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Excess air as indicator of recharge related nitrate pollution in groundwater of the semi-arid Kalahari, Botswana

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Introduction

"Excess air" usually denotes a gas component dissolved in groundwater that is in excess to the equilibrium solubility and to other known subsurface gas sources. It was first recognised in groundwater as a by-product of infiltration temperature calculations from dissolved noble gases [1]. Since then a number of studies established the ubiquitous presence of excess air in groundwater, which has to be accounted for in the interpretation of dissolved gases (e.g. noble gases, excess nitrogen, CFCs, SF_6). Several model concepts have been proposed and successfully applied that attribute excess air to the dissolution of small air bubbles trapped in soil pores during groundwater recharge, including the total dissolution (TD), closed-system equilibration (CE), and partial re-equilibration (PR) models [2]. Yet, most studies have treated excess air as a nuisance that must be corrected for to obtain the gas component of interest. However, a few noble gas studies in semi-arid environments [3-5] reported evidence that excess-air might reflect the conditions or processes during groundwater recharge.

Study area

Here we present hydrochemical and environmental tracer investigations in groundwater from the semi-arid Kalahari in Botswana where excess air provides information on the source of nitrate pollution if used as a recharge indicator. The study area is located on the Eastern fringe of the Kalahari close to the town of Serowe, Botswana [6]. Rainfall in the study area is restricted to one rainy season with a mean annual value of about 400 mm/yr. Groundwater samples were taken from 50 to 250 m deep wells tapping water from the fractured and mostly confined Ntane sandstone aquifer, which is affected by nitrate pollution. Because the investigated region experiences extreme water scarcity, an understanding of the origin of nitrate is of major importance for the management of the groundwater for water supply.

Results and Discussion

Nitrate concentrations in groundwater range from 2 to 210 mg/l. Stable isotopes of nitrate and water suggest that nitrate is derived from natural soil sources but not related to evaporative enrichment [6]. Combining noble gases with nitrate a strong linear correlation of nitrate with dissolved neon content is obtained for groundwater with elevated ^{14}C DIC content (Fig. 1). Neon concentrations in groundwater are consistently found in excess when compared to solubility equilibrium, which is attributed to excess air. In Fig. 1 high nitrate concentrations correspond to neon values close to solubility equilibrium, indicating low recharge rates where neon concentrations remain close to solubility equilibrium during the slow transport of water towards the groundwater table. By contrast, low nitrate concentrations are connected to high neon excess values, suggesting that

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this groundwater has been recharged at much higher rates, preventing occasionally trapped and dissolved air bubbles from complete re-equilibration. These findings indicate that nitrate concentrations are strongly correlated with recharge dynamics prevailing at different locations or times.

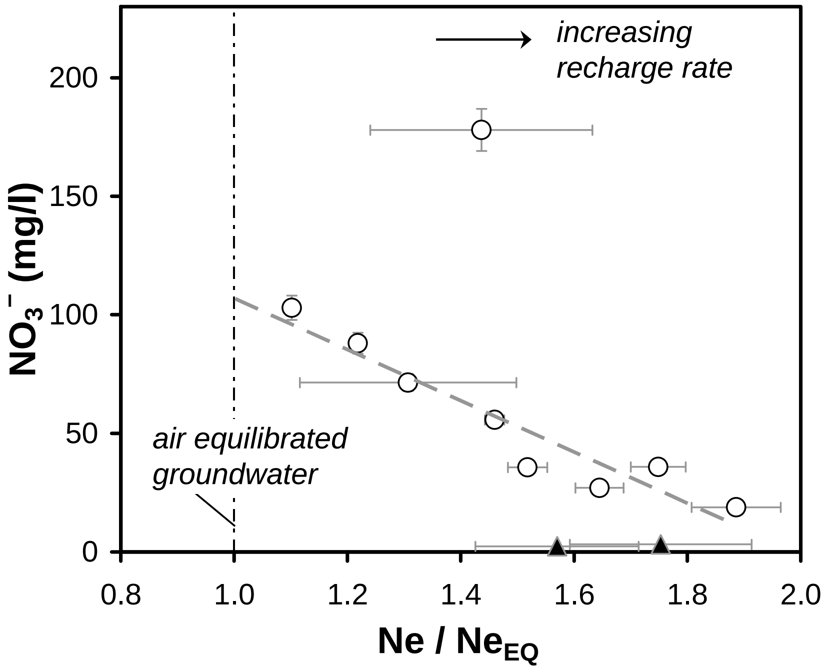

Fig. 1. Nitrate concentration versus neon concentration normalised to solubility equilibrium for the altitude (1200 m) and temperature (25°C) of recharge. Open symbols indicate ^{14}C rich, filled symbols ^{14}C poor samples. Error bars represent the error of measurement (2σ).

The application of excess air as proxy of recharge conditions is supported by ^{14}C dating which indicates that low recharge rates are associated with recently recharged groundwater. This is in full agreement with estimates for the current recharge rate of less than 10 mm/yr in the semi-arid Kalahari [7,8]. Higher recharge rates several thousand years before present are in reasonable accordance with climate proxies from the Kalahari, which give evidence that several wet phases have prevailed at the end of the Pleistocene and during the Holocene [9]. During such wet climate periods intense replenishment of the aquifer apparently lead to the formation of high excess air.

Therefore, increased nitrate concentrations after transition to a drier climate are most likely related to changes in the vegetation cover, soil water balance, and recharge dynamics.

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