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Assessing the impacts of anthropogenic activities on groundwater quality using nitrogen isotopes – Aveiro Quaternary aquifer (Portugal)

Galego Fernandes, P.^a, Carreira, P.M.^a, Nunes, D.^a, Condesso de Melo, M.T.^b, Marques da Silva, M.^b

^a Instituto Tecnológico e Nuclear, Departamento de Química, Sacavém, Portugal

^b Universidade de Aveiro, Departamento de Geociências, Aveiro, Portugal

E-mail: paulagf@itn.pt

The Aveiro region, situated on the northwest coast of Portugal is one of the most industrialized areas of Portugal, with a high demographic density and an intensive agriculture. The shallow Quaternary aquifer system, which consists mainly of detrital sediments of Pleistocene and Holocene ages, is still today an important water resource for this region despite growing evidence of diffuse pollution problems. Isotope techniques have been used to evaluate the aquifer vulnerability to nitrate contamination. Groundwater samples were collected from 30 wells and springs for isotopic analysis ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from NO_3 and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from H_2O). Nitrogen isotopes were used to identify nitrogen sources and assess agriculture, cattle-breeding, urban and industrial contribution to nitrogen cycle in Aveiro ecosystem, based on the fact that the main sources of nitrate in the area have isotopic distinct $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signatures. This methodology contributed for the identification of the main nitrate sources in the region (agriculture and industrial).

Dynamics of water transport through the Velika Morava catchment

Miljevic, N.^a, Golobocanin, D.^a, Milenkovic, A.^a, Nadezdic, M.^b

^a Vinca Institute of Nuclear Sciences, Belgrade, Serbia

^b Republic Hydrometeorological Service of Serbia, Belgrade, Serbia

E-mail: emiljevi@vin.bg.ac.yu

The Velika Morava (tributary of the Danube) is the largest river entirely situated in Serbia with an average annual outflow of 220 m³/s. Environmental isotopes (deuterium, tritium, oxygen-18) together with hydrochemical parameters (water temperature, pH value, electrical conductivity, major ions, and flow measurements) were applied to study dynamics of hydrological cycle in this macro-scale catchment (37.4 km² area). Used data are spanned a two-year period, September 2004 to December 2006. Stable water isotope composition of analyzed samples from three meteorological stations, seven sites for water quality and 25 piezometers followed the global meteoric world line indicating a common water origin and a relation between the flows of surface and shallow underground waters in the basin. Precipitation isotope composition exhibited strong seasonal variations, which although significantly damped within the catchment, were reflected in stream water at analyzed sampling sites. Using the sinusoid curve-fitting method for variations of oxygen-18 content in precipitation and stream water, the mean transit time of water in the catchment was estimated.

Isotope hydrology application in Cuba for assessment of water resource management in the most important basin of Havana City

Peralta Vital, J.L.^a, Gil Castillo, R.^a, Molerio León, L.^b, Leyva Bombuse, D.^a, Carrazana González, J.A.^a, Pin, M.^c, Dapeña, C.^d, Panarello, H.O.^d, Vera, M.C.^d, Ibarra, E.D.^d

^a Centro de Protección e Higiene de las Radiaciones (CPHR). Calle 20 No. 4113 e/ 41 y 47. Playa, C.P. 10600. A.P. 619. Ciudad Habana, Cuba

^b Compañía Especializada en Soluciones Integrales Geográficas y Medioambientales, CESIGMA. Ciudad Habana, Cuba

^c Empresa de Aprovechamiento Hidráulico de Ciudad Habana. Ciudad Habana, Cuba

^d Instituto de Geocronología y Geología Isotópica (INGEIS). Facultad de Ciencias Exactas de la Universidad de Buenos Aires, Buenos Aires, Argentina

E-mail: peralta@cphr.edu.cu

This paper shows the results obtained during the investigations carried out in two research and development Projects, a national Project (2002-2005) and an international collaboration Project between Cuba and Argentina (2005-2006). The isotope hydrology is applied to assessment the "Almendares-Vento" karstic basin, which is the main supplier to the Cuban capital. The basin is affected by the overexploitation of its water resources and discharges of industrial and urban wastewaters. Additionally, an extensive period of drought, justify the necessity of carrying out an integral Basin characterization for a better water resources management. Using a monitoring network of the groundwater and surface waters, a preliminary isotopic study (^3H , ^{18}O and ^2H) including the rainfalls analysis in the Basin was accomplished. Also a detailed geochemistry characterization, including the integral geologic study, the determination of the major anions and cations (HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , K^+), and physico-chemical parameters (electrical conductivity, pH, TDS) was achieved. The isotope composition indicates their meteoric origin. Groundwater and surface water fit on an evaporation line, but not all samples follow an evaporation pattern. The isotope variations respond to processes as selective infiltration or direct infiltration through preferential channels through the karst. The used models show good water mixing and the aquifer receives fresh recharge annually, but not in the whole extension. The aquifer is overexploited in the main water extraction point of the Basin. The vulnerable zones associated to the contamination by saline water intrusion and the human activities in the urban areas are observed in the basin west side. Also were clarified some geologic and hydrogeology uncertainties of the Basin. The utility of the isotope hydrology to assessment the water resources management was established.

Input of isotopic (^{18}O , ^2H and ^3H) and geochemical studies in the assessment of groundwater resources in Porto urban area (NW Portugal)

**Marques, J.M.^a, Carreira, P.M.^b, Afonso, M.J.^{c,d}, Chaminé, H.I.^{c,d},
Teixeira, J.^d, Fonseca, P.E.^e, Rocha, F.T.^d**

^a Instituto Superior Técnico, Centro de Petrologia e Geoquímica, Lisboa, Portugal

^b Instituto Tecnológico e Nuclear, Departamento de Química, Sacavém, Portugal

^c Instituto Superior de Engenharia do Porto, Departamento de Engenharia Geotécnica, Porto, Portugal

^d Universidade de Aveiro, Centro de Minerais Industriais e Argilas, Aveiro, Portugal

^e Universidade de Lisboa, Departamento de Geologia, Lisboa, Portugal

E-mail: jmmarques@mail.ist.utl.pt

This paper attempts to assess surface water / groundwater interaction in Porto urban area. The region is mainly characterized by Variscan granitic rocks. Several underground galleries were excavated throughout the centuries to conduct spring waters. Paranhos spring collection chambers constitute one of the galleries studied. Preliminary isotopic signatures of groundwaters indicate that: i) those collected along gutters present a homogeneous composition, ii) an isotopic depletion of about 1 ‰ in ^{18}O and 7.5 ‰ in ^2H was found, ascribed to groundwater samples collected from the granitic fractures. These groundwaters display ^3H concentrations higher than in the gutter groundwater samples. Coupled isotopic and geochemical signatures indicates that i) groundwaters collected along the gutter sampling points could be ascribed to meteoric waters infiltrated along the residual granitic soil, all over the years ii) groundwater samples collected from the granitic fractures could be ascribed to random precipitation events, resulting into a directly infiltration along the fissured granitic rocks. In the first case, sea water and agricultural fertilizers should be regarded as sole sources of the Cl and NO_3 , while in the second case wastewaters should be faced as typical sources of both Cl and NO_3 concentrations.

Detection of water leaks in Foug-El-Gherza Dam (Algeria)

Hocini, N., Moulla, A.S.

Centre de Recherche Nucléaire d'Alger (CRNA), Alger, Algérie

E-mail: nadahocini@yahoo.fr

The main objective of this work was to detect water leakage origin combining conventional, tracing and isotope techniques. The investigation was performed by a research team from the 'Algiers Nuclear Research Centre' in collaboration with engineers from the 'National Agency for Dams'. The chemical and isotopic results have shown no influence of dam water on the surrounding aquifers. Dye tracing has shown a faster water circulation through complex pathways for the right bank as compared to the left one.

A new contribution to the isotopic and geochemical characterization of the gas phase ascribed to the CO₂-rich mineral waters (N. Portugal)

Carreira, P.M.^a, Marques, J.M.^b, Carvalho, M.R.^a, Capasso, G.^c, Grassa, F.^c, Nunes^a, D., Neves, O.^b, Antunes da Silva, M.^d

^a Instituto Tecnológico e Nuclear, Departamento de Química, Sacavém, Portugal

^b Instituto Superior Técnico, Centro de Petrologia e Geoquímica, Lisboa, Portugal

^c Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy

^d Unicer Águas, S. Mamede de Infesta, Portugal

E-mail: carreira@itn.pt

In Portuguese mainland the most important HCO₃-Na CO₂-rich thermomineral waters issue in the Northern part of the country, linked to one major NNE-trending faults, the so-called Verin-Chaves-Régua-Penacova megalineament. Along this tectonic structure, different occurrences of CO₂-rich thermomineral waters are found: Chaves hot waters (78°C) and several cold (17°C) CO₂-rich waters. The gas phase composition and the isotopic ratios of ³He/⁴He and ¹³C/¹²C point out that 10 to 30 % of the gases have mantelic or magmatic source (typical MORB fluids). These primitive chemical signature decreases from S to N representing an increase of crustal contamination in that direction. Geochemical modeling applied to the hot and cold waters composition shows the water-rock interaction reactions are mainly controlled by the amount of dissolved CO₂(g) instead of the water temperature.

Assessment of groundwater salinization mechanisms in Santiago Island – Cabo Verde: an environmental isotopic approach

**Carreira, P.M.^a, Marques, J.M.^b, Pina, A.^c, Mota Gomes, A.^c, Almeida, E.^d,
Gonçalves, R.^d, Nunes, D.^a, Monteiro Santos, F.^e**

^a Instituto Tecnológico e Nuclear, Departamento de Química, Sacavém, Portugal

^b Instituto Superior Técnico, Centro de Petrologia e Geoquímica, Lisboa, Portugal

^c Instituto Superior de Educação, Departamento de Geociências, Praia, Santiago,
Cabo Verde

^d Instituto Politécnico de Tomar, Tomar, Portugal

^e Universidade Clássica de Lisboa, Departamento de Física, Centro de Geofísica,
Lisboa Portugal

E-mail: carreira@itn.pt

Two sampling campaigns were carried out at Santiago Island - Cabo Verde under the scope of an isotopic and geochemical research study. An evaluation of the groundwater systems was carried out through the application of environmental isotopes and geochemical data in order to answer questions such as: origin and mechanisms of groundwater recharge; relation between the hydrochemical evolution of the groundwater systems with the geological matrix (minerals dissolution) or mixture with seawater and aerosol marine influence; identification of seawater intrusion mechanisms and, determination of the apparent groundwater “age”. The results obtained so far are not conclusive on the identification of which process is responsible for the salinity increase. In general, all the data obtained seems to indicate that the waters have the same isotopic history but different geochemical evolution, which depends on the weathering and permeability of the rocks.

Application of isotope hydrology for the assessment of artificial ground water recharge in some areas of UAE

Ekaabi, A.S.

Head of Water Resources Section, Ministry of Environment & Water, Dubai, UAE

E-mail: asalmatri@moew.gov.ae

Due to recharge – discharge imbalance, severe depletion of groundwater table has occurred in most of the aquifers in United Arab Emirates. Evolved from its prime role to develop the water resources in the country, the Ministry of Environment and Water has constructed a large number of detention and retention dams across the main wadies. To assess groundwater recharge increase due to these dams, isotope methods were used to calculate such increase in three major wadies as Wuraiah, Bih and Tawean. Hydrochemical and isotopic data (^{18}O , ^2H and ^3H) have clearly showed a meaningful contribution to the recharge from the dams. A tentative isotopic balance based on stable isotopes of rains water stored by these dams drove to a quantification of the artificial recharge ranging from 20 to 40%.

Isotopic composition of precipitation and water from the Red River in Hanoi, North Vietnam

Nhan, D.D., Bich Lieu, D.T., Van Giap, T., Minh, D.A., Anh, V.T.,
Hong Thinh, N.T., Van Hoan, N.

Isotope Hydrology Laboratory, Institute for Nuclear Science and Technology, 5T-160 Hoang Quoc Viet, Cau Giay, Ha Noi, Vietnam

E-mail: ddnhan@mail.vaec.gov.vn

Results of 3 years (2003-2005) consecutive monitoring for isotopic composition of rainwater and water from the Red River in Hanoi (21°03N, 105°51E) are presented. The water samples were collected on monthly basis followed by the IAEA/WMO Technical Procedure for Sampling for ^3H , $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analysis. Maximum analytical uncertainties in ^3H , $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were $\pm 0.4\text{TU}$, $\pm 1.5\text{‰}$ and $\pm 0.15\text{‰}$ respectively. The accuracy of the analysis was proved by sample split with the IAEA Isotope Hydrology Laboratory and by using reference water with certified values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$. The monthly ^3H activity in rainwater of the Hanoi station (21°01N, 105°48E) varies within (3.58 ± 1.51) TU but that in water from the Red River was (4.14 ± 1.45) TU. The variation of monthly ^3H activity in the precipitation in Hanoi was fit well with a model derived from the regression of ^3H activities on latitude, altitude, precipitation and surface air temperature for the Asian region. The equation for local meteoric water line of monthly data was found to be $\delta^2\text{H} = 8.55 * \delta^{18}\text{O} + 15.16$ ($R^2 = 0.99$), while the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ relation for water from the Red River was $\delta^2\text{H} = 7.65 * \delta^{18}\text{O} + 7.02$ ($R^2 = 0.79$). The correlations of monthly $\delta^{18}\text{O}$ vs. monthly precipitation (PREC, mm) and surface air temperature (T, °C) were derived as $\delta^{18}\text{O} = -0.03 * \text{PREC} - 0.65$ ($R^2 = 0.64$) and $\delta^{18}\text{O} = -0.55 * T + 9.1$ ($R^2 = 0.41$), respectively. The obtained data are being used by the local scientists and managers to improve their sustainable water resources development in the Hanoi area. Additionally, the Hanoi station with its continued monitoring activity could be a potential member of the existing GNIP.

**Origin of the salinity of the alluvial aquifer of Geulta Zergua,
Morocco: a case study**

Zine, N., Abddaim, L., Zerouali, A., Krimissa, M.

Secretary of State in Charge of Water, Rabat, Morocco

E-mail: faqir@water.gov.ma

The city of Tantan, whose local water resources are very limited, is provided currently from the aquifer of Guelmim city. In the objective to relieve this aquifer and to meet the growing needs of the city of Tantan, a dam site has been identified on the Draa River for the artificial recharge of the alluvial aquifer of Guelta Zergua. This option will permit us to avoid the loss of Draa River water toward the sea and to exploit this resource by pumping for the socioeconomic development of the region. The chemical quality of the water of Guelta Zergua aquifer is mediocre, therefore a study based on hydro chemical and isotopic analysis have been done in the purpose to determine the origin of the salinity of water. The obtained results through these analyses agree perfectly with the findings getting from the hydrogeology analysis of the zone.

Use of the isotope techniques to estimate recharge sources of groundwater in the upper part of Nambo Plain (Vietnam)

Nguyen, K.C., Huynh, L., Le, V.K.

Center for Nuclear Techniques, Hochiminh City, Vietnam

E-mail: ttkthn@hcm.vnn.vn or nkienchinh@yahoo.com

Estimation of recharge ability to groundwater from surface water is part of the program on investigation, development and management of groundwater resources in Nambo plain, Vietnam. After the investigation on possibility of recharge from river water in the upper part of Nambo plain, isotope techniques were used to estimate the recharge to shallow groundwater from Dau-Tieng reservoir, the biggest reservoir in Nambo plain. According to the observation data of groundwater levels around the reservoir, a network of 45 sampling points was set up for groundwater, reservoir, and precipitation. Based on the obtained isotopic data of reservoir water, groundwater and local precipitation, the mixing ratio of reservoir water in adjacent shallow groundwater has been estimated. Isotopic results show that water from Dau-Tieng reservoir recharges the shallow groundwater with the contribution at some places up to 30%. Results obtained will be used to estimate recharge rate from the surface water sources in this area to the groundwater.

Geochemistry and isotope evolution of groundwater flow and recharge from the uranium production center in Brazilian semi-arid region (Caetité-BA, Brazil) – towards sustainability or shortage?

Lamego Simões Filho, F.F.^a, Aravena, R.^b, Fernandes, H.M.^a

^a Institute of Radiation Protection and Dosimetry (IRD/CNEN), Rio de Janeiro, Brazil

^b University of Waterloo, Ontario, Canada

E-mail: flamengo@ird.gov.br

The semi-arid region of the Northeast of Brazil is characterized by a lack of superficial waters due to the low pluviometric precipitation and high evaporation rates. Owing to these adverse climatic conditions, intense pressure is being put on the use of groundwater resources. However, there is still insufficient knowledge of the basic aquifers characteristics leading to an over exploitation of the water resources. The prevalence of crystalline rocks is connected to a fracture aquifer type of low productivity, where wells show, generally, yield rates lower than $3 \text{ m}^3 \cdot \text{h}^{-1}$. This work was developed in a semi-arid area located in the center-south region of Bahia State at 900 metres a.s.l., where were discovered several radioactive anomalies by aerogeophysical surveys performed during 70's decade, that allowed to set the uranium province named Lagoa Real. There were performed isotopic and geochemical analysis of groundwater sampled from twenty-five wells placed in crystalline rocks areas (granite or gneiss) covered by short layers of residual soil or alluvial sediments. The samples were analysed in a mass spectrometer for stable isotopic ratios, like $\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ (‰ VSMOW) and also measured for radiocarbon activity concentration (^{14}C) to calculate the percentage of modern carbon (PMC) by AMS. The values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ defined a local evaporation line (LEL) with slope equal to 4.6 against the value of 7.4 for the Local Meteoric Water Line (Salvador station from 1972 to 1976). The radiocarbon ages, corrected by carbonate dissolution (through $\delta^{13}\text{C}$ and DIC), showed very young waters that were recently recharged, perhaps during the last few years to several months. The supposed old ages for the fractured aquifer are not accomplished by radiocarbon dating, showing it is unconfined with no discharge of old groundwater through deep faults and short residence time. Thus, the groundwater offer for multiple uses (in terms of quantity) seems to be assured if the future demand does not increase too much.

Quantification of the heterogeneity in water transport through the unsaturated zone of sandy soils using environmental isotopes

Stumpp, C., Maloszewski, P., Stichler, W.

GSF-Institute of Groundwater Ecology, D-85764 Neuherberg, Germany

E-mail: christine.stumpp@gsf.de

A new method, which combines mathematical modelling with environmental and hydrological data, was investigated to estimate the heterogeneity of the unsaturated soils by separation of preferential and matrix flows, quantify both fluxes and determine their transit times. Finally, the transit time distribution functions were used to construct vulnerability diagrams of different soils without plants. The model complexity was simplified using a lumped parameter approach that combines an input and output function of environmental tracer contents with hydraulic measurements. Assuming a two parallel flow-paths model the environmental deuterium (^2H) with its seasonal variation in precipitation and in lysimeters outflow was taken to estimate the mean transit times as well as the amount of preferential and matrix flow and enabled to quantify the heterogeneity of seven sandy lysimeters ($L = 2 \text{ m}$, $A = 0.125 \text{ m}^2$) installed at the area of the GSF, Germany. The calculations were performed using weekly ^2H contents in precipitation and discharge during an eight year period. The fraction of preferential flow directly appearing in the outflow within one week, varied between 17% and 30%. The amount was practically independent from the texture and flow rates. The crucial parameter influencing the fraction of preferential flow was found to be the saturated hydraulic conductivity (K_s). The vulnerability diagrams yielded different patterns for all soil materials depending on the mean water content and the saturated hydraulic conductivity. Coarser material with low mean water content and high K_s showed a short mean transit time for the matrix flow (about 10 weeks) and mean preferential flow equal to or higher than 20%. Finer sand with lower K_s and higher mean water contents resulted in mean transit times of approximately 30 weeks and preferential flow of about 20%.

Compound-specific chlorine stable isotope of vinyl chloride by continuous flow-isotope ratio mass spectrometry (CF-IRMS)

Shouakar-Stash, O.^a, Frape, S.K.^a, Gargini, A.^b, Pasini, M.^b, Drimmie, R.J.^a, Aravena, R.^a

^a Department of Earth Sciences, University of Waterloo, 200 University Ave. W., Waterloo, Ontario, Canada

^b Department of Earth Sciences, University of Ferrara, Italy

E-mail: orfan@uwaterloo.ca

A new method for determining compound-specific chlorine stable isotope was developed for vinyl chloride (VC). The analysis is carried out on a continuous flow-isotope ratio mass spectrometer (CF-IRMS) with special collectors for m/z 64 and 62. The precision of this technique is better than $\pm 0.16\text{‰}$ (1σ) for pure phase gas injection and head-space SPME injection. The new methodology was tested in a confined sandy aquifer contaminated with VC located near the city of Ferrara, northern Italy. ^{37}Cl and ^{13}C data on VC showed the contamination is related to the use of VC in the production of PVC manufactured in the Ferrara region during the 70's and 80's. The isotope data also showed VC is attenuated by biodegradation along the groundwater flow system. The development of compound-specific isotope analysis (CSIA) for VC offers a new tool for fingerprinting sources and processes that affect VC in groundwater.

Isotopic study of the water exchange between atmosphere and biosphere at selected sites in Pakistan

Ali, M., Latif, Z., Fazil, M., Qureshi, R.M., Ahmad, M.

Isotope Application Division, Pakistan Institute of Nuclear Science and Technology,
P. O. Nilore, Islamabad, Pakistan

E-mail: mubarik@pinstech.org.pk and mubarik_ali2004@yahoo.com

Study of water exchange between atmosphere and biosphere was initiated to understand the ties between these two spheres. Main objective of this study is to acquire sufficient environmental isotopic data for the exploration of water cycle dynamics in selected areas of Pakistan, in order to contribute to the IAEA global network for the development of regional scale model on ecosystems. Isotope investigations (^{18}O , ^2H) help evaluate the major processes such as photosynthesis, respiration and evapotranspiration. From January 2005 to April 2005 non woody plants (wheat, grass) and soil samples from wheat and grass fields (from the surface and 7cm below the surface) were collected. Moisture contents from these samples were extracted using the vacuum distillation method and analysed for hydrogen and oxygen isotope contents. Air moisture was also collected in the field. Woody plants consisting of eucalyptus, pine, delbergia sisso, melia azedarch were sampled from Islamabad. Seventeen more species of woody plants are included in the study, from another site, located near Lahore. Data depicts that the leaves of the wheat plant are more enriched in ^{18}O and ^2H than other parts of the same plant and grass. It may be due to the process of evapotranspiration which is more rapid from the wider leaves as compared to the small ones. Rain effect was also observed on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the samples collected just two days after the rain event. Isotopic values of this rainwater were more negative as compared to other rain events that took place during this season. This depletion may be due to the “continental effect” in precipitation. More than 200 samples from woody plants of different species and soil were collected. Isotopic data of the moisture extracted from leaves and stems of the plants of different species indicate that leaves of all the plants are more enriched in ^2H and ^{18}O than that of the respective stems. There also seem some considerable species-specific effects transforming the isotope ratios of hydrogen and oxygen available for incorporation into plant metabolites relative to the water available for growth.

The necessity for monitoring the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ relationship during tracer experiments carried out with deuterium under monsoon conditions in lands under flood irrigation

Schumann, S.^a, Stichler, W.^b, Herrmann, A.^a

^a Institute of Geoecology, Technical University Braunschweig, Braunschweig, Germany

^b GSF-Institute of Groundwater Ecology, Neuherberg, Germany

E-mail: s.schumann@tu-bs.de

If environmental isotopes (^{18}O or ^2H) are used as artificial tracers in infiltration studies their natural variation can be established as an input function during the duration of the experiment. In on other study Stichler et al. proposed a mathematical formula to calculate the weighted input function of a mean constant infiltrating amount, which can be applied considerably well in temperate climates. Exemplarily will be shown that in areas with a monsoonal climate which underlay strong irrigation the establishment of such an isotope input function is not practicable. Here, the determination of the input function depends mainly on the mixing ratio of precipitation and irrigation water and on the permanently changing infiltration rates due to the irrigation. The investigation was carried out in Nepal at an experimental site that is characterised by a monsoon climate with a mean precipitation amount of 1250 mm/year, hereof 85% falling from May to September. The rain stable isotopic content falls, generalized, continuously from positive to negative values during the rainy season. The water for ponding and furrow irrigation is taken from a nearby river that shows a seasonal isotope variation with maximum in the end of May and minimum in November. The tracing experiment that aimed on the determination of the percolation flux for a transport study was carried out with 1 L 85% D_2O on a 10m^2 test field. The presented study shows that if deuterium is used under these conditions as an artificial tracer the results drawn from the tracer experiments may be misleading unless the deuterium excess is used as the parameter of interpretation instead of the $\delta^2\text{H}$ -value.

Tritium/Helium-3 dating of baseflow - Southern Vienna Basin

**Solomon D. K.^a, Rank, D.^b, Aggarwal, P.^c, Suckow, A.^c, Stolp, B.^a,
Gröning, M.^c, Vitvar T.^c**

^a Department of Geology & Geophysics, University of Utah, Salt Lake City, UT
84112, USA

^b Institut für Geologische Wissenschaften, Universität Wien, Vienna, Austria

^c Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: ksolomon@earth.utah.edu

Long-term time series of tritium in baseflow provide an indicator of the mean subsurface residence time (MRT) and hence a useful index of vulnerability/sustainability of surface water. Unfortunately, long-term times series are uncommon. We are investigating the use of tritium/helium-3 dating as a substitute for long-term time series in the Southern Vienna Basin, Austria. Preliminary results indicate that the apparent age of the water depends on sampling location and depth below the top of the stream. Apparent tritium/helium-3 ages range from about 1 to 7 years with the oldest ages occurring near or below the water sediment interface at upstream locations near springs and seeps. We have evaluated the exchange of helium-3 with the atmosphere by simultaneously measuring CFCs and applying a gas exchange model. The model was then used to predict the observed change in the helium-3 (and hence apparent tritium/helium-3 age) with excellent agreement to observed values. This result suggests that while gas exchange is an active mechanism for noble gases in streams, it is possible to predict this exchange and hence “correct” tritium/helium-3 ages for this process.

Radionuclide tracers of submarine groundwater discharge

Moore, W.S.

University of South Carolina, Columbia, SC, USA

E-mail: moore@geol.sc.edu

Radionuclide tracers have the ability to assess the flux of submarine groundwater discharge (SGD) over a range of temporal and spatial scales. Short-lived isotopes such as ^{222}Rn , ^{224}Ra , and ^{223}Ra can reveal sites where SGD impacts the coastal ocean and elucidate relationships between SGD and ocean forces such as tides and storms. Longer-lived isotopes such as ^{228}Ra and ^{226}Ra integrate the effects of SGD over longer scales. These isotopes can discriminate sources of SGD and evaluate total fluxes. This paper will investigate the application of radionuclide tracers to SGD in a variety of settings on different continents.

Possibilities for applying gamma-spectrometry software ANGLE in isotope hydrology analytical procedures

Jovanovic, S.^a, Dlabac, A.^b

^a University of Montenegro, Faculty of Sciences, Laboratory for Nuclear Spectrometry, P.O.Box 211, Cetinjski put bb, 81000 Podgorica, Montenegro

^b Centre for Eco-Toxicological Research of Montenegro, Department for Radiation Protection and Monitoring, P.O.Box 374, Put Radomira Ivanovica 2, 81000 Podgorica, Montenegro

E-mail: bobo_jovanovic@yahoo.co.uk

ANGLE software for gamma-spectrometry (semiconductor detector gamma-efficiency calculations, in particular) in its various forms has been in use for 15 years in numerous gamma-spectrometry laboratories all around. ANGLE is basically a semi-empirical model for efficiency calculations, which combines the advantages of both absolute and relative approach, while attempting to minimize their drawbacks. The physical model behind is the concept of the effective solid angle, which is calculated upon the input data on the geometrical and physical characteristics of (1) the source (including the container vessel), (2) the detector and (3) the counting arrangement (including intercepting layers between the latter two). It was shown earlier that only the simultaneous differential treatment of gamma-attenuation, geometry and detector response, as in ANGLE, is essentially justified for this type of calculations. The program can be applied to practically all counting situations encountered in laboratory practice: point, disc, cylindrical or Marinelli sources and any matrix composition. No standards are required, but a so called "reference efficiency curve" should be obtained ("once for ever") by measuring a set of calibrated point sources. As a summary, ANGLE is characterized by (1) a very broad application range, (2) satisfactory accuracy (of the order of a few percent), (3) easy data manipulation (under WINDOWS), (4) short computation times, (5) flexibility in respect with input parameters and (6) suitability for didactical purposes. Possibilities for applying ANGLE in isotope hydrology analytical procedures (e.g. with radioactive tracers involved), are discussed. Tracer techniques are of particular interest for water resources management in Mediterranean karstic regions, typically abundant with precipitation in winter, but scarce with ground waters in summer - like is the case with east coast of Adriatic, including the coastal part of Montenegro.

Contribution of isotopic indicators to the assessment of groundwater mixture between continental Intercalaire and Djeffara aquifers (South-Eastern Tunisia)

Trabelsi, R.^a, Charfi, S.^a, Chkir, N.^a, Abidi, B.^b, Zouari, K.^a

^a Radio-Analysis and Environment Laboratory , ENIS, Sfax, Tunisia

^b Direction of Water Resources, Commissariat au Développement Agricole in Gabes

E-mail: rimaenis@yahoo.fr

The Continental Intercalaire and the Djeffara aquifers are the most important groundwater resources in Southern Tunisia. Previous hydrogeologic and isotopic studies (^{18}O , ^2H , ^3H , ^{14}C) allow to define main hydrodynamic and hydrochemical characteristics for each aquifer. Continental Intercalaire aquifer which has important reserves is very old with low ^{14}C activities and very depleted values of stable isotopes (^{18}O , ^2H). That is why this aquifer is considered as fossil and non renewable resources. Compared to the Continental Intercalaire aquifer, Djeffara aquifer has more scattered stable isotopes values which confirms that there are different water origins. Near to the El Hamma faults, isotopic contents of Djeffara aquifer are very similar to the isotopic signature of the Continental Intercalaire indicating mixing flows between the two systems and showing that the recharge of Djeffara of Gabes is partially ensured by the discharge of the old water of the Continental Intercalaire through faults of the region.

Contribution of isotopic indicators to groundwater assessment and management in Grombalia Plain (North-Eastern Tunisia)

Ben Moussa, O.^a, Charfi, S.^a, Chkir, N.^a, Zouari, K.^a, Oueslati, M.N.^b

^a Radio-Analysis and Environment Laboratory, National School of Engineering, Sfax, Tunisia

^b Regional Direction of Water Resources Management, Nabeul, Tunisia

E-mail: najiba_chkir@yahoo.fr

Grombalia plain, situated in the Northeast of Tunisia, contains a very important multilayered aquifer. However, the exploitation rate of shallow groundwater resources reaches 170% in order to answer the increasing needs of socio-economic development and especially agricultural sectors. Irregular climate conditions combined with increasing human constraints have lead as main consequences to the depletion of water level and to the salinisation of groundwater along the coast enhancing the risk of marine intrusion. Multidisciplinary studies have been realised on this aquifer for the assessment of groundwater resources. Hydrochemical results indicate that shallow and deep groundwater show similar type of water facies highlighting vertical hydraulic communication between these different levels. Isotopic tracers (^{18}O , ^2H , ^3H , ^{14}C) confirm the existence of groundwater mixture between different depth and level. On the other hand, shallow groundwater present high ^{14}C activity indicating a direct infiltration of rainfall.

Isotopic and geochemical impact of water releases from the Sidi Saâd Dam on groundwater in Kairouan plain (Central Tunisia)

Belhadj Salem, S.^a, Chkir, N.^a, Zouari, K.^a, Beji, R.^b

^aRadio-Analysis and Environment Laboratory, National School of Engineering, Sfax, Tunisia

^bRegional Direction of Water Resources Management, Kairoun, Tunisia

E-mail: najiba_chkir@yahoo.fr

Kairouan plain, big endoreic sedimentary basin of 3000 km², contains the most important aquifer of Central Tunisia. The importance of this aquifer is due first to groundwater reservoir dimension and then to high recharge rates by the main wadis (Zeroud and Merguellil) floods and by direct rainfall infiltration. However, since the building of the great dam of Sidi Saâd on oued Zeroud to protect the plain against flooding, natural recharge decreases. Even if regulated dam releases are planning, a regular depletion of water level is observed due to over exploitation by high anthropic needs. Geochemical and isotopic studies have been realized in order to quantify the efficiency of artificial recharge. A short time-interval sampling campaign (15 days) has been carried out during the dam release of May 2005 in order to follow up the impact of dam water which geochemical and isotopic signatures are well identified on groundwater characteristics.

Spatial variations of environmental tracers distribution in water from a mangrove ecosystem: the case of Babitonga Bay (Santa Catarina, Brazil)

Barros, G.V.^{a,b}, Martinelli, L.A.^c, Pla, J.M.^d, Oliveira, N.T.M.^b, Ometto, J.P.^c, Sacchi, E.^d, Zuppi, G.M.^a

^a Dipartimento di Scienze Ambientali, Università Ca' Foscari, Dorsoduro 2137, 30123 Venezia, Italy

^b University of Univille, Joinville, Santa Catarina, Brazil

^c Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, Brazil

^d Dipartimento di Scienze della Terra, Università di Pavia, Via Ferrata 1, 27100 Pavia, Italy

E-mail: barros@unive.it

The hydrologic complex of Babitonga Bay (Brazil) forms a vast environmental complex, where agriculture, shellfish farming, and industries coexist with a unique natural area of Atlantic rain forest. The origin of different continental hydrological components, the environmental transition between saline and fresh waters, and the influence of the seasonality on Babitonga Bay waters are evaluated using isotopes and chemistry. The end of the dry season is marked by a fast response of continental water to the first rainfall, while in the Bay this change is delayed in time. At the end of the rainy season waters show a more homogeneous isotopic composition, suggesting the harmonisation of hydrological and hydrogeological systems. Moreover $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of DIC, and POM allows for the definition of the biogeochemical processes originating and transporting chemical compounds in the coastal and transition areas and for the determination of three distinct end-members: terrestrial, marine and urban.

Application of compound-specific carbon and chlorine stable isotopes for fingerprinting sources of chlorinated compounds in groundwater

Aravena, R.

Department of Earth Sciences, University of Waterloo, Waterloo, Canada

E-mail: roaraven@sciborg.uwaterloo.ca

The identification of contaminant sources is one of the key aspects that consultants and environmental agencies have to deal with when investigating groundwater contamination providing the basis for assignment responsibility for groundwater remediation. Environmental isotopes offer a unique approach for fingerprinting sources of organic contaminants in groundwater. This paper presents the first novel application of the combined use of ^{37}Cl and ^{13}C to evaluate the contribution of two sources to trichloroethene (TCE) contamination. The first source consists of an on-site TCE source, the second of an off-site TCE source producing TCE by biodegradation. The site is located in Pleasant Hill, California and the contamination is located in unconfined to semi-confined sand stringers within a fairly tight silty clay matrix aquifer and a deeper confined aquifer consisting of sand beds. The stable isotope data showed a very distinct and significantly different isotopic fingerprint for the primary source of TCE compared to the off-site source. The different signatures make it possible to relate downgradient contamination to the respective sources and clearly demonstrate that the off-site source contributes to TCE contamination at the site. These results demonstrate the great potential of the combined use of ^{37}Cl and ^{13}C for fingerprinting organic contaminant sources in groundwater.

Evaluation of origin of the Ayaş-Beyşehir geothermal waters with sulfur isotopes, Central Anatolia, Turkey

Çelik, M.

Ankara University, Engineering Faculty, Geological Engineering Department,
Tandoğan 06100 Ankara, Turkey

E-mail: alan.celikm@eng.ankara.edu.tr

The aim of this study is to investigate the origin of sulfate in deeply circulating thermal waters around the Ayas-Beyşehir region in Turkey. The waters of Ayas resorts and Çoban bath are of Na-Cl-SO₄ hydrochemical facies and waters of Kapullu and Dutlu thermal resorts are represented with Na-SO₄-Cl hydrochemical facies. Kirmir Formation gypsum minerals in Mio-Pliocene age have sulfur-34 isotopes between 17 and 25‰. According to oxygen-18 (SO₄) and sulfur-34 (SO₄) contents, sulfate in waters of Ayas and Dutlu resorts and Çoban bath is derived from gypsum of Kirmir Formation of primary source. Sulfates of Kapullu bath water and Karakoca mineral water may be originated from atmospheric and terrestrial environments, respectively. Among the cold groundwaters, sulfate of Tahirler fountain is derived from gypsum in the Kirmir Formation (primary source) and sulfate in Kapullu cold water is originated from a secondary origin (atmospheric). Sakarya River water sulfate is probable originated from atmospheric and terrestrial environments.

Surface water - groundwater interactions in transition environments: the example of the Rio de la Plata coastal plain, Argentina

Del Soldato, S.C.^{a,b}, Hernandez, M.^b, Kruse, E.^c, Panarello, H.^d, Pera Ibarguren, S.^{a,e}, Zuppi, G.M.^a

^a Dipartimento di Scienze Ambientali, Università Ca' Foscari di Venezia, Dorsoduro 2137, 30123 Venezia, Italy

^b CISAUA, Cátedra. de Hidrogeología. Universidad Nacional de La Plata, Calle 3 Nro. 584 – 1900, La Plata, Argentina

^c CONICET, Departamento de Geofísica Aplicada, Facultad de Ciencias Astronomicas y Geofisicas, Universidad Nacional de La Plata, Paseo del Bosque s/n, 1900 La Plata, Argentina

^d INGEIS, Instituto de Geología y Geocronología Isotópica, Ciudad Universitaria, 1428 Buenos Aires. Argentina.

^e Istituto Scienze della Terra, SUPSI, C.P. 72, CH-6952 Canobbio, Switzerland

E-mail: hector@ingeis.uba.ar

Environmental isotopes were successfully used to trace surface water-groundwater interactions in a multilayer aquifer system, and to propose a conceptual model for the hydrogeological systems of Rio de la Plata Coastal Plain. The objective of this work was to identify the surface water contribution to the recharge of the aquifers. A monitoring network of 50 wells for isotopic and geochemical analysis was established, covering different aquifers. According to the results a hydrogeological model has been proposed. The phreatic aquifer is directly recharged by the Rio de la Plata during level oscillations and indirectly during flooding events by feeding the marshes acting as recharge ponds. Artificial and natural channels act also as recharging lines. The recharge of the semi-confined aquifers occurs through lateral flow driven by the induced permanent landward gradients. River acts as a positive barrier, and beyond it, there is no possibility for the depression cones to expand.

Use of environmental isotopes of hydrogen and oxygen to determine Red River and groundwater mixing in Hanoi area of Vietnam

Van Giap, T., Dac Luc, H., Duc Nhan, D.

Institute for Nuclear Science and Techniques, VAEC, Vietnam

E-mail: tvgiap@mail.vaec.gov.vn

The paper presents the interaction between groundwater and surface water such as water of Red River together with water of large lakes in Hanoi area. The isotope data show that almost groundwater in study area is recharged in modern time and only one position in the south has the oldest age of 1100 years; Proportions of the Red River water in groundwater depend on the distance to the Red River; Groundwater of six Groundwater Production Stations is mostly recharged by Red River water in the rainy season when the water level of Red River is high; In the Ngoc Ha Station, producing groundwater relates to water of West Lake; Groundwater of Ha Dinh, Mai Dich, Phap Van Stations is the mixture of Red River water and meteoric water and the proportion of Red River water in these Stations is following 50%, 52% and 57%. Stable isotope ^{18}O was also used for determining the resident time of groundwater recharged by Red River water at some groundwater producing boreholes of Yen Phu Station.

Isotope and chemical techniques in assessing groundwater contamination from Metro Manila landfill

**Castañeda, S.S.^a, Almoneda, R.^a, Fernandez, L.^a, Sucgang, R.^a, Iblan, C.L.^b,
Bauí, D.G.^b**

^a Philippine Nuclear Research Institute, Commonwealth Avenue, Diliman, Quezon City, Philippines

^b Manila Water Company, Balara Road, Diliman, Quezon City, Philippines

E-mail: sscastaneda@pnri.dost.gov.ph

Investigations were conducted to establish benchmark isotopic characteristics of water sources and baseline concentrations of trace elements related to contamination from the Montalban landfill. Water samples were collected from the production wells and surface water in Rodriguez and in San Mateo, both in the province of Rizal. These municipalities are nearest to the Montalban landfill. Stable isotope characterization of the deep groundwater and rivers shows isotopic values clustering along the LMWL with $\delta^{18}\text{O}$ ranging from -7.5‰ to -6.5‰ and $\delta^2\text{H}$ ranging from -53.59‰ to -42.91 . The shallow groundwater are more isotopically enriched trending towards the evaporation line, with mean $\delta^{18}\text{O}$ and δD values of -6.46‰ and -44.14‰ , respectively, The mean isotopic signatures of surface water, with mean $\delta^{18}\text{O}$ of -7.19‰ , and deep groundwater, with mean $\delta^{18}\text{O}$ of -6.67‰ , in Rodriguez are significantly distinct. San Mateo groundwater appear to be more isotopically enriched, indicating recharge different from that of Rodriguez groundwater. Leachate from the landfill exhibits a distinct isotopic composition from the freshwaters, with most enriched δD values of $+5.84\text{‰}$ for the leachate run-off and $+16.55\text{‰}$ in the leachate pond. The significant differences in the isotopic signatures of the different water sources in the study area facilitates detection of contamination from leachate run-off to the surface water, and eventually, to the groundwater. Trace metals in the water samples collected, generally, were below the regulatory limits for drinking water and surface water.

Geostatistical methods for producing stable isotope maps over Central and Eastern Mediterranean

Argiriou, A.^a, Lykoudis, S.P.^b

^a Laboratory of Atmospheric Physics, Dept. of Physics, University of Patras, GR-265 00 Patras, Greece

^b National Observatory of Athens, Institute for Environmental Research, Athens

E-mail: argiriou@physics.upatras.gr

Stable isotopes of water, namely ^{18}O and ^2H , have been extensively used during the last decades to address key aspects of the water cycle. Several scientific disciplines, such as hydrology, meteorology, palaeoclimatology or ecology have adopted isotopes as powerful tracers characterizing certain systems and processes. As a result several isotope databases have been created yet in most cases, the use of the data has been restricted to specific applications, possibly due to their spatial coverage. Using geostatistical methods to develop isotope maps would allow for a much broader use of isotopic data in many countries. To that end GNIP-ISOHIS isotopic precipitation data were used to generate isotopic maps of the precipitation over the Central and Eastern Mediterranean. The monthly data set was checked for outliers and then local meteoric water lines were used to complete missing values wherever possible. Simple regression models were developed to relate monthly weighted average, annual and seasonal, point isotopic values with corresponding meteorological data extracted from the CRU CL 2.0TS 2.1 gridded climatologies. The empirical models were then applied to the full gridded data sets to produce gridded isotopic datasets. Finally the residuals of the empirical models were gridded using ordinary kriging and added to the isotopic grids. The resulting grids appear to reproduce the known isotopic patterns of the area. A crosschecking was attempted with gridded data obtained by objective analysis, yet a more detailed assessment of the performance of this methodology is needed.

**Isotopic and chemical study of Lake Massaciuccoli, Tuscany:
hydrodynamic patterns, water quality and anthropogenic impact**

**Baneschi, I.^a, Gonfiantini, R.^a, Guidi, M.^a, Michelot, J.-L.^b, Pennisi, M.^a,
Zuppi, G.M.^c**

^a Institute of Geosciences and Georesources, CNR - Via Moruzzi 1, 56124 Pisa,
Italy

^b UMR IDES CNRS-Université Paris-Sud, BAT 504 - 91405 Orsay, France

^c Department of Environmental Science, Università Cà Foscari - Dorsoduro 3246,
30123 Venezia, Italy

E-mail: i.baneschi@igg.cnr.it

Lake Massaciuccoli (7 km², 15 km north of Pisa, Tuscany), occupies a shallow depression on a coastal marshy plain. The lake is connected to the sea by 8 km channel with sluices flowing through an old sandpit pond. Hydrochemistry and stable isotopes are applied to investigate water, salt and nutrient inputs into the lake from drainage channels, groundwater and the sea. In general, the ion concentrations plotted versus Cl⁻ suggest mixing with seawater, but do not allow to discriminate between contributions of continental water versus seawater – which vary seasonally – nor between those from farming practices and redox processes. Vice-versa, hydrochemistry and isotopic tracers (²H, ¹¹B, ¹³C, ¹⁸O, ³⁴S) combined together, highlight the water mass dynamics and the role of continental waters, show the organic matter cycles and the anthropogenic contributions, and allow to define the main redox processes and their rates.

Origin and effects of nitrogen pollution in groundwater traced by $\delta^{15}\text{N}_{\text{-NO}_3}$ and $\delta^{18}\text{O}_{\text{-NO}_3}$: the case of Abidjan (Ivory Coast)**Oga Yei, M.S.^a, Sacchi, E.^b, Zuppi, G.M.^c**^a Université de Cocody UFR-STRM, Abidjan, Ivory Coast^b Università di Pavia, Italy^c Università di Venezia, Italy

E-mail: oga_oms@yahoo.fr

Groundwater resources of area of Abidjan are heavily impacted by nitrate pollution. A survey on 13 wells providing drinking water to the city was conducted in 2005, considering stable isotopes of the water molecule and of dissolved compounds (^{13}C and ^{15}N), major and trace elements. Nitrogen isotopes allow to define the origin of nitrate contamination, mainly from urban sewage, and the processes controlling its distribution. This information, coupled to hydrogeology and groundwater geochemistry highlights major changes in groundwater quality. Nitrate content is associated to an increased acidity of poorly buffered solutions in a geochemically open system and therefore is not affected by denitrification. Dissolved inorganic carbon confirms an input from organic matter decomposition, related to both pollution and diagenesis. This geochemical evolution is observed in both Quaternary and Continental Terminal aquifers, and is independent on depth. The comparison with previous hydrochemical data suggests a rapid decline in groundwater quality.

Hydrochemical and isotopic study of Al-Mouh Sabkha evaporatic system (Syria)

Abou Zakhem, B., Hafez, R.

Atomic Energy Commission of Syria (AECS), P.O. Box 6091, Damascus, Syria

E-mail: babouzakhem@aec.org.sy

Al-Mouh Sabkha is considered as one of the biggest and most important sabkhas in Syria; it represents the local hydrological basis and the final drainage area of surface water and of a great amount of groundwater. Whereas all the streams from surface basins terminate in the sabkha that dries in the summer but groundwater is still very near (0.5 to 2 m) to the ground level. The aquifer consists of Quaternary debris, which is sand and sandy clay with lense-shaped gypsum crystals sometimes have gravel shape. The salinity of water in the sabkha reached 200 g/L. Generally, this water is sodium chloride or calcium sulphate type characterized by very strong smell of H₂S gas. In the border of the sabkha there are many fresh water aquifers. However, deep aquifers are artesian, relatively fresh and good for agricultural purposes. In order to use isotopes, two profiles were drilled in the sabkha for preliminary estimation of evaporation values through the unsaturated zone, to apply the hydrochemical model to estimate the mixing ratio between the shallow water and the artesian Upper Cretaceous aquifer without evaporation process, and with an extensive evaporation process and precipitation of mineral phases in the sabkha. The isotope (¹⁸O and ²H) enrichment peak caused by evaporation is determined at 12 cm depth, the main evaporation front is located between the surface and 45 cm depth, the lower part of the unsaturated zone profile is prone to the capillary effect, where there is upward vertical movement. The evaporated water quantity through the unsaturated zone in the sabkha was determined to be about 18 Mm³/y using Barnes and Allison model, in addition to the direct evaporation quantity from the water surface in the flood period, and from the salt masles. The mixing ratio in the sabkha was evaluated using Hydrowin and Netpath programs, it was about 15-20% from surface water and 80-85% from groundwater in the upper cretaceous artesian aquifer through the upward infiltration. The mixing with extensive evaporation process and precipitation of mineral phases as calcite, dolomite then gypsum and anhydrite, finally, halite, chloride and H₂S gas, that causes a high salinity of residual water in the sabkha assuming that all the surface water is evaporated completely.

Tracing nitrification and denitrification processes in a periodically flooded shallow sandy aquifer

Sacchi, E.^a, Pilla, G.^b, Allais, E.^c, Guallini, M.^b, Zuppi, G.M.^d

^a Dipartimento di Scienze della Terra, Università di Pavia and CNR-IGG, Pavia, Italy

^b Dipartimento di Scienze della Terra, Università di Pavia, Italy

^c ISO4 s.s., Pavia Italy

^d Dipartimento di Scienze Ambientali, Università di Venezia, Italy

E-mail: elisa.sacchi@manhattan.unipv.it

The study defines the transfer mechanisms of nutrients and heavy metals from soil to groundwater operating in periodically water saturated soils. The study site is located in Lomellina (Po plain, Northern Italy), which is intensively cultivated with rice. Soils are dominantly constituted by sands, with acidic pH and low organic carbon content. The region generally displays low nitrate contamination in shallow groundwater, despite the intensive land use, while Fe and Mn often exceed drinking water limits. Monitoring performed through a yearly cycle closely followed the water table fluctuations in response to periodical flooding and drying of cultivated fields. pH, conductivity and Eh were measured in the field. Water samples were analysed for major ions, trace elements, nutrients and stable isotopes of DIN. Results evidence the seasonal migration of nutrients, the redox and associated metal cycling, and allow defining nitrification and denitrification processes.

A regional survey on nitrate contamination of the Po valley alluvial aquifer (Northern Italy)

Sacchi, E.^a, Pilla, G.^b, Gerbert-Gaillard, L.^c, Zuppi, G.M.^d

^a Dipartimento di Scienze della Terra, Università di Pavia and CNR-IGG, Pavia, Italy

^b Dipartimento di Scienze della Terra, Università di Pavia, Italy

^c ISO4 s.s., Pavia Italy

^d Dipartimento di Scienze Ambientali, Università di Venezia, Italy

E-mail: elisa.sacchi@manhattan.unipv.it

The origin, distribution and abatement of nitrate contamination in surface and groundwater are traced by hydrochemical and stable isotope analyses. The studied sector of the Po Valley is approximately 3,600 km² wide, extending from the Alps to the Apennine along a N-S transect. The phreatic aquifer is fed by local infiltration and by streams and irrigation channels, while the Po river represents the major discharge axis. The main diffuse source of nitrates is from synthetic fertilisers, exceedingly used for crop raising. Peak concentrations are instead associated to local leakage from sewage network. The distribution of groundwater contamination is closely related to the hydraulic characteristics of the unsaturated zone, to agricultural input and irrigation practices. Denitrification is observed along major draining rivers and below rice fields. Results are interpreted in terms of aquifer vulnerability, groundwater circulation and land use.

Location of recharge area of Gorgovivo Spring, Central Italy: a contribution from isotope hydrology

Tazioli, A.^a, Mosca, M.^b, Tazioli, G.S.^a

^a Marche Technical University, Ancona, Italy

^b Geologist Office, Chiaravalle (AN), Italy

E-mail: a.tazioli@univpm.it

The present study faces the problem of characterization of the recharge zone and the mechanisms of water renewal of the Gorgovivo spring, which feeds the aqueduct of the Ancona province. For achieving with precision the hydrogeological and geochemical dynamics, measures of chemical, isotopic and tritium contents have been used. The presence of different pluviometer stations for measure of rainfall heights and isotopic contents in the precipitations has allowed to draw the altitude gradient which correlates the oxygen-18 content in the underground waters with the isotopic height of infiltration. This value (about -0.24‰ per 100 m) allow to establish around 1400 m asl the intake altitude for Gorgovivo spring. Tritium contents (about 8-13 TU for shallow springs present in the area, 6-8 TU for Gorgovivo spring) and the different isotopic composition indicate the presence in groundwater of a double pathway. The first one is shallow and very fast: to this pathway belong the weeping springs in the studied area. The second pathway is slow and deeper. It reaches the bottom part of bedrock (Massive Limestone). As result, the groundwater recharging Gorgovivo spring can be found as a mixing between these two pathways. The liquid discharge of the spring is exceptional, thus Gorgovivo spring is one among the greatest Apennine springs for importance and quality. Isotopic composition and tritium contents have allowed to investigate the recharge area and the mechanisms of recharge of such spring.

Stable isotopes as indicators of soil water dynamics in watersheds

Brooks, J. R.^a, Barnard, H.^b, McDonnell, J.^b, Coulombe, R.^c, Burdick, C.^a

^a Western Ecology Division, U.S. EPA, Corvallis, Oregon, USA

^b Oregon State University, Corvallis, Oregon, USA

^c Dynamac Corporation, Western Ecology Division, U.S. EPA Corvallis, Oregon, USA

E-mail: Brooks.Reneej@epa.gov

Stream water quality and quantity depend on discharge rates of water and nutrients from soils. However, soil-water storage is very dynamic and strongly influenced by plants. Stable isotopes of oxygen and hydrogen were analyzed to quantify spatial and temporal changes in evaporation, transpiration and stream discharge in a gauged watershed with dry summers and wet winters. The isotope data indicate that plant and soil water have been affected by evaporation. In contrast, stream water is not evaporated, though discharge rates show diurnal cycles driven by transpiration. It is concluded that two separate pools of water are held within the soil. One is a faster moving pool held at relatively weak matric potentials, making it more subject to gravitational transport to streams. The other pool is held more tightly by matric forces, has a longer residence time within the soil, and will more likely be evaporated or taken up by plants.

First results of the isotopic study (^{18}O , ^2H , ^3H) of the Douala Quaternary aquifer (Cameroon)

**Ketchemen-Tandia, B.^a, Ntamak-Nida, M.J.^a, Boum-Nkot, S.^a, Wonkam, C.^a,
Emvoutou, H.^a, Ebonji Seth, C.^a, Aranyossy, J.F.^b**

^a Department of Earth Science, Faculty of Science, University of Douala, Cameroon

^b Agence Nationale pour la Gestion des Déchets Radioactifs (ANDRA) 1-7, rue Jean Monnet, Parc de la Croix-Blanche 92298 Châtenay Malabry CEDEX, France

E-mail: Ketchemen_tandia@yahoo.fr

The quaternary sandy aquifer of the Douala sedimentary basin generally indicates homogeneity in isotopic abundance (^{18}O , ^2H , ^3H) of water sampled at different depths. The large majority of these samples indicated a direct and fast infiltration of the precipitations, without significant evaporation. This homogeneity can moreover be accentuated under the pumping effects, putting in communication various levels of the multilayer aquifer. These results show that pollution from the surface can quickly reach the deeper layers, and seems to corroborate those obtained on the basis of field measurements and chemical analyses.

Characterization of bottled waters with stable isotopes of hydrogen, oxygen and carbon

Brencic, M.^a, Vreca, P.^b

^a Geological Survey of Slovenia, Dimiceva 14, SI-1000, Ljubljana, Slovenia

^b Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

E-mail: mbrencic@geo-zs.si

In recent years bottled waters became popular beverages and important part of the human diet. They are a food product that considerably depends on the environment from which it originates, not only at the place where it is produced, but predominantly on the conditions in the recharge area of the wells captured for bottling. These waters originate from various parts of the hydrological cycle and their natural origin is reflected in their isotopic composition. In stable isotope analyses of bottled waters two investigative approaches can be used; that from hydrology and the other from food analyses. In this study 58 domestic and foreign brands and 16 replicates of bottled waters, randomly collected on the Slovene market in 2004, were analysed for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}_{\text{DIC}}$. This investigation helped (1) to determine and test the classification of bottled waters, (2) to determine the natural sources of bottled water and (3) to discern between the natural and production processes.

Isotope hydrogeochemical investigation on the occurrence of fluoride in groundwaters of Alapuzha District, Kerala, India

Noble J., Shivanna K., Joseph T.B., Deodhar A., Navada S.V.

Isotope Applications Division, Bhabha Atomic Research Centre, Mumbai, India

E-mail: noblej@magnum.barc.gov.in

Environmental isotopes (^2H , ^{18}O , ^3H , ^{13}C and ^{14}C) along with hydrochemical and hydrogeological information were used to understand the source and mechanism of fluoride release into the groundwaters of a heavily exploited multilayered regional aquifer system in Alapuzha District, Kerala, India. The results of the study show that the shallow aquifers are uncontaminated whereas the deep Tertiary aquifers are contaminated with fluoride (up to 2.6 mg/L). The observed positive correlation of F^- with pH, alkalinity, Na^+ and ^{13}C and negative correlation with Ca^{2+} along the flow path point out that the leaching of fluorite bearing aquifer material is responsible for the release of fluoride into the groundwater. F^- vs. ^{18}O plot also confirms the leaching process. The rate of fluoride release is different in various flow paths and it depends upon the residence time of groundwater and length of the flow path. ^2H , ^{18}O , ^3H and ^{14}C data indicate that the contaminated groundwater is very old with ^{14}C ages varying from 15 to 30 ka B.P. in the down gradient and probably recharged during an arid climate in the past.

Submarine groundwater discharge into the Mediterranean Sea: a case study off Monaco

Scholten, J.C.^a, Schubert, M.^b, Schmidt, A.^b, Rutgers van der Loeff, M.M.^c, Schlüter, M.^c, Pham, M.K.^a, Knöller, K.^b, Comanducci, J.-F.^a, Sanchez Cabeza, J.A.^a

^a Marine Environment Laboratories, International Atomic Energy Agency; 4, Quai Antoine 1er, 98000 Monaco

^b Helmholtz Centre of Environmental Research - UFZ, Leipzig, Germany

^c Alfred-Wegener Institute, P.O. Box 120161, D-27515 Bremerhaven, Germany

E-mail: j.scholten@iaea.org

Submarine Groundwater discharge (SGD) is not only a potential fresh water resource, it also represents an important pathway for matter transfer from land to coastal seas. Here we investigate the SGD at Cabbé, a location near Monaco where groundwater from a karst aquifer discharges to the Mediterranean Sea. The discharge was monitored for 24 hours and several parameters (^{222}Rn , ^{223}Ra , ^{224}Ra , ^{228}Ra , ^{226}Ra , salinity, tidal range, nitrate) were measured. The flux of nitrate associated with the SGD to seawater off Cabbé amounts to $\sim 26.4 \text{ mmol}\cdot\text{day}^{-1}\cdot\text{m}^{-1}$ representing an important nitrate source for the local coastal environment. In contrast to ^{222}Rn radium isotope concentrations do not vary with the tidal range indicating that the SGD is not a source of radium at Cabbé. We therefore assume that radium isotopes may not be valuable tracers for SGD in cases of focused groundwater discharge from a karst aquifer. Along two ship transects in the Bay of Roquebrune we measured an increase of ^{222}Rn landwards towards Cabbé reflecting the influence of SGD on the composition of local seawater.

Hydrochemical and isotopic groundwater investigation in the Oltrepo region (Po Valley, Northern Italy)

Pilla, G., Sacchi, E., Ciancetti, G.

Dipartimento di Scienze della Terra, Università di Pavia, Italy

E-mail: gpilla@manhattan.unipv.it

A hydrogeologic investigation was conducted using hydrochemistry and isotope techniques in the lowland of the Oltrepò region (Po valley, Northern Italy). Groundwater generally displays a calcium bicarbonate facies. Along major discontinuities, the Po valley brines moves upward and mix with fresh groundwater. Stable isotopes of the water molecule indicate the main aquifer recharge areas, corresponding to the alluvial fans of the major rivers flowing from the Apennine towards the Po river. The observed different deuterium excess in groundwater relates to the origin of precipitation and the location of the river drainage basins. A hydraulic connection, underneath the Po river, between the deep aquifers of the Lomellina and the Oltrepò is also evidenced, implying that deep groundwater is recharged in the pre-alpine area and is several thousand years old.

Uranium isotopes in mineral waters of the Polish Carpathians

Dulinski, M., Michalec, B., Rozanski, K.

AGH University of Science and Technology, Krakow, Poland

E-mail: dulinski@novell.ftj.agh.edu.pl

Uranium isotopes and other isotopic tracers (tritium, stable isotopes) were investigated in selected mineral and therapeutic waters located in the Polish Carpathians. In total, 32 wells and springs were studied. They represent waters of different mineralization and different origin. In general, the investigated waters are poor in uranium. Its content and isotope activity ratios seem to be controlled mainly by redox conditions and availability of uranium in the rock matrix. In some cases very high uranium activity ratios were detected. They may originate from fluctuations of the redox front induced by changes in exploitation. The paper discusses also methodological issues related to analyses of isotopic composition of uranium in highly mineralized and CO₂-rich waters.

Long-term behaviour of Chernobyl radionuclides in the Dnieper River Basin

Zhukova, O., Bakarykava, Zh., Germenchuk, M.

The Republican Centre of Radiation Control and Environment Monitoring of The Ministry of Environment, Minsk, Belarus

E-mail: Us206@rad.by.mecom.ru

The analysis of formation of radioactive contamination of rivers of Belarus, entering the Dnieper basin (Dnieper, Sozh, Iput, Besed, Pripjat), after the accident at the ChNPP is given in the paper. The legitimacies and features of behavior of chernobyl radionuclides in surface waters and different types of soils on watersheds are detected. Radionuclide concentration dynamics in surface water of Dnieper river basin for period 1987-2006 are present. Transboundary migration of radionuclides through the river networks of Russia, Belarus and Ukraine is estimated. The transboundary migration of ^{137}Cs has decreased markedly with time. On the other hand, the transboundary migration of ^{90}Sr has fluctuated depending on the extent of annual flooding. Long-term behaviour of chernobyl radionuclides in the difference soil types of Dnieper River watershed is given. Linear velocity of ^{137}Cs , ^{90}Sr for different soil types are found. A forecast of vertical radionuclide migration is made.

Isotope study for relationship between surface and ground waters under a semi-arid climate: case of Souss-Massa catchment (South-West Morocco)

Bouchaou, L.^a, Hsissou, Y.^a, Ikenne, M.^a, Tagma, T.^a, Michelot, J.L.^b, Qurtobi, M.^c, Marah, H.^c

^a Laboratoire de Géologie Appliquée et Géo-Environnement (LAGAGE), Faculté des Sciences, Université Ibn Zohr, B.P 8106, Cité Dakhla, 80000 Agadir, Morocco

^b IDES, “Orsay Terre”, CNRS – Université de Paris-Sud, France

^c Laboratoire d’Analyses, CNESTEN, Rabat, Morocco

E-mail: lbouchaou@yahoo.fr

This study summarizes the application of stable isotopes as tools to infer water sources in the region. Hydrogen and oxygen isotope signatures reveal a significant infiltration before evaporation, indicating a recent recharge from Atlas Mountain and infiltration of surface water along the oueds and in the alluvial cones at the margin of the Atlas basins. ^{18}O , ^2H and tritium values indicate a mixing between recent and old groundwaters. The old groundwaters encountered in deep wells are not connected to modern recharge, indicating that water followed a long flow path. The slight evaporation recorded by stable isotopes in water from the southern margin close to the Anti-Atlas mountains indicates that these groundwaters are subject to a drier climate, marking the Anti-Atlas Mountains, which form a barrier against the influence of the Sahara. The upstream watershed, which is the place of condensation, shows more characteristic ^2H and ^{18}O -depleted waters. This finding can be explained by the altitude and the continental effects. On the other hand, ^2H and ^{18}O -enriched waters values towards the ocean, show an evaporation effect near the condensation source or the irrigation returns, especially in the irrigated zones. The rain isotope values indicate a main recharge from the Atlasic Mountain, whereas the contribution of the local rains is negligible in downstream.

Mean residence time of water from springs of the Plitvice Lakes and Una River area

Babinka, S.^a, Obelić, B.^b, Krajcar Bronić, I.^b, Horvatinčić, N.^b, Barešić, J.^b, Kapelj, S.^c, Suckow, A.^d

^a Leibniz Institute for Applied Geosciences, Hannover, Germany

^b Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

^c University of Zagreb, Faculty of Geochemical Engineering, Varaždin, Croatia

^d Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: Bogomil.Obelic@irb.hr

Within the FP5 project ICA2-CT-2002-10009 several tracers from springs that feed the Plitvice Lakes (Croatia) and springs in Una River valley (Bosnia and Herzegovina), as well as stable isotopes and tritium activity of precipitation from the Plitvice Lakes area were measured in the period 2003-2005. The aim of this work is to model the Mean Residence Time (MRT) by comparative measurements of concentrations of stable isotopes (^2H , ^{18}O), helium isotopes ($^3\text{He}/^4\text{He}$), chlorofluorocarbons (CFC-11, CFC-12, CFC-113), SF_6 and hydrochemical analyses. The complexity of the karst system required a multi-tracer approach, since one environmental trace substance alone leaves too much ambiguity in interpretation.

Installation of a laboratory for stable isotope analysis in Croatia

Roller-Lutz, Z.^a, Mandić, M.^a, Bojić, D.^a, Lutz, H.O.^b, Kapelj, S.^c

^a Laboratory for Environmental Studies, Medical Faculty, Rijeka University, Rijeka, Croatia

^b Physics Faculty, Bielefeld University, Bielefeld, Germany

^c Faculty of Geochemical Engineering, Varaždin Branch, University of Zagreb, Croatia

E-mail: roller@medri.hr

Croatia's first laboratory for stable isotope mass spectroscopy in hydrogeological studies has been set up at Rijeka University. Preliminary $\delta^{18}\text{O}$ results are obtained for the Gacka river catchment and interpreted together with data from the national meteorological and hydrological service.

Investigation of water resources and water protection in the karst area of Croatia using isotopic and geochemical analyses

Horvatincić, N.^a, Kapelj, S.^b, Sironić, A.^a, Krajcar Bronić, I.^a, Kapelj, J.^c, Marković, T.^d

^a Rudjer Boskovic Institute, Zagreb, Croatia

^b Faculty of Geotechnical Engineering, Varaždin, Croatia

^c Geo-Rudus, d.o.o., Sesvete, Zagreb, Croatia

^d Croatian Geological Survey, Zagreb, Croatia

E-mail: nada.horvatincic@irb.hr

Hydrogeological investigations using hydrochemical and isotopic methods have been performed to determine the sanitary protection areas of springs in the drainage area of the Vransko Polje near Biograd (North Dalmatia) and main springs in the drainage area of the Gacka River (Lika region). Both regions are situated in the karst area of Croatia. Water samples from springs and precipitation samples at both areas were collected monthly in the period 2005-2006. Hydrochemical results follow the variations caused by the main hydrogeological properties of particular aquifer and recharge conditions during different seasonal hydrologic and vegetation conditions. The mean ³H activity in all main springs in the Gacka River area is similar to that of precipitation, while in the springs of Vransko Polje the mean ³H activity is lower if compared with precipitation due to sea water infiltration. There is no seasonal fluctuation of ³H activity in all springs indicating fast circulation and good mixing of precipitation and ground waters.

Origin and age of groundwater in Araguari, Minas Gerais, Brazil

Bomtempo, V.L., Minardi, P.S.P.

CDTN/CNEN – Belo Horizonte, MG, Brazil

E-mail: vlb@cdtn.br

During the years 2004-2005 an investigation was carried out by CDTN and UFMG in the northwestern border of the state of Minas Gerais, Brazil, to assess the water resources related to the Guarani Aquifer System in the region of Araguari. The project was supported by the Fund of Universities (BNPPW/OAS) and was designed to cover a whole hydrological year. Main water supply for domestic, industrial and agricultural consumption derives from groundwater, and the system is under permanent stress. Among other classical tools, isotopic techniques were used to study groundwater origin, recharge processes and transit times. Environmental isotopic compositions (^{18}O , ^2H and ^3H) of 51 water samples were analyzed. The overall results show that the local waters fit fairly well to the GMWL, with a shift in the deuterium excess due to some evaporation; also, the groundwater is locally recharged. The exponential model was used to estimate groundwater transit time, and the results show that most of the waters (84%) are young waters with renewal time less than 30 years.

Use of natural tracers (major ions, total organic carbon, stable isotopes) to the understanding of volcanic aquifers functioning: an example from the Argnat Basin (Auvergne, France)

Bertrand, G., Celle-Jeanton, H., Chazot, G., Huneau, F.

Université Blaise Pascal, Laboratoire Magmas et Volcans, Clermont-Ferrand,
France

E-mail: G.bertrand@opgc.univ-bpclermont.fr

This work focuses on the chemical transfers within volcanic aquifers that are of special interest in Auvergne for they represent 30% of the water supplies (regional project PREVOIR financed by the Région Auvergne). A weekly monitoring of the chemical (major ions, TOC) and isotopic ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$) composition of rainfalls, unsaturated and saturated zone waters has been scheduled since November 2005. The evolution of the water quality is then followed during its transit towards the saturated zone. A combination of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and TOC measurements allow to approach the residence time of water within the unsaturated zone and to apprehend the processes which govern the quality of water during the hydrological cycle. Monthly investigations on the whole basin highlight the specificity of the volcanic environment. Carbon isotopic ($\delta^{13}\text{C}$) values range from -8.1 ‰ to -20.2 ‰ and then show a participation of deep CO_2 by the way of local faults.

Natural baseline quality within the lower Triassic sandstone of Lorraine (France): status and evolution

Celle-Jeanton, H., Huneau, F., Travi, Y.

Université Blaise Pascal, Laboratoire Magmas et Volcans, Clermont-Ferrand, France

E-mail: H.Celle-jeanton@opgc.univ-bpclermont.fr

The Triassic sandstones, that form an important aquifer on the Eastern border of the Paris Basin (France), have been intensively exploited by large scale pumping begun in the seventies that created a significant decrease in head level. Investigations using a combination of geochemical and isotopic methods have been carried out in 1979 and interpreted in terms of residence time of groundwater. This area appeared then of a special interest regarding the groundwater baseline evolution related to over-exploitation and matches the objectives of the EU BaSeLiNe project EVK1-1999-00024 as it allows to establish long term trends in water quality of a deep groundwater system. A new field campaign (major, minor, traces elements and isotopes) has been scheduled in 2001 in order to highlight the modifications of the water quality in relation with the modifications of the piezometric levels and the circulation flow paths that occurred after the large scale pumping.

The use of tritium in river base flow to understand long-term changes in water quality

Michel, R.^a, Aggarwal, P.^b, Kurttas, T.^b, Araguas-Araguas, L.^b, Kulkarni, K.M.^b

^a US Geological Survey, USA

^b Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: RLMichel@usgs.gov

To study the impact on water quality of changes in land-use, climate, or other factors, the residence times of water within the watershed must be understood. One manner of addressing this issue is through the use of tritium data. It has been over 50 years since thermonuclear weapons began producing tritium in large quantities, and over 40 years since the peak production of tritium by weapons testing in 1962. Since then, the tritium concentrations in the atmosphere have decreased and leading to a perception that tritium is no longer useful for determining physical parameters of surface waters. However, surface waters are frequently composed of a mixture of recent precipitation and baseflow, the latter of which can have residence times on the order of weeks to decades, or higher. The fraction of groundwater in surface flow and its age impacts the tritium concentrations of the surface flow. If the residence time of the waters composing base flow is decadal or longer, it is frequently possible to estimate the age of the active groundwater component in the river basin. Data from the Rocky Mountain area of Colorado is analyzed during three timespans: (1) the four years immediately after the bomb tests, (2) the decades after the tests (1970-2000), and (3) 2000 to the present. The early time period is found to be the best time to estimate the fraction of base flow in a system. Using the ratio of tritium concentration in precipitation/tritium concentration (C_p/C_r) in surface water, it is possible to estimate the residence times of water within watersheds both on historical and recent data.

Application of stable isotopes to evaluate groundwater recharge of a coastal aquifer in North-Central Chile and its role in vegetation dynamics

Aguirre, E.^a, Squeo, F.^b, Aravena, R.^c

^a Laboratorio de Isótopos ambientales, Comisión Chilena de Energía Nuclear, Chile

^b Departamento de Biología, Universidad de La Serena, Center for Advanced Studies in Arid Zones (CEAZA) & Institute of Ecology and Biodiversity (IEB), Casilla 599, La Serena, Chile

^c Department of Earth Sciences, University of Waterloo, Canada

E-mail: eaguirre@cchen.cl

The understanding of the water sources for plant growth is one of the key elements to evaluate the present and long term primary productivity in arid ecosystems. We use stable isotopes tools to evaluate the recharge mechanisms in a coastal aquifer located in the arid zone of north-central Chile. The main water sources in the study area, fog, rain and groundwater, were isotopically characterized over a decade. The isotope data confirmed that fog does not play any role in groundwater recharge. The water table and isotope data showed that during low water conditions (dry periods), the aquifer is maintained primarily by water recharged in the higher part of the Romeral basin. During high water table conditions (wet periods), recharge associated with local precipitation becomes a significant source of groundwater recharge. The aquifer responded very fast to rains with amounts over the average level for precipitation (like El Niño conditions), while no recharge was detected with precipitation events lower than the average value for precipitation. The recharge pattern can also influence the behavior of plants characterized by a dimorphic root systems than can perform hydraulic redistribution. Part of the fast recharge of the aquifer could be related to this water redistribution.

Characterization of marine intrusion and origin of the mineralization in the oriental coastal aquifer of Cap Bon (Tunisia)

Ben Hamouda, M.F.^a, Zouari, K.^b, Tarhouni, J.^c, Leduc, C.

^a Unité d'Hydrologie et de Géochimie Isotopique, CNSTN, Tunisie

^b Laboratoire de Radioanalyse et Environnement, ENIS, Sfax, Tunisie

^c Institut National Agronomique de Tunisie, INAT, Tunisie

^d Institut de Recherche pour le Développement, UMR G-EAU, MSE, France

E-mail: F.benhamouda@cnsn.rnrt.tn

The determination of the origin of the salinisation in the plio-quadernary oriental coastal aquifer of Cap Bon (North-East of Tunisia), and the understanding of its hydrogeological and geochemical behaviours were studied by the geochemical and isotopic tools. The climate of the region is semi-arid to sub-humid and of Mediterranean type. The long-term mean annual rainfall varies between 400 and 500 mm, and the mean annual potential evaporation is about 1100 mm. The overexploitation of the aquifer is characterized by the decrease of piezometry in the study area, reducing the discharge rate to the sea, and a continuous degradation of the chemical quality of water. Depression cones in various places have dropped to 5 to 10 m below sea level, which confirms the inversion of the hydraulic gradient and the invasion of seawater. The chloride is strongly correlated to the sodium for the majority of the samples. The predominance of sodium and chloride is explained by the proximity of the sea, via sea spray and/or a progress of seawater intrusion. The ^{18}O - ^2H plot shows that the composition of ^{18}O in the groundwater can be divided in two groups. In the first one the composition of ^{18}O varies between -4.3 and -5.5 ‰, this group is located between the global meteoric water line and the local water line; the hypothesis of an important contribution of the present rains to the recharge is probable. The second group is composed by the wells located in the region of the piezometric depression, near the sea where the salinity can reach 30 g/L. These waters are more enriched in ^{18}O and ^2H and fall on the mixing line of seawater; confirm the existence of marine origin.

The results of hydro-geochemical and isotopic studies suggested that the salinity is especially acquired by the dissolution of minerals through the return of water irrigation water in the aquifer system, by the contamination of nitrates and by a mixture with seawater, in particular in the area of Korba and Tefelloune, where we observe a negative piezometry and a very high salinity.

Deuterium and oxygen-18 ratios in rainfall and streamflow in a major drinking water catchment near Sydney, Australia, during drought

Hughes, C.E., Fischer, M., Stone, D.M., Hollins, S.E.

Australian Nuclear Science and Technology Organisation, Sydney, Australia

E-mail: Cath.Hughes@ansto.gov.au

The Warragamba catchment near Sydney, Australia, is in the midst of a major drought that is threatening water supplies for Australia's largest city. Over a period of 18 months 227 event based rainfall samples were collected at four locations, 74 streamflow samples were collected from the four major inflowing rivers and their tributaries and 45 reservoir samples were collected at various depths from Warragamba dam. The samples were analysed for δD and $\delta^{18}O$. These data provide a baseline dataset for establishment of a local meteoric water line for the Sydney region and for use in modelling of flow pathways and weather patterns in the Warragamba catchment.

Assessment of groundwater resources on La Digue Island in the Republic of Seychelles: a study proposal

Alcindor, H.A.^a, Taigbenu, A.E.^b, Araguas, L.J.^c, Jayawardena, L.P.^a

^a Public Utilities Corporation, Victoria, Republic of Seychelles

^b University of Witwatersrand, Johannesburg, South Africa

^c Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria.

E-mail: aalcindor@puc.sc

The objective of the study is to determine the groundwater potential of La Digue Island in the Seychelles Archipelago by mapping out the total extent of the aquifer available for abstraction of fresh water and estimating the recharge to the aquifer, including possible recharge enhancement, thereby estimating the safe yield of the resource. The proposed methodology to achieve the above task is discussed including the use of isotopic signature related to the precipitation inputs and their tracing through the aquifer. Moreover, the previous studies on the same plateau and similar areas are reviewed in order to identify the information gaps and thus the required additional studies that can be proposed to evaluate the impact of sea water intrusion with or without artificial recharge to the aquifer in relation to various water abstraction scenarios. All possible contamination sources due to the human activities are examined from the available water quality data.

The ^{14}C natural isotope as a tool for monitoring of groundwater exploitation

Abidin, Z., Brodjonegoro, A., Djiono

Center for the Application of Isotopes and Radiation Technology, Jakarta,
Indonesia

E-mail: his45@bit.net.id and ZAINL53@yahoo.com

The natural isotopes (^2H , ^{18}O and ^{14}C) have been used to monitor exploitation effect within interval of 10 years (1995 to 2005) in Bontang Basin, East Borneo, Indonesia. Groundwater exploitation from the basin was started in 1981 and at present the abstraction rate from more than 20 wells is about 59,000 m³/day. For isotope investigation of the groundwater water, samples were collected from different sources like rivers, springs, deep wells, seawater and rainwater in 1995 and 2005. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data show that the deep groundwater is recharged from local rainwater that infiltrates through in the breaking slope of sedimentary formation (Kampung Baru) in mountainous area of Lobang Batik. There is no indication of river water infiltration and sea water intrusion to the deep groundwater. The ^{14}C data show that the average age of deep groundwater in 4 wells located near the outcrop of Kampung Baru was 2300 year in 1995, while it is 1791 year in 2005. The decrease of about 500 year in groundwater age during the interval of 10 years of exploitation seems due to mixing with recent water recharged through the outcrop. The exploitation effect of groundwater is reflected by decreasing of groundwater age.

Groundwater resources from carbonate rocks in mountainous regions – hydrochemical and isotopic survey of groundwaters in the Western Pyrenees (France)

Huneau, F.^a, Rey, F.^a, Riss, J.^a, Pretou, F.^b, Celle-Jeanton, H.^c

^a Université Bordeaux-1, CDGA, Talence, France

^b CETRA, Laroin, France

^c Université Blaise Pascal, Clermont-Ferrand, France

E-mail: f.huneau@cdga.u-bordeaux1.fr

Carbonate rock aquifers are one of the main water supply sources for the French Western Pyrenees. The discontinuous structure of these reservoirs is a main obstacle to the development of such resources. By the way, since no other aquifer can be tapped, many communities have decided to improve their knowledge of the main springs over the whole region. Four sites have been considered from 2003 to 2006 and have been the object of multidisciplinary investigations including: geological mapping, geophysical investigations, dye tracing experiments and in situ hydrochemical survey. Stable isotopes have been analysed on both rainfall (¹⁸O, ²H) and spring's waters (¹⁸O, ²H, ¹³C, ³⁴S) in order to evaluate the origin of groundwaters, their residence time within the systems and to appreciate the occurrence of exchanges with other aquifers. Finally this study provides a good example of how to include hydrogeochemistry and isotopic tools in a water supply management policy.

New approaches for the detailed assessment of meromictic lakes by using stable isotopes

Seebach, A., Knöller, K.

UFZ Centre for Environmental Research, Leipzig, Halle, Germany

E-mail: anne.seebach@ufz.de

In recent years many approaches have been established in calculating lake water balances basing on meteorological/hydrological information supplemented with isotope data sets according to the mass and isotope balance equations. All of them have in common that the most important parameter - the evaporation flux - only can be obtained with an equation derived from the resistance model of the evaporation process introduced by CRAIG & GORDON in 1965. The preparation of field sampling systems for water vapour combined with in-lake evaporation pans shall improve the accurate determination of net evaporation fluxes. Therefore three several study sites within the Lusatian Lignite Mining District had been chosen to investigate lake-groundwater interactions and mixing dynamics of meromictic acidic mining lakes. A two-year data set of lake water, precipitation and air moisture sampled 10 cm and 100 cm above lake surface will be calibrated with pan evaporation and linked to meteorological data and groundwater samples of the lake's catchment area.

Examination of the source of salinity in water resources using isotope techniques. Case study: water resources of Shapoor River Basin

Hatami, F., Khalaj Amirhossainee, Y., Kuhpour, M.

Water Research Institute (WRI), Shahid Abbasspur Boulevard., East Vafarda Boulevard, Tehranpars 4th Square, Tehran, Iran

E-mail: Hatami_f@yahoo.com

The study area is located in south part of Iran, west part of Fars and the north part of Booshehr province. The area is situated between the longitudes 51°0' and 52°0' and latitudes 29°30' and 30°20'. The basin is a sedimentary area and hilly with gentle fold which is situated in a part of Zagros chain of mountains, in south-western of Iran. The length and width of the basin are approximately 95 km and 70 km respectively located in both side of Kazeroon fault. From the view of geology the formations of the basin are: series of Hormoz salt which is similar to salt domes, Asmari, Fars and Bakhtiari formations. The limestone formations with high permeability which make the fresh waters reservoirs of the basin are: 1) Asmari formations which is the calcareous main reservoir of ground waters and expands as a folded layer on the surface and depth of the study basin. 2) Sarvak limestone formation which is outcropped in central part of anticlines in east, north and northeast of the basin. The Shapoor river is the main river of the area which originates from the mountains of the east part of Arjan plain, then flows through the Kazeroon fault and after meeting some salt rivers of the middle part of the basin such as Salbiz, Malchesheikh, Chaharbisheh, Daregorg, Tanbakookar and Shekastian, It will enter into the Borazjan plain. Before arriving to the Kazeroon fault, water quality of Shapoor river is good but after contacting with salt rivers and moving through the salt formations of the west part of basin, it severely changes. The main objective of this study is examination of the sources of recharge of salinity resources and examination of all water resources in the study area for controlling water quality of Shapoor river. To access the following objectives more than 50 water samples were taken from different resources such as rivers, wells and springs in both wet and dry seasons. In this regard isotopes (¹⁸O, ²H, T) as well as hydrochemistry analysis and field measurements were carried out.

Using carbon and nitrogen isotope geochemistry to assess cultural eutrophication and remediation efforts in lakes

Teranes, J.L., Bernasconi, S.M.

Scripps Institution of Oceanography, University of California, San Diego;USA
Geological Institute, ETH-Zurich

E-mail: jteranes@ucsd.edu

Stratigraphic variations in the isotopic composition of carbon and nitrogen in lake sediment components are useful in assessing sources and cycling of organic matter, sources of nutrients and of the trophic evolution of lakes. Here we report carbon and nitrogen isotope ratios of sediment core material from two eutrophic lakes. Results show that the primary control of $\delta^{15}\text{N}$ values is typically external N inputs, modulated by relative availability of P and N in the photic zone. $\delta^{13}\text{C}$ values are influenced by both variations in the relative inputs of eukaryotic biomass, which becomes enriched in ^{13}C with increasing primary productivity, and the contribution of microbial biomass produced in the expanding anoxic bottom waters, which is typically depleted in ^{13}C . We conclude that carbon isotope fractionation within the organic matter– CO_2 – CaCO_3 system is best for accurate interpretation of $\delta^{13}\text{C}$ values in lake systems that have been heavily affected by cultural eutrophication.

Isotopic indicators for the processes from the chemoautotrophic ecosystem of the Movile Cave, Romania

Feurdean, L.^a, Feurdean, S.^a, Sarbu, S.^b, Gligan, M.^b, Stefanescu, I.^c

^a National Institute for R & D of Isotopic and Molecular Technologies, P.O. Box 700, Cluj-Napoca, Romania

^b Department of Biological Sciences of University of Cincinnati, Ohio, USA

^c National Institute of R & D for Cryogenic and Isotope Separation Technologies, Rm. Valcea, Romania

E-mail: luci@140itim-cj.ro or vfeurdean@gmail.com

Measurements of the natural isotopic content for hydrogen, oxygen, sulphur and carbon for samples collected from cave served as the basis for the characterization of the cave components and processes. Based on the water isotopes, the surveys have elucidated the origin of the water from cave. The water has meteoric origin, from modern and submodern precipitation fallen over a higher altitude than that of the emergence. The cave is the buffer system between the deep confined aquifer and the unconfined aquifer from Sarmatian deposits. The $\delta^{34}\text{S}$ values in the sulphide and sulphate from the Movile Cave and from the Black Sea present distinct values. The sulphide comes from deep aquifers and sulphate is produced in cave by sulphide oxidizing in presence of microorganisms. All forms of inorganic carbon are isotopically light. CO_2 in the cave atmosphere is a mixture of heavier CO_2 resulted from the dissolution of limestone and lighter CO_2 resulted from the oxidization of the organic matter and/or methane. The bicarbonate in water is at isotopic equilibrium with CO_2 . The organisms sampled from cave are isotopically light versus surface congeners, suggesting dependence on the chemoautotrophic production occurring in cave.

Deuterium as indicators of the natural and anthropic stress on the waters of the Danube Delta, Romania

Feurdean, V.^a, Feurdean, L.^a, David, C.^b

^a National Institute for R & D of Isotopic and Molecular Technologies, P.O. Box 700, Cluj-Napoca, Romania

^b Danube Delta National Institute for Research & Development, Tulcea, Romania

E-mail: victor@140.itim-cj.ro

The natural flow of water has been examined in the Danube Delta Biosphere Reserve Romania, the largest deltas in Europe, using deuterium (^2H) as a natural tracer. The understanding of the circulation of the water and pollutants into protected zones is essential to protect the maintenance of all ecological functions of delta. The isotopic content variations of water due to the climatic changes and anthropogenic activities are fast, the isotopic signature being indicators for the water flow-paths changes before irreversible environmental transformations occur. Contours maps of the mean deuterium concentrations have been used to reveal the changes of the water flow-paths from the running waters (Danube's distributaries, channels/canals with active, controlled or absent circulation of water) and the standing freshwater (lakes with active, reduced or controlled change of water). The isotopic maps show the changes of pathways due to the climatic changes that have the impact on the water balance, the erosion of coastal areas and the man made pressures on the Danube Delta.

Application of ^{15}N isotope to management of groundwater quality, Jabal Hasouna Wellfields, Great Man-Made River Project, Libya

Milne-Home, W.A.^a, Sahli, N.I.M.^b

^a University of Technology Sydney, Sydney, Australia

^b Great Man-Made River Authority, Benghazi, Libya

E-mail: William.Milne-Home@uts.edu.au

The Jabal Hasouna wellfields are located some 700 kilometres south of Tripoli, the capital of Libya, and are part of the Great Man-Made River Project for water supply to coastal areas. The wellfields include 484 deep wells with a total design production rate of 2.5 million cubic metres per day from the Cambro-Ordovician sandstone aquifer. The aquifer is unconfined in the southwestern portion of the wellfields and the remainder is confined, but most of the wells are located in the unconfined part. Water quality is good but concentrations of nitrate up to 133 mg/L occur in the wellfields, with slightly higher concentrations in the unconfined aquifer. Previous ^{14}C dating of the groundwater gave ages of $10.4 \text{ ka} \pm 0.4 \text{ ka}$ to $17.2 \text{ ka} \pm 0.1 \text{ ka}$ BP and stable isotope data indicate a meteoric origin from recharge during a humid climate phase of the Sahara. Analysis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ from groundwater nitrate showed a range of 7.11 to 12.64 ‰ for the $\delta^{15}\text{N}$ and 12.51 to 22.35 ‰ for the $\delta^{18}\text{O}$. At Jabal Hasouna these ranges suggest that soil nitrate may be the source. There appears to be a low rate of denitrification so high nitrate levels will be a long-term concern for water quality.

Transport processes of pharmaceuticals and personal care products during stream-aquifer interaction in the urban area of Halle/Saale, Germany

Osenbrück, K., Knöller, K., Strauch, G., Gläser, H.-R., Reinstorf, F., Möder, M., Wennrich, R., Weise, S.M.

UFZ Centre for Environmental Research, Halle/Saale, Germany

E-mail: karsten.osenbrueck@ufz.de

The urban aquatic environment is increasingly affected by low concentrations (but potentially harmful) of xenobiotica such as residuals of pharmaceuticals and personal care products (PPCP) and their metabolites. After release into the urban sewer system the PPCPs reach the surface water mainly by passing sewage treatment plants or by diffuse leakage from the sewer system into groundwater. In the city of Halle/Saale, Germany, we used stable isotopes (^{18}O , ^2H , $^{34}\text{S-SO}_4$) along with hydrochemical investigations to assess the exchange of river water with groundwater and its impact on the transport of selected PPCPs. The results indicate that attenuation of PPCP transport is mainly related to flood events with fast infiltration of river water into the aquifer (timescale of 5 days). By contrast, during slow infiltration linked to transport of PPCPs through the colmation layer (timescale of 150 days) no concentration changes have been found. These surprising differences in transport behaviour are attributed to the different hydraulic conditions with changing flow paths and river water chemistry.

Prediction of future nitrogen loading to Lake Rotorua, New Zealand

Morgenstern, U.

GNS Science, Lower Hutt, New Zealand

E-mail: u.morgenstern@gns.cri.nz

Groundwater that feeds streams and springs in the catchment of Lake Rotorua, New Zealand, has 15 - 130 years mean residence times in the aquifer. These long residence times of the water in the ground result in large time-delays of nitrogen loading from historical agricultural and urban development in the catchment. Currently observed increases in nitrogen loading in surface and groundwater are mostly due to the delayed impact of catchment development that occurred around 55 years ago. The time-dependence of the arrival of water to the Lake that was recharged since landuse development in the 1950's was calculated using the age distribution of the water derived from tritium, CFC and SF₆ data. The arrival of post-landuse water over time was then used to estimate the nitrogen load to the Lake for the time prior to landuse development, for the time since then, and for the future.

To use the environmental isotopes for wetlands: a case study from Kucuk Menderes River Coastal Wetland, Selcuk, Izmir, Turkey

Somay, A.M., Gemici, U.

Dokuz Eylul University, Geological Engineering Dept., Tinaztepe Yerleskesi,
35160, Buca, Izmir, Turkey

E-mail: melis.somay@deu.edu.tr

Environmental isotopes were used to identify the relationship between wetland and groundwater; and salinization processes, and to estimate the circulation time of the groundwater in the Selcuk Plain. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of wetland area samples range from -5.40‰ to -2.93‰ and from -35.1‰ to -19.55‰, respectively. The lakes and rivers are plotted on the mixing lines with slopes of 5.8 and 5.5 because they belong to the open system in the hydrologic cycle and there is a salinization in the plain. To identify the dominant process, $\delta^{18}\text{O}$ -Cl relationship was used. The river and the lake Kocagoz are plotted on the evaporation line. In addition, in rainy season the lake Akgol and in dry season the lake Gebekirse are plotted between evaporation and mixing line, which shows the effect the seawater on the lakes. In the light of the Tritium values, the groundwaters are recharges with modern rainfalls with 5-6 TU values and show the short circulation time of groundwaters.

Isotopic composition of meteoric water in Sicily

Liotta, M., Favara, R., Fontana, M., Gagliano, E., Pisciotta, A., Scaletta, C.

Istituto Nazionale di Geofisica e Vulcanologia (INGV) –Sez. di Palermo, Italy

E-mail: m.liotta@pa.ingv.it

The isotopic composition of meteoric water in Sicily (Italy,) was investigated from May 2004 until Jun 2006; a rain gauge network (50 sites) was installed and sampled monthly. During this same period most of the circulating groundwater in the investigated area was sampled from more than 560 springs and wells related to the main aquifers. The mean weighted precipitation values were used to define the weighted local meteoric water line (WLMWL) for several sectors of Sicily. The use of GIS tools, coupled with isotopic vertical gradients, allowed us to design an isotopic contour map of precipitation in Sicily. The defined meteoric compositions fitted well with most of the groundwater samples for each sector. However, in some areas fractionation processes occurring during and after rainfall, slightly modified the isotopic composition of the groundwater.

**Do water isotopes reflect differences in timber harvest practices?
Isotope ecohydrology in the Mica Creek watershed, Idaho, USA**

Koeniger, P., Link, T.E., Marshall, J.D.

Department of Forest Resources, College of Natural Resources, University of Idaho,
Moscow, USA

E-mail: koeniger@uidaho.edu

The impacts of timber harvesting techniques on the water balance and flow regime were studied at the catchment scale at the Mica Creek Experimental Watershed (97 km², 975 – 1,750 m a.s.l.) in northwestern Idaho, USA. These studies relied on stable isotopic techniques to assess the variation in water isotope fluxes of clear-cut, partial-cut (thinned), and unimpacted forest sites. Precipitation, stream flow, soil water, and sap flow, and stable isotope concentrations (deuterium and oxygen-18) of these components were measured on a monthly basis starting in fall 2004. The isotopic composition of sap flow appeared to reflect differential canopy interception losses, with greater enrichment under the densest canopies.

Origin and fate of nitrogen pollution in groundwater traced by $\delta^{15}\text{N}_{\text{-NO}_3}$ and $\delta^{18}\text{O}_{\text{-NO}_3}$: the case of the suburban area of Dakar (Senegal)

Re, V.^a, Cissé Faye, S.^b, Faye, S.^b, Gaye, C.B.^b, Faye, A.^b, Sacchi, E.^c, Zuppi, G.M.^a

^a Dipartimento di Scienze Ambientali, Università Ca' Foscari di Venezia, Venezia, Italy

^b Département de Géologie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal

^c Dipartimento di Scienze della Terra, Università di Pavia, Pavia, Italy

E-mail: re.vivi81@libero.it

In recent years, the rapid increase of the population in the region of Dakar, especially in suburban settlements, together with the lack of policies for urban waste management, has become a source of concern for water supply, needs, and quality control. Approximately 80% of water resources in the region come from groundwater reservoirs. In order to identify the origin of groundwater pollution a survey on 26 piezometers and wells was conducted in march 2006. In this study, both major and trace elements were measured as well as the stable isotopic signature of water molecules and dissolved compounds. Nitrates often exceed drinking water limits and are associated with microbiological pollutants, while sea water intrusion represents the major threat to rapidly declining groundwater quality. Stable isotopes of dissolved nitrates allow for the identification of urban sewage and fertilizers as a major source of contamination, and the ability to define the distribution of their impacts. The occurrence of denitrification processes, although limited, suggests the potential for auto-purification of the contaminated water, if the source of the pollution were to cease.

Tritium concentrations in the Yukon River Basin and their implications

Michel, R.L.^a, Schuster, P.F.^b, Walvoord, M.A.^c

^a US Geological Survey Menlo Park, CA 94025 USA

^b US Geological Survey Boulder, CO 80303 USA

^c US Geological Survey Denver, Colorado 80225 USA

E-mail: pschuste@usgs.gov

The tritium transient, produced by atmospheric nuclear weapons testing in the 1950s and 1960s, has been used to determine timescales for large-scale hydrologic processes such as the movement of water through river basins. A long-term tritium data base is available from downstream stations on the Yukon River from 1961 to the present. This data has been analyzed using a lumped-sum parameter model to obtain estimates of fraction of base flow and timescales for flow of water through the basin. The data shows that 63% of the water exported by the Yukon River has been retained in the basin less than a year. The average residence time for the older water is approximately 17 years.

Evaluation of the impact of groundwater resources on surface water in Chihuahua, Northern Mexico

**Hernández-Limón, L.G.^a, Mahlkecht, J.^b, Chávez-Rodríguez, A.^b,
Pinales-Munguía, A.^c, Aravena, R.^d**

^a Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Mexico

^b Universidad Autónoma de Chihuahua, Chihuahua, Mexico

^c Estudios y Proyectos en Agua Subterránea, SA de CV, Chihuahua, México

^d Department of Earth Sciences, University of Waterloo, Waterloo, Canada

E-mail: jurgen@itesm.mx

In water resources management it is very important to know the relationship between aquifers and surface water, to identify flow direction and quantify flows under given conditions, and eventually make use of groundwater resources for the environmental flow of rivers. The objective of this study was the assessment of the interaction between the Middle Conchos River in Chihuahua (semi-arid Northern Mexico) and the underlying Meoqui-Delicias aquifer which is heavily exploited for irrigation use, with the aim to know how to manage water resources for the improvement and conservation of damaged aquatic ecosystems. A 3-dimensional model domain has been developed which extends 30 km in length, includes 5 km at both sides of the Conchos River, and reaches a depth of 300 m. For the modeling process, a finite difference approach (MODFLOW) has been selected in combination with new, detailed hydraulic and geophysical data (100x100 m cell size). The surface water – groundwater interaction has been simulated with the streamflow routing package of MODFLOW. A two-step calibration strategy was applied to increase reliability of the model lacking of historical data: first, the model has been calibrated with piezometric data of dry and rainy seasons, and with streamflow data collected at 4 hydrometric gauges; then, tracer information (stable water isotopes and chlorofluorocarbons) was applied to calibrate the model. Once the model was calibrated, several scenarios considering the next 10 years have been evaluated as a response to the different water management alternatives. The predictions indicate that the ceasing of water production wells along and near the river, and measures to increase the river bed conductance would not increase significantly the baseflow. The best practice would be increasing the river flow via operation of the Boquilla Irrigation Dam in the Upper Conchos Basin, because this is the only way to sufficiently increase flow in the river for conservation of ecosystems. However, the operation must be done carefully to conserve the interests of the landowners of the irrigation district in the Middle Conchos Basin.

Internet GIS and water resource information

Deeprasertkul, P., Chitradon, R.

Hydro and Agro Informatics Institute, Bangkok, Thailand

E-mail: royol@haii.or.th

GIS is Geographic Information System, a computer system capable of integrating, storing, editing, analyzing, sharing and displaying geographically referenced information. At present, GIS is not only limited to cartography but also involves in various activities i.e. scientific investigation, natural resource management, environmental impact assessment, etc. Internet GIS allows more information sharing as many users can access GIS at the same time. Another progress in GIS is GIS/MIS where non geographical information (customized to users' purposes) regarding the particular area was overlaid with GIS. Internet GIS/MIS is useful for water resource management as it gives users better understanding of the overall picture i.e. GIS: locations of rivers/basins, topography of the flooded/drought areas, linkages of geographical factors and natural disasters occurred and MIS: water demand and supply thus gives users the ability to find best solution for each area and manage water resource in a sustainable manner.

Isotope techniques in groundwater contamination studies in urbanized and industrialized areas, Hat Yai Basin

Suwanlert, J.

Department of Groundwater Resources, Bangkok, Thailand

E-mail: Jittrakorn@dgr.go.th

Anthropogenic activities are mainly responsible for changing the hydrological cycle as well as the climate warming. Assessing the impacts of human activities on hydrological environments is becoming a wide-focused topic. In this research, the author attempt to link the urbanization, agricultural development, and the subsequent water resources exploitation with the change of water environments in Hat Yai Basin, southern of Thailand. The source of water for domestic use mainly comes from Utapao River which flows through the area. Now this area is facing the shortage of water in dry season and pollution due to domestic and industrial activities. Isotope techniques in conjunction with hydrological and chemical data can play the important role for identifying recharge mechanism and surface and groundwater interaction. By using the numerical model the information for proper groundwater management can be obtained. As a result, the quality of groundwater in Hat Yai Basin showed that the iron (Fe) content at many locations was higher than the permissible level for groundwater quality standards for drinking purposes in the Notification of the Ministry of Industry. Groundwater from such locations should not be used for drinking. The water types of Hat Yai aquifer were Na-Cl and Ca-HCO₃, while that of Khu Tao aquifer and Kho Hong aquifer were CA-Mg-HCO₃ and Ca-Mg-HCO₃, respectively. The origin of groundwater in Hat Yai aquifer is local rainfall. The origin of groundwater in Khu Tao and Kho Hong aquifers come from ancient rainfall indicating old water and low flow rate. The groundwater is recharged from the zones located in the eastern and western parts of Hat Yai Basin and flows to middle basin and northward to Songkhla Lake.

Assessment of viability of exploiting artesian aquifers for municipal water supply in parts of South East Nigeria using isotope techniques

Maduabuchi, C.^a, Eduvie, M.^b, Babarinde, S.^a

^a Federal Ministry of Water Resources, Abuja, Nigeria

^b National Water Resources Institute, Kaduna, Nigeria

E-mail: maduchristo@yahoo.com

The steady growth in Nigeria's population, now about 140million, and the continuing relocation of many citizens from rural to urban areas in pursuit of higher education and employment opportunities have placed considerable stress on social infrastructures particularly water supply in most of the State Capitals. In parts of the Middle Belt and South East, artesian flows have been encountered in boreholes tapping the False bedded Ajali Sandstone and Upper Coal Measures geological formations. The IAEA sponsored TC Project No. NIR/8/007: "Isotope-based Investigation of Groundwater in the Middle-Belt and South East" seeks to evaluate the source, recharge and hydrochemistry of these artesian aquifers through study of their hydro-geological setting, hydraulic and hydro-chemical parameters and isotopic compositions of the source water. Inventory of most of the existing artesian boreholes has been completed. Thirty-three water samples have been collected from surface and groundwater sources including artesian and non-artesian boreholes at varying depths, for isotopic and hydro-chemical analysis, which results, when available would be interpreted and discussed in a subsequent paper. This paper reviews the hydro-geology of the project area and outlines the way the project would progress with emphasis on the role isotope hydrology would play in resolving the sustainability question associated with exploitation of the artesian aquifers for municipal water supply schemes. It is envisaged that integrated interpretation of isotopic and hydro-chemical data to be acquired together with baseline data would provide informed advice to Water Resources Managers and Decision-Makers on the viability of planning large scale water supply schemes based on these artesian aquifers.

Isotope response of hydrological systems to long-term exploitation in the Singen aquifer system, Germany

Watzel, R.^a, Heidinger, M.^b

^a Geological Survey, State of Baden – Württemberg, D-79104 Freiburg, Germany

^b Hydroisotop GmbH, D-85301 Schweitenkirchen, Germany

E-mail: Ralph.Watzel@rpf.bwl.de

This study demonstrates the use of isotope tracers as a tool for monitoring groundwater resources, their depletion and recovery due to a phase of over-exploitation. It is based on spatial hydro-geological data of a Quaternary basin, a three dimensional numerical groundwater flow model and detailed hydraulic, hydro-chemical and isotope records over a period of more than 30 years at selected major production wells. Hydro-chemical data and tritium values have been used to comprehend the complex flow system throughout this period of exploitation. Tritium values in groundwater samples are influenced by the temporal tritium input function in precipitation, radioactive decay or residence time as well as by the mixing portion of various groundwater components due to exploitation. The mixing portions of groundwater components were dramatically changed by groundwater abstraction, especially during over-exploitation in the late 1960s and early 1970s. The long-term tritium record (1969-2001) demonstrates this change for the central part of the aquifer system where main discharge took and takes place. Various snapshots of calculated mean residence times prove increased flow dynamics in the system during the period of over-exploitation and the recovery of the system due to a more sustainable groundwater management. The combination of various investigation methods applied here resulted in a profound understanding of the flow and transport conditions within the studied groundwater reservoir under transient flow conditions over a time scale of more than three decades. The experience of a shallow, fast responding aquifer system is an encouragement for groundwater managers and experts dealing with (strongly) exploited aquifer systems to use isotope tracer techniques for monitoring purposes and to find adjustment of exploitation to sustainability.

Interaction surface water – groundwater: investigation in the Rhine Valley using environmental isotopes

Engesser, W.^a, Bertleff, B.^a, Maloszewski, P.^b, Stichler, W.^b

^a Geological Survey, State of Baden – Wuttemberg, D-79104 Freiburg, Germany

^b GSF Institute of Groundwater Ecology, D-85764 Neuherberg, Germany

E-mail: wolfgang.engesser@rpf.bwl.de

The investigation area is located in the Rhine Valley, a floodplain composed of Upper Quaternary sediments near Karlsruhe, Germany. The upper two gravel layers build highly permeable and productive aquifers which are used by many drinking water supplies. These two layers are partial hydraulically divided by an impermeable interlayer which does not exist everywhere. On the other hand many gravel extraction sites are dug out, which form small artificial lakes. To overcome the conflict between both, water supply and gravel industry, a precise knowledge of the interaction of surface water – groundwater is absolutely necessary. The hydraulic relationship between the groundwater storey, the gravel pit lakes, and the rivers could not be adequately explained using only water level measurements. Only with the aid of the results from the hydro-chemical and isotope-hydrological investigations ($\delta^{18}\text{O}$, $\delta^2\text{H}$, ^3H), the components of the regional groundwater recharge, Rhine bank infiltration, lake bank filtration, as well as local specifically marked water types could be identified, classified and quantified in surface – and groundwater. Utilizing these methods it was shown that the deep pumping wells of the water supply have over 90% Rhine riverbank filtration water and have no inflow from any of the investigated gravel pit lakes. The groundwater in the two investigated upper aquifers differ mainly isotope-hydrological and respectively in age, less pronounced in their hydro-chemical properties. In both aquifers there is a zone of ca. 1 to 3 km wide, in parts reaching to the gravel quarry lakes, which generally follows the Rhine with a flow of depleted isotopic Rhine filtration water with varying ages. From the east-southeast there is an inflow from the lower terrace of relatively young and identifiably anthropogenic influenced as well as almost totally reduced in nitrate, In the aquifer below, the water is usually tritium-free, i.e., older than 50 years, not anthropogenic influenced and reduced in sulphate. Modeling tritium data the local recharge rate could be estimated. In all investigated gravel pit lakes, a high percentage of Rhine bank filtration was proven. The inflow of groundwater to the lakes and the outflow of the lake water are identifiable because of isotope-fractionation due to evaporation. The environmental isotopes build together with the hydro-geological and hydro-chemical investigations the basis for a detailed understanding of this complex flow system.

The use of isotopes for karst water research in the Northern Calcareous Alps

Pfleiderer, S., Reitner, H., Heinrich, M., Rank, D.

Geological Survey of Austria, Vienna, Austria & University of Vienna, Austria

E-mail: sebastian.pfleiderer@geologie.ac.at

Since 1995, the northern Calcareous Alps at the border between Upper and Lower Austria have been studied intensively by the authors, integrating data on hydrogeology, isotope hydrology and tectonics. The area is dominated by dolomites and limestones which serve as large-scale karst water reservoirs. Monthly analyses of groundwater isotopic compositions (^3H , $\delta^2\text{H}$ and $\delta^{18}\text{O}$) reveal detailed information on groundwater flow, age, and areas of recharge. In moderately karstified dolomites, springs typically provide low and steady discharge draining a dense pattern of small-scale fissures. The aquifers possess large storage volumes, good retention capacity, long groundwater residence times and reduced effects of rainwater mixing. Springs in karstified limestone or dolomite, on the other hand, typically show highly dynamic hydrographs, short residence times and quick responses to daily rain events. Combining isotope data with information on precipitation and baseflow within a GIS allows to put constraints on size and location of recharge areas.

Relationship between stable isotopes of precipitation and atmospheric circulation - case study: application in a pilot basin in Central Anatolia

Tekeli, Y.I.^a, Unal Sorman, A.^b

^a Ministry of Agriculture and Rural Affairs , Soil and Water Resource Ankara Research Institute, Ankara, Turkey

^b Middle East Technical University Civil Engineering Dept., Water Resources Center, Ankara, Turkey

^c State Hydraulic Works, Technical Investigate and Quality Control Laboratory, Ankara, Turkey

E-mail: itekeli@lycos.com; inci-8@ttnet.net.tr

The stable isotope values of precipitation are strongly influenced by water vapor source and trajectory. It can be used as a tool for the evaluation of atmospheric circulation. This approach requires an understanding of how atmospheric circulation influence precipitation $\delta^{18}\text{O}$. This study presents to understand the relationship between atmospheric circulation and $\delta^{18}\text{O}$ of individual storm events for a micro scale basin in Central Anatolia. Circulation back trajectories and $\delta^{18}\text{O}$ values for 30 precipitation samples taken from 7 individual events were also examined to determine circulation type for each event. Results indicated that precipitation $\delta^{18}\text{O}$ was related with precipitation intensity. Precipitations originating from Siberia and Mediterranean-Africa air masses seen high frequently in study area yielded relatively depleted $\delta^{18}\text{O}$ values.

Infiltration processes and impact on shallow groundwater in agricultural dry land areas

**Garel, E.^a, Marc, V.^a, Ruy, S.^b, Doussan, C.^b, Simler, R.^a, Daniel, M.^a,
Tyson, F.^b**

^a Université d'Avignon, Laboratoire d'Hydrogéologie, Avignon, France

^b INRA, unité Climat Sol Environnement, Montfavet, France

E-mail: miliogarel@hotmail.com

An investigation of infiltration processes in a Mediterranean agricultural soil was carried out using environmental and artificial tracing. The objective was to assess the impact of the different vertical flow processes on the recharge of the underlying unconfined aquifer. A long term isotopic survey of rainwater, soil water and groundwater enabled us to estimate the seasonal influence of irrigation on the groundwater recharge. According to the rainfall time series over the previous months, the monthly proportions of irrigation ranged from 60 % to 98 %. These results point out the sensitivity of such shallow groundwater systems in the Mediterranean region, submitted to climate variability and depending on artificial recharge. At plot scale, preferential flow processes were investigated from a simulated rainfall using bromide as tracer (110 mm over 2h 52 min). The impact of this irrigation on the saturated zone was detected about 2 h after the start of the experiment. The hydrological contribution of this local infiltration to the groundwater was low owing to the high transmissivity of the saturated zone and the regional extent of the aquifer. But according to the concentration observed in soil water, solutes fluxes may be significant and local, short-term overtaking of allowable standards for water quality may occur. A rational management of shallow groundwater resources in agricultural regions should consider more explicitly these preferential flow processes in soils.

Advances in optical water isotope ratio measurements

Kerstel, E.

Center for Isotope Research, Department of Physics, University of Groningen, The Netherlands

E-mail: e.r.t.kerstel@rug.nl

Isotope ratio mass spectrometers routinely achieve impressive measurement precisions and high throughput. In spite of this, a number of fundamental and practical problems are encountered. These are most notable in the case of water, arguably the most important molecule in the environment. Optical techniques to measure stable isotope ratios are able to address at least some of these issues; particularly, in relation to sample pretreatment and the difficulty of *in-situ* measurements. After discussing some general design criteria for infrared laser-based isotope ratio spectrometers, the case made above will be illustrated with a number of different instruments in applications from earthbound to the atmospheric: From laboratory based ice-core water isotope analyses to *in-situ* water isotope measurements in the upper troposphere and lower stratosphere.

Environmental isotope and hydrochemical investigation on groundwater recharge and dynamics of the coastal sedimentary aquifers of Tiruvadanai, Tamilnadu State, India

Umayadoss, S.K.^a, Suman, S.^a, Deodhar, A.S.^a, Mohokar, H.V.^a, Navada, S.V.^a, Ganesan, S.^b

^a Isotope Hydrology Section, Isotope Applications Div., Bhabha Atomic Research Centre, Mumbai - 400 085, India

^b Tamilnadu Water Supply and Drainage Board, Sivagangai - 623 560, Tamilnadu, India

E-mail: vsk@magnum.barc.ernet.in

Recharge processes and dynamics of the Tiruvadanai aquifers were investigated using environmental isotopes and hydro-chemistry, in conjunction with hydrogeological data. Hydro-chemical characterization of the groundwaters indicated that the shallow (<200 m) Tertiary aquifers (unconfined/semi-confined), lying below the upper Quaternary alluvial deposits, contain no-dominant to saline type of waters and the deeper (350–500 m) Cretaceous aquifer (confined) is NaCl type. The concentration of various chemical species along the general groundwater flow direction (northwest to east) showed a trend with decrease in Mg^{2+} and Ca^{2+} and an increase in Na^+ and K^+ in both the aquifers. This could be attributed to ion-exchange process. A higher pH value of Cretaceous aquifer samples (7.4-8.6) could also be responsible for the lowering of Mg^{2+} and Ca^{2+} concentrations by facilitating precipitation of carbonates in them. δ^2H - $\delta^{18}O$ plot of the Tertiary aquifer samples fall on an evaporation line. Its 3H values near the ephemeral rivers range from 2 to 5 TU while those away from the rivers have <1 TU and $^{14}C_{DIC}$ model ages range from 1 to 13 ka BP. The Cretaceous aquifer samples measured 3H values <1.5 TU and their $^{14}C_{DIC}$ model ages are >20 ka BP, indicating palaeo-waters. Based on ^{14}C model ages, the groundwater velocity was estimated (Tertiary aquifers: $10^{-2} - 10^{-3}$ m.d⁻¹; Cretaceous aquifer: 10^{-3} m.d⁻¹). The $^{13}C_{DIC}$ enrichment along the flowpath of Cretaceous aquifer was observed and that could be due to carbonate minerals dissolution. From the investigation, four types of recharge processes to the aquifer system are discerned, with the overall modern recharge component being low. The Cretaceous aquifer contains fossil groundwaters and hence the resources may be finite and their exploitation is mining. The suitable river for implementing large-scale artificial recharge measures was identified.

Factors controlling the stable isotopic composition of recent precipitation in Spain

Díaz, M.F.^a, Rodríguez, J.^b, Pérez, E.^a, Castaño, S.^b, Araguás-Araguás, L.^c

^a Centro de Estudios de Técnicas Aplicadas (CETA), Centro de Estudios y Experimentación de Obras Públicas (CEDEX), Madrid, Spain

^b Instituto Geológico y Minero de España, Madrid, Spain

^c Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: jra@igme.es

Composite monthly samples of precipitation were collected for the period 2000-2004 at 16 meteorological stations included in the “*Red Española de Vigilancia de Isótopos en la Precipitación*” (REVIP), the Spanish Network for Isotopes in Precipitation. Oxygen-18 and deuterium results were used to review previous maps showing the spatial distribution of isotope contents over the Iberian Peninsula. Long-term mean weighted values of $\delta^{18}\text{O}$ over the Iberian Peninsula range from ca. -4.0 ‰ in stations from Andalusia to ca. -10.0 ‰ in the stations located in the northern plateau. The $\delta^2\text{H}$ - $\delta^{18}\text{O}$ relationship of the long-term weighted means is in good agreement with the GMWL, showing d-excess values only slightly above 10‰, indicating the relevance of air masses of Atlantic origin, as the main source of water vapour over the Iberian Peninsula. The spatial distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation over the Iberian Peninsula can be explained by a simple multiple regression model, based on two geographic factors: latitude and elevation. This polynomial model reproduces reasonably well the observed spatial distribution of the stable isotope composition of precipitation over Spain, facilitating the use of stable isotopes as a tool to trace the origin of surface and ground waters. Differences between measured and predicted $\delta^{18}\text{O}$ values with both global and local scale models are explained by other regional and local factors that influence the isotopic composition of precipitation.

Determination of transboundary groundwater flow by isotopic tracing

Dakoure, D., Gaye, C.B.

Programme VREO, Bobo-Dioulasso, Burkina Faso

E-mail: vreo@fasonet.bf

The hydrodynamics of the groundwater flow in large sedimentary basins are very difficult to establish since detailed topographic data are often not available in connection with the lack of adapted topographic levelling. The only available topographic maps are small scales ones at 1/200,000 with contour lines equidistant of 40 metres and do not allow a characterisation of large scale flows in the case of the large trans-boundary basins such as the south-eastern edge of the Taoudenni sedimentary basin shared by Burkina Faso and Mali. An isotope hydrology investigation has been carried out in the basin of Taoudenni shared by Burkina Faso and Mali. It shows that the combination of independent information derived from isotope data with groundwater flow modelling can highly improve the understanding of understand the system including its structure (mono or multi-layer), boundary conditions and recharge mechanisms as well as the groundwater reserves renewal processes.

Environmental isotopes in water cycle in the catchment of the Quequen Grande River, Argentina

Martinez, D.^a, Dapeña, C.^b, Betancur Vargas, T.^c, Panarello, H.^b, Quiroz Londoño, M.^d, Massone, H.E.^e

^a CONICET - Centro de Geología de Costas y del Cuaternario, U.N. de Mar del Plata, Argentina

^b CONICET-INGEIS (Instituto de Geocronología y Geología Isotópica), Argentina

^c Universidad de Antioquia, Colombia

^d FONCYT - Centro de Geología de Costas y del Cuaternario, U.N. de Mar del Plata, Argentina

^e Centro de Geología de Costas y del Cuaternario, U.N. de Mar del Plata. Argentina

E-mail: demarti@mdp.edu.ar

The catchment of the Quequen Grande River, in the Province of Buenos Aires, is about 10,000 km² occupying an important area in the Pampa Plain, the most important agricultural productive area in Argentina. The area is covered by Upper Cenozoic loess-like sediments forming an unconfined aquifer, and it is drained mainly by the streams. Most important aspects of its hydrology, like groundwater-surface relationship, recharge volume and area, etc., remain unknown at present. Moreover, before the starting of an IAEA CRP project in November of 2004, no isotopic data exists in the catchment. After about two years of data collecting some results are able to be communicated. Local meteoric water lines has been obtained for three sampling sites in the catchment, presenting clear differences between coastal an inland rainfalls. A clear difference has been stated between the isotopic composition of inland precipitation and the isotopic composition of coastal precipitation. This observation is partially due to continentally effect, but different precipitation sources can also be recognized. Preliminarily, the dominance of a recharge area in groundwater composition has been established. Stable isotope composition of groundwater is very homogeneous, corresponding to a well mixed system. The surface water composition is clearly dominated by groundwater discharge, with some evaporation effect, and some temporary changes related to strong rainfall events.

Isotope hydrology evolution in Haiti

Chery, M.C.

MARNDR, Port-Au-Prince, Haiti

E-mail: mellecar9@yahoo.fr

Water in Haiti needs a rational management. In fact, the availability of water in Haiti can be resumed in this manner: The country receives by means 40 milliards cubic meters of water. However, 70 % of this water was lost by evapotranspiration and the other part which shows the renewable water is distributed like that: 20 % of amount drain along of the surface through the river and go to the sea and 10 % filters through the aquifer. In Haiti water is not always on the use place it varies in an area to the other depending of some factors like: precipitation, geology, vegetation, etc. In fact, some difficulties lie in the regulation, protection and mobilization of this resource. Whereas, different needs of utilization sectors, water resources management become a need so as to be able to settle water in quality and in quantity sufficiently for natural preservation, ecosystem and else. In Haiti, we have many plains which contain aquifer. We can name them: Plaine de l'arbre, Cayes, Leôgane, Gonaives et Plaine du Cul-de-Sac. The last one is the most exploited because of geographical position. In fact, since 1980 many studies on isotope hydrology have been realized on these. About Plaine du Cul-de-Sac all studies realized show almost the same result: The exploitation limit of this aquifer. Some recommendations have been done in spite of, they still continue with the anarchical exploitation of this aquifer. Many years have been passed but nothing changed. In 2001, with the cooperation of IAEA, the project aquifer integrated management of Plaine du Cul-de-Sac has been started. We have some difficulties but I think it's the one of the best ways in order to solve this problem.

Environmental isotope investigation of fresh groundwater lenses at Al-Raudhatain area, Kuwait

Hadi, K.

Kuwait Institute for Scientific Research, P.O. Box 24885, 13109, Safat, Kuwait

E-mail: aalyaa@safat.kist.edu.kw

Fresh groundwater at Al-Raudhatain depression in northern Kuwait is mostly found in the upper saturated zones of the Kuwait Group aquifer as small fresh water lenses surrounded and underlain by brackish water. These lenses are formed from the local drainage system under low rainfall conditions due to the unique geomorphological and lithological conditions of the area. During the current study the environmental isotope investigations including ^{13}C , ^{14}C , ^{18}O , ^2H and ^3H , were utilized to characterize the groundwater system in Al-Raudhatain area and identify the sources of recharge and age of fresh groundwater lenses. The radioactive isotopes (^{14}C and ^3H) results indicate that the groundwater lenses at Al-Raudhatain contain significant portions of recharge from recent (less than 500 years) rainfall events, where results of stable isotopes (^{18}O and ^2H) support the allegation of the recharging rainfall events as during the last three to four decades. The $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot indicates that the evaporation process is minimal in controlling the water chemistry and it is taking place mostly during the early stages of infiltration of the recharging water. The effect of the mixing process between the recharged water and regional brackish to saline groundwater is evident from the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot of the groundwater samples with salinities exceeding 1000 mg/L. It was estimated using stable isotopic results that the mixing process is contributing from about 20% to more than 60% of the salts as the water percolates deeper, where the dissolution process remains a significant contributor.

Use of deuterated water as a conservative artificial tracer in the study of water movement in a coarse gravel unsaturated zone

Mali, N.^a, Urbanc, J.^a, Leis, A.^b

^a Geological Survey of Slovenia, Dimiceva ulica 14, SI-1000, Ljubljana, Slovenia

^b Institute of Water Resources Management, Hydrogeology and Geophysics,
Joanneum Research Forschungsgesellschaft mbH, Graz, Austria

E-mail: nina.mali@geo-zs.si

The processes in a coarse gravel unsaturated zone develop quite differently from those in aquifers with finer unsaturated zone granulation. The aim of a tracing experiment using a lysimeter in the Selniška Dobrava aquifer was to describe the transport processes in a high-permeable coarse gravel unsaturated zone. A combined tracing experiment was performed using both deuterated water and uranine. Deuterated water is known as an effective conservative tracer in hydrogeological studies, but only few studies have focused on the unsaturated zone. Due to its highest degree of conservativeness deuterium was chosen to study water movement, while uranine with its sorption capacity was used as a contaminant transport indicator. Based on the tracing experiment's results, the fastest and dominant flow velocities were estimated. Mean flow velocity and vertical dispersion were assessed by an analytical best-fit method using one-dimensional convection-dispersion-model. Deuterium was confirmed as an ideal conservative tracer and a more suitable tracer than dye (uranine) for the study of water flow in the unsaturated zone of a coarse gravel aquifer.

Stable isotope research as a basis for long-term exploitation plans on the Sorsko Polje aquifer, Slovenia

Urbanc, J.^a, Jamnik, B.^b

^a Geological Survey of Slovenia, Dimiceva ulica 14, Ljubljana, Slovenia;

^b Vodovod-Kanalizacija Public Utility, Vodovodna cesta 90, Ljubljana, Slovenia

E-mail: janko.urbanc@geo-zs.si

From the hydrogeological point of view, the Sorsko polje area is a sink, filled with porous conglomerate and gravel, where large quantities of groundwater are accumulated. The Sorsko polje aquifer is one of the richest regions of groundwater and represents an important water source reserve for the central part of Slovenia. The determination of the ^{18}O isotope composition in water ($\delta^{18}\text{O}$) represents an independent completion of previous hydrogeological investigations of Sorsko polje. Research results give more reliable information about water origin, as well as about the influence of local precipitation and the Sava river water on the dynamics of groundwater restoration in the aquifer.

Isotopic assesment of Trabzon mineral springs and Ayder (Çamlıhemşin-Rize) - Ilıcaköy (İkizdere-Rize) hot springs

Gültekin, F., Fırat Ersoy, A., Ersoy, H.

Karadeniz Technical University, Geological Engineering Department, Trabzon, Turkey

E-mail: fatma @ktu.edu.tr

In the study area generally, basalt, andesite and basaltic-andesitic pyroclastic and sandstone, sandy limestone and marl interbedded volcano-sedimentary rocks crop out. Age of these units ranged between Liassic and Quaternary. Volcanic rocks cropped out near the mineral springs are not aquifer because of the low permeability of volcanic rocks. Mineral springs generally are controlled with fault and contacts. The pH values of the cold mineral springs range from 5.5-6.23, electrical conductivity values range from 506-5070 $\mu\text{S}/\text{cm}$, total dissolved solid values range from 374-5098 mg/L. Bereketli, Selimoğlu and Durali mineral springs are in class of “carbonate and sulphate water”, İkişu and Kisarna mineral springs are in class of “salty and sodic water”. Ayder hot spring temperature is 57°C; pH value is 9.07; electrical conductivity value is 21 $\mu\text{S}/\text{cm}$; total dissolved solid value is 163 mg/L; the water type is CaHCO_3 . Ilıcaköy hot spring temperature range from 20-63°C; pH value range from 6.5-6.78; electrical conductivity values range from 4300-5500 $\mu\text{S}/\text{cm}$; total dissolved solid values range from 4012-4115 mg/L; the water type is NaHCO_3 . Environmental isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and tritium) were analyzed to clarify the relationship between surface and groundwater circulation, and recharge- discharge condition of the aquifers. According to oxygen-18 and deuterium values, mineral springs are close to General Meteoric Water Line. Transit time of the hot spring is the longer than mineral springs. Recharge elevation of the Ayder hot spring is the highest of all springs. Recharge elevation and transit time of the water system of the İkişu mineral spring is the longest considering to oxygen-18 and tritium values. Although Kisarna mineral spring and İkişu mineral spring have the same recharge elevation Kisarna mineral spring has a shorter transit time of the water system. Mineral springs have shallow circulation based on deuterium and tritium values.

Application of environmental isotope techniques to selected hydrological systems in Pampean, Argentina

Dapeña, C., Panarello, H.O.

INGEIS - CONICET -UBA, Buenos Aires, Argentina.

E-mail: dapenna@ingeis.uba.ar

The isotopic composition of precipitation in Buenos Aires station is of great importance to understand the hydrological Pampean Systems. The rain isotope content (^2H , ^{18}O and ^3H) is being recorded since 1978 at Ciudad Universitaria Station, belonging to the Red Nacional de Colectores de Argentina and the Global Network for Isotopes in Precipitation (IAEA-WMO). The annual weighted average of Buenos Aires isotopic composition is $\delta^{18}\text{O} = -5.5\text{‰}$, $\delta^2\text{H} = -30\text{‰}$ and the local meteoric water line ranges from $\delta^2\text{H} = 8\delta^{18}\text{O}+12$ to $\delta^2\text{H} = 8\delta^{18}\text{O}+14$. These data are being used like input function to local hydrologic systems. ^3H concentration varies between 0 TU and 17.7 TU; nevertheless, values higher as 40 TU were also measured, responding to the spring peak. At present, still higher values were found, in response to non-natural causes. Isotope techniques were used to investigate several regions from Buenos Aires province. This work presents relevant applications of environmental isotopes techniques to selected areas in the Pampean region.

Interaction between groundwater and surface water through the El Haouareb Dam (Kairouan plain, Central Tunisia)

Ben Ammar, S.^{a,b}, Zouari, K.^b, Leduc, C.^d

^a Centre National des Sciences et Technologies Nucléaires, 2020 Sidi Thabet, Tunisia

^b Laboratoire de Radio-Analyses et Environnement, E.N.I Sfax, BP W 38 Sfax, Tunisia

^c IRD, UMR G-EAU, BP 434, 1004 El Menzah 4, Tunis, Tunisia

E-mail: safouan_ammam@yahoo.fr

The alluvial aquifer of the Kairouan plain is the most important aquifer in the semi-arid central Tunisia and then the main water supply for agricultural and human needs. In 1989, the construction of the El Haouareb dam over a karstic sill completely changed the aquifer recharge process. Prior to the dam construction, recharge came from the infiltration of the Merguellil wadi floods in the plain and from the Ain el Beidha groundwater flow close to the dam site. Presently, recharge still comes from the Ain el Beidha aquifer but also from the dam reservoir through karstic fissures. A detailed isotopic survey (^{18}O , ^2H , ^3H , ^{13}C , ^{14}C) completed the hydrodynamic analysis. The new recharge pattern is identified and the progress of water infiltrated after 1989 is visible. Ratios of Ain el Beidha and dam waters in the karst or in the plain aquifer vary with time. A first water budget is proposed for the period 1998-2000.

C-14 and tritium concentrations along Romanian Danube Sector – preliminary results

Varlam, C.^a, Stefanescu, I.^a, Cuna, S.^b, Faurescu, I.^a, Popescu, I.^a, Varlam, M.^a

^a National Institute for Cryogenic and Isotopic Technologies, Rm-Valcea, Romania

^b National Institute for Isotopic and Molecular Technologies, Cluj, Romania

E-mail: cvarlam@icsi.ro

Danube River Basin is the second river basin in Europe comprising 18 countries. Lower Danube Basin covers the Romanian-Bulgarian sub-basin downstream of Cazane Gorge and the sub-basins of Siret and Prut River. Cernavoda Nuclear Power, a CANDU type reactor, is situated in this region upstream Danube Delta. Taking into account the future development of this important Romanian nuclear objective, the knowledge of the present condition of Tritium and C-14 concentrations levels becomes a necessity. Therefore, an extensive monitoring program for these isotopes, along the Romanian sector of the Danube River Basin, starting with Cazane Gorge and ending with the three branches of the Danube Delta, has been started. The tributaries from this sector: Cerna, Jiu, Olt, Arges are included also in this ongoing project. Preliminary results of tritium level measured in 17 locations within the mentioned areas are presented in the paper. This tritium level is compared with the tritium concentration in precipitation during the year 2006. In order to make an isotopic evaluation of water balance, the monitoring program will run during the year 2007 extending the scope of interest on stable isotopes: ^2H , ^{18}O , ^{13}C and a multivariate statistical analysis will be developed.

Rainwater tracing using the stable isotopes in the Western Mediterranean (case of Rif Chain in the North of Morocco)

Qurtobi, M.^a, Emblanch, C.^b, Marah, H.^a, Elmahboul, A.^c

^a Centre national de l'énergie, des sciences et des techniques nucléaires (CNESTEN), Morocco

^b Université d'avignon et des pays de vaucluse, UFR des sciences exactes et naturelles laboratoire d'hydrogéologie, Morocco

^c Agence du bassin hydraulique du loukous 'ABHL', Morocco

E-mail: qurtobi@yahoo.fr

Nine meteorological stations, distributed between 3 and 996 m of altitude, have been used as basis of an isotopic study of rainwater carried out in the Rif chain (Northern part of Morocco) during the hydrological cycles 2004 to 2006. This study allowed us to examine the isotopic variations during the year and to define the relationship between ^{18}O and ^2H . The altitude gradient established for ^{18}O is: -0.27‰ per 100 m. We have also used the relationship between emergence points altitudes of some studied springs and their ^{18}O contents to calculate the regional ^{18}O gradient. The selected springs are supposed to have nearest emergence altitudes to the ones of the neighbouring mountains. The ^{18}O content variation in the springs corresponds to an altitudinal gradient: -0.27‰ per 100 m. It is remarkable to note that this gradient is identical to that of the rainwater. Even if this isotopic study is reduced in time, it seems to be sustainable to establish a correct regional meteoric line. The constant difference associated to the regression (4.25 in groundwater and 4.87 in rainwater) remains to discuss. Before having a demonstrated value, we will use the gradient and the origin ordinate determined from the springs, gradient that takes in to account the rains evaporation before their infiltration.

The stable isotope of hydrogen as an indicator of Mediouna landfill leachate pollution (Casablanca, Morocco)

Fekri, A.^a, Wahbi, M.^b, Benbouziane, A.^a, Marrah, H.^c, Hammoumi, O.^a

^a Université Hassan II of Mohammedia Faculté des Sciences Ben M'sik, Boulevard
Commandant Driss el Harti B.P. 7955 Sidi Othman 20700 Casablanca, Morocco

^b Université Cadi Ayyad, Faculté des Sciences et Techniques-Gueliz, Marrakech,
Morocco

^c Centre National de l'Énergie, des Sciences et des Techniques Nucléaires
(CNESTEN) B.P. 1382 R.P. 10001 Rabat, Morocco

E-mail: ahmfekri@menara.ma

Since 1986 the municipal solid wastes produced by the city of Casablanca are stockpiled in Mediouna Landfill installed on old quarries without liner or leachate collection system. A previous study had shown an advance of the pollution plume from the landfill due to the faults affecting the fractured aquifer matrix. The aim of our study is to use the unique isotopic characteristics observed in landfill leachate as an indicator for confirming whether contamination is from landfill or from some other local sources. Oxygen-18 and deuterium investigation was undertaken on samples collected, from wells upstream and downstream the landfill. Compared to hydrogen and oxygen isotopes of local precipitation some wells' samples show an enrichment of hydrogen isotope. This data is used to delimit pollution plume extension. The deuterium is useful as an environmental indicator for municipal landfill pollution but not sufficient.

Isotopic and chemical investigation of water samples in Argolis Peninsula (Greece)

Matiatos, I.^a, Alexopoulos, A.^b

^a Isotope Hydrology Laboratory, Inst. of Physical Chemistry, N.C.S.R.,
“DEMOKRITOS”, Athens, Greece

^b National and Kapodistrian Univ. of Athens, Faculty of Geology and Geo-
environment, Athens, Greece

E-mail: imatiatos@geol.uoa.gr

The study area, located in the north-eastern part of Peloponnesus (Greece), is characterized by three major mountains (Arachnaio, Didima, Aderes), which constitute a complex orography and hydrogeology. The objective of the study was to gain the first regional picture of groundwater recharge in the area. However, groundwater circulation is not very distinct due to the geological diversity of the peninsula. Therefore, samples were collected from springs, wells and rain collectors and analyzed for environmental isotopes as well as major ions. The interpretation of the results was carried out in the light of other geological and hydrogeological information to determine the sources and mechanisms of recharge in the area. Arachnaio mountain, which shows the highest altitude and extent, appears to be the main recharge zone which replenishes a number of springs in the peninsula.

Cross-border groundwater management: the contribution of deep groundwater to Quaternary basins deduced from isotope data

**Althaus, R.^a, Heidinger, M.^b, Lorenz, G.^b, Purtschert, R.^a, Selg, M.^c,
Eichinger, L.^b**

^a Climate and Environmental Physics Division, Physics Institute University Bern,
Switzerland

^b Hydroisotop GmbH, Schweitenkirchen, Germany

^c Landesamt für Geologie, Rohstoffe und Bergbau, Regierungspräsidium Freiburg,
Baden-Württemberg, Germany

E-mail: althaus@climate.unibe.ch

In the frame of an EU Interreg IIIa project it is investigated to what extent the interregional upper Jurassic karst aquifer, which underlies parts of southern Germany and the area around Schaffhausen in Switzerland, contributes to the water budget of shallow Quaternary basins on both sides of the border. Special emphasis was put on isotope tracers because the differentiation between mixing end members based on chemical parameters is ambiguous. Proportion and spatial occurrence of deep karst water were determined based on ^3H , ^{85}Kr , ^{39}Ar , ^{14}C and Sr-isotope signatures. The data were interpreted based on a 3D-hydrogeological setup which was completely re-evaluated using reprocessed seismic profiles. The reviewed scientific results provide the basis for a sustainable groundwater protection and resource management overcoming national borders as the groundwater does.

Identification of groundwater recharge sources by using of ^{234}U excess and ^{34}S for the arid Ejina-Badain Jaran Interior Basin of Alxa Plateau in Inner Mongolia

Gu, W.-Z., Lu, J.-J., Wu, Y.

Nanjing Hydraulic Research Institute, Nanjing, China

E-mail: jjlu@nhri.cn

The Ejina-Badain Jaran depression of the Alxa Plateau of Inner Mongolia covers an area of 81,380 km² with annual mean precipitation of about 50 to 80 mm. It is composed of Gobi, Badain Jaran Shamo (Dune Desert) and two grasslands, Gurinai and Wendu Golei. The intermittent Black River ends into lakes in this depression. Precipitation, surface water, groundwater from dug wells, boreholes and springs are sampled. Big variations of U, $^{234}\text{U}_{\text{ex}}$, $^{34}\text{S}_{\text{sulphate}}$, ^{18}O , ^3H , and ^{14}C of waters are found especially that of U and $^{234}\text{U}_{\text{ex}}$ with ranges of 0.06 ppb to 1455 ppb and, - 0.408 eU to 13.91 eU respectively, it leads to the differentiation of groundwaters into groups as Gobi, Shamo and the grasslands. The $^{34}\text{S}_{\text{sulphate}}$ is also used for this purpose due to the sulphate in this huge nomad area. The recharge sources of groundwater are identified by using the end members with special reference to the Gurinai grassland. Three source waters of its phreatic groundwater are: the local precipitation, the Gobi groundwater and the leakage from deep aquifers. Three source waters of deep groundwater are: the Gobi groundwater, the deep groundwater from Shamo and the palaeowater. These recharge sources are checked by other isotopic ratios especially that of $^{34}\text{S}_{\text{sulphate}}$. The Gobi water appears to be the mixing of local precipitation, deep percolation from the Black River and the deep groundwater from different areas including that from Mongolia. From data of all the sampling sites distributed in Gurinai, an areal averaged contribution of every source water for both the phreatic and deep groundwaters are estimated by using of U and $^{234}\text{U}_{\text{ex}}$.

Isotopic and geochemical techniques applied to Efteni and Derdin Geothermal Systems, NW Turkey

Karakuş, H., Şimşek, Ş.

Hacettepe University, Engineering Faculty Geological Eng. Dept. 06800 Beytepe, Ankara, Turkey

E-mail: hkarakus@hacettepe.edu.tr

The Efteni and Derdin low-temperature geothermal areas are located in north-western Turkey. Surface manifestations of relatively low-temperature springs (22-43°C) emerge on the Düzce fault, a normal component dominated fault segment in the North Anatolian Fault System (NAFS). Ionic characteristics of the geothermal springs generally are $\text{Na} > \text{Mg} > \text{Ca}$ and $\text{HCO}_3 > \text{Cl} > \text{SO}_4$. Isotopic and chemical evaluations show that there are two separate geothermal reservoirs in the area. Geothermometrical analyses applied to the Efteni and Derdin springs, representing these two separate reservoirs, reveal 113-135°C and 80-104°C respectively. Strong ^{18}O shift has been observed in the Derdin spring which has ~2 TU of tritium content indicating recent recharges. In the scope of this study, the thermal reservoirs and the physical processes that affect both springs are distinguished, and the hydrothermal structures of the springs are determined by chemical and isotopic analyses. Geothermometric equations, which are used to estimate reservoir temperatures, have been correlated using isotopic techniques and, in particular, dilution processes, such as surface water mixing, have been distinguished in the Derdin Spring.

¹³C-isotope investigations for the determination and quantification of natural attenuation effects at the CHC contaminated site in Frankenthal, Germany

Ertl, S.^a, Heidinger, M.^a, Martin, H.^a, Schmidt, K.R.^b, Tiehm, A.^b, Leve, J.^c, Karch, U.^c

^a Hydroisotop GmbH, Schweitenkirchen, Germany

^b Dept. of Environmental Bio-technology, Water Tech. Center, Karlsruhe, Germany

^c DVGW - Research Institute Engler-Bunte at the University of Karlsruhe (TH), Karlsruhe, Germany

E-mail: MH@Hydroisotop.de

The investigations at the Frankenthal site are performed as a part of the German funding priority KORA (TV 3.6) of the BMBF (Federal Ministry of Education and Research). The aim of KORA is to develop technical and legal instruments, which will facilitate the evaluation and customised use of Natural Attenuation (NA) processes in the risk assessment and remediation of contaminated sites. The investigations show that by using compound specific isotope analysis (GC-IRMS, Gas Chromatograph Isotope Ratio Mass Spectrometry) evidence of NA processes on chlorinated hydrocarbons (CHC) can be provided. The amount of microbial degradation was quantified by using a Rayleigh-type-model approach with the weighted mean ¹³C-CHC-signature, the derived starting ¹³C-signature and the sum of site specific ¹³C-enrichment factors ϵ that were determined in laboratory experiments. The results indicate an ongoing degradation process, which is shown in diagrams under minimum criteria, which is the basis of the used quantification method. The diagram shows that the state of degradation is increasing with time (sampling campaign 2000-2004-2005-2006) and distance from the source. The methods will be implemented into guidelines for the use of Monitored Natural Attenuation processes in the risk assessment and remediation of contaminated water resources.

Stable isotope fractionation during PCE halo-respiration and aerobic *cis*DCE and VC biodegradation

Ertl, S.^a, Heidinger, M.^a, Martin, H.^a, Schmidt, K.R.^b, Tiehm, A.^b

^a Hydroisotop GmbH, Schweitenkirchen, Germany

^b Dept. of Environmental Biotechnology, Water Tech. Center, Karlsruhe, Germany

E-mail: MH@Hydroisotop.de

The objectives of our study were to identify the anaerobic/aerobic dechlorination mechanisms at two chloroethene-contaminated sites, to assess the isotopic enrichment factors in groundwater microcosms, and to evaluate microbial degradation in the field based on the isotopic signatures. In anaerobic microcosms, a transformation of PCE and TCE to *cis*DCE was observed. Halo respiration was accompanied by isotopic fractionation effects similar to previous publications. In aerobic microcosms, *cis*DCE and VC were degraded indicating a co-metabolic degradation of *cis*DCE in the course of VC degradation. In other experiments, only VC was degraded. Enrichment factors were determined during aerobic degradation of *cis*DCE and VC. These factors are significantly higher than factors published previously. This study demonstrates that isotope fractionation is suitable for assessing anaerobic/aerobic chloroethene degradation. However, the factors vary for different degradation pathways and micro organisms. Therefore, site-specific enrichment factors have to be determined in order to quantify natural attenuation processes in the field.

Assessing agriculture pollution in the Beja aquifer using nitrogen isotopes (South Portugal)

Paralta, E.^a, Carreira, P.M.^b, Ribeiro, L.^c

^a National Institute of Engineering, Tech. & Innovation (INETI), Hydrogeology Department, Estrada da Portela, Apartado 7586, 2720 Alfragide, Portugal.

^b Nuclear Technological Institute (ITN), Chemical Department, Est. Nacional 10, 2686-953 Sacavém, Portugal.

^c Lisbon Technical Univ. (IST), Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

E-mail: eduardo.parlata@ineti.pt

This paper intends to give scientific support for political decisions, considering the sustainable development of rural regions under semiarid conditions exploiting shallow aquifers, and promote appropriate use of nitrogen fertilizers, based on EC Water Framework Directive and EC Groundwater Framework Directive in the context of vulnerable aquifers. Stable nitrogen isotopes ($^{15}\text{N}/^{14}\text{N}$ ratios) can offer a direct way to identify the pollutant sources in groundwater systems. In the research area two major sources of nitrate were identified in agricultural areas, fertilizer and manure, which present different isotopic $\delta^{15}\text{N}$ signatures. The relative contributions of these two sources to groundwater or surface water can be estimated by mass balance. The analysis of nitrate $\delta^{18}\text{O}$ together with $\delta^{15}\text{N}$ improves the ability to trace nitrate sources and cycling. According to field practice in the rural area of Beja, major cause of pollution comes from fertilizers. Isotope results are not conclusive about the possibility that major source of nitrate-N in groundwater comes from agriculture as expected. Further work is required regarding seasonality sampling and laboratory techniques with sufficient accuracy.

The role of rivers and surface waters in the frame of Nisot, the Swiss network for the observation of isotopes in the water cycle

Kozel, R.^a, Leuenberger, U.^b, Schürch, M.^a, Stichler, W.^c

^a Federal Office for the Environment, Bern, Switzerland

^b Climate and Environmental Physics, Physics Institute, Univ. Bern, Switzerland

^c GSF – Institute for Groundwater Ecology, Neuherberg, Germany

E-mail: Marc.Schuerch@bafu.admin.ch

The Swiss network for the observation of isotopes in the water cycle aims at developing diagnostic tools for the public to detect and evaluate climate-induced changes in the qualitative behaviour of surface water and shallow groundwater. Water in rivers may originate from many sources with different isotopic composition depending on precipitation distribution and infiltration characteristics, residence time, or altitude of recharge areas of the contributing surface and groundwater components. The distribution of the natural tracers: tritium, deuterium, and oxygen-18 allows the separation of the water components as for instance surface run-off of precipitation or the contribution of groundwater. Depending on the size of the watershed, a single precipitation event or the seasonal change of snow cover for instance, may therefore determine the isotopic distribution of the run-off. During the last decades Switzerland went through the most substantial climatic change regarding temperature and precipitation distribution since the national climate measurement and observation network was established in 1864. Especially winter half-years experienced a sudden warming. According to this change the isotopic composition of river, surface water and shallow groundwater changed too. We will discuss to what extent the isotopic signature can be used to characterize local and regional conditions of surface-groundwater interactions and recharge mechanisms since 1985, the beginning of the isotope measurements in Swiss rivers.

Modeling the altitude isotope effect in precipitations and comparison with the altitude effect in groundwater

Gherardi, F.^a, Bono, P.^b, Fiori, C.^b, Diaz Tejeiro, M.F.^c, Gonfiantini, R.^a

^a Institute of Geosciences and Georesources, CNR, Pisa, Italy

^b Department of Earth Sciences, University “La Sapienza”, Rome, Italy

^c Centre of Studies and Applied Techniques, Ministry of Civil Works, Madrid, Spain

E-mail: r.gonfiantini@igg.cnr.it

A numerical model has been developed to account for the altitude effect on the isotopic composition of precipitation. The model allows to predict the isotope variations in rains produced by a marine air mass which moves inland, climbs up along a mountain slope and undergoes cooling and condensation under pseudo-adiabatic and pseudo-Rayleigh conditions. It is assumed that the isotopic fractionations between liquid water and vapor occur at equilibrium and the evaporation effects during the raindrop fall are negligible. Generally, the isotopic values observed in precipitation are in good agreement with those predicted by the model. For groundwater, the best agreement between model predictions and field observations is obtained for springs fed by small perched aquifers. The following relationships are obtained: (i) mean altitude gradients: $d(\delta^{18}\text{O})/dz = -1.8 \text{ ‰ km}^{-1}$ and $d(\delta^2\text{H})/dz = -14.2 \text{ ‰ km}^{-1}$ (model: -1.7 and -13.9 ‰ km^{-1} , respectively); (ii) local meteoric water line (valid up to an altitude of 2500 m a.s.l.): $\delta^2\text{H} = 7.53 \delta^{18}\text{O} + 13.5$ (model: $\delta^2\text{H} = 7.83 \delta^{18}\text{O} + 16.2$).

Isotopic approaches for monitoring potential contamination of shallow aquifers with produced fluids or gases from coalbed methane operations in Alberta, Canada

Mayer, B., Klassen, P., Cheung, K., Taylor, S.

Department of Geology & Geophysics, University of Calgary, Calgary, Canada

E-mail: bmayer@ucalgary.ca

Production of coalbed methane (CBM) or natural gas from coal (NGC) from shallow coal seams is a relatively new industry in Alberta (Canada) and constitutes a vital new source of natural gas supply in Western Canada. There are, however, significant environmental concerns; some of them are related to the potential negative impacts on shallow groundwater resources. Since 2004, we have analyzed the chemical and isotopic compositions of fluids and dissolved gases from more than 75 production wells in Alberta. Simultaneously, our research group has begun to generate an emerging database summarizing chemical and isotopic parameters for shallow groundwater and its dissolved gases in the vicinity of coal bed methane operations. Preliminary data indicate that carbon isotope ratios of coalbed-derived methane are often isotopically distinct from dissolved “background” methane in shallow groundwater. Therefore, carbon isotope measurements on dissolved or free methane in shallow aquifers may serve as a suitable tool for monitoring potential contamination of shallow groundwater resources with produced gases. As a consequence, the Alberta government has introduced mandatory baseline testing standards that include carbon isotope measurements in methane for water wells in the vicinity of CBM operations in Alberta.

Combining hydrological, chemical, and isotopic approaches to identify sources and fate of sulfate and nitrate in the South Saskatchewan River System, Canada

Mayer, B.^a, Wassenaar, L.I.^b, Rock, L.^a, McCallum, J.E.^a

^a Department of Geology & Geophysics, University of Calgary, Calgary, Canada

^b Science and Technology Branch, Environment Canada, Saskatoon, Canada S7N 3H5

E-mail: bmayer@ucalgary.ca

River water, seasonally sampled at 25 stations along the South Saskatchewan River and its tributaries between the headwaters in Alberta and mouth near Prince Albert (Saskatchewan), was analyzed for its chemical and isotopic composition ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{nitrate}}$, $\delta^{18}\text{O}_{\text{nitrate}}$, $\delta^{34}\text{S}_{\text{sulfate}}$, $\delta^{18}\text{O}_{\text{sulfate}}$). Sources and processes responsible for marked changes in riverine sulfate and nitrate fluxes were identified using stable isotope techniques. Geologic (evaporite) sulfate was the predominant sulfate source in the headwaters, while sulfate from anthropogenic sources in urban areas and from pyrite oxidation in the tills of agricultural regions caused markedly elevated sulfate fluxes with increasing distance. Nitrate fluxes in the headwater sections were low and N and O stable isotope data indicated that the nitrate was mainly derived from nitrification in forest soils. With increasing flow distance, there was clear evidence of nitrate loading from municipal waste water sources and agricultural return flows. This study demonstrates that stable isotope techniques are an effective tool for distinguishing natural and anthropogenic sources and the fate of sulfate and nitrate in large riverine systems, particularly if used in concert with hydrometric and complementary geochemical data.

Monitoring carbon dioxide injection and storage in aquifers and depleted oilfields using carbon and sulfur isotope techniques

Raistrick, M., Hutcheon, I., Shevalier, M., Mayer, B.

University of Calgary, Calgary, Canada

E-mail: mraistri@ucalgary.ca

Fluid and gas monitoring can be used to confirm the security and integrity of geological CO₂ storage. The distinct carbon isotopic composition of CO₂ from many industrial sources that process or combust hydrocarbons allows the use of isotopic and chemical analyses of produced fluids and gases to trace the injected CO₂ and quantify CO₂ storage processes in the subsurface. Our four year monitoring programme at the International Energy Agency Weyburn CO₂ Monitoring and Storage Project in Saskatchewan, Canada, featured frequent chemical and isotopic measurements of produced fluids and gases from around forty wells. Over the four year period, over four million tonnes of CO₂ were injected for storage and enhanced hydrocarbon recovery in the Weyburn Oilfield. CO₂ concentration and carbon isotopic measurements of produced fluids and gases trace CO₂, and confirm that the order of magnitude increase in the amount of CO₂ in the subsurface resulted from CO₂ injection. The amount of CO₂ stored as HCO₃⁻ can be quantified using HCO₃⁻ concentration and carbon isotopic measurements, while concentration and isotope data for SO₄²⁻ and H₂S indicate that bacterial sulfate reduction was not a major source of HCO₃⁻. To allow widespread application of geological CO₂ storage, reliable, cost effective monitoring of storage integrity will be essential. The produced fluid and gas monitoring techniques described here are based on chemical and isotopic techniques that are already widely employed and well understood by environmental isotope hydrologists, and have the potential to play an essential role in future geological CO₂ storage monitoring programmes.

Isotopic evaluation of geothermal waters in Konya region (Turkey)

Nalbantcilar, M.T.^a, Gocmez, G.^a, Kara, I.^b

^a Selcuk University Eng. and Arch. Faculty Geological Eng. Dept., Konya, Turkey

^b General Directorate of Mineral Research and Exploration, Turkey

E-mail: tahir111@hotmail.com

Konya region (Turkey) has three important geothermal subregion. These are Cihanbeyli, Beysehir-Seydisehir-Ilgın and Ismil-Eregli subregions. Geothermal waters in the region have temperature between 19.8-51°C, discharge between 0.1 - 130 L/s and total mineralization range from 852 to 5110 mg/L. The isotopic analysis evaluated according to $^{18}\text{O}/^2\text{H}$, $^{18}\text{O}/\text{TU}$, Cl/TU , pH/EC and Giggenbach diagrams. The geothermal water aquifers are recharged from higher altitudes and they are hardly affected by recent precipitations and these waters reveal meteoric origin. They have more negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and lower ^3H contents compared to cold waters. The reservoir rock temperature is 250°C, and water depths are ranging from 500 to 1000 m. The waters heat from volcanism and geothermal gradient.

Assessment of groundwater dynamics in Uganda using a combination of isotope tracers and aquifer hydraulics data

Tindimugaya, C.^{a,b}, Taylor, R.G.^b, Kulkarni, K.M.^c, Atkinson, T.C.^b, Barker, J.^b

^a Water Resources Management Department, Directorate of Water Development, P.O. Box 19, Entebbe, Uganda

^b Hydrogeology Group, Department of Geography, University College London, 26 Bedford Way, London, WC1H 0AP, UK

^c Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: ctindi.wrmd@dwd.co.ug

Groundwater is widely developed for low-cost town, water supplies in areas underlain by weathered crystalline rock in sub-Saharan Africa but the sustainability of abstraction is unknown. In this study, we assess groundwater dynamics in fluvial deposits and weathered-fractured crystalline rocks underlying the town of Rukungiri, Uganda using environmental tracers and aquifer hydraulics data. CFC and ³H concentrations in pumped groundwater highlight that mixing of groundwaters of different residence times has occurred. Application of lumped parameter models based on tracer concentrations and reconstructed input functions indicate that groundwater underlying Rukungiri Town is generally young (less than 50 years old). A change in groundwater flow dimension from 2 (radial) to 1 (linear) since the commencement of intensive abstraction 8 years ago combined with a steady decline in groundwater levels over the last 8 years give rise to a conceptual model of a locally bounded isotropic (gravel) aquifer. Our results suggest that current groundwater development in Rukungiri is unsustainable. To maintain current abstraction and plan for increased abstraction for rapidly growing towns, strategies to optimise groundwater abstraction and protection are therefore required to control overexploitation and possible pollution of the aquifer.

A deep, highly productive aquifer is identified using isotope, hydrochemical, and geophysical techniques

Verhagen, B.Th.^a, Butler, M.J.^b, van Wyk, E.^c

^a School of Geosciences, University of the Witwatersrand, Johannesburg, South Africa

^b Environmental Isotope Group, iThemba LABS (Gauteng), Johannesburg, South Africa

^c Directorate of Geohydrology, Department of Water Affairs and Forestry, Pretoria, South Africa

E-mail: verhagenb@staff.wits.ac.za

An environmental isotope and hydrochemical study was undertaken to assess a conceptual model developed earlier on which a major, regional rural groundwater supply from a basalt aquifer was to be based. Mean residence time and porosity figures indicated that recharge, and therefore sustainable extraction, could be as low as 10% of the model estimates. Variable chemical and isotope data also questioned model predictions of balancing drainage along a major fault line. These results, suggesting upwelling groundwater, prompted a major re-investigation of the area, involving further exploratory drilling and geophysics. A deeper sandstone aquifer, previously thought to be unproductive, was found to produce high yields of excellent quality groundwater and constituting a potentially major regional resource. Further work is aimed at its development and management through conjunctive exploitation.

Ground water input to a rare flood event in an arid zone ephemeral river identified with isotopes and chemistry

Verhagen, B.Th.^a, Butler, M.J.^b

^a School of Geosciences, University of the Witwatersrand, Johannesburg, South Africa

^b Environmental Isotope Group, iThemba LABS (Gauteng), Johannesburg, South Africa

E-mail: verhagenb@staff.wits.ac.za

Various isotope studies in temperate climates have shown that the shallow groundwater component feeding perennial rivers during rainfall events can be more important than surface runoff. We report here on possibly unique isotopic and chemical evidence of groundwater contributions to a rare flood event of the ephemeral Auob River during the exceptional rains of 1999/2000 in the arid/semi-arid Kalahari of south-eastern Namibia. The recognition of this process was enabled by a detailed knowledge of the isotope hydrology of groundwater in the area and provided insights into aspects of the palaeo-hydrology of the Auob River catchment.

Stable isotopes as tools for watershed hydrology model development, testing and rejection

McDonnell, J.J.^a, Vache, K.^b, Weiler, M.^c, Seibert, J.^d

^a Oregon State University, USA

^b Giessen University, Germany

^c University of British Columbia, USA

^d Stockholm University, Sweden

E-mail: jeff.mcdonnell@oregonstate.edu

Process representation in the watershed hydrology model structure continues to be a vexing issue in hydrology. Complex hydrological descriptions at the hillslope scale have been difficult to incorporate within a watershed modeling framework due to the disparity between the scale of measurements and the scale of model sub-units. As a result, parameters represented in many conceptual watershed hydrology models are often not physically-based or related to physical properties, and therefore cannot be established prior to a model calibration. While tolerable for predictions involving water quantity, water quality simulations require additional attention to transport processes, flowpath sources and water age. This paper examines how isotope hydrology studies, especially those where residence time can be quantified in surface waters and soil/ground waters may be used to subsume flowpath process complexity and provide a simple, scalable evaluative data source for water quantity-quality based conceptual models at the catchment scale. We present a set of simple distributed hydrologic models (from simple to more complex) along with a methodology to evaluate, through direct simulation, the residence time distribution of the model sub-units. Our results show that models that might otherwise be acceptable for flow may be wholly rejected for an inability to capture residence time dynamics. This process-based rejection framework can be very helpful in the evaluation of conceptual models that include chemistry.

**$\delta^{18}\text{O}$ isotope map-generation of European mineral waters,
applications and limits**

Voerkelius, S., Lorenz, G., Eichinger, L.

Hydroisotop GmbH, Schweitenkirchen, Germany

E-mail: S.Voerkelius@Hydroisotop.de

There is an increasing demand for independent analytical methods which can control the geographical origin of food. The EU project TRACE was started with the aim to develop a general understanding of the relation of the geo-bio-climatic environment and the isotope and elemental signature in food commodities. Besides mineral water, the agricultural products wheat, honey, olive oil and lamb meat are investigated. As one part of the study a detailed $\delta^{18}\text{O}$ map for groundwater will be generated by the isotope results of 600 samples of European mineral waters. These groundwater isotope maps provide a multitude of applications not only for authenticity of food, but for groundwater recharge and climate studies, criminal forensics as well as archaeology too.

Deuterium tracer experiment in the unsaturated zone of fractured karst aquifers

Cencur Curk, B.^a, Stichler, W.^b

^a IRGO – Institute for Mining, Geotechnology and Environment, Ljubljana, Slovenia

^b GSF – Institute of Hydrology, Munich, Germany

E-mail: Barbara.Cencur@irgo.si

In the frame of Association of Tracer Hydrology project a multi-tracer experiment was performed at the research field site (RFS) Sinji Vrh, which consists of surface set-up and a research tunnel, 15 m below the surface. A special construction (1.5 m long segments) for collecting water seeping from the ceiling of the research tunnel was developed. Deuterium (90 %), potassium bromide, lithium chloride, zinc sulphate, sulfonic acid, pyranine, naphthionate, uranine, Sulforhodamine B, micro spheres and bacteriophages P22H5 were used as tracers and injected into the borehole. Tracers appeared immediately after the first significant precipitation event, respectively four days after the injection. The most pronounced breakthrough appeared for uranine, deuterium and chlorine ions. This tracer experiment again confirmed the presence of fast flow through a channel above two sampling points (MP4 and MP5), where the response is rapid and the detected concentrations are high. After the injection of tracers, they remain in the microfracture systems of the unsaturated zone and are rinsed by subsequent larger precipitation events even up to several years (in this experiment at least three years) after the injection. The results from Sinji Vrh have shown that the unsaturated zone in the fractured and karstified rocks plays an important role in pollution retardation and storage.

Geochemical and isotopic characterization of groundwater resources in Maidere Basin (southern part of Morocco)

Ouda, B.^a, Marah, H.^a, Mokadem, K.^b, Zine, N.^c, Filali, M.^c, Lahmouri, A.^c, Mudry, J.^d

^a Centre National de l'Énergie, des Sciences et des Techniques Nucléaires, Morocco

^b Direction Régional du Bassin ziz-Rheris-Guir/Errachidia, Morocco

^c Direction Générale de l'Hydraulique, Morocco

^d Université Franche-Comté, France

E-mail: bouchra_ouda@yahoo.fr

Integration of geochemical and isotopes techniques in water resources investigations has contributed considerably to a better understanding of the aquifer hydrodynamic functioning in complex structural areas. Maidere Basin, located in south Morocco, is extending over 13,000 km² and limited by some orographical chains of Anti Atlas. Lithological formations outcropping in the basin are divided into compartments by major faults of NE-SW direction. This fault network helped to generate aquifers compartments with lateral hydraulic discontinuity. Five aquifers constitute the multilayer system: Precambrian, lower Cambrian, Middle Cambrian, Ordovician and Quaternary units. Ordovician outcrops are a large spread and constitute the more important aquifer in the basin. Furthermore, a smell gas like carbon dioxide is observed in some bores sampled from different aquifers. Geochemical and isotopic study has been undertaken in Maidere Basin in order to better understanding the hydrodynamic functioning of the aquifers units and to determinate the CO₂ gas origin. Correlations between saturation index towards calcite and the partial pressure of CO₂, have allowed distinguishing undersaturated water with a lower pCO₂ sampled from all of wells and oversaturated water with high values of pCO₂ sampled in boreholes. Modern carbon percentage analyses showed the presence of old water in the boreholes with high values of pCO₂. Carbon dioxide seems to come from deep levels and circulate through the deep faults network. The relationship between $\delta^{13}\text{C}$ and pmC (percent modern carbon) oppose the modern groundwater and impoverished in $\delta^{13}\text{C}$ (that keep the pedological marking of the carbon at the time of their infiltration) to paleowaters (<16 pmC) and having exchanged the carbon with an impoverished matrix and/or having dissolved a carbon dioxide of deep origin.

Isotopic and hydrochemical properties of hot and mineralized waters in SW Konya Geothermal Field (Turkey)

Gocmez, G., Nalbantcilar, M.T.

Selcuk University Engineering and Arch. Faculty Geological Engineering Dept.,
Konya, Turkey

E-mail: tahir111@hotmail.com

The study area is located at southwest part of Konya (Central Anatolia). The basement formation of the area is Çaltepe, deposited from Early Cambrian through Middle Cambrian. Seydişehir Formation which is composed of alternating slate, sandstone and metasandstone overlies conformably the overthrown Çaltepe Formation and is Upper Cambrian-Lower Ordovician in age. Seydişehir Formation is conformably underlined by Tarasçı Limestone, Neogene in age. Alluvium is Quaternary-Present in age. The hot and mineralized waters are located in the study area around Ilcatepe and Kavakköy village having temperature range between 31°C and 46°C, flow rate between 1.42 and 5.0 L/s and total dissolved solids between 2,218-3,500 mg/L. Aquifers of these waters are the porous limestone and dolomitic limestone of the Çaltepe Formation. The travertine cones occur as a result of water activity. The groundwaters are classified according to the AIH standards are Ca, Na, HCO₃, and B bearing hot and mineralized water. The oxygen and hydrogen isotope compositions of geothermal waters reveal meteoric origin. They have more negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and lower ^3H contents compared to cold waters. The geothermal water aquifers are recharged from higher altitudes and they are hardly affected by recent precipitations.

Assessing the applicability of global CFC and SF₆ input functions to groundwater dating in Britain

Darling, W.G., Goody, D.C.

British Geological Survey, Wallingford, United Kingdom

E-mail: wgd@bgs.ac.uk

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) are increasingly being used to date groundwaters. While these trace gases are generally well-mixed in the atmosphere, local atmospheric excesses (LAEs) have been found in some parts of the world, thereby affecting the interpretation of data from groundwater studies. To investigate the possibility of LAEs in Britain, mixing ratios of CFC-11, CFC-12 and SF₆ were measured in soil gases from two large conurbations (London and Birmingham) and a smaller urban area, Bristol. Most mixing ratios for CFC-12 and SF₆ were <10% above the current northern hemisphere atmospheric mixing ratio (NH-AMR) values. CFC-11 was more variable, but usually <20% above the NH-AMR value. Given the errors associated with trace-gas groundwater dating, there is little justification for factoring in the minor LAEs found in this study to urban groundwater investigations, and accordingly the use of CFC and SF₆ input functions based on the NH-AMR curves appears justified for Britain.

**The use of oxygen-18 and deuterium in the water dynamics
assessment in the Quaternary volcanic structure of Mount Vulture,
Southern Italy**

Bono, P.^a, Brun, C.^b, Fiori, C.^a, Gonfiantini, R.^c, Zucco, F.^a

^a Department of Earth Sciences, Università La Sapienza, Roma, Italy

^b Geokarst Engineering, Trieste, Italy

^c Institute of Geosciences and Georesources, CNR, Pisa, Italy

E-mail: paolo.bono@uniroma1.it

The Quaternary caldera of Mount Vulture, Southern Italy, hosts two small lakes, *Lago Piccolo* (0.16 km², 38 m deep) and *Lago Grande*, which are interconnected by a narrow channel and have a permanent emissary. Several springs gush out along the slopes and inside the caldera. Our objective is to assess the major flow paths of groundwater in the Quaternary volcanic structure by means of the isotopic composition and the main physical-chemical parameters (pH, temperature and electrical conductivity) of water. This investigation is a follow-up of a previous study, whose conclusions are revisited and updated by sampling a larger number of sites. The lakes were sampled at different depths to study the unusual water stratification, particularly evident in *Lago Piccolo*, resulting from recharge by bottom springs and surface heavy isotope enrichment by evaporation. Twenty-eight spring samples, with different chemical characteristics, allow establishing the isotopic gradient and recharging altitude.

Groundwater flow functioning in arid zones with thick volcanic aquifer units: North-Central Mexico

Carrillo-Rivera, J.J.^a, Cardona, A.^b, Edmunds, W.M.^c

^a Institute of Geography, National Autonomous University of Mexico, Mexico City

^b University of San Luis Potosí, SLP, México

^c Visiting Professor, Centre for the Environment, Oxford University, UK

E-mail: joeljcr@igg.unam.mx and jjoelcr@yahoo.es

Population increase in arid zones of Mexico has created the presence of 450 % new cities with more than 50,000 inhabitants, as related to 1950's. Due to the arid nature of the environment, the once enough spring and shallow water are becoming insufficient for the supply of those cities. An answer leans now in the sustainable development of deep groundwater. The geological features of the country permit the presence of thick fractured volcanic aquifer units with more than 1,500 m in thickness, which have a regional continuous extent of several hundred thousands of square kilometres. Groundwater development decisions need to consider, in the long span, inter-basin groundwater flow and the need to prevent environmental impacts in distant sites hydraulically connected with extraction centres. Radiocarbon is an excellent tool that initially has been applied to characterize groundwater in thick aquifer units in central Mexico to provide with evidence on the hierarchy of flow (local/regional) and water age from where the distance of regional recharge was inferred; obtained flow path length permits to postulate inter-basin groundwater communication; a potential for radiocarbon has been identified for future expansion of research and water management application.

Hydrochemical and isotope evolution in a deep carbonate aquifer in Northern Andalusia, Spain

**Núñez, I.^a, Araguás-Araguás, L.^b, González, A.^a, Pérez-Zabaleta E.^c,
Rodríguez Arevalo J.^a, Díaz, M.F.^c**

^a Instituto Geológico y Minero de España (IGME), Madrid, Spain

^b Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

^c Centro de Estudios y Técnicas Aplicadas, CEDEX, Alfonso XII, 5. Madrid, Spain

E-mail: i.nunez@igme.es

The Loma de Ubeda aquifer is formed by Jurassic carbonates with a mean thickness of about 80 m. The carbonate sequence is covered in the southern part of the study area by a thick sequence of Miocene sediments, and groundwater becomes confined. Groundwater samples in the phreatic zone contain tritium activities similar to present-day precipitation, as well as high nitrate contents, indicating the relevance of recent recharge. Further down-gradient, in the confined part of the aquifer, tritium contents become null. The $\delta^{18}\text{O}$ values in most groundwater samples are similar to those of present-day recharge. The uncorrected ^{14}C -DIC “ages” increase from recent up to 20-25 ka in the deepest part of the aquifer. Carbon-13 values in the confined part become progressively depleted (up to -21‰,) indicating the presence of a source of organic carbon in the aquifer. The $\delta^{34}\text{S}$ values in dissolved sulphate and the high concentrations of H_2S reflect the importance of sulphate reduction. Geochemical models suggest that the residence time of groundwater in the deepest part is up to 10,000 years younger than the uncorrected ^{14}C -DIC ages.

Hydrogeochemical and isotopic evaluation of thermal and mineralized waters of Terme (Kırşehir) and Kozaklı (Nevşehir) areas, Turkey

Pasvanoğlu, S., Gültekin, F.

University of Kocaeli, Faculty of Engineering, Geological Engineering Department,
Kocaeli-İzmit, Turkey

E-mail: suzan@kou.edu.tr

In the Central Anatolian Region, two neighboring cities of Kırşehir and Nevşehir have significant thermal and mineral water potentials. The Kırşehir massive and Cenozoic magmatic units are exposed around Terme and (Kırşehir) areas. Around Kozaklı (Nevşehir), the Kırşehir massive is overlain by thick salt layers such as gypsum type evaporitic rocks of Oligocene age. Thermal and mineral waters are mostly manifested through the normal faults. Lower parts of Oligocene deposits in Kozaklı are composed of conglomerate and sandstone. Thermal and mineral waters that form aquifer in fractures of marble and schists of the Kırşehir massive are accumulated via buried faults in Oligocene conglomerate and sandstones which comprise another aquifer with warmer temperature. On the contrary, in the Kırşehir area, faults that cut the Pliocene cover within the marble and massive pebbly schists transport the water to the surface. In Kırşehir-Terme, springs have discharge temperature of about 41°C, but temperature reach 60°C in the bottom hole. Temperature of waters in the Kozaklı area is 90-98°C while it exceeds 100°C in the bottom hole. The water types of Kırşehir and Kozaklı area are Ca-HCO₃ and Na-Cl, respectively. Environmental isotope results (¹⁸O, ²H, ³H, ¹³C) indicate that thermal waters have a meteoric origin and some of rainwater is percolated downward along fracture and faults and heated at depth and then rise to the surface along fracture and faults which act as hydrothermal conduit.

Characterization of the aquifers of the Essaouira Synclinal Basin (Morocco) by using ^2H , ^3H , ^{14}C and ^{18}O isotopes

Bahir, M.^a, Carreira, P.^b, Misdaq, M.A.^a, Silva, M.O.^c, Fernandes, P.^b

^a Laboratoire d'Hydrogéologie, Faculté des Sciences Semlalia, BP 2390, Marrakech, Morocco

^b Instituto Tecnológico e Nuclear, Sacavém, Portugal

^c Departamento de Geologia, Faculdade de Ciências da Universidade de Lisboa, Lisbon, Portugal

E-mail: bahir@ucam.ac.ma

The study has had framework the principal aquiferous of the Essaouira coast zone, while having for principal objectives, the datation of undergrounds waters of the region and while taking for samples the water principal points, that supply in drinkable water just as well the city, as the rural agglomerations. Different water samples have been collected from drillings, sources and wells belonging to the plioquaternary and turonian aquifers of the studied region. Water samples were collected for ^{18}O , ^2H and ^3H determinations. A meteoric local line was determined and compared to the world meteoric line. The apparent radiocarbon ages of the studied aquifers were evaluated. The recharge of the main aquifers of the studied region was investigated. It has been shown by this study that the recharge rate of the deep turonian aquifer is too low. This may cause a shortage of water supply to the Essaouira city and its surrounding region. Among the concerned aquiferous, the turonian that provides for more of 50 % in drinkable water of Essaouira city and rural villages must be the object of rational and durable exploitation to defect an epuishment of the resources.

Isotopes in deep groundwater in Northwest China: hydrological and paleoclimate implications

Pang, Z.^a, Qin, D.^a, Yang, Y.^b

^a Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China

^b Xi'an Institute of Geology and Mineral Resources, China Geological Survey, Xi'an, China

E-mail: z.pang@mail.iggcas.ac.cn

Depth-specific deep groundwater samples have been obtained from groundwater exploratory wells (down to 550 m) in Erdos Basin, a test drill-hole of the pilot high-level nuclear waste disposal site in Beishan, Gansu Province, both by using double packer sampling systems, and from well-cased geothermal water production wells (1500-3000 m) in Guanzhong Basin. Isotope variations (^{18}O , ^2H , ^{34}S , ^{86}Sr , ^3H , ^{14}C , ^{36}Cl) and stratigraphy as well as CFCs in the water samples evidence two types of groundwater circulation patterns in the aquifers: well mixed and essentially separated flows. Results from the test site in Beishan further reveal that the deep groundwater (phreatic) in the granite is not from the source of recharge previously suggested i.e. Mt. Qilian of Northwest China and doesn't participate in modern water cycle because it is ^3H and CFCs free.

Isotope hydrology and hydrochemistry of some nutrient enrichment sources to the Densu River Basin , Ghana

Fianko, J.R.^a, Osae, S.K.D.^a, Adomako, D.^b, Achel, D.G.^a

^a Department of Chemistry, National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon Accra. Ghana

^b Department of Physics, National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon Accra. Ghana

E-mail: dedehosae@fastmail.fm

Anthropogenic inputs of nitrogen, phosphorus and oxygen consuming materials to aquatic ecosystems can change nutrient dynamics, deplete oxygen and change abundance and diversity of aquatic plants and animals. The isotopic techniques in groundwater resource management in the Densu river Basin required a research and assessment program to establish the contribution of sewage discharge and agriculture to eutrophication in the Densu River and examine the source of nutrients and other pollutants in the aquatic ecosystem. This will improve the understanding of the interaction between nutrient input, dissolved oxygen and aquatic ecosystem productivity. Combining isotopic and hydrochemical characteristics of samples in the basin will show the influence of natural and anthropogenic source of nutrients in the Densu River Basin.

Radon-222 and tritium in the prevention of sea water intrusion and oil pollution in a coastal karst aquifer

Molerio Leon, L.F.

CESIGMA, S.A., P.O. Box 6219, CP 10600 Habana 6, Ciudad de la Habana, Cuba

E-mail: leslie@cesigma.com.cu

The partitioning properties of ^{222}Rn with organic liquids have been used efficiently to distinguish the presence of contaminations for hydrocarbons in the ground waters of a coastal karst aquifer of Northwestern Cuba. In presence of sea water intrusion ^{222}Rn and Tritium shows a different behavior. This property is used as an additional advantage for the identification of different sources of Chloride in groundwater; v.gr, sea water intrusion, formation waters or cooling waters used at the gas plants for electric generation. Isolated events of advance (and/or retreat) of sea water intrusion as well as oil spills from pipelines or during oil well completion were detected measuring the activity of the ^{222}Rn systematically in the ground waters.

Tritium as an indicator of groundwater overexploitation in a tropical karst aquifer

Molerio Leon, L.F.

CESIGMA, S.A., P.O. Box 6219, CP 10600 Habana 6, Ciudad de la Habana, Cuba

E-mail: leslie@cesigma.com.cu

Overexploitation of two huge Cuban karst aquifers is derived from Tritium sampling and isotope balance modeling. During the dry season no ^3H activity was measured in the ground waters discharged at the springs or either at some of the observation wells. Occasionally very high values for ^3H were recorded. These values are strongly correlated with rainfall that took place at the 1980 decade or a little older. On the other hand, ^3H activity linked with present precipitation has been also recorded. Therefore a good mixture of water of different origin and residence time moves through the aquifer. The change in the isotopic composition therefore, has been interpreted as an indicator of overexploitation as far as waters that are not replenished during the present hydrological cycle are pumped out of the aquifer. Residence time modeling applying Maloszewski and Zuber, and Zuber and Maloszewski, lumped model approach fits these no Tritium spring waters with waters with around 100 years of residence time. A more general conclusion is derived from the results obtained in the last years in both poljes relative to the mixing hydrodynamics in karst aquifers were flow stratification is associated with cave levels thus allowing that under certain conditions, old ground waters prevail in the mixing allowing important losses of ground water reserves that are not replenished during the present hydrological cycle.

Carbon-13 and carbon-14 contents of groundwater located in sandy aquifer outcrops: driving influence of the unsaturated zone

Gillon, M., Barbecot, F., Gibert, E., Marlin, C., Massault, M.

Laboratoire IDES UMR 8148 CNRS-Université Paris Sud 11, Orsay, France

E-mail: gillon@geol.u-psud.fr

Better assessment of carbon isotopes cycle in the Unsaturated Zone (UZ) is a key point for estimating the ^{14}C residence time of relatively young groundwater. In order to approach the UZ carbon cycle and to quantify C-fluxes, the distribution of the isotopic composition (^{13}C - ^{14}C) of each carbon phase (Dissolved Inorganic Carbon, CO_2 , carbonates) have been investigated on two experimental sites *i.e.* respectively the carbonate-free Fontainebleau sands (Paris Basin, France) and the carbonate Astian sands (South France). Similar matrix properties on both sites allowed identical *in situ* sampling protocols based on water-gas permanent samplers specifically developed for this work. In a carbonate-free UZ, the isotopic composition of water depends essentially on CO_2 diffusion. While, in a carbonated UZ, the carbonates force the isotopic composition of dissolved inorganic carbon and CO_2 . These carbon exchanges lead to a depletion of matrix carbonates by precipitation of secondary calcite.

Tracing stable isotope values from meteoric water to groundwater in the Cape Flats, South Africa: indicative tool for resource management

Adelana, S., Xu, Y.

Earth Sciences Department, University of the Western Cape, Bellville 7535, South Africa

E-mail: sadelana@uwc.ac.za

Urbanization and water resources management remains a central issue in the twenty-first century, partly because water is rapidly becoming a scarce resource and partly due to increasing population. Therefore, the global focus relating to water resources has shifted from a water development perspective to one of water management. In the Western Cape of South Africa water resources management even becomes crucial. This is a semi-arid region that receives precipitation amounts from 500-800 mm annually. Analysis of the long-term rainfall pattern has shown a drier condition in the last few decades. Stable isotopes have been measured for rainwater, surface water and groundwater samples around Cape Town in order to understand the inter-relationships between water resources of this area. This is being used in a qualitative sense to demonstrate present day recharge to the groundwater. The long-term weighted mean of precipitation for Cape Town is -12.8‰ and -3.28 ‰ respectively for $\delta^2\text{H}$ and $\delta^{18}\text{O}$. Surface water (rivers and reservoirs) falls on the evaporation line. The isotopic data indicate seasonal variations in the isotope composition of recharge to groundwater. The Cape Flats aquifer waters show similar stable isotope values but are distinguishable from those of the springs and the Table Mountain Group aquifer. The isotopic ratios tend to decrease with increasing distance from the coast. The indications and mechanism of recharge are integrated into the wide range of data, which are translated into a common language of the diverse actors in the water management process.

Impact of transboundary air pollution on our alpine water resources: application of a multi-isotope (N, O, S, Pb, Sr) approach

Kralik, M.^a, Humer, F.^a, Grath, J.^a, Nurmi-Legat, J.^a, Hanus-Illnar, A.^a, Halas, S.^b, Jelenc, M.^c, Lorenz, G.^d

^a Umweltbundesamt Austria (Federal Environment Agency Austria), Spittelauer Lände 5, A-1090 Vienna, Austria

^b Mass Spectrometry Laboratory, Marie-Curie-Sklodowska University, PL-20-031, Lublin, Poland

^c Geochronology Laboratory, Institute of Geological Sciences, University of Vienna, Althanstrasse 14, Vienna, Austria

^d Hydro-isotop GmbH, Woelkestrasse 9; 85301 Schweitenkirchen, Germany

E-mail: martin.kralik@umweltbundesamt.at

This paper shows possibilities to quantify the impact of air pollution on sensitive water resources (e.g. karst), to develop an innovative surveillance tool based on isotopes and meteorological considerations. Comparison of lead isotope measurements in precipitation, spring waters, soil profiles and dolomite bedrock in a relatively pristine and remote area at the front-range of the Northern Calcareous Alps in Austria with literature data indicate that radiogenic gasoline-lead still dominates with 60-80% the composition of the trace lead in the spring waters. In addition to the lead leached from the dolomite bedrock a third source contributes about 5-10%. This second long distance Pb-contribution may originate from coal burning and/or Ag-Pb-ore smelting in Central Europe in the past. The monthly precipitation (May and September 2005) samples show ¹⁸O-rich sulphate ions, whereas the soil sulphates have depleted ¹⁸O and higher ³⁴S values with depth. The spring waters and the bedrock dolomites show relatively low $\delta^{34}\text{S}$ values (4-9 ‰). Assuming the precipitation and the dolomite bed rocks are end-members the contribution of atmospheric sulphate is estimated to be 20% in the spring waters and between 10 to 45 % in the soil samples. The ⁸⁷Sr/⁸⁶Sr of the precipitation (0.7092) support at least a more radiogenic, far transported source in addition to a possible recycling of local dolomite and limestone (0.7080-0.7083) dust. Spring waters show similar ratios between 0.7083-0.7084 confirming Sr-isotopes are good indicators for groundwater contact with specific host rocks. The nitrate concentration in the precipitation is fairly low (2 mg/L) and increases in the spring and surface waters to 4.6-6.0 mg/L only by leaching the forest soils. The monthly precipitation show ¹⁸O-rich nitrate ions in spring and winter samples indicating higher concentrations of more atmospheric derived nitrate, whereas less ¹⁸O-rich and negative $\delta^{15}\text{N}$ nitrate ions in summer indicating more ammonium derived. Assuming mean $\delta^{18}\text{O}$ values of 10 ‰ in the nitrate ions for soil nitrification the atmospheric contribution of nitrate in the spring waters increases from 30% in summer to 50% in winter samples. Denitrification processes in the soil passage and karst rocks seem to be negligible.

Study of the Khoy geothermal area based on isotope and chemical investigations

Balderer, W.^a, Khalaj Amirhossainee, Y.^b, Hatami, F.^b, Kulkarni, K.M.^c

^a Engineering Geology, ETH Zurich, Switzerland

^b Water Research Institute, Tehran, Iran

^c Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: Balderer@erdw.ethz.ch

The study area is located in a severe active tectonic area in which different geological formations are set close together. The pressure direction is North-South (normal to the Ghatoor valley direction). There exist several Horst and Graben structures oriented parallel to the valley and filled with clastic sediments. The main thermal and mineral springs are observed along an approximately 2 km long segment of the north bank of the Ghatoor River. As effect of the tectonic structure different geological formations are set close to each other. A granitic batholith is detected at the depth of 200 m below the riverbed, using drilling and gravity investigations. The present isotope data show that two water systems interacting: i) the waters with actual recharge in the high mountain areas as the Almalu Spring No. 8 and ii) The deep thermal and mineral waters within a deep aquifer which is contained within tectonic fault zones (as the Qutur fault) and dominated by a high influx of CO₂ of deep (probably thermo - metamorphic) origin and the mixing with a deep seated high mineralized HCO₃ rich formation water. As an actual recharge based on the stable isotope data seems to exist a sustainable exploitation of this geothermal reservoir as long as the extraction rate does not exceed the natural recharge. As a rough estimate this rate will be in the range of 0.5 to 1.0 m³/s. If loss of the hydraulic pressure should be avoided (e.g. to maintain the natural out flowing hot springs with the touristically beautiful travertine deposits), the same amount of hot water extracted should be re-injected back directly into the same aquifer by additional boreholes.

Origin of the thermal waters of Stabio (Switzerland) and Sirmione (Italy) based on isotope and chemical investigations

Balderer, W.^a, Leuenberger, F.^a, Frei, Ch.^a, Surbeck, H.^b

^a Engineering Geology, ETH Zurich, Switzerland

^b University of Neuchatel, Centre d'Hydrogeologie, Neuchatel, Switzerland

E-mail: Balderer@erdw.ethz.ch

The study area is located in Southern Switzerland near the Swiss boundary and in Northern Italy, at the Garda Lake. The thermal waters of Stabio and Sirmione as well as the mineral water of Salo were investigated with hydrochemical and isotope methods as tritium, stable isotopes and also ³⁶Cl, radon and uranium. The results of these investigations clearly indicate that the waters of Stabio and Sirmione have a different origin than the normal shallow groundwater of the today's meteoric water cycle. They may be linked to the deep tectonic fault zones and induced flow systems. Also its chemical composition reflects a strong influence of water rock interaction processes or of a mixing component of an original deep sedimentary brine

Isotopic characterization of groundwater-seawater interactions

Povinec, P.P.^a, Aggarwal, P.K.^b, Kulkarni, K.M.^b

^a Comenius University, Mlynská dolina F1, SK-842 48 Bratislava, Slovakia

^b Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: povinec@fmph.uniba.sk

Studies of groundwater-seawater interactions (GSI) in coastal zones are important for better understanding of coastal processes, input of groundwater to the sea via submarine groundwater discharge (SGD), saltwater intrusion in groundwater reservoirs and coastal land, contamination of groundwater and coastal seawater by land based sources, and generally for proper management of fresh water resources in the region. Investigations of GSI using stable isotopes (^2H , ^{13}C , ^{15}N , ^{18}O , $^{87/86}\text{Sr}$ etc.) as well as radioactive isotopes (^3H , ^{14}C , Ra, radon etc.) have been recently carried out in several coastal regions. Stable and radioactive isotopes together with salinity and seepage measurements can thus provide a complex approach in GSI investigations, enabling separate estimation of fresh water as well as saline re-circulated groundwater fluxes to the sea. A Coordinated Research Project (CRP) on “Nuclear and Isotopic Techniques for the Characterisation of SGD in Coastal Zones” coordinated jointly by the IAEA’s Isotope Hydrology Section (Vienna) and Marine Environment Laboratory (Monaco), has recently been completed. The CRP was carried out in cooperation with UNESCO’s Intergovernmental Oceanographic Commission (IOC) and the International Hydrological Programme (IHP), and with several laboratories in Brazil, India, Italy, Japan, Russia, Slovenia, Turkey and USA. The aim of the CRP was to develop new isotope techniques for studying SGD and GSI. In the framework of the CRP several expeditions were carried out to Sicily, south-eastern Brazil and Mauritius. We present here a complex approach in characterisation of GSI as obtained by different techniques based on stable and radioactive isotopes and non-radioactive tracers.

Recent advances in modern ion chromatography for the analysis of environmental water samples: reagent free ion chromatography systems using recycled eluent and their applications

Ghirlanda, S., Jensen, D.

Dionex (Europe) Management, AG, Solothurnerstr. 259, 4600 Olten, Switzerland

E-mail: Sandro.Ghirlanda@dionex.ch

Ion Chromatography (IC) is one of the most important analytical techniques for the determination of inorganic ions in water samples. Designed to reduce the working load in modern analytical laboratories, automation in IC plays an important role for actual and future developments. Reagent Free Ion Chromatographs with eluent generation (RFIC-EG™) enable the user to perform a wide range of ion chromatographic separations using deionised water as the only carrier. RFIC-EG systems provide isocratic and gradient method flexibility for a wide range of IC applications. For laboratories using carbonate- and methanesulfonic-based eluents for isocratic separations Dionex expanded the properties of RFIC with a new technique called RFIC-ER™ (ER: Eluent Regeneration). We will discuss the principle of this operation mode for IC systems equipped with electrolytic suppressors. It utilizes the fact that the effluent from an electrolytic suppressor operated in the AutoSuppression® mode consists of mainly the eluent used in the IC separation process. The new IC operation mode uses a novel eluent purification cartridge and an efficient analyte trap column to remove electrolysis gases and purify the recycled eluent and is compatible with IC separations using carbonate/bicarbonate and methanesulfonic acid eluents. We will demonstrate the applications of the new IC operation mode in determination of common cations and anions in different sample matrices. RFIC-ER systems are designed specifically for a set of routine IC analyses, such as the determination of anions or cations in drinking water.

Isotope hydrology studies of water resources (Tabas area case study)

Khalaj Amirhossainee, Y., Hatami, F., Kuhpour, M.

Member of Scientific Board, Water Research Institute (WRI), Shahid Abbaspur Blvd., East Vafarda Blvd., Tehranpars 4th Square, Tehran, Iran

E-mail: khalajy@yahoo.com

Tabas Town with a surface area of 55,000 km² is located in north-east of Yazd City in the east of Iran. It is situated in western slopes of eastern heights of the country, on sediments of fourth era, on the edge of Kavir-e-Namak Desert. The study area falls between 56° to 57 °45' eastern longitudes and 32°15' to 34°15' northern latitude. The project aims at providing water for washing carbons, cooling systems and potable water purposes in Tabas carbon power plant. Investigating the origin, age and nature of different water resources and relationships between these resources is the main objective of conducting isotope studies in Tabas area. This will help in providing required water in the area. Determining under-investigation water resources, taking samples and isotope and chemical analysis of samples form methodology of present research. ¹⁸O and D stable environmental isotopes and T and ¹⁴C radioisotopes as well as results of chemical analysis of samples taken from different water resources have been used in studies. First stage of studies consists of sample-taking from 34 springs, 13 wells and 8 Qanats during both wet and dry seasons. Isotope and chemical analyses have been also made on taken samples. Main results achieved could be summarized as: 1) recharge centers of water resources are found in some parts beyond the study area; 2) regarding stable environmental isotopes tests results, recharge centers of water resources within the study area are mainly located in heights over 2,700 m; and 3) isotope and chemical tests results indicate a slight effect of evaporation on increasing salts contents of water resources in the area, whereas the increasing rate mainly depend on the rate of dissolving salts in evaporative and desert rocks on the course of groundwater flows.

Cooperative USGS-IAEA improvements in a sequential, time-integrated collector of precipitation, ground water and surface water for measurement of relative isotope-ratio amounts

Coplen, T.B.^a, Aggarwal, P.^b

^a U.S. Geological Survey, Reston, Virginia, USA

^b Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

E-mail: tbcoplen@usgs.gov

To collect precipitation samples for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water and $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of dissolved nitrate from four large land-falling cyclones at Cazadero, California, a sequential, time-integrated collector of precipitation, ground water, and surface water for analysis of isotopes was developed by the U.S. Geological Survey (USGS). Such major storms are sometimes supplied with vapour in “atmospheric rivers,” which are narrow regions of strong meridional water-vapour transport over the eastern Pacific Ocean that have caused heavy coastal rainfall and flooding of the U.S. West Coast. During several hours of a storm in March 2005, precipitation $\delta^{18}\text{O}$ variations of 6‰ were recorded in half-hourly samples of precipitation, suggesting changes in vapour sources and precipitation-formation mechanisms during the short-term evolution of the storm. Variations in $\delta^{15}\text{N}$ of dissolved nitrate between consecutive storms of as much as 5‰ may reflect different source regions for precipitation in these cyclones. IAEA recognized that the USGS sequential, time-integrating collector could be utilized for collection of precipitation samples in arid environments. It was envisioned that the collector might be modified so that when it rains, which presumably would be infrequent, the collector could collect precipitation samples at a designated interval, for example, every hour. After each rain storm, it is envisioned that the lid of the collector would close to protect it from dust, dirt, and animals and the collector would go into a sleep mode, awaiting the next rain event. In this manner, the collector could be operated in arid regions to collect sequential precipitation samples over a period of weeks to a month.

A practical approach to radiocarbon dating of groundwater

Herczeg, A. L.

CSIRO Land and Water, Adelaide, Australia

E-mail: andrew.herczeg@csiro.au

Radiocarbon dating of groundwater is widely used, but the calculated ages are often difficult to interpret for two reasons. Firstly, the ^{14}C age is ambiguous in that it depends on the sampling depth, sampling interval and flow system behaviour. Second, the age is in reality a 'carbon age' and the plethora of correction schemes that produce model water 'ages' are confusing to many practicing hydrogeologists. To simplify the process, I suggest that using relative 'ages' within a hydrostratigraphic context with minimal correction (with a nominal starting point of say 85‰mc) is more practical. For confined aquifers, the approximation of age difference along a transect or inferred flow lines may be used to estimate horizontal flow velocities. For unconfined aquifers, one would plot the 'age' as a function of depth incorporating the length of the screened interval to estimate recharge rates. The advantages are that it makes the data internally consistent and minimizes the large apparent errors inherent in the estimates of 'absolute' ages. The results have more meaning for those people requiring information to make groundwater management decisions.

Isotopes in precipitations of Kinshasa area: moisture sources and groundwater tracing

**Nndembo Longo, J.^a, Travi, Y.^b, Makoko Moyengo, L.^a,
Nlandu wabakaghanzi, J.^a**

^a Commissariat General a l'Energie Atomique, Kinshasa/ Rep. Dem. du Congo

^b Laboratoire D'hydrogeologie/Universite d'Avignon, France

E-mail: jndelongo@yahoo.fr

Event samples of rains have been collected for stable and radioactive isotopes data (¹⁸O, ²H and ³H) on Kinshasa area (Democratic Republic of the Congo) from September 2003 to November 2005 (AIEA TCP ZAI/8/013). $\delta^{18}\text{O}$ values for rainy seasons as a whole (September to May) show a relatively narrow range of variation (-0.05 to -7.79 ‰) compared with that is generally observed in tropical areas. The local meteoric line ($\delta^2\text{H} = 8.12\delta^{18}\text{O} + 15$) is distinct from World Meteoric Line. Mean values of deuterium excess are quite different in the main rainy season period (October – November in particular) with d-excess close to 10 ‰ associated with more depleted values, and in the more scarce rainfall event period (d-excess up to 22 ‰). These later data may be linked to significant local recycling of air moisture from equatorial forest and/or surface water (Pool Malebo on the Congo River). In the context of siliceous and non carbonate aquifer with short renewal time, these data may be used, together with tritium and post nuclear radiocarbon, for tracing groundwater recharge.

Use of environmental isotopes to evaluate the sources of submarine freshwater in the southern shoreline in Lebanon

Saad, Z.^{a,b}, Kazpard, V.^{a,b}

^a Lebanese University, Faculty of Sciences, Lebanon

^b Lebanese Atomic Energy Commission-CNRS, P.O. Box 11-8281, Beirut, Lebanon

E-mail: zsaad@cnrs.edu.lb

Geochemical and isotopic techniques are applied to evaluate the origin of submarine freshwater in the southern and northern shoreline in Lebanon. Submarine springs have different geochemistry reflecting a difference in the specific geology of southern and northern shoreline. Environmental isotopes including $\delta^2\text{H}$, and $\delta^{18}\text{O}$ in water and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in sulfate have proved the different geological features. A more enriched isotopic composition of submarine groundwater is investigated in the south where submarine springs are primarily artesian flows. The deep circulation of groundwater is affected by a high geothermal gradient. Also a high sulfate content is related to a fractionation in $\delta^{34}\text{S}$ isotopic composition. This is due to the dissolution of gypsum minerals and its reduction of marly limestones of the Upper Cretaceous and Lower Eocene in the confined aquifers. In the northern part, a slightly depleted isotopic composition is found for submarine and groundwater. The highly karstified northern region induces a fast infiltration of groundwater till its discharge as submarine springs.

Tracing sources of nitrate in groundwater by using hydro-chemical and isotopic methods: Beirut region and its suburbs

Kazpard, V.^{a,b}, Saad, Z.^{a,b}, El Samrani, A.^{b,c}

^a Lebanese University, Faculty of Sciences, Lebanon

^b Lebanese Atomic Energy Commission-CNRS, P.O. Box 11-8281, Beirut, Lebanon

^c Holy Spirit University of Kaslik, Faculty of sciences, Jounieh, Lebanon

E-mail: vkazpard@cnrs.edu.lb

Analyses of hydrochemical and stable isotopes of ^2H and ^{18}O were conducted on groundwater samples collected in Beirut city and its suburbs and tapped in a limestone aquifer. The analyses were done to document the chemical and isotopic characters of the natural groundwater and to determine its origin. Hydrochemical data are classified on the basis of dominant anions. Mineral groundwater quality was found affected by different pollution sources in the southern suburb of Beirut. Isotopic analyses delineate two major groups of groundwater. The first group is directly influenced by direct recharge into the aquifer from precipitation. The second group, showing elevated mineral characteristics, is influenced by a secondary evaporation process reflecting an isotopic enrichment in groundwater. $\delta^{15}\text{N}$ investigation of the isotopically enriched samples determines the origin of nitrate pollution from either infiltration of animal waste or septic systems to groundwater.

Water flowpaths in the mountainous watershed traced by oxygen-18 isotope: experimental approach

Sanda, M., Sobotkova, M., Cislerova, M.

Czech Technical University, Prague, Czech Republic

E-mail: martin.sanda@fsv.cvut.cz

Uhlirská, Jizera Mountains, Czech Republic, is a typical watershed with the crystalline bedrock forming Cambisols. It is situated in a humid mountainous region where soils are shallow and highly permeable with preferential pathways. As a result of these facts, outflow caused by storms can be of a quick response and high magnitude. Based on the observations performed since 1998, it becomes evident that soil profile plays dominant role in the rainfall-runoff transformation. Data collection of the water regime in the soil profile and the subsurface flow accompanied with the standard climatic and hydrological monitoring is performed. Due to the fact that the behavior of flow of water in the heterogeneous soil profile and hydrogeological structure is not fully understood, quantitative measurements are supplemented by the additional techniques of the tracing of stable oxygen isotope ^{18}O and silica since 2006 in rainfall, outflow and soil and groundwater.

Isotopic and geochemical investigations of groundwater from regional aquifer system of North Gujarat Cambay (NGC) region, Western India: insights into geohydrological processes

Deshpande, R.D., Gupta, S.K.

Physical Research Laboratory, Navrangpura, Ahmedabad, India

E-mail: desh@prl.res.in

A multi-parameter isotopic and geochemical investigation was undertaken in the North Gujarat Cambay (NGC) region in the Western India. The NGC region is characterized by a unique combination of geological, hydrological, tectonic, topographic and climatic features. The high fluoride concentration, high amount of dissolved helium and high groundwater temperatures were earlier reported in some parts of this region. In the present study the geographical distributions of fluoride, helium and groundwater temperature were determined and their origin and inter-relationship as well as their possible relationship with tectonic and geothermal regime of the NGC region were investigated. The age of groundwater and the rate of its movement in the regional aquifer system were determined employing various radiometric dating methods. The signals of alternating wet/dry climatic phases were reported earlier from the Quaternary sedimentary deposits in this region. Similar palaeoclimatic imprints were also identified in confined groundwater in this region during this study.

Identifying and dating the origin of groundwater resources in reclamation areas of Egypt

Aeschbach-Hertig, W.^a, El-Gamal, H.^a, Friedrich, R.^a, Dahab, K.^b, Kipfer, R.^c, Hajdas, I.^d

^a Institute of Environmental Physics, University of Heidelberg, Germany

^b Geology Department, Faculty of Science, Minufiya University, Egypt

^c Eawag, Dübendorf, and Isotope Geology, ETH Zürich, Switzerland

^d AMS Radiocarbon Lab, ETH Zürich, Switzerland

E-mail: aeschbach@iup.uni-heidelberg.de

So-called reclamation areas southwest of the Nile Delta, Egypt, depend almost exclusively on groundwater for irrigation of new agricultural land. We applied stable isotopes and noble gases to study the origin of the groundwater, and several environmental tracer methods (SF_6 , ^3H - ^3He , ^{14}C) to determine its age. The stable isotopes clearly identify the Nile River as the main source of the water, and due to the change of the river's isotopic composition in response to the construction of the Aswan High Dam, they also provide time information. The environmental tracers show that water recharged during the past 40 years is present only in wells close to surface water features. Further away from the surface water, ^{14}C data indicate ages up to a few thousand years. We conclude from the isotope data that the regional aquifers are recharged from the surface water, but the recharge and flow velocities are rather low.

Experiments on the formation of excess air in groundwater under various recharge regimes

Palcsu, L.^a, Aeschbach-Hertig, W.^a, Kopf, M.^a, Zechner, E.^b

^a Institute of Environmental Physics, University of Heidelberg, Germany

^b Environmental Geology, University of Basel, Switzerland

E-mail: palcsu@iup.uni-heidelberg.de

Excess air is a contribution to the gases dissolved in groundwater in addition to the solubility equilibrium component, formed by partial or total dissolution of air trapped during water level rises in the unsaturated zone. The amount of excess air can be quite large, mainly if the water level increase is significant, for example in case of recharge from ephemeral streams in semi-arid regions or artificial recharge. The increased gas amount, especially of oxygen, can have an influence on biological activity, water treatment, and quality. In order to investigate the applicability of excess air as a tool to identify recharge mechanisms, we examine the formation of excess air under field and laboratory conditions using all five noble gases. In laboratory experiments with plexiglas columns filled with different types of sand, we investigate how the excess air amount and composition depend on the hydrostatic pressure as well as the size distribution of the sand and the entrapped air bubbles. In field experiments we study the relationship between excess air and water level fluctuations. Two study sites were selected where the groundwater level increased due to artificial recharge (Basel, Switzerland) and due to river floods (Danube River, Hungary).

The preliminary study of groundwater recharge system in Kathmandu Valley, Nepal

Shrestha, S., Nakamura, T., Kazama, F.

Department of Ecosocial System Engineering, Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Kofu City, Japan

E-mail: sangam@ccn.yamanashi.ac.jp

This study aims to identify the groundwater recharge systems of Kathmandu Valley using isotopic compositions of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) along with other hydrochemistry data. The preliminary study consisted of 15 deep groundwater and 5 shallow groundwater samples that were collected from northern and central part of the valley. Three types of the deep groundwater isotope compositions were observed while $\delta^{18}\text{O}$ is plotted against $\delta^2\text{H}$. The results indicate that the deep groundwater has two main aquifers: north part and central part aquifers. In addition, the oxygen isotopic values of all samples when plotted against chloride indicate that deep groundwater is not being recharged by the shallow groundwater of the sampled area. It was also observed that the third type of groundwater is formed by the mixing of first and second types of groundwater. The next study will be focused on detailed investigation in finding source and recharge of this groundwater.

How isotopic tools can contribute to constrain groundwater – surface water interactions in a highly anthropized site? The Wolfen/Bitterfeld Megasite (Mulde Basin, Germany)

Petelet-Giraud, E.^a, Négrel, Ph.^a, Gourcy, L.^a, Schmidt, Ch.^b, Schirmer, M.^b

^a BRGM, 3 av. C. Guillemin, BP 6009, 45060 Orléans, France

^b UFZ, Centre for Environmental Research, Permoser-Strasse 15, 04318 Leipzig, Germany

E-mail: e.petelet@brgm.fr

The Bitterfeld/Wolfen region is a megasite with multiple contaminant sources from industrial activity for more than a century, which has a considerable impact on the environment. At present, the contaminated groundwater covers an area of about 25 km² and poses a threat for the surrounding aquifers and the Mulde River. This study focuses on the Schachtgraben, a man-made channel in the Mulde floodplain that collects the effluents of the industrial area. It aims to characterise the relationship between surface water (channels, rivers) and the groundwater in the shallow Quaternary aquifer. Waters are Ca-SO₄-type with TDS reaching 3.8 g/L in the industrial area. Stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) show that two of the rivers are recharged mainly by groundwater that can be divided into two groups. Strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) designate different geochemical end-members and enable the identification of mixing between natural and anthropogenic surface and groundwater.

Multi isotopic and geochemical constraints of interconnection and heterogeneities of water bodies in the Adour-Garonne district (SW France) – the CARISMEAU research project

Négrel, Ph.^a, Petelet-Giraud, E.^a, Brenot, A.^a, Millot, R.^a, Roy, S.^a, Dutartre, Ph.^a, Fournier, I.^b

^a BRGM, 3 av. C. Guillemin, BP 6009, 45060 Orléans, France

^b Agence de l'Eau Adour-Garonne, 90 rue du Férétra, 31078 Toulouse cedex, France

E-mail: p.negrel@brgm.fr

The main objective of the Water Framework Directive (2000/60/EC) is to prevent further deterioration and protect and enhance the status of aquatic ecosystems in Europe. The success of the WFD will be mainly measured by the status of water bodies. Aims of the research project *Carismeau* are to provide further characterization of the groundwater bodies which have been identified as being of primary importance and/or at risk in the Adour-Garonne district (1/5 of the French territory). For that purpose, combined geochemical analysis (major and trace elements), and isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$, $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$, strontium, boron, lithium, uranium and lead isotopes) are applied on one demonstrative water body named the Eocene sands aquifer. Preliminary results point out the extreme heterogeneity of water signatures between the selected water bodies but also within a single aquifer. The ongoing research will set out to demonstrate the role of lateral variation of facies and the interconnections between aquifers.

A decade of environmental isotope research in a low permeability aquitard system

Hendry, M.J.^a, Wassenaar, L.I.^b

^a Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada, S7N 5E2

^b Environment Canada, Saskatoon, SK, Canada, S7N 5E2

E-mail: jim.hendry@usask.ca

A decade of multi-isotope and hydrogeological research on a 160 m thick aquitard system has resulted in detailed, high-resolution profiles of stable and radiogenic isotopes (Tritium, δD and $\delta^{18}O$, ^{14}C -DOC and ^{14}C -DIC, ^{36}Cl , $\delta^{37}Cl$, 4He). The interpretations of these independent isotopic tracers reveal that late Pleistocene age porewater remains preserved in the aquitard between 35-55 m below ground. Transport modeling of isotopic profiles indicates this water was emplaced with the till upon deposition between 10ka - 20ka BP, and that the late Holocene glacial-interglacial climatic transition occurred in this area between 7ka – 12ka BP. Interpretation of the isotope profiles further shows transport of solutes in this aquitard is by molecular diffusion. These findings clearly demonstrate solute transport in homogeneous clay-rich aquitards is highly predictable over 20 ka and greater time scales. Long-term stability, plasticity, ease of access, and a high degree of confidence in transport predictability suggest thick aquitards could act as long-term repositories for the isolation and storage of hazardous and nuclear waste.

The integration of isotope data and hydrological models to support sustainable water resources management

Leavesley, G.H., Regan, R.S., Winter, T.C., Reddy, M.M.

U.S. Geological Survey, Denver, Colorado USA

E-mail: george@usgs.gov

The U.S. Geological Survey (USGS) Modular Modeling System (MMS) is an integrated system of computer software that has been used to support the development, coupling, and application of hydrological and resource-management models for use in making complex, operational decisions regarding sustainable water management. Estimates of the spatial and temporal distribution of water-balance components, including surface water, ground water, and evapotranspiration, are typically made using calibrated hydrological models with few measures to validate these estimates. Knowledge of the sources and magnitudes of water-balance components is critical to sustainable water-resources management. To provide improved model estimates of the explicit partitioning of water-balance components, simulation of the isotopes (^{18}O and ^2H) has been added to selected hydrological process modules in MMS. Isotope data can be used in combination with physical data to simulate water and isotope storages and fluxes within a basin at daily, monthly, or seasonal time scales. Models were developed, tested, and evaluated using the Shingobee River Headwater Basin, Minnesota, USA.

Flow and residence time in soil and unsaturated zone of Moravian Karst – an application of ^{18}O , ^3H

Vysoka, H., Bruthans, J., Churackova, Z., Silar, J.

Dept. of Hydrogeology, Charles University, Prague, Czech Republic

E-mail: helenavysoka@volny.cz

Mean residence time (MRT) and flow pattern were studied in unsaturated zone of the Ochoz Cave in Moravian Karst between 2001 and 2006. Two different localities of seepage water from the overlying 65 m thick unsaturated zone and up to 0.6 m thick soil profile were monitored. At one place the conductivity and yield of seepage waters was continuously measured with no contact of water with the cave atmosphere. In 2005 a gravitational lysimeter was added to the base of soil profile to help recognise the affect of both environments. To determine mean residence time and water mixing, $\delta^{18}\text{O}$ and ^3H were analysed in soil and seepage water during the whole period. Based on ^3H , there is roughly 20% of water present in seepage water infiltrated in the sixties and/or seventies. Components with MRT in months and first years are most important however. Based on $\delta^{18}\text{O}$ values, the mean residence time of water in soil is about 3-6 months and water is flowing in the form of piston flow with low mixing. In case of snow melt and major precipitation events, the discharge from unsaturated zone rises up to 2 orders of magnitude but direct inflow of the event water is at the same time very low (below 20% even during extreme events). TDS has inverse correlation with discharge. The study is demonstrating a complex flow in karstified limestone.

Isotope signatures of reverse osmosis desalinated seawater

Kloppmann, W.^a, Vengosh, A.^b, Pankratov, I.^c, Guerrot, C.^a, Millot, R.^a

^a BRGM, Orléans, France

^b Duke University, North Carolina, USA

^c Water Commission, Tel Aviv, Israel

E-mail: w. kloppmann@brgm.fr

Freshwater produced through desalination of seawater and saline groundwater can be no longer neglected in the water balance of technologically developed arid countries. Desalinated water can be released to the environment as wastewater, through irrigation and leakage. Here we present the first study on the isotope variations of freshwaters and residual brines from reverse osmosis (RO) plants in Israel. The Elat plant (18.5 MCM/year) operates at low pH conditions whereas the Ashkelon plant (100 MCM/year) operates under both low and high pH conditions for efficient removal of boron. At low pH, desalinated waters conserve typical seawater B isotope signature (39 ‰ vs. NBS951), whereas at high pH, permeates are enriched in ¹¹B and δ¹¹B reaches 60 ‰. No fractionation was observed for O and H isotopes. These isotopic signatures are different from natural fresh water, providing reliable proxies for tracing man-made waters in the environment.

Multi-isotope (B, Li, O, H) tracing of reverse osmosis treated waste water recharged artificially into a coastal aquifer (Torreele/Wulpen, Belgium)

Kloppmann, W.^a, Van Houtte, E.^b, Gaus I.^a, Guerrot, C.^a, Millot, R.^a

^a BRGM, Orléans, France

^b IWVA, Koksijde, Belgium

E-mail: w. kloppmann@brgm.fr

Artificially enhanced aquifer recharge is gaining importance in the active management of groundwater resources, in particular in coastal areas endangered by marine intrusion. Within the FP6 project Reclaim Water, the site of Torreele/Wulpen, at the Belgium North Sea Coast, was investigated, where secondary treated municipal wastewater is further purified through ultrafiltration and reverse osmosis (RO) before being infiltrated into the coastal dunes in order to reduce the extraction of natural groundwater for potable water production and hold back saline intrusion. B and Li isotopes as well as stable isotopes of oxygen and hydrogen were analysed to evaluate the extension of the injected water in the aquifer body. The infiltration and mixing of RO-treated wastewater with natural groundwaters could be intimately monitored. B isotopes performed particularly well due to a characteristic waste water signature and high contrasts of natural end-members (total range > 25 ‰ vs. NBS951)

Re-watering of Witwatersrand mining basins, South Africa – traced by stable light and stable radiogenic isotope systems

Horstmann, U.E.^a, Coetzee, H.^b, Verhagen, B.Th.^c

^a iThemba LABS, P/Bag 11, Wits 2050, Johannesburg South Africa

^b Council for Geoscience, P/Bag X112, 0001 Pretoria South Africa

^c School of Geosciences, P/Bag 3, Wits 2050, Johannesburg, South Africa

E-mail: horstmann@tlibs.ac.za

The relative proportions of discharge from underground mine water from abandoned and working gold and coal mines in the classical Witwatersrand goldfields were assessed by a variety of isotope systems. $\delta^{18}\text{O}$ and δD values show that direct ingress of surface water contributes only 30% to 40% to water in underground mine workings. Between 60% and 70% or more of mine water is derived from ground and/or fissure water sources. Owing to profound interaction with oxidative weathered Witwatersrand sulphides, S isotopes reveal a “Witwatersrand signature” with $\delta^{34}\text{S}$ values between 2‰ and 5‰ in mine water underground and/or emanating at the surface. A component/water mixing curve deduced from the relation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to $\delta^{34}\text{S}$ values points to water-rock interaction leaching Witwatersrand sediments. Component mixing is substantiated by $^{208}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios with a negative trend representing a mixing relationship between mine void water and ground water and/or surface water. A multiple isotopic label has great potential in tracing water in abandoned and/or active mine workings and can be used to apportion and quantify possible sources of such water.

Local-scale effects of surface – atmosphere interactions on the isotopic composition of atmospheric moisture

Yakir, D., Angert, A., Gat, J.

Environmental Science and Energy Research, Weizmann Institute of Science,
Rehovot, Israel

E-mail: dan.yakir@weizmann.ac.il

Observations of the isotopic composition of atmospheric water vapour are important for four main reasons: 1) It is not limited only to rainy days. 2) Isotopic information contained in newly formed raindrops is lost during rainout. 3) It is the principal tracer of water vapour sources, critical for eco-hydrology. 4) It is a key parameter in estimating the isotopic enrichment in leaf water, and therefore in the application the oxygen isotopic composition of CO₂ and O₂ as a tracer of land vegetation activities. More investigations are needed however into the controls over variations in the isotopic composition of water vapour across spatial and temporal scales. Here we address the effects of local air turbulence, wind direction and changes in mixing patterns over the daily and seasonal cycles on the isotope composition of water vapour by the admixture of evapotranspiration (ET) in vegetated areas, deviations from isotopic steady state in leaf transpiration and evaporation from water bodies.

Non-mass dependent oxygen isotope effect observed in water vapours from Alert, Canada

Lin, Y.^a, Huang, Y.^b, Clayton, R.N.^{a, c, d}

^a The Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, USA

^b Atmospheric Science and Technology Directorate/Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, Canada M3H 5T4

^c The Enrico Fermi Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637, USA

^d Department of Chemistry, the University of Chicago, Chicago, Illinois 60637, USA

E-mail: ying@uchicago.edu

Twenty-six precipitation samples from Chicago, IL and northwest part of Indiana were collected from 2003 to 2005. Twenty-five water vapour samples were collected at Alert, Canada (82.5° N, 62.3° W) from 2002 to 2005 by Environment Canada. Seven ice core samples from Dasuopu Glacier, Chinese Himalayas (28.2° N, 85.4° E) were drilled by Lonnie G. Thompson and prepared by Mary E. Davis. Sample of Standard Light Antarctic Precipitation (SLAP) is available in the laboratory. Water samples were reacted with bromine pentafluoride to produce oxygen, which was then purified and measured by Delta E gas source mass spectrometer. Oxygen isotopic compositions are reported in delta notations and relative to VSMOW. A $\lambda_{\text{MDF}}(\text{H}_2\text{O}) = 0.5292 \pm 0.0031$ (2σ) is determined from three-isotope plot of local precipitation samples. No oxygen isotopic anomaly is found in ice core samples from Dasuopu Glacier, Chinese Himalayas. $\Delta^{17}\text{O}$ of 0.076 ± 0.075 ‰ (2σ) is observed in water vapour from Alert, Canada. The SLAP possesses a positive anomaly of 0.059 ‰. Stacked seasonal trend of $\Delta^{17}\text{O}$ observed at Alert, Canada points toward a maximal value in late spring, which may be due to the lowering of the tropopause level, increasing tropopause folding events, and lowering the Planetary Boundary Layer (PBL) mixing height at the Arctic during spring time. Thus, the intrusion of stratospheric air is at its maximum.

Environmental isotopic study for groundwater of the North Plain of Huai He River, China

Ye, N.J., Gong, J.S., Ge, W.Y., Lu, J.J., Ha, C.Y., Gu, W.Z.

Nanjing Centre, China Geological Survey, Nanjing, China

E-mail: ynj2772@yahoo.com

The Huai He River, one of the seven main rivers in China, has a drainage area of 164,000 km² until Hongze Lake. The North Plain of Huai He River (NPH) covers an area of approximately 85,000 km². Due to the complex aluvial and diluvial depositional cycles, the aquifers are layered, discontinued, connected and, leaked. From hydrogeological settings and their isotopic features, shallow and deep groundwater are defined, the boundary of Lower and Middle Pleistocene is taken as the general boundary of them. Shallow groundwater is phreatic and/or slight confined while the deep groundwater is confined. The river water line of δD and $\delta^{18}O$ is close to that of the groundwater with depths of 0 - 30 m. The low flow of rivers is not only recharged from the Holocene deposit/aquifers but that of the Upper Plistocene. From the original composition of the shallow groundwater and the monthly mean composition of precipitation, it is found that the shallow groundwater is sourced from local precipitation and aquifers of the Upper Plistocene. Three recharge sources of deep groundwater are identified from uranium disequilibrium, the mixing diagram of uranium content U and $^{234}U/^{238}U$, also from that of ^{18}O versus ^{234}U excess, they are: the meteorological water from modern precipitation, the phreatic shallow groundwater and, the palaeowater. The recharge from the percolation of perched Yellow River situated to the north boundary of NPH to the deep groundwater is demonstrated by the profile of $\delta^{18}O$, the existence of tritium in groundwater even from the borehole with depth of 1300 m. The recharge extends about 150 km from the Yellow River.

Interactions between river and groundwater in an alluvial aquifer in Central Italy assessed by means of classic hydrogeological methods and natural tracers (^{222}Rn and water chemistry)

Stellato, L.^a, Petrella, E.^b, Terrasi, F.^a, Belloni, P.^c, Belli, M.^d, Sansone, U.^e, Celico, F.^b

^a Dipartimento di Scienze Ambientali, Seconda Università degli Studi di Napoli, via Vivaldi, 43, 81100 Caserta, Italy

^b Dipartimento di Scienze e Tecnologie per l'Ambiente e il Territorio, Università degli Studi del Molise, Contrada Fonte Lappone, 86090 Pesche (IS), Italy

^c Centro di Ricerca ENEA Casaccia, via Anguillarese, 301 - 00060 S. Maria di Galeria, Roma, Italy

^d APAT, Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici, Servizio di Metrologia Ambientale, via di Castel Romano, 100, 00128 Roma, Italy

^e IAEA, Agency's Laboratories Seibersdorf, Chemistry Unit, A-2444 Seibersdorf, Austria

E-mail: luisa.stellato@unina2.it

The seasonal changes of river-groundwater interactions in an alluvial aquifer in Central Italy have been investigated by ^{222}Rn and major ions measurements in river and groundwater. Stream discharge at various locations and water table levels all over the plain were also measured. The surveys carried out throughout the hydrologic year evidenced an area of groundwater inflow into the stream. Groundwater inflow to the stream was determined by means of ^{222}Rn data, corrected for the degassing, and stream discharge measurements used together in a two components mixing model. ^{222}Rn measurements in the stream were effective to determine fractions of groundwater inflow to the total discharge and to identify sections of flow-through condition. The integration of different approaches gave the best results in the investigation of such complex interactions.

Compound specific stable isotope analysis: research frontiers in isotope hydrology and water resources management

Sherwood Lollar, B., Chartrand, M.C., Hirschorn, S., Howlett, M., Biddleman, T.F., Jantunen, L.M., Mancini, S., McKelvie, J., Lacrampe-Couloume, G., Edwards, E.A.

Department of Geology, 22 Russell St., University of Toronto, Toronto, Ontario, Canada M5S 3B1

E-mail: bslollar@chem.utoronto.ca

Compound Specific Isotope Analysis (CSIA) - the characterization of stable isotope compositions of individual contaminant compounds dissolved in groundwater, sparked a revolution in the interface between isotope geochemistry and contaminant hydrogeology. Stable isotope fingerprints can provide diagnostic tools to identify and differentiate sources of contamination. Furthermore CSIA rapidly proved a novel method for investigation of abiotic and biotic remediation potential at contaminated sites. Several novel developments in CSIA are directly relevant to moving applications of this field from point source contamination to larger regional watershed and ground water resource management applications. The limits of sensitivity and detection limit are being pushed back to facilitate the application of CSIA to low concentrations of contaminants in more diffusive sources. Multi-isotope approaches such as incorporation of both carbon and hydrogen isotope signatures, which to date have been used primarily for non-chlorinated hydrocarbons, are now being extended to investigation of chlorinated hydrocarbon compounds. Improved detection limits and chromatography are facilitating applications of CSIA to new classes of compounds including pesticides, and chlorinated aromatics, where the presence of many isomers presents both an analytical challenge and a challenge for identifying promising lines of evidence for biodegradation.

Stable river water isotopic peak or valley of temporal variations is a good indicator to split wet and dry season at site

Lu, B.H.^a, Sun, T.T.^a, Wang, J.Y.^{a, b}

^aThe College of Water Resources & Environment, Hohai University, Nanjing 210098, China

^bInstitute of Geology and Geophysics, CAS, Beijing 10029, China

E-mail: lubaohong@126.com

The isotope compositions of hydrogen and oxygen in river water are very useful tools for tracing hydrological processes and hydrological cycle related to climate changes and anthropic activities in large-scale river basins. Since 2003, 170 water samples collected in the 1st sampling campaign and the samples regularly collected for one year from four stations along the main stem of Yangtze River are analyzed. As expected, the isotopic compositions (hydrogen- and oxygen-isotope) are progressively increased from upstream to downstream. New water body coming to the main stem of Yangtze River from different tributaries, evaporation and farming are the main reasons of isotopic spatial variations in river waters. The results revealed that temporal and spatial variations in the oxygen- and hydrogen-isotope of water sampled along the main stem of the Yangtze River strongly relied on the isotopic patterns of the regional precipitation. Moreover, signatures derived from influx of evaporatively enriched waters through the several reservoirs or lakes along the system will be resulted in d-excess values. Furthermore, a very interesting behavior of the river water isotopic temporal variations shows that the isotopic compositions are expressed as gradually increasing from the beginning to the end of the low water standing period at site. The increase or decrease of isotopic compositions in the river water depends on the dominant contribution from the ground water or surface water. The peak of the river water isotopic temporal variations corresponds to the boundary of the beginning for annual flooding period or of the ending for low water standing period at site. Obviously, the peak and valley can be used to determine the length of flooding period and low water standing period, and the peak and valley of the river water temporal isotopic variations is a good indicator to split wet and dry season at a given location for a water year.

**Groundwater and its function on the wetlands of the Doñana
Ramsar site (SW Spain): role of the environmental isotopes to
define the flow system**

Manzano, M.^a, Custodio, E.^b

^a Technical University of Cartagena, Cartagena, Spain

^b Technical University of Catalonia, Barcelona, Spain

E-mail: Marisol.Manzano@upct.es

Out of the largely fluctuating surface water marshes, many of the environmental values of the Doñana ecosystems depend on groundwater outflow and shallow watertable. Groundwater flow in the dominantly sandy Plio–Quaternary aquifer, is complex and is currently subject to important changes due to groundwater development. The use of environmental isotopes ^{18}O , ^2H , ^3H , ^{13}C , ^{14}C , ^{34}S , ^{39}Ar and ^{85}Kr has been very successful for defining recharge areas, flow patterns, transit times and the conceptual flow model. The importance of vertical groundwater flow in unconfined areas, as well as the behaviour of pre–Holocene confined water has been assessed. Thus, mixing patterns and chemical evolution can be explained. Lagoons mostly represent aquifer discharge areas in which water evaporates. Some of the solutes remain trapped in bottom sediments and some are flushed out in wet events. This pattern is being changed due to the intensive aquifer development in some areas and negative ecological impacts are appearing. Some wetlands receive anthropogenically impacted young recharge (less than 40 years), while others are fed by older, pristine water.

Isotopic concentration of carbon in pore-water of the unsaturated zone: implications for improved dating of groundwater with ^{14}C

Carmi, I.^{a,b}, Kronfeld J.^a, Yechieli, Y.^b, Yakir, D.^c, Stiller, M.^b, Boaretto, E.^c

^aTel-Aviv University, Tel-Aviv, Israel

^bGeological Survey of Israel, Jerusalem, Israel

^cWeizmann Institute of Science, Rehovot, Israel

E-mail: carmiisr@post.tau.ac.il

Dissolved inorganic carbon (DIC), $\delta^{13}\text{C}(\text{‰})$, $^{14}\text{C}(\text{pMC})$ and tritium were measured in pore water of the unsaturated zone (USZ) above the coastal aquifer of Israel in the nature reserve park of Nitzanim. The DIC and water were extracted from the sediments of the USZ by vacuum distillation. The vertical velocity of water in the USZ, 0.5m/year, was determined by the pulse of tritium from the thermonuclear tests of the 1960's. Thus, for each depth in the USZ an equivalent travel time of water, θ , from the surface to that depth can be assigned. The DIC showed a clear decreasing gradient with depth, suggesting carbonate precipitation in the USZ. The high DIC close to the surface is probably the result of soil CO_2 dissolution in the infiltrating water. The rate of carbonate precipitation (2.8%/year) was estimated by assuming first order reaction kinetics, as follows:

$$\frac{dQ_\theta}{d\theta} = \rho(Q_\theta - Q_{eq})e^{-\rho\theta}$$

where Q is the DIC concentration and ρ is the rate constant. The $\delta^{13}\text{C}$ of the DIC showed no variation with depth in the USZ and is very similar to that of groundwater in the coastal aquifer and of the solid carbonate fraction of the sediment in Nitzanim. The ^{14}C data also shows the effect of the thermonuclear tests of the 1960's. In the case of ^{14}C , the parameter Q_θ at each depth of the USZ is defined as the ratio between the measured ^{14}C to the atmospheric ^{14}C , θ years before sampling time. Presenting the ^{14}C data by the parameter Q_θ shows a clear gradient with depth, which suggests exchange between ^{14}C in pore water and the sedimentary carbonate of the USZ. The rate of exchange calculated as a first order reaction (by the above equation) is 4.1%/year. The gradient of Q_θ in the USZ indicates that at the entrance to the aquifer its value is 0.54. This value is the correction factor for the transfer of ^{14}C from the atmosphere to the aquifer. Thus a new tool to solve the long standing problem of dating groundwater with ^{14}C is added to the arsenal of the hydrologist.

Preliminary isotope studies of Poyang Lake, China

Zhou, W.B., Wang, M.L., Hu, C.H., Xiao, H.Y.

Nanchang University, China

E-mail: wbzhou@ncu.edu.cn

Poyang Lake is the largest fresh water lake in China, and the largest wetland protection area in Asia. The lake serves as the largest buffer for the Yangtze River as well. In order to make better understanding of the water dynamics, water balance, water chemistry, and the relations between lake, rivers and groundwater, isotope investigation has been carried out systematically for one and a half hydrological years. The paper will report the preliminary results from this program.

The interrelation between the sea and coastal aquifer deduced from analyses of radioactive isotopes

Yechieli, Y.^a, Kafri, U.^a, Sivan, O.^b

^a Geological Survey of Israel, Jerusalem, Israel

^b Department of Geological and Environmental Sciences, Ben Gurion University, Beer Sheva, Israel

E-mail: yechieli@gsi.gov.il

The present study used radioactive isotopes in order to get a direct estimate of the rate of seawater intrusion into the coastal aquifer of Israel. These isotopes were used also to determine the connection among the different sub-aquifers, and between them and the sea, by dating both fresh and saline groundwater. Groundwaters from the vicinity of the shoreline were analyzed for their ¹⁴C and tritium content, together with their chemical and stable isotope composition. The results indicate that there are several distinct sub-aquifers in the coastal aquifer near the shoreline, differing in their heads, water chemistry and ages. Stable isotopes were used in order to correct the ages for water-rock interaction. For example, oxidation of old organic matter in the aquifer results in relatively negative $\delta^{13}\text{C}$ values of DIC ($\sim -9\%$, compare to 0‰ in seawater), which should be taken into account for age estimation. The age of the intruding seawater is expected to be younger in the upper sub-aquifers, due to the rise of sea level since the last glacial period. Indeed, the saline groundwaters (no tritium and ¹⁴C <12 pMC) in the lower sub-aquifers are older than ca 10,000 years, while in the upper sub-aquifers they are younger than 50 years (contain tritium), indicating recent seawater intrusion. In most cases, groundwaters in the lower sub-aquifers are found to be fresh and old (older than ca 10,000 years - no tritium and ¹⁴C of <5 pMC). This implies that the flow to the sea in these sub-aquifers is blocked or restricted.

Hydro-isotope Mixing Cell Model for assessing fluxes in complex aquifers undergoing transient hydrochemical and isotopic evolution

Adar E.M., Halamish, N., Sorek, S.

Ben Gurion University of the Negev, Israel

E-mail: eilon@bgu.ac.il

The aim of this study was to develop a flow model that will enable identification of the hydraulic parameters and quantitative calculation of groundwater fluxes in a complex and transient hydro-geological system in which the piezometric heads and the spatial distribution of solutes varies with time. In such a system the boundaries and hydrological conditions along the boundaries are not sufficiently clear or distinct, and there is a lack of hydro-geological and hydro-chemical information. Thus it is difficult to construct, solve and calibrate a hydrological model based on the continuity equation. The algorithm proposed in this study is therefore based on a more simplistic approach in which the flow domain is sub- divided into pseudo-homogeneous flow cells forming a multi-compartmental flow model. The creation of the multi-compartmental structure is based on spatial distribution of dissolved ions and isotopes in a transient hydrological system.

Application of stable isotopes and fluid chemistry to understanding anthropogenic CO₂-brine-rock interactions in sedimentary basins: results from the Frio brine pilot tests, Texas, USA

Kharaka, Y.K.^a, Cole, D.R.^b, Thordsen, J.J.^a, Kakouros, E.^a

^a U. S. Geological Survey, Menlo Park, CA, USA

^b Oak Ridge National Laboratory, Oak Ridge, TN, USA

E-mail: ykharaka@usgs.gov

To investigate the potential for the long-term storage of CO₂ in deep saline aquifers in sedimentary basins, 1600 t of CO₂ were injected at 1500 m depth into a 24-m-thick “C” sandstone section of the Frio Formation, a regional aquifer in the U.S. Gulf Coast. Stable isotopes of water, gases and solutes proved powerful tools in mapping the distribution, transport and interactions of the injected CO₂, and in tracking its leakage into the local shallow groundwater, and into the overlying Frio “B” sandstone, separated from the “C” by ~15 m of shale and siltstone. Fluid samples obtained from the “C” before CO₂ injection showed a Na-Ca-Cl type brine with ~93,000 mg/L TDS at saturation with CH₄, but only 0.3% CO₂. Following CO₂ breakthrough, samples showed sharp drops in pH, pronounced increases in alkalinity, Ca, Fe and Mn, and significant shifts in the isotopic compositions of H₂O, CH₄, DIC, and Sr. Gas and isotopic signatures coupled with perfluorocarbon tracers demonstrated significant CO₂ migration into the “B” sandstone. Results obtained to date from four shallow monitoring groundwater wells show no brine or CO₂ leakage through the Anahuac Formation, the regional cap rock. The δ¹⁸O values for brine and DIC, used to calculate brine/CO₂ ratios in the reservoir, gave results comparable to those obtained by geophysical methods.

Isotope investigation of groundwater recharge by delay action dams in the arid region of Balochistan, Pakistan

Ahmad, M.^a, Akram, W.^a, Tasneem, M.A., Ali, M.^a, Jabbar, A.^b, Abdullah, M.^b, Kulkarni, K.M.^c

^a Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan

^b Pakistan Council of Research in Water Resources, Quetta, Pakistan

^c Isotope Hydrology Section, IAEA, P.O. Box 100, A-1400 Vienna, Austria

E-mail: manzoorriad@yahoo.com

Isotope techniques (^2H , ^{18}O , ^3H) were applied to investigate effectiveness of delay action dam reservoirs in Ziarat Valley of Balochistan. These reservoirs are meant to collect water in rainy seasons and supplement discharge of downstream karezes (subsurface water channels emerging on the ground surface after receiving groundwater through open wells) in dry season by recharging groundwater. The data indicate that the mean values of $\delta^2\text{H}$, $\delta^{18}\text{O}$ and tritium of precipitation are: -6.4‰ , -37‰ and 9 TU respectively. Ranges of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the groundwater samples (wells, karezes, springs) are -6.6 to -2.2‰ and -40 to -16‰ respectively. The reservoirs have ranges of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values from -6.7 to $+15.6\text{‰}$ and -42 to $+86\text{‰}$ respectively and they follow evaporation lines on the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plots. Isotope data indicate that there is no significant groundwater recharge from the Pechi Dam and Manna Dam reservoirs. Vouch Ghouski Dam has some contribution in groundwater recharge while Warchoom Dam reservoir is much effective in contributing to groundwater recharge. Results of tritium suggest that the residence time of groundwater is quite short (fresh water).

Linking water pathways and nutrient dynamics in a small head water catchment: results of a controlled sprinkler experiment using a deuterium tracer in western Oregon

Barnard, H.R.^a, Van Verseveld, W.^a, Graham, C.B.^a, Bond, B.J.^a, Lajtha, K.^a, Brooks, J. R.^b, McDonnell, J.J.^a

^a Oregon State University, Oregon, USA

^b U.S. EPA, Corvallis, Oregon, USA

E-mail: Holly.Barnard@oregonstate.edu

The linkages between subsurface flow paths, vegetation water use and nutrient dynamics are poorly understood. The few investigations that have explored such relations in forest systems have relied passively on natural rainfall and drainage events. As a result, it has been difficult to identify the first order controls on water-vegetation-biogeochemical processes. This work reports on a sprinkler experiment in Watershed-10 (WS10), H.J. Andrews, Oregon, USA. Discharge from the hillslope remained at steady state for 20 days. A pulse of deuterated water was applied for 24 hours on Day 1 of the experiment to investigate breakthrough of deuterium in hillslope runoff, soil and groundwater and trees. The peak in the hillslope deuterium breakthrough occurred within 24 hours of application. Deuterium enrichment was first observed in xylem samples 3 days following application. Weekly soil samples were taken for extraction of DOC, DON, NO₃⁻ and NH₄⁺, plot to investigate supply of nitrogen and carbon. Data analysis suggests carbon and nitrogen were mainly transport limited during the experiment.