake. This suggests that the source of the lake bottom springs is likely derived from Misaka Mountains.

Keywords: Fuji Five Lakes, springs, stable water isotopes

An isotopic study on origins of water and nitrogen pollution of shallow groundwater in densely populated areas of Kawasaki City, central Japan

*Takanori Futagami[1], Masaya Yasuhara[1], Seongwon Lee[1], Takashi Nakamura[2]

1. Rissho Univ., 2. Yamanashi Univ.

Around 30 water samples in Kawasaki City, the seventh largest city in Japan, was analyzed for water chemistry and isotope ratios of water (dD and $d^{18}O$) and nitrate ion ($d^{15}N$ and $d^{18}O$) to investigate the origins of water and nitrogen pollution of groundwater in the highly urbanized area. All groundwater samples are from either springs or private wells at a depth of less than 15 m. As a result of the dD and $d^{18}O$ analysis, it was proved that water leaking from drinking water mains is a major source of shallow groundwater recharge in the study area. The role of drinking water leakage in shallow groundwater recharge was found to be prominent for that in the lowland plains along Tama River, accounting for up to 40 % of the total groundwater recharge. With the help of nitrogen and oxygen isotopes of nitrate ion, we also found the serious effects of sewer leakage on shallow groundwater quality. Distribution of the nitrate ion concentration across the study area was highly heterogeneous, indicating the localized occurrence of denitrification as well as the effects of sewer leakage. Quantifying the effects of sewer leakage to both groundwater recharge and its quality is the subject of our future study.

Keywords: urbanized area, Kawasaki City, shallow groundwater, leakage from water mains, sewage leakage, nitrogen and oxygen isotopes of nitrate ion

Anomalous changes in groundwater and hot spring water after the 2016 Kumamoto earthquake

*Tsutomu Sato[1], Hiroshi A Takahashi[1], Kuniyo Kawabata[2], Masaaki Takahashi[1], Yuki Tosaki[1], Akinobu Miyakoshi[1], Akihiko Inamura[1], Hiroko Handa[1], Norio Matsumoto[1], Kohei Kazahaya[1]

1. Geological Survey of Japan, AIST, 2. Kagoshima University

We have investigated the groundwater at the 8 springs (A-H in Fig.1) to clarify the changes associated with the 2016 Kumamoto earthquake. We also conducted inquiring survey at the 21 hot springs and investigated spring water newly generated in Aso area (J in Fig.1).

Six of the eight springs (A-D, G, H) were the places where the measurement of flow rate and sampling was done from 6th to 10th March 2016 one month before the earthquake. The same survey was carried out in 2014 for the remaining two springs (E, F) as well. Such pre-earthquake survey revealed the changes in flow rate and major chemical concentration due to the 2016 Kumamoto earthquake.

The flow rate increased more than twice that of before the earthquake at the three springs (A-C) and decreased less than half at the two springs (G, H) (Fig.2). At the other springs (D-F), changes of the flow rate was less than 30 %. The former five springs are located within 7 km form the Futagawa and Hinagu faults that caused the 2016 Kumamoto earthquake.

To compare the flow rate changes and crustal deformation which might occur at the time of earthquake, we calculated the crustal strain changes based on the fault model by Geospatial Information Authority of Japan (2016) using MICAP-G (Okada, 1992, Naito and Yoshikawa, 1999). Spatial distributions of the flow rate changes and the crustal strain changes did not show a clear relationship (Fig.1).

As for the major chemical composition, there were clear changes only in the nitrate ion concentration (Fig.3). The pattern of change was the same for the all springs as follows. The nitrate ion concentration peaked in May 2016 and decreased until September 2016 than before the earthquake.

As the result of our inquiring survey at the hot spring facilities, it became obvious that there were hot spring wells and areas where self-discharge occurred or the amount of self-discharge was markedly increased. A good relationship in the spatial distribution between the changes and the calculated crustal strain changes was found.

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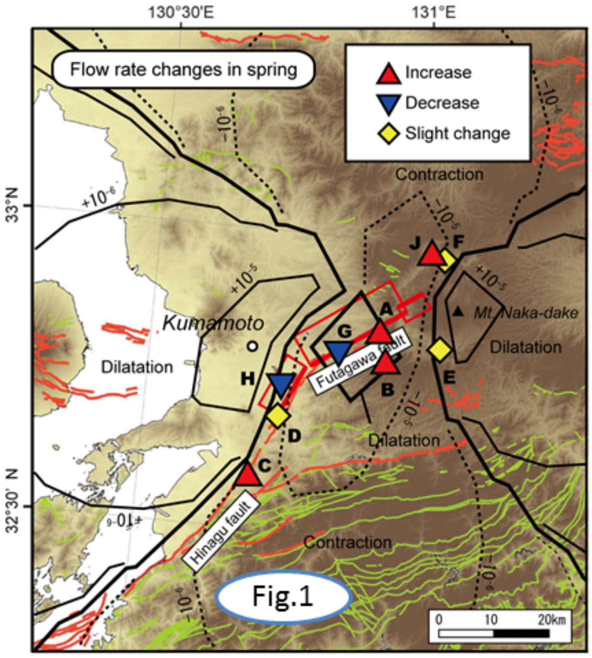
Fig.1 Spatial distribution of the flow rate changes of the springs in relation to the 2016 Kumamoto earthquake

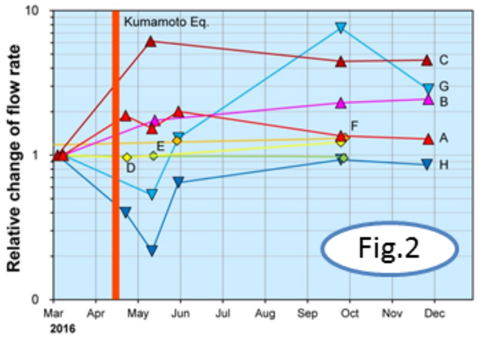
Fig.2 Relative changes of flow rate of the springs

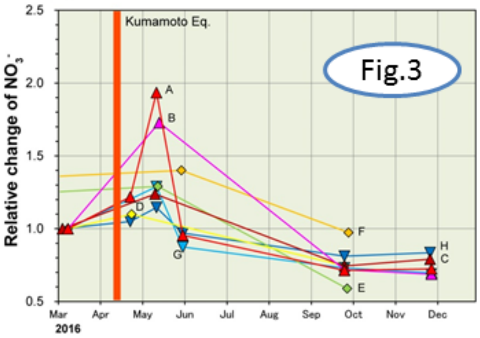
Fig.3 Relative changes of nitrate ion concentration of the springs

Keywords: The 2016 Kumamoto earthquake, groundwater, flow rate, nitrate ion, crustal strain changes, hot spring



The fault model by Geospatial Information Authority of Japan (2016)





Groundwater flow system in Fukushima Prefecture traced by tritium-^{3}He and ^{129}I dating methods

*Maiko Sakuraba[1], Hirochika Sumino[1], Teruyuki Maruoka[2], Hiroyuki Matsuzaki[3], Haruka Kusuno[3], Marina Kawamoto[3], Hironori Tokuyama[3], Katsumi Syouzukawa[1], Mayumi Hori[4]

1. Department of Basic Science,Graduate school,Arts and Sciences,University of Tokyo, 2. Faculty of Life and Environmrntal Scieences,University of Tsukuba, 3. Micro Analysis Laboratory,Tandem Accelerator,University of Tokyo, 4. College of Arts and Sciences,University of tokyo,Komaba

For developing and effective utilizing of groundwater resources, it is necessary to understand the large circulation of water from precipitation to use by residents (Mahara *et al.*, 1993). In particular, studying the residence time and source (recharge area) of the water is important in evaluating the groundwater flow system. In Fukushima Prefecture, although environmental behaviors of various radionuclides released by the accident of Fukushima Daiichi Nuclear Power Plant have been analyzed, there are few reports on the behavior and contamination status of groundwater by radionuclides, which are necessary to be assessed for safety use of groundwater resources in the future.

In this study, we investigated the groundwater flow system in Fukushima Prefecture and the anthropogenic contamination of groundwater caused by the nuclear accident using ^{3}H-^{3}He dating method, which is possible to acquire not only the age of groundwater but also the information on the water source based on the initial ^{3}H concentration, and ^{129}I, one of the radionuclides released by the nuclear accident.

Sampling was conducted in September 2016 and January 2017 mainly on groundwater and spring water at the Hama-dori region, Fukushima Prefecture. The water samples for ^{3}H-^{3}He dating method were collected and sealed in copper tubes with special care to atmospheric contamination and analyzed using a noble gas mass spectrometer at Department of Basic Science, University of Tokyo. After the first extraction of originally dissolved helium, the sample water was sealed in the copper tube again and stored for about a month, and then the amount of ^{3}He produced by the decay of ^{3}H was extracted by the second degassing and analyzed to obtain the initial ^{3}H concentration and the residence time. Water samples for iodine analysis were sampled in 1-L plastic bottles. Iodine in the sample water was extracted and back-extracted to yield silver iodide pellet, and then ^{129}I/^{127}I ratios and concentration of stable isotope ^{127}I was measured using an accelerator mass spectrometer and ICP-MS at Micro Analysis Laboratory, Tandem accelerator, University of Tokyo.

For example, in Minami Soma Sports Park located about 30 km north of the nuclear plant, the concentration of tritium-derived ^{3}He was approximately 2.2×10^{-18} mol/g. The current ^{3}H concentration has been determined by liquid scintillation counter to be 9.3 TU for a sample collected from the same locality (Yabusaki *et al.*, 2015). These values give the initial ^{3}H concentration of 10.1 TU and the residence time of about 1.5 years. This suggests the groundwater system in this region has already been almost completely refreshed since March 2011 due to the short residence time.

For ^{129}I/^{127}I ratios, most of the samples measured so far showed values below 1.0×10^{-11}, which is the lower limit of the isotope ratio including radioactive iodine of anthropogenic origin (Fehn, 2012). The low ^{129}I/^{127}I ratio of water from Minami Soma Sports Park is in the range of natural background, which is consistent with the short residence time obtained with the ^{3}H-^{3}He method.

Up to the present, it is not possible to confirm the apparent contamination due to the nuclear accident, but depending on the residence time of the groundwater, the possibility that polluted water will discharge in the future cannot be ruled out. We are planning to carry out further sampling to estimate the residence time and water source by the ^{3}H-^{3}He method and combine it with the ^{129}I results to investigate the environmental impact.

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10-Beryllium-contents of sediments in mountainous catchments topographically constrained by shallow landslides

*Hiro Ikemi[1]

1. Faculty of Engineering, Kyushu University

Recently, it is being important to understand sediment dynamics in a river basin for a well-balanced sediment management in the entire basin at view points of the national flood control and water resources. However, it is still unclear how much sediment has been produced in a mountainous stream, which is a basic information of the sediment dynamics. In this study, 10-beryllium-contents have been analysed for sediment samples of mountainous catchments in Fukuoka, Japan in order to fundamentally examine the sediment dynamics in the river basin. Since the late 1980s, beryllium isotopes of quartz extracted from rock or river sediment have been analysed to estimate rock- or catchment-scale denudation rates [1].

A lot of slope collapses are observed in the study area, of which the geology mostly consists of Mesozoic granites. Most of those failures were explained as a shallow landslide under around 1m in depth, which accompanied with an infiltration of rains and an increase of a groundwater table in weathering granite [2]. The sediment samples have been collected at four riverbeds and one hillslope in two different sub-catchments (A and B).

The samples that originated from weathering granite are composed of quartz, feldspar, mica and some organic materials. Firstly, they were washed by pure water and sieved over 250 μm to avoid a contamination from aeolian deposits. Then, the quartz was purified with acids and beryllium oxide was produced based on the method of Kohl & Nishiizumi [3]. Finally, beryllium isotopes were analysed with the accelerator mass spectrometer equipped by JAEA (JAEA-AMS-TONO).

As a result, the sample of the catchment B shows a little bit higher value in 10-beryllium-content that is 8.7 ±1.9 (x 10^4 atoms/g), than those of catchment A that show similar values ranging from 3.1 ±0.5 to 5.5 ±0.9 (x 10^4 atoms/g). This result indicates that the river sediment in the catchment B includes quartz grains that have been exposed on a ground surface for a long time compared with the catchment A because topographical settings of these two catchments are similar. It is also possible to think that the river sediment in the catchments A contains more landslide materials because the landslide materials, which have come from a deeper part, might have a lower value in 10-beryllium-content. This result is consistent with distribution of the shallow landslides in 2003.

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Keywords: topography, beryllium isotopes, sediment dynamics

Dynamics of Lake and Groundwater

*Meseret Dawit Teweldebrihan[1]

1. Delft University of Technology

Soils and forests are deteriorating; grazing lands are degraded; water points, sources and lakes are drying, and underground water levels are lowered. This could largely be attributed to the employed traditional inappropriate resource management methods; severe soil erosion and degradation reducing infiltration and resulting in sedimentation of water sources and lake basins. Bad cultivation practices, burning and cutting of perennial vegetation, overgrazing and grass fires increase the runoff causing soil erosion and consequently sediment transport to the lake resulting to decrease its storage capacity and quality of stored water.

The present investigations also include the runoff-rainfall studies combined with estimation of sediment transport, pollution of water and rating decrease in storage capacity. The lake discharge has been decreased according to preliminary analysis. The main aim of this research is to quantify the interactions between groundwater and surface water. A multi-disciplinary approach will be used to quantify interactions between groundwater and surface water in the catchment. The methods include modelling, isotopes, hydrochemistry, hydraulic, and temperature approach. These methods will be applied at various spatial and temporal approach. With the help of different GIS/Remote Sensing equipment’s, different maps and imageries will be developed and further investigation will be done to evaluate the present mode of land situation and its degradation. Hydrological data and other related data will be collected from the different sources. Analysis of soil samples for different physico-chemical properties and water sample for testing its quality will be done by standard procedures and methods.

The status of land and water surface will be counter checked by ground truth. The results will provide a solid scientific basis on integrated approach of groundwater and surface water. Moreover, depending on the analysis and result, suggestions can be made for adopting some strategies to improve water resource management.

Keywords: lake, groundwater, SWAT & MODFLOW