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Rare earth elements as indicators of groundwater mixing in the North China Plain: A case study in the area of Hengshui city, China

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Abstract

Water samples were taken from five couple wells of salty-mixed irrigation (SMI), Hengshui test site (HTS) wells and surface drainage, in order to characterize REE geochemistry of different waters and determine mixing ratio of deep groundwater to shallow groundwater. Results showed that shallow groundwaters had similar total REE concentrations (58.8–167.1 ng/L, average 119.1 ng/L) to deep groundwaters (48.0–216.1 ng/L, average 107.9 ng/L), while surface waters generally showed higher values (162.4–257.7 ng/L, average 193.3 ng/L). Fractionation between light and middle REEs ($R_{(M/L)}$) and between middle and heavy REEs ($R_{(H/M)}$) showed that all water samples were consistently depleted in light REEs, with the largest enrichment in middle REEs ($0.68 < R_{(M/L)} < 0.92$, average 0.82) being observed in surface waters, followed by shallow groundwaters ($0.55 < R_{(M/L)} < 0.75$, average 0.75) and deep groundwaters ($0.35 < R_{(M/L)} < 0.66$, average 0.55), although comparable enrichment in heavy REEs was found in shallow ($0.37 < R_{(H/L)} < 0.50$, average 0.44) and deep groundwaters ($0.29 < R_{(H/L)} < 0.55$, average 0.43). The variations in aqueous REE patterns demonstrated that surface waters were preferentially accumulated in middle and heavy REEs over light REEs; shallow groundwater increasingly enriched in heavy REEs was possible due to interactions with aquifer sediments during infiltration; deep groundwater showed decreasing enrichment in middle REEs when receiving recharges from shallow groundwater, although heavy REEs enrichment degree exhibited different trends, likely because of difference in solution complexation. Mixing calculation showed that shallow groundwater recharge consisted of about 40% of deep groundwater. This investigation would help in effectively managing groundwater resources for sustainable development in the NCP under the great influence of human activities.

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Keywords: rare earth elements; groundwater; fractionation; enrich; North China Plain

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1. Introduction

It is vitally important to delineate groundwater flow and groundwater mixing with regard to better understanding hydrogeological systems and sustainable development of groundwater resources, particularly in the North China Plain (NCP) where groundwater has extensively been over-exploited¹. However, groundwater flow systems in the confined aquifers beneath the NCP are poorly-characterized due to anthropogenic interference and the complicated sedimentation, although hydrology and hydrogeochemistry of the NCP Quaternary aquifers have been studied over the last several decades¹. Rare earth elements (REEs) coherent and predictable behaviors have spawned considerable attention in their potential utility as indicators of groundwater-rock reactions, groundwater origin and recharge processes²⁻⁴. Furthermore, groundwater mixing calculations have been performed using normalized REE patterns with both North American Shale Composite (NASC) and upper continental crustal (UCC) as normalized references^{5,6}. Although previous investigation has shown that REE concentration and distribution pattern (i.e., normalized to NASC) are key parameters for demonstrating recharges of shallow groundwater into deep aquifers through efficient pathways due to long-term over-exploitation of deep fresh groundwater⁷, calculation of mixing ratio is one of the challengers owing to the insufficient data concerning groundwater end-members. Limited data showed that about 44.43 % of deep groundwater recharge was derived from shallow aquifers in the northeastern NCP on the basis of groundwater balance calculation and modeling⁸. Mixing calculation for deep groundwaters using normalized REE patterns would help in effectively managing groundwater resources for sustainable development in the NCP under the great influence of human activities. Therefore, the main objectives are: (1) to investigate REE characteristics of groundwater from different aquifers; (2) to identify groundwater mixing end-members; (3) to evaluate mixing of deep groundwater and shallow groundwater with normalized REE patterns.

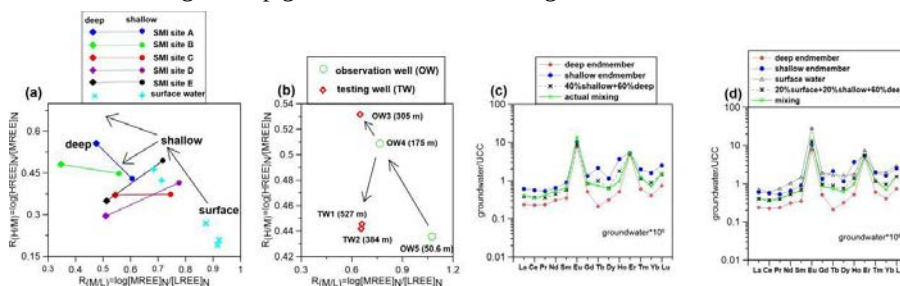


Fig.1 (a) and (b): REE patterns as ratios of middle over light REEs ($R_{(M/L)}$) and heavy over middle REEs ($R_{(H/M)}$) ((a): salty-mixed irrigation samples; (b): Hengshui test site samples); (c) and (d): mixing calculation using UCC-normalized REE pattern. ($R_{(M/L)} = \log(Gd_N/3 + Tb_N/3 + Dy_N/3) / (La_N/3 + Pr_N/3 + Nd_N/3)$; $R_{(H/M)} = \log(Tm_N/3 + Yb_N/3 + Lu_N/3) / (Gd_N/3 + Tb_N/3 + Dy_N/3)$).

2. Methods and materials

Total twenty water samples (including seven shallow groundwater samples, eight deep groundwater samples and five surface water samples) were taken from five couples of salty-mixed irrigation (SMI) wells (shallow and deep) (sites A, B, C, D, E), Hengshui test site (HTS) and surface drainage (river and spring) (see previous studies^{7,9}). Depths of the investigated wells ranged from 25 to 527 m. Groundwater was sampled from each well after pumping for 20 min. All samples were filtered through 0.45 μ m membrane filters before being stored in sampling bottles and transported to laboratory. Physiochemical parameters, including water temperature, electrical conductivity (EC), pH, ORP, and alkalinity were measured in the field. Methods for REEs determination, as well as major and trace components analysis were specifically described in previous studies⁷.

3. Results and discussion

3.1. Chemical characteristics

Sampled waters were primarily distinctive in total dissolved solids (TDS), which ranged between 319 and 11226 mg/L with the lowest in surface waters (spring) and the highest in shallow HST groundwater. Generally, shallow

groundwaters exhibited much higher in TDS than deep ones. Shallow SMI groundwaters had pH ranging between 6.98 and 7.81 (average 7.37), which was less than deep SMI groundwater values of 8.22~8.58 (average 8.42). Shallow and deep HTS groundwater had pH of 7.50~8.38 (average 7.94) and 8.72~10.32 (average 9.39) respectively. The pH of surface water samples were of 7.18~9.23 (average 8.33).

Aqueous REE concentrations were broadly similar to circumneutral pH groundwater values with La, Ce and Nd being the most abundant elements. Although total REE concentrations of deep groundwaters (average 107.9 ng/L) were generally comparable to shallow groundwaters (average 119.1 ng/L), shallow SMI groundwater samples in sites A (167.1 ng/L) and B (141.4 ng/L) were about three times higher than deep SMI groundwaters. The HTS groundwaters showed a slight increase in total REE contents with depth with shallow groundwater of 58.8~67.9 ng/L (average 63.4 ng/L) and deep groundwater of 48.0~124.8 ng/L (average 87.1 ng/L), although the lowest value was observed in observation well 3 (OW3). Surface waters had generally higher total REEs ranging between 162.4 and 257.7 ng/L (average 193.3) than groundwaters, with the highest value in river water samples, reflecting the role of pH value in the formation of stronger REE complexes^{2,3}.

Sampled waters exhibited strikingly similar normalized REE patterns with primarily enrichment in middle and heavy REEs with respect to light REEs, as indicated by fractionation indexes of $R_{(H/M)}$ and $R_{(M/L)}$ ratios³, which ranged between 0.19 and 0.55 and between 0.35 and 0.92, respectively. It likely reflected geochemical reactions between groundwater and aquifer minerals. One possible mineral phase was fluorapatite, which is typically exhibited enrichment in middle REEs, and the possible source of high groundwater F^- which were commonly found in study area⁹. Typical positive Eu anomalies (4.64~31.98) observed in samples resulted from preferential dissolution of Eu-bearing minerals in aquifer sediments as discussed in previous investigation⁷.

3.2. Implications for aqueous REE signature

The characteristics of aqueous REE signatures were elucidated by variations in $R_{(H/M)}$ and $R_{(M/L)}$ ratios. As compared to shallow SMI groundwaters, higher $R_{(M/L)}$ ratios and lower $R_{(H/M)}$ ratios were observed in surface water samples. The $R_{(M/L)}$ ratios generally shifted to lower value in deep SMI groundwater samples in comparison with shallow SMI groundwaters, although two trends of $R_{(H/L)}$ ratios were observed, sites B, C and D decreasing, yet sites A and B increasing (Fig. 1a). Strikingly similar trends for HTS groundwater $R_{(H/M)}$ and $R_{(M/L)}$ ratios were observed (Fig. 1b). These indicated that surface waters were characterized by preferential accumulation in middle and heavy REEs over light REEs evolved towards patterns increasingly enriched in heavy REEs and decreasingly enriched in middle REEs when infiltrated into shallow aquifers. This was possibly due to interaction with aquifer sediments, as well as salt-induced coagulation as fresh groundwater mixed with salty shallow groundwater, during which light REEs were preferentially scavenged as compared to heavy REEs¹⁰. With long-term over-exploitation of deep groundwater, recharges of shallow groundwater into deep aquifers occurred⁸, which influences deep groundwater REE patterns. It is, therefore, reasonably to believe that deep SMI groundwaters from sites C, D and E were actually mixtures of original deep groundwaters and shallow groundwaters, evidenced by their consistent decreases in both $R_{(H/M)}$ and $R_{(M/L)}$ ratios (Fig. 1a) and, more importantly, their strikingly similar REE concentrations and normalized patterns (data not shown), although the geochemical controls on the variations of groundwater REE patterns still remains better understanding. Whereas in sites A and B, deep SMI groundwaters showed greatly distinguished REE concentrations with coherent elevated $R_{(H/M)}$ ratios in compared with shallow SMI ones (Fig. 1a). Meanwhile, REE pattern and concentration of HTS OW3 exhibited very similarly with SMI sites A and B deep groundwater. Consequently, we proposed that deep groundwaters in SMI sites A and B, and HTS OW3 were characteristic of an end-member groundwater that only interacted with deep aquifers.

3.3. Evaluation of groundwater mixing

Calculation of groundwater mixing were carried out with UCC-normalized REE patterns. Previous investigation have shown that groundwaters collected from deep aquifers normally had characteristics of mixtures of deep groundwaters and shallow groundwaters⁷. Hence, average REE contents of SMI deep groundwaters (except for sites A and B, and OW3) and HTS deep groundwaters, as well as deep groundwaters presented in previous study⁹ were regarded as mixed groundwater. Similarly, average REE contents of all shallow groundwater samples were treated

as an end-member of shallow groundwater. The end-member representing original deep groundwaters without inter-aquifer influx input were the averaged REE content of SMI deep groundwaters in sites A and B and deep groundwater in HTS OW3 mentioned above. Initially, 40% shallow groundwater and 60% deep groundwater were used to fit normalized REE curve of mixed groundwaters (Fig. 1c). However, the result was not satisfying due to the poor reproduction of Pr, Nd, Tb and Ho concentrations. An additional water which has greater concentrations of Pr and Nd and lower concentrations of Tb and Ho must contribute to the mixture, which was assigned to the surface water. Consequently, a combination of roughly 20% surface water, 20% shallow groundwater and 60% deep groundwater were found to better fit the normalized REE pattern of mixed groundwater (Fig. 1d), which were in good agreement with previous study with water balance analysis⁸.

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