WATER RESEARCH COMMISSION

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The WRC operates in terms of the Water Research Act (Act 34 of 1971) and its mandate is to support water research and development as well as the building of a sustainable water research capacity in South Africa.

TECHNICAL
BRIEF

Tracking trace constituents in groundwater

This project looked to improve observation and prediction of naturally-occurring hazardous trace constituents in groundwater.

Natural trace constituents in groundwater

In the last few years, geological risk mapping and sampling studies have indicated that there are relatively large zones within South Africa where groundwater is at risk of being contaminated by arsenic and uranium. In addition, parts of the Eastern Bushveld area are rich in chromium bearing minerals.

While arsenic and chromium can occur in groundwater at naturally high concentrations, groundwater abstraction practices can also play an important role in facilitating movement of these elements from bedrock into groundwater and at the same time promote speciation changes from relatively benign to toxic forms.

Clearly, there is a need to safeguard groundwater consumers from exposure to toxic trace elements by providing water authorities with relevant knowledge and reliable tools for predicting and managing natural groundwater contamination. To assist in meeting this need, an investigation comprising three main components was initiated. These components were:

- Field sampling and subsequent analysis of groundwater and rock chemistry at selected sites.
- Leaching tests on rock samples to confirm the presence and concentrations of potentially harmful elements.
- Construction and verification of geochemical models to predict water quality.

Establishing the extent of groundwater contamination

The main purpose of the field component of the investigation was to determine concentrations of a range of chemical constituents in groundwater and rock samples in order to assess the extent of trace element contamination and thus the suitability of the water for drinking. Another important purpose was to support the remaining components of the investigation (leaching tests and geochemical modelling) through the provision of the necessary rock samples and analytical data, respectively.

Groundwater and associated rocks were sampled across a broad range of South African geological settings, including the Giyani and Gravelotte greenstone belts, the Eastern Bushveld, the Rooiberg tin fields, the Karoo coal fields, Bushmanland and the Beaufort West and Sutherland areas. In total, 44 boreholes were sampled, with pH, redox potential, temperature and conductivity being measured concurrently in the field.

The groundwater samples were subsequently analysed in the laboratory for ionic as well as major and trace element constituents. Rock samples obtained in close proximity to the sampled boreholes were similarly subjected to laboratory analyses for major and trace constituents. An assessment of water quality in the different regions was obtained by interpreting the results of water chemistry analyses in relation to the South African and World Health Organisation water quality guidelines.

Arsenic was found to occur at harmful levels in samples from only one Giyani and three Beaufort West boreholes. However, there was potential for speciation of arsenic in the more toxic arsenite form (As III) at about 10% of boreholes sampled. Chromium was not present at harmful levels in any borehole water samples, although most registered low chromium concentrations.

There was potential for speciation in the more toxic hexavalent form (Cr VI) at only one Karoo borehole. Potentially harmful levels of uranium were measured in samples from 13 boreholes (mainly on farms) in Bushmanland and Beaufort West, and low levels in samples from other boreholes. However, according to water quality guidelines, the uranium levels measured on the farms should not pose a threat to most healthy individuals.

At a number of boreholes there were high levels of several trace elements and, additionally, a broad spectrum of ions was present in samples from most regions. Ion concentrations often exceeded both human and livestock water quality guidelines. Of main concern were the high nitrate and fluoride levels at a number of sites, mainly in the Bushmanland region. While the water quality guidelines give good information for individual elements, little is known of the synergistic effects of consuming water containing multiple elements at elevated concentrations.

Leaching tests

Leaching tests seek to establish the leachability of metals and other potentially hazardous components from solid rock samples. The tests employed in the investigation utilised three types of internationally accepted, standard leaching procedures and also considered the effects of different liquid to solid ratios, pH and redox conditions on leachability. In general, the tests on rock samples yielded relatively minor quantities of the contaminants of main concern (As, Cr and U). The results generally correlated very weakly and non-significantly with analyses on groundwater samples from borehole locations corresponding to the rock sampling sites.

Verification of geochemical models

The main aim of the modelling component of the investigation was to assess how useful and efficient geochemical models would be in predicting the concentrations of potentially harmful trace elements in groundwater based on geological data.

Water and rock chemistry data collected in the field investigation were used as a basis for assessing the usefulness and effieciency of models. Two potentially valuable modelling applications were considered, namely element speciation and definition of mineral phases in equilibrium with sampled borehole water.

Element speciation modelling is important for determining both the toxicity and mobility of elements of concern. It was found that chromium in water samples from all boreholes was in the less toxic trivalent (Cr III) form. Arsenic speciation was similar, in that the less toxic arsenate (As V) form was most common, although there were about six boreholes were arsenite speciation resulted. With the exception of only four boreholes, uranium existed mainly in the highly mobile U (VI) form.

Overall, it appears that the concept of the groundwater solution from a borehole approaching geochemical equilibrium with the host rock matrix in an aquifer is an oversimplification of a rather complex process. For all three elements of main concern (As, Cr and U), it was found that borehole-specific conditions drive the release of trace metals from the bedrock and that few broad regional generalisations can be made.

An important exception, the reasons for which have yet to be clarified, is in Bushmanland, where relatively high uranium concentrations in groundwater are found despite relatively low concentrations in the bedrock.

Conclusions and policy implications

Satisfactory modelling of groundwater chemistry based on geological knowledge alone is made difficult by variable geology, compounded by factors which determine element mobility and release such as changes in redox and pH conditions brought on by groundwater pumping over time. Morever, the failure of leaching test results to correlate closely with observed groundwater chemistry means that naturally elevated levels of hazardous trace elements in groundwater are more likely to result from localised, anomalous geochemical zones within aquifers than from simple reactions between groundwater and the surrounding aquifer material.

Consequently, neither geochemical modelling nor leaching tests alone would be accurate enough for risk assessment purposes where human health is at stake. For this reason, knowledge of the actual borehole conditions remains necessary to provide certainty about water quality and ensure safety of consumers.

While focusing on the local scale, it remains important to recognise regional problems (e.g. widespread fluoride contamination) where they exist and to have appropriate institutional structures and regional management plans to cope with these.

Policies that relate to water quality and water quality monitoring need to recognise problems of natural contamination of groundwater by trace elements, as well as groundwater usage habits which can lead to or exacerbate such problems. Specifically, repeated drawdown and recharge of aquifers can lead to changes in redox chemistry and contaminant release into groundwater.

Trace element monitoring including arsenic, chromium and uranium should become standard practice, with pH and redox potential being measured in the higher risk areas to address speciation effects.

The South African Water Quality Guidelines could become a more robust management tool through future inclusion of trigger levels for boron, nitrite, nickel and barium which may be toxic at levels measured in some regions. Multi-element analysis and synergistic health risk effects of multiple elements should also be accommodated in possible future revisions.

Further reading:
To obtain the report, *To Calibrate and Verify a Prediction Model for the Incidence of Naturally Occurring Hazardous Trace Constituents in Groundwater* **(Report No: 1431/1/08)** contact Publications at Tel: (012) 330-0340; Fax: (012) 331-2565; E-mail: orders@wrc.org.za; or Visit: www.wrc.org.za