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POSTER SESSION 2

Laser Spectroscopy Advances
Analytical Methods
Isotopic Hydrological Modeling
Nutrient Cycles and Contamination
Water Pollution Studies

Laser Spectroscopy Advances

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Hydrogeochemical indicators for radioactive waste disposal site survey to the east of Nile delta, Egypt (IAEA-CN-225-364) .................................................. 153
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Abstract: Stable isotopes of water ($\delta^2$H, $\delta^{18}$O) are unique tracers of many hydrological processes including evaporation, precipitation, reservoir mixing and residence time. Historically, discrete water samples have been collected and analyzed via either Isotope Ratio Mass Spectrometry, or more recently laser-based spectroscopic methods, such as Cavity Ring-Down Spectroscopy (CRDS). However, the analysis of discrete samples precludes the ability to construct high resolution water isotopes data sets through time and space. Previously, research groups have developed laboratory-built diffusive samplers for extracting water vapor from liquid [1,2] and then analyzed that vapor via CRDS instruments, whose continuous flow design and high frequency measurement interval (< 1 Hz) makes them uniquely suited to real-time, high throughput measurements. Here we present details of the first commercially-available Continuous isotopic Water Sampler (CiWS) coupled to a Picarro L2130-i for isotopic water analysis. The CiWS device utilizes an expanded polytetrafluoroethylene (ePTFE) membrane to extract water vapor into a dry air stream. The resultant water vapor is analyzed by a Picarro L2130-i for $\delta^2$H and $\delta^{18}$O. An automated software program provides user-specified time-averaged data and switches between four ports to enable easy calibration. Tight temperature and flow rate control regulates fractionation across the membrane. In-lab testing demonstrates that the system can achieve a raw precision (1σ of 3 minute average) better than 0.05/0.15 ‰ ($\delta^{18}$O/$\delta^2$H), respectively, and a reproducibility of 0.15/0.5 ‰ ($\delta^{18}$O/$\delta^2$H) over seven days (Figure 1), even under variable ambient air and water temperature conditions.
The system was tested in October 2014 during a small boat surface water transect across the northern Sacramento River Delta. In addition to water isotopes, nitrate, chlorophyll, dissolved organic matter (DOM) fluorescence, and other water quality parameters were also measured continuously. We found that as you travel northeast up the delta, surface waters become progressively more enriched in $^{18}$O and $^2$H, while nitrate decreased in concentration and chlorophyll and DOM increased. In concert with other data collected from the Sacramento River Delta, we suggest the lower region represents a mixture of river waters derived from the Sierra Nevada Mountains and the more marine waters from the mouth of the San Francisco Bay. Moving NE up the Delta into shallow sloughs through flooded wetlands, evaporative enrichment increases as shown by the increasing deviation of the real-time isotope data below the local mixing line constructed using discrete water samples from the Bay, Delta and river.
Correlations between the water isotope and chemical data suggest that the extent of evaporative enrichment of real-time water isotope data from this environment may prove a useful proxy for water residence time.

**REFERENCES**


DEVELOPMENT OF IN-SITU VAPOUR SAMPLING FOR STABLE ISOTOPES OF WATER WITHIN UNSATURATED MINE WASTE

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Abstract: The development of in-situ vapour sampling methods to measure the natural, stable isotopes of water in the pore-water of unsaturated profiles will enhance our ability to monitor water movement through mine waste. In order to develop appropriate field sampling methods, a laboratory study was first undertaken to evaluate potential materials and sampling methods by which vapour samples from unsaturated mine waste could be collected and analyzed. Test results show that HDPE or stainless steel tubing should be used for sample collection; however it should be flushed with at least five pore volumes of vapour prior to sample collection or analyses. Analyses can either be performed on-site using field portable laser analyzers or in the laboratory. The vapour samples can be collected for later analysis using Flexfoil bags; the maximum storage time in the bags was determined to be 48 h. Prior to sample collection in the bags, they should be flushed with vapour sample at least three times prior to sample collection. Field methods developed based on these findings were tested at two mine sites using either direct analyses of the vapour with a portable analyzer or sample collection and storage prior to analyses. The field sites included a series of deep (> 100m) multiport profiles within a coal waste rock dump and open wells installed in a sand tailings dyke at an oil sands mine. The final isotope values were compared to the results obtained directly from samples of drill core collected at the sites.

1. INTRODUCTION

Conventional methods of soil water analysis for stable isotopes of water include liquid-water sampling from standard piezometers, pore-water sampling from multiple methods of extraction [1-3] or through the use of vapour equilibration methods on soil cores [4]. If the vapour equilibration method provides a reliable method of obtaining the stable isotope of water composition of pore water in core samples [4], then it should be possible to directly sample and analyze soil vapour taken directly from an unsaturated soil profile to yield the $\delta^2$H and $\delta^{18}$O of the pore water. The successful development of this approach would allow the isotopic compositions of pore waters to be rapidly and repeatedly measured in situ, and in doing so, provide a means of tracking water movement through unsaturated mine waste. The goal of this study is to develop a method for field based sampling and analysis of vapour in unsaturated mine waste such as waste rock or tailings.
2. METHODS

There have been a number of recent studies into measuring the isotopic signature of water vapour under controlled laboratory conditions [5, 6] although these methods are not well suited to sampling within deep profiles of unsaturated mine waste. The initial phase of this study evaluated potential materials and methods under controlled laboratory conditions [7]. This study evaluated a variety of tubing and sample bags with a focus on defining the fractionation associated with losses to the tubing or bags during sampling (i.e. memory effects). Three types of tubing commonly installed in multiport systems were examined for memory loss effects including stainless steel, HDPE and nylon. The tubing was flushed with water vapour with a known isotopic composition and the δ²H and δ¹⁸O values were analyzed over multiple pore volume flushes until a stable reading was obtained. To assess sampling bag memory losses, Flexfoil gas sample bags were flushed with known quantities of standard sample vapour and analyzed for δ²H and δ¹⁸O at each flush until a stable reading was obtained. The last set of testing explored the effects of changing relative humidity values in the water vapour as cold vapour samples in the soil profile warm up prior to analyses. Standard vapour samples were injected into Flexfoil bags and mixed with dry air at specific ratios from 20-100% RH and analyzed for δ²H and δ¹⁸O to establish a correction for the specific analyzer and RH conditions. All δ²H and δ¹⁸O analyses were made using a Picarro L1102-i.

The field sampling campaign was undertaken in two different mine wastes and sampling systems; Waterloo multiport gas sampling profiles (n=4) installed in waste rock at a coal mining operation in the Elk Valley, British Columbia and standpipe piezometers (n=24) in a sand tailings dyke at an oil sands mine near Fort McMurray, Alberta. Sampling the multiports was performed in two ways: direct connection the analyzer to the sampling tube in the field and collecting vapour samples in Flexfoil bags for later analysis on the Picarro L2120i. Flushing volumes and storage times identified in the laboratory testing program were used to define the field sampling protocols. The Waterloo multiport sampling tubes were constructed from HDPE tubing. As a result, 4-5 pore volumes of vapour were flushed with an SKC Grab Air Sample Pump™ prior to analysis or sample collection. The sample bags were also flushed with 1.5 L of vapour (three pore volumes) prior to sample collection. Results from the Waterloo sampling were compared to high spatial resolution sampling developed from drill core using the H₂O⁻H₂O vapour equilibration technique. In the case of the standpipe piezometers, HDPE tubing was lowered down the standpipe to 10 cm above the phreatic surface or base of the riser if the well was dry, and the top of the riser was then sealed from the atmosphere. Five pore volumes of vapour were flushed through the tubing, and the vapour was then collected in Flexfoil bags following the same procedures as described above. The bags were placed in a cooler and analyzed at the end of the day. In standpipes in which a water sample could be collected, these samples were also analyzed using the vapour equilibration method for comparison to the vapour samples. At many of the standpipe piezometer locations, the test results can also be compared to a nearby (less than 10 m) high resolution drilling core profile of δ²H and δ¹⁸O developed using the vapour equilibration method. All δ²H and δ¹⁸O analyses were made using a Picarro L2120i.

3. RESULTS

A snapshot of the results obtained from each portion of the study are presented below. Figure 1 highlights the number of pore volumes required to minimize memory effects for the different types of tubing (a) and the volume of vapour needed to be flushed through a Flexfoil bag prior to obtaining a usable sample (b). The results demonstrate that nylon tubing is not
adequate for sample collection. Its high gas permeability makes it difficult to eliminate memory effects and consequently it never attains the values of the standards used. HDPE and stainless steel tubing require a minimum flushing of 3 pore volumes of sample vapour prior to sample collection. Flexfoil bags also show memory effects up to 1.5 L mL (3 bag volumes) of vapour flushing prior to sample collection.

Figure 1. (a) Tubing memory effects and stabilization and (b) bag memory effect

Preliminary results from the field sampling campaign are shown in Figure 2. Sampling of the Waterloo system showed a similar trending of \(\delta^{18}O\) with depth for the two different sampling procedures (Figure 2a).

Figure 2b, shows the results from the bag sampling campaign within the oil sands sand dyke in comparison to a drill core taken from the same location. The standpipe piezometers sample across a greater depth interval and consequently do not provide as high resolution profiles as those obtained from the drill core taken a previous year. The single water sample collected from this location yields comparable values with the sample taken from the soil core the previous year.

4. CONCLUSIONS

Preliminary results of this study suggest that field based methods of establishing the natural, stable isotope of water profiles for pore water in unsaturated mine waste can be obtained by collecting and analyzing pore vapour. However, memory effects in tubing and sample bags must be addressed. Further, it must be ensured that corrections be applied for analyses for vapour samples that are not water saturated (results not presented).
REFERENCES


THE LASER REVOLUTION IN THE HYDROGEOLOGY GROUP IN MAR DEL PLATA, ARGENTINA

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Abstract: The Hydrogeology Group of the National university of Mar del Plata, Argentina, has about 30 years of existence, but since 2008 its activities were strongly improved by the donation from IAEA of a laser spectroscopy Los Gatos research DLT-100. The Group, without any previous experience in Mass Spectrometry (MS) analysis, has produced 3000 results of stable isotope in water, which leads to an important academic production. The capabilities of the group for analyzing and understanding the hydrological cycle in the Pampa Argentina environment was increased producing a revolution in the conceptualizing of the systems in the Pampa plain.

1. INTRODUCTION

The Hydrogeology Group in the University of Mar del Plata, Argentina, was formed in 1985 and during more than twenty years the research lines were Groundwater Flow Modeling, Environmental Hydrogeology and Hydrogeochemistry. In year 2004 thanks to the possibility to participate in its first Research Coordinated Project (CRP) the group started to be involved in isotopic projects with the IAEA, working in cooperation with the National Institute of Geochronology and Isotope Geology (INGEIS), a Institute with a large trajectory in the subject. In the year 2008 the Group received as a donation of the IAEA into an ARCAL project a Laser Spectroscopy Los Gatos Research DLT-100.

2. METHODS

The Laser Spectroscopy was installed in a Laboratory space (Figure 1) specially disposed by the University, and in 2008 Orlando Mauricio Quiroz Londoño PhD was trained in Vienna for the laser machine operation. The laser spectroscopy is being operated by the authors and the results are available on line in a database designed by Quiroz Londoño (http://www.mdp.edu.ar/hidrogeologia/BDusuariosexternos/index.php). Starting from the standards provided with the machine, five internal standards were developed for the team (Table 1)
Table 1. Internal Standards used for the Hydrogeology Group in Mar del Plata, Argentina.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Water origin</th>
<th>δ²H</th>
<th>δ¹⁸O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Correntoso Lake (Patagonia)</td>
<td>-59.9</td>
<td>-8.64</td>
</tr>
<tr>
<td>B</td>
<td>Groundwater from Lobería city</td>
<td>-25.7</td>
<td>-4.78</td>
</tr>
<tr>
<td>C</td>
<td>Mixing of Mar del Plata groundwater and La Salada lake water</td>
<td>-31.8</td>
<td>-5.46</td>
</tr>
<tr>
<td>D</td>
<td>Water from a creek in the Andes in Mendoza at 3000 masl.</td>
<td>-111.0</td>
<td>-15.8</td>
</tr>
<tr>
<td>E</td>
<td>Distilled water of La Brava lake</td>
<td>-2.2</td>
<td>-0.07</td>
</tr>
</tbody>
</table>

3. RESULTS

At present 3390 samples has been analyzed for δ²H and δ¹⁸O (Figure 2). The results allowed the Research Team to achieve the following achievements:

- Participation in five CRPs.
- Five PhD Thesis were successfully finalized including isotopic date provided by the isotope Hydrology laboratory of the Group.
- Seven papers based on the isotope data have published in indexed journals (ISI) since 2008, and other four are under consideration.
- More than twenty Congress presentations using stable isotope data.
- Cooperation with other research groups and Governmental Organizations.
- Sustainability of a monitoring program in the Quequen Grande River, including stable isotope analyses of weekly samples of river water from two sites during the last ten years and continuing.
Figure 2. Number of samples analyzed for the hydrogeology group of Mar Del Plata National University.

- Participation in a Fourth interlaboratory comparison exercise for $\delta^2$H and $\delta^{18}$O analysis of water samples (WICO2011)
- Four stable isotopes in precipitation gages are operating giving information and local meteoric water lines for the southeast of the Buenos Aires province.
- Training in the used of laser spectroscopy to visitors from Ecuador, Colombia and South Africa.

4. CONCLUSIONS

Laser spectroscopy introduced a real revolution in the development of the hydrogeological research in Mar del Plata, Argentina. A small group without any experience in laboratory or mass spectrometry became able to produce water stable isotope data; increasing its capabilities and giving the chance of introduce new conceptual criteria for solving hydrological problems in the region. PhD thesis approved, new young researchers incorporated, scientific projects granted by national agencies, a large increase in the scientific productivity expressed as papers in indexed journals, etc. arises as a consequence of the possibility of generate isotope data.

The advantages of laser spectroscopy transformed the hydrogeologic research in the Mar del Plata’s group and also other groups in Argentina that can now access to isotope, giving to the society new ideas, possibilities and elements to solve hydrologic problems in Argentina.
DATING WITH ATOM TRAP TRACE ANALYSIS OF $^{39}$AR – THE $^{39}$AR-ATTA-APPARATUS

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Abstract: We have developed an Atom Trap Trace Analysis setup for $^{39}$Ar as well as an extraction and separation system for water and ice samples. Our results reveal the potential of this tabletop experiment based on laser cooling techniques to routinely measure small samples down to 0.1 mL STP of argon within less than a day. For the first applications to date groundwater we achieved a stable atmospheric count rate of $3.58 \pm 0.10$ atoms/h.

1. INTRODUCTION

Atom Trap Trace Analysis (ATTA) is an ultra-sensitive counting method for rare isotopes [1]. It is based on the high selectivity of resonant photon scattering during laser cooling and trapping distinguishing the rare isotope from the abundant ones. The special strength of this method is that for dating with long-lived isotopes only small sample sizes are required for practical measurement time.

2. METHOD

Our ATTA-apparatus follows the concept as the ones described by Jiang et al. [2, 3]. It consists of a liquid nitrogen-cooled metastable argon source driven by a RF-field. In different stages the divergent atom beam is collimated, focused and slowed down longitudinally below the capture velocity of the magneto-optical trap. With that a single atom can be detected observing its fluorescence light with an avalanche photo diode. The $^{39}$Ar concentration is inferred by the observed atom counts per time normalized by the carefully determined count rate of an atmospheric sample (commercial bottled argon). This approach requires a stable and reproducible performance of all components of the apparatus leading to robust $^{39}$Ar detection efficiency. Therefore, before and after each measurement different control measurements of the stable isotopes such as the $^{38}$Ar loading rate of the magneto-optical trap and the $^{40}$Ar atom beam profile are performed. Furthermore, we measure and stabilize all laser powers and frequencies actively and monitor the metastable atom flux, the laser powers and frequencies and locking signals during $^{39}$Ar measurements.

There are two different modes in which our apparatus can operate. In throughput configuration, where the sample is pumped out of the vacuum chamber, 0.5 to 1 L STP of argon is necessary for a 15- to 30-hour measurement. In recycling mode the gas circulates in a closed vacuum system. Thereby, less than 0.1 mL STP of argon is needed to run the system. Since the abundance of $^{39}$Ar ($^{39}$Ar/Ar = $8.23 \times 10^{-16}$) is about 600 times lower than that of $^{81}$Kr and about 25,000 times lower than $^{85}$Kr, enriched samples have been used to get a sufficient count rate for optimization and characterization of our setup. This however has induced a detectable contamination embedded in the vacuum system, which accumulates while operating in recycling mode. We can deduce from the accumulated background in recycling mode that its contribution is less than 2% in throughput configuration.
3. RESULTS

By systematic optimization with enriched samples we achieved an atmospheric count rate of 3.58 ± 0.10 atoms/h. A total number of 1162 $^{39}\text{Ar}$ atoms were counted within 324 hours distributed over 28 single measurements each with a length of 3h to 21h. The statistics indicates the behavior of the expected Poissonian distribution. A small long-term drift could be correlated to the deterioration of the source monitored with our beam diagnostics tools. This count rate and stability are sufficient for dating of groundwater samples with $^{39}\text{Ar}$-ATTA [4]. An agreement on the 1σ-confidence level with the concentrations measured by Low-Level Counting in the underground laboratory in Bern was achieved. In addition, synthetic samples with known concentration covering the whole dating range also show excellent agreement.

4. CONCLUSIONS

Current developments such as more efficient cooling techniques and a source with a higher flux of metastable argon atoms aim to enhance the count rate. Shorter measurement times together with a reduction of statistical uncertainties thus are possible. Due to the contamination in the apparatus, we chose the throughput mode of operation and analyzed argon gas of several tons of water. It should be possible to reduce the contamination for recycling sufficiently by replacing the affected vacuum parts. In this case we expect a reduction in the needed argon to 0.1 mL STP, corresponding to about 0.25 L of water or 0.1 kg of ice.

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DATING WITH ATOM TRAP TRACE ANALYSIS OF ARGON-39: METHODS OF SAMPLE PREPARATION

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Abstract: We have developed an Atom Trap Trace Analysis setup of $^{39}$Ar as well as an extraction and separation system for water and ice samples. For the first explicit demonstration of dating with $^{39}$Ar-ATTA, we took large groundwater samples, degassed them in the field and separated the argon with a gas chromatographic technique. The argon purification of ice samples is realized with a setup based on a titanium getter. With argon purities of about 98% and recoveries above 90%, the setup fulfills the sample requirements of the ATTA apparatus for $^{39}$Ar dating.

1. INTRODUCTION
The radioactive isotope $^{39}$Ar with a half-life of 269 years is the ideal and only tracer for dating water and ice in the time range of 50-1000 years. However, its routine application is hindered by its extremely low atmospheric abundance of $^{39}$Ar /Ar = 8.23 x 10$^{-16}$ [1]. Besides Low-Level Counting, the laser based atom counting method Atom Trap Trace Analysis (ATTA) is the only feasible technique for the detection of $^{39}$Ar with a maintainable effort. For the application of this technique to environmental samples, various sample preparation setups are required.

2. METHODS
Preparation of groundwater samples:
Groundwater is degassed in the field by an extraction setup based on membrane contactors. For this purpose, up to 2500 L of water are pumped through a two-stage filtering system and degassed by a 6 x 28 Extra-Flow membrane contactor [2]. The gas phase is then compressed to a maximum of 7 bar onto a 9 L sampling cylinder. Although the degassing efficiency slightly varies between different elements, isotope fractionation of argon is negligible.

For the gas chromatographic separation of argon we use a similar setup as developed at the University of Bern [3]. The extracted gas is loaded on 9 columns filled with zeolite, which is cooled down to -130°C. By using helium as a carrier gas, the different gas components are flushed from the columns. The process is supervised by a quadrupole mass spectrometer which analyzes the gas at the outlet of the columns. Argon leaves the columns first as it interacts weaker with zeolite than the other gas components. It is then captured on an activated charcoal trap and finally transferred to a container for the transport to the ATTA setup.

We demonstrated that the gas chromatographic system is also capable of separating the krypton fraction of a gas sample. Further developments for routine krypton preparation are currently underway.

Preparation of ice samples:
Roughly 10% of the volume of an ice block is trapped air. By melting the block under vacuum conditions, the trapped air is released and then guttered to remove the reactive gases [4].
remaining gas fraction consists to more than 98% of argon, which is transferred to a container for \( ^{39} \text{Ar} \) analysis with ATTA.

3. RESULTS

The extraction unit for groundwater requires about 75 minutes for one sample of more than 60 L of gas with a degassing efficiency of about 90% for argon. With the argon separation system, 5 to 65 L gas samples can be processed, which takes about 7 hours. We obtain argon purities above 98% while recovering more than 96% of the argon from the gas sample. First tests of krypton purification led to a purity and recovery of about 60%.

The argon extraction from ice blocks of between 0.5 kg and 10 kg takes about 3 hours and results in an argon purity of above 98% and a recovery of at least 90%.

4. CONCLUSIONS

Two different systems for the preparation of argon were developed, one for large groundwater samples and the other for ice samples. Both systems fulfil the requirements for the \( ^{39} \text{Ar} \) analysis via the ATTA apparatus and process the samples within a satisfying period of time. Current developments focus on the preparation of small ocean and lake samples, as well as on an improved krypton separation routine.

REFERENCES


NITRATE ISOTOPIC ANALYSES BY COMBINING THE DENITRIFIER METHOD WITH LASER SPECTROSCOPY

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Abstract: Anthropogenic nitrate inputs into the global nitrogen cycle have increased considerably and are negatively impacting aquatic ecosystems and human health. Nitrate sources in water can be identified using stable nitrogen and oxygen isotopic compositions ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) of nitrate. Several methods have been developed for such analyses, but they involve intensive cost and maintenance for an accurate and precise analysis using on-line isotope-ratio mass spectrometry (IRMS). Moreover, all methods need a preliminary sample preparation step to convert the nitrate from water to obtain an appropriate substance to be analyzed (e.g. N$_2$O, from the bacterial denitrification method or the cadmium reduction method via headspace analysis; nitrate salt from the ion-exchange method via high-temperature conversion). Our proposed method is based on the isotopic analysis of N$_2$O produced from the conversion of NO$_3^-$ by cultured denitrifying bacteria in an isotopic N$_2$O laser analyzer (Los Gatos Research, Inc.) employing cavity enhanced laser absorption spectroscopy. The reaction stops at N$_2$O since the denitrifying bacteria Pseudomonas aureofaciens lack N$_2$O-reductase activity, and the N$_2$O is extracted from the vial to be injected into the laser analyzer. Accuracy and precision of the method is estimated at different nitrate concentrations analyzing reference materials and in-house standards with known isotopic composition as well as unknown samples. Blank and drift correction is considered for each run. This high throughput isotope analytical technique improves the isotopic analysis of nitrates (i) providing precise measurements of isotopic ratios of $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_{\alpha}$, $\delta^{15}\text{N}_{\beta}$) and $\delta^{18}\text{O}$ without pre-concentration, (ii) by eliminating interferences by other gas substances (water and CO$_2$), and (iii) reducing extensive and costly maintenance of mass spectrometers. Application of this novel technique will assist with the determination of relative contributions of nitrate sources using (Bayesian) isotope mixing models, which increases our knowledge of nitrogen cycling in aquatic ecosystems.
LASER SPECTROSCOPIC ANALYSES OF H AND O ISOTOPE COMPOSITIONS IN FLUID INCLUSIONS: APPLICATIONS IN PALEOCLIMATE/HYDROLOGY

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Abstract: Inclusion-hosted water may provide direct information on the isotopic composition of the drip water from which cave deposits formed. The water content of stalagmites is generally in the thousand ppm range that makes the stable isotope analyses of the H\textsubscript{2}O possible by different techniques. In the last decades stable H isotope analyses were usually conducted by mass spectrometric measurements, O isotope compositions were seldom determined due to the rather tedious and sophisticated methods required. Laser-based spectroscopic analyses of water δD and δ\textsuperscript{18}O values, however, became routine in the last decade and the number of applications on fluid inclusion-hosted H\textsubscript{2}O measurements is growing nowadays. We have developed a technique to analyse δD and δ\textsuperscript{18}O values in inclusion-hosted waters using a Los Gatos Ltd. laser spectrometer (LWIA-24d) and a preparation line (Czuppon et al., 2014). The method applied here is slightly modified after Czuppon et al. (2014) to conduct vacuum crushing in helium flow to reduce the possibility of H\textsubscript{2}O-CaCO\textsubscript{3} oxygen isotope exchange during the extraction. The accuracies of δD and δ\textsuperscript{18}O data were tested by analysing recently forming stalagmites where dripwater compositions are known and calcite samples whose isotopic compositions had been determined by independent mass spectrometric measurements. Although good agreements between the different methods and laboratories have been achieved, the application of the method for paleotemperature calculations is rather limited due to diagenetic alterations of speleothem deposits. The method is best suited for analyses of inclusion water trapped in oxygen-free host minerals (e.g., fluorite). The study was financed by the Hungarian Research and Development Office and the Hungarian Scientific Research Fund (OTKA CK 80661).

REFERENCES

A NEW TRITIATED WATER MEASUREMENT METHOD WITH PLASTIC SCINTILLATOR

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Abstract: A new tritiated water measurement method with plastic scintillator (PS) by using liquid scintillation counter was developed. The PS used was a pellet of 3 mm in both of a diameter and a length. A low potassium glass vial was filled with the pellets and tritiated water was applied to the vial from 5 to 100 µL. This method needs no liquid scintillator, so no liquid organic waste fluid is produced. The measurement efficiency with the pellets was approx. 50% when a solution was 5 µL. Relationship between count rate and activity showed perfect linearity. The pellets were able to be used repeatedly. The PS pellets are useful for environmental radioisotopes measurement without radioactive wastes.

1. INTRODUCTION

Tritium ($^3$H) exists in our environment approx. 11 EBq at 2013. Measurement of $^3$H including tritiated water is important for not only environmental researchers but life science researchers and radioactive wastes managers. Tritium is generally measured by a liquid scintillation counter (LSC). A LSC is a superior machine for low energy pure beta emitters because energies emitted from radioactive samples transfer to liquid scintillator with 4 π (all) directions. So, $^{14}$C and higher energy emitters can be measured with high measurement efficiency (more than 90%) by using a LSC. On the other hand, a maximum range of $^3$H in a solution is approx. 6 µm, measurement efficiency of $^3$H is almost under 50% even when a LSC is used. Nevertheless, high measurement efficiency for beta-ray emitters is the most important merit with LSC measurement. A demerit of LSC measurement is to produce radioactive organic waste fluid (WASTE) because of using liquid scintillator.

For avoiding producing WASTE, there were some studies using other scintillators which were used as substitutions for liquid scintillator. All these attempts had some issues; for examples, low measurement efficiency [1], low reproducibility [2], impossibility of low energy detection [3]. Especially in our studies [4, 5], using plastic scintillator sheets (PS sheet) with and without modification of their surface, tritiated water was impossible to measure with high measurement efficiency. Because the PS sheets method needs to dry up samples on the PS sheet, it is good for nonvolatile compounds. However, little tritiated water remains on it. So, another method was attempted for tritiated water: the sample was put on a PS sheet and put another sheet on the sample without drying, then put the pair of sheets in a glass vial for measurement by LSC. The sample solution was vaporized from the sheets slowly in the vial. Unfortunately, the measurement efficiency of this method for tritiated water was not so high compared with that of LSC. Other methods are required for reduction of WASTE. A new measurement method was developed for tritiated water.
2. METHODS

Figure 1 shows a diagram of the new measurement method. Points of the method are as follows: 1. Tritiated water is put in a low potassium glass vial for LSC in which is filled with plastic scintillator pellets; EJ-200 (G-tech Co. Japan). 2. The size of the pellet is approx. 3 mm in a length and 3 mm in a diameter. 3. Soon after the sample is applied to the pellets, the vial is screwed a lid on, which has a cone gum inner to avoid leaks (uGV2, Meridian Biotechnologies Ltd.).

![Diagram of measurement procedure](image)

**Figure 1.** A) A photo of pellets, B) A photo of a vial with pellets and lids for this measurement system. C) A diagram of the measurement procedure.

By this method, 1) relationship between measurement efficiency and elapsed time, 2) relationship between count rate and activity, 3) detection limits calculated with the back ground counts of PS pellets, and 4) possibility of reuse of the pellets were studied. For the efficiency calculation, the activity (dpm) was determined by measuring liquid scintillator (LS: ACS-2, Amersham). The measurement efficiency (Eff.) and detection limit count rate \( (n_D) \) were defined as follows [6]:

\[
\text{Eff.} \, (\%) = \frac{\text{cpm}}{\text{dpm}} \times 100
\]
\[ n_D (\text{cpm}) = \frac{k^2}{2} \left( \frac{1}{t_s} + \frac{1}{t_B} \right) + \frac{1}{k^2} \left( \frac{1}{t_s} + \frac{1}{t_B} \right) \]

where \( k \) is a coverage factor corresponding to a confidence interval of 95% when \( k \) equals 2. The \( t_s \) and \( t_B \) are measurement time of the sample and back ground, respectively. Also the \( n_B \) is the count rate of back ground. A detection limit activity concentration \( (\text{AD}) \) was defined as

\[ \text{AD} (\text{dpm/mL}) = \frac{nD}{\text{Eff}/100} / \text{sample volume (mL)}. \]

The LSC used was Tri-Carb3110TR (PerkinElmer) and the measurement time was 2 min for each sample. The radioactivity was approx. 1KBq/5µL except for linearity study.

3. RESULTS

1) Relationship between measurement efficiency and elapsed time: Fig. 2 shows measurement efficiency of tritiated water of 5 µL with LS, PS pellets and PS sheets.

![Figure 2. The measurement efficiency with PS pellets: It was higher than that of LS and PS sheets. Also the measurement efficiency agreed well among 3 samples.](image)

2) Relationship between count rate and activity: Figure 3 shows the linearity between the count rate and activity of tritiated water. In this case, the sample used was 50 µL and the activity was from 76 to 6600 Bq/mL. When the sample used was 50 µL, the measurement efficiency was approx. 25% for every concentration.

Other results will be shown at the symposium.

4. CONCLUSIONS

Without liquid organic waste fluid, tritiated water was measurable by using plastic scintillator pellets with a liquid scintillation counter. The measurement efficiency was as high as that of liquid scintillator. Reproducibility of the pellets measurement was good. The pellets could be reused by rinsing in a hot water. The pellets are able to measure other tritium labeled compounds and other radionuclides. The measurement method is suitable for a new detector of a monitoring post for environment researches.
Figure 3. Relationship between count rate and radioactivity: It shows good linearity. Under 4 Bq of tritiated water measurement was possible by PS pellets in the vial for LSC.

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Abstract: The IAEA Terrestrial Environmental Laboratory is developing wood standard material that will be characterized for hydrogen stable isotopes to aid in the verification of the geographical origin of timber. However, after a tree is harvested hydrogen bound to oxygen and nitrogen continues to exchange with moisture in the ambient air obscuring the original δD isotopic signal. Here we compare δD measured in bulk wood analysed using a traditional equilibration method with δD liberated from lignin methoxyl groups. Data will be presented for five woods from Austria, Mongolia, and Canada.

1. INTRODUCTION

The international trade of illegally logged timber is an issue with far reaching environmental and economic consequences. In response to the European Union Action Plan on Forest Law Enforcement, Government, and Trade (FLEGT), the IAEA Terrestrial Environmental Laboratory is developing wood standards characterised for light stable isotopes to aid in the verification of the geographical origin of timber. The adoption of laboratory methods to validate the stated origin of timber being imported into the European Union (EU) has the potential to elevate legal proceedings to a scientific arena rather than relying on documentation, which can easily be falsified.

Light stable isotopes, particularly δD, have long been employed to authenticate the origin of a range of organic materials of economic importance including food [1] and wine [2] by capitalizing on the characteristic global distribution of δD [3, 4]. The δD isotopic composition of wood reflects the δD isotopic signal of rainfall in the location where the tree was grown, with a correction factor related to the depletion of $^2$H during the incorporation of hydrogen during photosynthesis. However, after a tree is cut hydrogen bound to oxygen and nitrogen continues to exchange with moisture in the ambient air obscuring the original δD isotopic signal as the wood moves from the location it was harvested through the export process. The traditional method for analysing hydrogen stable isotopes in materials which contain exchangeable hydrogen requires the equilibration of samples with two different waters of known composition to obtain the amount of exchangeable hydrogen in the unknown sample and calculate the true value of δD [5]. This method is not well suited for routine verification of wood samples for import, which requires rapid analysis of samples. A recently developed method for analysing δD of lignin methoxyl groups capitalizes on hydrogen bound to carbon, which is non-exchangeable with ambient moisture [6]. This method eliminates the need for equilibration and therefore the analytical time required is reduced relative to the traditional equilibration method.
2. METHODS

Here we compare δD measured in bulk wood analysed using a traditional equilibration method with δD liberated from lignin methoxyl groups. Results will be presented for five woods: two woods from Mongolia, *Larix sibirica* and *Haloxylon ammodendron*, one local wood, *Fagus sylvatica*, and two woods from Canada, (*Juglans nigra* and *Acer negundo*). Under the equilibration method bulk samples of each wood ground to 250 µm are freeze dried for five days, equilibrated with two waters (δD values of -43.2‰ and -399.8‰) for five days, then freeze dried a second time prior to analysis. In the methoxyl method hydroiodic acid (HI) is added to samples to cleave the ether bonding the methoxyl groups to lignin; the methoxyl groups are converted to methyl iodide (CH$_3$I).

3. RESULTS

Preliminary results for the methoxyl method performed with samples of local wood, *Fagus sylvatica*, give a value of -249.7 ± 2.9‰. Local mean annual precipitation values for δD are -57‰ [7], giving an epsilon (ε) value between wood methoxyl δD and local mean annual precipitation δD of -204.7 ± 6‰. This value for ε is within error of those published by Keppler, -216 ± 19‰ [6].

4. CONCLUSIONS

These preliminary results represent the first step towards our goal to provide a rigorous characterisation and best practice recommendations for wood standard material targeted at laboratories providing stable isotope determination for the verification of the geographical origin of imported wood.

REFERENCES

PRESENT STATUS AND STRATEGIC PLAN FOR THE STABLE ISOTOPE REFERENCE MATERIALS AT THE IAEA

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Abstract: The presentation will focus on the historical overview of the Stable Isotope Reference Materials under distribution by the IAEA, on current approaches and capacities related to material testing and production.

Future plans include directions as follows:

• Maintaining the scale-defining Stable Isotope Reference Materials (SI-RMs) at the highest level and introducing replacement SI-RMs when needed;

• Addressing the most critical applications (environmental applications, human health, food safety studies etc) and newly emerging analytical isotope techniques by suitable high-level SI-RMs;

• Performing all measurements aimed to characterisation of SI-RMs and the uncertainty evaluation in accordance to the latest metrological concepts.

The presentation will demonstrate in details the steps related to production and characterization of new SI-RMs, with the example of a range of water RMs produced.
Abstract: The worldwide metrological comparability of stable isotope measurement results is presently achieved by linking them to the conventional delta scales. Delta scales are realized by scale defying reference materials, most of them being supplied by the IAEA. In fact, these reference materials are artefact materials, characterized by a network of laboratories using the current best measurement practice. Presently there is no link between the delta scale and international system of units (SI). This is important when the reference materials have to be replaced. In order to maintain the scale, the new materials need to be linked with the original scale defining materials. A good example is the replacement chain: SMOW => VSMOW => VSMOW2 and SLAP2.

This process of replacement somewhat increases the measurement uncertainty associated with the assigned property values, as it is the case for VSMOW2 and SLAP2 which are used in everyday analytical practice as calibrators for working standards in laboratories.

In assessing and reporting their measurement results, the laboratories using VSMOW2 and SLAP2 and/or other stable isotope reference materials should account for the uncertainty associated with the values assigned to these reference materials. In order to support laboratories in their everyday practice for reporting results of stable isotope measurements, a generic scheme of uncertainty evaluation will be presented.
Abstract: The three most important concerns related to δ\(^{13}\)C reference materials include:

- urgent need for introducing the replacement of NBS-19, the δ\(^{13}\)C scale defining reference material;

- climate change related measurements and associated metrological requirements: small measurement uncertainty, long term stability for the low value δ\(^{13}\)C reference material(s); and

- the need for a range of reference materials addressing existing and newly emerging analytical techniques, e.g., optical isotopic analysers.

In this presentation an overview of the current status of the δ\(^{13}\)C reference materials will be presented and the strategic plan of developments discussed.
A NEW SET OF SINGLY AND DOUBLY STABLE ISOTOPE LABELED REFERENCE WATERS FOR RESEARCH USING ISOTOPE LABELLING

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Abstract: Two new sets of three reference waters enriched in the stable isotopes have been produced and certified: one set singly labeled waters, only enriched in $^2$H and another set of Doubly Labeled Waters, enriched in both $^2$H and $^{18}$O. These reference waters have been prepared gravimetrically, and the process has led to highly accurate isotopic values for these waters. The three parent waters: natural water, pure $^2$H water and highly $^{18}$O enriched water have been thoroughly assessed for their isotopic compositions. This set of certified reference materials, covering enrichments in the range of 800-1600‰ and 100-2000‰ for $\delta^2$H and $\delta^{18}$O, respectively, is now available (called IAEA-604 to 609). They will be distributed by the IAEA in 5-mL aliquots in borosilicate ampules and are valuable as reference materials for biomedical research, and all other fields where water isotope labeling is used. The two waters with the lowest enrichments will also be useful as anchor values for isotope measurements around the natural range.

1. PRODUCTION

The basis of the production of the new reference materials is gravimetric mixing of a distilled natural water sample with isotopically pure $^2$H water and highly $^{18}$O enriched water. We filled three 30-liter stainless steel containers for singly labelled waters initially with about 20 kg of demineralized local tap water and three other containers for doubly labelled waters with about 10 kg (for all 6 reference waters from the same single supply tank) and determined the mass of the water to a precision of better than ±1 gram (better than 1:10$^4$). Isotopically enriched parent solutions, $^2$H and $^{18}$O water, were served in small vials such that the quantities (ranging from 1.5 to 56 grams) could be weighed to 0.01 mg to 0.1 mg precision (better than 1:10$^5$). Care was taken to restrict evaporative losses to the very minimum by covering the vials, and working quickly. The set of the three singly labelled waters was made by immersing the small glass vials filled with the $^2$H water into their three containers for thorough mixing with the demineralized waters. Then the containers were tightly capped. The three doubly labelled enriched waters were produced by immersing simultaneously the filled small vials with the $^2$H and those filled with the highly enriched $^{18}$O water into their three
containers. The all airtight containers were stored for three weeks in which period they were regularly moved/rolled to ensure complete mixing.

The isotopic composition of the natural water had been characterized via an interlaboratory comparison involving five stable isotope laboratories. The isotopic composition was determined to values of $\delta^2\text{H}=-42.7\%_\text{o}$ and $\delta^{18}\text{O}= -6.32\%_\text{o}$ with very low quantified uncertainty.

The highly $^2\text{H}$ enriched water used for preparation of our reference materials had a high $^2\text{H}$ purity grade of 99.993%, certified by the supplier (Sigma-Aldrich) for this specific batch through $^1\text{H}$-NMR spectroscopy. We relied on the stated purity, but used a conservative uncertainty estimate of $\pm 0.005\%$ in this value.

Contrary to the deuterated water, the $^{18}\text{O}$ enriched water was not certified with satisfactory accuracy for our goal. This is caused by the fact that a purity of virtually 100% cannot be reached in the thermo-diffusion process by which $^{18}\text{O}$ is enriched. Furthermore, the other rare isotope of oxygen, $^{17}\text{O}$, gets enriched as well. An independent determination of the $^{18}\text{O}$ enrichment level was thus essential. We did this by gravimetrical dilution of the $^{18}\text{O}$ enriched water by naturally depleted water, such that the end product is close to VSMOW in its isotopic composition. Using this procedure we were able to determine the abundances to be $96.05\pm0.12\%$ for $^{18}\text{O}$ and $1.176\pm0.020\%$ for $^{17}\text{O}$.

We also carefully determined the oxygen enrichment of the highly enriched $^2\text{H}$ water, and the deuterium enrichment of the enriched $^{18}\text{O}$ water. In both cases, enrichment levels in the non-specified isotopes were considerable too: the $^{18}\text{O}$ abundance in the deuterated water was close to 0.9%, and the $^2\text{H}$ abundance in the $^{18}\text{O}$ water was nearly 0.18%. These results were used in our mixing calculations.

2. RESULTS

Based on the above determinations of the full isotopic composition of the two enriched waters, the final delta values of the six new reference waters could be calculated using self-developed mixing spreadsheets.

The values, along with their (1-sigma) combined uncertainties, and also the equivalent isotopic abundances are given in table 1. This combined uncertainty is valid for the bulk waters, and excludes as yet a potential component of heterogeneity from ampoule bottling. For the calculation of the final combined uncertainties, up to four uncertainty sources were significant for the $\delta^2\text{H}$ values (though not for all six waters). For $\delta^{18}\text{O}$, the uncertainty in the enriched waters is entirely due to the uncertainty in the $^{18}\text{O}$ abundance of the $^{18}\text{O}$-water.

3. VALIDATION AND CONCLUSIONS

Provided all procedures went as expected, the gravimetric values for these reference waters are superior to directly measured ones in terms of combined uncertainty. However, to check if procedures all went right, an experimental verification of the values was performed. We analyzed the prepared reference waters IAEA 604-609 in two laboratories, CIO and IAEA, with a variety of techniques. All measurements showed good agreement with the assigned values within the spread of the methods used. For $\delta^2\text{H}$, the uncertainty in the assigned values of the new reference waters is minute compared to the spread of all experimental methods, making the new reference waters a huge improvement in terms of precision and accuracy. For
The gain in accuracy is not as impressive as in the $\delta^2$H case, but the improvement is still very significant.

Based on our experimental results we can be confident that the reference waters have indeed been prepared according to plan and that the values presented in table 1 are reliable.

The significant improvement in accuracy that these waters provide will be of use in a number of fields, where water isotope labelling is performed. The lowest enrichments will be even useful for isotope measurements in the natural range, for which they can serve as high anchor point. The reference waters IAEA-604 through -609 are now available through the usual IAEA channels for isotope reference materials. They will be distributed in 5 mL aliquots in borosilicate ampules.

**Table 1. Isotopic compositions of the new reference waters, expressed both in delta values and isotopic abundances, with their combined uncertainties (excluding heterogeneity, to be assessed by IAEA) in brackets.**

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\delta$-values and combined uncertainties(‰)</th>
<th>Absolute Isotopic abundances (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^2$H</td>
<td>$\delta^{18}$O</td>
</tr>
<tr>
<td>IAEA-604</td>
<td>799.9 (0.3)</td>
<td>-5.86 (0.03)</td>
</tr>
<tr>
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<td>736.4 (0.8)</td>
</tr>
<tr>
<td>IAEA-609</td>
<td>16036.4 (1.0)</td>
<td>1963.7 (2.2)</td>
</tr>
</tbody>
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**17O-EXCESS IN HIGHLY EVAPORATED NATURAL WATERS FROM THE SISTAN DESERT (IRAN)**

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**Abstract:** The combination of $\text{H}_2^{17}\text{O}/\text{H}_2^{16}\text{O}$ and $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ isotope ratios allows discrimination between equilibrium and kinetic processes during mass dependent fractionation of water [1]. Excessive enrichment of the $^{17}\text{O}$ species in residual water during evaporation is strongly controlled by effects of relative humidity and may provide second order information on the environment. Here, we present first triple oxygen isotope data of natural, evaporated water bodies in the hyper arid desert of Sistan (Iran) where evaporation is high and freshwater supply by the Helmand River is hardly restricted. Water samples were analyzed by CoF$_3$ fluorination and subsequent mass spectrometric analysis of released oxygen. Samples from perennial lakes and residual groundwater-fed ponds originating from earlier floods evolve along typical evaporation trends as a function of relative humidity (Figure 1).

The high depletion of $\text{H}_2^{17}\text{O}$ can be assigned to a strong diffusive contribution which is controlled by low relative humidity. Measurement data is in excellent agreement with model predictions which are based on a closed-basin evaporation model interacting with atmospheric moisture [2]. Our results suggest the applicability of $^{17}\text{O}$-excess as a tracer for relative humidity and emphasize the importance of water-vapor interaction in natural environments.

**REFERENCES**

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Figure 1: Isotopic composition of average freshwater (solid blue dot) and evaporated water bodies and lakes (diamonds) in the Sistan Basin, Iran. Increasing evaporation degree is indicated by increasing $\delta^{18}O$ and accompanied by a decrease of $^{17}O$-excess. The lines show predicted isotopic evolution for 30 %, 35 % and 40 % relative humidity.
PROGRESS ON AMS MEASUREMENT FOR δ¹¹B MEASUREMENTS AT CIRCE.

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Abstract: Boron (B) commonly exists in groundwater as a minor constituent (concentration < 0.05 mg/L). Other non-natural sources in waters include anthropogenic use in fertilizers and final goods (0.1–1.5 mg/L in sewage effluent, >1mg/L in liquid manure, up to 22 mg/L in mineral fertilizer leachate). The two stable isotopes of boron, ¹⁰B and ¹¹B (natural abundances ≈ 19.9 and ≈ 80.1 atom percent, respectively), undergo isotopic fractionation during boron speciation (e.g.: ¹⁰B is preferentially incorporated into B(OH)₄ versus B(OH)₃, Tonarini et al., 2003). Therefore, the isotopic composition of dissolved boron in groundwater can be used for source apportionment. Boron behaves as a conservative element in groundwater and surface water systems and the isotopic signature of boron is very useful together with other stable isotope (e.g. δ¹⁵N-NO₃, δ¹⁸O-NO₃) to identify the sources of nitrates (Tirez et al., 2010; Widory et al., 2004; Widory et al., 2005). We present a method for boron chemical purification as B(OH)₃ in natural water samples by ion exchange chemistry and measurement of boron isotopic composition (δ¹¹B) by AMS (Accelerator Mass Spectrometry). At CIRCE, the extracted solid B(OH)₃ is loaded into little cones (cathodes) in the source of a 3 MV Pelletron tandem accelerator that allows to measure 40 samples in a single run. The sample is ionized by Cs⁺ sputtering, producing B ions which are accelerated and analyzed through an Electrostatic Analyzer, a Low Energy Magnet and a High Energy Magnet. The ions are collected on Faraday Cups. We tested whether isotopic fractionation occurred during chemical preparation, measuring chemically treated and untreated samples. The preparation method does not seem to introduce any significant isotopic fractionation. In summary, we have developed a suitable chemical method for AMS measurement of δ¹¹B that can be applied to samples with boron concentrations as low as 0.1 ppm. The precision obtained on δ¹¹B measurements so far is around 5-10 ‰.

1. INTRODUCTION.

High precision (≤ 0.1‰) measurements of ¹¹B/¹⁰B isotopic ratios are usually achieved by TIMS (Thermal Ionization Mass Spectrometry), others measurement technique such as ICP-MS (Inductively Couple Plasma-Mass Spectrometry) and MC-ICP-MS (Multi-Collector-Inductively Coupled Plasma-Mass Spectrometry) achieve precision about 6.7‰ and 0.81‰, respectively (Gonfiantini et al., 2003). The aim of this paper is to present the entire procedure (chemical purification and measurement technique) that we have adopted in our laboratory and its evaluation by measurement of the NIST SRM 951 reference material. The method is developed for boron (as Boric acid, B(OH)₃) in natural ground waters and surface waters samples. The ratio between the two stable boron isotopes, ¹¹B/¹⁰B, is usually expressed with the δ¹¹B notation.
\[
\delta^{11}B = \left[ \frac{^{11}B}{^{10}B} - 1 \right] \times 10^3
\]

NIST SRM 951 (boric acid) is the international reference material for the abundance of B isotopes with a certified isotopic ratio \( ^{11}B/^{10}B = 4.04362 \pm 0.00137 \) (2\( \sigma \)).

The mass spectrometer used in this study is Accelerator Mass Spectrometry (AMS). Note that the applicability of \( \delta^{11}B \) measurement is limited by the boron concentration in the source materials. To determine the \( \delta^{11}B \) signature of a sample, detectable boron concentrations are a pre-requisite. Preliminary tests show this mass detection limit to be 0.5 mg. The AMS ultra-sensitivity ensures that the isotopic ratio \( ^{11}B/^{10}B \) can be estimated with good precision (i.e. 0.1-0.001). The precision (\( \geq 5 \% \)) achieved would allow us to measure differences of 15 \( \% \).

2. METHODS.

2.1. Chemical extraction.

An AMS system needs a chemical pre-treatment to extract boron as boric acid (solid) from a water sample, and to eliminate other interfering compounds (organic matter), which can influence the mass spectrometric measurement. First, a column made of perfluoroalkoxy alkane PFA is filled with 0.7 mL of the boron specific ion exchanger resin (Amberlite IRA 743). The boron pre-concentration includes a resin cleaning and seasoning by pumping HCl 2 M and 3 M ammonia solution (flow rate: 2 mL/min) through it to remove chlorides. Then the pH samples is adjusted to 7-9 by adding NaOH 0.1 M, the water samples are pumped (flow rate: 0.5 mL/min) on top of the column where borate is fixed as ester chelate. The other compounds in the sample passed through the column are eliminated by eluting with water and ammonia solution 3M. Boron is collected in PFA containers by passing 14 ml of HCl 0.1 M. Mannitol is added to the eluate to avoid evaporation and isotopic fractionation when drying it at 70°C by thermo block (Xiao et al. 2003; Simonnot et al. 2000; Eisenhut et al. 1996; Barth 1998).

2.2. AMS analyses.

Samples of pure B(OH)\(_3\) have been weighed and loaded into cones (cathodes) placed into the AMS source wheel. Different masses in the range 0.05-2 mg have been tested to determine the minimum amount of B required to perform the analysis. The results (not shown) suggest that a mass around 0.5-1 mg is sufficient to get a sufficiently high signal in the Faraday cups (100 nA). The samples are ionized by sputtering with Cs\(^+\) heated up to 136°C producing B\(^-\) ions, which are accelerated at 60 keV and analyzed through an Electrostatic Analyzer and Low Energy Magnet (L.E.M.). The ionization process produces an isobaric interference of \( ^{11}B: ^{10}BH \). To remove \( ^{10}BH \), the sample beam is stripped through an Argon cell at 12\( \mu \)Torr in the accelerator tank, forming B\(^3+\) as the main charge state of B ions in the high energy sector (after the accelerator tank). Ion currents are detected on Faraday cups in offset (outside the beam line). \( ^{11}B \) and \( ^{10}B \) beams are alternatively injected by using the Magnet Bounces System (MBS), which allows to quickly changing the L.E.M. chamber voltage. The suppression of \( ^{10}BH \) is demonstrated by the higher \( (^{11}B/^{10}B) \) ratio in the low energy sector than that in the high energy sector. Two different samples have been used to test the precision of the method: pure B(OH)\(_3\) from the local pharmacy (PHARM) and pure B(OH)\(_3\) from
SIGMA-ALDRICH (SIGMA). We also tested how different masses influence the precision, and whether any isotopic fractionation is associated with the preparation method. To do this, four replicates of PHARM (0.5 mg and 1 mg), and four replicates of SIGMA (0.5 mg and 1 mg) were prepared with and without chemical treatment. Finally, different natural waters samples from the Po plain (north of Italy) have been measured in a sequence together with five NIST 951 (pre-treated) and two NIST 951 (with no treatment).

3. RESULTS.

The purpose of this study is to develop a new measurement method for the determination of $\delta^{11}\text{B}$ in water matrices, undergoing a chemical purification using a selective resin, followed by measurement of the isotopic ratio $^{11}\text{B}/^{10}\text{B}$. This method can be applied to samples with boron concentrations as low as 0.1 ppm. The precision obtained on $\delta^{11}\text{B}$ measurements so far is around 5-10‰. The average $\delta^{11}\text{B}$ of the samples is normalized with the average $\delta^{11}\text{B}$ of NIST (mass 0.5 mg). The precision can be improved by increasing the number of replicates measured during the AMS run. Between each sample, an untreated NIST SRM 951 0.5 mg was measured as the reference value for calibration. The results in Fig. 1 show that a significant offset (~5‰) was observed below 1 mg. This is especially true for the PHARM sample. The influence of the mass needs to be better explored. The treatment seems to introduce an isotopic fractionation (2.7‰, fig.2). The ground and surface natural waters samples show very similar $\delta^{11}\text{B}$ values (Fig. 3), comparable with others laboratory (Gonfiantini R. et al. 2005; Xue D. et al. 2009).

**Fig. 1. Comparison $\delta^{11}\text{B}$ between different mass.**

**Fig. 2. Isotopic fractionation.**
Future work will address the limited precision achieved so far, by better constraining the factor influencing the AMS stability (sample cleanliness, number of replicates, etc…). We will also match the information derived from measurements of δ$^{15}$N and δ$^{18}$O of nitrates with our results on water natural samples to better constrain the source of nitrates in water.

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USE OF WATER STABLE ISOTOPES AS NATURAL TRACERS OF GROUNDWATER IN THE ENGENHO NOGUEIRA WATERSHED IN MINAS GERAIS, BRAZIL

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Abstract: Isotope Ratio Mass Spectrometry is the best method to determine with high precision the ratio of stable isotopes of light elements. Accordingly, it has been used in environmental research, especially in hydrological studies as a natural tracer requiring no injection procedures. The present paper reports a method for the analysis of water isotopes ($\delta^{18}$O and $\delta^2$H), implemented at the Laboratory of Isotope Ratio Mass Spectrometry at the Center for Development of Nuclear Technology (CDTN). The method has been applied to studies of groundwater in the Engenho Nogueira watershed, located inside the Federal University of Minas Gerais (UFMG) Campus, in the northern area of Belo Horizonte city, Brazil.

In recent years this watershed has been studied from several viewpoints and for different purposes [1]. However, the method of natural water isotopes has never been used in this site. This technique can help to expand the amount and quality of information on the local aquifer, helping to fill several gaps in the understanding of its dynamics. Besides, it can be used to confirm previously obtained data and be used to improve the hydrogeological conceptual model of the aquifer the site.

The expansion of the academic and administrative units of the UFMG considers that the rational management of the local aquifer is an important requirement for its sustainability, inasmuch as the demand for water is steadily increasing. According to Ribeiro (2013) a population of 30,254 students, 2267 faculty, and 4323 staff attends the campus on a daily basis. The water supply is partly provided by a local public water supply company, except for some of the CDTN facilities, sited inside UFMG Campus, which are supplied by two pumping wells, located within its premises [2].

The steps for the implementation of the stable isotope methodology involved:

(i) Sample collection campaigns conduct during the dry and rainy periods;
(ii) Spectrometric analysis by IRMS, in which the operational procedures set by the equipment manufacturer were followed [3] and the results validated by comparison with primary and secondary reference materials [4], statistical treatment of the data;
(iii) Organization of results and evaluation of active transport processes in the sampled environmental system (aquifer), comparing the correlations between $\delta^2$H and $\delta^{18}$O in the samples.
A sample collection campaign has been performed and one further campaign is being planned to take place at the beginning of the rainy season. The instrument calibration was performed and the results were satisfactory. The analysis of samples collected during the dry period has been completed and the results are being organized and treated statistically.

REFERENCES


NOVEL TOC/TN IRMS INTERFACE FOR SIMULTANEOUS DETERMINATION OF $\delta^{13}C$ AND $\delta^{15}N$ OF DISSOLVED ORGANIC CARBON AND TOTAL DISSOLVED NITROGEN IN AQUEOUS SAMPLES

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Abstract: Investigation of transformation and transport processes of carbon and nitrogen in ecosystems plays an important role to understand and predict their dynamics and role in biogeochemistry. Consequently, suitable and accurate methods for concentration as well as stable isotopic composition analysis of carbon and nitrogen in waters and aqueous solutions play a significant role. Traditionally dissolved carbon and nitrogen stable isotope analysis (SIA) is performed using either offline sample preparation followed by elemental analysis isotope ratio mass spectrometry (EA/IRMS) or modified wet chemical oxidation based device coupled to IRMS. Recently we presented a high temperature combustion system (HTC), which significantly improves upon these methods for dissolved organic carbon (DOC) SIA. The analysis of $\delta^{15}N$ of dissolved nitrogen still has large limitations. Its low concentration makes EA/IRMS laborious, time and sample consuming. Systems based on wet chemical oxidation-IRMS bare the risk of sensitivity loss as well as of fractionation due to incomplete mineralization. In addition, the high solubility of molecular nitrogen in water remains a technical challenge, as it requires additional separation steps to distinguish between physically dissolved nitrogen and bound nitrogen.

Further development of our HTC system lead to the implementation of the $\delta^{15}N$ determination which now coupled, into a novel total organic carbon (TOC) analyzing system, especially designed for SIA of both, carbon and nitrogen. Integrated, innovative purge and trap technique (peak focusing) for nitrogen with aluminosilicate adsorber and peltier element based cooling system, in combination with high injection volume (up to 3 mL) as well as favorable carrier gas flow significantly improves sensitivity. Down to 1ppm and less total nitrogen can be measured with precision of $\leq 0.5\%$. To lower the background caused by physically dissolved nitrogen new, membrane-vacuum based, degasser was designed for online separation of physically dissolved nitrogen. This novel HTC system, “iso TOC cube”, provides an innovative tool with large potential in investigation of biogeochemical carbon and nitrogen cycles.
Abstract: The dual measurement of stable isotopes of nitrogen ($\delta^{15}$N-NO$_3^-$) and oxygen ($\delta^{18}$O-NO$_3^-$) in nitrates is currently used to identify sources of nitrates in environmental samples (e.g.: soil, fertilizers, groundwater, surface water, sewage, etc.). At CIRCE (Centre for Isotopic Research on Cultural and Environmental heritage, Caserta, Italy) lab, $\delta^{15}$N-NO$_3^-$ and $\delta^{18}$O-NO$_3^-$ measurements are performed by means of Temperature Conversion/Elemental Analyzer Isotope Ratio Mass Spectrometry (TC/EA-IRMS), quality controlled by means of Quality Assurance/Quality Control (QA/QC). This procedure involves data normalization through raw data calibration with $\delta$ values of Reference Materials (RM) and drift/QC sample analyses. Before analysis, nitrates are extracted from the bulk material and converted to AgNO$_3$. The sample preparation can affect the original isotopic ratios of nitrates. In order to i) test the accuracy and the reproducibility of nitrates extraction procedure; ii) check the quality (i.e. accuracy and precision) of measurements, we currently apply a QA/QC method based on the analysis of different Reference Materials (RM) undergoing the extraction protocol, for data normalization. The RMs must be chemically similar to the sample to simulate possible isotopic fractionations eventually occurring during preparation. International Reference Materials covering a range of $\delta$ values (USGS34: $\delta^{15}$N -1.8 ± 0.2‰ and $\delta^{18}$O -27.9 ± 0.6‰, USGS32: $\delta^{15}$N 180 ± 1‰ and $\delta^{18}$O 25.7 ± 0.4‰, USGS35: $\delta^{15}$N 2.7 ± 0.2‰ and $\delta^{18}$O 57.5 ± 0.6‰, IAEA NO$_3^-$: $\delta^{15}$N 4.7 ± 0.2‰ and $\delta^{18}$O 25.6 ± 0.4‰) were used to characterize a number of Internal Standards (SIAL KNO$_3$: $\delta^{15}$N 5.3 ± 0.4‰ and $\delta^{18}$O 23.5 ± 0.1‰, CIRCE KNO$_3$ 1: $\delta^{15}$N 5.3 ± 0.4‰ and $\delta^{18}$O 23.5 ± 0.1‰, CIRCE KNO$_3$ 3: $\delta^{15}$N 26.9 ± 0.8‰ and $\delta^{18}$O 23.8 ± 0.1‰).

In this paper, protocol and overall performances (e.g. accuracy and precision) based on experimental distributions of measured RM and QC datasets will be discussed. Preliminary results show a precision of extraction protocol, determined as the standard deviation (1σ) of measures of AgNO$_3$, equal to 0.8‰ and 0.2‰ for $\delta^{15}$N and $\delta^{18}$O, respectively. The accuracy, obtained by the comparison between the direct combustion and the extraction protocol of RMs at different $\delta^{15}$N and $\delta^{18}$O, results to be 14.3 ± 1.7% for $\delta^{15}$N and 4.9 ± 0.3% for $\delta^{18}$O.

The machine precision obtained by means of QA samples (n= 120) is 0.13‰ (mean error) for $\delta^{18}$O and of QA samples (n=103) 0.07‰ for $\delta^{15}$N.
REFERENCES


SYRINGE LIFE AND MEMORY EFFECTS IN ISOTOPIC ANALYSES PERFORMED BY LIQUID WATER ISOTOPIC ANALYSERS – A CASE STUDY FOR NATURAL WATERS IN CENTRAL EUROPE

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Abstract: Syringes are the most expensive consumables in the LWIA (Liquid Water Isotope Analyser) analyses. Result of a simple procedure improving the syringe lifetime is presented. Influence of the number of injections on the final δ¹⁸O and δ²H values is studied using isotopic ranges typical for the highest part of the Carpathians. The results indicate that syringe lifetime can be rather long, although material failures are frequent as well. The number of injections (6 or 9) significantly influenced only analyses of δ²H conducted by Picarro2120i. The differences for Picarro 2130i were not significant.

1. INTRODUCTION

Laser water isotopic analysers (LWIA) become available to many laboratories in recent years. They can run for a long time without significant issues. Syringe life is typically the weakest point during the routine operation. Syringes are expensive and sometimes have very short lifetime [1].

Multiple injections of the same sample are typically used during the analyses to cope with the between-sample memory effect. Higher number of injections allows obtaining more accurate results. On the other hand it increases the time of the analysis and consumption of syringes.

The objective of this contribution is to share the experience obtained during analyses of natural waters (precipitation, snowpack, soil water, shallow ground water and rivers) in central Europe (Western Carpathians). Over 2200 samples between May 2013 and October 2014 were analysed. We have managed to obtain high average syringe lifetime (over 3600 injections) with Picarro 2120i and 2130i analysers.

2. METHODS

The analyses were made by the Picarro 2102i analyser equipped with the G2000 autosampler and the Picarro 2130i analyser equipped with the PAL HTCx autosampler (CTC Analytics AG). Each sample was filtered before the analysis. SGA syringes with volume 5 microliter and 8 mm silicon transparent blue vial septa were used in the analyses. Vial septa were not penetrated more than 14 times. Injection port septa (Restek Blue Ice, diameter 9.5 mm) was replaced after 200-300 injections. Six or seven injections per sample were routinely used and each sample was analysed three times in three different vials on different days. LIMS for Lasers [2] with template for 20 samples was used for data evaluation. Values of the laboratory standards determined by the IAEA laboratory in Vienna are given in Table 1.

We have analysed 2214 samples. Majority of them represents natural waters in the highest part of the Carpathian Mountains (northern Slovakia), but several samples from lower latitudes were analysed as well (Georgia, Israel, Eritrea, Malawi). The ranges of δ¹⁸O and δ²H
are shown in Figure 1. The isotopic composition generally varies in a rather large interval. However, the box plots in Figure 1 show that majority the samples had the δ^{18}O between -10 and -12 ‰ and δ^{2}H values between -70 and -80‰. Electrical conductivity of the samples varied between less than 10µs.cm-1 (precipitation) and 1460 10µs.cm-1 (groundwater).

**Table 1. Isotopic composition of standards used in the analyses.**

<table>
<thead>
<tr>
<th></th>
<th>δ^{18}O [‰]</th>
<th>δ^{2}H [‰]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy standard</td>
<td>-2.45</td>
<td>-16.6</td>
</tr>
<tr>
<td>Light standard</td>
<td>-28.3</td>
<td>-215.7</td>
</tr>
<tr>
<td>Light standard 2</td>
<td>-23.65</td>
<td>-176.8</td>
</tr>
<tr>
<td>Control standard</td>
<td>-10.7</td>
<td>-76.6</td>
</tr>
</tbody>
</table>

Figure 1. Position of the analysed samples along the global meteoric water line (left) and the box plots of the δ^{18}O and δ^{2}H (right); the box plots from the top to bottom represent IQR*1.5, upper quartile, median, lower quartile, IQR*1.5; IQR stands for the interquartile range (the difference between the upper and lower quartiles).

Syringes were changed twice a day, after about 80-100 injections. The autorun was always ended after the last injection at a particular vial, the syringe was removed and washed about 20 times with the deionized water. Acetone was used only rarely. If the plunger did not move smoothly after the washing, the syringe without the plunger was placed into a basin filled with distilled water and kept there until the next syringe exchange. Another syringe was used in such a case to continue the analysis.

Number of injection per vial influences the accuracy and duration of the analysis. We analysed 20 samples with contrasting isotopic composition (δ^{18}O between -4.1 and -13.9‰) by the above setup. In both machines we used the same syringes and injection port septa. Nine injections were applied and each sample was measured three times. LIMS was used to evaluate the measurements. First 6, 7, 8 and 9 injections were considered during processing of the raw data. The results were compared for differences between the number of injections used in raw data processing and analyser model.

3. RESULTS

Maintenance of the syringe according to the simple rules mentioned above resulted in a high number of injections conducted during the lifetime of many syringes (Figure 2). If excluding the first two syringes which broke during installation or the very first injection, the average number of injections during the syringe life was 3678. However, Figure 2 reveals that there are big differences among individual syringes. Although 25% of the syringes could do more than 4000 injections, as much as 30% did less than 1000 injections. Bending of the needle at
the very first infection of a new vial septum is rather common reason of failure. Interestingly, only one syringe broke in the HTC PAL autosampler so far. Red vial septa which we originally used with standards often caused problems (either needle damage or too high concentration peaks). Their replacement by the standard blue septa significantly reduced the problems.

![Figure 2](image2.png)

**Figure 2.** Number of injections done by each of 28 syringes; letter W above the bars indicates that the syringe still works.

Although the syringe could do even 200 injections before the replacement and washing, the typical numbers during our analyses varied around 80-100 injections (Fig. 2). We generally analysed clean waters with low EC (when the EC was higher, we inserted a vial with distilled water after the sample with a highly mineralized water). However, when the syringe did too many injections (more than about 120), it often needed more washing or longer time in the distilled water before it could have been used in the next analysis. Therefore, replacement of the syringes two times per day appears to be the practice which results in least problems.

![Figure 3](image3.png)

**Figure 3.** Number of injections between syringe replacement for syringes which were used more than 10 times; the S number is identical with syringe numbers given in Fig. 1; the whiskers are IQR*1.0.
4. CONCLUSIONS

Syringe life may not be such a serious issue if the syringes are properly maintained and replaced two times per day. 28 syringes were needed to analyse 2214 samples and five of them still work. However, a good syringe should be always available to replace the one which does not work satisfactorily. Seven injections are used as a reasonable compromise between the duration and accuracy of the analysis. Further improvement consists of applying nine injections at the first vial after syringe replacement.

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A NEW TRITIUM ENRICHMENT UNIT WITH CONTINUOUS WATER FILLING AND HIGH ENRICHMENT FACTOR

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Abstract: The bomb tritium peak has almost decayed and the environmental tritium concentration has reached to its natural level of production. It has posed a problem in the correct measurement of low level tritium concentrations in natural water samples with the conventional tritium enrichment units. Wherever possible, T-He technique is being used for measuring low tritium contents at few specialized laboratories, but it is beyond the reach of most of the users. Moreover, the conventional tritium enrichment units (TEU), currently being used by most of the member states of IAEA, are capable in general to enrich 500 mL of water sample that yield enrichment factor around 30 while it is not possible to measure low tritium concentrations in groundwater with this enrichment factor. In addition, there are many disadvantages with the conventional TEU, among them four major drawbacks are: 1) the enrichment factor is limited by fixed sample amount, 2) it is not possible to determine the enrichment factor based on the actual performance of each individual electrolysis cell in a particular run, 3) the post-electrolysis processes are tedious (neutralization of enriched sample and removal of electrolytes) and time consuming, and 4) the combination of the TEU which has relatively lower enrichment factors and a counting system which has relatively lower detection limit may be very costly. This increased a pressure on IAEA to design a compact unit with considerable reduction in size and cost but should have improved efficiency of tritium enrichment for measuring low level tritium concentration in natural water samples.

The IAEA TRIC 2012 exercise concluded recently also emphasised to have higher tritium enrichment factor to improve precision in tritium measurements and to measure low concentrations of tritium. The other important recommendation was to introduce deuterium enrichment technique for determining tritium enrichment factor of each sample with individual cell, for reducing error in tritium measurements, instead of using average enrichment parameter of few cells to estimate enrichment factor of each sample.

A new compact unit for tritium enrichment in water samples has been developed and tested successfully at the IAEA Isotope Hydrology Laboratory, Vienna, Austria. The new tritium enrichment unit uses water to cool the system and it can enrich water samples up to 2000 ml in one electrolysis run through automatic filling of sample into the electrolysis cell. The electrolysis cell has been kept relatively of smaller capacity (200 ml) to reduce the overall size of TEU. The post-electrolysis process of NaOH neutralization has been simplified by using CO₂ gas instead of adding PbCl₂. Vacuum distillation of the enriched water is carried out directly from the cell to avoid loss of enriched water and deuterium fractionation. The tritium enrichment factor can be determined on the basis of actual performance of each cell using the deuterium enrichment factor of each cell. Tritium enrichment factor can be achieved >80 with samples of 2000 mL of water.
The device is comprised of a glass sample bottle (2L of volume) connected to the electrolysis cell. The sample water is transferred from the reservoir bottle into the electrolysis cell automatically when the level of water goes down in the cell below to a particular level. Automatic water filling into the cells is very reliable due to a special design of automatic filling system. Electrolytic enrichment can be done with a maximum 10 A current in such a way that even with a relatively smaller cell (200 ml), the enrichment of 500 ml sample can be completed within a week time. The new TEU requires as less as care needed in case of conventional TEU during enrichment run.

The cost of the new TEU is comparably less than the conventional TEU (500 mL capacity). With the new TEU, the total cost of tritium measurements can be further reduced because 1) it is possible to measure water samples with tritium concentrations < 0.5 TU with satisfactory accuracy (since the tritium concentration in the enriched water can be > 80 times than the original sample with 2L water sample). This avoids using more costly and time-consuming measurement techniques such as tritium-ingrowth (combined with mass spectrometry measurements); and 2) the measurement can be carried out by a less expensive counter which may have slightly higher background counts. Thus, the new TEU is particularly beneficial for laboratories in developing countries.

The design of new tritium enrichment cell and a photograph of 10 cells TEU are given in Figures 1 and 2 respectively. This paper describes the design and operational aspects of the new TEU with the high tritium enrichment factor that can be achieved along with details of deuterium enrichment technique to determine tritium enrichment factor of each sample with individual cell.

Figure 1: Electrolysis cell (mild steel cathode and stainless steel anode) along with a mechanism that controls automatic water filling into the cell. 1) Mild steel cathode; 2) Stainless steel anode; 3) A cut in the tube for water-inflow; 4) Rubber stopper with hole for escaping gasses; 5) Rubber stopper with hole for escaping water; 6) Polycarbonate tube; 7) Teflon piece for separating cathode and anode; 8) Stainless steel tube; 9) Teflon spacer with hole and grove; 10) Teflon disc (φ37mm); 11) Swagelok T-connector; 12) Stainless steel tube; 13) O-ring
Figure 2: A front side photograph of a 10 cells Tritium Enrichment Unit developed at Isotope Hydrology Laboratory, IAEA, Vienna, Austria.
CALIBRATION OF DISSOLVED NOBLE GAS MEASUREMENTS BY AIR EQUILIBRATED WATER

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Abstract: Measurements of noble gases in water samples require calibration against known concentrations. Air equilibrated water (AEW) is often used as quasi-matrix-equivalent standard for dissolved gases in groundwater, because of the well-known and constant fractions of noble gases in the atmosphere. AEW standards are only reliable if temperature and pressure of the gas-water equilibrium can be controlled precisely, and if contamination of laboratory air (or partial sample degassing) can be prevented during sampling. These requirements make it challenging to create in the laboratory what is common in nature. As a result, air pipettes are frequently used for day-to-day calibrations, making estimation of overall analytical uncertainties for unknown water measurements difficult to estimate. Details of air equilibrated water sample production at the IAEA will be presented, which consists of a 600 L tank filled with deionized water and held at a constant temperature using a heat exchanger. Temperature and total dissolved gas in the tank are constantly measured, as are atmospheric pressure and temperature in the laboratory. Reproducibility of this system for production of air saturated noble gas samples will be demonstrated.
ASSESSMENT OF AN AUTOMATIC TDCR LIQUID SCINTILLATION COUNTER FOR USE IN LOW-LEVEL TRITIUM MEASUREMENT

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Abstract: A recently developed, low-cost, triple-to-double coincidence ratio (TDCR) decay counting and analysis system (Hidex 300 SL) was directly compared with a traditional ultra-low-level decay counting system (Perkin Elmer Quantulus 1220) in order to assess the applicability of TDCR for low-level tritium (³H) analysis by electrolytic enrichment of 500 mL natural water samples. Test samples included six IAEA tritium inter-comparison (TRIC2012) samples with known low tritium contents (0.43-7.5 TU), as well as duplicate precipitation samples obtained from the IAEA Global Network of Isotopes in Precipitation (GNIP). The TRIC2012 samples were processed in triplicate using routine IAEA electrolytic tritium enrichment procedures. All test samples, blanks and standards were first measured on a Quantulus 1220 decay counting instrument; thereafter the sample vials were placed into a Hidex 300SL TDCR instrument (Hidex Oy), and counted for an identical time (500 minutes, 10 cycles of 50 minutes). Results demonstrated that the Hidex TDCR-based instrument produced tritium results that were similar to that of the traditional decay counting method when an advanced statistical spectral fitting algorithm was applied to account for the higher but exceptionally stable background count rates. Our tests revealed that the Hidex SL300 was capable of producing accurate results to at least 0.4 TU when using samples electrolytically enriched from 500 mL to ~15 mL.
KRYPTON ISOLATION AND PURIFICATION FROM GROUNDWATER FOR $^{81}\text{Kr}$ AGE DATING

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Abstract: In many parts of the world, groundwater levels are rapidly dropping commensurate with population expansion, commercial agriculture, and as a result of changes in precipitation patterns. For areas where aquifers contain water that recharged a long time ago, and/or recharge slowly, use of this non-renewable water resource can pose a significant risk of taps and irrigation systems going dry. Accordingly, it is of critical importance to identify and assess size and recharge rates associated with aquifers containing appreciable ancient water. The Isotope Hydrology Laboratory, in cooperation with Argonne National Laboratory (USA) have now established an IAEA capability to date groundwater up to one million years, using the long-lived krypton-81 isotope. The method is similar to tritium and radiocarbon dating, in which a radioactive isotope is produced naturally and becomes entrained in surface water, subsequently entering groundwater systems. At that time, these particles begin to decay away leaving an amount that depends only on the time since being removed from the atmospheric production. Whereas $^{81}\text{Kr}$ is an ideal natural tracer for very old water, Krypton is quite rare in the gas extracted from groundwater (one part in a million). This presents a technical challenge to produce enough pure Krypton for analysis, and due to the fact that there are only a few appropriate purification systems available worldwide, the IHL deemed it appropriate to develop our own system. The IHL has recently begun use of Kr extraction and purification system which was constructed in-house and completed in spring 2014. In brief, a portion of gas extracted in the field is passed through a small cryogenic trap to remove bulk gases and subsequently purified with a home-built gas chromatograph mass spectrometry system. A typical 10 L gas sample yields some 10-20 µL of pure Krypton, which is packaged and shipped to collaborators in the USA for measurement. Details of the separation apparatus from several study units will be presented.
RESULTS AND ANALYSIS FROM THE IAEA INTERNATIONAL TRITIUM INTERCOMPARISON 2012 (TRIC2012)

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Abstract: A world-wide intercomparison was undertaken to evaluate the performance of laboratories conducting low level tritium (3H) assays of surface and ground waters. Eight test samples were prepared by dilution of a high-level tritium standard with tritium-free groundwater. The test water samples were comprised of one tritium-free water and five water samples with low ratios between 0.43 - 7.51 TU. These low-level tritium test samples encompass 3H concentrations currently observed in modern precipitation, surface and ground waters, whereupon each participating laboratory employed routine pre-treatment or electrolytic enrichment procedures and 3H counting methods. Two higher-level samples were to be measured without any pre-treatment or enrichment to evaluate performance of laboratories utilizing decay counting. Fifty-eight laboratories reported test data to the IAEA for all, or a sub-set, of the eight test samples. Forty-three laboratories used liquid scintillation counting (LSC) with electrolytic enrichment, 7 laboratories utilized LSC without electrolytic enrichment, 6 laboratories utilized 3He accumulation and mass-spectrometry, and 2 laboratories used gas proportional counting. Of these laboratories, approximately half demonstrated a good ability to generate tritium results sufficiently accurate for groundwater age dating purposes, with an additional 25% reporting results that were reasonable within their reported uncertainties, but inadequate for high-precision age dating applications. Details and analysis of submitted results will be presented.
AN ONLINE TEMPERATURE CONTROLLED VACUUM-EQUILIBRATION PREPARATION SYSTEM FOR THE MEASUREMENT OF $^2$H OF NON-EXCHANGEABLE-H AND OF $^{18}$O IN ORGANIC MATERIALS BY ISOPORE-RATIO MASS-SPECTROMETRY

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Abstract: Measurement of $\delta^2$H in non-exchangeable H ($\delta^2$H$_n$) and $\delta^{18}$O in organic environmental samples are inconsistent among laboratories worldwide due to varied and lengthy approaches in controlling for H isotope exchange (for $\delta^2$H$_n$) and removal of trace moisture ($\delta^2$H$_n$ and $\delta^{18}$O), which undermines the comparability of organic $\delta^2$H and $\delta^{18}$O data produced among different laboratories.

An online preparation system was developed for measurement of $\delta^2$H$_n$ and $\delta^{18}$O values of organic samples, coupled to isotope-ratio mass spectrometers. The system features a 50 position auto-sampler and isolation valve where samples are 1) held isothermal between ambient to 40-120 ± 0.1 °C for H isotopic exchange experiments ($\delta^2$H$_n$) and drying of hygroscopic samples ($\delta^2$H$_n$ and $\delta^{18}$O), 2) evacuated to <5 mbar and flushed with helium for moisture and N$_2$ removal, and 3) allows injection of up to 500 µL of H$_2$O for controlled vapour exchangeable-H experiments.

Results showed the system provides highly reproducible and precise non-exchangeable $\delta^2$H$_n$ isotope estimates for a range of organic keratinous standard powders over a wide range of experimental temperatures. A reproducible sample processing regimen can now be applied to a wider range of organics and hygroscopic samples that are currently hampered by poorly controlled preparative methods amongst laboratories.

Rapid and reproducible online vacuum equilibration of samples and standards for the routine measurement of non-exchangeable $\delta^2$H$_n$ and $\delta^{18}$O values is now possible using the online equilibration system, with the added benefit that sample processing times for organic $\delta^2$H values are reduced from weeks to hours.
ANTIMONY ISOTOPIC FRACTIONATION DURING THE
ADSORPTION PROCESS DEMONSTRATED BY ANION-EXCHANGE
CHROMATOGRAPHY

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Abstract: Antimony isotope fractionation factor was determined by anion-exchange
chromatography for the first time. The magnitude at 25°C was 0.5 (=10^4 × ln S), indicating
that the heavier isotope ^{123}\text{Sb} was preferentially enriched into liquid phase, whereas the
lighter ^{121}\text{Sb} was in resin phase. The tendency of the isotopic enrichment was agreeable with
Sb isotope effect between seawater and sediment in literature.

1. INTRODUCTION

Antimony (Sb) has two oxidation numbers: Sb\text{III} and Sb\text{V}. The latter generally occurs more
predominately in nature than the former. It has been reported that the more reduced form is
the more toxic form. The Sb\text{III}-compounds were found to be chemically and toxicologically
similar to those of As\text{III} [1] and have been designated as acute toxic substances by many
governmental agencies [2]. In fact, high concentrations of Sb were found in soil near where
the Sb mining and smelting processes occur [3]. Stemming from these sources, the
distribution and environmental mobility of Sb has been reported [4,5], and the Sb enrichment
in soil samples has been studied with respect to adsorption to the following natural materials:
humic acid [6], hydrous Mn oxides [7], aluminium and/or iron hydroxides [8], goethite
[9,10], amorphous iron [11], and natural diatomite [12]. Because the Sb is mobile in nature,
one it has been reduced to its highly toxic state, the high toxicity Sb distributed in
environments could threaten human health. Therefore, it is important to know the behaviour
and natural fate of the Sb. For this purpose, the stable isotopes of Sb will be useful tracers of
Sb-bearing compounds in nature.

Antimony has two stable isotopes (^{121}\text{Sb} and ^{123}\text{Sb}) and their relative abundance ratio was
reported as 0.7479 (^{123}\text{Sb}/^{121}\text{Sb}) [13]. Isotopic variation of Sb is expressed as \varepsilon^{123}\text{Sb} =
\left\{\left(^{123}\text{Sb}/^{121}\text{Sb}\right)_{\text{sample}} / \left(^{123}\text{Sb}/^{121}\text{Sb}\right)_{\text{standard}} -1\right\} \times 10000 using the notation of \varepsilon-unit. Significant
variation was observed in several studies analysing naturally occurring Sb-bearing substances
[14] and Sb-bearing chemical reagents [15]. For instance, the \varepsilon^{123}\text{Sb} values of several
geological materials varied from -3 \varepsilon-unit to +15 \varepsilon-unit [14]. In this report, a difference in the
\varepsilon^{123}\text{Sb} values between sea water (ca. +3.7 \varepsilon-unit) and oceanic sediments (+1.7 \varepsilon-unit)
suggested that the magnitude of the fractionation factor between them would be estimated as
2 \varepsilon-unit. This difference would not be negligible if the homogeneity of the \varepsilon^{123}\text{Sb} values of
the crustal rocks and the consistency of the value of the seawater were verified. It was
verified that the \varepsilon^{123}\text{Sb} values of silicate rocks and basalts were similar to those of the oceanic
sediments, and the $^{123}\text{Sb}$ value of seawater against varying depth was constant at 3.7±0.4 ε-unit [14]. Furthermore, soil samples had a wide range of $^{123}\text{Sb}$ values: from 0 ε-unit to +5 ε-unit. The remarkably high value was found in Sb-sulphide minerals that occurred in deep ocean hot springs. To understand this phenomena, Rouxel et al. [14] conducted a redox reaction experiment, $\text{Sb}^{\text{V}} + 2e^- \rightarrow \text{Sb}^{\text{III}}$, and obtained a large depletion of up to 5.5 ε-unit. This fact implied that the Sb isotopic fractionation associated with the redox reaction was an important path to changing the Sb isotopic composition in nature; nonetheless, data of the Sb isotopic effect under basic conditions has not been reported except for in one article [14]. In this study, to facilitate Sb isotopic geochemistry, we first determined the Sb isotopic fractionation factor by performing anion-exchange chromatography.

2. METHODS

To precisely determine an Sb isotopic separation factor by anion exchange chromatography, we employed a chromatographic column (50 cm long with a 0.50-cm inner diameter) made of Pyrex glass with a water jacket, temperature of which was kept constant at 25.0 ± 0.2 °C. The column was packed with a strongly basic anion-exchange resin, Muromac 1x8 Analytical grade (mesh size, 200-400 mesh; ionic form, Cl⁻; total exchange capacity, 1.2 eq L⁻¹; cross linkage, 8% DVB; and moisture, 45-55%). The resin was at first conditioned into the hydroxide form by feeding 2 M NaOH into the column using a high pressure pump (Nihon Seimitsu). Secondly, the resin was rinsed with distilled water to flush sodium ions out of the column. The resin bed height in the column was 20 cm and its volume was 39 mL.

We employed 8.0 mmol L⁻¹ K$\text{Sb}^{\text{V}}$$(\text{OH})_6$ as a feed solution to form a $\text{Sb(OH)}_6$⁻ adsorption band in the column. The feed solution was fed from the top of the column with a constant flow rate of 1.5 mL min⁻¹ using a pressure pump. The effluent from the bottom of the column was automatically fractionally collected in polypropylene tubes. The volumes in the tubes of each recovered fraction were 9.9 mL, and the total volume of the effluent was 1188.0 mL. For the elemental Sb content analysis, an aliquot of the each fraction was used. For the isotopic Sb analysis, portions of each fraction that had been diluted by distilled water to have concentrations of 0.19 µmol L⁻¹ of the solution were employed.

The Sb concentration in each fraction was measured by the inductively coupled plasma atomic emission spectrometer (ICP-AES, Seiko-700) with analytical errors of 0.1%. The standard solution for the ICP-AES analysis was the feed solution diluted from 8.0 mmol L⁻¹ to 7.6 µmol L⁻¹. The Sb isotopic ratio was measured using the quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS, HP-4500). As a lab standard solution for the analysis, we employed 0.19 µmol L⁻¹ of K$\text{Sb(OH)}_6$ diluted from the feed solution. This lab standard solution was analysed multiple times to evaluate the reproducibility of the isotopic analysis.

3. RESULTS

Analytical results of the $^{123}\text{Sb}^{121}$Sb ratio of the Sb standard solutions by Q-ICP-MS show a population standard deviation of 5 ε-unit (1σ) and a reproducibility of ±0.05% (1σ). The reproducibility would be acceptable for Sb samples that were isotopically enriched. The accuracy was not calculated because no certified standards existed.

The experimental results on chromatography are shown in Figure 1. The first 287.1 mL of the effluent was Sb free. The Sb concentration then quickly increased up to 7.89 mmol L⁻¹ and
was nearly constant approximately 8.0 mmol L\(^{-1}\). After 297.0 mL of the effluent had passed through the experimental column, the Sb concentration was less than 0.09 mmol L\(^{-1}\). This rectangle shape of chromatogram implies that the breakthrough chromatography was carried out ideally. The ε\(^{123}\)Sb values of this experiment are plotted in Figure 1. From left to right in the figure, the ε\(^{123}\)Sb values quickly decreased from the highest value of 23 ε-unit near the beginning of the Sb chromatogram to the original value of 0.0 ε-unit. The ε\(^{123}\)Sb value of the effluent fraction collected between 287.0 mL and 297.0 mL containing 0.09 mmol L\(^{-1}\) of Sb could not be obtained. A profile of the ε\(^{123}\)Sb values showed that the lighter isotope was depleted in the front part of the chromatogram, which means that the \(^{121}\)Sb was preferentially fractionated into the ion-exchange phase and that the \(^{123}\)Sb was preferentially fractionated into the solution phase. To evaluate the magnitude of the Sb isotopic effect observed in the present experiment, the single-stage separation factor expressed as \(S\) for the \(^{123}\)Sb/\(^{121}\)Sb isotopic pair (Eq 1) was calculated. The \((10^4 \times \ln S)\) value was calculated as at least 0.5 for the initial part of the experiment, which gave an Sb isotopic fractionation factor of 1.00005 at 25.0 °C. This experiment demonstrated that Sb isotopic fractionation by anion-exchange chromatography could at least achieve a 0.3% enrichment of \(^{123}\)Sb in the solution at 25 °C. The \(^{123}\)Sb molar fraction of the standard solution was \(R_0 = 0.4279\), and the \(S\) value was \((10^4 \times \ln S) = 0.49\). It is smaller than the Sb isotopic fractionation during the Sb adsorption onto oceanic sediment reported where \((10^5 \times \ln S) = 2.0\) [14].

Figure 1. The ε\(^{123}\)Sb values and Sb concentration profiles of the experiment. The solid lines show the Sb concentration profiles (the scale is on the left vertical axis). The closed circles represent the ε\(^{123}\)Sb values (the scale is on the right vertical axis). The fitting regression curve is shown as an isotopic enrichment curve. The ε\(^{123}\)Sb value of the feed solution, shown as the broken line, is defined as 0.0 ε-unit in this study.

4. CONCLUSIONS

The major findings of this experimental study are: (1) the Sb isotopic separation was achieved by strongly basic anion-exchange chromatography with 8.0 mmol L\(^{-1}\) K\(\text{Sb}^\text{V}(\text{OH})_6\) operated in the band displacement manner, (2) the Sb isotopic fractionation factor for a single-stage separation was \((10^4 \times \ln S) = 0.5\) at 25.0 °C with a reproducibility of 0.05% (1σ), (3) the heavier isotope, \(^{123}\)Sb, was preferentially fractionated into the aqueous phase, and the lighter isotope, \(^{121}\)Sb, was enriched in the resin phase.
REFERENCES


DETERMINING $\delta^2$H IN FOOD USING CH$_3$I AND THERMOCHEMICAL ELEMENTAL ANALYSIS

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Abstract: Measurements of the hydrogen isotope ratio in foodstuffs provide an important tool for verifying the origin of that food. Hydrogen isotope ratios in food show large variations that are regionally consistent and predictable due to the close relationship with well-characterised environmental variables (precipitation and temperature). Thus isoscapes of food $\delta^2$H are a key component of an origin verification system. However, the measurement of hydrogen isotopes in food is difficult due to a number of factors:

- A portion of the hydrogen in the food is weakly bound (acidic) and therefore exchangeable with ambient water.
- Analysis of hydrogen in solid materials requires special equipment including a high temperature furnace (1400 °C) and a zero-bank autosampler.
- The lack of suitable solid reference materials available for two-point calibration of hydrogen isotopes.

Here we present an analytical system whereby non-exchangeable H is extracted from methoxy groups in the food as CH$_3$I. The $\delta^2$H of the CH$_3$I is measured using a TC/EA adapted to allow injection of water for calibration with a separate injector for the large volumes (>2 mL) of samples gas required. The setup can be used with a TC/EA (glassy carbon, 1400 °C) or a conventional EA (chromium, 900 °C). It does not require a zero-blank autosampler and calibration is achieved using water standards.
Abstract: The importance of surface soil water (rooting zone) has become evident with climate change affecting rainfall patterns and crop production. The use of Cosmic Ray Neutron Probe (CRNP) for measuring surface soil water has become increasingly popular. The advantage of CRNP is that it is a non-invasive technique for measuring soil water content at an area-wide scale, in contrast to more conventional techniques which measure mainly at field scale (point level). This paper describes the calibration and validation of the CRNP.

1. INTRODUCTION

The cosmic-ray method is a passive and non-invasive way to monitor water content integrated over the top several centimetres (20-40 cm) of soil or the water-equivalent depth of snow up to 20 cm. With the cosmic-ray method, one obtains a spatial average over a large lateral radius, approximately 300 m at sea level, providing an unprecedented scale of observation [1]. It appears to be a promising near field method to measure large scale soil moisture contents for remotely observing soil moisture over a circular area of about 600 meters in diameter. In autumn 2013 a Cosmic Ray Neutron Probe was installed within the
Hydrological Open Air Laboratory (HOAL) in Petzenkirchen, Austria. This study will give an overview of the installation, calibration and validation of the CRNP.

2. MEASUREMENT PRINCIPLES

2.1 THEORY

Cosmic-ray neutrons are an ever-present part of the land-surface radiation environment. They are a by-product of chain reactions initiated at the top of the atmosphere by primary cosmic rays. The primary radiation is composed of highly energetic particles, mainly protons and helium nuclei, which are believed to have been accelerated in shock waves associated with supernovas occurring throughout the Milky Way. These particles collide with atmospheric gas molecules, unleashing cascades of secondary protons, neutrons and other subatomic particles, some of which penetrate down to sea level. Fast neutrons are generated by cascading particles (primarily cascade neutrons) throughout the atmosphere and in the upper few meters of Earth’s crust [2].

2.2 RADIUS OF INFLUENCE

A unique characteristic of the cosmic-ray technique is the spatial scale over which it averages. This spatial scale is determined by the average distance a neutron travels from where it is emitted from a nucleus to where it is detected in the sensor.

3. FIELD CALIBRATION

For a wide range of soil characteristics, a “universal” shape-defining function can be used to convert neutron counting rates to soil water content for typical silica-dominated soils. This function is valid for neutrons in the epithermal to the faster flux of the spectrum (10^5-10^6 eV), where neutron absorption is minor. The N_0-method is a site-specific calibration parameter that depends mainly on the characteristics of the surroundings. The N_0 method is described as:

\[
\theta_p = \frac{0.0808}{N_0} + 0.372 - 0.115 + \theta_{LW} + \theta_{SOC_{eq}}
\]

where the values 0.0808, 0.372 and 0.115 are constant in time and independent of soil characteristics from a semi-analytical solution of a neutron diffusion equation [3], θ_p is pore (or gravimetric) water content (g/g), θ_{LW} is lattice water content (g/g), θ_{SOC_{eq}} is soil organic carbon water content equivalent (g/g), ρ_{bd} is dry soil bulk density (g/cm^3), N is the corrected neutron counts per hour (cph), and N_0 is an instrument specific calibrated parameter that represents the count rate over dry silica soils (cph). θ_{LW} and θ_{SOC_{eq}} can be determined in the laboratory (e.g. Actlabs Inc. of Ontario Canada or in muffle type furnace where oven-dry soil is heated up to 800 °C, so, that only the mineral components remain). On average sandy soils have lower θ_{LW} values (~0 to 0.03 g/g) than clays or volcanic soils (~0.03 to 0.1 g/g). Samples should be taken around the footprint area to determine a reasonable average (e.g. 108 samples from 18 locations, sampling every 60° and radii of 25, 75, and 200 m, and 6 depths every 5 cm down to 30 cm)[4]. The pattern of sampling described above was chosen such that each sample location (and representative area) is given equal weight in the cosmic-ray neutron probe sensitivity. Note that the sample locations should not be biased by human judgment. The standard gravimetric method is used to obtain the wet soil weight and dry soil...
weight following oven drying at 105°C for 24 to 48 hours until constant soil weight is reached. At the time of soil sampling, N will be measured and then \( N_0 \) can be estimated from the above equation, to be used thereafter for the calculation of the \( \theta_p \), or volumetric water content after multiplying by the soil bulk density. However, the \( N_0 \) values have to be tested from time to time to assure their stability at different soil wetness conditions and avoid too high uncertainty.

4. VALIDATION

Because no other instrument operates at a comparable scale, field validation is inherently difficult due to different crop establishment and agricultural practices. It is therefore probably best accomplished by comparing the CRNP readings to an aggregate of point samples. The preferred method is to compare the probe against the most reliable direct measurements of water content determined from oven-dried soil cores. This should be done at different times, with each point in time representing different average water contents. While this procedure is accurate, it has the drawbacks of being labour intensive and only capable of providing intermittent data. Some investigators [4, 5, 6] have therefore used dense networks of buried electromagnetic probes (Time Domain Reflectometry; TDR or Time Domain Transmission; TDT) for an indirect comparison of soil moisture, which has the advantage of providing continuous data for analysing soil moisture dynamics. The drawback is that the independent measurements are then indirect, and their accuracy and bias have to be measured also.

Being the first in Austria, a CRNP (CRS 1000/B model) consisting of two neutron counters (one tuned for slow, the other one for fast neutrons), a data logger and an Iridium modem, has been installed at Petzenkirchen research station of the Doctoral Programme for Water Resource Systems (TU Vienna) at 48.14 latitude and 15.17 longitude, 100 km west of Vienna, in late autumn 2013. The research station is located in an undulating agricultural landscape, characterized by heavy Cambisols and Planosols, and winter wheat and barley as main crops in winter, and maize and sunflower in summer [7]. In addition, an in-situ soil moisture network has been established, consisting of 32 stations of TDT sensors measuring soil water at 4 depths (0.05, 0.10, 0.20 and 0.50 m) over an area of 66 ha [8]. This TDT network is used to validate the use of the CRNP technique. In addition, TDR probes were used in the upper 15 cm of the soil during two field campaigns in April 2014 to further validate the CRNP (Figure 1). The results showed that CRNP reflects rainfall patterns and snow incidents (Figure 1). The TDT also showed agreements with CRNP readings especially when no crop was present.

5. CONCLUSIONS:

The CRNP is a unique tool for measuring soil moisture at intermediate scales. However, just like other soil moisture sensors, it requires proper calibration. The preliminary study carried out here showed that similar results with TDT or TDR were only achieved if crop cover was not dominance in the field.
Figure 1 Calibration and validation of Cosmic Ray Neutron Probe at Petzenkirchen station (2013-14 seasons).

REFERENCES

THE INTERNAL DOSE CALCULATION BY USING HYDROLOGICAL BASED LUMPING METHOD

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Abstract: In the present work, we aim to provide readily-understandable internal dose calculation which corresponds to hydrological lumped model. We place the internal exposure and rainfall-runoff in the same problem. We treat the human body as a single vessel. We demonstrate our method reproduces the previous standard internal dose calculation method in radiology.

1. INTRODUCTION

Fukushima Daiichi Nuclear Power Plant accident on March 2011 caused diffusion of several radioisotopes. Those leaked from the reactor containment vessels have been observed in the east Japan after the accident. The leakage amount of radioesium is largest among the leaked radioisotopes, it has been particular attention. On April 2012, Japanese government revised the regulatory value of radioesium on general food from 500 Bq/kg to 100 Bq/kg [1]. Thus, health effects of radioactivity on food supply have become an issue great interest.

Computational human phantom is accepted as a standard method for internal dose calculation [2-3]. There is no doubt that it is exact method to calculate the accurate internal dose. However, it is challenging not only for the public but also general technologists for its complexity due to the reproduction of accurate imaging of the human body. Here, we propose a readily-understandable method to calculate the internal dose. Our method corresponds to hydrological lumped model. The existing method might correspond to distributed model. The simplification by lumping has been made a great deal of effort in hydrology [4-5]. That is, the aim of the present work is to expand the simplification by lumping from hydrology to radiology. It should be noted that our method do not replace the existing method. We emphasize that our method of internal dose calculation is a methodology for readily understanding. The present work partially overlaps with our previous researches [6-7].

2. METHODS

In the present work, we treat the human body as a single vessel as shown in Figure 1. The conservation relationship between the number of radioactive atoms in the human body $N(t)$ with the effective runoff of radioactive atoms from the human body $q_{ea}(t)$ and ingestion amount per unit time of a number of radioactive atoms $r_a(t)$ is described for a single vessel in Figure 1 (b). They are treated as a function of time $t$. Effective outflow of radioactive atoms $q_{ea}(t)$ is the sum of $q_{pa}(t)$ and $q_{ba}(t)$ as:

$$q_{ea}(t) = q_{pa}(t) + q_{ba}(t) = (\alpha_p + \alpha_b)N(t) = \alpha_eN(t),$$  

where the attenuation constants $\alpha_p=\ln T_p$, $\alpha_b=\ln T_b$ and $\alpha_e=\ln T_e$. Then, $T_p$ is physical half-life
The ingestion number flux of radioactive atoms $r_a(t)$

Outflow of radioactive atoms by excretion $q_{ba}(t) = \alpha_b N(t)$

Outflow by radioactive decay of radioactive atoms $q_{pa}(t) = \alpha_p N(t)$

Storage of the number of radioactive atoms in the human body $N(t)$

Effective outflow of radioactive atoms: $q_{ea}(t) = q_{pa}(t) + q_{ba}(t) = (\alpha_p + \alpha_b) N(t) = \alpha_e N(t)$

Figure 1. The conservation relationship between the storage of the number of radioactive atoms in the human body $N(t)$ with ingestion amount per unit time of radioactive atoms $r_a(t)$, physical outflow of radioactive atoms $q_{pa}(t)$ emerges from radioactive decay, biological outflow of radioactive atoms $q_{ba}(t)$ emerges from excretion, the effective outflow $q_{ea}(t)$, and, which in (a) is described schematically, and in (b) is described as a single vessel.

emerges from radioactive decay, $T_b$ is biological half-life emerges from excretion. That is, $N(t_0 + T_p) = N(t_0)/2$ and $N(t_0 + T_b) = N(t_0)/2$ are satisfied independently. Effective half life $T_e$ is described as:

$$\frac{1}{T_e} = \frac{1}{T_p} + \frac{1}{T_b}$$

(2)

from Eq. (1) and relational expressions attenuation constants with half-life. The conservation relationship between $N(t)$ and ingestion flux of the number of radioactive atoms $r_a(t)$ is described by the continuity equation:

$$\frac{dN(t)}{dt} = r_a(t) - \alpha_e N(t)$$

(3)

The intensity of radioactivity is $\alpha_p$ times the number of radioactive atoms. Eq. (3) is rewritten as the conservation of the intensity of radioactivity in the human body $h(t)$:

$$\frac{dh(t)}{dt} = r_a(t) - \alpha_e h(t)$$

(4)

where $h(t) = \alpha_p N(t)$, $r_a(t) = \alpha_p r_a(t)$. Solving Eq.(4), we can get

$$h(t) = \int_0^t e^{-\alpha_e(t-\tau)} r_a(\tau) d\tau$$

(Bq).

(5)

Internal total exposure dose $I(t)$ is obtained from time integration of $h(t)$ as:

$$I(t) = \int_0^t h(\tau) d\tau$$

(6)

Eq. (6) gives the effective dose $H_{eff}(t)$ as:

$$H_{eff}(t) = \frac{I(t) \times \langle E \rangle \text{(MeV)} \times 1.6 \times 10^{-13} \text{(J/MeV)}}{\text{body weight (kg)}}$$

(Sv),

(7)
where \( \langle E \rangle \) is the energy absorbed into the human body per radioactive decay. We calculate \( \langle E \rangle \) by applying the mean kinetic energy of \( \beta \) ray [8] and the absorptivity of a \( \gamma \) ray in the human body [9].

3. RESULTS

We demonstrate the accuracy of the present method to calculate the intensity of radioactivity in the human body, Eq. (5). Figure 2 compares the intensity of \(^{137}\text{Cs}\) radioactivity of the measurements by using a whole-body counter given by Rühm et al. [10] after the Chernobyl accident with analytic solution obtained by our method. Both are comparable. We can say that the present method to calculate the intensity of radioactivity in the human body shows sufficient accuracy.

![Figure 2. Typical \(^{137}\text{Cs}\) body burden of a male. Plots are measurement values using a whole-body counter according to Rühm et al. (1999). The solid line is the analytic solution provided by the present method.](image)

![Figure 3. Comparison of the committed effective dose coefficient from previous research (ICRP Publ. 72) with the present method.](image)

Next, we demonstrate the accuracy of the present method to calculate the effective dose, Eq. (7). Figure 3 compares the committed effective dose determined by previous research of International Commission of Radiological Protection (ICRP) [11] with the present method. Iron and zinc are modified by considering absorptivity from digestive organs [12]. Strontium is modified by considering the bone-seeking [13]. Iodine is modified by considering the tissue weighting factor [9]. Thus, we can get comparable result with previous research of ICRP as shown in Figure 3. The accuracy of the present method to calculate the effective dose is demonstrated.

4. CONCLUSIONS

In the present work, we propose the internal dose calculation by using hydrological based lumping method. It is demonstrated that our method is comparable with previous researches in radiology. The merit of our method is readily-understandable calculation. It is noteworthy
in hydrology that correct lumping enables the description of complex natural phenomena with no reduction in accuracy. It may provide a better understanding of the influences on internal exposure not only radiologists but also general technologists.

REFERENCES


HOW MUCH DO HUMAN ACTIVITIES INFLUENCE SHALLOW GROUNDWATER RECHARGE? AN EXAMPLE OF USING ISOTOPE LUMPED PARAMETERS MODELS TO INVESTIGATE THE IMPACT OF IRRIGATION PRACTICES IN TWO MEDITERRANEAN ALLUVIAL AQUIFERS

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Abstract: Many shallow aquifers in the Mediterranean irrigation area are today threatened by global changes. An isotope ($^{18}$O) lumped parameters model was used to improve our understanding of the behavior of two French Mediterranean alluvial aquifers. A monthly $^{18}$O monitoring highlighted predominant contribution of irrigation water to the recharge and showed changes of this contribution in space and time. The correct agreement between the modeled $\delta^{18}$O of groundwater and the observations enabled us to (1) validate the assumptions concerning input data i.e. amount and proportion of irrigation water and rainfall to recharge aquifer and (2) estimate the mean residence time of groundwater. These first results open up new perspectives in the use of environmental tracers in highly transient hydrosystems.

1. INTRODUCTION

Many shallow aquifers in the Mediterranean area are mainly recharged by gravity irrigation. These aquifers are often used as a major resource for drinkable water supply. However, these resources are today threatened by the reduction of available irrigation water, the reduction of irrigation surface, the urban expansion, the increasing groundwater demand, and the climate changes [1][2]. In order to evaluate the real impact of global changes on these resources, the groundwater behavior must be well defined and the respective influence of the different input variables must be identified. We propose here to use an isotopic approach ($^{18}$O/$^{2}$H) to improve our understanding of the recharge processes in two French Mediterranean alluvial aquifers: plain of Crau and plain of Avignon [3][4][5]. The recharge of these aquifers occurs by irrigation (main source of water) and rainfall. The comparison between isotopic recharge signal (irrigation and rainfall) and isotopic groundwater signal makes it possible to quantify the distribution of residence times of water in these aquifers and to propose a conceptual model of recharge.

2. METHODS

Groundwater has been monthly sampled during two years for the Crau aquifer, and one year for the Avignon aquifer. The input variables (irrigation water and rainwater) have been collected over the same 2 years period at the Crau plain while time series of 8 years are available at the Avignon plain. At the beginning of irrigation period and when large rainfall events occurred, the sampling was carried out on shorter period for Crau aquifer.
In the traditional lumped parameter approach [6], output concentrations are calculated from input concentrations by using the well known convolution integral whose core is a transfer function. Usually, the flow pattern is supposed to be constant, so that only the tracer concentrations are convoluted. In the case of transient systems, this is the flux of tracers that should be convoluted instead. In this study, isotope transfer modeling was carried out using both variable rainfall and irrigation rates and respective tracer concentrations as input functions. The model was made of 2 in-series boxes, the first one simulating an exponential drainage ("good mixing" model) and the second one a piston flow. As a first attempt, the model has been applied on the Avignon groundwater system only. In the Crau area, irrigation rates need to be better quantified before applying the model.

In theory, the exponential model can be used in shallow, unconfined groundwater systems where transit time through the unsaturated zone is negligible in comparison with the total transit time. The shape of the transfer function assumes that very short transit times can be observed which is in agreement with our hydrogeological situations. Combining exponential and piston flow models result in a new transfer function which is usually called EPM (Exponential-Piston Flow model). A typical situation where EPM model is applicable is the case where the upper unconfined part of the aquifer is becoming confined downwards. In the confined part of the system, it is assumed no dispersion and all the flow lines have the same transit time. In the Avignon alluvial aquifer, the use of the EPM model in a partly confined aquifer is in keeping with the downwards increasing thickness of a low permeable loamy cover.

Before the exponential and piston flow in-series reservoirs, a traditional water balance approach was used to estimate the effective input rate. As long as the amount of water stored in the soil is not enough to satisfy the evapotranspiration, infiltration is zero. Once the readily available supply in the soil (RAS) is overtaken, infiltration is estimated from the difference between gross water input (rainfall + irrigation) and actual evapotranspiration. The model was developed with the system dynamic modeling platform Vensim (version 6.1) [7] at a monthly time step. The number of parameters is 3 which are RAS, the mean residence time in the exponential reservoir and the mean residence time in the piston flow reservoir. RAS was estimated from in situ soil investigations. The initial isotope content in the "soil reservoir" where water mass balance is applied was assumed to be the weighted mean $\delta^{18}O$ value over the observation period (rainwater + irrigation). The initial water levels in the exponential and piston flow reservoirs were supposed equal to the weighted mean value of the effective input (rainwater + irrigation) over the observation period whereas the initial isotope content was the $\delta^{18}O$ mean value weighted by the effective inputs.

3. RESULTS

For both groundwater systems, the $\delta^{18}O$ in rainwater and irrigation water ranged between -9‰ and -2‰ and between -12‰ and -8‰, respectively (Figure 1). Irrigation water is more depleted in $^{18}O$ compared to rainwater due to the origin of the water irrigation. Irrigation channels are fed by the Durance River which is native from high elevation recharge areas in the south Alps. The groundwater $\delta^{18}O$ range between $\delta^{18}O$ of irrigation water and $\delta^{18}O$ of rainwater (-11‰ to -9‰), highlighting the respective role of the two water sources of recharge but with a greater influence of irrigation water. In the Crau aquifer, a seasonal signal was observed: the $^{18}O$ depletion of groundwater occurred with a delay of 1 to 2 months compared to the beginning of $\delta^{18}O$ decreasing in the irrigation water whereas the signal was enriched during the non irrigation period. A similar behavior was observed in the Avignon area but the seasonality was much smaller than in the Crau aquifer. This difference is
probably the result of a larger mean residence time of water in the Avignon aquifer than in the Crau aquifer.

Figure 1. Temporal evolution of $\delta^{18}O$ of rainwater, irrigation water and groundwater in the two alluvial aquifers (example for three boreholes).

The figure 2 shows the modeling results in the Avignon aquifer for 2 observation points located in the irrigated area (point 30) and in the urban area (point 19).

Figure 2. Observations vs simulated $\delta^{18}O$ values in the Avignon aquifer (shaded areas are for model initialization periods)

In the irrigated area, the aquifer is unconfined, so that the simulation was performed using the exponential transfer only. The mean residence time was 6 months which gives a mean actual velocity of water of 8 m/d by taking a 1.4 km as the mean distance from the recharge area to the sample point. This value is in keeping with velocity calculated from the Darcy law [5]. In the case of the point 19 in the urban area, a full EPM model was needed to account for the progressive confinement of the groundwater under the increasing loam thickness. The isotope signal variation was smoother than in the irrigated area and highly time shifted. The simulation of the observed values required a mean residence time of 10 months for the exponential reservoir and 7 months for the piston flow part.

Overall, observations were correctly reproduced in both cases. In the case of the poorly simulated monthly values, at least 2 reasons can be given:
the monthly time step might not be convenient according to the groundwater dynamics (preferential flow are not considered). This means that an instantaneous water sample may not be representative of the monthly average.
- the actual input rates are still poorly known, especially regarding the irrigation part.

4. CONCLUSIONS

Stable isotopes of water ($^{18}$O/$^2$H) were used to investigate water transfer to groundwater in two Mediterranean shallow aquifers. A transient modeling approach was carried out using in-series reservoirs to account for the monthly variable input rates from irrigation and rainfall. The correct agreement between the modeled $\delta^{18}$O of groundwater and the observations enabled us to (1) validate the assumptions concerning input data i.e. amount and proportion of irrigation water (anthropogenic recharge input) and rainfall (natural recharge input) to recharge aquifer and (2) estimate the mean residence time of groundwater.

In a context of high time variability of fluxes and isotope, the lumped parameter approach carried out in the Avignon aquifer made it possible to simulate the amount of infiltrated water as well as the change in isotope content of waters involved in the recharge processes. In the Crau aquifer, a hydrogeological model is already available [1]. A similar lumped parameter method applied on the Crau data will allow validation of recharge data implemented in the hydrogeological model.

These first results open up new perspectives in the use of environmental tracers in highly transient hydrosystems. More flexible modeling approaches will be required in the future if we intend to implement in the mixing models high frequency data from new spectroscopy laser technology.

REFERENCES

HYDROCALCULATOR - A NEW TOOL FOR ESTIMATION OF EVAPORATIVE LOSSES USING STABLE ISOTOPE COMPOSITION OF WATER

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Abstract: Evaporative losses from water bodies are important elements of the terrestrial hydrological cycle, particularly in arid and semi-arid regions. However, accurate determination of evaporation losses can be challenging, especially in minimally gauged catchments. Stable isotope methods offer an alternative approach to often labour intensive and time consuming hydrological monitoring. Isotope methods are also relatively inexpensive as estimation of evaporative volume loss from a water body requires the stable isotope analysis of just two water samples, basic weather data and estimation of the stable isotope composition of ambient air moisture. The water stable isotope composition needs to be analysed only at the beginning and at the end of the observation period (non-steady state model), or in inflowing and outflowing water from a water body (steady state model) [1-3]. However, the complexity of calculations can be challenging and time-consuming for users unfamiliar with stable isotope methodologies.

We have designed the "Hydrocalculator", which is user-friendly software, based on the revised Craig-Gordon model (C-G) [2, 3]. Hydrocalculator allows quick and robust estimation of evaporative losses based on water isotope composition [3]. We also assessed the accuracy of the C-G model and tested the software against results from field pan evaporation experiments as well as published data from other regions. For the pan evaporation experiments we used a normalized evaporation pan of 1.2 m diameter and surface 1.13 m\(^2\) (following the Australian Bureau of Meteorology standard) located at an automatic weather station that recorded air temperature, relative humidity and solar radiation. The pans were filled with groundwater (TDS = 350 mg/L, 225L). Pan water level was measured (±0.5 mm) and water samples for analyses of the stable isotope composition (2 mL
each) were collected every morning over eleven days (Fig. 1A). The mean evaporative losses calculated based on changes in the water stable isotope composition (mean calculated from $\delta^2$H and $\delta^{18}$O) were in good agreement with calculations based on water level observations ($R^2 = 0.998$, $p<0.001$, Fig. 1B). Differences between measured and calculated evaporative losses were on average 0.2% and always <2.2% (Fig. 1B). The main constraint and source of uncertainty in these types of calculations lays in the estimation of ambient moisture isotope composition.

The Hydrocalculator is available free of charge from the publisher’s web site [3] and the authors’ web site [4].

Figure 1. The pan evaporation experiment conducted in the Hamersley Ranges, Western Australia (23.0°S 119°E, altitude 700 m a.s.l.), air temperature 28-30°C, RH 19-26%. A – comparison between $\delta^{18}$O and the evaporative volume losses from two pans as observed in the field; B – comparison between the measured and the calculated, using Hydrocalculator, evaporative volume losses; the difference given between observed and calculated values.

REFERENCES

VERIFICATION AND CALIBRATION OF GROUNDWATER FLOW MODEL OF Szigetköz AREA (NW HUNGARY) USING ISOTOPE TOOLS

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Abstract: MODFLOW model was developed and calibrated by isotope data to detect the effects of human impact on the groundwater flow regime in Szigetköz and surrounding area. Some seepage parameters and boundary conditions of MODFLOW model should have been changed for the sake of best fitting of the position of modeled and measured tritium peaks of 1963. Transit time and ratio of older (tritium free) water are increasing with distance from Danube up to 75 years and 50% respectively by lumped parameter Dispersion Model (DM) [3 and 4]. These data were validated by $^3$He/$^3$H dating. Verification of a one-dimensional model and calculation of flow velocity as 425 m/a and longitudinal dispersivity as 250 m was performed by $^{36}$Cl data [6] in good agreement with results of tritium evaluations. $^3$H, $^3$He, $^{36}$Cl, $\delta^{18}$O and $\delta^2$H isotope data are excellent tools for validation and calibration of conceptual and mathematic models of young groundwater bodies as Szigetköz and surrounding area including lumped parameter DM and one dimensional flow models.

1. INTRODUCTION

Drastic human interventions in 1992, as diversion of Danube, operation of a huge reservoir (in Slovakia) and lowering the Danube level with 3 to 4 meters changed the natural conditions of the regional groundwater flow regime in the thick gravel aquifer at Szigetköz and surrounding area. MODFLOW model was developed and calibrated by isotope data to detect the effects of these interventions to the groundwater flow regime. Isotope data of two great campaigns first in 1991-93 (related to the natural conditions) and second in 2011-12 (related to the present status, measured in the framework of IAEA RER8016 TC project) complemented with periodical data of 1997 to 2012 are used for verification and calibration of the MODFLOW model.
2. METHODS

$\delta^{18}$O and $\delta^2$H data were used to prove the origin of groundwater (Danube water, local infiltration from precipitation, upward migration of deep groundwater, transboundary recharge from Austria and Slovakia). Former and present position of tritium bomb-peak served an excellent tool for MODFLOW model calibration. Groundwater transit time, flow velocity and dispersion coefficient of aquifer were calculated by dispersion lumped parameter model [4, 5] using tritium records compiled from previous and new data. Results of lumped parameter model were validated by $^3$He/$^3$H dating and $^{36}$Cl [6] data.

3. RESULTS

Previous environmental isotope studies proved that Danube River is the main source of this flow regime; local infiltration and upward migration of deep (Ice-age) groundwater are negligible ([1], [2], [3]). Complementary isotope data confirmed this finding but revealed the importance of transboundary recharge from Austria (Parndorfer Platte) and Slovakia (Danube) at the external areas of Szigetköz. Previous evaluations [1, 2, 3] have considered these groundwater resources as mixture of Danube water and locally infiltrated precipitation.

Position of groundwater tritium peaks in natural conditions was found 3 to 15 km along pathlines from Danube (red crosses on Fig 1.) designating the 28 to 30 years isochrones (i.e. the temporal difference between exploration and 1963). These points did not fit well to the position of the 29 years transit times calculated by the MODFLOW model (red lines on Fig 1/a) so we had to change some seepage parameters and boundary conditions. Hydraulic conductivity data and rate of discharge (i.e. supposed evapotranspiration of the swampy Hanság area) were enhanced. Performing these corrections the position of modeled and measured tritium peaks of 1963 are fitting better (Fig 1/b). Parameters of this calibrated model are used for reveal of effects of human interventions for the groundwater resources. This new MODFLOW model and its validation are in progress.

Lumped parameter Dispersion Model (DM) [3 and 4] was used for estimation of groundwater transit time, flow velocity and dispersion coefficient of gravel aquifer along the main groundwater flow path. Input tritium data were available from periodical (five years frequency) analyzes of some wells from 1992 to 2012. The source of Danube tritium data was the GNIP of IAEA beside of our data. Transit time and ratio of older (tritium free) water are increasing with distance from Danube up to 75 years and 50% respectively. These data were validated by $^3$He/$^3$H dating.
Verification of a one-dimensional model and calculation of flow velocity as 425 m/a and longitudinal dispersion as 250 m was performed by $^{36}$Cl data [6] in good agreement with results of tritium evaluations.

4. CONCLUSIONS

$^3$H, $^3$He, $^{36}$Cl, $\delta^{18}$O and $\delta^2$H isotope data are excellent tools for validation and calibration of conceptual and mathematic models of young groundwater bodies as Szigetköz and surrounding area including lumped parameter DM and one dimensional flow models. Furthermore these isotope data are usable to prepare hydrogeological evaluations.

General conclusions by joint evaluation of available isotope data arisen from 1992 to 2012 are that groundwater in the gravel aquifer of Szigetköz are:

- fresh (less than 50 years old)
- originates mainly from the Danube, local infiltration and deep origin are negligible
- horizontal flow velocity from Danube is high (up to 500 m/a)
- coefficient of longitudinal dispersivity $a_L=250$ - 300 m via the main flowpath
- hydraulic conductivity of aquifer is high, up to 700 m/day

REFERENCES


HYDROTHERMAL GASES IN A SHALLOW AQUIFER AT MT. AMIATA, ITALY: INSIGHTS FROM STABLE ISOTOPES AND GEOCHEMICAL MODELLING

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Abstract: We investigate the interaction between hydrothermal gases and groundwater in a major aquifer exploited for potable supply in the geothermal-volcanic area of Mt. Amiata, Central Italy. The chemical and isotope composition of more than 80 water samples from two springs emerging on the southwestern side of the volcanic edifice has been processed with geochemical modelling techniques. Best fitting conditions between analytical data and model outputs have been achieved by numerical optimization, allowing for a quantitative description of gas-water-rock interactions occurring in this aquifer.

1. INTRODUCTION

Mt. Amiata, a large Pleistocene volcano in Tuscany (Central Italy), represents the most recent manifestation of the silicic volcanism of the Tuscan Magmatic Province. Its latest activity dates back to about 200 ka ago. The area has been investigated since longtime for geothermal purposes. Two distinct geothermal fields, Bagno and Piancastagnaio, are located on the southern slopes of the volcano. Discovered in the late 1950s and early 1960s, these fields are producing steam from both a shallow carbonate reservoir and, since late 1970s, from the fractured rocks of the metamorphic basement underlying the shallow carbonate reservoir ([1]). The total installed capacity is now 88 MWe ([2]). Acceptability problems with the local communities have hindered further geothermal developments over the last years. Some of the most controversial debate topics are focused on the possible connection between the shallow aquifer exploited for potable supply and the deep geothermal aquifer(s). Geothermal pollution is of concern at Mt. Amiata because local volcanics host one of the most important groundwater resources of the region, that provides drinkable water to more than half a million people. In an effort to gain some understanding of the interactions occurring between geothermal fluids and groundwater, in this study we processed with geochemical modelling techniques the chemical and isotope signature of waters from two selected springs regularly sampled over the last ten years.

2. GEOLOGY

The Mt. Amiata volcano (1738 m of elevation) rests on the Tuscan Nappe sequence made up by, from top to bottom: i) allochthonous flysch-facies units (Ligurids); ii) Mesozoic carbonate-evaporite and carbonate formations of the Tuscan Nappe; iii) variable piling up of carbonate-evaporite and clastic sequences belonging to the basal part of the Tuscan Nappe, and to the underlying metamorphic units; iv) Paleozoic metamorphic basement, made up of phyllites, micaschists and gneissess. Flysch formations at the top of the sequence act as an impermeable caprock. Below, two distinct geothermal reservoirs have been identified from geological and mineralogical data. Hosted in carbonate-evaporitic rocks at depths between 500 to 1000 meters, the upper reservoir has a temperature of about 200-230°C. The second
reservoir, formed by metamorphic rocks of the Paleozoic basement, has a temperature of 300 to 350°C at about 3000 m depth ([1], and references therein).

3. METHODS

The interaction between geothermal fluids and cold waters likely occurring in the shallow volcanic aquifer of Mt. Amiata is investigated under the assumption that both the mechanisms of conductive heat flow [3] and vapor/gas migration [4] contribute to the transfer of heat and mass from the geothermal reservoir(s) to near-surface environments. For this purpose, two low salinity (TDS < 250 mg/L) springs (Santa Fiora and Bagnore), emerging on the southwestern side of the volcanic edifice at different temperatures (11.3 ± 0.5 and 21.8 ± 0.7°C, respectively), were considered for their chemical composition and the stable isotope composition of dissolved carbon (δ¹³C-TDIC) and sulfur (δ³⁴S-SO₄). Compared to Santa Fiora, the Bagno thermal spring is characterized by higher contents of solutes, lower pH values and higher P⁵⁷CO₂ and P⁴⁰H₂S values.

A zero-dimensional, multicomponent geochemical model has been implemented and applied to spring waters to decipher the reactive mechanisms governing the evolution of waters circulating through the local volcanic aquifer. In this model, Santa Fiora and Bagnore waters are considered as the starting and the end-point, respectively, of a reaction path driven by the inflow of hydrothermal gases (vapor, CO₂(g) and H₂S(g)) into the volcanic aquifer. Primary and secondary minerals taken from the literature (e.g. [5], and references therein) are allowed to dissolve/precipitate under kinetic constraints. The goal of the numerical exercise is to obtain a reasonable matching between numerical predictions and analytical data, i.e. the concentration of major chemical components and the stable isotope composition of total dissolved carbon and sulfur. The solution of this inverse problem is inherently non-unique. In order to circumscribe the problem, a sensitivity analysis has been then performed by varying the input parameters of the model. From this analysis, it emerges that numerical results sensitively depend on: i) the inflow rate of hydrothermal CO₂(g) and H₂S(g); ii) the stoichiometry, thermodynamic solubility and kinetic parameters of volcanic glass; iii) the amount and reactive surface area of carbonate cement; iv) the isotopic composition of CO₂(g), H₂S(g) and calcite.

4. RESULTS

Analytical data and numerical simulations indicate that the inflow of hydrothermal CO₂(g) and H₂S(g) into the volcanic aquifer enhances the reactivity of circulating waters. The progressive decrease of pH suggests that the acidity produced via continuous solubilization of hydrothermal gases overwhelms the buffer capacity of the rock + water system. Because of this enhanced reactivity, the concentration of dissolved species progressively increases. Low chloride concentrations (up to a maximum of ~18 mg/kg at Bagnore) indicate that the mixing with geothermal water (Cl concentration of several hundred up to more than 1900 mg/kgw at reservoir conditions) is negligible, whereas the presence of measurable amounts of tritium (up to ~2.5 TU) testifies about the predominant meteoric recharge of the aquifer, and the relatively short underground circulation paths of groundwater. Most of the chemicals in solution are acquired by leaching of primary solid constituents (volcanic glass and anorthite) and secondary carbonatic cement, after absorption of hydrothermal gases.

δ¹³C-TDIC values of Santa Fiora waters are significantly depleted in¹³C (-15.1 ± 0.9‰ vs. VPDB) compared to those of the Bagno spring (-7.76 to -11.13‰), and are compatible with an edaphic origin of oxidized carbon in solution. The relative enrichment in¹³C at Bagno is
interpreted as an effect of mixing between soil CO$_2$(g) (depleted in $^{13}$C, as observed for Santa Fiora) and deep-seated CO$_2$(g) of hydrothermal origin. The numerical model accounts for this process considering that the □ $^{13}$C of the hydrothermal component is in the range of -1.4 to -7.1‰, in agreement with CO$_2$(g): i) discharged from local vents at Mt. Amiata (-2.0 to -4.7‰; [6]), ii) produced in the lab through pyrolysis experiments on phyllite specimens from local metamorphic basement rocks (-6.0 ± 0.5‰; [7]) and/or iii) discharged from geothermal wells of the high-enthalpy geothermal field of Larderello (-1.4 to -7.1‰; [8]), located some 80 km northwest of the Mt. Amiata edifice. Best fitting conditions between analytical (chemical and isotopic) data and numerical outputs have been achieved (Fig. 1A) with $\delta^{13}$C-CO$_2$ of -6.5 ± 0.5‰, and $\delta^{13}$C of carbonate cement of -2 ± 1‰, after addition of about 2.4 mmol-CO$_2$(g)/kgw. Under these conditions, the numerical model fits the most $^{13}$C-enriched TDIC value measured at Bagnores (-7.8‰), but it is not able to explain the more negative $\delta^{13}$C-TDIC values, down to -11.13‰. This reinforces the hypothesis of mixing between CO$_2$(g) produced via hydrothermal metamorphism and $^{13}$C-depleted CO$_2$(g) of biogenic origin (up to ~30% contribution, depending on the initial conditions of the model). The assumption of more positive $\delta^{13}$C-CO$_2$(g) values for the CO$_2$(g) hydrothermal component, would shift the red curve of Figure 1A towards the top of the plot, worsening the fit with the $\delta^{13}$C-TDIC values measured at Bagnores. Under these conditions, the gap between numerical and analytical values can be minimized by invoking a progressively larger (i.e. increasing with the $\delta^{13}$C-CO$_2$(g) of the hydrothermal component) contribution of $^{13}$C-depleted, biogenic CO$_2$(g).

![Figure 1. Comparison between numerical predictions (red curves connecting the starting point “Santa Fiora” to the end-path point “Bagnores”) and stable isotope analytical data (grey areas), under the assumption of water-rock interactions driven by the inflow of hydrothermal CO$_2$(g) and H$_2$S(g) into the shallow aquifer. Box A: $\delta^{13}$C-TDIC vs. mmoles of CO$_2$(g) per kgw; box B: $\delta^{34}$S-SO$_4$ vs. mmoles of H$_2$S(g) per kgw.](image-url)

The $\delta^{34}$S-SO$_4$ values of -6.4 ± 0.5‰ (VCDT) measured at Bagnores, significantly depleted in $^{34}$S compared to Santa Fiora ($\delta^{34}$S-SO$_4$ = +5.11‰), are interpreted as the result of the quantitative oxidation of hydrothermal H$_2$S(g) entering the volcanic aquifer from the geothermal reservoir. This H$_2$S(g) is supposed to derive from the thermochemical reduction of Upper Triassic anhydrites (Anidriti di Burano and/or Calcare Cavernoso formations; $\delta^{34}$S = +15.5 ± 0.4‰ [9]), possibly via the following reaction: SO$_4^{2-} + 8 \text{Fe}^{2+} + 10 \text{H}^+ \rightarrow \text{H}_2\text{S}_2\text{(g)} + 8 \text{Fe}^{3+} + 4 \text{H}_2\text{O}$. This hypothesis is corroborated by the fact that relatively high Fe contents (up to 0.68% as Fe$_2$O$_3$, [10]) have been measured in a number of rock specimens from Mesozoic carbonates in southern Tuscany. This conceptual framework is also validated by the numerical model. Best fitting conditions between numerical outputs and analytical data (in
this case, the $\delta^{34}$S-SO$_4$ of Bagnore spring) are achieved after addition of 1.1 mmol/kgw of hydrothermal H$_2$S$_2$(g), with $\delta^{34}$S in the range -6.7 ± 0.5‰ (Fig. 1B). Based on the sulfur geothermometer by [11], these $\delta^{34}$S values indicate that the thermochemical reduction of local anhydrites may occur at a temperature of 270 ± 10°C, in good agreement with the temperatures effectively measured in the deeper horizons of the geothermal system.

5. CONCLUSIONS

The chemical concentration of major aqueous constituents and the stable isotope composition of total dissolved carbon ($\delta^{13}$C-TDIC) and sulfur ($\delta^{34}$S-SO$_4$) of two springs draining a major volcanic aquifer have been investigated to gain some understanding of the interactions occurring at Mt. Amiata between geothermal fluids and local groundwater. More than 80 water analyses have been processed with geochemical modelling techniques. Numerical calculations support a conceptual model that considers water-rock interactions to occur in the volcanic aquifer after inflow of deep-seated gases (CO$_2$(g) and H$_2$S(g)), in absence of mixing with geothermal waters. Best fitting conditions between numerical outputs and analytical data were achieved for $\delta^{13}$C-CO$_2$(g) and $\delta^{34}$S-H$_2$S(g) values of -6.5 ± 0.5‰ and -6.7 ± 0.5‰, respectively, indicative of a predominant hydrothermal origin of both the gases.

REFERENCES

CONCEPTUAL AND NUMERICAL MODELING OF FLOW AND GROUNDWATER AGE DISTRIBUTION ON THE SOUTHERN PORTION OF GUARANI AQUIFER SYSTEM (GAS)

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Abstract: The Guarani Aquifer System - GAS is a transboundary aquifer shared by Brasil, Paraguay, Uruguay and Argentina, extending for some 1100000 km². Doubts have been raised in relation to the existence of discharge/recharge zones in the Argentinean sector of the aquifer (Figure 1) and their relationship with the surface water system. This area is well known for its ecological wealth, which is dependent on water resources, both surface as well as groundwater; therefore it is important to know the relationship between these two systems. However, in comparison with other sectors of the GAS, the region has scarce data, particularly on groundwater. On the other hand, ¹⁴C measurements on the entire aquifer resulted in groundwater ages over 40000 years in vast, deep areas, including the south. Therefore, a new hydrogeological conceptual model for the South region of the GAS was developed, considering a multilayer system, consisting on a surface aquifer and a deep aquifer (the GAS) hydraulically connected through altered basalts. Based on hydrochemical and isotopic analyses, the existence of deep waters discharge zones into overlying units in Corrientes state, Argentina, and to selected reaches along the Paraná and Uruguay rivers was postulated. The conceptual model was validated by means of numerical simulation under steady state conditions using the code TRANSIN under the VISUAL TRANSIN interface. The flow model calibration was satisfactory and the water balance consistent with current knowledge of the system and previous modeling efforts. Figure 2 shows simulated piezometric levels in the two aquifers. Novel groundwater age modeling results for the GAS were obtained based on the new flow model. Prior to calculating GAS groundwater age, synthetic cases were simulated to evaluate the distribution of groundwater age under different hydrogeological settings defined based upon real hydrogeological conditions identified on the GAS. The surface aquifer would have groundwater ages under 30000 years old (Figure 3a). The deep aquifer would have older waters, exceeding 40000 years (Figure 3b), a consistent result, however the calculated ages do not match adequately well ages inherent to this type of aquifers. New simulations including pre-GAS formations besides pos-GAS formations would be necessary to assess the effect of all potential inter-layers interactions on GAS groundwater age. Equally important is the need to validate simulated groundwater ages with isotopic field data.
Figure 1. Location of the Southern sector of GAS with respect to entire aquifer.

Figure 2. Simulated piezometric levels of GAS (left) and surface aquifer (right).

Figure 3. Simulated groundwater age of GAS (left) and surface aquifer (right)
THE USE OF ENVIRONMENTAL ISOTOPEs TO ESTABLISH A HYDROGEOLOGICAL CONCEPTUAL MODEL IN BELENE LOWLAND – NORTH BULGARIA

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Abstract: The present paper summarizes the hydrogeological and isotopes investigations, carried out in Belene – Svishtovska lowland, which are used to create conceptual model. The Belene-Svishtovska lowland is an important industrial urbanized territory using mainly groundwater to satisfy the water supply demands. There are three relatively big towns Svishtov, Belene and Nikopol with various industries. Furthermore the planned Nuclear Power Plant “Belene” would increase the potential risk of radioactive pollution. That significantly augments the importance of the present investigation looking at the future. The analyses of the environmental isotopes in water aimed to define age and origin of the groundwater, its contemporary renewal and mixing of different water sources. For the purpose the quantity and quality monitoring networks have been established. Monthly water level measurements and four sampling (isotopic) campaigns have been made during investigations. Groundwater samples from the alluvial aquifer (the Belene aquifer), Senonian limestone aquifer, Aptian sandstone aquifer and surface Danube River have been isotopically analysed. The results confirm that the main recharge source for the Belene aquifer is the Danube River. They show partially recharge from Senonian limestone in the west, Aptian sandstone in the east, from loess and deluvium deposits in the south boundary. The discharge is through the Danube River and drainage systems. The situation is very complicated with seventh different inflow sources, a complex drainage system, and numerical unknown pumping wells and needs of elaboration of conceptual model. In the material is presented the developed conceptual model for the Belene area using analysed data. The conceptual model is a base for numerical model using finite elements or finite differences techniques. Finally the FeFlow and PEST are selected for further modeling stand on the already created conceptual model.

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EVALUATION OF TRACER TRANSPORT INTO A TUNNEL BY VARIOUS NUMERICAL MODELS

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Abstract: We study the water flow in fractured granite between the surface and the tunnel, using a numerical model to interpret data from natural tracers (described in a separate paper by Sanda et al. [1]). The main features are the distinction of the shallow permeable zone and a permeable fracture/fault from remaining compact rock is included in the 3D model variant. First, we solve the pulse transport and compare the mean residence time with the lumped parameter model results (both the stable isotopes $^2$H and $^{18}$O and the $^3$He/$^4$He data). Second, we input and fit the real stable isotopes concentration sequences in the surface and the tunnel respectively, for the shallow parts of the tunnel. In both cases, mobile water volume (porosity of permeable structures) is estimated together with hydraulic parameters from the inflow rates.

1. INTRODUCTION

One of the difficulties for describing fractured hard rock is the inhomogeneity of flow, which is even different from the hydraulic point of view (flow rates) and from the transport point of view (particle velocity). An opportunity to observe the flow in rock in a larger scale than e.g. borehole tests is observation of a tunnel inflow, including both the flow rates and natural tracer sampling. We study a particular site in Bohemian granite massif, in the Jizera mountains in the north of the Czech Republic [2]. It is a water supply tunnel in Bedrichov, from a reservoir to the water processing plant, which is 2.6 km long in up to 150 m depth. Most of the inflow is in the shallow parts from the permeable zone, while the inflow in the deeper hard rock is concentrated to several fractures or sub-vertical fault zones. The water inflow measurement and tracer sampling follows the previous geological research from 2003.

We analyze the combined water flow and tracer transport by a numerical model, which is a compromise of the conceptual and geometric simplification against keeping the main features of inhomogeneity, appropriate to the level of details and precision in the measured data. Formerly, we used a catchment-scale 3D model of water flow, with digital terrain model, positions of the shallow permeable zone and the vertical faults (permeable features) from geological maps and geophysics [3]. The hydraulic conductivities or transmissivities of all the subdomains were found which resulted to simplified distribution of inflow (homogeneous from the rock continuum and concentrated from the discrete features). On the other hand, this model was not so suitable for tracer transport simulation, due to computational cost (requiring much finer mesh then for the hydraulics only) and less insight into the influence of various parameters.

The numerical model as described below is also part of the Decovalex-2015 project, which is intended to a comparison of various numerical codes by different research teams, to improve the credibility of models for nuclear waste repository safety assessment. Even the site is not in a candidate area, the study of the migration through granite is a generic interest for this kind of repository host rock.
2. METHODS

The aim of the modelling is to derive properties of the rock from measuring and sampling in the tunnel and on the surface. By the hydraulic model, we calibrate the hydraulic conductivities from flow rates of the tunnel water inflow (discharge). Consequently, given a flow field, we calibrate porosity (mobile water volume ratio) from the tracer transport. As the first simpler approach, we fit the mean water residence time of an fictitious tracer pulse to the residence time (water age) derived previously by lumped parameter models, in contrast to more complex case of fitting the concentration sequences directly.

The presented work uses a set of models representing the particular inflow points in the tunnel with their neighborhood. For the tunnel in hard rock, they all use the same concept of regular geometry and distinction of the shallow zone, vertical fracture/fault and rock continuum (Figure 1 left). The shallow zone is not fully represented here and its role is like a buffer between the infiltration and a deep percolation. We define a separate model for the tunnel inflow in the shallow zone (Figure 1 right), where the relation between variable infiltration and water table and the flow path pattern can be represented more realistically.

The hydraulic problem for the deeper inflow is considered steady state, which corresponds to measured variations under 20%. The tracer pulse injection is realized by a short period (single time step in the order of 1000 s) of unit concentration. The simulation time is between 100 and 1000 years, depending on the resulting residence time, which was necessary to cover the long tails of the breakthrough curves in the tunnel, including a mass from near-stagnant zones in the model. We use the in-house developed simulation software FLOW123D with a feature of connecting 3D continuum and 2D fracture domains [4].

The “measured” residence time was considered a value obtained by the lumped-parameter model for the stable isotopes $^2$H and $^{18}$O in the more shallow inflow (125 m and 142 m positions) and directly from the $^3$H/$^3$He dating for the deeper fault zone inflow (1565 m position). We used the dispersion model in the FLOWPC software [5].

![Figure 1. Models of tunnel water inflow for various locations along the tunnel – the left is for the tunnel in the deeper hard rock with dominant inflow from a fracture or fault, the right is for the tunnel in the shallow zone (distributed inflow).](image-url)
3. RESULTS

Examples of result visualization are in Figure 2 – piezometric head, velocity field, and concentration field in a selected time. As expected, horizontal flow dominates in the shallow zone and most of the infiltration leaves the domain, as the terrain-controlled flow. The deeper percolation is deviated by the tunnel drainage, splitting the water between the tunnel and the bottom boundary. The important parameters are collected in the Table 1, together with the calibration results. We determine the 3D domain hydraulic conductivity from the distributed inflow (intensity per unit length of the tunnel) and the 2D fracture/fault transmissivity from the concentrated inflow rate. Then the discrete fracture apertures (independent of the hydraulic aperture related to the transmissivity by the cubic law), interpreted as the mobile water volume, are determined from fitting the fraction of the residence time in the deeper hard rock, after subtracting the shallow zone contribution to the residence time.

The shallow zone parameters, hydraulic conductivity $10^{-6}$ m/s and porosity 0.02 are chosen partly artificially, to keep the important features – reasonable slope of the water table and the contribution of the residence time equivalent to the value measured in the shallow part of the tunnel (3 years). They also correspond to values calibrated from the 3D model of the shallow inflow (figure 1 right, resulting data not presented). The shallow zone porosity is below the expected value, which can be influenced by the geometric simplification and the presence of artificial stagnant zone in the model.

4. CONCLUSIONS

The presented work extends the results of [1] by alternative numerical model, which will also be used for comparison of more numerical codes. The model allowed to interpret hydraulics together with the natural tracer dating, as well as to connect fitting the data for different hydrogeological domains – shallow zone, small fracture in shallow hard rock and a fault in deeper hard rock part. The resulting hydraulic parameters and mobile water volume estimations are mostly appropriate to the rock types.

After the calibration of the 3D transport model for the pulse tracer transport, simulations with the same parameters for the real stable isotope concentration sequences were run. Results comparable to the lumped-parameter model were obtained for the shallow inflow and 142 m inflow. These results will be presented on the conference poster.

<table>
<thead>
<tr>
<th>Position [m]</th>
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<th>142</th>
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<td>Fault zone</td>
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<tr>
<td>Hydr. conductivity 3D [m/s]</td>
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<tr>
<td>Frac. transmissivity [m$^2$/s]</td>
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Figure 2. Examples of the deeper inflow model results – two for the hydraulics and one for the fictitious pulse tracer transport.

ACKNOWLEDGEMENT

The work described in this report/paper was conducted within the context of the international DECOVALEX Project (DEmonstration of COupled models and their VALidation against EXperiments). The authors are grateful to the Funding Organisation who supported the work, i.e. the Radioactive Waste Repository Authority (RAWRA/SURAO), contract nr. SO2013-077. The views expressed in the report/paper are, however, those of the authors and are not necessarily those of the Funding Organisations. The results were also obtained through the financial support of the Ministry of Education, Youth and Sports from the project LO1201 in the framework of the targeted support of the "National Programme for Sustainability I".

The used data were obtained in the IAEA contract no. 16335 of the Czech Technical University.

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IDENTIFYING AND QUANTIFYING TRANSIENT GROUNDWATER FLUXES INTO COMPLEX GROUNDWATER SYSTEMS BY MIXING CELLS MODELING APPROACH – THE MATHEMATICAL ALGORITHM OF MCMusf MODEL

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Abstract: A Mixing Cells Modeling (MCM) approach has been developed to elaborate on complex and vague groundwater flow systems. It was applied to identify and quantify hidden sources of contaminants percolating into groundwater reservoirs. It provides the user with the ability to assess the groundwater fluxes in a complex and transient hydrological system in which the spatial distribution of pollutants vary 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 impossible to construct, solve and calibrate a transport hydrological model based on the continuity approach. The proposed alternative MCM algorithm is based on a more simplistic, yet practical approach, in which the flow domain is sub-divided into pseudo- homogeneous flow cells forming a multi-compartmental MCM flow model. The creation of the multi-compartmental structure is based on spatial distribution of dissolved contaminants, environmental isotopes and hydrochemistry in a transient hydrological system. This presentation demonstrates the use of the MCMusf (unsteady flow) mathematical algorithms for identifying and quantifying groundwater fluxes, recharge and hidden fluxes of pollutants into complex aquifer system. The MCM modelling scheme is solved by an optimization scheme which is based on water and the dissolved minerals and chemicals constraints.
CONTRIBUTION OF HYDROCHEMICAL AND ISOTOPE TOOLS TO ELUCIDATE THE ORIGIN OF NITRATE CONTAMINATION IN THE COASTAL AQUIFER OF THE MITIDJA PLAIN (NORTH EAST OF ALGIERS)

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Abstract: This study was carried out within the framework of a Technical Co-operation project supported by IAEA (ALG/7/005- Protecting and Safeguarding Vulnerable Areas Against Contamination and Mapping Vulnerability and Risks of Groundwater Pollution), and the investigation was performed by a research team from the Algiers Nuclear Research Centre (CRNA) in collaboration with engineers from the National Agency of Hydraulic Resources (ANRH). The main objective of the study is to combine conventional methods and isotope techniques, especially $\delta^{15}N$ and $\delta^{18}O$ of nitrates, to trace the sources of contamination in the Mitidja aquifer.

1. INTRODUCTION

The Mitidja plain, located North East of Algiers, hosts an alluvial aquifer delimited to the North by the Mediterranean Sea. Groundwater resources are exploited mainly for agricultural and drinking water use, and often to the limit of their availability. In recent years, a considerable piezometric decrease and a degradation of groundwater quality has been recorded, mostly affecting the deeper parts of the aquifer (sea water intrusion) and shallow wells (nitrate pollution) [1]. The main objective of the study is to combine conventional methods and isotope techniques, especially $\delta^{15}N$ and $\delta^{18}O$ of nitrates, to trace the sources of contamination and understand the transfer mechanisms from the surface to depth. The investigated area covers part of the Mitidja area, where both agricultural activities and urban areas are present.

2. METHODS

Twenty-six samples from boreholes and piezometers were collected in the Mitidja plain. Temperature and conductivity were measured in the field. Hydrochemical analyses were conducted at the ANRH chemical laboratory. The isotopic composition of dissolved nitrates was analysed at ISO4, Italy, using the method described by [2].

3. RESULTS

The results of hydrochemical analyses indicate that groundwaters are calcium bicarbonate type, for the less mineralized, with relatively high levels in calcium and sulphate, turning to sodium chloride facies with increasing mineralization. Nitrate concentrations are generally higher than 50 mg/l, ranging between 100-200 mg/l. These high nitrate levels have forced the distributors to dilute pumped water in order to reduce their concentration, and ultimately to
disconnect numerous wells for drinking water supply. Isotope results are shown in Fig. 1. \( \delta^{15}N \) values are always higher than +7‰, indicating a strong contribution from anthropogenic organic matter (AOM - manure, septic effluents, sewage) [3].

Based on nitrate isotope compositions, samples were grouped into three types: the first group is constituted by a mixture of synthetic fertilizers and organic matter (MIX, pink group in Fig. 1); the second group is strongly affected by inputs of anthropogenic organic matter (AOM, blue group in Fig. 1). Finally, some samples appear to be affected by partial denitrification, indicating an ongoing natural attenuation process (green group in Fig. 1). Unfortunately, no clear relationship with the geographic position was observed, nor any relationship with land use and anthropogenic activities [3].

4. CONCLUSIONS

Hydrochemical and isotopic results indicate that the studied zone is very complex and strongly affected by hydrodynamic perturbations and anthropogenic contamination. In order to better understand the hydrodynamics of the aquifer system and the coupled effects of human activities, additional investigation should be conducted. In particular, in order to assess the origin of the anthropogenic organic matters causing the nitrate contamination, the boron isotope systematics will be used.

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EVALUATION OF SEASONAL NITRATE SOURCES AND DENITRIFICATION IN THE KARST CATCHMENT

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Abstract: A karst catchment with developed conduit networks was selected as studied area to understand the nitrate sources and transformation processes based on water chemistry and dual isotopes in the southwestern China. The results suggested that nitrate sources in the water samples mainly derived from oxidation of reduced fertilizer. Meanwhile denitrification would shift the isotopes of nitrate significantly during the wet seasons according to isotopic proof. There is relative slight denitrification in the underground stream compared with that in the surface stream.

1. INTRODUCTION

Karstic aquifers are particularly vulnerable to anthropogenic pollution because of their conduit networks and sinkholes, which quickly respond to rain events and anthropogenic inputs [1-2]. There are not only hydrodynamic interactions between ground water and surface water, but also interactions of nutrient transportation between them. The latter is complicated and important for water management. Karst rocky desertification is a severe problem in southwestern China. This desertification process involves soil losses, increased exposure of bare rocks, and the appearance of a desert-like landscape [3]. Nutrients easily flow away from the fragile and thin soil layer, which is concerned by local governments and agricultural populations in karstic area of the southwestern China (Liu et al. 2008). Understanding the sources and fate of nitrate between surface water and groundwater is critical to improve management practices to reduce nutrient loss in infertile environment and protect water quality.

2. METHODS

The drainage basin of the Houzhai River has an area of 81 km$^2$ and is a typical karst catchment, lies at the center of the Southeast Asian karst region [4]. The Houzhai catchment with its well-developed karst conduits was selected for understanding nitrate sources and transformation processes. A monsoonal climate often results in about 80% of the annual precipitation during wet season (Generally May to Oct.) and much less precipitation during other seasons. The land in the basin can be divided into four types: cultivated land, forest land, grassland and bare rock land. Sample waters were collected monthly in 2013. The major cations ($\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{K}^+$, and $\text{Na}^+$) and the anions ($\text{ALK}$, $\text{SO}_4^{2-}$, $\text{Cl}^-$, and $\text{NO}_3^-$) were analyzed. Deuterium and oxygen isotopes of water were measured by Liquid-Water Isotope Analyzer (LGR Company, America). The denitrifier method was used for measurement of isotopes of nitrate.
3. RESULTS AND DISCUSSION

Ca$^{2+}$ and Mg$^{2+}$ are the major cations and accounted for more than 90% of the total cations in the water from the Houzhai catchment. HCO$_3^-$ was an important anion in the studied water for most water samples. SO$_4^{2-}$ was the second most important anion. The water chemical compositions general showed that the water chemistry was controlled by carbonate weathering.

The waters from the studied area have a range from -65.1‰ to -50.6‰ and -9.5‰ to -7.1‰ for δD and δ$^{18}$O, respectively. The plots between δD and δ$^{18}$O fit well with GMWL line for the most water samples. As indicated by Fig.1, the evaporation would shift the isotopic compositions for some waters, especially during the dry seasons. The waters in the dry seasons generally enriched heavy isotopes due to longer water residence time relative to that during the wet seasons.

Fig.1 Scatter plots for the correlation between δ$^{18}$O and δD in water samples at the Houzhai catchment, SW China.

The nitrate content of the waters varied widely in the Houzhai catchment. Some headwaters in the catchment had high concentrations of nitrate, which suggested nitrate sources enter the water system quickly in the upper reaches of the watershed due to the sparse vegetation cover. The spatial distribution of contents and isotopes of nitrate in waters represented the heterogeneity and complexity in the typical karstic conduit system, SW China. There is big difference between outlet of surface stream and underground stream/total outlet during the dry seasons and little difference during the wet seasons. The export of nitrogen from the whole catchment is mainly from surface stream in the wet seasons, but strongly dominated by the underground system in the dry season.

The δ$^{15}$N-NO$_3^-$ reflected that nitrate is mainly affected by nitrification [5, 6] due to a narrow range between 0‰ and 10‰ in most water samples (Fig.2). Nitrate generally enriched heavy isotopes in the water samples during the dry seasons compared with that during the wet seasons. The dual isotopic pattern indicated that nitrate in most water samples mainly derived from a mix of chemical fertilizer and manure during the wet season and more impacted by manure sources during the dry season because thin soil lack of enough SON. There is strong negative relationship between δ$^{15}$N and ln[NO$_3^-$] and a positive relationship between δ$^{15}$N and δ$^{18}$O-NO$_3^-$ values from water samples collected at the wet seasons. The denitrification would occur in the wet seasons with high temperature and rainfall, especially during the depression.
with relative thick soil zone in this catchment. Meanwhile, nitrate generally has higher isotopic values in the surface stream compared with that in the underground stream at the outlets of this catchment, which might indicate there is relative strong denitrification for the nitrate in the surface stream.

Figure 2. Scatter plots between $\delta^{15}N$ and $\delta^{18}O-NO_3^-$ in different seasons of 2013 at the Houzhai Catchment, SW China

4. CONCLUSIONS

This study presents a detailed analysis of the water chemistry and multiple stable isotopes to identify the sources and fate of NO$_3^-$ in an agricultural catchment at the center of the Southeast Asian karst region. The $\delta$D- and $\delta^{18}$O-H$_2$O values demonstrated that water was slightly affected by evaporation during the dry seasons. The nitrate fertilizers and rain were not the major source of NO$_3^-$ in the water samples due that the $\delta^{18}$O-NO$_3^-$ values mainly reflected the nitrification characteristics in the Houzhai catchment. The relative strong denitrification signal was found in the surface stream compared with that in the underground stream at the outlets of the whole catchment based on the isotopic proof. Denitrification would remove the part of nitrate in this catchment and shift the isotopes of nitrate, especially in the depression with thick soil at the Houzhai catchment.

REFERENCES


COUPLING ISOTOPE HYDROGEOCHEMISTRY AND SOCIAL SCIENCES TO ASSESS AGRICULTURAL AND DOMESTIC IMPACTS IN RURAL ZONES: THE BIR AL-NAS APPROACH

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Abstract: The paper presents a new bottom-up integrated approach combining hydrogeochemistry and social sciences for tackling groundwater issues in rural areas. Under the need to assess anthropogenic impacts due to combined agricultural and domestic pollution, the proposed Bir Al-Nas approach couples hydrogeology and isotope hydrogeochemistry with socio-economic assessment of the investigated zone. The main objectives of this approach are to: (i) foster public participation of local farmers; (ii) retrieve information on local issues and agricultural/domestic practices, (iii) raise awareness on groundwater vulnerability, and (iv) make the best use of the information obtained by using isotope tracers, as the most powerful tools for the identification of groundwater fingerprint, recharge and pollution origin.

1. INTRODUCTION

Groundwater represents the largest volume of all unfrozen fresh water on Earth. However the knowledge and understanding of this precious resource is very limited, if compared to surface water, especially when considering the general public and policy makers. Nonetheless groundwater abstraction for human needs significantly increased in the past sixty years [1], playing a major role in agricultural production and the support to rural livelihoods [2]. In rural areas, when groundwater is withdrawn for irrigation and domestic purposes, water scarcity and overexploitation issues might be exacerbated. In addition, due to the possible lack of sanitation facilities and the impacts of agricultural return flow, nitrate pollution might occur, resulting in dissolved nitrate concentration exceeding the WHO statutory limit for drinking water (50 mg/L; [3]). Indeed when contaminated groundwater is used for agricultural and drinking purposes this can have severe consequences on food security and human health, as the well-known child’s methemoglobinemia and gastric cancer [4-5].

In the framework of hydrogeochemical investigations in rural zones, environmental isotopes have proven to be an excellent tool for the identification of water fingerprint and contamination origin [6]. In particular, when dealing with nitrate it is widely recognized how $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ are fundamentals tracers for the identification on nitrogen sources and cycle [7]. In particular these isotopes allow for a clear distinction between the domestic and agricultural NO$_3^-$ contamination origin, which is one of the main problem of rural zones, especially in developing nations. However, any information obtained with the best available tool has no value if it is not translated into a set of best practices shared by final groundwater users (and polluters). This is why, in order to make the best use of high quality data and information, a dialogue with the interested stakeholders (including marginalized groups) must be an asset.
Based on these assumptions, a bottom-up integrated approach for sustainable groundwater management is proposed as a replicable example of an integrated methodology combining hydrogeochemistry and social sciences for tackling groundwater issues in rural areas.

2. METHODS

The Bir Al-Nas approach (Bottom-up IntegRated Approach for sustainabLe grouNdwater mAnageMent in rural areaS) is proposed as a framework to better support groundwater management strategies tailored on the real needs and issues of local populations. In Arabic bir al-nas means the “well of people” and emphasizes the effective inclusion of the social dimension into hydrogeological investigations.

The overall objective is meant to be achieved through an integrated hydrogeochemical and social analysis, finalized to obtain robust and reliable information for providing advices and supporting integrated management practices for rural development (Figure 1). The key aspect of Bir Al Nas is the implementation of socio-economic assessment into hydrogeochemical investigations evaluating the impacts of human activities on groundwater quality and quantity. In practical terms this is done through:

• A Stakeholder analysis prior to the hydrogeochemical and hydrogeological study. This analysis allows for the identification of the main actors involved in the studied water issue, their power relations and possible existing conflicts.
• The direct engagement and confrontation with final water users while performing the monitoring activities. This represents a moment for knowledge and information sharing that can facilitate a better understanding of local issues while also retrieving direct information on groundwater use and agricultural practices.

The socio-economic assessment, coupled with the hydrogeochemical investigation will result in a more complete understanding of local issues, pollution sources and processes. The latter will be obtained thanks to the use of isotope tracers allowing to identify groundwater origin and recharge processes (δ²H, δ¹⁸O and δ¹³C) as well as to assess NO₃⁻ contamination drivers (δ¹⁵NNO₃ and δ¹⁸ONO₃) and to discriminate between agricultural and domestic NO₃⁻ pollution (δ¹¹B). If correctly implemented this approach can lead to a more effective understanding since the early stages of a project, pave the way for shared actions for groundwater quality protection and consent scientists to make the best use of their scientific findings.

3. PRELIMINARY RESULTS ON THE APPLICATION OF BIR AL-NAS TO A PILOT CASE STUDY

The Bir Al-Nas approach is currently tested in the Grombalia Region, which is one of the main agricultural regions of Tunisia, interested by groundwater salinization, aquifer overexploitation and NO₃⁻ contamination issues [8].

As a part of the public engagement component during the hydrogeochemical sampling campaign carried out between February and March 2014, structured questionnaires were administered to 35 farmers and landowners included in the monitoring network, in order to retrieve information on groundwater use, irrigation practices, and crop production (including fertilizers type and application rate). Furthermore questions concerning their perception about recent and past water issues, as well as knowledge of climate change were also included.

Additionally a Stakeholder Analysis was performed in order to identify and sort individuals or groups that could affect or be affected by NO₃⁻ contamination in the Grombalia Region. In
particular the Social Network Analysis was applied using the Net-Map toolbox [9] in order to identify stakeholders’ network and their relationships regarding the investigated issue [10].

Results for both phases allowed for a better understanding of local issues and the perception of groundwater contamination problems for local wellbeing and agricultural development. Based on the interviews it was possible to highlight that farmers and landowners generally do not have the perception to hold an influential role in groundwater pollution contamination and reduction.

In addition it was possible to identify the most influential stakeholders likely to favor the implementation of new, science-based management strategies for groundwater protection: (i) the Ministry of Agriculture and the Regional Commissioner to Agricultural Development, as the more influential decision-maker and control actors; (ii) the farmers, as the final water user and (iii) the Groups of Agricultural Development and farmers’ trade union, as mediating actors between the authorities and the local water users [10]. Those will be the key stakeholder groups to discuss with once the NO$_3^-$ contamination sources will be identified with the application of environmental isotopes. Results of the ongoing isotopic investigation are presented elsewhere [11].

Figure 1. Conceptual scheme of the Bir Al-Nas approach

4. CONCLUSIONS

Given the need to adequately assess nitrate contamination origin in rural regions in order to protect human health and food security, it is of paramount importance to identify nitrate contamination origin with the best available technologies, as environmental isotopes. Nevertheless it is also fundamental that the scientific outcomes are adequately shared with the general public in order to promote groundwater protection and raise awareness on both its relevance and vulnerability to anthropic pressure. This, on the one hand, implies the implementation of science-based management practices, clearly resulting from sound
hydrogeological and hydrogeochemical investigations, but also to start considering the social impacts of scarce and/or polluted water.

Bir Al-Nas is therefore proposed as a new approach for integrating social sciences into hydrogeochemical investigations in rural areas. The final outcomes are expected to be an increase of the awareness of groundwater issues from the rural community, eventually resulting in a more proactive behavior in terms of groundwater protection. On the other hand, from the scientists’ perspective, the engagement of farmers and well’s owners will favor both the comprehension of local issues and needs, and will help bridging the gap between science and society.

Acknowledgements

This research was supported by a Marie Curie Fellowship within the EU 7th FP for Research and Technological Development (FP7-PEOPLE-2012-IOF n.327287). The author wishes to thank Dr. Elisa Sacchi for the critical review of the synopsis.

REFERENCES

THE USE OF NITRATE ISOTOPES TO ASSESS AGRICULTURAL AND DOMESTIC IMPACTS ON GROUNDWATER QUALITY IN RURAL ZONES. THE EXAMPLE OF GROMBALIA BASIN (TUNISIA)

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Abstract: In recent years, the increased groundwater withdrawal for agricultural practices coupled with the widespread use of natural and synthetic fertilizers has affected both groundwater quality and quantity in the Grombalia Plain (Tunisia). In particular, the region is experiencing an increase in nitrate concentration that can have severe effects on human health and food security. In order to identify the origin of groundwater pollution a survey on 48 wells was conducted in between February and March 2014, as the first step for a complete nitrate vulnerability assessment of the region. In most of the investigated sites nitrates exceed the drinking water limits and the isotopic and hydrogeochemical investigation associated their origin to agricultural and domestic inputs. The occurrence of denitrification processes has been highlighted, suggesting the potential for self-remediation of the contaminated waters.

1. INTRODUCTION

As many coastal regions along the Mediterranean, the Cap Bon Peninsula (Tunisia) is an important agricultural area, where rural population mainly relies on groundwater as water-supply and irrigation source. In addition, the increasing withdrawal for urban and industrial purposes, coupled with extensive agricultural activities, result in severe groundwater quantity and quality issues. As an example of generalized water related problems, many aquifers in the region are experiencing a significant decrease of the piezometric level and an increase of human-induced groundwater pollution [1]. Based on a review of the available hydrogeological and hydrogeochemical data, the Grombalia aquifer, covering a surface of about 720 km², has been chosen as priority area to assess the links of regional agricultural activities with aquifer overexploitation and salinization. The area is in fact characterized by high groundwater salinity and elevated NO₃⁻ concentrations, both in the shallow and deep aquifer, raising concerns for the local population’s health and food security.
We present the preliminary results of a complete assessment on groundwater pollution origin in the Grombalia aquifer, aimed at discriminating the different sources of contamination and at supporting regional development. In particular, the main objectives of the present study are to examine patterns of NO$_3^-$ concentrations and δ$^{15}$N in 48 wells distributed across the aquifer and to identify NO$_3^-$ pollution origin. Isotopic and hydrogeochemical results, coupled with a socio-economic analysis, will be used to promote alternative, science-based, management strategies to ensure a more sustainable use of available water resources in the region.

2. METHODS

A field campaign, performed between February and March 2014, allowed for the collection of 48 groundwater samples from hand dug wells and boreholes in both the shallow (27 samples) and deep aquifers (21 samples), in the whole Grombalia plain. Electrical Conductivity, pH, Eh and groundwater temperature were measured directly in the field. Samples for major ion analysis were analyzed at the Laboratory of Radio-Analysis and Environment of the National Engineering School of Sfax (Tunisia). The δ$^{15}$N$_{NO_3}$ and δ$^{18}$O$_{NO_3}$ were determined following the procedures described by [2 - 3] and reported relative to V-AIR and V-SMOW [4]. The uncertainties are ±0.5‰ and ±1‰, respectively. All samples were prepared and analyzed on a Finningan™ MAT 250 Mass Spectrometer at ISO4 s.n.c., Turin, Italy.

3. RESULTS

Hydrochemical results allow to classify Grombalia groundwater as Ca(Na)Cl(SO$_4$) water type. Electrical conductivity ranges from 1.04 to 9.18 mS/cm (mean 3.81 mS/cm) in the shallow aquifer and from 1.04 to 7.13 mS/cm (mean 2.29 mS/cm) in the deep one. Mineralization processes are relevant and concern areas where farming and agricultural activities can seriously affect the groundwater quality.

The abundance of major ions, especially of nitrates, chlorides and sulphates, indicates an alteration of physical-chemical properties due to anthropogenic activities, thus constituting a serious threat for public health and crop production. In particular, the nitrate content is very high in most of the wells. Almost 75% of the wells in the shallow aquifer and 43% in the deep one have concentrations exceeding the WHO statutory limit for drinking water (50 mg/L; [5], Figure 1). Several studies [6-7] have pointed out how a nitrate excess in water used for drinking and agricultural purposes can be the driver for serious diseases, especially concerning children (i.e. methemoglobinemia and gastric cancer). This is why an adequate characterization of these inputs is of paramount importance for the local development of the Grombalia region.

In order to identify the different sources of nitrate in the studied site, the isotopic composition of nitrogen and oxygen has been investigated. In Figure 2 the comparison between [NO$_3^-$] and δ$^{15}$N$_{NO_3}$ shows that the highest nitrate concentrations are associated with enriched isotopic compositions, indicating the dominant role of anthropogenic organic matter as a source of contamination.
Figure 1. Plot of $[\text{NO}_3^-]$ vs. $[\text{Cl}]$ for the samples collected in the shallow and deep aquifers in the Grombalia Plain between February and March 2014.

Figure 2. Simplified characterization of nitrogen pollution sources [based on 8] for the samples collected in the shallow and deep aquifers in the Grombalia Plain.

Figure 3. Isotopic composition of nitrates for the samples collected in the shallow and deep aquifers in the Grombalia Plain. Modified after [2].
Despite the well-known widespread use of fertilizers in the whole Grombalia region [1] the isotopic compositions of the samples do not show a dominance of mineralized synthetic fertilizers as contaminants. However, this diffuse pollution source, associated to irrigation and agricultural return flow and might be subject to transformations in the soil resulting in an isotopic enrichment [9]. In addition, in the plot of $\delta^{15}$N$_{NO_3}$ versus $\delta^{18}$O$_{NO_3}$ (Figure 3) denitrification processes are observed in both aquifers, suggesting an original composition of dissolved nitrates from fertilizers and anthropogenic organic matter.

4. CONCLUSIONS

The increasing nitrate contamination in the Grombalia Plain requires an unequivocal identification of pollution sources in order to promote new management and agricultural strategies that support both local development and environmental protection. The use of nitrate isotopes has proven to be a useful tool for the preliminary identification of nitrate inputs in groundwater and the identification of the occurrence of denitrification processes. Ongoing investigation is focusing on a complete nitrate vulnerability assessment, evaluating all the possible anthropogenic pollution sources and the links with the regional geological settings.

AKNOWLEDGEMENTS

This research was supported by a Marie Curie Fellowship within the EU 7th FP for Research and Technological Development (FP7-PEOPLE-2012-IOF n.327287).

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GROUNDWATER DATING FOR PREDICTING FUTURE EVOLUTION OF NITRATE CONCENTRATIONS

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Abstract: In the Gäu aquifer, Switzerland, nitrate leaching from agriculture caused increasing nitrate concentrations in several production wells and subsequently measures were taken to reduce the nitrate input. In this study, several factors that determine the nitrate concentrations in the wells and their future evolution were identified and quantified. A crucial factor is the travel time of the water from the surface to the wells, which was assessed with multiple environmental tracers: $^3$H/$^3$He, $^{85}$Kr and $^{39}$Ar. The presence of a thick unsaturated zone (UZ) of up to 35 m requires an extended lumped parameter modelling approach. Total residence times of up to 22 years were found from which a considerable portion is in the unsaturated zone. These data are the basis for predicting the future evolution of nitrate concentrations in the aquifer.

1. INTRODUCTION AND SITE DESCRIPTION

In the Gäu aquifer (Canton of Solothurn, Switzerland), which is an important source of drinking water locally, high nitrate concentrations are threatening the water quality. Measurements in several production wells in the aquifer since 1988 reveal increasing nitrate concentrations above the target value of 25 ml/g required by the water protection regulations. To prevent the concentrations from exceeding 40 mg/l – the maximum allowable concentration for drinking water – farmers, water suppliers and the environmental office of the Canton of Solothurn jointly started a project to reduce nitrate input from agriculture in the year 1999. From 2000 to 2011, the agricultural area under contract rose from 0 to 10.5 km$^2$. However, the reduction of nitrate concentrations in the production wells is lower than expected, until now. This raised the question why the measures taken are not (yet) effective.

The Gäu aquifer with a total area of 33.9 km$^2$ is located in the central lowlands of Switzerland and is bounded by the Jura Mountains (limestone) in the north and the Gäu Hills (molasses) in the south. It consists mostly of gravel deposited after the glacial retreat at the end of the Würm glacial and porosity is typically around 15 %. In large parts of the aquifer the gravel is overlain by 1 to 3 m of clayey silt. The central and southeastern parts of the aquifer have a
very thick unsaturated or vadose zone (UZ) of up to 35 m which increases in thickness from north east to south west. Water balance modelling showed that direct infiltration of precipitation, infiltration from streams and lateral inflows all contribute roughly equally to the total groundwater recharge of around 1000 mm/a [1, 2].

2. METHODS

Samples were taken from six of the production wells in the aquifer, as well as from several shallow piezometers just below the water table. Factors that control nitrate concentrations are a) the temporal evolution of nitrate input concentrations, b) denitrification, c) the dilution of the nitrate-rich local infiltration with low-nitrate water, d) the travel time of the nitrate-rich water component and e) multi-annual climatic conditions.

Nitrate concentrations in nitrate-rich direct infiltration were estimated based on the general nitrate trends in Switzerland (Figure 1). Denitrification was assessed with the stable isotopes of nitrate [3].

Dilution of nitrate-rich direct infiltration was quantified by major ions and other chemical tracers, as the earlier quantification based on water balances was quite uncertain. Based on geological conditions six end-members were identified, some of which only apply for a part of the aquifer. The relative amounts of these end-members were estimated for each well in a mixing calculation based on Cl\(^{-}\), HCO\(_3\)^-, SO\(_4\)^-, SiO\(_2\) and acesulfame concentrations using least squares.

To determine travel times of the water and thus nitrate from the surface to the production wells [4] the transient tracers \(^{3}\)H/\(^{4}\)He, \(^{85}\)Kr and \(^{39}\)Ar [5, 6] were measured. Since direct infiltration and infiltration from streams are distributed along the whole length of the aquifer, an exponential age distribution lumped parameter model (with the mean residence time \(T_\theta\) as a free parameter) is considered to be a good approximation for modelling the saturated zone (SZ) [7]. Gas transport through the UZ was modelled in 1D using a simplified, analytically resolvable version of the equation from Cook et al. [8] (free parameter: tortuosity \(\tau_g\)). For water transport in the UZ (also in 1D) again an exponential distribution was assumed to account for preferential flow paths (free parameter: mean vertical velocity \(v\)). Subsurface mountain block recharge (MBR) from the Jura [9, 10] was considered as an additional component \(m\) of \(^{3}\)H- and \(^{85}\)Kr-free old water as indicated by \(^{39}\)Ar measurements. Multi-parameter fitting (error weighted least squares) was used to interpret the tracer data sets. Uncertainties were determined with the Monte-Carlo method.

On time scales of a few years, nitrate concentrations can also be influenced by climatic conditions because nitrate leaching varies with precipitation. This was not quantitatively assessed in this study.

3. RESULTS AND DISCUSSION

The analysis of the stable isotopes of nitrate showed that denitrification is negligible in the aquifer.

The dilution with low-nitrate water was found to be less than suggested by the water balance with the direct infiltration fraction being 60 to 90 %. The only exception was one well in the west of the aquifer where MBR is more dominant. The low-nitrate water was found to be lateral inflow (11 – 22 %) and infiltration from streams (1- 17 %). The nitrate concentration distribution obtained from these mixing calculations and assumed nitrate concentrations of the mixing end members agree well with the measured distribution (\(r^2 = 0.70\)).
Groundwater dating showed that the travel times are longer than expected based on previous investigations. This is mainly caused by the consideration of the previously neglected unsaturated zone (UZ). Mean travel times in the saturated zone (SZ) were found to be between 4 and 12 years with an uncertainty of 1-2 years; the oldest ages are located in the central part of the aquifer where the SZ is the thickest. For the UZ, the obtained travel times are between 2 and 10 years with quite a high uncertainty related to the model selection (the uncertainty due to measurement errors is again in the order of 1-2 years). In total, this results in travel times of 6-22 years from the surface to the production wells.

With these results, the future evolution of nitrate concentrations in the production wells can be predicted. Figure 1 shows two examples for long and short travel times.

![Figure 1](image.png)

**Figure 1. Past and future evolution of nitrate concentrations in two selected wells: a) Neufeld (total travel time 21 years) and b) Gheid C (total travel time 8 years).**

In both examples the shift in time and a smoothing of the nitrate input curve is visible both at the groundwater level and in the production wells. Naturally, both effects are more pronounced in wells with longer mean travel times. At the water table, nitrate concentrations react immediately to surficial nitrate reducing measures in both wells. This is in agreement with measurements in shallow piezometers which already show a reducing trend in nitrate concentrations. However, the nitrate concentrations decrease slower than the nitrate input at the surface, as a consequence of the age distribution. In the production wells themselves, the peak nitrate concentration can be delayed with respect to the beginning of the nitrate reducing measures for wells with longer travel times, like Neufeld.

A comparison of the modelled nitrate concentrations with measured concentrations in the production wells, where available, served as a verification to identify wells where the proposed approach works well and where it has its limitations. The measured data also show that multi-annual variance in nitrate concentrations are between 2 and 5 mg/l. Before and after the predicted peak concentration, nitrate concentrations might stay within 5 mg/l of the peak for up to a decade, implying that the actual peak year can be shifted by up to 10 years by variations in the multi-annual climatic conditions.
4. CONCLUSIONS

Using a modelling approach that takes into account the unsaturated zone to interpret the tracer measurements it could be shown that the system reacts slower than expected. Based on the groundwater dating and an estimation of the dilution of nitrate rich local infiltration we were able to predict how nitrate concentrations will likely evolve in response to the measures taken to reduce nitrate input.

ACKNOWLEDGEMENTS

We thank the local water suppliers for granting us access to their production wells for sampling.

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THE IMPACT OF SURFACE WATER - GROUNDWATER INTERACTIONS ON NITRATE CYCLING IN THE RIPARIAN AND HYPORHEIC ZONES ASSESSED BY MEANS OF HYDROGEOLOGIC AND ISOTOPIC TECHNIQUES IN THE ALENTO RIVER BASIN (ITALY)

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Abstract: The knowledge of the mechanisms regulating the concentration of nutrients in rivers is of fundamental importance in maintaining the ecological functioning of streams. In particular, in the riverbed sediments, where the biogeochemical activity is enhanced, the study of retention mechanisms becomes crucial in order to determine the restoring capacity of a watercourse. In case of groundwater inflow, hot-spots in the recycling of nutrients within the riparian and hyporheic zones can be observed, influencing the nutrient load transported into the stream depending on retention mechanisms. Hence, the study of biotic and abiotic factors affecting retention within the riverbed sediments, and the study of processes occurring at the interface of groundwater and surface water (i.e., the hyporheic zone) are fundamental in understanding the mechanisms of retention and transport, which regulate the concentration of nutrients, and in particular nitrates, in streams.

The main scope of the present project, within the framework of the IAEA Coordinated Research Project (CRP) “Environmental Isotopes and Age Dating Methods to Assess Nitrogen Pollution and Other Quality Issues in Rivers”, is to find a reliable methodology to, spatially and temporally, quantify groundwater inflows to a river in order to study nitrates contamination of a groundwater dependent river ecosystem.
This goal will be achieved focusing on three main objectives:

1. The identification and quantification of spatial-temporal variation of the connectivity between groundwater and surface water in the considered river basin.
2. The identification of the nitrate contamination sources of shallow groundwater in the considered alluvial aquifer.
3. The study of the nitrates retention and recycling mechanisms in riverbed sediments in critical effluent river reaches (key sites) in order to determine the importance of hyporheic and riparian zones in the considered catchment.

Here, the preliminary results of the hydrogeological, chemical and isotopic monitoring are presented and discussed.
APPLYING DUAL-ISOTOPE NITRATE TRACING THROUGH GROUND AND SURFACE WATER IN NEW ZEALAND CASE STUDIES

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Abstract: New Zealand's pastoral agriculture drives the nation's top export commodities but introduces nitrate contamination into freshwater. Identifying opportunities to reduce hot spots and hot moments of nitrate loss would therefore be economically and environmentally beneficial. N and O isotopes can be used to trace the source and fate of the nitrate molecule from its creation in soil through to impacts in receiving freshwater environments. H and O isotopes in water, tritium dating, and other tracers provide important additional tools for identifying the spatial and temporal nature of ground and surface water interactions. This presentation synthesises findings from case studies in several catchments and regions, including the Upper Manawatu, Mangatarere, Canterbury and Southland. We find that most catchment-scale nitrate follows a 1:1 line on a δ^{15}N vs δ^{18}O biplot. The positioning of this line may vary, presumably as a result of winter-versus-summer differences in soil water δ^{18}O contributing to the formation of the nitrate. We find a lack of evidence for widespread denitrification or DNRA, implicating assimilatory processes as the main contributor to observed fractionation. Data from nearly 200 streams, drains and wells from across the Southland region confirms that δ^{15}N vs δ^{18}O of nitrate has unique tracer value, showing variation not captured in other variables including δ^{11}B and δ^{13}C DIC. These results may have utility in identifying management practices targeted reducing winter or summer periods of nitrification.

1. INTRODUCTION

New Zealand's pastoral agriculture drives the nation's top export commodities but introduces nitrate contamination into freshwater. Identifying opportunities to reduce hot spots and hot moments of nitrate loss would therefore be economically and environmentally beneficial. N and O isotopes can be used to trace the source and fate of the nitrate molecule from its creation in soil through to impacts in receiving freshwater environments. New Zealand situation is relatively unique in being able to use O isotopes in NO_3 in the absence of strongly elevated atmospheric and fertilizer δ^{18}O-NO_3. As a result, δ^{18}O-NO_3 can be expected to trace the δ^{18}O-H_2O present during the formation of NO_3. H and O isotopes in water, tritium dating, and other tracers provide important additional tools for identifying the spatial and temporal nature of ground and surface water interactions. This presentation synthesises findings from case studies in several catchments and regions, including the Upper Manawatu, Mangatarere, Canterbury and Southland.
2. METHODS

N and O isotope measurements in NO$_3$ have been made using a modified Cd-Azide reduction method.

3. RESULTS AND DISCUSSION

Extended campaigns of monthly samples across ~15 stations in the Upper Manawatu catchment have identified that catchment-scale nitrate follows a 1:1 line on a $\delta^{15}$N vs $\delta^{18}$O biplot, and catchments are positioned on this plot with $\delta^{15}$N-NO$_3$ and $\delta^{18}$O-NO$_3$ both proportional to the level of agricultural intensity in the catchment.

Extended campaigns and high spatial resolution sampling in the Mangatarere catchment confirm differing sources of winter and summer nitrate, and highlight that surface water exchanges with groundwater over relatively short distances.

Data from nearly 200 streams, drains and wells from across the Southland region confirms that the $\delta^{15}$N vs $\delta^{18}$O of nitrate has unique tracer value, showing variation not captured in other variables including $\delta^{11}$B and $\delta^{13}$C DIC. Using this data, we find a lack of evidence for widespread denitrification or DNRA, implicating assimilatory processes as the main contributor to observed fractionation.

4. CONCLUSIONS

We find that most catchment-scale nitrate follows a 1:1 line on a $\delta^{15}$N vs $\delta^{18}$O biplot. The positioning of this line may vary, presumably as a result of winter-versus-summer differences in soil water $\delta^{18}$O contributing to the formation of the nitrate. These results may have utility in identifying management practices targeted reducing winter or summer periods of nitrification.
NITROGEN SOURCES, TRANSPORT AND PROCESSING IN PERI-URBAN FLOODPLAINS

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Abstract: Peri-urban floodplains are an important interface between developed land and the aquatic environment and may act as a source or sink for contaminants moving from urban areas towards surface water courses. With increasing pressure from urban development the functioning of floodplains is coming under greater scrutiny. A number of peri-urban sites have been found to be populated with legacy landfills which could potentially cause pollution of adjacent river bodies. Here, a peri-urban floodplain adjoining the city of Oxford, UK, with the River Thames has been investigated over a period of three years through repeated sampling of groundwaters from existing and specially constructed piezometers. A nearby landfill has been found to have imprinted a strong signal on the groundwater with particularly high concentrations of ammonium and generally low concentrations of nitrate and dissolved oxygen. An intensive study of nitrogen dynamics through the use of N-species chemistry, nitrogen isotopes and dissolved nitrous oxide reveal there is little or no denitrification in the majority of the main landfill plume, and neither is the ammonium significantly retarded by sorption to the aquifer sediments. A simple model has determined the flux of total nitrogen and ammonium from the landfill, through the floodplain and into the river. Over an 8 km reach of the river, which has a number of other legacy landfills, it is estimated that 27.5 tonnes of ammonium may be delivered to the river annually. Although this is a relatively small contribution to the total river nitrogen, it may represent up to 15% of the ammonium loading at the study site and over the length of the reach could increase in-stream concentrations by nearly 40%. Catchment management plans that encompass floodplains in the peri-urban environment need to take into account the likely risk to groundwater and surface water quality that these environments pose.
APPLICATION OF ISOTOPE TECHNIQUE TO ESTIMATE ORIGIN OF NITROGEN COMPOSITION OF GROUNDWATER IN HANOI AREA

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Abstract: Groundwater in Hanoi area as well as in some other areas in Bacbo Delta of Vietnam is being contaminated by nitrogen compounds and arsenic. In order to exploit and manage sustainable groundwater served for production and live, it is necessary to estimate the origin of nitrogen compounds and arsenic in groundwater in Hanoi area. The paper presents the procedure to analyze the isotope ratio $^{15}\text{N}/^{14}\text{N}$ in NH$_4^+$ and NO$_3^-$ of water samples using diffusion method and isotope ratio mass spectrometer and origin of nitrogen composition of groundwater. Total 40 groundwater samples were collected in the study to analyze ammonium and composition of $^{15}\text{N}(\text{NH}_4^+)$. The data of isotope composition $^{15}\text{N}$ in groundwater samples show that portion of NH$_4^+$ produced from organic matter of aquifer in groundwater is higher than that from inorganic fertinizer used in agriculture activities. The model of isotope mass balance is applied to calculate the contribution of NH$_4^+$ origined from organic matter and inorganic fertinizer of groundwater and portion of NH$_4^+$ produced from organic matter of aquifer in groundwater is from 23% to 97%. The results of total nitrogen, concentration of NH$_4^+$ and NO$_3^-$, and isotope composition of $^{15}\text{N}$ in two aquifer columns of 40m depth show that soil layers of aquifer consist of organic matter produced from wastes of crop plants with high concentration of nitrogen, and in the mineralization, the organic matter is disintegrated into ammonium
APPLICATION OF STABLE ISOTOPES IN THE IDENTIFICATION OF NITRATE POLLUTION SOURCES IN AQUIFERS INFLUENCED BY LAND-USE

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Abstract: The present study presents the preliminary results of the stable isotope measurements (δ\(^{15}\)N-NO\(_3\), δ\(^{18}\)O-NO\(_3\)) performed in groundwater samples collected in April 2013 from River Asopos basin (central Greece), which is considered to be one of the most degraded areas of Greece in terms of water resources, with a large number of established industries (e.g., textile, metal processing, chemicals, food, fertilizers, paint) and an intensive agriculture and livestock breeding. The catchment is characterized by three basic land-use types: the agricultural area with complex cultivations (e.g., celery, carrots, potatoes, olive oil trees), the arable agricultural area (cultivated in places), and the industrial-urban area. The western part of the study area is used mainly for agriculture and is characterized by elevated nitrate concentrations (up to 134.2 mg/L NO\(_3\)-N) and δ\(^{15}\)N values ranging between -2.6 and +6.5 ‰ indicating that a mixture of chemical fertilizers, soil and manure is responsible for groundwater contamination. In the central and eastern part of the study area, where complex cultivations are the predominant land-use, the nitrate concentrations showed a maximum of 125.0 mg/L NO\(_3\)-N and the δ\(^{15}\)N values ranged between +1.7 and +9.2 ‰ exhibiting that manure and septic wastes are the main sources of nitrate pollution. The industrialized and urban part of the study area showed high nitrate values in places (up to 72.7 mg/L NO\(_3\)-N) and δ\(^{18}\)O values ranging between +7.3 and +10.7 ‰ that was attributed to sewage wastes or other nitrogen-enriched wastes originating from industry as well as to manure. The comparison of sample groups originating from the different land-use areas showed a transition from light N-isotope values in the less cultivated agricultural area to heavy N-isotope values in the industrial-urban area. Stable isotopes were used to identify nitrate pollution sources and assess land-use (agriculture, urban and industrial) contribution to nitrogen cycle in River Asopos basin, based on the fact that the main sources of nitrate exhibit different δ\(^{15}\)N and δ\(^{18}\)O signatures.

1. INTRODUCTION

Although naturally occurring as part of the nitrogen cycle, nitrate (NO\(_3\)) is a typical contaminant with different origins (e.g., synthetic and natural fertilization, bacterial production, atmospheric deposition and leaking septic systems), which classifies it as one of the most widely spread contaminants in groundwater resources. Moreover, biogeochemical processes can also modify nitrate concentrations such that different forms of nitrogen (NO\(_2\), NH\(_4\), NH\(_3\)) can be transformed into nitrate [1].

Nitrate sources show different isotope “fingerprints” of nitrogen (\(^{15}\)N/\(^{14}\)N) and oxygen (\(^{18}\)O/\(^{16}\)O), hence the determination of both nitrogen and oxygen isotopic composition can provide meaningful insight for tracing sources of NO\(_3\) in groundwater. This dual isotope approach (δ\(^{15}\)N-NO\(_3\) and δ\(^{18}\)O-NO\(_3\)) has been applied successfully to the identification and quantification of a) diffuse nitrate inputs into water bodies [2-7] and b) the transformation pathways of nitrate and, in particular, denitrification processes [8-11].
The objective of the present study was to identify the contamination sources of nitrate in groundwater bodies affected by different natural and anthropogenic activities (e.g., urban, agricultural) in a heavily polluted area of central Greece.

2. METHODS

A sampling campaign for nitrate ions and isotopes was performed in Asopos River basin (central Greece) in April 2013, when the groundwater samples were collected from 26 boreholes. The samples were filtered through 0.45 µm filters and collected in acid-rinsed 100 mL polyethylene bottles. Once the samples were collected, they were stored at 4°C until analysis. Nitrate concentrations were analyzed on a continuous flow analyzer (AutoAnalyzer 3, University of Athens, Greece). The δ\textsubscript{15}N–NO\textsubscript{3} and δ\textsubscript{18}O–NO\textsubscript{3} values were determined by the “Bacterial denitrification method”, adopted and modified by a number of researchers [10-12] which allows for the simultaneous determination of δ\textsubscript{15}N and δ\textsubscript{18}O of N\textsubscript{2}O produced from the conversion of NO\textsubscript{3} by denitrifying bacteria (e.g., *Pseudomonas aureofaciens*) (Fig.1). A trace gas preparation unit (ANCA TGII, SerCon, UK) coupled to an isotope ratio mass spectrometer (IRMS) (20-20, SerCon, UK) was used for the δ\textsubscript{15}N and δ\textsubscript{18}O analysis of the produced N\textsubscript{2}O.

The stable isotope ratios are expressed in delta (δ) units and a per mil (‰) notation relative to an international standard:

\[
\delta_{\text{sample}} (‰) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000
\]

where \(R_{\text{sample}}\) and \(R_{\text{standard}}\) are the \textsuperscript{15}N/\textsuperscript{14}N or \textsuperscript{18}O/\textsuperscript{16}O ratio of the sample and standard for δ\textsubscript{15}N and δ\textsubscript{18}O, respectively. Values of δ\textsubscript{15}N are reported relative to N\textsubscript{2} in atmospheric air (AIR) and δ\textsubscript{18}O values are reported relative to Vienna Standard Mean Ocean Water 2 (VSMOW 2).

3. RESULTS

To primarily identify the predominant NO\textsubscript{3} sources in the study area, a dual isotope bi-plot approach (δ\textsubscript{15}N–NO\textsubscript{3} vs. δ\textsubscript{18}O–NO\textsubscript{3}) was used based on Kendall classifications [13] (Fig. 2):
Although classified as arable agricultural land-use, according to Corine-2000 classification, the western part of the basin is cultivated in places (e.g., celery, carrots, potatoes, olive oil trees). The isotopic results showed elevated NO$_3$ concentrations (10.9 – 134.2 mg/L NO$_3$-N) and δ$^{15}$N values of nitrate between -2.6 and +6.5 ‰ which is attributed to a mixture of chemical fertilizers, soil and manure. The central and eastern part of the study area is occupied mainly by a complex agricultural land-use, where the NO$_3$ concentrations are ranging between 4.0 and 125.0 mg/L NO$_3$-N and the δ$^{15}$N values between +1.7 and +9.2 ‰. The results exhibit that manure and septic wastes are the predominant NO$_3$ sources of pollution in this area. The industrialized and urban part of the study area showed high nitrate values in places (0.9 – 72.7 mg/L NO$_3$-N) and δ$^{15}$N values of nitrate ranging between +7.3 and +10.7 ‰ that is attributed to manure as well as sewage wastes or other nitrogen-enriched wastes originating from industry.

4. CONCLUSIONS

Stable isotopes were applied to a highly polluted area of central Greece to investigate possible nitrate pollution sources and assess land-use (agriculture, urban and industrial) contribution to nitrogen cycle, based on the fact that the main sources of nitrate exhibit different δ$^{15}$N and δ$^{18}$O signatures. The comparison of sample groups originating from different land-use areas showed a shifting from light N-isotope values in the less cultivated agricultural area to heavy N-isotope values in the industrial-urban area.

ACKNOWLEDGEMENTS

This work was supported by a STSM Grant from the COST Action ES0806 SIBAE. The author would like to thank Prof. P. Boeckx, Head of the Isotope Bioscience Laboratory and the rest of the Laboratory staff for the training on the nitrate isotope measurements. The
author also wishes to express his gratitude to Dr. V. Paraskevopoulou, at the Department of Chemistry of the University of Athens (Greece), for providing the nitrate measurements.

REFERENCES


Abstract: In Lithuania low and intermediate level radioactive waste generated from medicine, industry and research were accumulated at the Maisiagala radioactive waste repository. Short-lived low and intermediate level radioactive waste, generated during the operation of the Ignalina Nuclear Power Plant (INPP) and after the dismantling of INPP will be disposed of in the repository near the INPP. Extensive data sets of the hydraulic properties, water content and isotope composition of unsaturated zone soil profiles of the two radioactive waste disposal sites (Maisiagala radioactive waste storage facility site and Stabatiske near surface repository site) has been collected and summarized.

1. INTRODUCTION

There have been no long-lasting and detailed unsaturated zone experimental research to characterize two sites of nuclear facilities with different hydrogeological conditions. Globally widespread radionuclide tritium (\(^{3}\text{H}\)) and hydrogen and oxygen isotope ratio (\(\delta^{2}\text{H}\) and \(\delta^{18}\text{O}\)) distribution features were determined in precipitation, unsaturated zone soil moisture profiles and groundwater. Two unsaturated zone soil profiles were characterized by the soil density, moisture content and hydraulic conductivity.

2. METHODS

The research methods include collection and analysis of undisturbed and disturbed soil samples of the unsaturated zone, determination of the soil physical–mechanical properties and hydraulic conductivity values of the unsaturated zone profile; systematic monitoring of ground water level; monthly precipitation amount; analysis of the isotopic composition of groundwater, precipitation and the unsaturated zone moisture. To perform pore water extraction from the unsaturated core samples for the isotopic analyses, a moisture extraction system was designed [1]. The beta decay counting of \(^{3}\text{H}\) was run for a scintillation cocktail and 8 ml of water electrolytically enriched with \(^{3}\text{H}\). As extracted the moisture from soil samples were only a few ml, the specific activity of the \(^{3}\text{H}\) was determined by direct measurement (without enrichment), in which the uncertainty can reach 2-4 TU. Since the monthly precipitation and monthly groundwater sampling volume was 600 ml and a sufficient to perform the enrichment of \(^{3}\text{H}\) in these cases \(^{3}\text{H}\) specific activity was determined by measuring electrolytically enriched water with \(^{3}\text{H}\), in this case uncertainty can reach only 0.1-0.2 TV. \(^{18}\text{O}/^{16}\text{O}\) and \(^{2}\text{H}/^{1}\text{H}\) ratios of water molecules determined as \(\delta^{18}\text{O}\) and \(\delta^{2}\text{H}\) values with respect to international standard (VSMOW) [2].

The investigations have been carried out using IRMS DELTA V Advantage and GasBench II system or Picarro L2120-i Cavity Ring-Down Spectrometer. Stable isotopes data are presented as per mille deviations from internationally accepted standards with the reproducibility of \(\pm 0.1\%\) for \(\delta^{18}\text{O}\) and \(\pm 1\%\) for \(\delta^{2}\text{H}\).
3. RESULTS AND CONCLUSIONS

Periodical measurements of $^{3}$H, $\delta^{18}$O and $\delta^{2}$H in the water samples have been performed. Preliminary relationship between $\delta^{2}$H and $\delta^{18}$O for the precipitation (monthly samples of two years 2010 and 2011 from two sampling sites) in East Lithuania was determined in term of the Local Meteoric Water Line (LMWL) (Figure 1):

![Figure 1. $\delta^{18}$O and $\delta^{2}$H distribution in precipitation, ground water and the unsaturated zone soil moisture.](image)

According to the two years precipitation $\delta^{18}$O and $\delta^{2}$H studies in the two areas preliminary local meteoric water line was established, which is for the eastern part of Lithuania expressed as a linear equation ($\delta^{2}$H=7.8×$\delta^{18}$O+7.2; $R^{2}$=0.9). Isotopic composition of the groundwater is close to the annual isotopic composition of precipitation in Lithuania. The weighed annual mean $\delta^{18}$O and $\delta^{2}$H values for atmospheric precipitation are respectively -9.9‰ and -70‰. The $\delta^{18}$O and $\delta^{2}$H values in the groundwater vary respectively from -12.1 to -9.3 ‰ and from -82 to -70‰. The majority of groundwater samples in diagram are situated near the GMWL and LMWL indicating groundwater recharge by modern atmospheric precipitation.

![Figure 2. $^{3}$H concentration in groundwater (Maisiagala) and precipitation (Vilnius).](image)
Variations of $^3$H in the groundwater are very small compared with precipitation, but the summer period is characterized by slightly higher $^3$H concentrations (Figure 2). The $^3$H activity in the groundwater of the study areas can be related with $^3$H variation in atmospheric precipitation and in surface water as groundwater recharge sources. The mean annual $^3$H activity in atmospheric precipitation is approx. 10 TU.

The pattern of stable isotopes seasonal variation occurring in the precipitation almost disappear in the unsaturated zone soil moisture and especially in shallow groundwater, but a slight seasonal peak traces remain.

Figure 3. $\delta^{18}O$ change in groundwater (Maisiagala) and precipitation (Vilnius).

The $\delta^{18}O$ and $\delta^2H$ values of moisture in the Maisiagala unsaturated zone profile vary within wide ranges: from 2.1‰ to -9.1‰ and from -37.5‰ to -70.3‰, respectively. In terms of water isotopic composition, the upper part is much heavier (less negative values) due to enrichment because of evaporation and moisture uptake by plant roots. With the depth of the unsaturated zone profile stable isotope values become more negative.

At the Stabatiske site unsaturated zone profile, the $\delta^{18}O$ and $\delta^2H$ values of the soil moisture ranges from -10.2‰ to -18.4‰, and from -74.6‰ to -135.6‰, respectively. At the Maisiagala site $\delta^{18}O$, $\delta^2H$ and $^3$H seasonal peak traces are slightly more contrast than in Stabatiske site, due to unsaturated zone moisture transit times are shorter at the Maisiagala site, and the measured hydraulic properties of the unsaturated zone at Maisiagala site (eolian sand deposits) is much higher than in the Stabatiske site (till deposits).

REFERENCES


INSITU ARSENIC REMOVAL DURING GROUNDWATER RECHARGE THROUGH UNSATURATED ALLUVIUM

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Abstract: Arsenic in excess of the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) of 10 micrograms per liter (µg/L) occurs in aquifers throughout much of the southwestern United States and the world. A field-scale experiment was done in Antelope Valley, Calif. to test the feasibility of insitu removal of arsenic by sorption to naturally-occurring iron and aluminum oxides on the surfaces of mineral grains. Between December 2010 and July 2012, more than 120,000 cubic meters (m$^3$) of high-arsenic groundwater was pumped from a deep aquifer into a 0.11 hectare pond and infiltrated though an 80-meter thick unsaturated zone to recharge a water-table aquifer. Downward movement of the wetting front and changes in water chemistry were monitored using instruments in a borehole adjacent to the pond. Infiltration rates from the pond were as high as 0.4 meters per day, and the wetting front moved downward about 25 centimeters per day (cm/d) to a depth of about 50 m. Clay layers at that depth slowed the downward movement of the wetting front to about 5 cm/d. Lateral movement of the wetting front was monitored using sequential direct-current (DC) surface and sequential electromagnetic (EM) and DC borehole resistivity. Most lateral movement occurred on the clay layer about 50 m below land surface. Infiltrated water reached the water table in January 2013. At the water table, the “wetted footprint” of water infiltrated from the pond was about 13 hectares. Arsenic concentrations decreased from 30 µg/L to 2 µg/L as a result of sorption to iron and aluminum oxides on mineral grains within the unsaturated zone. Although arsenic concentrations sorbed to the surfaces of mineral grains within the upper meter of alluvium increased as a result of infiltration from the pond, Toxicity Characteristic Leaching Procedure (TCLP) data show concentrations were not classified as hazardous. Some preexisting arsenic and uranium, possibly associated with past agricultural activities at the site, was mobilized from a salt-affected clay layer at a depth of 14 m and resorbed on deeper materials. Other oxyanions (including antimony, chromium, selenium, and vanadium) were not mobilized during the experiment. Batch experiments done using radiolabeled arsenic-73 (a man-made isotope, having a half-life of 80.3 days) show arsenic-73 was initially sorbed to surface exchange sites, but was incorporated into more refractory crystalline iron and aluminum oxides within one year. Data from the field experiment agree with laboratory column experiments that show arsenic strongly sorbed to aquifer materials over a range of pH’s from 6 to 8. Unsaturated alluvium underlying the pond contains 3.6 and 1.2 kilograms per cubic meter of elemental iron and aluminum sorbent on the surfaces of mineral grains, respectively. Given lateral spreading within the unsaturated zone, water infiltrated from the pond encountered 4.5 x 10$^6$ m$^3$ of unsaturated alluvium having enough iron and aluminum oxide to treat 60 x10$^5$ m$^3$ of water having 30 µg/L arsenic to a concentration less than the MCL of 10 µg/L. The cost of arsenic treatment and recharging the shallow aquifer was the cost of pumping the water from the deeper aquifer, about $120 per 1,000 m$^3$. 

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INDUSTRIAL AREA INVESTIGATION USING STABLE ISOTOPES

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Abstract: Hydrology studies using isotopes are an important topic in the current research field due to increased human activity, translated in high demand of resources (fresh water, energy, process water, etc.) and pollution. The hydrological basin of an important chemical industrial platform in Romania, the Rm. Valea industrial area, was characterized in terms of the chemical and stable isotope composition (by continuous flow - isotope ratio mass spectrometry CF-IRMS). The surface waters in the industrial area are used for chemical processing, discharge of wastes and electricity production. Throughout a period of one year, water samples from the Olt River and its more important tributaries were collected monthly in the industrial area, when the seasonal and spatial isotope patterns of the surface waters and the main sources of pollution were determined.

1. INTRODUCTION

Hydrology studies are an important topic in the current research field due to increased human activity, translated in high demand of resources (fresh water, energy, process water, etc.) and pollution. Considered as core elements in establishing the origin, path and history of a water source, environmental isotopes are recognized tools applied to investigate hydrological systems [1-7].

2. METHODS

Analysis were carried out on water samples collected from 11 locations in the industrial area of Rm. Valea town, on Olt River and its main tributaries, for chemical and isotopic characterization. The surface waters in the industrial area are used for chemical processing, discharge of wastes and electricity production. Another set of samples were represented by the mean precipitation for each month for the sampling area that were also isotopically characterized. The sampling was done monthly from November 2012 to October 2012, when the environmental conditions were registered. All the water samples were analyzed at the National R&D Institute for Cryogenics and Isotopic Technologies (ICIT) at Rm. Valea (Romania) and the isotopic measurements were done using a Delta V Plus (Thermo Scientific) continuous flow - isotope ratio mass spectrometer (CF-IRMS).

3. RESULTS

The seasonal and spatial isotope patterns of the surface waters and precipitation from the industrial area were determined. The results were correlated with the chemical composition, in particular, contaminants, to determine the source of pollution.
4. CONCLUSIONS

The isotopic values for Middle Olt Basin were distributed along the local meteoric water line, when the Olt River presents distinct isotopic composition than its tributaries, having smaller seasonal variations and being more depleted in deuterium and oxygen-18. The main sources of pollution were determined.

REFERENCES

TRITIUM AND IODINE-129 IN PRECIPITATIONS AT TSUKUBA, JAPAN, AFTER THE MARCH 2011 FUKUSHIMA DAIICHI NUCLEAR PLANT ACCIDENT

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Abstract: The earthquake off the Pacific coast of Japan and the subsequent tsunami on 11 March 2011 triggered a series of accidents in the Fukushima Daiichi Nuclear Power Plant. The accidents caused the release of a mixture of radioactive substances into the environment. The concentrations of tritium and iodine-129 (129I) were analyzed in rainwater samples collected at Tsukuba, 170 km southwest of the plant over the first year after the accident. High tritium and 129I concentrations were observed in the rainwater samples collected within 4 weeks after the power plant explosions. The tritium concentrations of subsequent rainwater samples decreased steadily with time and returned to the levels before the accident. Concentrations of 129I also decreased as did tritium; however, several pulses of high 129I concentrations were observed. The incorporation of 129I into the atmosphere occurred at the time of the explosions, and also several times thereafter.

1. INTRODUCTION

The earthquake off the Pacific coast of Japan and the subsequent tsunami on 11 March 2011 triggered a series of accidents in the Fukushima Daiichi Nuclear Power Plant (FNPP1). The accidents caused the release of a mixture of radioactive substances into the environment, which were produced in the nuclear reactors and stored in the spent-fuel.

Tritium (t1/2 = 12.32 yr) released from the nuclear reactor was initially in the form of tritiated water vapor (HTO) that was washed out of the atmosphere as precipitation and incorporated into the natural hydrologic cycle. Tritium measurements in precipitation are useful for tracing hydrological processes and provide a better reconstruction of the mechanism and history of emissions from the accidental release of radioactivity.

Iodine-129 (t1/2 = 1.57×10^7 yr) has been used to reconstruct the distribution of iodine-131 (131I) (t1/2 = 8 days) after the accident. Iodine -131 is one of the most harmful radionuclides produced in nuclear reactors; therefore, the activity of 131I around the accident site should be precisely evaluated to estimate the health impact. However, 131I has a short half-life and is no longer detectable after several months. Therefore, the distribution and behavior of 129I in the
environment should be evaluated, as it remains much longer in the environment and moves identically with $^{131}$I.

We report the concentrations of tritium and $^{129}$I in precipitation at Tsukuba, 170 km southwest from the FNPP1 over the first year after the accident.

2. METHODS

Rain samples were collected at Tsukuba over the first year after the accident. Individual rainfalls were collected in pan-shaped containers. Tritium analysis was carried out in the Isotope Hydrology Laboratory of the International Atomic Energy Agency by electrolytic enrichment followed by liquid scintillation spectrometry with a detection limit of about 0.1 TU [1].

Concentrations of $^{129}$I were determined using accelerator mass spectrometer (AMS) at MALT (Micro Analysis Laboratory, Tandem accelerator) of the University of Tokyo [2]. The standard used for the determination of $^{129}$I/$^{127}$I ratio was Z94-0596 prepared by Prime Lab., University Purdue. Cation compositions (K, Na, Ca, Mg, Al, Fe, and Mn) were determined using ICP-MS at Gakushuin University.

3. RESULTS

Particularly high tritium concentrations were observed in the rainwater samples collected within 4 weeks after the power plant explosions. The tritium concentrations of subsequent rainwater samples decreased steadily with time and returned to the levels before the accident, indicating that tritium in the atmosphere was washed out by precipitation.

Concentrations of $^{129}$I also decreased after the explosions; however, several pulses of high $^{129}$I concentrations were observed (>$10^{-6}$ Bq/kg: more than two orders of magnitude higher than the minimum concentration for the year). This means that incorporation of $^{129}$I in the atmosphere occurred at the time of the explosions and also several times after the explosions. No evidence of continuous release of radiogenic volatile substances from FNPP1 was detected after the explosions. Therefore, the source of the $^{129}$I pulses was most likely atoms that had been deposited on the soil surface and then redistributed back into the atmosphere. This conclusion is supported by the correlation between Fe/Na and $^{129}$I/Na observed only for the high $^{129}$I rainwaters, because soils are generally enriched in iron as iron oxides, and iron oxides are strongly absorbed iodate ions (IO$_3^-$).

4. CONCLUSIONS

Tritium and $^{129}$I concentrations in precipitation at Tsukuba, Japan, were analyzed. Although concentrations of both radioactive substrates decreased steadily with time and returned to the normal levels before the accident, several pulses of high $^{129}$I concentrations were also observed. The concentrations of $^{129}$I were accompanied by those of iron. Because iron oxides are absorbed iodate ions (IO$_3^-$) and are generally rich in soils, the high-$^{129}$I pulses were likely induced by the redistribution of $^{129}$I from soils.
REFERENCES


THE $\Delta^{14}$C, $\delta^{13}$C, $\delta^{15}$N AND PLUTONIUM ISOTOPES SIGNATURES IN THE BALTIC SEA SUSPENDED PARTICULATE MATTER AND BOTTOM SEDIMENTS

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Abstract: Anthropogenic radionuclides as well as stable C and N isotopes were applied to study sources and fate of organic matter in the Curonian Lagoon and the Baltic Sea including chemical warfare agents dumping areas. The $\Delta^{14}$C, $\delta^{15}$N, $\delta^{13}$C of TOC and $^{137}$Cs, $^{241}$Am, Pu isotopes in bottom sediments (BS) and suspended particulate matter (SPM) as well as $\Delta^{14}$C, and $\delta^{13}$C in humic substances (HS), lipid and phospholipid (PL) fractions isolated from the BS samples collected in the Curonian Lagoon and in the open Baltic Sea were investigated.

1. INTRODUCTION

This study was performed to assess characteristic isotope ratios in SPM and bottom sediments with the aim of their possible application to trace the pollutants in the Baltic Sea. Activity concentrations of $^{137}$Cs, $^{241}$Am and Pu isotopes were also analyzed in soil, seawater, BS and SPM samples collected in the Baltic Sea and the Curonian Lagoon during 1997–2014. The Baltic Sea is supposed to be sensitive to contamination compared to other marine systems because of its semi-closed nature and specific biochemical conditions. Since the 19th century it has been exposed to a wide range of organic and inorganic pollutants, including chemical weapons. Due to the shallow average depth of the Baltic Sea and the wave-induced resuspension occurring in large areas of the sea, the resuspended organic matter (OM) might be kept in suspension for a long time and be redistributed over large areas [1]. Data on plutonium and carbon isotopic ratios in SPM and BS can provide important information on the pollutant transfer between sources and sinks.

2. METHODS

BS samples were collected using a Van Veen grab and Gemini Corer samplers during the sampling campaigns in the frame of the State monitoring and several other investigations in 1997–2014. Surface water samples (0.5-1 m depth) for SPM analysis were taken at 10 stations in the Lithuanian part of the Curonian Lagoon and at 16 stations of the Baltic Sea (Fig. 1). The water for the stable carbon analyses was sampled with a 5-L bathometer. Samples were stored in the dark in the laboratory until further preparation. Water samples were filtered in the laboratory through 47 mm GF/F filters, which were pre-weighed and pre-
combusted (at 450 °C, for 3 h). After filtration filters were dried at 50 °C for 4 h and re-weighed [2]. In order to remove inorganic carbon the filters were exposed to HCl fumes for 4 h in desiccators [3].

**Figure 1. Sampling locations in the Curonian Lagoon and the Baltic Sea.**

$^{137}$Cs activities were measured with an intrinsic germanium detector (resolution 1.9 keV/1.33 Mev and efficiency 42%). Am and Pu in BS and SPM were separated by the TOPO/cyclohexane extraction, then purified using UTEVA, TRU and TEVA resins (100 - 150 µm) and measured by alphaspectrometry [4,5]. Pu was then de-plated from the stainless steel disks used for alphaspectrometry, and after additional cleaning using UTEVA resins it was analyzed for the 240Pu/239Pu ratio with ICPMS (ELEMENT-2, Thermo Fischer Scientific).

Total lipid fractions (TLF) were extracted using dichloromethane, methanol and phosphatebuffermixture. The TLF were gently evaporated under the nitrogen stream at 37°C and stored at -20°C until further analysis. Neutral lipid (NL), glycolipid (GL) and phospholipid (PL) fractions for $\delta^{13}$C measurements were separated by chromatography.

The content and isotopic ratios of carbon in the samples were measured using a Thermo Scientific Delta V Advantage mass spectrometer coupled to a Flash EA 1112 elemental analyzer. Measurements of $\delta^{13}$C in individual PL biomarkers were carried out with Finnigan Trace GC ultra-gas chromatograph, equipped with a 30 m long non polar 5% phenylmethylpolysiloxane capillary column (DB-5; 0.25 mm, 0.25 µm), connected to the Thermo
Finnigan Delta plus Advantage stable isotope spectrometer. Helium was used as a carrier gas. Humic acids were separated using the conventional alkali extraction. The Shimadzu Multi-Dimensional GC/GCMS System was applied for hydrocarbon (HC) determination in BS. Measurements of $\Delta^{14}C$ in BS and in different classes of organic substances extracted from BS were carried out using a 1.0MV HVE Tandetron AMS.

3. RESULTS

Activity concentrations of $^{239,240}$Pu in surface samples of the 0 – 3 cm BS ranged from $0.023 \pm 0.002$ Bq/kg to $4.3 \pm 0.3$ Bq/kg (mean value – $1.0 \pm 0.1$ Bq/kg) while in SPM they ranged from $0.13 \pm 0.01$ Bq/kg to $1.3 \pm 0.1$ Bq/kg. Activities of $^{241}$Am varied from $0.13 \pm 0.03$ Bq/kg to $1.2 \pm 0.2$ Bq/kg and from $<0.002$ Bq/kg to $2.4 \pm 0.3$ Bq/kg in SPM and BS samples in 2012-2014, respectively. $^{238}$Pu/$^{239,240}$Pu activity and $^{240}$Pu/$^{239}$Pu atom ratios have shown that the Chernobyl-derived Pu in SPM varied from 5% to 38% with the largest amount in the smallest SPM of 0.2 – 1 µm in size collected at the Klaipėda Strait in 2011 – 2012. The contribution of the Chernobyl-derived Pu in BS collected at the sampling station in the open sea was rather small. $^{240}$Pu/$^{239}$Pu atom ratios in the BS collected at the chemical warfare agent dumping sampling stations varied from 0.179 to 0.190. The obtained data indicated transport of the Chernobyl-derived plutonium from the land to the Baltic Sea. Contrary to Pu isotopes the data on activity concentrations of $^{137}$Cs in the BS indicated its redistribution in the Curonian Lagoon – the Baltic Sea system that points to certain limitations in the application of $^{137}$Cs in the tracer studies.

The $\delta^{13}C$ values in BS varied from -30.7‰ to -23.7‰ while the highest values were found at the stations in the open sea waters. The $\delta^{13}C$ values of particulate organic carbon (POC) in the Curonian Lagoon surface waters ranged from -37.2‰ to -25.4‰ whereas in the Baltic Sea surface waters they varied from -31.9‰ to -21.3‰. The $\delta^{15}N$ in SPM showed broad variations at the studied sampling stations (from 1.2‰ to 8.7‰) in the Baltic Sea and from 0.9‰ to 11.3‰ in the Curonian Lagoon. The isotopic signatures of $\delta^{13}C_{POC}$ and $\delta^{15}N_{PON}$ in POC in the Baltic Sea in all seasons revealed the transport of the SPM from the Curonian Lagoon. The contribution of the non-marine organic matter was estimated via application of a carbon isotope mixing model [6]. It was found to be about 90% in the Curonian Lagoon and 50% in the Baltic Sea coastal waters [7].

$\Delta^{14}C$ of the total organic carbon (TOC) and the TLF extracted from BS varied -453‰ to -7‰ and from -820‰ to -103‰. Generally, $\Delta^{14}C$ of the TLF has shown depleted values and bigger variations (down to -800‰) than in the TOC. There has been no correlation with the water depth layer above the sediments. $\Delta^{14}C$ values of TOC, total hydrocarbon (THC), diesel hydrocarbon (DHC) and mineral oil hydrocarbon (MOHC) fractions in bottom sediments of the Curonian Lagoon (KM10 station) and in the open Baltic Sea were measured. No correlation was observed between $\Delta^{14}C$ and HC fractions (Pearson corr., sig.: THC = -0.015, 0.957; DHC = -0.026, 0.926; MOHC = -0.001, 0.996). The $\delta^{13}C$ values of TOC, HS and the TLF extracted from BS varied between -29 and -24‰, usually with lower values in the TLF. The $\delta^{13}C$ values in the L, GL and PL fractions isolated from BS varied between -30 and -28‰. The $\delta^{13}C$ values in individual PL biomarkers estimated by the application of the compound specific techniques showed the widest variations (from -37.6‰ to -25.1‰).

4. CONCLUSIONS

Large variations in Pu isotope activity and atom ratios showed the possible application of the Chernobyl-derived Pu to trace the pollutants of the terrestrial origin. The $\Delta^{14}C$ and $\delta^{13}C$ of TOC in BS, HS, lipid and PL fractions isolated from the BS varied with different substances and
sample locations ($\Delta^{14}C$ for TOC – from -453‰ to -7‰ and for the TLF – from -820‰ to -103‰ as well as $\delta^{13}C$ for TOC – from -31‰ to -23‰ and for TLF – from -34.5‰ to -27.9‰). Large variations (and differences) between $\delta^{13}C$ and $\Delta^{14}C$ values of the TOC and the TLF values in BS were found. Comparison of the data of $\delta^{13}C$ with $\Delta^{14}C$ has indicated that the $\delta^{13}C$ measurements are important pre-requisite for obtaining valuable radiocarbon data. Results indicated that the organic compounds containing a significant amount of old carbon can affect the $\Delta^{14}C$ values, so that the TOC of the BS needs to be determined before $^{14}C$ dating. The obtained data can be used for the estimation of sources and redistribution of organic substances in the studied area.

ACKNOWLEDGEMENT

Financial support provided by the Research council of Lithuania (contract Nr. MIP-080/2012).

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HIGH URANIUM CONCENTRATION ON A BOTTLED BRAZILIAN MINERAL WATER

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Abstract: Testing several bottled mineral water produced at Rio de Janeiro State; it was observed that one brand presented high uranium content. It was verified that in fact this company has several producing wells presenting a large gradient on the uranium concentration reaching up to 62 µg L\(^{-1}\). Based on the chemical analysis, it was verified the presence of, at least, two different water bodies, and also a strong relationship between the uranium and the fluoride concentration.

1. INTRODUCTION

During the countrywide survey carried out during early 2000, the highest uranium concentration observed on over 200 Brazilian mineral water brands was 7.5 µg L\(^{-1}\) [1]. In fact, national surveys shows that uranium concentration in bottled mineral water above the current WHO limit (30 µg L\(^{-1}\)) is quite unusual, among 158 Italian brands only one presented uranium above this value or the highest value observed after the analysis of 908 bottled water in Germany the highest observed concentration was 16 µg L\(^{-1}\) [2, 3].

In general, it has been observed that the presence of uranium in groundwater is determined by the existence of a uranium rich mineral phase associated with presence of uranium complexing agent in the water such as fluoride or bicarbonate [2-4].

2. METHODS

Two kinds of water samples were analyzed: samples bought at the local market and samples taken directly from the wells existing at the producer facility. The following parameters were determined on every sample: pH, conductivity, alkalinity, sulfate, nitrate, chloride, fluoride and elements (ICP-MS).

Durov and Piper diagrams as well as Stiff diagrams were draw using the RockWare Aq QA software.

3. RESULTS

At the beginning, the uranium concentration in this particular brand was monitored buying it at the local market. During one year, 15 samples were analyzed with uranium content ranging between 8.5 and 32 µg L\(^{-1}\) and, based on the labels, two springs should be in operation. It was verified that the uranium concentration was highly correlated with both fluoride and
bicarbonate. However, the chemical composition didn’t fit with the label values and trace elements like uranium had quite uneven values.

During a visit realized to the facilities, it verified the existence of three producing wells and another three new wells under commissioning process. Samples were taken not only from these six wells but also of the bottled water under production at that time.

The uranium concentration on the three producing wells were 1.5, 5.2 and 60 µg L⁻¹. Based on the, the first conclusion is that what is found on the bottle is a mixture from the well containing 60 µg L⁻¹ with the other two wells, which explains the observation about the chemical composition.

Two of the three new wells presented uranium concentration around 60 µg L⁻¹ and the other one below 1 µg L⁻¹. Based on the results of these six wells, it was possible to delimitate the region where high uranium content were observed and orientate the company about the future policy related with the use these wells.

Stiff diagrams show the existence of two end members and also of wells containing a mixture of them. Based on plots like uranium versus fluoride and uranium versus bicarbonate it is possible to verify and to calculate the mixing ratio between the low and the high uranium content waters.

4. CONCLUSIONS

The water sold at the market not represents in fact what exists on the label but a blend of the existing wells. It was possible to delimitate the region where high uranium waters is observed enabling the producer to avoid it. The existence of two end members is possible to be verified on the chemical composition as well as on the geographical distribution of the wells inside the facility.

REFERENCES

USE OF STABLE AND UNSTABLE ISOTOPES TO STUDY THE EFFECT OF THE DISPOSAL OF FLY ASH ON THE POLLUTION OF SHALLOW GROUNDWATERS: THE EXAMPLE OF THE KORADI AND KHAPERKHEDA THERMAL POWER PLANTS (MAHARASHTRA, INDIA)

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Abstract: An increasing amount of fly ash from thermal power plants is produced in India every year. Its disposal is generally done in ponds after it is mixed together in suitable proportion of water to make it in a slurry form.

In this work we studied the impact on local water resources of fly ash produced in the Koradi and Khaperkheda thermal power plants (district of Nagpur, Maharashtra - India) where sludge is disposed in three large ponds established in an area where the population of many small villages uses groundwaters for drinking and domestic purposes.

Here, groundwater locally exceeds the concentration limits recommended by the World Health Organization for Mg$^{2+}$, Ca$^{2+}$, NO$_3^-$, SO$_4^{2-}$, Total Dissolved Solids (TDS) and for some minor elements like As, Mo, V and U.

As a first step a new geological map of the study area has been prepared to understand the possible water-rock interactions. Then, an extensive geochemical survey of groundwater, stream water and fly ash was also carried out to identify the possible origin of the pollutants and to discriminate between geogenic and anthropogenic sources.

Analyses carried out on oxygen and hydrogen isotopes suggest scarce interaction between the water temporarily stored in the ponds and groundwaters. Data also highlight that the high salinity measured in the polluted wells cannot be produced by evaporation and subsequent infiltration of stream waters draining from the ponds in the local aquifer. $^{87}$Sr/$^{86}$Sr values, when associated with Sr/Ca ratios, point out the main role of industrial waters on the share of pollution due to sulphates in the villages of Masada, Khairi and Kawatha. Here, the analytical results suggest that a large part of the sulphates in the groundwater of the villages of Masada, Khairi and Kawatha originate from the infiltration of industrial water from tens of factories that mix fly ash with relatively high quantities of gypsum and lime for the production of bricks.

Uranium isotopic analyses clearly show the evidences of the interaction between groundwaters and aquifer rocks and confirm again the scarce influence of sludge waters. A new conceptual model based on the study of the isotopes of radium was proposed and used to estimate the short residence times of groundwaters. This model highlights that high salinity can't be in any case attributed to a
prolonged water-rock interaction but it is probably due to the influence of untreated waste waters of domestic and/or industrial origin on the shallow and vulnerable aquifer.

In addition, the interaction with the relatively U-rich Gondwana units, like Talchir formation, is probably the cause of the high concentration of this element. Results showed how the relatively high concentrations of Mo, As, B and F in circulating waters are linked to the leaching from fly ash, also pointing out a direct spatial correlation between the concentration of fluorides in the groundwater and their closeness to the ash ponds.
Abstract: The agriculture represents the main activity in Argentina with an intensive use of agrochemicals. Among them, nitrates and organochlorine pesticides, highly persistent, were used since 1945, but nowadays are forbidden. Particularly endosulfan was the last organochlorine banned (July 2012). Agrochemical transport and fate are influenced by many processes, including volatilization, runoff, absorption, biochemical decomposition and leaching, with the potential contamination of groundwater. The aim of this work is to establish the relationship among organochlorine pesticides, nitrate and groundwater residence time, in the Pampeano aquifer at the southeast of the Province of Buenos Aires, Argentina. Groundwater samples were taken from four groups of nested piezometers in different locations: Vivoratá, INTA, San Manuel, Lobería. Each group included concrete isolation wells to 12m, 24m and 48m. The highest pesticide concentrations were found at deepest layers with a predominance of endosulfans and coincident with residence times of about 50 yr. At shallow depth ($^3$H/$^3$He apparent age, 12-20 yr) the occurrence of pesticides and nitrates was more related to interactive effects of agricultural practices, and local geologic features through local flow systems, being endosulfans the main organochlorine pesticide group found in all wells.

1. INTRODUCTION

The extensive agriculture constitutes one of the main activities in Argentina. During the last 30 years, soybean cropping area grew 600% in Argentina; it was associated
with the adoption of direct seeding technique and agrochemical uses. The use of organochlorine pesticides started 70 years ago, with the launch of DDT in 1945. Nowadays all of them are forbidden but due to the high persistence they are still present in all matrixes. Particularly endosulfan, the most widely used insecticide on soybean cultures, was banned in Argentina in 2012. Moreover, since the mid-19th century, nitrate has been used in the agricultural system to boost productivity. As a result, agricultural systems contain nitrogen well above natural levels. Increased use of agrochemicals in agricultural fields has become one of the major environmental threats to water resources. Agrochemical transport and fate are influenced by many processes, including volatilization, leaching, adsorption and biochemical decomposition. Among them, leaching receives particular attention due to their potential impact on groundwater resources. Moreover, recharge by rain or irrigation water and the adsorption–desorption interactions with soil particles would determine the extent of agrochemicals mobility through the soil profile. The concentrations or these compounds in groundwater will be directly related with physicochemical characteristics of pollutants and the residence time of groundwater sample.

The aim of this work is to establish the relationship among organochlorine pesticides, nitrate and groundwater residence time, in the Pampeano aquifer at the southeast of the Province of Buenos Aires, Argentina.

![Figure 1](image1.png)

*Figure 1. Location of the nested piezometers (a) and design of the sampling wells (b).*

2. METHODS

Groundwater samples were taken from four groups of nested piezometers in different locations: Vivoratá, INTA, San Manuel, Lobería (Figure 1). Each group included a shallower 12 m depth, an intermediate 24 m depth with concrete isolation until 12 m, and a deeper 48 m depth with concrete isolation until 24 m. Groundwater residence time was determined by $^3$H/$^3$He method according to the procedure described in Martínez et al. [1]. Nitrate was determined by spectrometer UV-VIS. $\delta^{15}$N-NO$_3$ and $\delta^{18}$O-NO$_3$ were determined at the laboratories of the Waterloo University (Canada). For organochlorine pesticide analyses, all samples were handled on glass or aluminum material pre-washed with hexane and spiked with PCB #103 as internal standard. Solutions were liquid–liquid extracted according to Gonzalez et al., 2012 [2]. Briefly, solutions were horizontally shaken for 2 h with a mixture of dichloromethane:hexane (2:1), obtaining the organic layer for further clean up. Pesticides
were quantified according to Miglioranza et al. (2003) [3], using a Shimadzu GC-ECD 17A equipped with a fused-silica capillary column of 30 m, SPB-5.

3. RESULTS

Nitrate concentrations ranged between 10.5 and 92.5 mg/L. The isotopic relationship of the nitrate isotopes $\delta^{15}$N-NO$_3$ vs $\delta^{18}$O-NO$_3$ into the scheme developed by Kendall [4] showed that its main source is manure and septic waste. The nitrate concentrations decreased with depth according to the expected behavior, excepting for the INTA piezometers where an opposite distribution was observed. The $\delta^{15}$N-NO$_3$ vs NO$_3$ (mg/L) relation indicates that denitrification can be taking place in the top layers in this case.

![Figure 2. Organochlorine pesticides in wells at different depths (12, 24 and 48 m) and $^3$H/$^3$He apparent age (years).](image)

Organochlorine pesticides showed values in the range of 0.5 ng/L to 50 ng/L, with the highest concentrations in wells from INTA. The area belongs to the National Institute of Agriculture where many practices about pesticide behavior are carried out since 60 years ago. In most sampling areas the highest pesticide concentrations were found at deeper layers in accordance with the most aged depth (around 50 years). A predominance of endosulfan was found in all deepest layers with a relation $\alpha$-/\(\beta\)-endosulfan >1. It is remarkable that endosulfan is the pesticide with lowest Kow that enhance the movement to deeper layers and it has been applied since 50’s.

In the shallow layers from INTA and Loberia, a particular behavior was found. In both areas a predominance of trans-nonachlor and/or heptachlor was observed at 12m, corresponding to residence times in the order of 25 years. It agrees with the intensive use of these pesticides in the area, mainly on potato cultures during the period 1990-2013.

The lower pesticide levels in the middle depth of the wells could be explained by several facts, such as heavy rainfall during those periods (1980, some flooding episodes) could lead to dilution effect, affecting all areas.
4. CONCLUSIONS

The occurrence and fate of nitrate (NO$_3^-$) and pesticide levels in groundwater were evaluated in four groups of nested piezometers in different locations: Vivorató, INTA, San Manuel, Lobería, adjacent to agricultural watersheds in the Atlantic coastal plain. It was related to the groundwater residence times using isotopic analyses, in order to understand possible sources and events in chemicals enter to saturated zones. The results demonstrate the interactive effects of agricultural practices, groundwater residence times, and local geologic features on the transfer of NO$_3^-$ and pesticides through local flow systems, being endosulfans the main organochlorine pesticide group found in all wells.

REFERENCES


Abstract: If not properly disposed, wastes can lead to contamination of surface and groundwater. In the developing countries the correct destination of wastes often remains a great challenge. São Francisco do Sul Island, Brazil, is located on the northern coast of the Santa Catarina State in Babitonga Bay estuary vicinity. The use of different techniques (geophysical surveys, SPT, classical chemical) and isotopic tracers ($\delta^{13}C$, $\delta^{2}H$, $\delta^{18}O$) were proposed to identify contamination in an area of inadequate waste disposal. Results will provide data to safeguard water resources and to direct environmental remediation actions.

1 INTRODUCTION
Correct waste disposal remains one of the major challenges in developing countries. If not properly disposed, wastes could lead to contamination of surface and groundwater in their immediate environment [1-3]. In Brazil, efforts have been made in order to develop policies in this area, identifying environmental liabilities and recovering the degraded areas by improper waste disposal. The leachate impact of an unlined closed dumpsite on groundwater and water resources was evaluated in São Francisco do Sul Island, Southern of Brazil. This site received different types of wastes from 1980 to 2002, when it was closed by using classical engineering solutions with coating the area with compacted clay. The area has no leachate collection. Conventional assessing programs involve sampling of ground and surface waters surrounding a dumpsite for chemical indicators of contamination, such as ammonium, chloride, and heavy metals. This conventional methodology may not be effective in environments where the background levels of many of these chemical indicators are already high, such as shallow groundwater areas (especially coastal areas) or sites with contamination that pre-dates the disposal. So, additional tracers have been adopted, as $\delta^{13}C$ from dissolved organic carbon (DIC) to identify biogeochemical processes, as methanogenesis, within the dumpsite area, and $\delta^{2}H\delta^{18}O$ from water to verify possible mixing or isotopic exchange with other sources. This work applies different techniques and isotopic tracers to identify contamination in an area of inadequate waste disposal. Results will provide data to safeguard water resources and to direct environmental remediation actions.

2. SITE DESCRIPTION
The region is located in the southern Brazilian coast and rests against crystalline massifs that forms the Serra do Mar coastal range. Its most prominent geomorphological characteristic is the scarped coastal range that, when intersecting the coastline, creates coastal embayments where strandplains, and less frequently estuarine systems, are found [4]. São Francisco do Sul Island is located on the northern coast of the Santa Catarina State in Babitonga bay estuary vicinity. It covers an area of about 280 km$^2$ with an approximate length of oceanic coastline of 40 km. The facing inner shelf is identified by a low-gradient slope (~ 0.01%) with the –
50 m contour at around 45–75 km away from the shore [4]. The climatic oscillations, which occurred during the Holocene, shaped terraces, beach dune ridges, and barrier beaches. The climate is subtropical (Cfa, according to Koppen's classification) with wet summers and moderately dry winters. The annual rainfall varies between 1500 and 2000 mm and the mean average temperature is 18°C. The interactions between tropical and extratropical atmospheric systems control the climate in southern Brazil [5].

3. METHODS

In order to explore the area different techniques were employed. First of all, a planialtimetric investigation was performed to carry out geophysical surveys by means of vertical electrical sounding (VES) and electrical profiling methods inside the dumpsite area and standard penetration test (SPT) inside and outside of the area. After this first approach, piezometers and monitoring wells (MW) for groundwater were executed to allow the collection of groundwater samples. The MW location followed water table level being two in upstream (PM1 and PM4) and downstream (PM3) of the area. Six water samples were collected: 4 from groundwaters (PM1 to PM4), being only one inside disposal area (PM2). Two points from rivers (upstream and downstream of the area) were also sampled. In situ measurement involved electrical conductivity and temperature using an Aquaread-2000 probe calibrated before the campaign. Samples for stable isotope analysis were collected and prepared according to standard procedures [6, 7], respectively. Chemical analysis where performed in Brazil according to standard methods [6]. All gases were analysed on a Finningan™ MAT 250 Mass Spectrometer at ISO4 s.n.c., Turin, Italy.

4. RESULTS

The research started from zero, because no information about type of waste disposed, volume, etc. was given. The planialtimetric survey provided necessary data to visualize the geometry of massive and surface water flow direction and georreferencing points to vertical electrical sounding and electrical profiling. Results (Figure 1) identified four geoelectric layers: landfills / coverages, waste and Quaternary sediments until reaching the weathered rock (at depth 30m, not exhibited in the Figure 1).

![Figure 1: Geoelectric layers](image)

In addition it was possible to investigate ground boundaries of the waste disposal area. It is also observed that in the eastern portion of the waste deposit, it presents higher resistivity than in other portions of the deposit area. This may be representing a different residue and/or even compacted waste, the first hypothesis is the most suitable. It is possible also observe that there is flow from the massive to the surroundings. The main flow directions are west and northwest (indicated by arrows in the images), until depth 12.2m. VES allowed identifying heterogeneities in the disposal materials that directly influence the interpretation of
geoelectric layers. Variations ranged from 0 to 16000 ohm.m, depending on the layer, the most conductive materials (waste, soil amendments) have less than 20 ohm.m. From the VES result it can be seen that the coating layer has an average thickness of 0.3 m, the layer of residue has an average thickness of 6.5m. The mean water table level, indicated by the decrease in resistivity curve, inside the waste massive is at 4.75m depth. From these results, SPT, piezometers and monitoring wells for groundwater were performed to identify water table in surroundings and to collect water samples inside and outside the massive. Results are presented in Figure 3 a), and Table 1. From the analysis it can be observed:

1. PM2, inside the area, presents δ\(^{13}\)CDIC isotopic composition consistent with leachate, δ\(^{13}\)C: +12.01‰, caused by methane-producing bacteria, moreover, it presents also highest EC among the monitoring points. Other point that presented more enriched δ\(^{13}\)CDIC is PM3, δ\(^{13}\)C: -3.94‰, located in the outside area in the same direction of the arrows in Figure 1. This result can be explained by a mixing of leachate, groundwater, and stream water located around the area, in fact, SPT results show that the water table is at depth of 0.10m. Other points presented more depleted values (mean δ\(^{13}\)C: -15.06‰). For upstream and downstream stream water δ\(^{13}\)CDIC value lies within the expected range of δ\(^{13}\)C values that have been previously reported for stream water [8, 9] suggesting no contamination in surface water.

2. Stable isotopes of water molecule Figure 3b) show more enriched values in accordance to coastal waters and deviate from the Global Meteoric Water Line. Little enrichment in δ\(^{2}\)H was observed, even at PM 2 (and could indicate gas leak by drains located in the massive), nevertheless δ\(^{2}\)H results display more enriched values than other wells in the region [10].
Exception is point PM4. The isotopic composition of PM4 is very similar to groundwaters from Bacia Hidrografia do Rio Cubatão [10], this can suggest an interconnection among groundwaters in the region. SPT results confirm that PM4 monitoring well is the only in the area that reached the bedrock (and a fracture could explain this more depleted value). The samples (excepting PM4) that are most enriched in $\delta^{18}O$ show a trend of minor EC, and can evidence mixing between surface (minor EC and $\delta^{18}O$ values) and subsurface groundwaters.

5. CONCLUSION

The use of different techniques in an area with no preliminary data allowed for a an integrated view of the processes in a zone subject to improper disposal of waste without proper sanitary measures required. Results confirms that human activities, specially when made subsidiary by public authorities, change natural characterististics of natural resources. Classical engineering solutions have reduced the effects of groundwater contamination in the area, but measures of underground drainage and treatment of the leachate within the waste are needed. Furthermore, results spotted a possible groundwater interconnection in the region, previously mooted by the author. Also, the importance of assessing the aquifers in the region (this is not done) and the possible interconnections between them proper to protect the water source from environmental contamination of impacted areas.

REFERENCES

ISOTOPE HYDROGEOCHEMISTRY OF ARSENIC INFESTED GROUNDWATERS IN TA KHMAU AREA, CAMBODIA – PRELIMINARY OBSERVATIONS

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Abstract: Groundwaters in Ta Khmau area, south of Phnom Penh, Cambodia are infested with high concentrations of arsenic. River Basak, a tributary of River Mekong, flows through the area. The area consists of almost flat alluvial sediments and has numerous ponds/lakes, wetlands and small rivers. Sampling campaign was undertaken during September 2013 for stable isotopes of hydrogen and oxygen, tritium and chemistry. A total of 24 water samples were collected and analyzed. Stable isotope composition shows wide variation from -4.08‰ to -9.29 ‰ for $\delta^{18}O$ and samples fall along a regression line $\delta^2H = 6.34\delta^{18}O - 5.76$ (n=24; $r^2=0.98$) showing some evaporation effect. The river water is highly depleted in stable isotopes ($\delta^{18}O = -9.29 ‰$) and probably precipitation as well. Bangkok precipitation data with precipitation weighted least square regression was used as a reference meteoric water line represented by the equation $\delta^2H = 7.678\delta^{18}O + 7.24$ (n=355; $r^2=0.97$). A few arsenic-infested groundwater samples are tritium-free whereas some show measurable amount of tritium. In general, the tritium content varies from 0 to 2.1 TU. The lower tritium and depleted stable isotopes are thought to be the result of land-based sources of atmospheric moisture.

Chemically, the groundwaters are mostly of Ca-Mg-Na-HCO$_3$ type with signs of base exchange reactions as seen from Piper diagram. Arsenic concentration varies from <5 µg/L to 960 µg/L. Fe, Mn and Sr are present in µg to mg levels. A few samples show presence of fluoride, maximum being 2.8 mg/L, but most samples have fluoride levels below detection limit. Trace elements like Cd, Cr, Cu, Ni, Pb, Zn, Hg were found to be below detection limits. High concentrations of As are accompanied by relatively higher concentrations of Fe and Mn.

Comparatively enriched stable isotope values and presence of tritium in some of the arsenic-infested groundwaters indicate that ponds/lakes and wetlands play an important role in release of arsenic from sediment to groundwater under anoxic conditions. The observed variations are attributed to facies changes and heterogeneity of sediments in the area.
CHEMICAL AND ISOTOPE STUDIES OF THE IMPACTS OF LANDFILL ON WATER QUALITY IN THE SITE OF ANDRALANITRA, ANTANANARIVO-MADAGASCAR

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Abstract: The present study deals with the impacts of the landfilling practices in the site of Andralanitra on the surrounding water resources, using chemical (Ca$^{+2}$, Mg$^{+2}$, Na$^{+}$, K$^{+}$, Cl$^{-}$, SO$_{4}^{2-}$, HCO$_{3}^{-}$, NO$_{3}^{-}$) and isotope tools ($^{2}$H, $^{18}$O, $^{3}$H). Results showed that the landfill has negative impact on groundwater just down gradient of it (highly contaminated with high major ions concentrations and tritium contents, up to 22 TU). Upstream and further downstream the landfill; groundwater has low TDS values, but high nitrate and chloride concentrations, probably originating rather from the on-site sanitation and farming at the vicinity of the water points than from the landfill leachate. The abrupt drop of the tritium contents from 22 TU to natural values (2-3 TU), measured further down gradient, seems to confirm a lesser influence of the landfill further from the waste disposal site, assuming the tritium decay and the rapid percolation through the sandy aquifer. The stable isotopes results showed a direct infiltration of rainfall. Similarities of the stable isotope composition between geographically close spring and dug well waters seem to indicate that they are of the same origin. The presence of impervious layers at greater depth may prevent contamination to spread over into the aquifer.

1. INTRODUCTION

Antananarivo, the capital city of the nation island of Madagascar is the most populated city in the country, with about 3 million inhabitants [1], of which half belong to the Antananarivo municipality (AM) alone. The landfill site of Andralanitra has been used by the AM for household wastes disposal for more than 45 years and is used without neither external protection nor leachate collection system [2]. Originally planned to receive waste within an area of 130,000 m$^{2}$, the site is currently overloaded due to the increasing population over the years and occupies 50,000 square meters more than the authorized area. With a total weight of waste between 450 and 600 tons daily, the site height reaches 10 to 15 m [3]. The site is a high risk of contamination source for the different water bodies in the landfill’s surroundings. The present work aims to study the impact of the landfill on the water quality using chemistry and isotopes.

2. SITE DESCRIPTION

The study area is located in the Central Highlands Plateau, District of Northern Antananarivo, and region of Analamanga. It is located at about 10 km northeast from Antananarivo. The
landfill site is almost surrounded by paddy rice fields, except in the north western part, where it is limited by small agglomeration of households. The Ampasimbe River, downstream of the landfill site, limits the study area on the south-eastern side (figure 1).

Figure 1. Geographical location of the study area, with sampling points displayed

The climate can be divided into two distinct seasons: the hot and rainy season from October to April, and the cold and dry season from May to September. The Central Highlands Plateau is underlain by Archaean and Neoproterozoic igneous and metamorphic rocks of the Basement Complex [4]. The main aquifer reservoir of the study area is composed of thick layer (more than 10 meters) of alluvial sand, which covers the whole plain area. The underlying bedrock covers tens of centimetre layers of coarse sand, playing the role of drainage, considering its permeability. The immediate overlying formation of the basement rocks is composed of mica enriched sandy clay material, kaolin feldspar and ferromagnesian minerals. The aquifer underlying the clayey formations is semi-confined, in particular on the interfluves, while it is confined at the bedrock level and in the alluvial plain. The network of fractures of the crystalline basement serves as water storage amid the substratum [5]. The occurrence of several emerging springs in the alluvial plain allows the flooding of paddy rice fields, even during the low flow period [6].

3. METHODS

Two sampling campaigns were performed in October 2011 and August 2012, almost on the same sampling sites. Twenty one samples, collected from 14 traditional dug wells, 5 springs, the Ampasimbe River, and a small lake were collected. Sampling points were located within 500 m upstream and downstream the landfill site. Physical parameters including pH, Eh, EC, T, DO,
TDS, and alkalinity were measured in the field. All samples were collected in plastic polyethylene bottles: 50-mL bottle for stable isotope analysis, 1000 mL bottle for tritium analysis, 50-mL bottle each for anion and cation. Samples for cation analysis were treated with three drops of concentrated nitric acid. The analyses were carried out in parallel by the Water and Climate Unit, CNESTEN-Morocco and the National Institute for Nuclear Science and Technology-Madagascar (for intercomparison purpose within RAF8048 regional project, entitled “Building Capacity in Support of Regional and Sub-Regional Water Resources Planning, Development and Management in Africa).

4. RESULTS

Isotope (table 1) and chemical (table 2) results are given below:

<table>
<thead>
<tr>
<th>Table 1. Isotope results from the 2011 sampling campaign</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Well</strong></td>
</tr>
<tr>
<td>Minimum</td>
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<tr>
<td>Maximum</td>
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</tbody>
</table>

| **Spring** | |  |
| Minimum | -7.69 | -51.67 | 1.58 |
| Maximum | -6.43 | -41.89 | 2.36 |

| **River** | -2.78 | -25.81 | 3.23 |

| **Lake** | 2.26 | 3.97 | 2.54 |

<table>
<thead>
<tr>
<th>Table 2. Chemical results from the 2011 sampling campaign</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Well</strong></td>
</tr>
<tr>
<td>Minimum</td>
</tr>
<tr>
<td>Maximum</td>
</tr>
</tbody>
</table>

| **Spring** | |  |
| Minimum | 1.11 | 0.49 | 2.94 | 2.36 | 1.58 | 4.80 | 0.00 | 9.90 |
| Maximum | 8.98 | 5.89 | 26.32 | 13.40 | 26.70 | 13.6 | 0.35 | 77.00 |

| **River** | 5.9 | 2.06 | 10.26 | 4.76 | 5.16 | 40.2 | 2.78 | 5.58 |
| **Lake** | 9.41 | 3.81 | 45.10 | 16.76 | 55.94 | 61.5 | 1.54 | 15.58 |

Concentrations are in mg/L, 10 out of 14 well water samples have nitrate concentration higher than the WHO admissible value of 50 mg/L.

5. DISCUSSION

The highest tritium value refers to well water (W1) collected from dug well located just down gradient the landfill. A tritium value of 10.43 TU was also measured in another well close to W1. The chemical and tritium values of those two well waters differ substantially from those of the well waters located upstream and further downstream of the landfill, except for chloride and nitrate, which are also high in most of the latter samples. This is likely due to on-site sanitations and farming at the vicinity of the water points rather than from the landfill. The landfill has negative impact on the water quality just down gradient of it but seems to have lesser influence further downstream. The abrupt drop of the tritium contents from 22.82 TU to natural values (2-3 TU), measured further down gradient, seems to confirm that assumption, assuming the tritium
decay and the rapid percolation through the sandy aquifer. The stable isotopes results showed a direct infiltration of rainfall, with dug well and spring waters plotting along the local meteoric water line (Figure 2). Similarities of the stable isotope composition between geographically close spring and dug well waters seem to indicate that they are of the same origin. The presence of impervious layers at greater depth may prevent contamination to spread over into the aquifer.

Figure 2. Stable isotope composition of the different types of water samples in the study area

6. CONCLUSION

Chemical and isotope results showed that the landfill is negatively affecting the groundwater quality just down gradient of the waste disposal site. The low major ions concentrations, except for nitrate and chloride, and the tritium content of natural origin, measured in the groundwater samples further from the landfill, suggest that contamination from the landfill leachate does not reach the aquifer downward, due probably to the presence of impervious layers at greater depth. The high nitrate and chloride concentration in the well waters would rather originate from the presence of on-site sanitation and/or farming close to the water points.

REFERENCES

URANIUM ISOTOPES IN SURFACE WATERS AND GROUNDWATER IN PORTUGAL

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Abstract: Activity concentrations of uranium isotopes and $^{234}\text{U}/^{238}\text{U}$ isotope ratios are reported in surface waters from uranium mine drainage, to rivers, estuaries and the ocean. Uranium isotope concentrations are reported also in groundwater from several geological formations in Portugal. Activity concentrations varied widely and uranium isotope ratios were not constant in the hydrosphere. Average isotope ratios are presented for several hydroic domains and discussed. High $^{234}\text{U}/^{238}\text{U}$ isotope ratios in groundwater are indicative of potential radiation exposure of humans above radiation safety guidelines if groundwater is used as drinking water.

1. INTRODUCTION

Uranium in continental waters originates in salts dissolution from earth crust. Ratios of uranium isotopes in the lithosphere are well established and are nearly constant [1]. Uranium isotope $^{234}\text{U}/^{238}\text{U}$ ratios in dissolved uranium are however variable in some water bodies depending on a number of chemical and physical factors that may facilitate dissolution of $^{234}\text{U}$ isotope in comparison with $^{238}\text{U}$. This is likely due to the effect of atom recoil following the radioactive decay of $^{238}\text{U}$ with partial destruction of mineral lattice [1]. Uranium isotope concentrations and uranium isotope ratios in several water bodies, ranging from groundwater to ocean water, were determined to identify patterns of isotopic ratios in such waters.

2. METHODS

Analyses of radionuclides were performed on 0.45 μm pore size membrane filtered water samples from uranium mine drainage, rivers, estuaries and Atlantic Ocean. Radionuclides were separated and purified by radiochemistry methods and determined by alpha spectrometry using techniques described elsewhere in detail [2,3]. In brief, spikes of isotopic tracers ($^{232}\text{U}$, $^{229}\text{Th}$), were added to each sample as internal tracers to allow for determination of the chemical recovery yield. Radionuclides once electroplated onto stainless steel discs, were measured with low background silicon surface barrier or ion implanted detectors from ORTEC EG&G. Quality assurance of analytical results was provided through analysis of certified reference materials and frequent participation in international intercomparison exercises [3, 4].

3. RESULTS

Activity concentrations of uranium isotopes $^{238}\text{U}$ and $^{234}\text{U}$ determined in continental surface waters (rivers and lakes) are displayed in Figure 1. The whole set of these samples correspond to oxygenated waters (6.6-11.6 mg O$_2$/L), with pH between 6.27-7.61, and redox potential (Eh) between 150-360 mV. The range of activity concentrations determined for $^{238}\text{U}$ and $^{234}\text{U}$ was large, from 3.4 to 25 mBq/L of $^{234}\text{U}$, and mainly depended upon the composition of contact rocks or soils which ultimately are the uranium source. The mean
activity ratios $^{234}\text{U}/^{238}\text{U}$ was 1.04±0.04 (n=29), and no statistically significant trend or deviation from unity was observed.

Dissolved uranium in uranium mine drainage, potentially an important source of dissolved uranium and often discharged into streams and rivers, displayed varying concentrations depending upon chemical parameters. A large data set from uranium mine drainage in Portugal showed concentrations ranging from 15 to 20,100 mBq/L of $^{238}\text{U}$ with an average $^{234}\text{U}/^{238}\text{U}$ isotope ratio of 0.93±0.23 (n=18) (Figure 1).

Uranium may have a conservative behavior in river water flowing through estuarine ecosystems with a gradient of total uranium concentrations resulting from the mixture of waters (saline and freshwater), such as reported for several estuaries. However, the isotopic composition of uranium in water was not kept constant in the transition from continental/river waters to the ocean, such as observed in the estuary of Tejo with an average $^{234}\text{U}/^{238}\text{U}$ ratio of 1.13±0.04 (n=10) (Figure 2). In several estuaries similar change of the $^{234}\text{U}/^{238}\text{U}$ isotopic ratios were noticed, and most data describes $^{234}\text{U}/^{238}\text{U}$ isotope ratios above unity in estuarine water. In seawater the $^{234}\text{U}/^{238}\text{U}$ ratio is consistently >1 also and the average ratio of 1.14±0.03 was proposed the world ocean [5].

In groundwater from Portugal, activity concentrations of $^{238}\text{U}$ and $^{234}\text{U}$ uranium isotopes displayed a wide range, roughly comparable to surface waters but with a different isotopic composition. The $^{234}\text{U}/^{238}\text{U}$ activity concentration ratios in groundwater varied from 1 to 15. At the low end of this range were the samples from aquifers in the granite region of Beira province, while at the high end of the range were the samples from aquifers in shale regions of Alentejo province. The exact chemical conditions of the aquifers that produced such isotopic ratios were not fully investigated yet. These high isotopic ratios are striking and have been reported also for aquifers elsewhere [4]. The interpretation of such high ratios has been proposed based on chemical effects of atom recoil [5]. The nuclear disintegration of $^{238}\text{U}$ atoms and subsequent radioactive decay of its progeny cause destruction of the mineral lattice rendering the dissolution and displacement of $^{234}\text{U}$ atoms easier in comparison to the parent $^{238}\text{U}$, although both have the same chemical properties. Dissolution/displacement of $^{230}\text{Th}$ from the mineral lattice is also facilitated by $^{234}\text{U}$ decay and further damage of mineral lattice.

Isotope ratio $^{234}\text{U}/^{238}\text{U}$ values higher than 1 in groundwater are due to higher activity of $^{234}\text{U}$ isotope dissolved from the rocks compared to $^{238}\text{U}$. However, when this occurs the mass of total uranium in water (99.3% is due to $^{238}\text{U}$ isotope, $T_{1/2} = 4.5\times10^9$ y) practically does not change. However, the enhanced dissolution of $^{234}\text{U}$ causes a noticeable increase in the alpha activity of water due to the much higher specific activity of $^{234}\text{U}$ isotope ($T_{1/2} = 2.5\times10^5$ y) (Figure 3).

For toxicological protection of humans the World Health Organization (WHO) has recommended a limit of 15 µg U per L in drinking water. With dissolved uranium displaying a $^{234}\text{U}/^{238}\text{U}$ isotopic ratio of 1, this uranium mass concentration would correspond to the uranium activity concentration of 0.5 Bq/L of water. The regular consumption of such water as drinking water would deliver an effective radiation dose to the consumer of 0.1 mSv/y, i.e., 10% of the annual dose limit for members of the public. However, in groundwater with the isotopic ratio $^{234}\text{U}/^{238}\text{U}$ =20 and the same uranium mass concentration of 15 µg/L, the alpha
Figure 1. Activity concentrations of $^{238}U$ and $^{234}U$ in water from uranium mines, river, and groundwater. Correlation of uranium isotopes in surface waters is $R^2 = 0.999$. Groundwater samples are outliers.

Figure 2- $^{234}U/^{238}U$ activity ratios against salinity in several water types.

Figure 3- Alpha activity of water for several $^{234}U/^{238}U$ activity ratios [6].
activity concentration would 10 Bq/L and its consumption as drinking water would give rise to an effective radiation dose largely exceeding the annual radiation dose limit recommended for radiological protection of the public [6].

4. CONCLUSIONS

The $^{234}\text{U}/^{238}\text{U}$ isotopic ratio in water was determined consistently at values slightly below unity (0.93±0.23) in mine drainage and leachates from surface uranium rocks. This isotope ratio was closer to unity in surface waters in rivers (1.04±0.04) flowing across a wide range of geological settings. In estuaries the same isotope ratio increased to values higher than unity. Indeed, uranium in the particulate phase of river water discharge dissolves in saline water of the estuary and this is accompanied by an increase of the isotope ratio to 1.13±0.04. This ratio remained unchanged in seawater. In the open ocean the $^{234}\text{U}/^{238}\text{U}$ ratio in seawater averages 1.14±0.03 [4].

In contrast with aerated surface waters, groundwater from continental aquifers showed a significant departure of $^{234}\text{U}/^{238}\text{U}$ isotope ratios reported above and displayed values from 1 up to 15. Groundwater from several aquifers and in a concentration range of 0.24 to 2900 mBq/L of $^{238}\text{U}$, displayed those high isotopic ratios. This isotopic disequilibrium does not cause meaningful changes of uranium mass concentration in water, but from the radiation point of view its consumption as drinking water will originate much higher radiation dose to members of the public. Therefore, the use of groundwater as drinking water must include careful radiological risk assessment and determination of uranium isotopes by alpha spectrometry instead of mass based analytical methods.

REFERENCES


NATURAL RADIOACTIVE ISOTOPES AND WATER QUALITY IN A URANIUM MINING REGION

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Abstract: Uranium mining and milling activities in the Centre North of Portugal took place for almost one century. Concentrations of isotopes of the uranium decay series in acid mine water, treated water discharges, and river water are presented and discussed in the light of radionuclide behavior in aquatic freshwater systems and implications on radionuclide transfer to humans through water consumption.

1. INTRODUCTION

Uranium mining for nuclear fuel supply takes place worldwide. Some regions were mined since the beginning of the last century, initially for radium production followed by uranium production later. Exposure of uranium ores and uranium leaching with sulfuric acid, followed by surface disposal of milling tailings under oxidizing conditions, modify the chemical conditions of the uranium ore and contribute to dissolution and transport of uranium series radionuclides in surface waters. The distribution of naturally occurring radioactive isotopes in surface waters in an area impacted by uranium mining at the center of Portugal was investigated.

2. MATERIAL AND METHODS

The main study area selected was the catchment of River Mondego and of River Távora in the central area of Portugal, where several uranium mines and milling facilities were operated during most of the 20th century. Some of the mine sites were remediated in the last 10 years and direct discharge of acid mine waters was reduced. Several abandoned old mines still exist in the area and open pits are flooded with acidic mine water. Treated and untreated mine waters are discharged into streams that are tributaries of River Mondego, the largest river in the region flowing into the North-east Atlantic. The artificial lake of Aguieira Dam in River Mondego supplies drinking water to human populations in the region [1].

Samples of mine waters were collected in mine open pits, in mine discharges and in rivers in October 2013. Water samples were filtered on site through 0.45 μm pore size membrane filters for separate analysis of radionuclides in dissolved and suspended particulate matter (SPM) fractions. Radionuclide analyses were performed with addition of isotopic tracers and complete dissolution of SPM in a microwave digester (Mars 6, CEM). Radiochemical separation of radioelements was performed with ion exchange columns followed by electro-deposition on silver and stainless steel discs. Radioactivity measurements were performed with ion implanted 450 mm² silicium detectors and alpha spectrometers OctetePlus (ORTEC), according to radio-analytical protocols described and validated previously [2]. Results are expressed in activity concentrations (Bq/L or Bq/kg dry weight).
3. RESULTS AND DISCUSSION

Radionuclides dissolved in water from stagnant ponds in open pit abandoned mines (long contact time of water with uranium bearing rock) showed very different activity concentrations in the soluble phase. In flowing river water under different pH, redox potential (Eh), and dissolved oxygen (DO) conditions, the radionuclide concentrations and activity concentration ratios varied widely also (Figure 1).

In general, in aerated surface waters uranium was highly dissolved and thorium was very insoluble, while $^{226}\text{Ra}, ^{210}\text{Pb}$ and $^{210}\text{Po}$ radioisotopes displayed intermediate solubility. Mine water from underground mine drainage with low dissolved oxygen such as, for example, Fonte Velha Mine in the catchment of River Tâvora, displayed a different load of radionuclides with low uranium and high radium concentrations in the dissolved phase. Transport of dissolved radionuclides from mine water discharges of Cunha Baixa Mine into stream water was previously reported in the catchment of River Mondego also [3].

Although uranium series radionuclides might have been in radioactive secular equilibrium in uranium ore deposits, once exposed to oxidizing conditions radioelements underwent significant departure from radioactive equilibrium due to distinct chemical behavior. In addition, the use of sulfuric acid for in situ uranium leaching and natural acid ($\text{H}_2\text{SO}_4$) formation enhanced the dissolution of radionuclides. Chemical behavior and solubility in particular, controlled de transportation of dissolved radionuclides in surface waters [4].

The relative contribution of radionuclides to total activity of water from flooded open mine pits and rivers is exemplified in Figure 2. In water from open mine pits, $^{238}\text{U}$ and $^{234}\text{U}$ accounted for more than 90% of the radioactivity of dissolved phase, and other isotopes such as $^{226}\text{Ra}, ^{235}\text{U}, ^{210}\text{Pb}$ and $^{230}\text{Th}$ accounted for much smaller percentages in total activity. In oxygenated waters, pH may enhance the dissolution of several radionuclides such as uranium isotopes. In contrast to this the mine water from Fonte Velha Mine (underground mine, water drainage with low dissolved oxygen) displayed the largest concentrations of $^{226}\text{Ra}$ and smallest concentrations of uranium. In this mine water, the activity concentrations of dissolved $^{210}\text{Pb}, ^{210}\text{Po}, ^{238}\text{U}$ and $^{234}\text{U}$ were all low. The stream Ribeira da Pantanha, a tributary of River Mondego receiving mine drainage and seepage from milling tailings at Urgeiriça mine area, displayed high activity and a relative composition similar to water from open mine pits. This contrasted with radioactivity in Mondego water at the source (upstream mines) and in water at Aguieira Dam reservoir, located many km downstream and after strong dilution of Pantanha discharge.

The relative contribution of radionuclides in suspended particles for total activity concentration (mBq/L) in water from open mine pits was 10-29% for $^{238}\text{U}$ and similar percent to $^{234}\text{U}$, while $^{226}\text{Ra}$ accounted for 5-37%, $^{210}\text{Pb}$ accounted for 12-16% and $^{210}\text{Po}$ for 20-22%. In contrast with these surface and oxygenated mine waters, in mine water from underground Fonte Velha mine the activity concentration of radionuclides in particulates were the highest for $^{210}\text{Pb}, ^{226}\text{Ra}, ^{210}\text{Po}$ and smallest for U isotopes.
FIGURE 1. Radionuclide activity concentrations in the dissolved phase of open pit mine waters and river waters in the uranium region of center of Portugal.

FIGURE 2. Percent contribution of radionuclides to total activity in the dissolved phase of open pit mine water (Mine Boco), in drainage from an underground mine (Mine Fonte Velha) and in river waters non-impacted (Mondego source) and impacted by mine drainage discharge (Ribeira da Pantanha).
Per unit of water volume, radioactivity in the dissolved phase and in the particulate phase contributed each to about half of total activity, with variations depending on pH and particle load. Nevertheless, specific activity concentrations of radionuclides in the particulate fraction of mine waters were much higher than concentrations in soluble phase. For example activity concentrations in SPM from Mondego Sul mine were 49500±1560 Bq/kg of $^{238}$U, 8110±640 Bq/kg of $^{226}$Ra and 27500±2000 Bq/kg of $^{210}$Pb. These concentrations were about 2 to 3 orders of magnitude higher than in surface soils and river sediments in the region [1, 5]. Besides transport in dissolved phase, a significant transport of these radionuclides is associated also with suspended particulate matter in surface waters.

The dissolution of naturally occurring radionuclides in rivers flowing across uranium regions may enhance the ingestion of radionuclides with the daily intake of water and foods locally grown. In particular, the contribution of radionuclides such as $^{226}$Ra, $^{210}$Pb, $^{210}$Po and to some extent uranium isotopes as well, requires thorough radiological risk assessment. However, it must be pointed out that water with high radionuclide concentrations do occur naturally also and without relationship with mining activities [6].

4. CONCLUSIONS

In uranium regions with radioactivity enhanced by mining activity, uranium series radioisotopes get oxidized and thus may dissolve further in surface waters. In a region with uranium deposits and old uranium mines, isotopes from uranium series naturally occur in water in activity concentrations higher than in other regions of the country. In areas receiving discharges from old uranium mines, often with low pH due to sulfuric acid from in situ uranium leaching, the low pH of water is associated with higher radionuclide concentrations.

Mine drainage from underground mines and seepage from sealed waste piles, often have lower pH and low dissolved oxygen and contain in solution much higher concentrations of radionuclides such as $^{226}$Ra, $^{210}$Pb, and $^{210}$Po. Treatment of this mine drainage is required prior to discharge in order to reduce contamination of surface waters with alpha emitting radionuclides ($^{226}$Ra, $^{210}$Po) that represent a radiological hazard, actually greater than the uranium radiological hazard.

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ISOTOPIC AND GEOCHEMICAL APPROACHES TO CHARACTERIZING WATER MOVEMENT THROUGH ABANDONED MINE WORKINGS, NELSON-WOOSTER-HUMPHREY TUNNEL, CREDEE, COLORADO

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Abstract: Long term acid mine drainage (AMD) discharging from the portal of the Nelson Tunnel near Creede, CO is currently impacting water quality in West Willow Creek and the Rio Grande River. The interior of the mine has been structurally rebuilt so that we could safely go into the mine for a distance of two km to collect samples. The study utilized multiple techniques including physical hydrologic parameters, hydrogeologic information, solute chemistry, applied tracers, and a suite of isotopic analyses. The stable isotope ($^{18}$O) of the mine water is steady at $-14.82 \pm 0.15 \, \%o, \ n= 25$ throughout the year, suggesting a well-mixed groundwater system composed of equal parts winter snow ($-19.38 \pm 0.37 \, \%o$) and summer monsoon rain ($-8.89 \pm 3.13 \, \%o$). Tritium ($^3$H) values within the tunnel are primarily “tritium-dead” indicating water that is at least older than the “bomb-spike” waters of nuclear weapons testing in the 1960s. Dissolved inorganic carbon (DIC) $\delta^{14}$C values indicate mine water apparent ages of 5,000 to 10,000 years. To provide age verification for the DIC $\Delta^{14}$C results the mine water samples were also analyzed for the $\Delta^{14}$C of dissolved organic carbon (DOC) and provided ages similar to the DIC values. Additionally, three-dimensional fluorescence analyses of the DOC provided characterization of the DOC and help verify that it represented DOC that was picked up from the soil zone at the time of source water recharge and not from microbial processes in the water column. Isotopic ratios of strontium ($^{87}$Sr/$^{86}$Sr) were also analyzed to provide an additional geochemical tracer to differentiate between waters flowing along pathways having different host rock geochemistry. Results therefore suggest that mine waters are largely not directly connected to surface waters, or to the shallow groundwater (sampled from springs and domestic wells), but rather are comprised of deeper groundwater likely entering the tunnel via a system of faults associated with the graben structure. The results from this study have been used to develop a hydrogeologic conceptual model of the mine complex, which will aid in the development and feasibility analysis of targeted remediation strategies.
HYDROGEOCHEMICAL INDICATORS FOR RADIOACTIVE WASTE DISPOSAL SITE SURVEY TO THE EAST OF NILE DELTA, EGYPT.

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Abstract: The present work introduces a hydrogeochemical indicator for surveying the area to the east of Nile Delta in Egypt, to select, screen out and rank potential sites for radioactive waste disposal facility. The index and overlay methodology exemplified by DUPIT index, has been applied to determine the susceptibility of groundwater contamination through unsaturated zone reach. This provides a basis for classifying the study area into subareas and mapping them according to their suitability for hosting radioactive waste disposal facility, from hydrogeochemical point of view.

The environmental isotopes (oxygen-18, deuterium, tritium and carbon-14) have been used for verifying the results of waste disposal siting survey. The transit time of chosen six radionuclides (T, C-14, Co-60, Tc-99, Ni-59 and Sr- 90) through the unsaturated zone reach, has been calculated, based on simple hydrological / pollutant retardation model. A considerable consistency exists between the calculated radioisotopes transit times and the corresponding waste disposal suitability index. A high adoptability has been proven for using the employed indicator methodology for siting survey of radioactive waste disposal facility.