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A neutron activation study on the hydrogeochemistry of the natural waters of Haikou, Hainan Island, China

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Abstract Rainwater, river water and groundwater were sampled from Haikou, Hainan Island, China. Annual mean samples were analysed by the neutron activation method. The elements Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Fe, K, La, Mg, Mn, Na, Sb, Sc, Sm, Th, Ti, V and Zn were detected in all waters; in addition Lu was detected in river water and groundwater; Se, Sr and U were detected only in groundwater. Concentrations of elements in Haikou waters were compared with those in waters sampled simultaneously from another nine sites distributed in various climatic regions of China, and with those of world freshwaters reported by Bowen (1979). It was found that contents of Al, Cl, Cs, K, Sb and Zn in rainfall and contents of Ba, Ca, Cr, Mg, Na, Sb and Sc in river water and groundwater are lower than the other sampling sites and rivers in China. Contents of Ba, Cs, Sc, V and Zn in rainfall and of Co, Cs, Lu, Sm, V and Zn in river water exceed the median values reported for world freshwaters, which reveals the anthropogenic impacts. By comparing the type and concentration of elements in waters, it seems that river water is mainly recharged by rainfall but elements in groundwater are sourced from both the rainfall and the local lithosphere.

Estudio de activación de neutrones en la hidrogeoquimica de aguas naturales de Haikou, Isla de Hainan, China

Resumen Se tomaron muestras de aguas pluviales, fluviales y subterráneas de Haikou en la isla de Hainan. Se analizaron muestras de promedios anuales por el método de activación de neutrones. Se detectaron elementos de Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Fe, K, La, Mg subterráneas y Se, Sr, y U únicamente en aguas subterráneas. La concentración de elementos de las aguas de Haikou se compararon con muestras de agua tomadas simultáneamente de otros nueve sitios distribuidos en diversas regiones climáticas de China y con las de agua dulce comunidadas por Bowen (1979). Se vio que los contenidos de Al, Cl, Cs, K, Sb y Zn en aguas pluviales y los contenidos de Ba, Ca, Cr, Mg, Na, Sb y Sc en aguas fluviales y subterráneas son los más bajos de todos los muestreos. Los contenidos de Ba, Cs, Sc, V y Zn en aguas pluviales y los de Co, Cs, Lu, Sm, V y Zn en aguas fluviales exceden los valores medios conocidos del agua dulce a nivel global, lo que revela el impacto antropogénico. Al comparar los tipos y concentraciones de elementos en el agua, parecería que el agua de los ríos se recarga principalmente por precipitación, y que los elementos contenidos en el agua subterránea provienen tanto de la precipitación como de la litosfera local.

INTRODUCTION

It is very important to understand the chemical composition and the natural balance of waters in an area to evaluate the pollution of water bodies, to establish local environmental standards, to make rational development of water resources, to probe into the nature of endemic disease, etc. Information obtained from current hydrochemical analyses for waters is certainly important, but it seems insufficient to see the overall situation for above purposes. The intention of this case study is to provide a preliminary geochemical survey for natural waters including rainfall, river water and groundwater from Haikou, Hainan Island, China, and to make geochemical comparisons between Haikou waters, those from other climatic regions of China and those reported from elsewhere in the world.

MATERIALS AND METHODS

Site and sampling

Rainwater was sampled from Haikou Hydrological Station at 20°02′N and 110°21′E with altitude of about 14 m a.s.l. The mean annual rainfall is about 1570 mm resulting mainly from monsoon and typhoon rain. River water was sampled in Nandu Jiang River having a drainage area of 6841 km^2, originating from Wuzhi Mountain and draining mainly the area of platform, coastal plain and a few hilly/mountainous areas. The mean annual runoff is about 980 mm. Phreatic groundwater was sampled from drinking wells situated in the plain area in the vicinity of Haikou.

In order to make geochemical comparisons, natural waters including rain/precipitation water, river water and groundwater were sampled simultaneously at ten hydrological stations distributed in different climatic and geomorphological regions of China with latitudes from 20°02′N to 47°21′N, altitudes from 5 m a.s.l. to 3660 m a.s.l., mean annual precipitation from 35 mm to 1570 mm. Annual mean samples, taken for research purposes were averaged from samples of all months of 1992, weighted by monthly precipitation and monthly runoff for precipitation water samples and river water samples, respectively.

Analyses

The water samples were clean in general; the suspended particles of turbid samples were removed by a millipore filter. Then samples were pre-concentrated by freeze-drying and low-temperature evaporation by the vacuum method. The standard reference materials, the dried samples and one of their containers (the blank plastic bag) were led into the active space of a heavy-water cooled nuclear reactor and irradiated by a thermal neutron flux up to 3×10^{13} n cm^{-2} s^{-1}. The flux rates, irradiation decay and counting times differ according to the half-lives of the nuclides of interest. The kinds and concentrations of various activated elements were determined using a gamma spectrometer with large volume Ge(Li) detectors (Hoste, 1971).

RESULTS AND DISCUSSION

Rainwater

Twenty-three elements were detected, namely Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Fe, K, La, Mg, Mn, Na, Sb, Sc, Sm, Ti, Th, V and Zn.

The concentration of Al, Cl, Cr, Cs, K, Sb and Zn were lower than in precipitation water sampled from the ten stations distributed over the country. The contents of Ba, Cs, Sc, V and Zn were higher than the median values of world freshwater reported by Bowen (1979) as shown in Fig. 1. Element concentrations of rainwater are classified in Table 1.

The sources of many elements in rainfall in Haikou are aerosols with various origins including tropospheric, marine and local processes. Ocean elements Cl, Na, Ca, Mg and Br are introduced mainly from marine aerosols. However, concentration of Ca in Haikou rainwater (Table 1) is much higher than that in the concentration rank of elements in marine aerosol (Raemdonck & Maenhaut, 1986). It must have been superimposed by another local sourced aerosol. It is worth noting that anthropogenic sources have important contributions to the high concentrations of As, Br, Sb, V and Zn in rainwater. This is caused mainly by coal/petrifactive burning. The high concentrations of Ba, Cs, Sc, Th, etc., may be contributed from coal burning too, because the contents of these elements in Chinese coal (averaged from more than one hundred coal mines) are much higher than those of American coal, for example. Of course, the contribution from natural aerosols formed from wind-blown dust, for example, could not be excluded.

River water

Twenty-four elements, with the element Lu in addition to those found in rainwater, were detected in river water.

Concentrations of Ba, Ca, Cr, Mg, Na and Sb were the lower than in river waters sampled simultaneously from ten major rivers in China, including the Yangtze River at Nanjing, the Yellow River at Yinchuan, etc. This is mainly due to the element content of the rainfall with large annual amounts and the shorter turnover time of this island river water. From Table 1 it can be seen that the concentration of most elements in the river water are of the same order as in rainwater. It therefore follows that the water of this river is recharged substantially by rainfall, and the geological effect currently met in many other rivers seems less important. However, contents of Zn, V, Co, Cs, Sm and Lu are higher than the highest values of world freshwater reported by Bowen (1979). It shows both the anthropogenic impact from burning/industrial pollution and the enrichment of some lithosphere elements such as Lu during the runoff process.

Groundwater

The groundwater contains all the elements detected from rainfall and river water with additional Se, Sr and U. There are 12 elements with concentrations higher

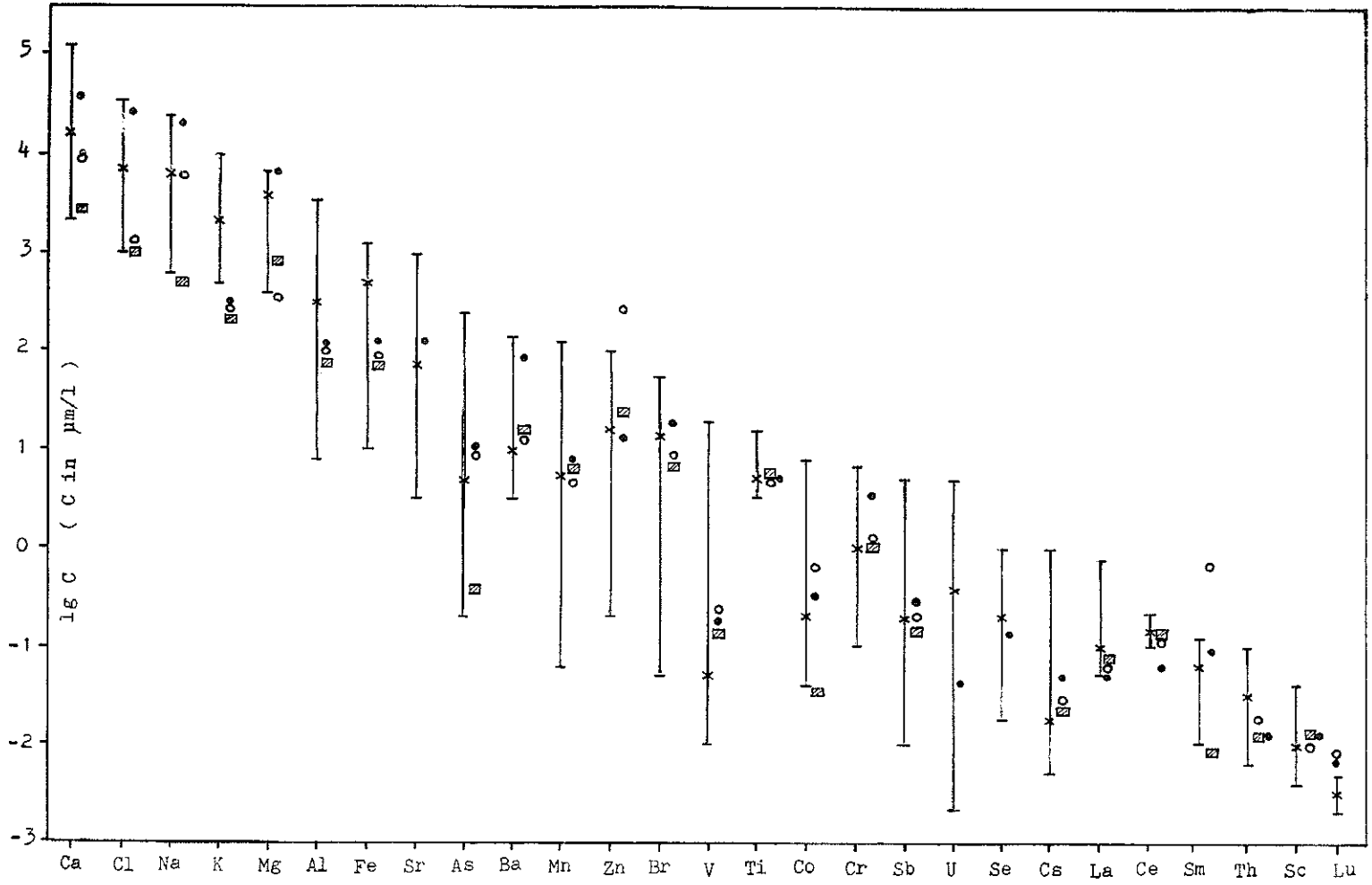

Fig. 1 Comparison of the variations of element concentrations determined by neutron activation of rainwater (□), river water (o) and groundwater (•) in Haikou, Hainan Island, China, with the concentration ranges of world freshwaters reported by Bowen (1979) (bars) and their median values (×).

Table 1 Element composition and element concentrations of rainwater, river water and groundwater of Haikou, Hainan Island, China, determined by neutron activation.

Concentration (ppb)	Element composition of:		
	Rainwater	River water	Groundwater
$>10^4$			Ca Cl Na
10^3–10^4	Ca	Ca Cl Na Zn	Mg
10^2–10^3	Cl K Mg Na Zn	K Mg	Fe K Sr
10–10^2	Al Ba Fe	Al Ba Fe	Al Ba Br Zn
1–10	Br Cr Mn Ti	As Br Mn Ti	As Cr Mn Ti
0.1–1	As Ce Sb V	Ce Co Cr Sb Sm V	Co Sb Se V
0.01–0.1	Co Cs La Sc Th	Cs La Sc Th	Ce Cs La Sc Sm Th U
0.001–0.01	Sm	Lu	Lu

than the median values of Bowen (1979) as shown in Fig. 1. The natural abundance of rare elements and rare-earth elements in the Earth's crust ranks in the order Sr > Ba > Ce > La > Se > Sm > Th > U > Cs > Lu > Sb. In the groundwater of Haikou, the ranking is similar, but the elements Cs, Sb, Sm and U, which move easily in water, are enriched and so ranked higher.

Concentrations of most elements in groundwater are higher than those in river water and rainwater except for the contents of Zn, Co, Sm and Lu—their highest values occur in river water. The comparison of the element composition of waters as listed in Table 1 reveals that elements Br, Cr, Fe, Lu, Mg, Se, Sr and U in groundwater are sourced mainly from the lithosphere, because either they are not detected in rainfall or they are enriched in groundwater.

CONCLUSIONS

Twenty-three, twenty-four and twenty-seven elements were detected in rainwater, river water and groundwater, respectively. Concentrations of Al, Cl, Cr, Cs, K, Sb and Zn in rainfall are the lowermost ones while Ba, Ca, Cr, Mg, Na, Sb and Sc were the lowermost ones between all sampling stations distributed in various climatic regions of China, including main rivers of this country. However, high contents of Ba, Cs, Sc, V and Zn in rainfall and of Co, Cs, Lu, Sm, V, Zn in river water, which exceed the median values of world freshwater reported by Bowen (1979) reveal the anthropogenic impact from burning and industrial pollution.

In this typical humid tropic basin, in shows that river water is mainly recharged by rainfall, groundwater is sourced from not only the rainfall, but also the local lithosphere.

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