

# Distribution of As and As<sub>(V)</sub> adsorption potential onto topsoil in the Datong Basin, northern China

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**Abstract.** Datong Basin is a typical groundwater irrigation area in northern China contaminated by As. In order to reveal the distribution of As and the adsorption behavior of As<sub>(V)</sub> onto topsoil in the Datong Basin, a total of 40 topsoil core samples were collected from a 2 m core. Samples were used for chemical composition analysis and an isothermal adsorption experiment. Results show that the collected samples are not contaminated. The adsorption capacity ( $S_{\text{tot}}$  value) of topsoil for As<sub>(V)</sub> at the study site ranged from 257 to 1027 nmol/g with an average of  $505.2 \pm 200.2$  nmol/g. Vertically, both  $S_{\text{tot}}$  value and topsoil components exhibit a vertical zoning with a positive correlation between the  $S_{\text{tot}}$  value and K<sub>2</sub>O, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> contents while Na<sub>2</sub>O and SiO<sub>2</sub> are inversely correlated. Fe<sub>2</sub>O<sub>3</sub> content shows a strong positive correlation with As content while Al<sub>2</sub>O<sub>3</sub> does not. Moreover, the correlation between  $S_{\text{tot}}$  value and Al<sub>2</sub>O<sub>3</sub> is much better than Fe<sub>2</sub>O<sub>3</sub>. These results indicate that Fe minerals are the main reservoirs of As in the natural topsoil at the study site. Furthermore, both Fe minerals and clay minerals can adsorb As<sub>(V)</sub>, but clay minerals have a greater storage potential. This result indicates that a combined effect of Fe minerals and clay minerals for As<sub>(V)</sub> accumulation onto topsoil should be considered during geochemical modeling and further agricultural management.

## 1 Introduction

Datong Basin is a typical distribution area of As-contaminated groundwater in northern China. Endemic arsenism due to drinking water contamination has occurred since the end of last century at Datong Basin. In recent years, the endemic arsenism has been eradicated by replacing the drinking water source. However, As-contaminated groundwater is still being exploited for agricultural usage at this region due to water resource shortages and high demands for agricultural water. This irrigation practice has been confirmed to result in an uptake of As by crops, posing a further risk to public health [1]. Moreover, it can also cause the accumulation of As in topsoil, and this may result in a longer-term risk than irrigation itself [2]. The As-contaminated groundwater often contains a low concentration

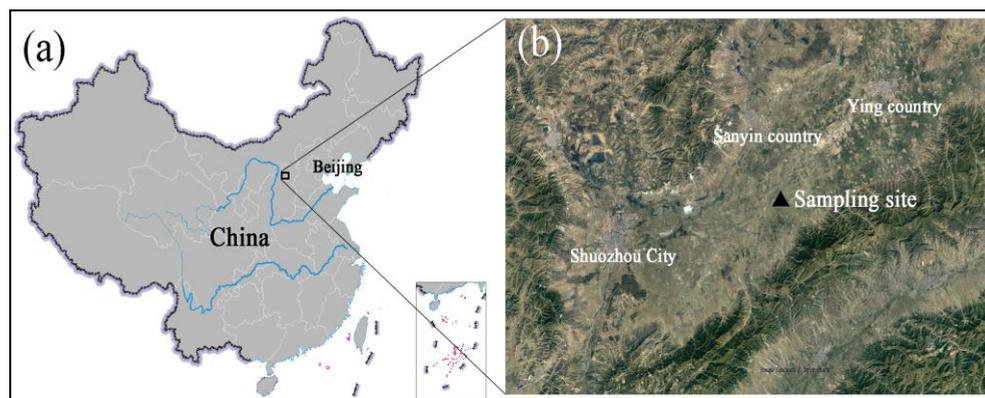
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of  $\text{Fe}_{(\text{II})}$  due to the significant sulfate reduction and precipitation of  $\text{FeS}$  at Datong Basin [3]. This means the co-precipitation of  $\text{As}$  and  $\text{Fe}_{(\text{III})}$  minerals may not so significant during irrigation. Thus, the main process controlling the  $\text{As}_{(\text{V})}$  accumulation into topsoil is likely to be the adsorption behavior. The main objectives of this study are (1) to investigate the adsorption capacity of topsoil for  $\text{As}_{(\text{V})}$  at the selected study site, (2) to reveal the natural reservoirs of  $\text{As}$  in topsoil of Datong Basin, and (3) to uncover the main adsorbents for  $\text{As}_{(\text{V})}$  in topsoil of Datong Basin.

## 2 Methodology

Topsoil core samples were collected from Datong Basin using a manual geotome during July 2017. Since the basin center is the main agricultural region as well as  $\text{As}$ -contaminated groundwater distribution area of Datong Basin, and an uncontaminated soil is favorable for us to obtain the exact  $S_{\text{tot}}$  value through isothermal adsorption experiment. The sampling site is located in an uncultivated land at the center of the Datong Basin. Topsoil samples were collected every 5 cm without interval (the 5 cm depth was all taken and homogenized). Thus, a total of 40 samples were obtained from a 2 m core. All the samples were then air-dried and rubbed to 200 mesh using an agate mortar. The ground samples were used for soil component and loss on ignition (LOI) measurements. During component analysis, all the samples were dissolved using ultrapure  $\text{HNO}_3$  and  $\text{HF}$  at  $190\text{ }^\circ\text{C}$  and the obtained solutions were measured for  $\text{K}$ ,  $\text{Ca}$ ,  $\text{Na}$ ,  $\text{Mg}$ ,  $\text{Al}$ ,  $\text{Fe}$  concentration using ICP-OES (ICAP 7400, Thermo) and  $\text{As}$  concentration using an atomic fluorescence spectrometer (AFS-9700, Beijing Haitian Instruments). Samples were placed into a porcelain crucible and maintained in  $1000\text{ }^\circ\text{C}$  for 3 h using a muffle furnace for LOI analysis. The unground samples were used for an adsorption experiment. During the experiment, topsoil samples were being mixed with a series of  $\text{As}_{(\text{V})}$  solutions ( $0\text{--}2500\text{ }\mu\text{g/L}$ ) with a solid-to-liquid ratio of  $1:50$  and equilibrated for 24 h with a  $180\text{ r/min}$  shaking. The initial solution and equilibrium solution were both sampled for  $\text{As}$  concentration analysis, and the adsorption quantity of  $\text{As}_{(\text{V})}$  was calculated. The  $\text{SiO}_2$  content was calculated using the difference between  $100\%$  and the sum of other oxides and LOI. The  $S_{\text{tot}}$  value of soil sample was obtained via a Langmuir fit based on the adsorption experiment data using Origin 9.1. All the analyses were performed at the Environmental School, China University of Geosciences in Wuhan. Random duplicates (1 in 10) of all analyses were within  $5\%$ , and laboratory blanks were below detection limits for all species.

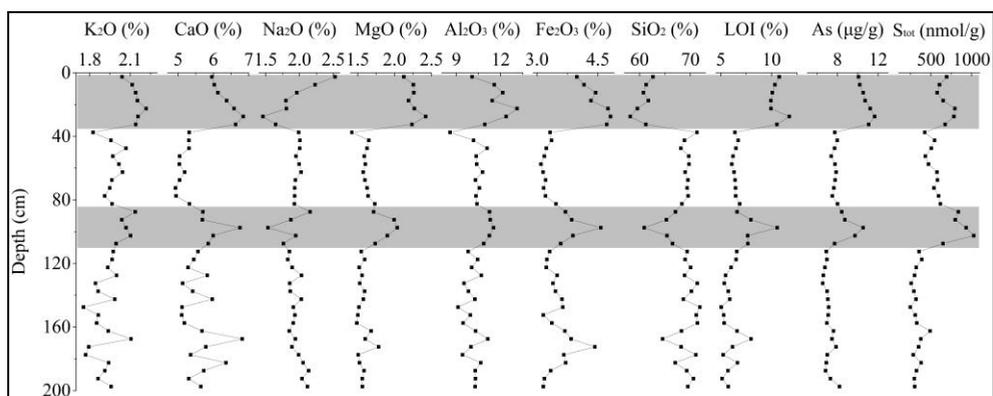


**Fig. 1.** Location map showing the Datong basin (a) and the sampling site (b).

### 3 Results and discussion

#### 3.1 Vertical variation of soil characteristic

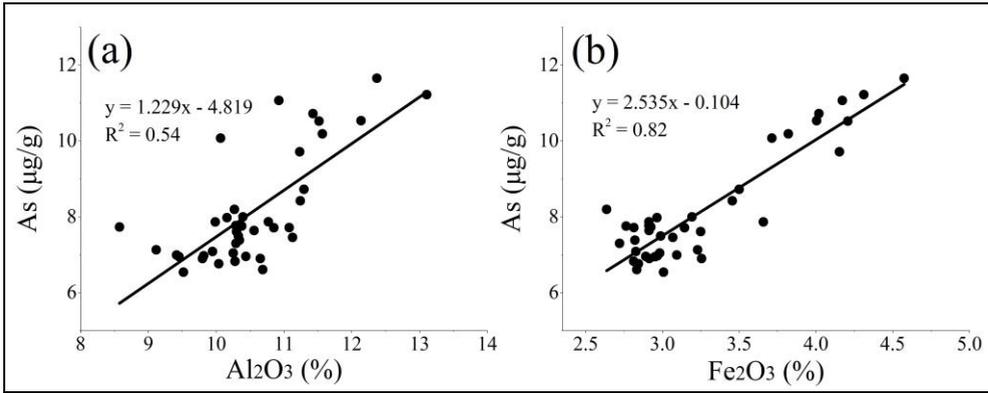
The As content of topsoil samples ranged from 6.54 to 11.7 mg/kg with an average of  $8.1 \pm 1.4$  mg/kg, which indicates that samples from the study site are not contaminated (the screening value of agricultural soil for As in China is 25 mg/kg).  $S_{tot}$  value of topsoil for  $As_{(V)}$  at study site ranged from 257 to 1027 nmol/g with an average of  $505 \pm 200.2$  nmol/g, which is less than the  $S_{tot}$  value ( $8.4 \mu\text{mol/g}$ ) of  $As_{(V)}$  for Holocene aquifer sediments from Vietnam [4]. The  $S_{tot}$  value exhibits an obvious vertical zoning at the study site (Fig. 2). The  $S_{tot}$  value of samples with a depth from 0 to 35 cm and 85 to 105 cm is much higher than other samples. The soil components show an almost identical vertical zoning. The trends of  $K_2O$ ,  $CaO$ ,  $MgO$ ,  $Al_2O_3$  and  $Fe_2O_3$  content all vary consistent with the  $S_{tot}$  value, while the  $Na_2O$  and  $SiO_2$  are inversely correlated. This indicates that both Fe minerals and clay minerals may be the adsorbents of  $As_{(V)}$  in the topsoil of study site.



**Fig. 2.** Vertical change of soil components, LOI and adsorption capacity of  $As_{(V)}$  at study site. The grey bars shows the vertical zoning of As content and  $S_{tot}$  value.

#### 3.2 As reservoirs in topsoil

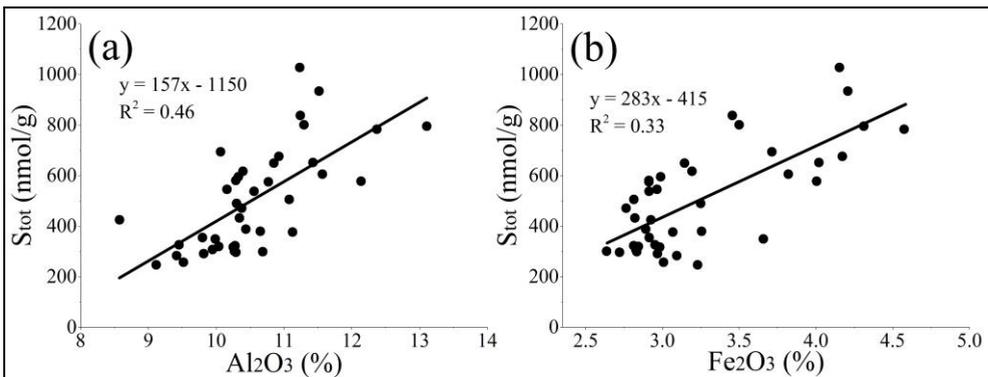
The samples show a positive correlation between As and  $Fe_2O_3$  content with an  $R^2$  value of 0.82 (Fig. 3b). However, a poor correlation can be observed between As and  $Al_2O_3$  content ( $R^2 = 0.54$ , Fig. 3a), which indicates the natural reservoir of arsenic is mainly iron minerals at the study site. This result is consistent with the common expectation. Compared to other elements, Fe content is typically correlated best with As in sediments, and this is why the release of As is often associated with the reductive dissolution of hydrous Fe oxides [5]. However, our previous study has shown that only a small fraction ( $< 5\%$ ) of total As exists in the form of adsorbed-As in topsoil of study site [6]. The vast majority of total As is co-precipitated with Fe minerals, maybe as a result of the dissolution-precipitation cycle of Fe minerals. This indicates that the positive correlation between As and  $Fe_2O_3$  content does not prove the Fe minerals as the single adsorbent of As onto topsoil. There is an inference that Fe oxides are probably the most important adsorbents in sandy aquifers because of their high abundance and the strong binding affinity [5]. However, clay minerals in topsoil are much more abundant than a sandy aquifer.



**Fig. 3.** Correlation between As and Al<sub>2</sub>O<sub>3</sub> content (a) and Fe<sub>2</sub>O<sub>3</sub> content (b).

### 3.3 Adsorbents of As(V) in topsoil

Clay minerals such as kaolinite, illite, montmorillonite are known to potentially adsorb As. As shown in Figure 4(a), the  $S_{tot}$  value of topsoil samples show a positive correlation with Al<sub>2</sub>O<sub>3</sub> content with a  $R^2$  value of 0.46. However, there is only a weak positive correlation between the  $S_{tot}$  value and Fe<sub>2</sub>O<sub>3</sub> content ( $R^2 = 0.33$ , Figure 4b). This indicates that clay minerals may be the more important adsorbents for As than Fe minerals in topsoil at the study site. As shown in Figure 2, the vertical variation of  $S_{tot}$  value is always consistent with the K<sub>2</sub>O, MgO and Al<sub>2</sub>O<sub>3</sub> contents, and all three are the main ingredients of clay minerals. This also indicates the clay content can influence the  $S_{tot}$  value of topsoil. The discrepancy of main adsorbents for As<sub>(V)</sub> between this study and previous studies (the adsorbents of As<sub>(V)</sub> into sediment is generally considered as Fe minerals) can result from the difference in clay content between topsoil and sandy aquifer medium. Although some synthetic Fe minerals are better adsorbents than clay minerals for As<sub>(V)</sub> [7], the Fe minerals in topsoil are more complicated than synthetic and may have adsorbed other anions such as HCO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>. In addition, they may have oxidized coatings. Both competing adsorption reactions and less reactive surfaces may result in a decrease in  $S_{tot}$  of Fe minerals during extended water-rock reaction times. However, the importance of Fe minerals during As<sub>(V)</sub> adsorption onto topsoil cannot be neglected.



**Fig. 4.** Corrections between  $S_{tot}$  value and Al<sub>2</sub>O<sub>3</sub> content (a) and Fe<sub>2</sub>O<sub>3</sub> content (b).

## 4 Conclusions

The adsorption capacity of topsoil for As<sub>(V)</sub> exhibit an obvious vertical zoning at the study site with samples from 0 to 35 cm and 85 to 105 cm displaying much higher S<sub>tot</sub> values than other depths. The variations of K<sub>2</sub>O, CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> content are all consistent with the S<sub>tot</sub> value, while the Na<sub>2</sub>O and SiO<sub>2</sub> are inversely correlated, which indicates the importance of Fe minerals and clay minerals for As<sub>(V)</sub> adsorption onto topsoil. The As content shows a stronger positive correlation with Fe<sub>2</sub>O<sub>3</sub> content and only a weak correlation with Al<sub>2</sub>O<sub>3</sub> content, indicating that Fe minerals are the main reservoir of As. However, the S<sub>tot</sub> value shows a stronger positive correlation with Al<sub>2</sub>O<sub>3</sub> content and only a weak correlation with Fe<sub>2</sub>O<sub>3</sub> content. This indicates that clay minerals may be the more important adsorbents of As<sub>(V)</sub> than Fe minerals in topsoil at the study site if As contamination increases. Above conclusions indicate that a combined effect of Fe minerals and clay minerals for As<sub>(V)</sub> accumulation onto topsoil should be considered during geochemical modeling and further agricultural management.

The research work was financed by the National Natural Science Foundation of China (Grants No. 41521001 and No. 41772255).

## References

1. A. Spanu, et al., *Env Sci Technol*, **46**, 8333-8340 (2012)
2. Z.Y. Chi, et al., *Sci Total Env*, **637-638**, 191-199 (2018)
3. Y.X. Wang, et al., *J Hydrol*, **519**, 414-422 (2014)
4. N.T.H. Mai, et al., *Geochim Cosmochim Acta*, **142**, 587-600 (2014)
5. P.L. Smedley, D.G. Kinniburgh, *Appl Geochem* **17**, 517-568 (2002)
6. Z.Y. Xiao et al., *J Hydrol*, **564**, 256-265 (2018)
7. S. Goldberg, *Soil Sci Soc Am J*, **66**, 413-421 (2002)