Isotopes and tracers in hydrology & Henry Darcy Lecture 2009

International symposium organized by the Netherlands' National Committee IHP-HWRP and the VU University Amsterdam, together with the Netherlands Hydrological Society (NHV), the Netherlands' Chapter of the International Association of Hydrogeologists (IAH), and the US National Ground Water Research and Educational Foundation (NGWREF) – 5 November 2009, Amsterdam, The Netherlands

Isotope hydrology is a field of hydrology that uses isotopic dating to estimate the age and origins of water and of movement within the hydrologic cycle. The techniques are used for water-use policy, mapping aquifers, conserving water supplies, and controlling pollution. It often supplements past methods of measuring rain, river levels and other bodies of water.

Environmental tracers can reduce uncertainty of hydrological predictions in all environments, but are particularly valuable in highly heterogeneous groundwater systems, where spatial variations in aquifer hydraulic conductivity may range over several orders of magnitude, and so hydraulic approaches are inherently uncertain. Despite the rapid growth of environmental tracers during the past few decades and their adoption by the research community, they are not widely used in routine hydrogeological assessments.

On 5 November 2009, the Netherlands National Committee IHP-HWRP and the VU University Amsterdam, together with the Netherlands Hydrological Society (NHV), the Netherlands' Chapter of the International Association of Hydrogeologists (IAH) and the US National Ground Water Research and Educational Foundation (NGWREF), organized a symposium on the recent progress in the use of environmental isotopes and other tracers in hydrological research.

Seventeen years earlier, on 19 November 1992, the Netherlands Hydrological Society had organized a meeting on isotopes in hydrology, which resulted in the first special publication[1] of the society. Also the VU University has a longstanding record of courses in isotopes hydrology, most importantly those given by Prof. W.G. Mook. His university reader was expanded and subsequently published by IAEA and UNESCO in six volumes[2]. This was a major contribution of the Netherlands to the framework of the International Hydrological Programme (IHP) of UNESCO. The publication series 'Environmental isotopes in the hydrological cycle: Principles and applications' is still an important reference for many students worldwide.

Dr. Vincent Post, *VU University*, welcomed the participants as a good host and gave a short introduction on developments in the isotope and tracer courses taught at the VU University in Amsterdam. This started with the course by Prof. Wim Mook and his earlier-mentioned reader. Dr. Post reiterated the importance of isotopes and tracers in the verification of models.

Introduction to the use of environmental isotopes and tracers in hydrology

– Prof. Stefan Uhlenbrook, VU University Amsterdam and UNESCO-IHE Institute for Water Education

As a first speaker, Prof. Stefan Uhlenbrook, introduced the use of environmental isotopes and tracers in hydrology. He aptly put this in the framework of the many changes that the world is undergoing: global change including climatic change and changes in land-use. Looking at the equations for precipitation, interception, surface water, soil moisture and groundwater, changes are possible for all parameters. Environmental isotopes can be used to investigate the various components of the water cycle and for validation of models of the water cycle.

Uhlenbrook concluded that the world is changing, and so should hydrology. Environmental isotopes can help us to understand changes and their impacts. The use of isotopes constitutes innovative ways to observe hydrological processes, in particular in combination with other methods such as geophysics and models. Whereas today the focus of water-related isotope research is mostly in the usage of ^{18}O, ^{2}H and ^{3}H, components of the water molecule, the current trend is towards 'isotope biogeochemistry' using ^{15}N, ^{13}C and ^{34}S, or other dating techniques noble gases, metals.

Environmental Tracers in Modern Hydrogeology: Reducing Uncertainty in Ground Water Flow Estimation

— Dr. Peter Cook, 2009 Darcy Lecturer, CSIRO Land and Water

In his lecture, Dr. Peter Cook illustrated the potential of environmental tracers through illustration using field sites in North America and Australia, and discussed

1 **Van der Valk, M.R. (2002)** Isotopen in de hydrologie: the state of the art (in Dutch); NHV-special 1, Nederlandse Hydrologische Vereniging, Delft, 103 pp.

2 The complete six volumes of «Environmental isotopes in the hydrological cycle: Principles and applications», can be downloaded free of charge from www.hydrology.nl.

methods for bridging the gap between research and practice.

Quantitative hydrogeology is often traced back to Darcy who, in the mid-19th century, observed a linear relationship between flow rate and hydraulic gradient, the proportionality constant later becoming known as hydraulic conductivity. Even today, groundwater flow rates are most frequently determined as the product of measured hydraulic gradients and hydraulic conductivities, the latter determined using pumping tests. Although the past 150 years have seen considerable improvements in interpretation of pumping tests, and understanding of isotropy and heterogeneity, estimations of aquifer hydraulic conductivity values at appropriate scales remains a significant source of uncertainty. Within the past few decades, however, environmental tracer methods have been developed that can provide independent estimates of groundwater flow rates, which have helped to overcome some of the problems associated with hydraulic approaches, particularly in heterogeneous systems. However, despite the ability of environmental tracers to constrain conceptual models of groundwater systems and significantly reduce uncertainties in prediction, the methods are underrepresented in hydrogeological textbooks and are still not widely used for hydrogeological assessment.

There are a large number of environmental tracers, all with different properties and hence different potential uses. While environmental tracers that readily undergo chemical reactions can sometimes be used to determine reaction pathways, tracers that behave more conservatively may yield information on transport processes. The calculation of groundwater residence times is one of the more common applications. Tracers that can be used for this purpose include radioactive isotopes, which decay at a known rate (e.g. ^{14}C, ^{3}H), tracers that are produced and accumulate in the subsurface (e.g. He), and tracers that are neither produced nor consumed in the subsurface, but have a variable and well-known input history (e.g. CFCs, SF_6). Groundwater residence times in unconfined aquifers can be used to infer aquifer recharge rates, whereas in confined aquifers they allow quantification of horizontal flow velocities. Tracers present in much higher concentrations in groundwater than in surface water have great potential for quantifying groundwater discharge to surface water. In particular, dissolved gas tracers such as radon and helium will rapidly volatilise from surface water and so provide important tracers of recent groundwater inflow. Radon (with a half-life of 3.8 days), in particular, can be used in quantifying rates of groundwater discharge to streams, wetlands, and to the ocean, and also to determine the rate of water exchange between a river and its underlying hyporheic zone.

Dr. Cook excellently showed the impact of magnitudes and scale on hydraulic properties. The various techniques available for different situations, including the coupling of tracers with more 'classical' hydraulics were clearly explained. Where previously isotopes and other tracers were used as a reconnaissance tool in remote areas, with quantitative interpretation based on highly idealized models, there is nowadays an important role for tracers used in conjunction with hydraulics to improve prediction, particularly in heterogeneous groundwater systems. Given the general lack of uncertainty analysis in hydrogeology, tracers can improve accuracy of prediction in heterogeneous environments.

Dr. Cook concluded that in *homogeneous aquifers*, both hydraulic and environmental tracer approaches can accurately characterize groundwater flow. In *heterogeneous aquifers*, tracers may have advantage over hydraulics because they provide spatially averaged information. In *moderately heterogeneous aquifers*, environmental tracers can be used in conjunction with hydraulics, to improve calibration of groundwater models. In *highly heterogeneous systems*, uncertainty of hydraulics is so high that perhaps we have no alternative than to pursue environmental tracer methods for estimating rates of groundwater flow.

Multitracing of artificially recharged Rhine River water in the coastal dune aquifer system of the Western Netherlands

– Dr. Pieter Stuyfzand, KWR and VU University Amsterdam

The coastal dunes of the Western Netherlands are locally recharged by pre-treated water form the River Rhine in order to supply drinking water to large cities like Amsterdam, The Hague, Leiden, Haarlem and Alkmaar. This has happened on a large scale since 1955, when the drawdown of groundwater tables and aquifer salinization became unacceptable. Ecological interests and both national and EU legislation now compel the water utilities to monitor the expansion of the resulting artificial groundwater bodies amidst the surrounding, natural dune groundwater.

That monitoring requires, however, multitracing techniques in order to unambiguously identify the infiltrated Rhine water amidst coastal dune groundwater, because both water types show a large variation in water quality yielding overlapping tracer contents. In addition, the identification is becoming more difficult due to a reducing contrast between both waters.

In his contribution Dr. Stuyfzand showed the performance of various environmental tracers, both single and in various combinations (multitracing), for diverse levels of the aquifer system. Uncertainties in the discrimination were also quantified.

Dr. Stuyfzand showed results of mapping the extension of the infiltrated Rhine water, with special attention to so-called rainwater lenses on top of laterally migrating Rhine water, groundwater dating and hydrological information (hydraulic conductivity, dispersivity) as derived from the observed spatial patterns.

Dr. Stuyfzand concluded that more tracer studies are needed, in this specific case due to a strong increase of interaction between Rhine water and groundwater in the Netherlands, as a result of artificial recharge, land reclamation, polders, drainage, irrigation, shipping canals and river bank filtration. The best tracer combination of Rhine water in the Netherlands is Cl/Br + ^{18}O; the cheapest being HCO_3 in combination with electrical conductivity. Additional good tracers are ^{2}H, Cl and SO_4. Multitracing helps to reduce uncertainties in origin detection, deriving mixing ratios and hydrological models.

Degassing of $^{3}H/^{3}He$, CFCs and SF_6 by denitrification in the Netherlands

– Dr. Ate Visser, Deltares

Groundwater dating has proven to be a valuable tool for environmental research, for example for the demonstration of trend reversal in groundwater quality. Modern groundwater dating techniques are based on the transport of dissolved gases in groundwater, such as noble gases, CFCs or SF_6. These tracers are chemically inert, but are sensitive to the formation and flow of a gas phase below the groundwater table. A gas phase below the groundwater table, for example as the result of a geochemical reaction, causes secondary partitioning between the water and gas phase and obstructs the conservative transport of groundwater age tracers. Ordinary methods to interpret groundwater age tracers are then no longer valid.

Since 2001, a total of 95 screens of the groundwater quality monitoring network in Brabant, the Netherlands, located 10 m or 25 m below the surface, have been sampled for $^{3}H/^{3}He$, 34 of which have also been sampled for CFCs and SF_6. About half of these samples showed the effects of noble gas depletion (degassing). The absence of nitrate in degassed samples indicated that denitrification had causes degassing. CFCs appeared to be subject to significant degradation in anoxic groundwater and SF_6 was highly susceptible to degassing. Therefore $^{3}H/^{3}He$ appears to be the most reliable method to date degassed groundwater.

Conclusion: enormous opportunities for the use of isotopes in water resources research

As was stated by various speakers, research involving environmental tracers such as isotopes is still not common usage, let alone their monitoring on a regular basis. This is rather unfortunate, as environmental tracers have the ability to constrain conceptual models of groundwater systems and significantly reduce uncertainties in prediction.

It was therefore good to see the broad attention given to the subject by participants from many different organizations, although participants were mostly working in research rather than in water management and water policy. The broad attention and the improved possibilities for relatively inexpensive analyses give lead to more structural monitoring of essential parameters, possibly by governmental water managers, as part of the standard analyses suite. This would be to honour the importance and specific opportunities that isotopes and other tracers merit, amongst others, for the calibration of models, both in groundwater and surface water research and management.

Michael R. van der Valk

▶ The presentations of the symposium can be downloaded from www.hydrology.nl.

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