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ABSTRACT

Arsenicosis and fluorosis, two endemic diseases known to result from exposure to their elevated concentrations in groundwater of north China used by many rural households for drinking, have been major public health concerns for several decades. Over the last decade, a large number of investigations have been carried out to delineate the spatial distribution and to characterize the chemical compositions of high As and F groundwaters with a focus on several inland basins in north China. Findings from these studies, including improved understanding of the hydrogeological and geochemical factors resulting in their enrichments, have been applied to guide development of clean and safe groundwater in these endemic disease areas. Survey efforts have led to the recognition of iodine in groundwater as an emerging public health concern. This paper reviews the new understandings gained through these studies, including those published in this special issue, and points out the direction for future research that will shed light on safe guarding a long-term supply of low As and F groundwater in these water scarce semi-arid and arid inland basins of north China.

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1. Introduction

China, a country with the largest population in the world and an average GDP growth of 10% since 1980 (International Monetary Fund), has inadequate water resources that are unevenly distributed. In arid north and northwest China, groundwater has been over-exploited (Currell et al., 2012; Ji et al., 2006; Wang et al., 2008). Irrigated areas have increased from 16% to 35% of cultivated land between 1949 and 2000, accounting for 68% of combined water withdrawal from surface water and groundwater in 2000 (FAO, 2000; Scanlon et al., 2007). Increasingly, groundwater has been utilized to irrigate especially in the North China Plain (Cao et al., 2013; Zhang et al., 2004). More importantly, groundwater provides for about 70% of the drinking water in the arid north and northwest China (Qu, 1991). Sustaining the rapidly growing economy threatens the quality of groundwater. Each year, an estimated 190 million Chinese become ill as a result of polluted water from industrial and agricultural activities, causing 60,000 premature deaths (Chan and Griffiths, 2010). Although the degradation of water quality has been most evident and wide spread in surface water, groundwater quality surveys have identified regional scale nitrogen pollution and point-

sourced metal and organic contaminations (Wen et al., 2012). This special issue does not address groundwater quality issues from anthropogenic sources. Instead, it reports new hydrogeochemical findings on naturally occurring substances including arsenic (As), fluorine (F), and iodine (I) in groundwater of northern China that are linked to endemic diseases through drinking water exposure.

Elevated concentrations of As in groundwater ($>10\mu\text{g/L}$, or $>50\mu\text{g/L}$ in older literature) have been reported at many locations around the world in the last 2 decades. Consumption of this water adversely affects the health of over 100 million people mostly in Asia (Ravenscroft et al., 2009). About 10,000 arsenicosis patients who had been chronically exposed to As from drinking As-rich groundwater and burning As-rich coals were identified in a survey targeting endemic areas between 2003 and 2005 in China (Yu et al., 2007). This led to accelerated mitigation measures by the Chinese government that began in 2000 with initial support from UNICEF. Arsenicosis from groundwater exposure was first reported in 1983 for Kuitun city, Xinjiang Uygur Autonomous Region, China (Wang and Huang, 1994). Investigations have identified several aquifers in inland basins of northern China where groundwater frequently contains $>10\mu\text{g/L}$ As, the current drinking water standard of China for public water supply, and have delineated endemic arsenicosis areas where groundwater frequently contains $>50\mu\text{g/L}$ As, the current drinking water standard of China for individual household and small ($<1000\text{m}^3/\text{day}$) water systems serving $<10,000$ people. This paper provides a review of studies in Yinchuan, Hetao and Songnen Plains, as well as Huhhot, Datong and Yuncheng Basins (Table 1 and references therein) and an overview of 5 papers on As hydrogeochemistry in this special

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Table 1
Chemical characteristics of high arsenic groundwater in inland basins of Northern China.

Area of interest	Groundwater [As] ranges ($\mu\text{g/L}$)	Climate	Aquifer	High-As aquifer location	High-As Depth	High-As (>50 $\mu\text{g/L}$) water chemistry	Hydraulic gradient
Yinchuan Plain ^a , 7300 km ² , Ningxia Hui Autonomous Region	<1 to 177	Continental semi-arid, precipitation of 183 mm/yr, evaporation of 1955 mm/yr	Holocene alluvial and lacustrine sediments deposited in a Cenozoic extensional fault basin.	North Yinchuan Plain with a distinct strip-like regional pattern along two paleo Yellow River channels	Primarily shallow (<40 m), [As] <1 to 47.3 $\mu\text{g/L}$; average = 7 $\mu\text{g/L}$ in deep groundwater (40 to 250 m)	Weakly to moderately alkaline environment (pH: 7.5–8.5) with ORP from –200 to +100 mV, but is more frequent when ORP is negative. Groundwater TDS is from 225 to 7388 mg/L, dominated by Na·Ca–HCO ₃ , Na–HCO ₃ ·Cl, and Na·Ca–HCO ₃ ·Cl types. [As] is positively correlated with [NH ₄ ⁺], [PO ₄ ³⁻] and is negatively correlated with [SO ₄ ²⁻]. Variable [As] over time for depths of 8–20 m but is less for depths of 30–80 m.	<0.4‰
Hetao Plain ^b , 10,000 km ² , Inner Mongolia	<1 to 1860	Continental arid and semi-arid, precipitation of 130–220 mm/yr, evaporation of 1900–2500 mm/yr	Fault-bounded Cenozoic rift basin over the last 50 Ma, Quaternary aquifer is composed of alluvial–pluvial sand, sandy silt, lacustrine and fluvial–lacustrine sandy silt, silty clay and clay. Sediment is rich in organic carbon (0.44%–5.57%) in the central part of the basin.	Very high [As] in central low-lying alluvial–lacustrine plain within dark gray fine sand layers north of the Yellow River alluvial plain. Lower [As] south of the Langshan Mountain piedmont alluvial fan. [As] higher in western Hetao than in eastern Hetao.	Mostly shallow, 2m–35 m. Highest [As] between 10 m and 29 m, but sample from 100 m has up to 340 $\mu\text{g/L}$ [As]. [F] and [B] can also be high.	Neutral to strongly alkaline (pH: 6.9–9.4) with reducing (min ORP: –431 mV) groundwater. TDS is 350–7460 mg/L with frequent brackish (TDS > 1500 mg/L) groundwater of Na·Mg–Cl·HCO ₃ and Na·Mg–Cl types. Fresh groundwater is of Na·Mg–HCO ₃ type, although Mg is not important in western Hetao's high As groundwater. High [DOC] (0.7 to 35.7 mg/L), [HCO ₃], [NH ₄], [Fe] and sulfide, dominance of As(III), occasionally elevated [CH ₄]. The [SO ₄] and [NO ₃] of high arsenic waters are less than those of low arsenic groundwater; [As] is locally positively correlated with [NH ₄ ⁺], [PO ₄ ³⁻] and [Fe]. Bulk sediment [As] ranged from 5 mg/kg to 73 mg/kg, maximum between 15 and 25 m of depth. Colloidal As, possibly as As–NOM complexes, exists. Little As(V) in central Hetao.	Usually <0.8‰
Huhhot Basin ^c , 4800 km ² , Inner Mongolia	<1 to 1493	Continental arid, precipitation of 440 mm/yr, evaporation > precipitation	Quaternary (largely Holocene) lacustrine and fluvial sediment aquifer in a fault-bounded Cenozoic rift basin, bounded to the north by the Da Qing Mountains, to the south and east by the Man Han Mountains and to the west the Yellow River.	In both the shallow (<100 m) and deep (100–500 m) aquifers, groundwaters evolve from oxidizing conditions along the basin margins to reducing conditions in the low-lying central part of the basin where high As concentrations occur	Mostly shallow <35 m. but a sample from 280 m has 308 $\mu\text{g/L}$ [As]. High [F] in shallow groundwater of Na–HCO ₃ type.	Neutral to moderately alkaline (pH: 6.7–8.7) and reducing (min ORP: –74 mV) groundwater with H ₂ S smell. High As in anaerobic groundwaters is associated with moderately high dissolved Fe as well as high Mn, NH ₄ , DOC, HCO ₃ and P concentrations. Deep groundwaters have [DOC] up to 30 mg/L. From the recharge area in the north to the discharge area in the south, groundwater evolves from Ca–Mg–HCO ₃ and Mg–CO ₃ types to Na–Mg–HCO ₃ and Na–Mg–HCO ₃ –Cl types to Na–Cl–HCO ₃ type, with TDS increasing from 500 mg/L to >3000 mg/L. Mostly As(III). Sediment [As] is from 3 to 29 mg/kg.	Low

Datong Basin ^d , 7440 km ² , Shanxi Province	<1 to 1932	Continental semi-arid, precipitation of 370–420 mm/yr, evaporation of 1980 mm/yr	Quaternary alluvial, alluvial–pluvial and alluvial–lacustrine aquifers (5–60 m, 60–160 m, >160 m) with gray to blackish, organic-rich reducing lacustrine sediment interlayered with alluvial sands deposited in a fault-bounded Cenozoic basin of the Shanxi rift system.	Groundwaters evolve from oxidizing conditions along the basin margins to reducing conditions towards the low-lying floodplain in south-central Datong Basin mostly between the Sanggan and the Huangshui Rivers.	Very high As between 15 and 40 m, and high As between 100 and 150 m. High [F] in groundwater with soda water chemistry.	Weakly to strongly alkaline (pH: 7.2 to 9.7) reducing environment (min ORP –242 mV) with H ₂ S and CH ₄ . Concentrations of SO ₄ and NO ₃ are very low in high arsenic waters. Concentrations of PO ₄ , Fe (>0.5), Mn (>0.1), HCO ₃ are high. [DOC] ranges from 1.4 to 17.5 mg/L. High As groundwater is mostly of Na–HCO ₃ or Na–HCO ₃ –Cl type with >80% as so called soda water (Na/(Cl + SO ₄) > 1). The TDS ranges from 205 to 10,700 mg/L. Mostly As(III) in reducing groundwater. Sediment As is from 0.3 mg/kg to 44 mg/kg, with biodegraded petroleum. Desorption is postulated to cause As enrichment in deeper groundwater whereas reductive dissolution is more prominent in shallow groundwaters.	Low
Yuncheng Basin ^e , 4946 km ² , Shanxi Province	<1 to 27	Continental semi-arid, precipitation of 550 mm/yr, evaporation of 1900 mm/yr	Quaternary aquifer of interlayered sediments up to 500 m thick, including a shallow unit (<70 m), a deep unit (>120 m), and an intermediate unit (70–120 m). The sediment is mostly aeolian loess containing quartz, feldspar, calcite, clays and mica, that comprises a series of depositional layers, mostly 2–5 m thick, separated by thinner (<1 m) palaeosol layers. The loess is also interlayered with alluvial sands and lacustrine clay Lenses in a fault-bounded Cenozoic basin of the Shanxi rift system.	Both F and As concentrations are highest in the northern Sushui River Basin where groundwater flow converges. One groundwater sample from 58 m depth near Kaolao contained 4870 µg/L of As but might be due to an anthropogenic source.	>10 µg/L As mostly found between 100 m and 150 m with very high F at <100 m	Weakly to moderately alkaline (pH: 7.2 to 8.8) but oxid (DO:1 to 6.5 mg/L) with considerable dissolved SO ₄ and NO ₃ . TDS ranges from 260 and 8450 mg/L. Groundwater with high As and F concentrations has a distinctive major ion chemistry, being generally Na-rich, Ca-poor and having relatively high pH values (>7.8). [As] is positively correlated with pH, [HCO ₃], and Na/Ca ratio and [F], suggesting desorption as an enrichment mechanism.	Low
Songnen Plain ^f , 188,400 km ² , Jilin Province and Heilongjiang Province	<1 to 179	Continental semi-arid sub-humid precipitation of 350–600 mm/yr, evaporation of 1500–2000 mm/yr	Meso–Cenozoic fault basin where neo-tectonic depression filled by alluvial lacustrine deposits.	In areas where Huolin and Tao'er Rivers merge and end, the inter-channel depression and lowland plain in the Southern part of the Songnen Plain.	Quaternary phreatic aquifer (<20 m) and confined aquifer between 20 and 100 m, with highest As between 30 and 50 m. High F detected.	Moderately to strongly alkaline (pH: 8.0–9.3) reducing groundwater. Arsenic is positively correlated with Fe, HCO ₃ ⁻ , Mn, Cl ⁻ , PO ₄ ³⁻ and TDS (265–2006 mg/L) and negatively correlated with SO ₄ ²⁻ and Se. High [As] water is of Na·Mg–HCO ₃ type with TDS up to 1054 mg/L, and is further enriched in As and becomes Na(K)–HCO ₃ –Cl type with TDS up to 2006 mg/L, possibly influenced by evaporation. [As] is low in Ca–HCO ₃ type water.	low

References for each region with high As groundwater, arranged in the sequence from west to east (Fig. 1) are as follows:

^a Yinchuan Plain: Han et al., 2010, 2013.

^b Hetao Plain: Bo and Luo, 2010a,b; Deng et al., 2009a, 2009b, 2011; Fujino et al., 2004, 2005; Gao, 1999; H.M. Gou et al., 2009, 2010, 2011, 2012; Q. Gou et al., 2008; X.J. Guo et al., 2003, 2006; He et al., 2010; T. Luo et al., 2012; Mao et al., 2010; Neidhardt et al., 2012; Yang et al., 2008; Zhang, 2004; Zhang et al., 2002, 2010c.

^c Huhhot Basin: Mukherjee et al., 2009; Smedley et al., 2003.

^d Datong Basin: H. Guo et al., 2003; Guo and Wang, 2005; Xie et al., 2008, 2009a, 2012a, 2012b.

^e Yuncheng Basin: Currell et al., 2010, 2011, 2012.

^f Songnen Plain: Bian et al., 2012; Tang et al., 2010.

issue. In addition, it summarizes the occurrence of high As ($>10\mu\text{g/L}$) in groundwaters throughout China (Table 2 and references therein).

Fluorosis associated with high F in drinking water has been reported in many but mostly low income countries around the world, including India (Ayoob and Gupta, 2006), China (Tian, 1989; Wang et al., 1999), Tanzania, Mexico, Argentina, and South Africa (Amini et al., 2008). The drinking water standard for F is 1.0 mg/L in China and the guideline value is 1.5 mg/L by the World Health Organization (WHO, 2008). Fluorosis associated with drinking water exposure was first identified in the Miao ethnic group from southwestern Guizhou (Kweichow) province by a British doctor Kilborn (Lyth, 1946). A national cross-sectional study carried out in 2008–2009 has documented a significant population level reduction in F concentrations of drinking water and urine, as well as reduction in prevalence rates of dental and skeletal fluorosis in children and adults in endemic fluorosis areas in 27 provinces of China resulting from the supply of fluoride-safe water (Wang et al., 2012a). The endemic fluorosis areas have been classified into three geochemical environments: soda groundwater rich in sodium from the arid and semi-arid regions of northern China, high total dissolved solids (TDS) and brackish groundwater in coastal aquifers influenced by marine transgression in northern China, and iron-rich soil in semi-humid southern China where F leaching and bioaccumulation occurs (Liu et al., 1980). Since the 1980s, the distribution of high-F groundwater and technologies for F removal from drinking water have been investigated, although most publications were in Chinese (Tian, 1989). It is worth noting that the spatial distribution of F in groundwater (Wang et al., 1999) tends to be of regional scale (about 1000 km²) in northern China but is of local scale ($<100\text{ km}^2$) in southern China (Fig. 1). This paper provides a review of hydrogeochemical studies of high F groundwater in Guide, Zhangye, Huhhot, Datong, Taiyuan and Yuncheng Basins, along with Hetao and Songnen Plains (Table 3 and references therein). It provides an overview of 4 papers on hydrogeochemistry of

high F groundwater and 2 papers on hydrogeochemistry of high I groundwater. Iodine is an essential element of the thyroid hormones. Iodine deficiency disorder is a well-recognized public health hazard that has been gradually mitigated through iodized salt. However, high intakes of iodine can cause some of the same symptoms as iodine deficiency for individuals with high susceptibility, including goiter and hypothyroidism (Pennington, 1990). The dietary reference intake level recommended by the Food and Nutrition Board of the National Academy of Sciences is 150 mg/day for adults (Munro, 2001). A summary of groundwater fluoride occurrence is tabulated (Table 4 and references therein).

Following a description of the geological setting of the Mesozoic–Cenozoic semi-arid and arid inland basins in northern China where groundwater frequently contain elevated concentrations of As and F (Section 2), the hydrogeochemical conditions and mechanisms resulting in As and F enrichment are reviewed and discussed (Sections 3 and 4) for several basins that have been extensively studied and the processes of As and F release to groundwater are best understood. A brief overview of iodine in the groundwater of China follows (Section 5). Finally, recommendations for future research relevant to water resources management conclude this paper (Section 6).

2. Geology of Mesozoic–Cenozoic sedimentary basins in northern China

Sedimentary basins in northern China and several Asian deltas where high As groundwater frequently occurs have sequences of sediment several km to $>10\text{ km}$ in thickness, usually deposited during rapid subsidence related to orogeny or rifting (Zheng, 2007). The sedimentary basins in northern China containing high As and F groundwater range from small ($<2000\text{ km}^2$) to vast ($>200,000\text{ km}^2$) (Tables 1 and 3), with high F groundwater occupying areas larger than that of high As

Table 2
Occurrence of arsenic in groundwater of China.

Province/autonomous region	County	Max. As ($\mu\text{g/L}$)	References
Shanxi	Shanyin, Yingxian, Shuozhou as part of Datong Basin; Fenyang, Xiaoyi, Pingyao, Wenshui, Jiexiu, Yuci, Qixian, Tianzhen, Xiaodianqu, Qingxu, Loufan, Dingrang, Yicheng, Yanhu, Yoongji	1932	Gao et al., 2013; Guo and Wang, 2005; Jin et al., 2003; Pei et al., 2005; Wang et al., 2010; Xie et al., 2008; XJ. Xie et al., 2011
Inner Mongolia	Dengkou, Linhe, Hangjinhouqi, Wuyuan, Wulateqianqi, Wulatehouqi, Wulatezhongqi, Tuoketuo, Tumotezuqi, Tumoteyouqi, Alashanzuoqi, as Hetao Plain; Keshenketengqi, Sunidyouqi, Sonidzuqi, Naimanqi, Ewenkizuzizhiqi, Xinbaragzuqi, Taibusqi, Horinger	1860	Bo and Luo, 2010a; H. Guo et al., 2008; He et al., 2010; Luo et al., 2006; Luo, 1993; Yang et al., 2008
Anhui	Fuyang, Dangshan, Wuhe, Tianchang	1146	Jin et al., 2003; Li et al., 2006; Qin and Xu, 2010; Yu et al., 2007
Xinjiang	Kuiteng, Wusu, Tacheng, Sulei, Bachu, Luntai, Awat, Shawan, Bohu,	830	Huang et al., 1985; Wang et al., 1993; Yu et al., 2007; Zhu et al., 2009
Yunnan	Tengchong, Gengma, Eryuan, Changning, Mengla	687	Chen et al., 2012; H. Liu et al., 2009; Yang et al., 2011; Yu et al., 2007
Taiwan	Jiayi, Tainan	600	Chen et al., 2003; Lin et al., 2006; Tseng et al., 1968
Jilin	Tongyu, Yaonan, Daan, Shuangliao as part of Songnen Plain	≥ 500	Bian et al., 2012; Tang et al., 2010; Yu et al., 2007
Henan	Qixian	≥ 500	Li et al., 2010; Yu et al., 2007
Jiangsu	Sihong, Nantong, Xuyi	333	Han et al., 2009; M. Zhang et al., 2010;
Qinghai	Guide, Datong, Menyuan	318	Jin et al., 2003; Shi et al., 2010
Sichuan	Jinchuan, Luding	287	Deng et al., 2004
Gansu	Yumen, Qin'an, Datong, Menyuan	≥ 250	Jin et al., 2003; Yu et al., 2007
Heilongjiang	Lindian, Zhaoyuan, Dorbod, Anda as part of Songnen Plain	200	Hao and Xing, 2010; Yu et al., 2007
Ningxia	Pingluo, Helan, Huinun, Qingtongxia, Xixia as part of Yinchuan Plain; Zhongwei, Zhongning	177	Han et al., 2010; 2013; Yu et al., 2007
Beijing	Shunyi	143	Pang et al., 2003; Jin et al., 2003
Zhejiang	Nanxun, Tongxiang	80	Jiang et al., 2010; Jin et al., 2003
Shandong	Dongchangfu, Yanggu, Yuncheng, Tengzhou, Jiexian, Guanxian, Liangshan	≥ 50	Shen et al., 2005; Yu et al., 2007
Hunan	Shimen	≥ 50	Yu et al., 2007
Liaoning	Kangping	25	Liu et al., 2003
Guangdong	Fuoshan	21	Huang et al., 2010

*Bold font indicates the locations where hydrogeochemical research of arsenic in groundwater are summarized in Table 1.

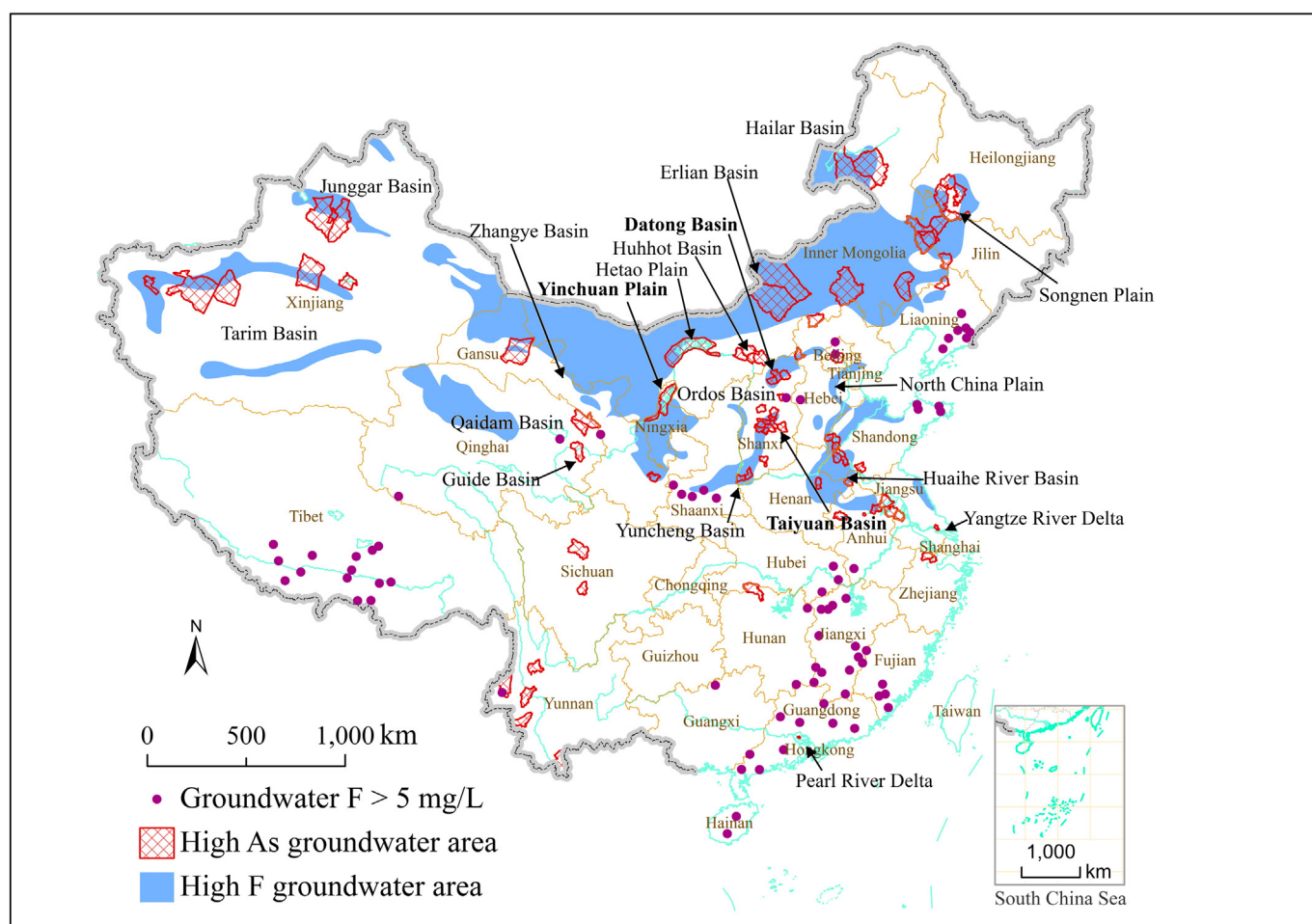


Fig. 1. Occurrence of high As and F in groundwaters of China based on compilation of literature data in Tables 2 and 4, and also maps in Liu (1988) and Tian (1989) and results in Shen et al. (2005).

groundwater. For most basins, groundwater with both high As and F occur in parts of the basins (Fig. 1), although the exact overlap is difficult to determine because of spatially heterogeneous distribution at the local scale for both. The health effects from chronic As and F exposure have been the most severe in densely populated central north China (Jin et al., 2003; Wang et al., 2007). Therefore, hydrogeochemical investigations have focused on the densely inhabited or endemic disease ridden basins along the Yellow River: the Yinchuan and Hetao Plains, and the Yuncheng–Taiyuan–Datong Basins of the Shanxi rift system (Fig. 1).

Although there are no papers in this special issue discussing the basins in the northwest, the Junggar (130,000 km²), Tarim (560,000 km²), and Qaidam (120,000 km²) basins all have elevated groundwater F concentrations and two have high As concentrations (Fig. 1). These arid basins are massive but have few inhabitants limited to areas surrounding the few oases. Each basin contains relic back-arc deposits formed behind the newly risen orogenic belts after arc-continent collisions during the Late Paleozoic, with part of the basin filled in as pull-apart basins (Hsu, 1989). The stratigraphic sequence of Junggar Basin is such that thinner red-beds deposited during the Upper Jurassic and Lower Cretaceous overly a thick sequence of Mesozoic euxinic marine sediments totaling of about 5 km thickness. The 4 mega-sequences had maximum sedimentation rates of 0.03 to 0.08 mm/yr (Eberth et al., 2001). In Junggar Basin, groundwater As has been found to increase gradually with depth to 660 m (Wang and Huang, 1994), but the reason for this depth trend is not understood. The Tarim Basin developed as an inland basin at the beginning of the Mesozoic. During the Miocene, the Tarim

Basin subsided to form a large depression, in which a series of terrestrial red sandstones, shales, and mudstones up to 9 km thick were deposited with interbeds of shaly gypsum and bedded salt, with a sedimentation rate of about 0.15 mm/yr (Tian et al., 1989). The Qaidam basin is petroliferous. The maximum sediment thickness is 16 km, deposited since the Mesozoic with a 3.2 km-thick Quaternary sequence including a 1.6 km-thick organic rich, dark colored, argillaceous formation of Pleistocene age with a sedimentation rate of 1.23 mm/yr (Gu and Di, 1989).

The Hexi Corridor (100,000 km²), a flat stretch of highland bounded by the Qiliang Mountain to the south and the Longshou and Heli mountains to the north, has more than 20 sedimentary basins filled with variable thicknesses of Meso–Cenozoic deposits (Xu et al., 1989). Zhangye (4240 km²) Basin is a pull-apart basin controlled by two strike slip thrust faults along the north and south side of the basin (Wei and Li, 2007). High F groundwater occurs in a small area, primarily in the piedmont of Longshou Mountain and to a less extent in the down gradient alluvial fan that consists of Quaternary sediment; the high F content is attributed to leaching from bedrock (J. He et al., 2013). The basin has orange–red–brown colored sandstone, siltstone and mudstone deposits of >1 km thickness deposited since the Miocene that are overlain by Quaternary unconsolidated diluvial and lacustrine sediment. To the west of Zhangye Basin, Yumen–Tashi Basin shows high As and F groundwater (Fig. 1). To the east of Zhangye Basin, groundwater from Wuwei and Minhe basins displays a high F concentration; and groundwater from two other intermountain basins displays a high As concentration

Table 3
Chemical characteristics of high fluoride groundwater in inland basins of Northern China.

Area of interest	Groundwater [F] ranges (mg/L)	Climate	Aquifer	High-F aquifer location	High-F depth	High-F (>1 mg/L) water chemistry
Zhangye Basin ^a , 4240 km ² Gansu Province	0.2–3.1	Continental semi-arid and arid, precipitation of 128 mm/yr, evaporation of 2020 mm/yr	Quaternary unconsolidated diluvial and lacustrine sediment	High [F] (mostly >1 mg/L) in the piedmont of Longshou Mountains to the east. Low [F] (<0.5 mg/L) in the piedmont of Qilian mountain to the west. The fine soil plain in between has [F] from 0.2 to 2.8 mg/L.	Wells (14 m–180 m) in the diluvial sediments of Longshou mountain show >1 mg/L F with no obvious depth trend.	Only basin without soda water chemistry. Weakly alkaline (pH: 7.5–8.3) water of Na–Mg–SO ₄ –Cl type. TDS: 0.72–2.3 g/L. [F] is positively correlated with [Na + K] and also [Ca]. High F groundwaters have positive cation exchange index values, and can be thousands of years old.
Hetao Plain ^b , 10,000 km ² , Inner Mongolia	0.3 to 6.0	Continental arid, precipitation 130–220 mm/yr, evaporation 1900–2500 mm/yr	Quaternary aquifer is composed of alluvial–pluvial sand, sandy silt, lacustrine and fluvial–lacustrine sandy silt, silty clay and clay, and can be organic-rich	Most high F groundwater samples are located in the low-lying areas in front of the Yin Mountain where the groundwater flow converge to discharge	Mostly shallow, with highest [F] found between 15–35 m, although F is still >1 mg/L at 80 m.	Unlike other basins, [F] decreases with TDS (range: 0.35–7.5 g/L). Concentrations of Cl, Br and I increase with TDS. High F groundwater is weakly alkaline (pH: 7.0 to 8.22) and of HCO ₃ –Cl–Na or HCO ₃ –Na type. Undersaturated with respect to fluorite. PCA analysis show that processes to enrich F are different from those of the Datong Basin with less influence of evaporation.
Huhhot Basin ^c , 4800 km ² , Inner Mongolia	0.1 to 8	Continental arid, precipitation of 440 mm/yr, evaporation > precipitation	Quaternary (largely Holocene) lacustrine and fluvial sediment aquifer in a fault-bounded Cenozoic rift basin.	Between Ha Su Lake and Man Han Mountain in central and southeastern southern parts of the Basin. As occurs also in this region but not strongly correlated with F.	Mostly shallow (<100 m). Deep (>100 m) with 0.13 to 2.35 mg/L F, median [F] 0.7 mg/L (n = 14)	Na and HCO ₃ rich but Ca poor groundwater that is weakly alkaline (pH: >7.5). In the discharge areas in the south, groundwater evolved to become Na–Mg–HCO ₃ –Cl and Na–Cl–HCO ₃ types, with high TDS. Groundwaters are undersaturated with respect to fluorite.
Datong Basin ^d , 7440 km ² , Shanxi Province	0.1–22	Continental semi-arid, precipitation of 370–420 mm/yr, evaporation of 1980 mm/yr	Quaternary alluvial, alluvial–pluvial and alluvial–lacustrine aquifers (upper 5–60 m, middle 60–160 m, >160 m) with gray to blackish, organic-rich reducing lacustrine sediment interlayered with alluvial sands deposited in a fault-bounded Cenozoic basin of the Shanxi rift system.	Very high [F] (max: 22 mg/L) in <50 m groundwater occur in the discharge or evaporation zone in the low-lying central and northern basin. High [F] in >50 m groundwater (max: 8.3 mg/L) occur in the western mountain front area.	No clear depth trend although Most of the wells deeper than 50 m contain much less fluoride except for W-Central areas.	Soda water of Na–HCO ₃ (Cl) type occur widely, with TDS between 0.2 and 2.9 g/L (max TDS: 10.7 g/L). High F waters are of HCO ₃ –Na(Mg), HCO ₃ –SO ₄ –Na(Mg), and SO ₄ –Cl–Na(Mg) types, with low [Ca] and high [Na] and [HCO ₃]. Conditions favorable for F enrichment are: weakly alkaline pH (7.2 to 8.2), moderate TDS with Na–HCO ₃ as dominant ions. Nearly all of the

Taiyuan Basin ^e , 6159 km ² , Shanxi Province	0.1–6.2	Continental semi-arid, precipitation of 425–520 mm/yr, evaporation of 1739 mm/yr	Upper (0–50 & 50–200 m) and Lower (200–400 m) Quaternary alluvial–pluvial and alluvial–lacustrine aquifers with Tianzhuang Fault line separates the N and S flow regime.	High [F] (>2 mg/L) located in the discharge zones with shallow groundwater table (<4 m) N. of the Tianzhuang fault and in southern plain of the basin	Depth trend not known.	high F samples are oversaturated with respect to calcite and undersaturated with respect to fluorite. Weak alkaline (pH: 7.2 to 8.8) of Na(Ca,Mg)–HCO ₃ (SO ₄ , Cl) type. TDS range 0.4 and 7.0 g/L. High F (>1.5 mg/L) waters have higher pH, Na, HCO ₃ and TDS content than low F (<1.5 mg/L) waters. Geochemical modeling supports dissolution of fluorite, gypsum, halite dolomite and montmorillonite and precipitation of calcite, kaolinite.
Yuncheng Basin ^f , 4946 km ² , Shanxi Province	0.1–6.6	Continental semi-arid, precipitation of 550 mm/yr, evaporation of 1900 mm/yr	Quaternary aquifer of interlayered sediments up to 500 m thick, including a shallow unit (<70 m), a deep unit (>120 m), and an intermediate unit (70–120 m).	In the northern Sushui River Basin where groundwater flow converges. [F] increases from the loess highland and piedmont plain to the alluvial plain and the boundary between brackish water and fresh water NW of the salt lake	Very high F in <100 m. Most high [F] occurred in the shallow groundwater with depth from 20 m to 40 m	For waters with low TDS, Na-rich, Ca-poor water having pH values (>7.8) favor F enrichment. [F] is positively correlated with pH, [HCO ₃], and Na/Ca ratio. Due to intrusion of salt lake water, TDS of water increases (range: 0.26–8.5 g/L), with brackish water being Na–Cl or Na–SO ₄ types with pH between 7.7 and 8.0
Songnen Plain ^g , 188,400 km ² , Jilin Province and Heilongjiang Province	0.5–10	Continental semi-arid sub-humid precipitation of 350–600 m/yr, evaporation of 1500–2000 mm/yr	Meso–Cenozoic fault basin where neo-tectonic depression filled by alluvial lacustrine deposits. Quaternary unconfined aquifer with silt and sand, and confined aquifer consisted of sediments deposited in the Pleistocene and the Pliocene. Quaternary phreatic aquifer (<20 m) and confined aquifer between 20–100 m	The central plain where phreatic groundwater is high in F. the edge of plain, F ion content decreased. However, in retention region at the western piedmont area of Songnen Plain, F ion content is also very high.	Mostly in shallow phreatic groundwater and confined (<80 m) ground water. At >80 m depth, most waters still contain >1 mg/L.	Three hydrochemical types along the flow path from the leaching–migrating area–accumulating area are: HCO ₃ –Ca(Mg), HCO ₃ (Cl)–Na–Ca, then HCO ₃ –Na. Average [F] is 4.6 mg/L for phreatic groundwater <10 m deep with 94% samples with >1 mg/L F. High F groundwater in two “accumulating areas” in the plain and lowland have the pH of 7.9 and 8.1, TDS of 2–3 and >4 g/L, and [F] of 1.2 and 6.0 mg/L, respectively.

References for each region with high As groundwater, arranged in the sequence from west to east (Fig. 1) are as follows:

- ^a Zhangye Basin: J. He et al., 2013.
- ^b Hetao Plain: X. He et al., 2013; Hu et al., 2013.
- ^c Huhhot Basin: Smedley et al., 2003; Wang et al., 1999.
- ^d Datong Basin: Hu et al., 2013; Li et al., 2012; Su et al., 2013; Wang et al., 2009; Xie et al., 2013.
- ^e Taiyuan Basin: Q.H. Guo et al., 2007; Li et al., 2011b.
- ^f Yuncheng Basin: Currell et al., 2011; Gao et al., 2007.
- ^g Songnen Plain: Wang et al., 1999; Zhang et al., 2003.

Table 4
Occurrence of fluoride in groundwater of China.

Province/autonomous region	Maximum concentration (mg/L)	Comment	Reference
Guangdong	25.1	Hot springs of Shantou City and Meizhou City displayed [F] of >25.0 mg/L. The Shantou City, Meizhou City, Chaoyang City and Jieyang City were among the most serious fluorosis areas	Wu et al., 2001
Xinjiang	21.5	Maximum [F] found in Kuitun area. In parts of Tarim Basin, [F] was up to 4.6 mg/L	Shao et al., 2006; F.C. Zhang et al., 2010
Tibet	19.6	Geothermal water in the Yangbajing geothermal field contained up to 19.6 mg/L of F	Q. Guo et al., 2007
Liaoning	16.0	Maximum [F] detected in hot springs from Xiu County	Li et al., 2004
Inner Mongolia	15.5	Maximum [F] found in Sunit region, and Alashan desert area	Li et al., 2008; Liu and Zhu, 1991
Guizhou	15.3	Maximum [F] found in groundwater of siliceous terrigenous clastic rocks area in Tongren City	Chen, 2001
Fujian	13.5	Maximum [F] found in the geothermal groundwater of Lanjing County, Fuding County, Yong'an, County, and Zhenghe County used before alternative water sources were developed	Lin and Chen, 1995
Shanxi	12.5	Maximum [F] found in Yuncheng City, Linyi County and Yongji City, among the most serious fluorosis areas. Groundwater [F] reaches 9.0 mg/L in Shanying County	Liang, 1992
Shaanxi	11.8	The highest fluoride occurred in Dali County	R. Liu et al., 2009; Zhao et al., 2009
Shangdong	11.0	The highest fluoride was up to 7.8 mg/L in Mudan District of Heze City, up to 6.5 mg/L in Shouguang City, up to 11.0 mg/L in Gaomi City	Sun et al., 2012; Wang et al., 2011, 2012b
Gansu	10.0	Maximum [F] found in the Piedmont fault zone of Zhangye City	J. He et al., 2013
Jilin	10.0	Maximum [F] found in Qianan County and Songyuan City	Zhang et al., 2003
Hunan	8.4	The fluoride content originated from deep geothermal groundwater for water supplies reached to 8.41 mg/L before water improvement project in Ningxiang County	Guo et al., 2002
Beijing	8.0	The [F] in bedrock well water of Tongzhou District reaches 8.0 mg/L	Liu, 2008
Hebei	7.0	Groundwater [F] in Daming County of Handan City is up to 3.5 mg/L; and up to 7.0 mg/L around Cangzhou and Wuqiao City	Zhao, 1993
Jiangsu	7.0	Maximum [F] detected in deep groundwater of Fengpei County	Chen, 1993
Yunnan	6.9	F content in one spring used for drinking in Shuifu County was 6.9 mg/L	K.L. Luo et al., 2012
Heilongjiang	6.1	Maximum [F] detected in the middle Pleistocene confined groundwater in Anda City	Li et al., 2011a
Guangxi	5.7	Maximum [F] detected in thermal groundwater from He County	Yan et al., 1995
Ningxia	4.9	Maximum [F] was 4.9 mg/L and 2.40 mg/L for Yanchi District and Pengyang County, respectively	Dou and Qian, 2007; Li and Qian, 2010
Anhui	4.1	The mean [F] in the northwest Huaibei plain is >2.0 mg/L	Xu et al., 2009;
Henan	4.0	Maximum [F] detected in Xihua County	Liu et al., 2012
Tianjin	4.0	Maximum [F] detected in deep groundwater in villages near Tianjin	Liu et al., 2010
Hubei	3.7	Maximum [F] found in Zhongxiang City, a dental fluorosis area. Shallow groundwater in Zaoyang City are usually high in F, reaching up to 2.8 mg/L	Q.H. Guo et al., 2010; Lang and Zhou, 2007
Qinghai	3.6	High [F] (>1.0 mg/L) found in Guide, Hualong, Huzhu, Huangyuan, Tongren, Wulan, Jianzha, Minhe, Datong and Haiyan County	Zhang et al., 2008
Zhejiang	3.0	Maximum [F] found in karst water in Huzhou City	Jiang et al., 2010
Chongqing	2.2	Maximum [F] found in Fuling District	Chen et al., 2008

(Fig. 1). The depressions that led to the basin formations in the Hexi Corridor resulted from foredeep development, faulting and subsidence with accumulation of up to several km of sediment since the Cretaceous but varies from basin to basin.

Guide Basin at 1600 km² is the smallest basin reviewed in this paper. Enrichment of As and F in groundwater has been associated with deep geothermal water. The basin belongs to the Qilian–Helan Stratigraphic Zone and the Zhamashan Mountains sub-region. The Neogene system consists of a set of red piedmont fluvio-lacustrine sediments that is 1330 m thick, with an unconformable contact with the underlying Proterozoic or Triassic basement and an unconformable or conformable contact with the overlying Quaternary deposits (Gu et al., 1992).

Some of the most well-known arsenicosis and fluorosis endemic areas are from the Inner Mongolia Autonomous Region and Shanxi Province (Sun, 2004). From west to east along the Yellow River there is the Yinchuan Plain (7300 km²), Hetao Plain (10,000 km²) and Huhhot Basin (4800 km²). To the east, there are the Datong (7440 km²)–Taiyuan (6195 km²)–Yuncheng (4946 km²) Basins of the Shanxi Rift System (Fig. 1) that are sometimes considered as part of the Yellow River basins (E. Zhang et al., 2009), and are also known as Fenhe River and Weihe

River basins (Hsu, 1989). These graben basins (Weihe–Shanxi and Yinchuan–Hetao) around the Ordos Block (Basin) result from late Cenozoic extension of northern China (Zhang et al., 1998). The majority of the massive Ordos Basin (250,000 km²) does not have high As groundwater but has high F water towards the south (Fig. 1). The Ordos Basin is a result of collision between the North China Craton and the Yangtze Craton in the Late Triassic Period that produced the Qinling range in Central China to the south of the Ordos.

Between the Ordos Basin and the Helan Mountain to the west lies the Yinchuan Plain with high As groundwater (Fig. 1). The intensive faulting induced the subsidence of Yinchuan Graben and forced the rapid uplift of Helan Mountain to its west (Zhao et al., 2007). Sedimentation began in the Eocene for the Yinchuan Graben which had a maximum sedimentation rate of 0.11 mm/yr during the Eocene and Oligocene, 0.10 mm/yr during the Miocene, 0.52 mm/yr during the Pliocene and 0.62 mm/yr during the Quaternary periods. Drilling revealed that the maximum thickness of Quaternary sediment is 1605 m, where As rich (>50 µg/L) groundwater was found usually at depths <40 m, although there were also groundwaters with As between 10 and 50 µg/L at depths of ~200 m (Han et al., 2013).

On the northern periphery of the Ordos Basin, Hetao plain lies south of the Yin Mountain and the Huhhot Basin is south of the Daqing Mountain (Fig. 1). They are formed by extension induced by the Neogene faults, resulting in >10 km Cenozoic sediment deposition (Zhao et al., 1984). Because the Hetao Plain and Huhhot Basin are located to the north of the Ordos basin, the sediment in these basins is more likely to have been derived from the mountains in the north that belongs to the earlier Variscan Orogeny belt. The sediment accumulation rate was 0.1 mm/yr in the early Pleistocene, but increased by 5 to 10-fold towards the present. It was ~0.6 mm/yr in the Mid-Pleistocene and ~1.2 mm/yr in the Holocene (Li et al., 2007). The Holocene strata (16–36 m) with the most frequent and very high As groundwater (Table 1) were accumulated at a rate of ~0.9 mm/yr in Hetao Plain, but high As groundwater was detected up to 400 m depth in Huhhot Basin, also within the Holocene deposits (Smedley et al., 2003) that appears to locate within the Huhhot trough (Zhang et al., 1998).

The Shanxi rift, bordered by the Ordos Massif to the west and the Taihang Mountain Uplift located within the North China block to the east, became reactivated since the late Mesozoic (Xu and Ma, 1992). Extension of the Shanxi rift may have started in the Miocene, but the present graben formed since the Pliocene (He et al., 2003). The rift was a result of right-lateral displacement of the Ordos block relative to the north China block and did not produce a single strike-slip fault but a series of en-echelon half grabens. The rift system is composed of a series of linear and rectangular-shaped intermountain basins about 20–50 km wide (Xu et al., 1993). The age and thickness isopachs of the basin-filling sediment reveal the timing, extent and rate of sedimentation during basin development (Xu et al., 1993). Data from boreholes in the Datong basin with as much as 2.5 km of Cenozoic deposits show that the thickness of the Early Pleistocene sediment is 400 m, which is equivalent to a sedimentation rate of 0.24 mm/yr. The shallow Quaternary aquifer of the Datong is usually consisted of 60 m deposits of lacustrine and alluvial-lacustrine medium-fine sand, silty clay and clay, and are gray to blackish (Wang et al., 2009). The upper 500 m of Quaternary deposits with three aquifers of the Shushui River Basin part of the Yuncheng Basin, on the other hand, consists of interlayered sediments, primarily aeolian loess, along with lacustrine clays and fluvial sands and gravels (Currell et al., 2010). In the E'mei Plateau region of the Yuncheng Basin there is no shallow aquifer (<70 m) but groundwater is present in confined sand layers below 120 m of depth, under a thick accumulation of massive, low porosity loess (Currell et al., 2010).

The Songnen Plain (188,400 km²) in northeastern China has two areas in the west (Heilongjiang Province, Hailar Basin) and the east (Jilin Province, Songliao Basin) where high As and F groundwater simultaneously occur, and the high As–F groundwater region also includes an area of the Erlian Basin (100,000 km², Fig. 1). The Songliao basin is the most important oil province of China, where subsidence started in the late Jurassic, accelerating during the early Cretaceous (Hsu, 1989). The Quaternary strata is typically about 140 m thick and consists of alluvial fan and flood plain deposits (Feng et al., 2010), where high As and F groundwater has been found (Tables 1 and 3). Both Erlian and Hailar Basins also resulted from rifting that began in the Late Jurassic–Early Cretaceous periods (Ren et al., 2002).

Although further studies are required to ascertain whether rapid sediment accumulation due to basin subsidence or rifting is a prerequisite for enrichment of As in the groundwater of north China, most basins with high As groundwater do share these common geological characteristics.

3. Arsenic in groundwater

3.1. Occurrence

Areas where high-As groundwater is mapped to the county level are shown on Fig. 1 using information compiled in Table 2. Individual

wells display considerable variability of As concentrations at a local spatial scale of 10 to 1000 m (Sun et al., 2003). Therefore, areas marked as “high As groundwater” in Fig. 1 should not be interpreted to indicate that all groundwater from this area contains >10 µg/L As. Instead, it indicates that a certain percentage of groundwater samples analyzed for As exceeds 10 µg/L typically, with this percentage referred to as occurrence.

There are also incidents of As contamination of groundwater due to mining activities in Southern China but they are not included in Fig. 1. For example, in the Xiangjiang watershed, a non-ferrous metal and rare earth element mining area (Q. Zhang et al., 2009), groundwater As content was found to increase between 2002 and 2008, although As concentrations are only slightly greater than 10 µg/L (Chai et al., 2010).

Estimates for the population exposed to As through groundwater-sourced drinking water vary. Recent official data from the Ministry of Health of China reported that 1.85 million people are exposed to >50 µg/L As (He and Charlet, 2013). Between 2001 and 2005, 445,638 wells in 20,517 villages in 292 counties in 16 provinces from China were tested. Results show that about 5% of wells contained >50 µg/L As, affecting an estimated 0.58 million people (Yu et al., 2007). These villages were selected for testing because they had been known or were suspected to have arsenicosis patients. Although the population ever exposed to high-As in drinking water is almost certainly more than 0.6 million, mitigation measures since 2000 likely have reduced the exposed population, especially those to high dose (Pers. Comm. China CDC). Our compilation indicate that 68 counties in 20 provinces of China, including Taiwan (Table 2) have confirmed the occurrence of elevated As in groundwater, with the highest value of 1932 µg/L reported for Datong Basin (Table 1) located in Shanyin county of Shanxi Province (H. Guo et al., 2003). A predictive model using survey data and geological and hydrogeochemical parameters as proxies of processes that affect arsenic mobilization in groundwater aquifers estimates that the population at risk of exposure to >10 µg/L As in China can be 19.6 million, although the authors caution that such results must be confirmed with field measurements (Rodríguez-Lado et al., 2013).

3.2. Hydrogeologic and hydrogeochemical conditions favoring high As groundwater

The mechanisms contributing to the occurrence of high As groundwater in several inland basins of north China are discussed by reviewing most published studies for the Yinchuan, Hetao and Songnen Plains, the Huhhot and Datong Basins (see references in footnote of Table 1). For these arid and semi-arid inland basins of north China, high As groundwater occur frequently in aquifers with organic-rich fluvial-lacustrine deposits, where the flat, low-lying topography leads to long residence time of groundwater that evolves to be weakly alkaline and frequently strongly reducing (Guo and Wang, 2005; Mukherjee et al., 2009; Smedley et al., 2003). Sediment As concentrations are often elevated (>10 mg/kg) in sands where high As groundwater occur in Hetao Plain (Deng et al., 2011), Huhhot Basin (Smedley et al., 2003) and Datong Basin (Xie et al., 2009b, 2009c) but are less elevated in Yinchuan Plain (Han et al., 2013).

3.2.1. Hydrogeological conditions

It has been known that two hydrogeological conditions favor accumulation of aqueous As that is mobilized from aquifer sediment (Smedley and Kinniburgh, 2002). First, the aquifer consists of sediment, which is typically geologically young and the syndepositional As has not been flushed out. Second, groundwater has a long residence time as a result of sluggish flow in flat areas such as deltas or flood plains. That the history of flushing is relevant has been shown to not only account for spatial heterogeneity of As distribution in the shallow Holocene aquifer of Bangladesh (Stute et al., 2007; van Geen et al., 2008) but also account for the contrast between and

low and high As aquifers also in Bangladesh (Zheng et al., 2005). This is also the case for inland basins in north China where the centers of the basins are usually topographically low and flat, with regional groundwater flow converging from the surrounding high terrains. This convergence of flow to topographic low results in discharge through evapotranspiration and may cause further enrichment of As in shallow groundwater (Table 1). Although the sediments in the basins are of various ages and can be significantly older than the Holocene (see Section 2), the rapid subsidence of the basins are interpreted to indicate that the sediments are likely incompletely flushed of labile As.

In Yinchuan Plain where the Quaternary sediment reaches a depth of 1.6 km, a study in this special issue investigates high As groundwater in the unconfined alluvial lacustrine aquifer in the northern part (Han et al., 2010) and finds that where the hydraulic gradient is $<0.4\%$, As concentration is high (Han et al., 2013). Despite the heterogeneous As distribution at the local scale, two clusters of high As wells are aligned along two elongated southwest–northeast trending “strips” approximately 100 km in length in northern Yinchuan Plain to the west of the Yellow River (Fig. 2). Prior to sediment deposition, these two high As strips were low topographic areas resulted from faulting (i.e. paleo-lakes) or erosion (paleo-river channel). Both were

then filled with thick sequences of lacustrine and alluvial deposits as the Yellow River meandered.

This strip-type spatial pattern of high As groundwater is similarly observed in the Hetao Plain of Inner Mongolia (H. Guo et al., 2008). In addition, the high As zones identified by analyzing 63 wells were found to correspond to the subsidence center of the basin, with lacustrine organic sediment strata displaying particularly elevated contents of As in sediment and groundwater (Yang et al., 2008). In this special issue, Zhang et al. (2013) sought to demonstrate how groundwater arsenic (As) concentration are related to and are dependent on regional hydraulic gradients in Hetao Plain. Groundwater samples ($n = 165$) were collected along three representative transects in the western, central and eastern parts of the Hetao Plain, spanning a wide range of groundwater As concentrations ($0.36\text{--}916.7\ \mu\text{g/L}$) and hydraulic gradients ($0.11\text{--}23.31\%$). Along all three transects, high groundwater As usually corresponds to low hydraulic gradients ($<0.8\%$) except for the discharge areas where both the As concentration and hydraulic gradient can be high. Results from the three transects permitted an empirical relationship to be established between the groundwater As concentration and groundwater hydraulic gradient. Assuming a typical hydraulic conductivity range of fine sand

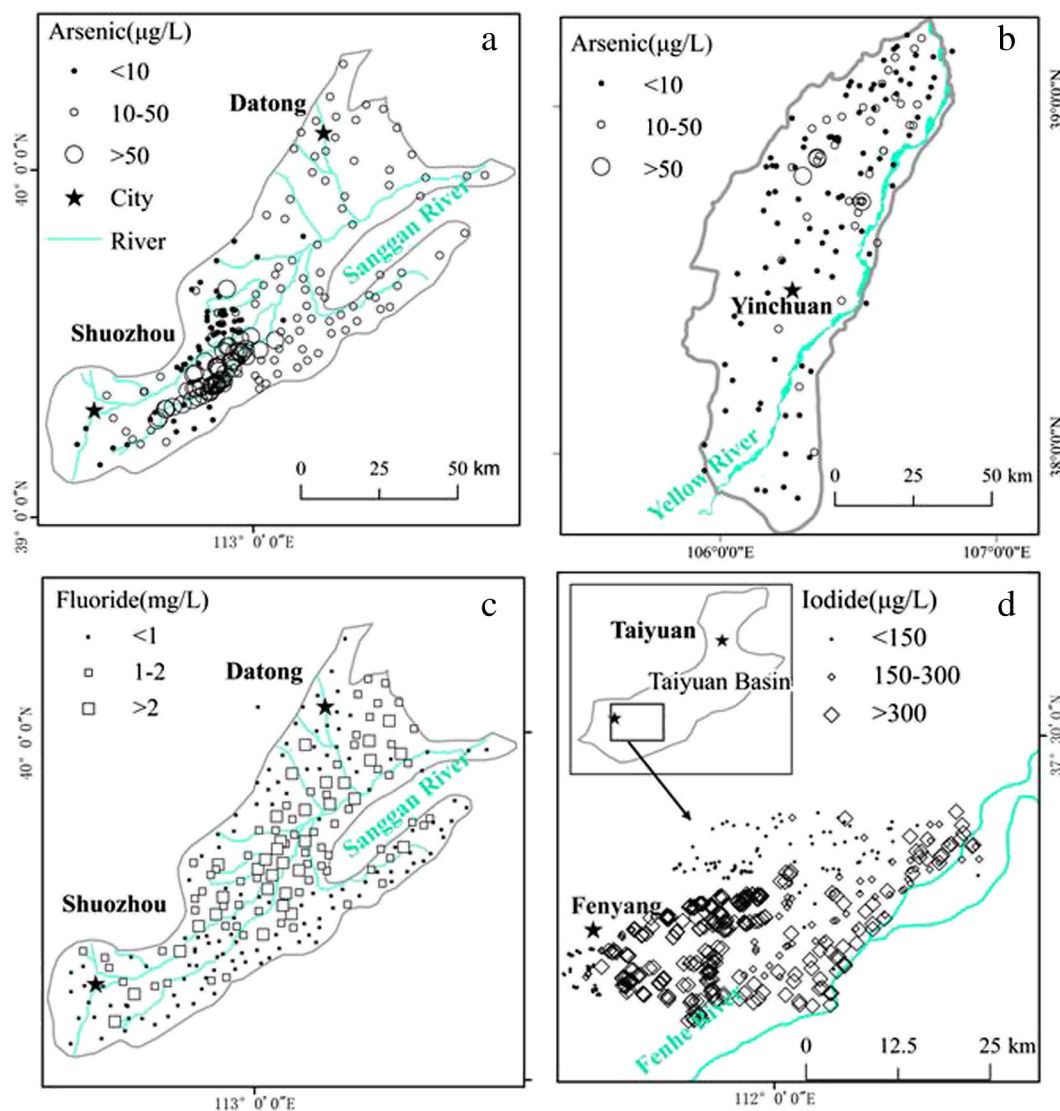


Fig. 2. Spatial heterogeneity of concentrations of a) groundwater As in Datong Basin (Source: China Geological Survey), b) groundwater As in Yinchuan Plain (Han et al., 2010), c) groundwater F in Datong Basin (Source: China Geological Survey), and d) groundwater I in Taiyuan Basin (Tang et al., 2013).

ranges from 2×10^{-7} to 2×10^{-4} m/sec, the groundwater flow rate in a fine sand aquifer corresponding to a hydraulic gradient of 0.8‰ is thus from 1.4×10^{-3} to 1.4 cm/day. This flow velocity, even at the high end, is too slow to flush As out of the aquifer because it has been shown that at a flow rate of 5 cm/day typical of the Ganges–Brahmaputra Delta, it will take thousands of years to transport (or flush) As over a distance of 1 km (van Geen et al., 2008).

Other inland basins of north China (Table 1) where the groundwater As occurrence rate is high also tend to be flat and low lying, although the hydraulic gradients are not specifically reported. It was noted that groundwater flow from the piedmont front to the discharge area in Datong Basin ranged from 0.20 to 0.58 m/day which is very high and may be in error (Xie et al., 2009a) but the flow in the central plain was not reported.

3.2.2. Hydrochemistry: major ions and pH

Investigations thus far have identified that weakly alkaline to alkaline pH conditions are common for the high As groundwater in inland basins of north China (Table 1), suggesting enhanced mobility of As because adsorption of As to the iron minerals that are carrier phases (Xie et al., 2008, 2009c) is poor under alkaline pH conditions. Bicarbonate (HCO_3^-) is typically the most abundant anion, with some waters being Cl dominant. In all the basins, groundwaters evolve from Ca-dominant to Na-dominant and sometimes Cl-rich when evaporation plays a role in the low lying parts of the basins. Yinchuan Plain has the least chemically evolved water as it still contains significant Ca (Han et al., 2013).

In the Huhhot Basin (Smedley et al., 2003), as groundwaters flow from the basin margin towards the low-lying area, shallow groundwaters generally of Ca– HCO_3^- type become more saline with Na– HCO_3^- dominant or of mixed-ion types with Na–Mg as dominating cations and HCO_3^- –Cl as dominating anions, with some waters enriched in SO_4 (Mukherjee et al., 2009). Deep artesian groundwaters are also predominantly of Na– HCO_3^- or mixed-ion types. A later study also found that in general the groundwater is of a mixed-ion composition with nearly equal proportions of Ca and Na + K, and follow a similar geochemical evolution from the recharge area in the north to the discharge area in the south where TDS (total dissolved solid) concentrations increased from 0.5 g/L to >3 g/L (Mukherjee et al., 2009).

The groundwater major ion chemistry evolution is similar for the nearby Hetao Plain. Along a flow path with a length of about 9 km, groundwater evolves from Ca– HCO_3^- – SO_4 , to Mg–Ca– HCO_3^- –Cl, to Na–Cl– HCO_3^- from the recharge zone to the discharge zone (H.M. Guo et al., 2010). In addition to As, groundwaters displayed high salinities (Gao, 1999). The hydrochemical types of brackish groundwaters are Na–Mg–Cl– HCO_3^- and Na–Mg–Cl, and are of Na–Mg– HCO_3^- type for fresh groundwaters (Deng et al., 2009b). Both fresh and brackish groundwaters may have high As.

Beneath the Songnen Plain, groundwater from the recharge area at the mountain front is also of Ca– HCO_3^- type with TDS ranging from 0.37 to 0.54 g/L and contains little As (Bian et al., 2012). Down gradient, the dominant groundwater anion is HCO_3^- whereas cations in decreasing order of abundance are Ca, Mg, K and Na, with TDS ranging between 0.52 and 1.05 g/L. At the end of the flow path in the center of the basin, water composition is influenced by strong evaporation. Here, the groundwater has evolved to be of Na–K– HCO_3^- –Cl type with TDS ranging from 0.37 g/L to 2.01 g/L with the highest As concentration.

The Datong basin groundwaters with high As (Table 1) are of Na– HCO_3^- or Na– HCO_3^- –Cl type with >80% qualifying as soda water ($\text{Na}/(\text{Cl} + \text{SO}_4) > 1$). A hydrogeochemical study following evolution of water types from recharge to discharge have identified five zones in this basin: a large leaching zone (Ca– HCO_3^- type with TDS of 0.25–0.79 g/L) and two small oxidizing zones (Ca–Mg– SO_4 with TDS of 0.28–1.04 g/L) in the piedmont area, a converging zone (Ca–Mg–Na– HCO_3^- type with TDS of 0.24–1.02 g/L) where much agricultural activities take place, and finally, evaporating

(Na– HCO_3^- –Cl– SO_4 type water with TDS 0.44–8.90 g/L) and reducing zones (Na– HCO_3^- or Na– HCO_3^- –Cl soda water type with TDS 0.28–3.24 g/L) in the central low lying area where groundwater As is elevated (Guo and Wang, 2005).

Oxic groundwaters with high As (maximum concentration = 27 $\mu\text{g}/\text{L}$) in Yuncheng Basin display similar major ion chemistry as the aforementioned basins in that it is Na– HCO_3^- rich and Ca poor with high pH (>7.8) (Currell et al., 2011). The Yuncheng Basin is the case in the point that weakly alkaline conditions can promote As mobilization without anoxia, although the degree of As enrichment is far less compared to anoxic groundwater (see below).

3.2.3. Hydrochemistry: redox condition

There are a range of redox conditions for which elevated As in groundwater occurs in the aquifers of these inland basins of north China. Most are characterized by reducing environments with a variably high contents of dissolved Fe, Mn, HCO_3^- , DOC, PO_4 , NH_4 , CH_4 , and H_2S , and depletion of SO_4 and NO_3^- (Table 1). The groundwater becomes progressively reducing from recharge to discharge within each basin. This has been suggested to reflect progressive reaction of electron acceptors with organic carbon which increases HCO_3^- concentration. This progression is consistent with the changing lithology of sediments from relatively coarse marginal alluvial deposits to finer lacustrine sediments (Smedley et al., 2003). A number of these water chemistry parameters correlate with As concentrations. For example, PO_4 has a good correlation with As in both Datong Basin and Hetao Plain (Deng et al., 2009a; T. Luo et al., 2012).

In Yinchuan Plain, high As groundwater occurs in a primarily Fe reducing environment in the shallow aquifer of the northern region, with dissolved Fe concentrations reaching 3.6 mg/L (Han et al., 2013). However, positive ORP values are frequently encountered with the presence of dissolved oxygen, suggesting a less reducing environment than the other inland basins at comparably shallow depths.

The groundwaters display a strong redox gradient between the basin margins and the low-lying central parts of the Huhhot basin (Smedley et al., 2003). Both shallow and deeper groundwaters are oxic along the basin margins but become anoxic down the gradient. The oxic groundwaters contain abundant NO_3^- and SO_4 , particularly in the shallow aquifer. These concentrations diminish to below detection limits in the anoxic sections of the aquifers. Dissolved Fe in shallow groundwater reached 4.0 mg/L (Mukherjee et al., 2009) or 4.5 mg/L but the 90th percentile values was only 1.2 mg/L (Smedley et al., 2003).

The redox gradient develops similarly along the flow path in the Hetao Plain (H.M. Guo et al., 2010). Eh and other redox indicators (i.e., dissolved Fe and H_2S) indicate that oxic–suboxic conditions with onset of denitrification for groundwaters proximate to the recharge zone (0–1 km) and also immediately to the southeast of the groundwater drainage canal. Between 1–2 km along the flow path, Fe reduction occurs. The increase in H_2S concentration, or sulfate reduction, occurs between 2 and 3.5 km into the basin. Arsenic concentration is negatively correlated with the Eh value. Although one well displayed dissolved Fe as high as 2.5 mg/L (H.M. Guo et al., 2010), most groundwaters were <1 mg/L (H.M. Guo et al., 2010; T. Luo et al., 2012). Taken together, the central Huhhot basin and Hetao Plain are dominated by groundwater that has reached sulfate reduction stage and beyond.

Although data were available, the redox conditions along the flow path in Songnen Plain were not delineated in relation to As occurrence (Bian et al., 2012). Nonetheless, high As groundwaters are found in both phreatic and confined aquifers with similar redox characteristics to aforementioned basins. Most notable are very high dissolved Fe contents that reach 11.2 mg/L.

In the Datong Basin, five hydrochemical zones were identified from recharge to discharge (Guo and Wang, 2005). Across these

zones, the redox condition evolves to become anoxic with decreases in SO_4 and accumulation of H_2S with high PO_4 , although Fe and Mn concentrations are usually $< 1 \text{ mg/L}$. Reduction of As, Fe and Mn occurred in the pe range -4 to -2 , or equivalent to Eh values of approximately -240 to -120 mV (T. Luo et al., 2012). Principal component analysis yielded high loadings for Fe, Mn, redox potential, and As in one cluster in the Datong Basin, suggesting that reductive dissolution of Fe and Mn oxides releases the sorbed As into groundwater (T. Luo et al., 2012).

The Yuncheng Basin is different from all other basins in that it hasoxic groundwater throughout (Currell et al., 2011), although here the As level did not exceed $27 \mu\text{g/L}$.

3.2.4. Mobility of sediment As

Sequential leaching and laboratory incubation experiments have been employed to evaluate the mobility of sediment As for the Hetao Plain, and Huhhot and Datong Basins. Although the approach of the investigators differed somewhat, the results are considered comparable. A significant fraction of sediment As was extracted by treatments intended to dissolve the amorphous Fe oxyhydroxides phases. The mobility of As was further enhanced by microorganisms inoculated to experimental systems incubating sediment under a variety of conditions. The percentage of oxalate-extractable As is greater for sediments from Hetao Plain than those from Datong Basin, although the reasons for this difference are not clear.

Twelve sediment samples of clay, silt and sand from Huhhot Basin were subjected to extraction using a 0.2 M acid ammonium oxalate solution to compare extractable amounts to bulk sediment As concentrations determined by a mixed acid ($\text{HNO}_3\text{--HClO}_4\text{--HF}$) digest (Smedley et al., 2003). Concentrations of bulk sediment As ranged from $3\text{--}29 \text{ mg/kg}$ and showed a correlation with total Fe, with up to 30% of the As being oxalate-extractable, or associated with amorphous Fe oxyhydroxides.

Three sediment cores penetrating to 50 m of depth from Hetao Plain have bulk sediment As concentrations between 3.0 and 58.5 mg/kg ($n = 51$) (Deng et al., 2011). A subset of these samples were subject to an 8-step sequential extraction procedure. Not only the total sediment As and Fe correlated, but also the oxalate-extractable As and Fe. Results show that 24% to 37% of total As was phosphate extractable as adsorbed As and that 18% to 38% of total As was oxalate-extractable as As in amorphous iron oxides. About 10% of As in the aquifer sediment is associated with pyrite, but it is not known whether this pyrite is a recently precipitated As sink, a possibility consistent with some groundwater compositions (see Section 3.2.3 above).

Five freshly collected sediments with a deep gray to yellow color from shallow aquifers of the Hetao Plain were subjected to anaerobic incubation experiments with three treatments: unamended, amended with glucose, or autoclaved (H.M. Guo et al., 2008). Microcosms of unamended sediments released a smaller quantity of As (equivalent to $0.03\text{--}0.30 \text{ mg/kg}$ than those amended with glucose ($0.71\text{--}3.81 \text{ mg/kg}$)). The quantity of As released with glucose accounted for 60–70% of As bound to Fe/Mn oxides in the sediments, with 2–4% of the sediment Fe also released. Introduction of labile organic C into the yellowish sediment aquifers with As-free groundwater would reductively dissolve a significant proportion of the Fe(III) oxyhydroxides and increase groundwater As concentrations.

Sediment samples ($n = 76$) from three boreholes penetrating to 50 m of depth from the Datong Basin show bulk sediment As concentrations ranging from 4.9 to 118.2 mg/kg with a mean value of 18.6 mg/kg (Xie et al., 2008). Bulk sediment As and Fe are moderately correlated, so were the extractable As and Fe by hydroxylamine hydrochloride in 25% acetic acid (Xie et al., 2009b). A subset of 18 sediment samples from one sediment core (DY) was subjected to an 8-step sequential-extraction procedure, showed that most As was strongly adsorbed or co-precipitated. Scanning electron microscopy

demonstrated the universal presence of iron oxides/oxyhydroxides in the magnetically separated fractions, which have a high content of As. Using X-ray diffraction, iron oxides/oxyhydroxides with residual magnetite and chlorite, illite, iron oxides/oxyhydroxides-coated sand grains, and ankerite are identified as the major minerals in the magnetically separated fractions. Investigation of magnetic properties of 21 sediment samples from two bore holes (DY and SHX) from Datong basin found high correlation coefficients between arsenic concentrations and two magnetic parameters, saturated isothermal remnant magnetization (SIRM) and isotherm remnant magnetization (IRM) (Xie et al., 2009c), although most sediment samples analyzed were clay/silt. This was interpreted to suggest that the ferrimagnetic minerals including maghemite and hematite are the dominant carrier for As. A follow up study assessed the quality of the organic matter in the sediments and found that all the sediments contained natural petroleum-sourced hydrocarbons which may have undergone biodegradation, as evidenced by the carbon preference index, C29 sterane, and the distribution pattern of hopanes (Xie et al., 2012a), similar to the findings of West Bengal (Rowland et al., 2006) and Cambodia (van Dongen et al., 2008). In this special issue, column experiments using Datong basin sediment samples show a large increase in the effluent As concentration when the $\text{Ca}(\text{NO}_3)_2$ electrolyte solution was followed by Na_2HPO_4 or NaHCO_3 (Gao et al., 2013). However, columns were under oxic conditions thus it is not known whether the observed behavior will be the same under anoxic conditions.

Compared to the Hetao Plain, much less As was mobilized when sediment samples from Datong Basin were incubated with the addition of a labile carbon source, even with inoculation of microbes. Arsenic-resistant strains isolated from aquifer sediments of a borehole from Datong basin were used for inoculation, with glucose and sodium acetate as carbon sources in microcosms using a gray fine silt sample from 12 m of depth of borehole DY (Duan et al., 2009). The amount of As mobilized decreases for the four treatments in the following order: microbe plus carbon, carbon, microbe, and unamended. The most As mobilized was equivalent to about 10% of sediment As. Similar results were observed when a sandy loam sample from a $1.8\text{--}11.6 \text{ m}$ depth interval was incubated and inoculated with *Bacillus cereus* isolated from Datong Basin sediment (Z.M. Xie et al., 2011) whereby addition of labile carbon and microbes released at most 5.7% of sediment As (original total As concentration = 11.7 mg/kg). Interestingly, the As concentration in the treatment with both bacteria and sodium citrate or glucose increased rapidly in the first 18 days then declined. Using a redox–pH control system that maintained a constant pH of 8.0 and a range of Eh values (-410 , -330 , -160 , -30 , 60 , and 150 mV), microcosm experiments using a clay sample from 46 m of depth of Datong Basin DY borehole showed that the As release peaked at -30 mV , after which the As concentration decreased with the Eh value, reaching minimum at -410 mV where the Fe level is also low (Xie et al., 2009b). Considered collectively these results suggest that the lower mobility of sediment As in Datong Basin may be due to Fe-sulfide mineral trapping.

Batch sorption experiments using two samples from Datong Basin borehole DY from 24 m and 50 m of depth show much higher sorption partitioning coefficients for As(V) (K_d : $1060\text{--}1434 \text{ L/kg}$) than those for As(III) (K_d : $149\text{--}275 \text{ L/kg}$) (Hu et al., 2012). However, it is unclear what equilibrium As concentration these K_d values are calculated for because K_d values vary with As concentration (Jung et al., 2012).

3.2.5. Particulate, colloidal and dissolved As

Groundwater samples ($n = 583$) from 120 wells located in Bamen, western Inner Mongolia (Bayan Nur, Inner Mongolia, part of Hetao Plain) were reported to contain particulate matters accounting for $39 \pm 38\%$ (median 36%) of the total arsenic (Gong et al., 2006). However, because samples were frozen at -20°C without acidification it is likely that at least part of the particulate As was due to sorption or co-precipitation of Fe-oxyhydroxides formed post

sample collection. This is likely because on-site filtration (0.45 μm membrane filter) and speciation separation of 6 well water samples by the same authors found substantially less particulate As (range: 10%–22% with a mean of 16%). The speciation of As in these 6 samples was on average 54% As(III) and 30% As(V). Later studies exercised more caution to prevent settling of large particles and also exposure to air. Five groundwater samples were filtered in the field through a progressively decreasing pore size (10, 5, 3, 1, 0.8, 0.45 μm) under nitrogen and within 5–10 s (H.M. Guo et al., 2009). By comparing 43 paired filtered and unfiltered samples, it was found that a small proportion of As (about 15%) is associated with large-size Fe complexing particles (>0.45 μm) when groundwaters are saturated with respect to pyrite and siderite. Larger amounts of As are trapped with small size organic colloids (<0.45 μm), which has been confirmed by the ultrafiltration (Guo et al., 2011). The authors returned to the same area and sampled 8 wells. After 20 min of pumping, groundwater samples were filtered in the field through a progressively decreasing pore size (0.45 μm ; 100, 30, 10, 5 kDa) using a filtration technique under nitrogen. Concentrations of As in the 5 kDa ultrafiltrates (dissolved) range between 55% and 80% of those in the 0.45 μm filtrates (dissolved and colloidal). For most samples, DOC and Fe concentrations in the 5 kDa ultrafiltrates account for 15–60% and 3–25% of those in the 0.45 μm filtrates, respectively. Arsenic is more likely to be associated with the smaller organic colloids than with larger Fe colloids. Additionally, SEM images, EDS analysis and synchrotron XRF analyses confirmed the association of As with natural organic matter (NOM) with molecular weights of 5–10 kDa.

The new finding of As–NOM colloidal association has implications for As mobility for aquifers with high dissolved organic matter concentrations. This is because the As–NOM complex may not be easily immobilized by adsorption (Redman et al., 2002) and thus will remain in groundwater. That As–NOM complex or colloid is difficult to immobilize is consistent with an observation that >90% of As in 63 well samples from Hetao Plain is thought to exist as As(III) (Yang et al., 2008). The speciation was done using the MetalSoft cartridge based on a selective aluminosilicate adsorbent (Meng et al., 2002) that selectively sorbed inorganic As(V) but not As(III). However, any As(V) complexed with NOM may not have sorbed and thus could have been misclassified as As(III). Yang et al. (2008) noted that most wells smelled of sulfide, contained methane that could be lit, and is yellowish in color suggesting the presence of humic substances. The maximum DOC concentration was 650 mg/L.

3.2.6. Geothermal As

Arsenic found in groundwater of Guide Basin has been attributed to geothermal origins, although the sample size is very small ($n=3$). Guide is a small basin located in the northeast of Qinghai Province where two tributaries merged into the east flowing upper Yellow River. The alluvial and piedmont plains in this basin are underlain by Quaternary and Neogene unconfined and confined aquifers. Since 1978, more than 20 wells with depths between 200 m and 600 m were installed, encountered well water with temperatures ranging from 24.5 to 64 °C, which increased with depth (Shi et al., 2010). One groundwater from the unconfined aquifer did not contain detectable As (<10 $\mu\text{g/L}$), and so was a surface water sample. However, the As concentration of three artesian wells (depth: 251 to 319 m, temperature: 16.0 to 45.9 °C) from confined aquifers ranged from 112 to 318 $\mu\text{g/L}$. These artesian well waters, and many more, also contained elevated F concentrations and high TDS values, suggesting hydrothermal leaching of As from the organic-rich fine lacustrine evaporite deposits of the Neogene Guide group.

In this special issue, hot spring sourced As has been invoked to explain the enrichment of As found in the upstream tributaries of the Indus (Singe–Tsangpo) and Brahmaputra (Yarlung–Tsangpo) rivers (Li et al., 2013).

3.2.7. Irrigation and groundwater As

Several of the inland basins use diverted Yellow River water for irrigation, with groundwater a smaller component. Considering the long-standing debate of whether infiltration of surface water derived organic matter enhanced by irrigation pumping is key in mobilizing As in shallow aquifers of Bangladesh (Harvey et al., 2002; van Geen et al., 2003), studies from the north China inland basins can provide useful insights. In the Yinchuan Plain, there is a longer late spring to summer irrigation period from later April to mid-August and a shorter fall irrigation period from later October to early November each year that depends primarily on diverted Yellow River water. There were significant temporal changes of As concentration based on 3 years of monthly data for monitoring wells at 8, 12 and 15 m depth, with lesser changes (<10%) reported for wells at 20, 30 and 80 m of depth (Han et al., 2013). Despite a clear rise in water tables for the wells between 8 and 15 m of depth corresponding to each irrigation period, the resulting As concentrations did not always increase, and even if they did, not always to the same level. Thus, it is plausible that temporal variations of shallow groundwater As concentrations may be driven by infiltration of the Yellow River water, although additional evidence is needed to evaluate mechanisms responsible for the changes.

In the Hetao Plain, one mine water, one Yellow River water and 4 groundwater samples (distance from the mine: 0.5, 11, 30 and 44 km) were analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ and ^{208}Pb , ^{207}Pb , ^{206}Pb , ^{204}Pb isotopes, along with dissolved As, Sb, Cd, Cu, Pb, and Zn (Zhang et al., 2002). The authors suggest that As-rich mines in the Yin mountains to the north is the ultimate geological source of As in the aquifer, although the data are too few and alternative explanations cannot be ruled out. The Yellow River water has high $^{87}\text{Sr}/^{86}\text{Sr}$ but low $^{207}\text{Pb}/^{208}\text{Pb}$ ratios. For mine water, both isotopic ratios are high. Because the Sr concentrations were not reported, it is difficult to ascertain the influence of the Yellow River water or mine water, although the authors suggested that three of the 4 groundwater samples showed Yellow River influence. Perhaps more convincing evidence supporting mine sourced As from Yin Mountain is that concentrations of As in soils are higher closer to the Yin Mountain, and decrease southward to the Yellow River (Zhang, 2004). A study in this special issue examines the possibility of Yellow River water influence on temporal variation of As groundwater but the evidence for both the change and the cause of change are weak (Guo et al., 2013). The authors determined As concentrations in groundwater samples ($n=30$, depth = 9 m to 30 m) collected in July/August from 2006 to 2010 but found no statistically significant change. A smaller set of samples ($n=23$) were obtained in November 2006. The November dataset displayed generally higher As concentrations than measured in the July samples. It was suggested that more reducing conditions induced by flood irrigation using diverted Yellow River triggered more As release.

A study in the Datong Basin used environment isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) and Cl/Br ratios in groundwater to trace groundwater recharge in relation to geochemical processes for arsenic mobilization (Xie et al., 2012b). All the groundwater samples are plotted on or close to the meteoric water line. In contrast to other basins, there has been intensive extraction of groundwater for irrigation over decades from wells deeper than 50 m in the Datong Basin. Thus, irrigation return flow and the salt it leaches can impact the groundwater chemistry. Indeed, a group of groundwater samples ($n=18$) displayed a large increase in Cl concentrations from <30 mg/L to >600 mg/L but with little increase in $\delta^{18}\text{O}$ values. Further, the increase of Cl concentration coincided with an increase of the Cl/Br ratio, supporting halite dissolution and leaching as a key process. Of these 18 groundwater samples, 14 contained >10 $\mu\text{g/L}$ As. In comparison, a second group of groundwater samples with low Cl concentration but increasing $\delta^{18}\text{O}$ values from evaporation during lateral recharge, and a third group of groundwater samples with increasing Cl concentrations and $\delta^{18}\text{O}$ values interpreted to be result of evaporation had only a few samples containing >10 $\mu\text{g/L}$ As. Taken together, the results suggest that irrigation return flow in Datong Basin may contribute to As mobilization.

3.2.8. Modeling As risk

A question that has intrigued hydrogeochemists studying As occurrence is whether the As risk could be predicted based on a set of hydrogeological parameters. Empirical statistical models have shown various degrees of success at various spatial scales (Ayotte et al., 2006; Winkel et al., 2008; Yang et al., 2012). A similar approach using step-wise logistic regression was applied to analyze the statistical relationships of a dataset of arsenic (As) concentrations in groundwaters ($n = 5081$) of Shanxi rift basins (Yuncheng–Taiyuan–Xinzhou–Datong Basins) with a set of environmental explanatory parameters (Zhang et al., 2012). From the 23 initial variables, 7 parameters are identified as significant. EVI7 (a principal component derived from the “enhanced vegetation index” (EVI) from the moderate resolution imaging spectroradiometer or MODIS remote sensing data), topographic wetness index and the presence of Holocene sediments are positively associated with high As levels while EVI1, EVI6, gravity, and distance to rivers are negatively associated. The spatial patterns of the risk maps (probability exceeding $10 \mu\text{g/L}$ and low vs. high As binary type) agreed well with the already established high As contaminated areas and highlighted new areas with high potential for As pollution. The moderate accuracy values obtained in the validation process indicates these areas with potential for As pollution should be targeted for As screening. The study estimates that the area at risk exceeding $10 \mu\text{g/L}$ As occupies approximately 8100 km^2 in 30 counties in Shanxi province. A similar modeling approach was recently employed to predict geogenic As risk in China through classifying safe and unsafe areas with respect to the threshold of $10 \mu\text{g/L}$ of As (Rodríguez-Lado et al., 2013). It predicts that 19.6 million people are potentially at risk of exposure to $>10 \mu\text{g/L}$ As. The overall validation dataset indicates that there is a 42% false positive (e.g. when observed datum is $<10 \mu\text{g/L}$ As, the model predicts that it has $>10 \mu\text{g/L}$ As) and a 9% false negative. Therefore, the large uncertainty especially the tendency to over-estimate by the model implies that risk models should not be used to substitute for water testing of individual wells.

3.2.9. Geological sources of arsenic

A review of the geological environment of endemic disease areas has suggested that the geological sources of arsenic originate from As-rich strata surrounding these inland basins (F.C. Zhang et al., 2010). In the northern part of the Helan mountain adjacent to Yinchuan plain, concentrations of As in coal beds are found to range from 2 to 10 mg/kg at the Sabatai mine. The Hetao plain is surrounded by mountains from the west, north and east sides. To the north, the Lang and Daqing Mountain consisted of gneiss and marble that host mineralized As in metal-sulfide ore deposits exposed at ground surface or at shallow burial depths. Arsenic concentration in ore deposits ($n = 9$) ranged from 3.3 to 43.6 mg/kg with an average value of 29.4 mg/kg in Tanaokou, Lang mountain (Gao, 1999). In the mountains surrounding Datong Basin, concentrations of As ranged from 0.5 to 22 mg/kg (average = 18.7 mg/kg) in the Carboniferous–Permian sedimentary rocks. The coal strata to the west of Datong Basin contain on average 102.8 mg/kg As. The U–Pb ages of detrital zircon have shown that sediment with high As concentrations in the aquifers of Datong Basin are influenced by the younger Carboniferous–Permian sedimentary rocks (As concentration = 0.37 to 22 mg/kg) to the west of the basin while sediment with low As concentrations in the aquifers of Datong Basin are exclusively from the older Hengshan Complex (As concentration 0.37 to 4.14 mg/kg) to the east (X.J. Xie et al., 2011).

3.2.10. Huaihe River Plain and Pearl River Delta

In addition to the inland basins, Huaihe river plain also has several clusters of groundwater As occurrence (Fig. 1) identified through As screening efforts (Yu et al., 2007). The Huaihe River Basin has an area of $330,000 \text{ km}^2$ and encompasses 5 provinces: Henan, Anhui, Jiangsu, Shandong and Hubei. The Basin has

abundant coal deposits. The Huaihe River, the abandoned paleo-Yellow River and the Yangtze River contribute to deposition of fluvial and deltaic aquifers. To date, studies have not been conducted to evaluate mechanisms resulting in As enrichment in the Huaihe River Plain. A water quality survey of 450 well water samples randomly selected from Tianchang city, Wuhe and Tangshan counties in Anhui province found 15 samples containing $>50 \mu\text{g/L}$ As (Li et al., 2006). Screening of 9427 well water samples (depth = 5 – 65 m) in Jiangsu province found that 220 samples contained $>50 \mu\text{g/L}$ As, with most of the high As wells in Sihong and Xuyi counties along the Huaihe River and close to Hongze Lake (M. Zhang et al., 2010).

Elevated arsenic up to $161 \mu\text{g/L}$ is also found in the groundwater of a confined Quaternary aquifer of the Pearl River Delta in southern China (Wang et al., 2012c). The Pearl River drainage basin resulted from an uplifting of the Tibetan Plateau during the Tertiary and Quaternary periods. The Late Quaternary stratigraphic sequence consists mainly of two terrestrial (T1 and T2) and two marine (M1 and M2) units that have been subjected to marine transgressions of the Pleistocene glaciation. Arsenic is enriched in both fresh and brackish groundwater that is anoxic with negative Eh values, weakly alkaline, and has abnormally high concentrations of ammonium and dissolved organic carbon, but low concentrations of nitrate and nitrite, consistent with the reductive dissolution of Fe-oxyhydroxide as a key process of mobilizing As. The groundwater arsenic concentrations are regulated by precipitation of authigenic pyrite in the sediments (Wang and Jiao, 2012), causing arsenic concentrations in groundwater closer to the sea to be less elevated than those located farther from the coast.

4. Fluoride in groundwater

4.1. Occurrence

Areas with high-F groundwater are mapped to the county level for northern China (Fig. 1) based on compilation of data in Table 4. Although there is also spatial heterogeneity in groundwater F distribution at various scales, the occurrence of groundwater fluoride in southern China tends to be more local in a spatial extent (Liu et al., 1980) and thus is represented by locations where $>5 \text{ mg/L}$ F has been detected in a national survey (Tian, 1989) instead of classifying the entire county as a high F area (Fig. 1). The regions noted in Fig. 1 are similar to those identified on a map of groundwater F concentrations published earlier (Wang et al., 1999). Like As, areas marked as “high F groundwater” in Fig. 1 should not be interpreted to mean that all groundwater from this area contain $>1 \text{ mg/L}$ F. Widespread occurrence of fluoride in the groundwater of northern China (Liu and Zhu, 1991) is one of many stress factors for a region low in water supply (Currell et al., 2012).

Endemic fluorosis has been reported in all 29 provinces, autonomous regions and municipalities except Shanghai (Fawell et al., 2006; Wang and Huang, 1995). Populations suffering from dental and skeletal fluorosis has been estimated to be 26 million and 1.7 million, respectively (Liang et al., 1997) and has also been estimated to be 45 million and 2.6 million, respectively, (Yang et al., 2003). The exposure to F is not limited to drinking water because air and food are contaminated through use of high F coal in SW China for heating and food processing (Finkelman et al., 1999; Luo et al., 2004).

Since 1978, the Chinese government began to construct fluoride-safe drinking water supply schemes in areas with high-fluoride drinking water and also those affected by endemic fluorosis. A national cross-sectional study was conducted in 2008–2009 to assess the efficacy of decades of fluoride mitigation work (Wang et al., 2012a). Based on fluoride in drinking water screening data collected between 2005 and 2007 from 231,175 villages in 27 provinces, the villages were classified to three groups with F concentration ranges of 1.2 – 2 mg/L , 2 mg/L – 4 mg/L , and $>4 \text{ mg/L}$. For each group, 4% of

the villages were randomly selected. The prevalence rates of dental fluorosis were compared between 1318 villages that received fluoride safe water and 558 villages that did not, and was similarly done for skeletal fluorosis. There is a 5 to 6-fold reduction in prevalence rates for dental and skeletal fluorosis, with the maximum reduction observed for villages that received fluoride safe water for the longest period of time (>10 yrs). Despite this progress, the data also suggest that about one third of the villages with high fluoride water still do not have fluoride safe water as of 2008–2009. Thus, hydrogeochemical studies to identify low fluoride groundwater sources for these villages are still needed.

4.2. Hydrogeologic and hydrogeochemical conditions favoring high F groundwater

In the following, conditions favoring high F groundwater in semi-arid and arid inland basins of northern China (35°–50°N) are described (Table 3). Elevated fluoride concentrations in the soils of Southern China and associated fluorosis endemics result from a different geochemical environment (Liu et al., 1980). In northern China, geothermal F has been identified in addition to dissolution of fluorine-rich minerals as sources for F in groundwater. Groundwater that has weakly alkaline with so-called “soda-water” characteristics, namely $\text{HCO}_3\text{-Na}$ type water with $\text{Na}/(\text{Cl} + \text{SO}_4)$ (meq) greater than 1, has been shown to contain high F levels in shallow groundwater, with evapotranspiration causing further enrichment (Wang et al., 2009). For example, concentration of F in phreatic water in the Alashan Desert reached 15.5 mg/L (Liu and Zhu, 1991). Marine transgression also brought sea water sourced F to affect deep groundwater in North China Plain.

There are also regional groundwater F spatial patterns. Along the hydraulic gradient from the piedmont area to the basin center, F concentration in groundwater usually increases (Q.H. Guo et al., 2007). Because evapotranspiration enriches F, depths where high F concentration groundwater occurs tend to be very shallow, with F concentration in shallow groundwater generally greater than that of the deep groundwater although there are exceptions when geothermal sourced F is involved. An emerging consensus of studies reviewed below is that F enrichment appears to be in discharge zones where regional groundwater flow converges.

4.2.1. Geothermal F

Fluoride is enriched in geothermal fluids (Ellis, 1977). At the Yangbajing geothermal field of Tibet, concentrations of F ranged from 17.9 to 19.6 mg/L in the shallow ($n = 7$, about 200 m and 100 °C) thermal groundwater and is 18.0 mg/L for a deep ($n = 1$, 1500 m, 159 °C) thermal groundwater (Q. Guo et al., 2007). F is more enriched in the shallow thermal water than is Cl assuming that both are from mixing between deep thermal groundwater with high Cl and F and cold groundwater/surface water with low Cl and F (<1 mg/L). This suggests another source of F to shallow thermal water through ion exchange of OH^- for exchangeable F^- in hydroxyl-minerals such as muscovite and biotite under alkaline pH. At the Yangyi geothermal field of Tibet with a higher temperature reservoir (>200 °C), concentrations of F ranged from 20.4 to 22.7 mg/L for thermal spring waters ($n = 4$, about 80 °C), and were from 13.0 to 20.5 mg/L in the thermal groundwaters ($n = 4$, about 300 m or 900 m and 80 °C) (Q.H. Guo et al., 2009). Water samples collected from the Qialagai Stream ($n = 1$) and the Luolang River ($n = 3$) that received geothermal water discharge either directly or indirectly contained $\text{F} < 1$ mg/L. Although Na^+ is the dominating cation in geothermal waters from both fields, the major anions of geothermal waters from Yangyi are HCO_3 , SO_4 and Cl whereas those from Yangbajing are Cl, HCO_3 , and SO_4 .

In the central Yunnan–Guizhou Plateau of SW China near Zhaotong city, concentrations of F in river, fissure and hot spring waters ranged

from 0.05 to 0.22 mg/L ($n = 9$), 0.03 to 0.47 mg/L ($n = 73$) and 1.0 to 6.9 mg/L ($n = 4$), respectively (K.L. Luo et al., 2012). Like in Tibet, river waters displayed much lower F concentrations and generally met the Chinese drinking water standard of F (1 mg/L), although there were significant temporal changes in F concentration. Concentrations of F in two hot springs of a fluorosis endemic area in Yuexi County of Anhui Province are 4.6 and 4.8 mg/L, respectively (Lan et al., 2008). Exposure however appears to mainly result from crops grown in fields irrigated by these high-F waters, because the hot springs are not a significant source of drinking water.

Concentrations of F in the groundwater of Guide Basin (Table 3) ranged from 0.3 to 4.6 mg/L ($n = 16$), increasing with increasing depth (100 m to 600 m) and well water temperature (Shi et al., 2010). Most of the groundwater has $\text{pH} > 8$ with TDS ranging from 0.2 to 0.5 g/L, and is of $\text{Cl-SO}_4\text{-HCO}_3\text{-Na}$ type water. Two hot spring water samples (about 90 °C) displayed F concentrations of 8.0 and 8.5 mg/L, and were of $\text{SO}_4\text{-Cl-Na}$ type water. Further supporting that F is of geothermal origin is the similarity in F concentration and temperature contours at 200 m of depth. Drilling of about 20 boreholes in the basin identified widespread fine-grained and organic-rich lacustrine strata within the aquifers of Guide Basin although it is not known whether F is leached from these strata.

A study sampled 14 water samples from bedrock ($n = 4$), Quaternary ($n = 7$) and Karst ($n = 3$) aquifers near Zhongxiang City, Hubei Province of central China and found 5 samples containing 1 to 3.67 mg/L F, three of which were warm (30 °C to 48 °C) spring waters (Q.H. Guo et al., 2010). In addition, F concentration is >1 mg/L when the Na/Ca molar ratio is >1 except for one sample from the Karst aquifer. Warm spring waters contain more SO_4 and Cl than cold well waters. Hydrolysis of F-bearing silicate minerals and fluorite dissolution were suggested as sources of F to groundwater. For the Quaternary aquifer waters at 2-m and 6-m depths, evaporation is likely important due to high TDS observed for these two high F samples.

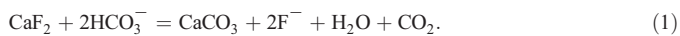
4.2.2. Dissolution of fluorite and hydrolysis of F-rich minerals

Dissolution of fluorite, an accessory mineral in granites, has been shown to result in up to 4.2 mg/L of F during low discharge periods in stream waters of a boreal watershed consisted of glacial till over a granitic intrusion, with a correlation with Li concentration (Berger et al., 2012). The limited data of F concentrations in igneous rocks suggest that F abundance is related to alkalinity and to some extent to the volatile contents of the rocks (Edgar et al., 1996). There are two F-bearing series: the alkali basalt-ultrapotassic rocks in which F increases with increasing K and the alkali basalt-phonolite-rhyolite series with F showing positive correlation with both total alkalis and SiO_2 . A statistical model constructed to assess fluoride occurrences in groundwater also relies on the knowledge that various minerals, such as fluorite, biotites, topaz, and their host rocks including granite, basalt, syenite, and shale, contain F that can be released into groundwater (Amini et al., 2008).

It has been noted that water bodies near fluorine-rich deposits such as fluorite and apatite in semi-arid and arid basins of north-western China tend to have high F water (Wang and Cheng, 2001). In the Quaternary lacustrine deposit aquifer of the Tarim Basin, groundwater TDS (1–9.7 g/L) and F concentration (1–3.6 mg/L) increase with depth, with the highest TDS and F concentration values at 80 m of depth. Groundwater F concentration is just above 1 mg/L for water with TDS of about 1 g/L between 35 m and 60 m of depth. Groundwater F concentration in the Junggar Basin also increases with depth. It has been noted that in the lower reaches of the Kuitong River, F concentration was <1.5 mg/L in surface water, 2.5–5.1 mg/L in shallow groundwater and 6.3–10.3 mg/L in deep confined groundwater. Here, groundwaters with high F concentrations tend to be weakly alkaline (pH : 7.2 to 8.8) with low Ca and SO_4 but high K + Na. Fluoride displays a weak positive correlation with TDS and HCO_3 . This

association of “soda water” with fluorite dissolution (Liu and Zhu, 1991; Wang et al., 2009; Zheng, 1983) has been for the majority of high F groundwater in northern China (Table 3), and is discussed further in Section 4.2.3.

Dissolution of fluorite (Eq. (1)) in high HCO_3^- groundwater has been described as follows (Q.H. Guo et al., 2007):



The same authors suggest that hydrolysis (OH^- in water exchanges for F^-) of F-bearing silicates such as muscovites (Eq. (2)) and biotites (Eq. (3)) in alkaline soda water is also common:



In this special issue, a hydrochemical study of the Zhangye Basin that is located in the central Hexi Corridor and is part of the Hehei River Basin favors dissolution of F-bearing silicates (muscovite and biotite react with dissolved carbon dioxide to form kaolinite, releasing dissolved K, Na, Mg, silicate and bicarbonate) than dissolution of fluorite as source of F to groundwater (J. He et al., 2013). The authors favored a source from F-bearing silicates because unpublished data show that groundwater from the biotite-, sericite-, and mica-containing fractured bedrock aquifer in the Longshou mountain contain very high F contents. Concentrations of Ca, as well as Na + K, increase with groundwater F concentrations. Because fluorite dissolution in a soda-water environment tends to result in association of high F water with low Ca water, the authors interpret opposite association here as supporting evidence for lack of fluorite dissolution. However, because the mixed cations and $\text{SO}_4\text{--Cl}$ type water is more consistent with an earlier stage of groundwater evolution than those characterized by soda-water chemistry, additional evidence is necessary to rule out the dissolution of fluorite. Earlier studies have also reported shallow (2–12 m) groundwater from Heihe River Basin with F concentration ranging from 1 to 2.7 mg/L (Wang and Cheng, 2001).

4.2.3. Soda water and evaporation

The notion that soda water and groundwater F enrichment are related has been supported by many studies, with the role of soda water eloquently discussed in a study of Datong Basin (Wang et al., 2009). The Na– $\text{HCO}_3(\text{Cl})$ type water is a subgroup of soda water defined as with $\text{Na}/(\text{Cl} + \text{SO}_4)$ (meq) greater than unity. Incongruent dissolution of aluminosilicates such as anorthite and albite produces kaolinite plus OH^- and dissolved cations including Ca. Because Ca is subsequently precipitated as calcite under alkaline pH with abundant CO_2 (possibly sourced from organic matter respiration) in the water, dissolution of fluorite (reaction 1) is enhanced, resulting in F-rich and Ca-poor groundwater whereby nearly all data points on the Ca vs. F plot would fall below the solubility curve of fluorite. Unlike Ca and Mg which is captured in precipitating carbonate and clay minerals, Na does not have other mineral precipitation reactions to restrict its increase in water, this results in a Na dominant water over a wide range of TDS from <0.5 g/L to 4.2 g/L at Datong Basin. Although both Na and Cl show nearly perfect correlation with TDS, there is always more Na than Cl on the molar basis, suggesting that in addition to evaporative enrichment of Cl and Na, there is an additional source of Na to groundwater from silicate dissolution and possibly cation exchange. The influence of evaporation on F enrichment has been demonstrated using stable isotopes of water (Xie et al., 2013). The low-lying northern and southwestern parts of the Datong Basin or the discharge areas (through evapotranspiration) are where the shallow groundwater F concentrations are high (Li et al., 2012)

and where the stable isotopes of water are less negative. Furthermore, the high F groundwater fell below the local and global meteoric line with a slope of 5, consistent with the influence of evaporation.

In this special issue, further aqueous geochemical characterization in one study (Su et al., 2013) augmented by principal component analysis in another study (Hu et al., 2013), strengthen the evidence for calcite and fluorite solubility control for F concentrations in Datong Basin (Table 3). It is worth noting that the largest data set consisted of 486 groundwater samples unequivocally show that elevated F concentrations also occur in deep groundwater (>50 m), sometimes together with high As (Li et al., 2012).

In the Taiyuan basin, 4 hydrochemical zones have been recognized to span a pH range from 6.00 to 8.80, although the TDS of most groundwaters ($n = 59$, depth not reported) were <1.5 g/L with a maximum value of 8.0 g/L (Q.H. Guo et al., 2007). Groundwaters in recharge and flow through zones contain low F (average = 0.6 and 0.9 mg/L), with levels increasing towards the discharge zones located just north of the Tianzhuang fault line (average F concentration = 2.0 mg/L, $n = 12$) and in the low-lying southern plain (average F concentration = 1.8 mg/L, $n = 4$). Compared to low F groundwaters, both Na and HCO_3^- content are dominant in the high F groundwaters although those by the fault line have very high SO_4 . A subsequent study which sampled 34 groundwaters also found similar spatial patterns of F distribution in the Datong Basin (Li et al., 2011b). Although F concentration increases with increasing $\delta^{18}\text{O}$ for most groundwater samples suggesting evaporation as an important mechanism for F (along with Cl) enrichment, several high F groundwater samples displayed low TDS values (<1 g/L) with depleted $\delta^{18}\text{O}$ values, providing support that F-mineral dissolutions or hydrolysis as source of F to groundwater (Li et al., 2011b).

In the Yuncheng Basin, water infiltrated from a salt lake located in the southeastern part of the basin was shown to contribute to groundwater F enrichment through introduction of Na that in turn promoted fluorite dissolution (Gao et al., 2007). Of 73 groundwater sampled (depth = 17 m to 347 m), 27 wells showed elevated F concentrations (1.5–6.6 mg/L) usually with high Na/Ca ratios (Currell et al., 2011). In addition to dissolution of F-bearing minerals in a soda-water environment, the role of evapotranspiration is evident because F/Cl ratios of most high F groundwaters from shallow (<50 m) and intermediate (~100 m) depths are similar to those of precipitation. Only a smaller fraction of high F groundwaters display F/Cl ratios higher than those of precipitation.

Two studies in this special issue delineate spatial patterns of groundwater F in the Hetao plain and note that concentrations of F do not increase with TDS. Like the other basins, concentrations of groundwater F ($n = 97$) are elevated in the low-lying flat area south of the Yin Mountain front where regional groundwater flow from N and S converge to discharge (X. He et al., 2013). Unlike the other basins, groundwater F concentrations display a decreasing trend with TDS and are the highest when the TDS < 2 g/L and not when it is very high (up to 7.4 g/L) (X. He et al., 2013). That F concentration are highest when TDS values are intermediate is confirmed by a second study in this special issue that used principal component analysis to compare water chemistry between Datong Basin and Hetao plain (Hu et al., 2013). Both studies propose that fluorite dissolution is responsible for F enrichment. Significantly, F concentration data (900 to 2423 mg/kg) reported for rocks ($n = 12$) from Yin Mountain have higher than average crustal F concentrations, with granite, gneiss and schist showing the highest water soluble fluorine concentrations (22–29 mg/kg). Severe fluorosis (Wang et al., 1999) and high dissolved fluoride contents have been reported for Huhhot Basin of Inner Mongolia for both shallow (<100 m) and deep (100–300 m) groundwater (Smedley et al., 2003). In the Huhhot Basin, high F groundwater displayed soda water chemistry. That evaporation also plays a role in F enrichment was supported by a study in the Sunit region NE of Huhhot (different from Huhhot Basin located to the SW of Huhhot) where groundwater

F concentrations ($n = 44$) were found to decrease with depth, with the highest F concentration of 14.8 mg/L at 2 m of depth (Li et al., 2008).

The Songnen Plain in northeast China has high F (Wang et al., 1999) at a regional scale (Fig. 1). A hydrogeochemical study which sampled 2373 wells in western Songnen Plain has identified soda water with high TDS in the groundwater “accumulation area” in the plain and low-land (Table 3) as favoring F enrichment in unconfined shallow groundwater (Zhang et al., 2003).

4.2.4. Marine transgression

In this special issue, concentrations of F were reported for shallow (depth < 100–150 m) and deep (depth > 100–150 m) aquifers in the North China Plain (Zhang et al., 2013). Shallow groundwater F concentration ranged from <0.1 to 8.5 mg/L ($n = 4390$) with a mean and median value of 0.7 and 0.5 mg/L, respectively. Deep groundwater F concentrations ranged from <0.1 to 7.5 mg/L ($n = 1708$) with a mean and median value of 1.7 and 1.5 mg/L, respectively. A much larger percentage (60.4%) of deep groundwater contained >1.5 mg/L F compared to that (6.5%) of shallow groundwater. Four marine transgression events occurred during the Quaternary period and left a sea water signature that resulted in the enrichment of Na–Cl, and other minor components such as borate, F, Br, etc. The transgressions are thought to be especially important for enrichment of F in deep groundwater of the North China Plain.

5. Iodine in groundwater

The aforementioned study of groundwater in the North China Plain investigated the hydrogeochemical processes responsible for iodine occurrence (Zhang et al., 2013). The drinking water standard for iodine is 150 $\mu\text{g/L}$ in China. About half of the groundwater samples, either shallow or deep, contain $[I] > 150 \mu\text{g/L}$. When principal component analysis was applied to a subset of 46 shallow and 48 deep groundwater samples, it was shown that three factors (sea water, carbonate mineral dissolution, and decomposition of organic matter) accounted for 87% of the variance in 9 hydrogeochemical parameters including I. The majority of I is thought to be from organic matter decomposition in the marine strata.

In this special issue, a second study analyzed total and inorganic iodine concentrations and iodine species (iodide and iodate) in 950 groundwater samples from Taiyuan Basin (Tang et al., 2013). Iodine concentrations are about twice as high in the shallow (<50 m) groundwater as those from the intermediate (50–200 m) and deep (>200 m) depths. The main species is iodide ion, with organic iodine a minor component. In addition to leaching of I from soil subjected to evaporation to enrich I in shallow groundwater, the authors suggest that organic-rich marine strata uplifted during Yanshanian tectonic period are sources of I in these groundwaters.

6. Recommendations

In water scarce arid and semi-arid north China, the widespread occurrence of F and I in groundwater, and to a lesser extent As, has been a challenge for drinking water safety. Despite progress, there are still hundreds of thousands of people affected by >50 $\mu\text{g/L}$ of As and millions more affected by >1.0 mg/L of F in groundwater, and for the very unfortunate, affected by both. New findings of high I in groundwater of the North China Plain presents a new challenge and has implications for where iodized salt should be promoted.

Between 2001 and 2005, the Chinese government implemented a program of As mitigation and management jointly supported by UNICEF. Subsequently, the management of endemic diseases due to As and F exposure has been fully incorporated to the Chinese government policy. The State Council released a “Twelfth National Five-year Plan for Prevention and Control of Endemic Diseases” and called for the

following measures: 1) Further improve the control and monitoring system for endemic diseases, in particular, to strengthen the monitoring of severe endemic disease areas; 2) Continue defluoridation and As removal for drinking water sources; and 3) Provide health education and prevention knowledge for residents in endemic areas. The plan also called for hydrogeochemical studies to understand the occurrence of As and F in groundwater and to investigate alternative safe water sources. New insights gained from these investigations, some of which are published in this special issue include:

- 1) A study that used U–Pb ages of detrital zircon in the Datong Basin concluded that sediments with low As concentrations were derived exclusively from an older rock unit with low As concentrations whereas sediment with high As concentrations included sediment from a younger Carboniferous–Permian sedimentary rock unit that contained up to 22 mg/kg As. This suggests that an abundance of As in the source region influences groundwater As enrichment in basins down the gradient. Sediment provenance studies for other inland basins are needed to aid the evaluation of the risk of arsenic in groundwater.
- 2) Although it has been recognized that sluggish flow favors As mobilization, two studies in Hetao and Yinchuan Plains show that a hydraulic gradient of 0.8‰ appears to be a threshold value below which reducing geochemical environment favoring As mobilization can develop. This also supports the use of groundwater in the piedmont alluvial fan area for water supply where hydraulic gradient is usually higher than this value.
- 3) From the basin margin where groundwater recharges to the center of the basins where groundwater discharges to the low-lying plain, groundwater chemistry evolves from being Ca/Mg dominant to Na dominant with increasing HCO_3^- concentration, TDS and pH values, and becomes increasingly reducing. Basins vary in degree of reduction. The Yuncheng Basin is mostly oxic, the Yinchuan Plain is mostly Fe-reducing, but other basins are sulfate-reducing or beyond. The Yuncheng Basin is where low levels of As enrichment (10–50 $\mu\text{g/L}$) are achieved through desorption in weakly alkaline water. The extent to which evaporation further enriches As and also F in the discharge zone of the inland basins has not been fully quantified.
- 4) In the Datong Basin where groundwater has been extracted most extensively for irrigation, a study shows that groundwaters impacted by irrigation return flow with high Cl concentrations but similar $\delta^{18}\text{O}$ values are frequently enriched in As compared to those that are not impacted by irrigation return flow, suggesting that irrigation return flow may have enhanced As mobilization there. However, in Yinchuan Plain, large scale irrigation using diverted Yellow River water and resulting water table fluctuations are thought to be related to temporal changes in shallow groundwater As concentrations but the biogeochemical mechanism for this fluctuation is not understood. Further studies are needed to differentiate the effects of irrigation using groundwater or river water on As mobilization, and whether these irrigation practices present a risk to mobilize sediment As to groundwater currently low in As.
- 5) Colloidal As has been shown to be a significant fraction of dissolved As in groundwater from Hetao Plain through ultrafiltration, with much of it complexed to dissolved organic matter. How common the organic matter complexed colloidal As is in these inland basins with organic rich lacustrine sediment needs to be assessed because it will likely affect As removal efficiency as some regions will have to rely on treatment because high As groundwater is the only source of fresh water.
- 6) Enrichment of fluoride in groundwater results from water–rock interactions of F-bearing silicates and dissolution of fluorite, with further enrichment through evapotranspiration occurring in the discharge areas. The Na rich and Ca poor aqueous environment is conducive for fluorite dissolution. The Na dominated

groundwater tends to occur either at the end of the groundwater flow path close to the discharge areas or in the case of the Zhangye Basin, in the piedmont fractured bedrock aquifer. Although substantial progress has been made, the mitigation of F in groundwater is still a work in progress due to the magnitude of the problem.

- 7) Wide spread iodine enrichment in the groundwater of North China Plain in both shallow and deep groundwaters is related to decomposition of organic matter in marine strata, deposited during episodes of Neogene marine transgressions.

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