Ecological and geochemical conditions of the groundwater in the Jianghan Basin, Hubei Province, China

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Abstract: The Jianghan Basin of the Hubei Province in China is an area of high population density, and intensive agricultural use. It is shown that the groundwaters of this region is generally fresh with a total range of TDS from 0.4–1.1g/L and pH 7.1–8.0. Major portion of these waters are naturally clean and only part of it polluted with the ions: Cl, SO_4, NO_3, PO_4, Ca, Mg, K. The sources of these elements are mineral fertilizers, which local people use for productivity of soils during long period.

Riassunto: *Il Bacino dello Jianghan nella Provincia di Hubei in Cina è un'area ad elevata densità di popolazione ed intenso utilizzo agricolo. È stato dimostrato che le acque sotterranee di questa regione sono caratterizzate da valori di TDS compresi tra 0.4-1.1 g/L e valori di pH compresi tra 7.1-8.0. Le acque presentano perlopiù buone caratteristiche qualitative con solo la presenza locale in concentrazioni elevate di Cl, SO_4, NO_3, PO_4, Ca, Mg, K. Queste situazioni sono legate all'utilizzo di fertilizzanti minerali utilizzati per lunghi periodo al fine di aumentare la produttività agricola dei suoli*

Keywords: Chlorite; Nitrate; Sulphate; Fluorine; Zone of hypergenesis; Equilibrium of groundwater

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Introduction

In recent years, issues of environmental ecology and groundwater geochemistry have taken on new importance worldwide. Almost one third of the world's population consumes poor-quality water. The result has been an avalanche of publications on understanding these issues, by the industrial and scientific communities. Groundwater is considered one of the major sources of fresh water, as a result the ecological geochemistry of groundwater has taken on a special importance in the past couple of decades (Deutsch, 1997; Domenico and Schwartz, 1990; Fetter, 1993; Hutzinger, 1991; Jorgensen at al., 1998; Soliman at al., 1992; Pinneker, 1999; Shvartsev, 2008).

The study area of interest is the Jianghan basin of China, the area is densely populated and has been settled for a long time in the area of the Yangtze River (Fig. 1).

The Short Characteristic of the Study Area

The Jianghan plain is located in the central and southern part of Hubei Province with a subtropical climate. The region is characterized with four distinct seasons and abundant rainfall. The spring and winter seasons are short while the summer and autumn seasons are long. In Hubei Province the summers are hot and wet and the winter is relatively cool and dry. The average annual temperature of the Jianghan plain is approximately 16˚C. The average winter temperature ranges from 1–6˚ C, while for the summer season ranges from 24–30˚C. Active rainfall occurs between June and August.

The average annual precipitation is 1000–1300 mm. It increases from north to south and is relatively equal between east and west. Precipitation during the spring months ranges between 268–483 mm, accounting for 30%–37% of total annual precipitation. During the summer rainfall ranges between 390–495 mm, which is 35%–39% of total annual amount. The autumn weather is primarily controlled by cold air flow and normal precipitation of 213–264 mm (17%–23% of the whole year). The cold winter is characterized by low precipitation, which accounts for 7%–10% of the annual average. The average annual evaporation rate is only 200 mm and allows for the formation of active runoff year round.

The Yangtze River is the largest surface water system in China, flowing through the entire region from the west to the east. It is one of the most important factors that control the surface water and the groundwater for the study area. The Hanshui River is the second major river system in the region it flows into the Hubei province from the north. The Hanshui River performs an important part in controlling groundwater recharge and surface water runoff and discharge for the northern region. The Yangtze and Hanshui Rivers meet in Wuhan, the capital of Hubei Province. This low-lying area is characterized by deep alluvial deposits, many small rivers and numerous large and shallow lakes all formed by the meandering Yangtze River.

Today, under the influence of technogenic factors the plain landscape has changed considerably and the territory is characterized with a high population density of about 800 people/square km. The

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territory has been settled for more than 2800 years.

The alluvial plain is a honeycomb of waterways bordered by natural levees, and the depressed areas encompassed by these waterways are dish-shaped in cross-section. Mountain ranges surround the eastern, southern and western sides as well as part of the northern side of the plain (Fig.1).The mountains are remains of the Palaeozoic basement on the surface combined with limestone and sandy-argillaceous shale crumpled in folds. The intermountain basin consists of Eocene, Neocene and Quaternary rocks.

There are three main water-bearing rock groups in the study area. The three groups are the shallow pore groundwater petrofabric, an upper confined pore groundwater petrofabric and the lower confined facture pore groundwater petrofabric (Zhang, 2005).

The shallow pore groundwater petrofabric is composed of Quaternary Holocene, while the upper confined pore groundwater petrofabric is composed of Pleistocene and Middle Pleistocene. Since there is no aquiclude between them, and the hydraulic connection is small, the clay between them is lens shaped, there is no formed aquitard and thus is an aquifer.

There is a clay aquitard between the middle and lower Pleistocene, while between the lower Pleistocene and the Upper Tertiary there is no obvious aquitard. Water quality and groundwater dynamics are very similar to one another and could not be separated for evaluation. Therefore the lower confined fracture pore groundwater petrofabric, is taken to be an aquifer.

The water-rich conditions vary greatly in different sections. The maximum thickness is 280m, the thinnest is several meters. The maximum thickness of the shallow pore groundwater petrofabric is 120–140 m, while the maximum thickness for the aquifer is 90 m and the thinnest is several meters. The lithology of the aquifer is clay, silt, silt sand, sand and gravel. Generally it contains mud, however the content is uneven, with it being higher in the center of the basin than at the edge, and it contains little or no sand and gravel (Zhang, 2005).

The recharge routes for the unconfined pore groundwater are meteoric water and infiltration of surface water, with surface water being the primary recharge route. The river is the primary recharge source for areas surrounding the river and recharges when the river level rises. The surface and meteoric water are the main recharge sources as well as an important discharge place of unconfined pore groundwater. Besides the ways mentioned above, evaporation, artificial discharge to the vicinity region are also the major discharge ways in unconfined pore groundwater and the evaporation discharge amount is the largest. Because the level of unconfined pore groundwater is often higher than the upper confined pore groundwater, the former will leak discharge to the other naturally. The runoff path of unconfined pore groundwater is short, the particle size of aquifer medium is fine, and the water holding of the aquifer medium is good.

The major recharge sources for the confined pore groundwater include leaking from the shallow unconfined pore groundwater, the upward recharge of the lower confined fracture porous groundwater and the seepage recharge around. Both the Yangtze River and the Han River cut through the top of water-resisting layer. This puts the surface water and the upper confined pore groundwater directly in contact, shortening the way of seepage and thereby allowing surface water to be an important source of recharge.

The terrain of Jianghan Plain is flat, the roof of the aquiclude is almost horizontal, the difference of water level is small and as a result the hydraulic gradient is low. The major routes of discharge for the groundwater are runoff discharge into adjacent areas and aquiferous rock formations along with artificial discharges in populated areas. The flat relief of the territory show a small and even depth for the water table of the order 2-10 m (Fig. 2). The groundwater is widely used by the local population as a source of drinking and potable water. In these areas of the unsaturated zone, impermeable clay is localized, resulting in a water table that is poorly protected from penetration of surface pollution.

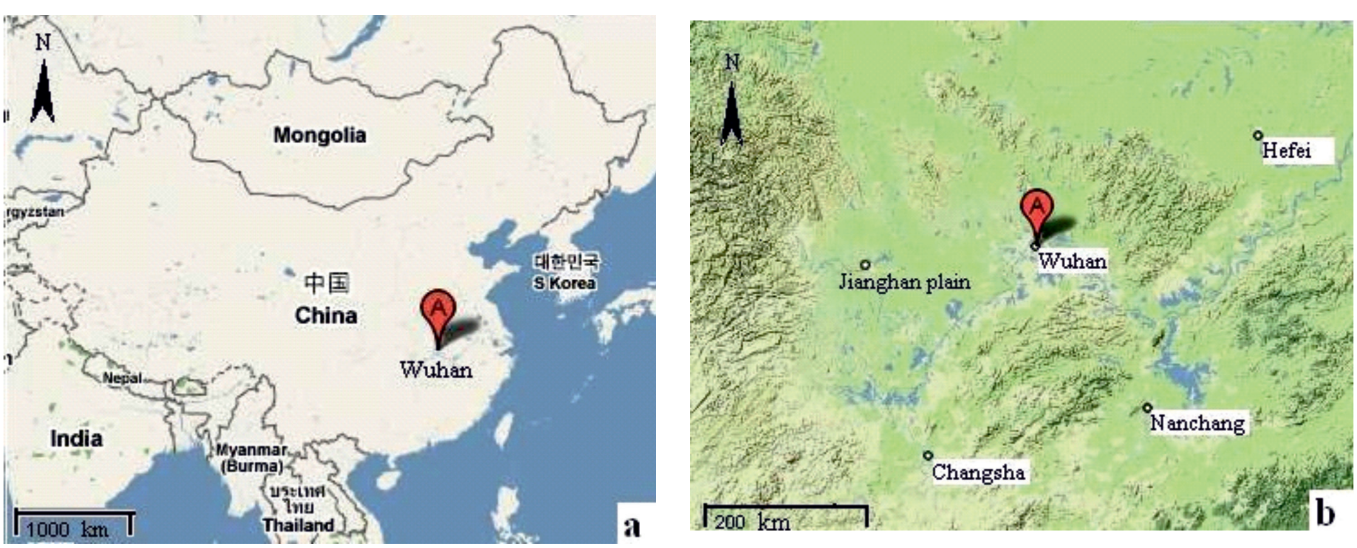

Fig. 1: *Maps showing: (a) the geographical location of Hubei Province in China; (b) topographical map of Jianghan Plain.*

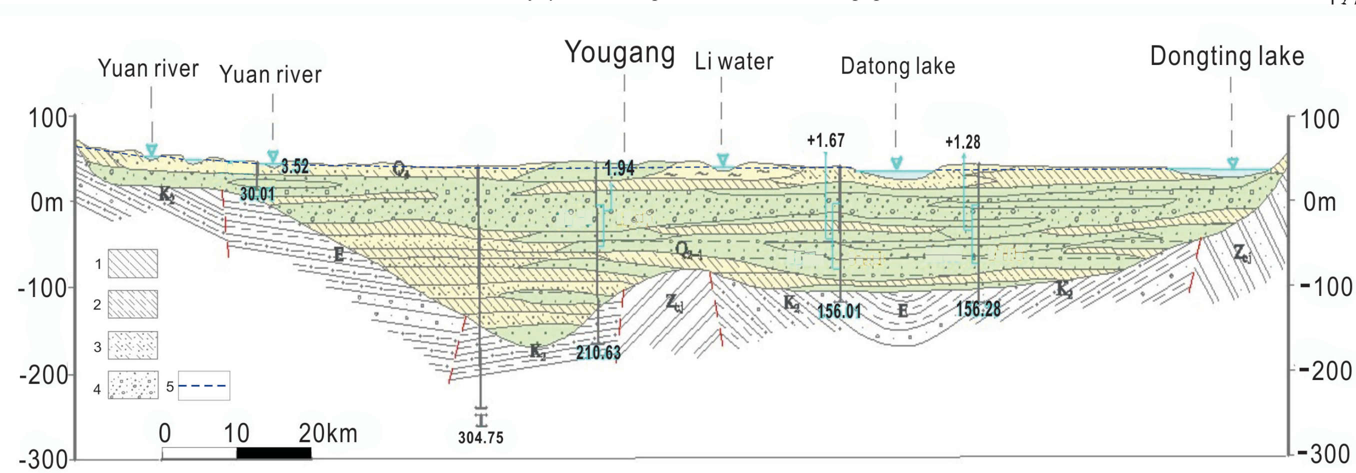

Fig. 2: *A typical hydrogeologic cross-section of Jianghan Basin.1 – Clay; 2 – Sandy clay; 3 – Clay sand; 4- Sandy gravel; 5 – Water level (from Zhang, D., 2005).*

Geochemistry of Groundwaters

The study program was divided into two stages. The first stage conducted in January 2007, consisted of 60 water samples being selected (Fig. 7). In December 2008 the second part was done. 20 more water samples were obtained from the same wells. All the water samples were obtained from wells used by local people for drinking and household needs. In total, 80 water samples were selected and analyzed. The well pump range was generally narrow in the range of 4 to 20 m with rare cases the pumps reaching 30 to 40 m and in one instance it reached 80 m. The temperature of water fluctuates from 8.7 to 20.3 ºC. Water analysis was performed by the accredited laboratories of China University of Geosciences (Wuhan City) and Tomsk Polytechnic University (Tomsk City).

Typical analyses of the groundwater for this region are shown in table 1 and represented at Piper Plot (Fig. 3). The data shows that the groundwater of the study area is basically fresh water with a TDS range of 0.4 to 1.0g/L with a rare increase to 1.5g/L. pH values fluctuated from 6.8 to 8.1, but generally stayed in the range of 7.2–7.6, with the water in the neutral range and slightly alkalescent. All water samples are carbonate except one sample which has SO_4-HCO_3 composition. Cation composition was more varied, calcium is dominant, but Ca-Mg and Ca-Na are high as well, HCO_3-Na is inherent. Concentration levels of SO_4 and Cl were low in the majority of samples, though in separate points it reached 204 and 80 mg/L respectively. In separate tests high concentrations of NO_3, F and PO_4 were also observed. This demonstrates possible localized technogenic pollution of water in the study area. We will consider this question in more detail. First of all, we will look how composition of water varies with a depth.

The analysis showed that pH and TDS of water did not increase with depth. The most alkaline and mineralized water was at a shallow depth, not exceeding 6m (Fig. 4). TDS of the deepest water was only 0.6–0.7g/L with a pH range of 7.3–7.4, although pH and TDS of water must be growing slightly with depth.

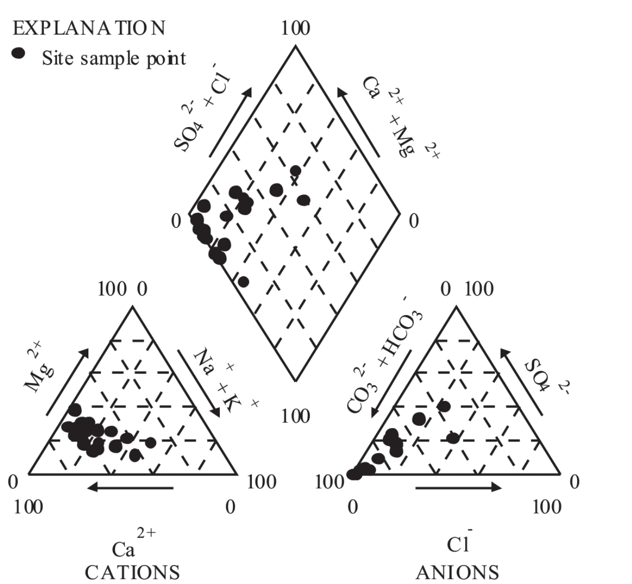

Fig. 3: *Piper hydrochemical plot of typical groundwaters of Jianghan Plain.*

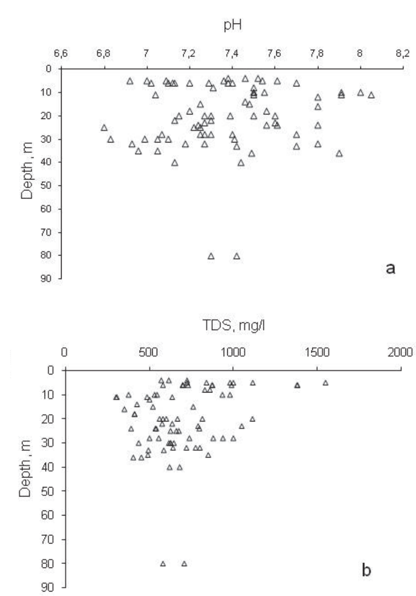

Fig. 4: *Dependence between pH (a) and TDS (b) of a depth of groundwater occurrence.*

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Tab. 1: *Chemical composition of typical underground waters of Jianghan basin.*

Sample No.	pH	HCO_{3-}	SO_4^{2-}	Cl^-	NO_{3-}	NO_{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	TDS	PO_4^{3-}	F^-	Chemical type
4	8,0	332	11,8	6,1	3,05	<0,001	70,2	11,2	33,0	0,66	468	0,005	0,16	HCO_3-Ca
11	7,2	311	0,13	1,73	0,01	0,005	50,1	16,0	31,1	0,63	411	0,005	0,33	HCO_3-Ca-Na-Mg
12	7,6	512	0,03	1,94	0,51	0,005	95,0	31,8	24,5	0,71	667	0,24	0,89	HCO_3-Ca-Mg
13	7,7	640	17,9	19,89	0,77	0,005	135	53,4	5,72	0,33	873	0,005	0,17	HCO_3-Ca-Mg
14	7,6	803	22,9	8,8	3,67	<0,001	122	20,8	139	7,36	1128	0,10	4,92	HCO_3-Na -Ca
25	7,6	799	0,09	1,28	6,10	0,005	160	40,8	42,3	0,73	1 050	0,14	0,34	HCO_3-Ca-Mg
27	7,8	597	0,06	2,6	16,0	0,005	120	38,4	21,5	1,06	797	0,39	0,19	HCO_3-Ca-Mg
29	7,8	585	0,01	5,28	4,52	0,005	125	30,6	23,5	0,78	775	0,11	0,043	HCO_3-Ca-Mg
30	7,3	719	0,09	5,48	0,12	0,005	160	42,1	10,5	0,42	938	0,45	0,32	HCO_3-Ca-Mg
31	7,7	378	0,13	0,25	0,23	6,730	80,3	17,3	16,4	0,82	493	0,25	0,031	HCO_3-Ca
33	7,9	341	0,13	0,83	0,11	0,005	64,4	13,5	30,5	0,72	451	0,005	0,21	HCO_3-Ca
35	7,5	542	47,9	26,39	6,20	0,005	140	24,6	40,0	2,89	830	0,005	0,16	HCO_3-Ca
36	7,1	378	84,4	22,5	31,7	0,005	115	15,0	48,4	1,66	697	0,005	0,11	HCO_3-Ca
37	7,3	536	0,04	0,92	6,80	0,005	113	31,8	15,8	1,84	707	0,029	0,017	HCO_3-Ca-Mg
39	7,5	189	95,8	30,81	78,8	0,005	75,4	15,2	51,4	8,71	545	1,14	0,21	HCO_3- SO_4-Ca-Na
40	7,5	158	63,9	78,25	159	0,005	57,2	20,3	96,8	1,17	635	0,005	0,18	HCO_3- NO_3-Cl-Na-Ca
41	7,3	829	0,13	2,25	22,3	0,005	189	40,5	29,3	1,06	1 114	0,24	0,13	HCO_3-Ca
42	7,4	372	102	19,03	51,5	0,005	120	18,1	48,3	5,95	738	0,005	0,18	HCO_3-Ca
43	7,1	475	0,01	1,55	0,38	0,077	101	20,2	26,5	0,71	626	0,072	0,3	HCO_3-Ca
44	7,2	671	142	66,25	159	0,005	200	58,8	80,5	4,83	1 383	0,005	0,6	HCO_3-Ca-Mg
56	7,4	555	86,8	61,66	40,2	0,005	160	42,0	41,3	1,59	989	0,005	0,15	HCO_3-Ca-Mg
57	7,5	231	204	81,0	172	0,005	104	33,2	101	7,54	935	0,72	0,3	SO_4- HCO_3-Ca-Na

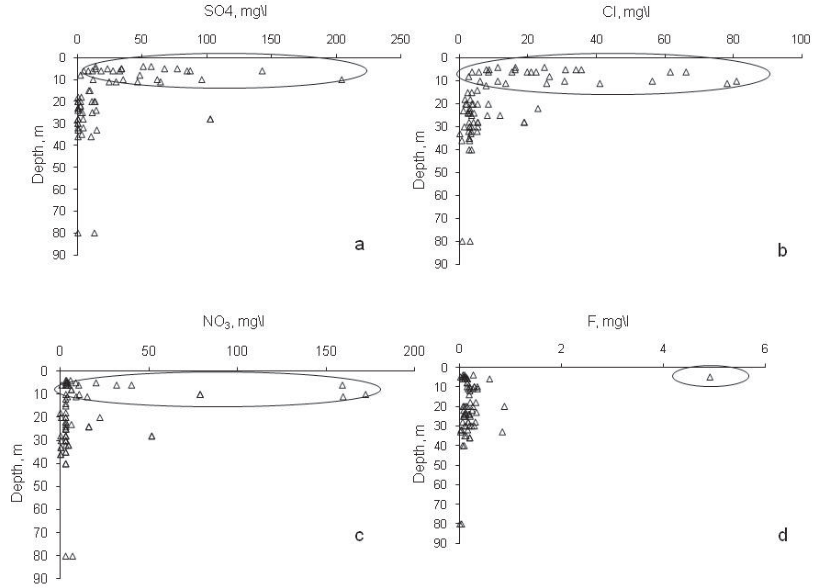

Fig. 5: *Concentration of sulphate ion (a), chlorine (b), nitrate (c) and fluorine (d) in underground waters according with their depth of occurrence.*

Interestingly the plots of the other anions (Cl, NO_3, SO_4, F) are all rather similar. Concentration of these components all occur at shallow depths (Fig. 5).

In a normal case for underground waters formed under natural conditions of a zone of hypergenes, the concentration of elements increases with depth as well as their TDS and pH values (Deutsch, 1997). A possible explanation for this case, is that enrichment of underground waters by abnormal concentrations of elements occurs not at the expense of dissolution of bearing rocks as it would under natural conditions, but due to their inflow from the unsaturated zone.

Ecological Condition of Underground Water

If we compare concentrations of separate elements with existing maximum permissible limit, it is observed that only a small group of elements increase (Table 2). It is apparent from the results table that not only a small number of elements but also the quantity of points that are characterized with a high concentration of said elements is insignificant and makes up 10% of the total, essentially data points 39, 42, 52, 54, 55, 57, 58 and 59.

Therefore in investigated basin ecologically pure water which satisfies requirements of maximum concentration limit is developed basically. Only the small area of groundwater was polluted by such compounds as NO_3, Cl, SO_4, and more rarely by PO_4, F, Fe. Accordingly in separate samples TDS and pH values exceeded. The chemical compounds that exceeded the maximum concentration limits indicate that the groundwater contamination occurs from agricultural production. Such compounds are common agricultural pollutants where mineral fertilizer, nitrogenous associations and pesticides are used. Observe that HCO_3 concentrations behaved differently, as the HCO_3 high concentrations meet at different depths (Fig. 6).

The sampling points with high concentrations of pollutants reside compactly on two sites of the north-eastern part of the study area (Fig. 7). With the available data it was determined that sites with contaminated water, had no blocking clay layer to impede infiltration. It was also found that individual sample points only have high concentrations of one anion (F or SO_4) which indicate water pollution at these locations.

It was discovered that high concentrations of phthalate esters were also found in the investigated area. The interesting aspect of this phthalate discovery was that the maximum concentration of phthalate (> 1000 ng/L) correlates with the same points as the other pollutants, namely sample points: 52, 57—59 and also 47, 48, 50 and 53. The phthalate esters are probably indicative of earlier contamination other than the other pollutants (Liu at al., 2009; Zhang at al.,2008).

Equilibrium of Groundwaters with Enclosing Rocks

As explained earlier the geochemistry of groundwaters of Jianghan basin are defined by two basic processes: 1) dissolution of enclosing rocks and 2) contamination by technogenic products. Accordingly, the rocks and soils including the technogenic products also serve as the basic source of the chemical elements. To comprehend the role the rock play as the source of groundwater enrichment

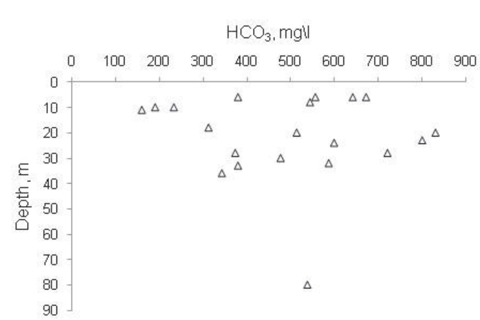

Fig. 6: *Dependence of maintenance of hydrocarbonate ion in underground waters of a depth of their occurrence.*

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Tab. 2: *The comparative concentration analysis of some elements in underground waters of Jianghan basin with maximum concentration limit.*

Elements, associations	Permissible limit, mg\l				Maximum maintenances in water	Quantity of points which exceeding maximum concentration limit	
	China (III)	Russia	USA	WHO*		Russia	USA
pH	6.5-8.5	6-9	6.5-8.5	7.0-8.5	8.1	0	0
TDS	1000	1000	500	1500	1550	3	45
Cl	250	350	250	600	81	0	0
SO_4	250	500	250	400	201	0	0
NO_3	20	45	45	45	172	2	2
NO_2	0.02	0.5	3.3	-	6.7	2	2
PO_4	-	0.3	-	-	1.14	4	-
F	1.0	0.7-1.5	2.0	0.6-0.9	4.92	1	1
Ca	-	200	-	200	200	0	-
Mg	-	75	-	150	58.8	0	0
Na	-	200	-	-	139	0	-
Fe	0.3	0.3	0.3	1.0	0.82	7	7
Mn	0.1	0.1	0.05	0.5	6.42	6	10

* - World Health Organization

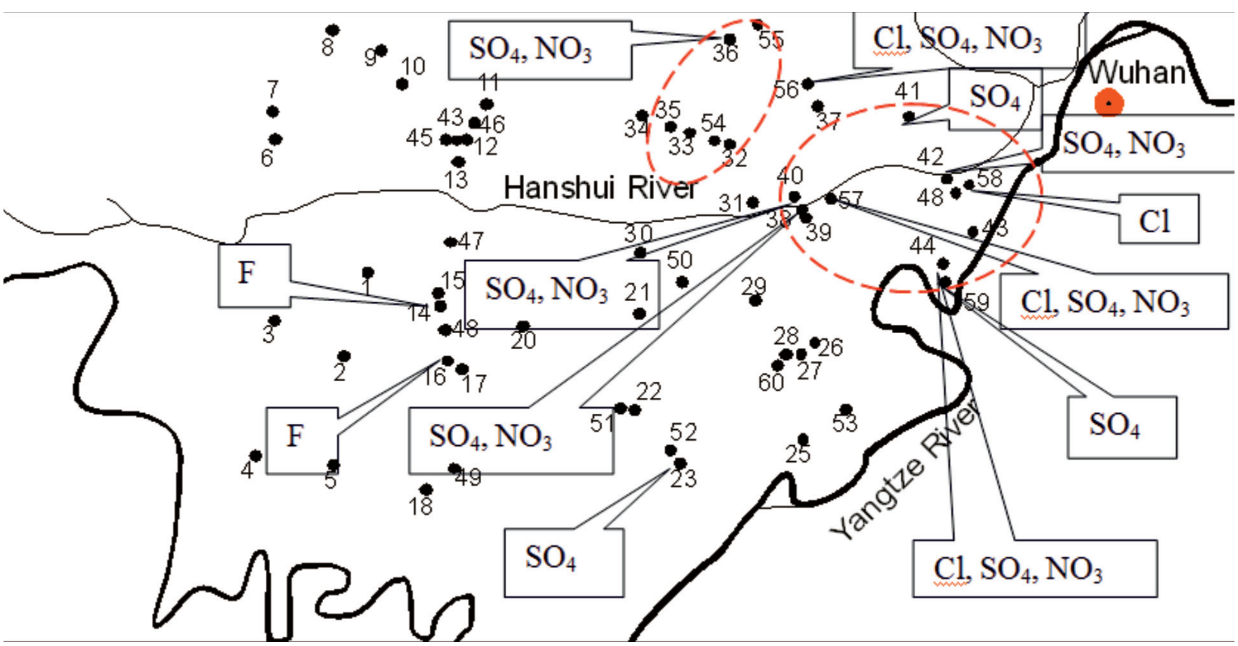

Fig. 7: *Map of water points location with drawing of data of abnormal high concentration of polluting elements: Cl>40, SO4>50, NO3>30, F>1mg/L in groundwaters.*

due to various elements, the equilibrium condition in the water-rock system will be considered.

As water enclosing rocks contains prevail aluminosilicate and carbonates, as illustrated earlier, it is important to consider the equilibrium with these rocks, starting first with the carbonates.

As illustrated in Fig. 8 almost all water in the study area is in equilibrium with calcite, the basic carbonate mineral. The sole exception was sample point 40. It is therefore impossible for the carbonate to be the source for the chemical elements. The carbonate rocks can only change the character of the geochemical environment.

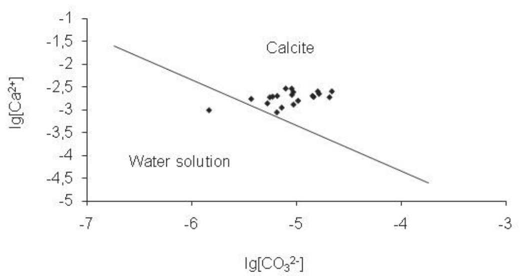

Fig. 8: *Degree of groundwaters saturation with calcite at 25°C in Jianghan basin.*

Characterizing the equilibrium for groundwater in contact with aluminosilicates is far more difficult (Fig. 9). The majority of points fall within the field of montmorillonite stability of different structure and partially in the field of illite and kaolinate. Concurrently all was is in a state of non-equilibrium with anorthite, albite, muscovite, i.e. with minerals endogenic genesis and also Mg-chlorite.

The obtained data confirm conclusions drawn earlier by Shvartsev (2008) that the character of groundwater equilibrium for as zone of hypergenesis has an equilibrium / non-equilibrium character which provides for a continuous balance of endogenic minerals, the water is in a state of non-quilibrium with such minerals. The continuous formation of clay minerals such as montmorillonites and illite where the water is in a state of equilibrium with such minerals. Unfortunately it is not possible to calculate the scale of this phenomenon due to the lack of data on the rate of undergrounf runoff. However, it is shown that fresh waters HCO_3-Ca-Na and Ca-Mg types with a TDS <0.8 g/L and pH <7.6 are formed due to dissolution of aluminosilicates. Such water can act as addition sources to add to the chemical background for waters of the given region. Other waters with high concentrations of NO_3, Cl, SO_4, PO_4, F have additional sources of contamination due to mineral or organic fertilizers used in agriculture.

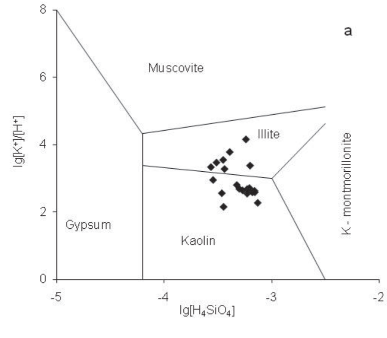

Fig. 9a: *system H_2O-Al_2O_3-CO_2-CaO-SiO_2.*

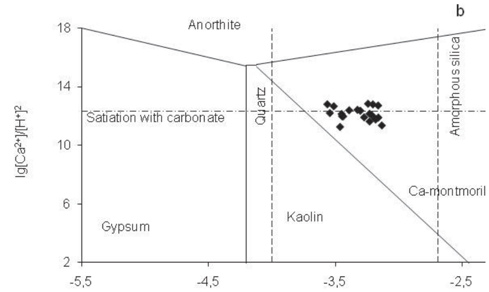

Fig. 9b: *system H_2O-Al_2O_3-Na_2O-SiO_2*

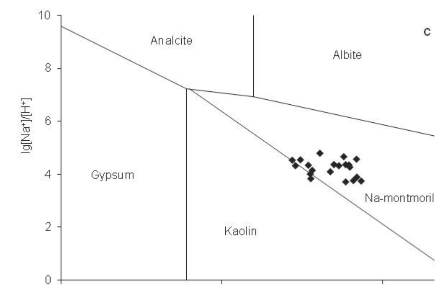

Fig. 9c: *system H_2O-Al_2O_3-MgO-SiO_2*

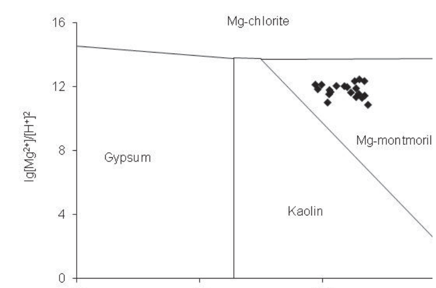

Fig. 9d: *system H_2O-Al_2O_3-K_2O-SiO_2*

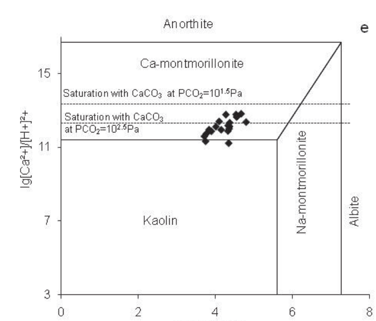

Fig. 9e: *system H_2O-Al_2O_3-CO_2-Na_2O-CaO-SiO_2 at $lg[H_4\ SiO_4] = -3.5$*

Fig. 9a-b-c-d-e: *Diagrams of equilibrium of groundwaters of Jianghan basin with aluminosilicate at 25°C.*

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Conclusion

The geochemistry of the groundwater for the intermountain Jianghan basin are defined by two basic processes: 1) natural interaction of a penetrating atmospheric precipitation with the enclosing rocks which is not significant due to active water exchange. These processes form waters on depth, approximately 80 m with a TDS nearby 0.6–0.7g/L and pH 7.3–7.4 and HCO_3-Ca-Na structure. All other elements are found at normal concentrations as defined by the geochemical type of water. It is possible to name such waters as a background waters; 2) contamination of atmospheric precipitation in the soil horizon during the process of dissolution of technogenic products from the application of agricultural fertilizer. Depending on the type of fertilizer used concentrations of NO_3, Cl, SO_4, PO_4 or F increase in different combinations in water and also naturally with Na, Ca or Mg. The amount of technogenic products depends on many factors such as, whether a clay waterproof deposit is present or absent in the unsaturated zone and on the quantity and type of fertilizer used.

Despite high population density, rapid land development, the longevity of human occupancy, superficial bedding groundwater and the rather weak security form anthropogenous influence, the water for the most part remains uncontaminated and fresh. Anthropogenous influence has only impacted a small part of the investigated groundwater and that is unique. The study of the hydrogeology of this region is therefore of great interest.

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