

EUG XI



Symposium AI04

Plumbing the Depths:
Groundwater in the Third Millennium:
Hydrology and Hydrogeology

Convenors

Mike Price
Paul Ashley

AI04 Hydrology and Hydrogeology

Tuesday AM Session

AI04 : TUam01 : F1

Deep Groundwaters in the Alluvial Aquifer of the Rhine Valley. Groundwater Flow and Salinity Transport Inferred from Environmental Isotopes (O, H, C, S, B)

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Systematic investigations of the isotopic characteristics of deep groundwaters in the alluvial aquifer of the Rhine valley have been undertaken since 1993 both in France and Germany. Over 180 samples from wells attaining 240 m of depth were obtained by pumping from the Quaternary and in some cases Tertiary clastic sediments. The first form a complex but continuous aquifer system containing one of the most important groundwater resources of Europe. The samples were analysed for major, minor and trace elements, stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$), tritium, carbon isotopes, and for a restricted number of samples S and O isotopes of sulphates and B isotopes. The aim of the study is to constrain flow conditions (recharge mechanisms and groundwater residence times) as well as the origin of dissolved species in particular with respect to groundwater salinisation.

The influence of infiltration of Rhine water produces a sensible depletion in ^{18}O and ^2H in all wells lying closer than 1.5 km from the bank and it penetrates into the aquifer to depths of more than 100 m. Outside this zone, groundwater flow from the Vosges and the Black Forest is the dominating recharge component besides local precipitations.

A post-1953 tritium containing component was found in all French wells and the majority of the German wells. This young waters penetrate into depths of more than 140 m. Only a few wells on both sides of the Rhine contain an old component with residence times of several thousand years. Two of them show typical Pleistocene stable isotope signatures with ^{14}C -activities below 10 pmc. In several other cases, mixing with a Pleistocene component can be assumed.

High salinities were encountered in both young and old groundwaters. In the first case, an anthropogenic origin of the salt contents cannot be excluded in particular in relation with the influence of the potash salt mining activities. Leaching of evaporitic levels in the underlying Tertiary and Mesozoic strata is suggested by the isotopic composition of dissolved sulphates in the older saline groundwaters. The $\delta^{11}\text{B}$ values display a very large range of +5.2 ‰ to +57.1 ‰ vs. NBS 951 within the same well. Boron isotopes thus reveal a potential tool for distinguishing natural and anthropogenic origin of salinity in the Rhine valley.

AI04 : TUam02 : F1

Water Chemistry Calculation by Hydrological Methods: Example of the Druance Small Agricultural Watershed (Normandy, France)

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Surface waters, collected at the watershed outlets, are mixtures of variable contributions that can be attributed to the individual discharge of at least three specific reservoirs :

groundwater, hypodermic runoff and surface runoff (Roche, 1962). Chemical mixing models are usually employed in order to estimate the contribution of these different components to the total stream water. These models are based on assumptions about the chemistry of each of the components (Boeglin & Tardy, 1997). We have worked on the experimental Druance small agricultural watershed (Normandy, France). We have chosen to use the unit hydrograph method in order to build a synthetic hydrological cycle. Hypotheses about hydraulic characteristics of groundwater, hypodermic runoff and surface runoff allow us to distinguish them in the global hydrograph, without using their respective chemical compositions. The composition of each component is deduced from the measured concentration-flow curves and is supposed to remain constant. The water chemistry is calculated using together the obtained compositions and the three different contributions to the daily total flow. Results of this calculation are compared to yield measurements and show a good high frequency reconstruction of the stream water variability for (Si), Mg^{2+} , Ca^{2+} , HCO_3^- , Na^+ and SO_4^{2-} , that are elements which are not affected by agricultural supply. The extraction of these calculated values from the yield measurements shows that the stream flow chemical composition is characterized by a cyclic variability at an annual scale. The depletion of solute concentration during the winter period was observed by Foster (1978) and interpreted as the consequence of both the increases in runoff with increased rainfall, and the flushing effect in the reservoirs of the watershed. Our approach allows to separate the two effects and leads us to discuss the constant concentration of the three components at the seasonal scale.

Boeglin JL & Tardy Y, C. R. Acad. Sci., *Earth & Planetary Sciences, Paris*, **325**, 125-131, (1997).

Foster IDL, *Catena*, **5**, 151-163, (1978).

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AI04 : TUam03 : F1

Influence on the Water Quality of the Mineralizations Occurring in the Grande River Basin (San Luis, Argentina)

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The reservoir of La Florida is the main water source for the city of San Luis (San Luis Province, Argentina). This reservoir is located in The Grande River Basin. Many different types of mineralizations (Ag, Au, Be, Bi, Co, Cr, Cu, Li, Mn, Nb, Ni, Sn, Ta, Pb, REEs, V, U, W, and Zn) occur in the basin before the river water arise the reservoir. The main mining district is Carolina, located at a mountainous region 80 km north of San Luis, where gold epithermal were exploited since the late 1700s.

Results of surface water samples of the Grande River Basin are presented. The parameters pH, specific conductivity, temperature, dissolved oxygen, TOC, Ca, Mg, Na, K, Si, Cl, HCO_3^- , SO_4 , NO_3^- , NO_2^- , Ag, Al, As, Au, Ba, B, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr have been monitored in thirteen sampling stations.

The hydrochemical processes of dilution, pH change and adsorption of potentially toxic trace elements (e.g., As) onto surfaces of iron oxyhydroxides act as natural controls to the extent and amount of pollution from the mineralizations.

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AI04 : TUam04 : F1

Characterisation of the Artesian Aquifers in the Friuli Plain (NE Italy) by Means of Low-Quality Hydrological Data

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The Friuli alluvial Plain is characterised by a northern sector consisting of highly pervious gravel and sand which contain a single freatic aquifer, and by a southern sector containing a complex multistrata aquifer system economically remarkable. The southern sector is a fertile and densely populated area, subject to a capillary drawing from more than 20,000 wells for domestic, potable, irriguous, industrial and trout breeding use. In several areas, the wells represent the only source of water supply, being integral part of a keen popular culture. This fact led to the absence of an aqueduct system.

In spite of the widespread exploitation of underground water, the available technical and hydrogeological data on wells and aquifers are collectively fragmentary and of low quality. We have collected a data set comprising fair information on approximately 1,000 wells of a total of 20,000 existing wells (Martelli and Roda, 1998; Granati, Martelli and Roda, 2000).

Notwithstanding the modest quality of the collected data, it has been possible to gain some relevant results with regard to the hydrology of the Friuli Plain. In fact, the data on wells for which a simplified lithostratigraphy is available from local drilling operators, has provided a spatial distribution of the most continuous and productive aquifers as well as evidence on the provenance of the sediments. The depth of wells increases with drilling date and this is a consequence of the progressive depletion and pollution of the more superficial aquifers.

In order to estimate the groundwater amount yearly drawn from the area of the low Friuli Plain, we have considered either the small number of wells provided with pumping data (essentially sources of huge water supply for industrial and trout breeding use), or the great number of wells lacking in pumping data. For the latter, appropriate analogical criteria have been adopted. On this basis, the groundwater supply reaches the very high value of 761 millions of cubic metres per year, which corresponds to an annual average flow of more than 30 l/s per square kilometre. Finally the correlation between wells depth and groundwater drawing has allowed to share the recovered water among the artesian aquifers.

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AI04 : TUam05 : F1

Rare Earth Element and Yttrium Distribution in Aqueous Crustal Fluids

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The REE and Y abundances (combined to REY) in water are dependent on the composition, type and alteration of the source rocks. REY are less dependent on the compositions of rock-forming minerals (with exception of carbonate rocks in which the carbonates largely host REY) than on REY-bearing accessory minerals. Water derived from igneous rocks are richer in REY than those from their corresponding metamorphites. REY abundance patterns of aqueous fluids with temperatures between 10 to 400°C vary over many orders of magnitudes. In contrast, the source-rock-normalised REY/Ca patterns of water and steam characterise the fluids from different types of source rock (Möller in press). Waters often show anomalous behaviour of Ce, Eu, and Y. Some of the anomalies are inherited from the source rocks, others are acquired by sorption processes, and chemical reduction and oxidation. The acquired anomalies yield information on the water-rock interaction, whereas the inherited ones point to the source rocks. Low-temperature waters from granites that normally are characterised by negative Eu anomalies can show no or even positive ones due to leaching of excess Eu which represents the fraction of divalent Eu during the solidification of the granites. All geothermal fluids with temperatures above 250°C are marked by an acquired positive Eu anomaly

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because the thermochemical reduction to Eu^{2+} is less sorbed onto mineral surfaces than the trivalent REE and is therefore more mobile. Negative Ce anomalies are present in all oxygen-rich waters irrespective of the source rocks and is due to catalytic oxidation of Ce to Ce^{4+} on FeOOH surfaces (Bau 1996). Waters from limestones often inherit the negative Ce anomaly from seawater. In metasomatic carbonates such as dolostones this primary anomaly can completely be removed because of the REY exchange during the metasomatic reaction. Y is mostly enriched in water because of less chemical complexation at mineral surfaces. This behaviour is only observed as long as the system has not reached a steady state. In highly productive geothermal well fluids such as those used for electric power generation Y anomalies are absent because the source rocks are depleted in easily leachable Y.

Bau M, *Geochim. Cosmochim. Acta*, **63**, 67-77
Möller P, *Hydrogeology of crystalline rocks*, Kluwer academic publ., in press

AI04 : TUam08 : F1 Characterization of Paleofluids by SIMS Analysis of Minor and Trace Elements in Fracture Calcite

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Geochemistry of minerals that line or fill fractures in rock masses allow characterisation of paleofluid transfer through those rocks (e.g. Denniston *et al.*, 1997), adding constraints to hydrogeological modelling. The present study aims at characterizing paleotransfers in and around Callovian-Oxfordian strata at the site of the proposed ANDRA underground laboratory in eastern France.

As a part of a scientific cooperation program between ANDRA and Ecole des Mines de Paris, fractures have been sampled in the HTM102 drill hole. Twelve samples have been collected in massive and clayey limestones below Callovian-Oxfordian Clays, and sixteen samples in marls above the Clays. In surveyed drill cores, no fracture-filling material has been observed in Callovian-Oxfordian Clays hosting the projected laboratory. Petrographical examination shows that calcite is the predominant mineral phase in fractures, leading to the choice of minor and trace elements Mg, Mn, Fe, Sr, and LREE as geochemical tracers. The small size of fractures, often less than 1 mm wide, and the need to keep control of the analyzed material with respect to fracture structure (especially walls), orientated the choice of the analytical tool towards secondary ion mass spectrometry (SIMS), using the CAMECA IMS6f equipment installed in Centre-d'Informatique-Géologique labs at Ecole des Mines de Paris in Fontainebleau.

Analytical procedures still are under development and are tested using homogeneous and chemically known calcite standards. A primary beam of ca 100nA is used. O⁻ primary ions are accelerated at *12.5 kV, focused and rastered on sample surface, yielding a crater approximately 100x100µm in size. The use of dynamic-transfer capabilities of IMS6f means that the analyzed area has the same size. Homogeneity of the analyzed area is simultaneously checked on the ion-imaging facility, allowing for the presence of REE-rich phases to be detected, and corresponding analyses to be discarded. Other working parameters include moderate mass resolution (ca 1000) and a transfer-field pair at around 30µm. After acquisition, signals are normalized to ⁴⁰Ca, then corrected for interference if needed (e.g. ⁴⁴Ca²⁺ on ⁸⁶Sr⁺, or ¹³⁶Ba¹⁶O⁺ on ¹⁵¹Eu⁺), and converted into atomic abundance and mass concentration by comparison with calcite standard ccCigA whose homogeneity has been checked and composition had previously been determined by bulk methods (INAA and ICP-MS). Further analytical developments are under way. Preliminary results point out that calcites from the upper layers are richer in minor elements than calcites from lower layers. Further analyses of the whole sample set are scheduled for confirming that trend. Finally, scattering of minor-element concentrations in one sample located at the footwall of the clay layer suggests an influence of carbonate-rich host rock on fracture-filling calcite.

Denniston, R.F., Shearer, C.K., Layne, G.D., Vaniman, D.T., *Geochimica et Cosmochimica Acta*, **61**, 1803-1818, (1997).

AI04 : TUam09 : F1 Chemical and Isotopic Features of Interstitial Water and Isotopic Evolution of the Matrix in the Sainte Colombe Borehole (France)

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A 700 meters borehole cored in the Chalk of the Paris Basin has crossed below the Tertiary sediments through all the superior Cretaceous. The chalk samples was packaged in watertight buckets in order to avoid the iso-topic fractionation of water elements. The interstitial water was analyzed for chemical composition (electrical conductivity and major elements) and isotopic content (¹⁸O, 2H), the matrix was analysed in the aim to study the water-rock interaction. The strongly porosity decreases with the depth from 50% to 5%, this could be explained : - either by the increase of the lithostatic pressure with the depth - or by recrystallizations of carbonates in the depth. In a 2H vs ¹⁸O diagram, all samples are below the GMWL (Global Meteoric Water Line) and plotted along a line with slope of 3.1. In the same time, the electrical conductivity increases highly with the depth from 5 to 40 mS.cm⁻¹. This evolution take place according to mixing between a meteoric water and a salty water enrich in heavy stable isotopes and enrichment water (this could be a connate evolved water (Sofer *et al.*, 1975)). To explain the evolution and the origin of the interstitial water, the study of the Cl⁻ concentration has been performed. The increase of this element with the depth is not very important and paint out a mixing between a connate water and a meteoric water. Moreover the shape of the evolution reflect a Cl⁻ diffusion through the porous media. The excess of Na⁺ content towards halite saturation can be explain by a cation exchange process between Na⁺, K⁺ and Ca²⁺.

Forty Chalk samples were analysed in ¹⁸O and the ¹³C in the aim to identify some recrystallizations in the the lower part of the Chalk. The ¹⁸O of the samples show a decrease from -1 to -4‰ vs PDB and an increase from 0 to 3.0‰ vs PDB with the depth. However the dolomites present a enrichment of +2.8‰ in ¹⁸O and +0.2‰ in ¹³C compared to surrounding calcium carbonate, that is to say if we refer to the study of Fritz and Smith (1970) this enrichment can only be explained by a dolomitization of a classical Chalk whereas a dolomite crystallised in the same environment of a calcite must present a enrichment of +5-6‰ in ¹⁸O. The decrease of the ¹⁸O of the carbonates and the augmentation of the Activity ¹⁴C of samples with the depth can only be explain by a recrystallization more important with the depth.

Fritz, P., Smith, D.G.W., *Geochimica et Cosmochimica Acta*, **34**, 1161-1173, (1970).
Sofer, Z., Gat, JR, *Earth and Planetary Science Letters*, **26**, 179-186, (1975).

AI04 : TUpo01 : PO Geothermal Fluids from the Granitic and Sedimentary Basement of the Rhine Valley: B, Sr, Nd, U, O, H-Isotope Systematics

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The deepening of the geothermal well GPK-2 at Soultz sous Forêt (France) from 3883 to 5093 m between February and May 1999 allowed to obtain representative samples of formation waters from about 5000 m of depth in the granite basement of the Rhine graben. These samples are currently analysed for major and minor ions, rare earth elements, as well as for Nd, Sr, U, B, O, H isotopes. In the aim to better situate these superdeep formation waters in the regional hydrogeological context, the same analytical program has been carried out on thermal waters from the Triassic sedimentary cover and the crystalline basement on a EW striking profile through the Rhine graben. All mineral waters on the EW profile are Na-Ca-Cl waters with TDS values ranging from 4.8 to 23.3 g/l for the sedimentary cover and 2.9 g/l for the granitic basement of the Black Forest which can be compared to a mean value of 100 g/l for the deep Na-Cl brines at Soultz. The samples from the sedimentary cover and the Black Forest granite show a clear heavy REE (HREE) enrichment ((Lu/La)_N from 5 to 32). REE patterns are quite homogeneous for the Soultz

reservoir with a much less pronounced HREE enrichment ((Lu/La)_N from 0.7 to 5) and a slight middle REE enrichment. The ⁸⁷Sr/⁸⁶Sr ratios of the sedimentary mineral waters cover a narrow range between 0.710956 and 0.711566 and all the Soultz brines are comprised in this interval with values ranging from 0.711308 to 0.711454. The granite mineral water sample is more radiogenic with a ⁸⁷Sr/⁸⁶Sr of 0.718091. The εNd(0) values (vs. CHUR) vary between -12.6 and -8.8 for the sedimentary fluids at near constant Nd concentrations around 5 ng/l. The granite water sample shows a more radiogenic value of -6.8 together with a higher Nd content of 8.56 ng/l. Both εNd(0) values and Nd contents as well as the ⁸⁷Sr/⁸⁶Sr ratio of the granite mineral water sample agree with typical values of mineral waters in granite environment (Négrel *et al.*, 2000). All sedimentary fluids show positive δ¹¹B values ranging from +1.74 to +8.38 ‰ vs. NBS951 which lies in the field of groundwaters from Triassic sediments from N Switzerland and S Germany (Barth, 2000a). The granite water is depleted in ¹¹B, the δ¹¹B value of -7.17 ‰ is similar to the values obtained from Hercynian granite hosted fresh waters (Barth, 2000b, Casanova *et al.* in press). The deep fluids from the Soultz geothermal wells show isotopic signatures which are similar to the those in the overlying sedimentary reservoirs and clearly different from thermal waters from the Black Forest granite.

Barth SR, *Appl. Geochem.*, **15**, 937-952, (2000).
Barth SR, *J. Hydrol.*, **235**, 72-87, (2000).
Négrel Ph., Guerrot C., Cocherie A., Azaroual M., Brach M & Fouillac C, *Appl. Geochem.*, **15**, 1345-1367, (2000).
Casanova J., Négrel Ph., Kloppmann W & Aranyosy JF, *Geofluids*, in press

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Tuesday PO Session

AI04 : TUpo02 : PO Geochemical Investigation of the Recent Sediments of the Kuzuluk, Armutlu, *Karailica* and Tuzla Hot and Mineralized Water Springs, Marmara Region, Turkey

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The hot and mineralized water springs make alteration and element enrichment at some locations in the Lithosphere. For this purpose, geochemical investigations of the recent sediments of Kuzuluk (Akyazi), Armutlu (Armutlu), *Karailica* (Çan) and Tuzla (Ayvacik) hot water springs located in the Marmara Region have been carried out. Therefore, hot water, recent sediment, rock and soil samples were collected from the study site.

According to the results of the water chemistry analyses of the hot water springs, it has been determined that hot water includes SiO₂ more than 50 ppm and it is rich in Na, Ca, K cations and at Cl, SO₄ and HCO₃ anions. According to the results of the major element analyses they are rich in SiO₂ in samples KRP4 and KTRP2; rich in CaO in samples ARP6 and rich in Fe₂O₃ in the sample TRP12.

As per the enrichment coefficient range of metals existing in the recent sediment, rocks and soil samples received from the discharging locations of the hot water springs, the most enrichment are made by Sb, As, Ni, and Au metals, and Fe in the Armutlu and Pb in the *Karailica* and Tuzla have accompanied to the above ones.

AI04 : TUpo03 : PO Spatial and Temporal Variability of Water Quality in a Mediterranean River Basin: The Llobregat River Basin in Northeastern Spain

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The water quality of Llobregat River is a very important concern for the sustainable management of water resources in NE Spain. The Llobregat basin supports a high pressure of both economic activities (industry and agriculture) and highly dense populated area. In fact, the water supply needs of more than 4 million inhabitants are related with the water quality of the basin.

The sampling protocol has been designed in order to obtain the geographic and temporal inorganic profile of the Llobregat basin. Ten sampling stations have been established to complain with this objective, seven on the Llobregat river and three on its main tributary, the Cardener river.

The parameters monitored are: pH, specific conductivity, temperature, dissolved oxygen, TOC, Ca, Mg, Na, K, Si, Cl, HCO₃⁻, SO₄²⁻, NO₃⁻, Ag, Al, As, Au, Ba, B, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr.

The main features of Llobregat watershed are: 1) the low mineralization of the headwaters, a direct consequence of the geochemical characteristics of the detrital geological formation occurring in the Pyrenees; 2) the high salinity occurring after Cardona-Súria-Balsareny-Sallent salt mining district, that mainly affects the Na, K, Mg, Br, Rb, Li and Sr concentrations; and 3) the trace element pollution of the low valley of Llobregat, where the Al, B, Co, Mn, Ni, Mo and Pb concentrations increase.

In relation with the temporal behaviour of the elements studied, this is erratic for Ca, Mg, Si, Li, B, Cr, Ni, Cu, Zn, As, Rb, Sr, Mo, Sb, Ba and U, without relation to river flow

or water temperature in the middle part of the basin. The concentrations of Na, K and Br decrease in large floods, and NO₃⁻, Al, V, Mn, Fe & Pb follow an annual sinusoidal curve, similar to the seasonal variability of the water temperature in the central part of the basin. This general behaviour is obliterated in the low valley due to the pollution.

AI04 : TUpo04 : PO Natural and Anthropogenic Influences in the Water Quality of the Ter River (Northeastern Spain)

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The Ter River basin together with the Llobregat River basin supply the water needed for the city of Barcelona and its metropolitan area. More than 4 million inhabitants and the associated economic activities depend of the sustainable management of these basins.

The Sau-Susqueda-Pasteral reservoir system, located in the central part of the basin, supplies high quality raw water to the Ter Drinking Water Treatment Plant, water that finally is addressed to the city of Barcelona and surrounding areas. This reservoir system, with a total capacity of 400 hm³, regulates the hydrological basin of the River Ter.

As input for the decision support system of the management of Ter River, the parameters pH, specific conductivity, temperature, dissolved oxygen, TOC, Ca, Mg, Na, K, Si, Cl, HCO₃⁻, SO₄²⁻, NO₃⁻, Ag, Al, As, Au, Ba, B, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr are monitored monthly in seven sampling stations.

The results obtained through this monitoring allow us to determine the natural and anthropogenic influences in the water quality of the Ter River and to establish their geographic and temporal variations. The influences on the water quality of the Sau-Susqueda-Pasteral reservoir system are one of the most important objectives of the work.

AI04 : TUpo05 : PO Flow-Transport of Pollutions Pesticides in Unsaturated Zone of Pistoia Plain (Italy) using Artificial Neural Networks

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In Geological sciences one - dimensional flow - transport models of pollutions (pesticides) in unsaturated zone actually show several limits. Particularly, during the study about absorbment of nutriments from root plant, also most diffuse models underestimate pollutions diffusion in the zone near land surface. This problem is due from lack of information about longitudinal dispersivity of pesticides that are used from garden centres. Water and pollutions flow-transport equations result inadequate to a correct description of phenomenon for two reasons: the wide fissures, due drying up, control kind of flow; the absence of evaluation of pesticides gaseous phase. Moreover initial and boundary conditions don't agree with reality because chemical and hydraulic propriety of ground can change both in the spatial and in a non-linear way in the time. So it becomes difficult to characterize these conditions. These limits grow if research is on a little area like our research. Recently a new computing technology has been used in the construction of environmental models: Artificial Neural Networks (ANN). ANN are particular computational structure for numerical elaboration. After learning phase using example data, the nets are able to map the input/output relationships. For their characteristics ANN can estimate phenomena apart from a perfect knowledge of them. In the

last years some researchers applied neural networks for meteorological quantities estimation, for runoff hydrograph evaluation, for land drainage engineering. Aim of this research is to carry out a flow - transport model, based on ANN, of pollutions in unsaturated zone for most accurate management and conservation of vulnerable esteemed aquifers. Study, calibration and validation of the model will be done in Pistoia plain where several garden centres are located.

AI04 : TUpo06 : PO Isotope Determination on H₂O Samples Ranging from 0.5 Microliter-5 Milliliter by Equilibration, Chromium Reduction and Carbon Reduction Techniques

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Recent developments have extended the capabilities for D/H and ¹⁸O/¹⁶O determinations in water. While most of the basic developments were driven by the needs of the field of hydrology, creating the field of isotope hydrology, the new applications in the fields of biology, food adulteration, and medicine have become increasingly important as a driving force for instrumental developments. Specifically, requirements for higher sample throughput, smaller sample size, higher precision and easier sample handling has led us develop new peripheral devices and to introduce new technologies. There are currently four separate ways to measure the isotopes of water:

1. Water-CO₂/H₂ equilibration using the dual viscous flow inlet system. The sample size is 1-5 ml water and the precision is better than 0.05 ‰ for δ¹⁸O and 1 ‰ for δD. Water-H₂ equilibration was first described in references 1 and 2. It is commercialized by Finnigan MAT as the HDO II water equilibrator, which succeeds the H₂O I; there are about 100 such units in the field.

2. Water-CO₂/H₂ equilibration using helium as a carrier gas. The sample size is 0.5 ml water and the precision is better than 0.08 ‰ for δ¹⁸O and 3 ‰ for δD (reference 3). These applications are automated on the Finnigan MAT GasBench II.

3. Chromium reduction, in which H₂O is reduced to H₂ using chromium using the dual viscous flow inlet system. This technique, first developed by at UFZ in Leipzig, is fully automated and has proven to be the most precise and accurate method available for the analysis of D/H. The sample size is <0.5µl H₂O and the precision is better than 0.5 ‰ δD. The technique is patented (reference 3, under exclusive license to Finnigan MAT), and is commercialized in the H/Device. The same technique can be used in CF-IRMS mode, but with a significant diminution in precision and with no tangible benefits.

4. Carbon reduction at elevated temperature (the water-gas reaction, often incorrectly referred to as pyrolysis), H₂O + C = CO and H₂, at T=1400°C, using helium as a carrier gas. Because ¹⁸O and D can be analyzed from one reaction, this recent development offers significant increased sample throughput, reduced sample sizes, and good precision. In six minutes, from one injection of 0.5µl of H₂O, precision of 0.3 ‰ for δ¹⁸O and 3 ‰ for δD are attainable. Analysis can be completely automated by the use of a GC autosampler (5). It is commercialized by Finnigan MAT as the TC/EA high temperature elemental analyzer.

The peripherals can be combined, so that one autosampler can be shared between two peripherals, extending the range of applications.

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AI04 Hydrology and Hydrogeology

AI04 : TUpo07 : PO

Hurst's Phenomenon in Karstic Springs

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Hurst's phenomenon is well known for hydrologists ever since the construction of the Aswan dam on the Nile river. Roughly speaking, it means that the order of magnitude of growth in time of the normalised range declines from one half for certain classes of stochastic process. These processes have the peculiarity that they do not belong to the domain of attraction of the Brownian motion, and cannot be described by finite linear models such as e.g. ARIMA ones. We show that the 10600 days long registered water capacity data of karstic springs in North-Eastern Hungary provide strong evidence for Hurst's phenomenon to be present. Hurst's phenomenon usually is associated with long memory processes. Mathematical models exist however, that show this "virtually" long memory to be resulted from the aggregation of numerous short memory models with randomly chosen parameters. In view of the great variability of the local aquifers, this may serve as a realistic explanation for Hurst's phenomenon in water capacity data of karstic springs.

