

## **Impact of transboundary air pollution on sensitive karst water resources by means of N-, O-, Pb-, S- and Sr-isotopes**

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### *Introduction*

The impact of air pollution is a substantial European and global problem which was observed even in the most remote areas of our planet. Not only surface water, but also groundwater re-sources are partly endangered by dry and wet deposition from the air. Karst and other sensitive aquifers contribute up to 90 % to the total drinking water supply in some European regions. However, they are more vulnerable to contamination than other aquifers due to short transfer times from recharge to source. Therefore, the main objective of this paper is to show possibilities to quantify the impact of air pollution on sensitive water resources (e.g. karst), to develop an innovative surveillance tool based on isotopes and meteorological considerations.

In a pilot study on a small number of samples as precipitation, soil, rock and spring waters were collected in the North front of the Northern Calcareous Alps to test the application of isotope analyses to estimate the amount of far transported contaminants and their impact on the spring water quality. The hydrochemistry and the isotopic composition of nitrate, sulphate, strontium, lead and the water molecule itself has been analysed in five laboratories, each of them specialised in a certain group of isotopes.

### *Investigation site*

The Federal Environmental Agency Vienna runs an UN-ECE-Integrated Monitoring station (Zoebelboden) within a karstified dolomite. The Zoebelboden-site is located south of Linz (Upper Austria) in the front range of the Northern Calcareous Alps in form of steep mountain ridges at an altitude of 500-950 m. The monitoring sites are divided in plateau and

slope areas. The natural mixed mountain forest (beech, fir) is often displaced by production forest dominated by spruce. Transeuropean air masses coming mainly from NW are washed out by relatively high precipitation rates (1650 mm/year). On this Zoebelboden-site in the National Park “Nördliche Kalkalpen” a geology, hydrology and hydrogeology research program is running since 1993. Hydrogeological and hydrochemical well studied springs are accessible in winter time. Studies with fluorescence tracers showed passage times of about 20 hrs during storm events.

### *Materials and Method*

#### *Sampling*

The precipitation was collected as monthly sample either in a wet only sampler (WADOS) in-stalled on top of a research container with immediate cooling (4°C) or with three large containers as open deposition during May till December 2005.

The spring water samples and their suspended matter were all collected during August and December 2005 in 0.1 to 10L containers. The samples for cation analysis and lead isotope analysis were pressure filtered through pre-weight teflon filters (SS). The filters were dried and equilibrated in an exsiccator before reweighing the filters. Two water blanks were transported into the field and treated like the other water samples.

The humic top layer was cut with a 0.3x0.3m frame. The top soil (0-5cm) and the mineral soil (5-40cm) samples were taken with a 7cm diameter corer. In the core sample the outer rim was peeled off to avoid downward contamination. The carbonate rocks were sampled (1997 and 1998) from outcrops in 5m diameter as unweathered carbonate chips in the total weight of 1-2kg.

#### *Sample preparation for isotope analyses*

5-10 L water samples were evaporated on a water bath or in a heating cabin (130°C) down to 0.5-0.3 L. 0.05-0.2 kg soil sample (105 °C dried and screened < 2mm; stored deep frozen) was leached with 0.8-1.2 L deionised water with continuous stirring over 24-34 hrs. The leachate was concentrated by heating (130°C) to 0.5-0.3 L. The BaSO<sub>4</sub> was precipitated after acidification (pH 3-4) with 2N HCl and adding 5-10 ml of 0.2N Ba Cl<sub>2</sub>·2H<sub>2</sub>O at moderate temperature (40-60 °C). The nitrogen, sulphur and oxygen isotopes of nitrate and sulphate were analysed by the labs of Univ. Lublin (Poland) and Hydroisotop Ltd (Munich, Germany).

Sr and Pb isotope analyses of water, soil and carbonate rock samples were performed in the Laboratory of Geochronology, University of Vienna and in the lab of the Environment Agency Vienna.

### *Results and discussion*

To quantify and manage the problems resulting from the impact of air pollution on sensitive karst groundwater resources nitrogen-, sulphur- and lead-isotopes are used as key-indicators for a wide range of contaminants. Therefore they will be used for a new cost efficient control system, applied especially for surveillance of sensitive and remote areas.

In spite of strong efforts initiated by the European Union and other international organisations in the past 20 years, air pollution from industry, traffic and agriculture is still significant. Transboundary transport processes by atmospheric circulation are responsible for its long-range distribution. There is evidence that even remote mountainous regions in the Pyrenees or Alps as well as the Mediterranean islands are contaminated by inorganic and organic airborne pollution. This is most evident on the surface, but also penetrates into the aquifers, particularly in carbonate areas with strong karstification, characterised by dolines, karst shafts, caves and large springs. Special attention is therefore given in this project to karst aquifers: They are particularly vulnerable, but very important in many regions of Europe. Indeed, in many regions they are the only natural resources for drinking water supply.

In order to protect these water resources effectively the amount of the far transported pollutants should be identified and quantified at an early stage. For many transboundary pollution problems the time between recognition and relieve measures are in the range of ten years or more. In the last years, the monitoring was focused on surface water. However, airborne pollution of groundwater was rather neglected. To avoid the long term degradation of aquifer systems, new management tools and innovative alarm systems are urgently necessary. The UN-ECE-Integrated Monitoring station (Zoebelboden) is a background station with a very low sulphur (4-5 mg/l) and lead (0.2 µg/l) and a low nitrogen (5-7 mg/l) content in the karst water.

First results of this pilot investigation, which had to overcome the problem of extremely low concentrations will be shown in this presentation and further recommendation for the usage as surveillance tool will be given.

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