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Fluoride-leaching simulation of aquifer sediment and its influence on groundwater fluoride levels along coastal plains

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ABSTRACT

Seawater intrusion and drinking-water fluorosis are frequently documented along coastal plains. Groundwater is characterized by high OH^-, Na^+, total dissolved solids, and low Ca^{2+} because of seawater intrusion, and such conditions favor sediment fluoride-leaching and fluorosis. But the geological process of seawater intrusion has not been noticed when high-fluoride groundwater along coastal areas is discussed. The groundwater and sediments in a typical seawater intrusion and fluorosis area are gained, and fluoride-leaching simulation experiments are performed. Sediment fluoride levels are equal to or lower than average sediment fluoride levels in China and Shandong province, but strong fluoride-leaching in aquifers is observed. Compared with the supplied water from the non-intruded neighboring area, the local groundwater has higher fluoride levels, together with higher pH, total dissolved solids, HCO_3^-, Cl^-, Br^-, SO_4^{2-}, Na^+, K^+, and low Ca^{2+} because of seawater intrusion. Aquifer sediment fluoride-leaching ability increases with an increase in seawater (brine water) mixing ratios, and NaCl or $NaHCO_3$ levels, but with a decrease in $CaCl_2$ levels. This directly confirms that seawater (brine water) intrusion promotes sediment fluoride-leaching, and the high pH, Na^+, HCO_3^-, and low Ca^{2+} levels caused by seawater intrusion are responsible for the high-fluoride groundwater along coastal plains.

Key words: coastal plains, drinking-water fluorosis, fluoride-leaching, Laizhou Bay, seawater intrusion

HIGHLIGHTS

- The local groundwater is characterized by seawater intrusion and high fluorine levels, while the aquifer sediments show low fluorine levels.
- The fluorine-leaching ability of aquifer sediments increases with higher ratios of seawater or brine water, higher levels of NaCl and $NaHCO_3$, and lower levels of $CaCl_2$.
- Seawater intrusion is an important dynamic of groundwater fluorine enrichment along coastal plains.

INTRODUCTION

Fluorine is an essential micro-nutrient for human health. High fluoride concentration in water may result in damage to the teeth or bones by long-term and frequent consumption of high-fluoride groundwater. Consumption of groundwater that has fluoride levels of more than 1.0 mg/L may cause dental fluorosis, and of fluoride over 3.0 mg/L brings about skeletal fluorosis (Rezaei *et al.* 2017).

Drinking-water fluorosis along coastal areas such as Yingkou, Panshan, Jingzhou, Huludao, Tianjing, Lianyungang, Yancheng, Suzhou, Wuxi, Wenzhou, Xiangshan, Tiantai, Xinchang, Zhangzhou, Xiamen, and Quanzhou in China (Zheng *et al.* 2001; Wang *et al.* 2013; Xia *et al.* 2017), Thoothukudi District in India (Reddy *et al.* 2010; Singaraja *et al.* 2013), Gaza Strip on the Mediterranean Sea (Al-Agha 1995), Al Musanaah in Oman (Askri 2015), Florida Bay side of Fiesta Key, Florida (Machusak & Kump 1997), and northern Israel (Kafri *et al.* 2002) has been widely recorded. High fluoride in groundwater is also widely distributed in Laizhou Bay, Shandong province, China. It was reported that 640,285 people suffered from fluorosis, including 610,194 dental fluorosis and 30,091 skeletal fluorosis respectively (Han 1997; Chen *et al.* 2012, 2014). The groundwater fluoride levels and distribution, epidemiology, and health-related impacts in this area have been well investigated, but its enrichment mechanisms and influencing factors are still unknown.

Seawater intrusion, a universal geological process along coastal plains, greatly changes the groundwater geo-chemical properties and results in high pH, Na^{+}, total dissolved solids (TDS), and Cl^{-}, and low Ca^{2+} (Chae *et al.* 2007; Liu *et al.* 2015; Rao *et al.* 2018). Such changes favor sediment fluoride-leaching and high-fluoride groundwater (Gao *et al.* 2007; Chen *et al.* 2012, 2014; Jia *et al.* 2019). But there is still no direct proof detailing the fluoride-leaching laws and mechanisms of soils (rocks) with the conditions of seawater intrusion, and especially without the direct simulation experiments, which deeply impedes our further understanding of groundwater quality and the scientific use of groundwater resources along coastal plains.

In this research work, groundwater samples and sediment core in Buzhuang Town along Laizhou Bay were acquired, and simulation experiments of fluoride-leaching were performed in laboratory, with the aims to: (1) characterize fluoride levels in sediment core and groundwater and discuss their relationship with fluorosis; (2) directly reveal the effect of seawater intrusion on fluoride-leaching of aquifer sediments through simulation experiments; and (3) discuss the potential enrichment dynamics and mechanisms of high-fluoride groundwater along coastal plain.

MATERIALS AND METHODS

Studied area

Buzhuang Town is located in the northeast of Changyi City, Shandong province, China. The town has an area of 143.11 km^2 (Figure 1) and is a typical area of seawater intrusion and high-fluoride groundwater. The area is adjacent to the Bohai Sea and mainly consists of alluvial, proluvial, and marine sediments of late Pleistocene to Holocene, and Quaternary. The deposition types include alluvial-diluvial, alluvial-marine, and marine sediment, with the thickness varying from less than 100 m in the south to over 300 m in the north (Chang *et al.* 2018).

Laizhou Bay experienced three glacial-interglacial alternation periods since the Late Pleistocene, accompanied by the Cangzhou transgression during 124.6–72 ka B.P., the Xianxian transgression during 60–24.4 ka B.P., and the Huanghua transgression during 10.2–4.0 ka B.P. (Gao *et al.* 2015). During the transgressions, lagoon water bodies were detained in the sediments, forming brine by evapo-concentration of ancient seawater (Chang *et al.* 2018). The brine water flowed through the ancient alluvial sand layer due to the overexploitation of fresh groundwater since the late 1970s, and the local groundwater is suffering from serious brine water/seawater intrusion (paleo-seawater intrusion).

Sampling methods

Groundwater samples were gathered from 14 villages located near Buzhuang Town. Besides, supplied water in two villages (Liujia and Bajia) was also sampled. The supplied water was directly pumped to the villages without any treatment. The supplied water was the groundwater from the neighboring area unaffected by saltwater intrusion. All the local groundwater samples were from supply wells or irrigation wells. The groundwater was generally from the available wells along the

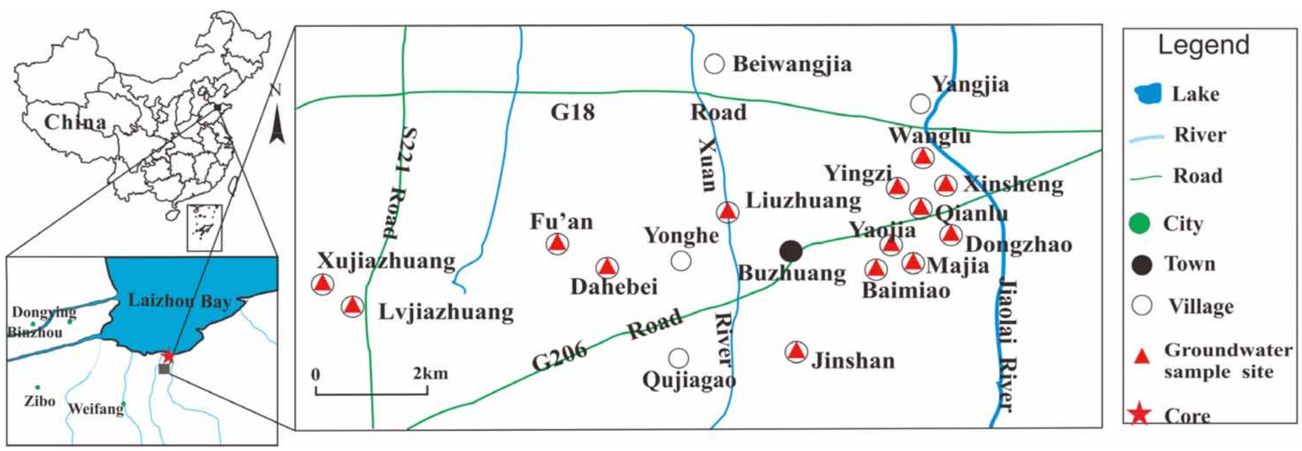

Figure 1 | Sampling locations of groundwater and sediment core.

north-south line (Jinshan-Wanglu) and west-east line (Xujiazhuang-Dongzhao). The well depths were 9–30 m according to the visit of proprietors. The groundwater was from the first aquifer layer, belonging to shallow groundwater. Multiple samples were obtained in every village. The water was directly pumped from the wells in October and collected using pre-cleaned polyethylene containers. 0.45 μm membrane filters were used to filter the water after sampling.

One sediment core was gained by drilling with a depth of 80 m at geographic coordinates of N37°03′17.3″ E119°32′13.9″. Four aquifers were involved and used for simulation experiments. The mineralogy in the aquifer sediments mainly consisted of quartz, anorthite, albite, dolomite, and calcite (Xue *et al.* 2000).

Simulation experiment methods

Different solutions were prepared for simulation experiments, including freshwater, 1:1 freshwater and seawater, 1:1 freshwater and brine water, seawater, brine water, 0.1 mol/L NaCl, 1 mol/L NaCl, 0.1 mol/L $NaHCO_3$, 1 mol/L $NaHCO_3$, 0.1 mol/L $CaCl_2$, and 1 mol/L $CaCl_2$. The effects of seawater or brine water intrusion or single ion on groundwater fluoride levels were detected by comparing the fluoride-leaching under different solutions. The freshwater is water distilled in the laboratory, seawater is from the Bohai Sea, and brine water is from a brine deposit in Changyi City.

Four aquifer sediments were used for simulation experiments. The sediments were dried naturally in laboratory and finely powdered into particles less than 100 mesh using an agate ball mill and sieve. For every aquifer sediment, 11 fresh beakers were prepared, and 1,000 mL solutions were added to each 50 g sediment sample, giving a total of 44 beakers for four aquifers. The beakers were let stand at room temperature after magnetic stirring for 1 minute. Aliquots of 120 mL were sampled at 8, 16, 24, 48, 96, and 192 h after stirring.

Sample analysis

The combustion-hydrolysis method employing a fluoride-selective electrode (PF-1C, Shanghai, China) was used to determine sediment fluoride levels according to Feng *et al.* (2004). Aliquots of 0.3–0.5 g powered sediment and 0.1 g quartz sand were put into a silica boat, and the boat was combusted at 1,000–1,100 °C. An aqueous solution of 0.2 mol/L NaOH was used to receive the condensate.

For fluoride analysis, an ionic strength adjusting buffer was prepared as follows: 145 g NaCl and 7.35 g $Na_3C_6H_5O_7.2H_2O$ were dissolved in 143 mL $C_2H_4O_2$. The solution had 40% NaOH added to adjust the pH to 5.0–5.5 and was diluted into 1,000 mL by distilled water. 0.5% phenolphthalein and 2 mol/L HNO_3 were used to adjust the solution pH to 7.0, and 5 mL ionic strength adjusting buffer was added. Finally, the solution was diluted to 50 mL and a fluoride-selective electrode method was used to determine the solution's fluoride levels. The sediment's fluoride levels were estimated like this: sediment fluoride level $= 50 \times$ (fluoride level in solution − fluoride level in blank)/sample weight. Sediment fluoride level was in mg/L; the unit for fluoride level in solution and blank was mg/L; and sample weight was in g.

A fluoride-selective electrode was used to determine the fluoride levels in water and solution. An accuracy of 40 mL sample was used, and the analyzing procedure was similar to that mentioned above. The fluoride levels in groundwater and solutions were calculated by the formula: $F = 5 \times L/4$; F: the fluoride level in groundwater or the solutions (mg/L), L: the measured solution fluoride level (mg/L).

A PH-3C pH meter was calibrated by pH = 4.01, 6.86, 9.18 solutions, and used to analyze pH. HCO_3^- was analyzed by 0.01 mol/L HCl titration. Cl^-, Na^+, K^+, Ca^{2+}, and Mg^{2+} were determined using ICS-90 ion chromatography.

For quality control, the blank samples, parallel samples, standard samples (GBW07403; GBW10010; GSB 07-1194-2000), and repeated samples were analyzed. The working standard curve was established with the standard solutions, known fluoride levels, and the errors were less than 5%.

Estimation of fluoride-leaching

Considering the different initial fluoride levels in solutions, the leached fluoride was estimated by the formula: leached fluoride = fluoride levels in simulation solution − initial fluoride levels, and the unit was in mg/L.

RESULTS

The fluoride levels of sediment core and groundwater

The sediment core has fluoride levels of 130–468 mg/kg, with mean of 324 mg/kg (Figure 2). Fluorine in rock, soil, or sediment is generally considered to determine groundwater fluoride levels (Usham *et al.* 2018; Chen *et al.* 2020a). However, the

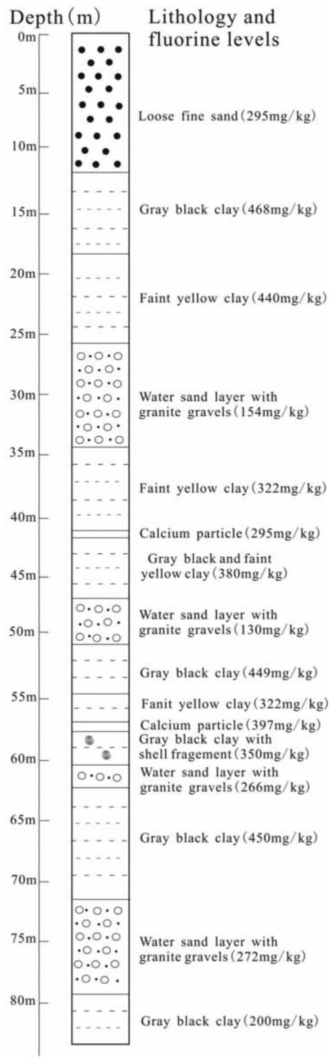

Figure 2 | Sediment fluoride levels in Buzhuang Town [after Chen *et al.* (2014)].

sediments in Buzhuang Town have lower fluoride levels than the average soil (sediment) fluoride level in China (478 mg/kg) and soil fluoride levels in Shandong province (499 mg/kg) (Chen *et al.* 2020a). Therefore, the sediment fluoride level itself can't well explain the high-fluoride groundwater in Buzhuang Town. Moreover, the sediments in the four aquifers have fluoride levels of 154, 130, 266, and 272 mg/kg, which are obviously lower than those in other layers. These facts indicate that a lot of fluorine in the aquifer sediments has leached into the groundwater. So stronger fluoride-leaching ability may be an important factor controlling groundwater fluoride enrichment in Buzhuang Town.

The local groundwater in Buzhuang Town has higher fluoride levels (0.7–9.9 mg/L) than the supplied water (0.5 mg/L) (Table 1). And 78% samples of local groundwater have exceeded the limit of 1.0 mg/L prescribed by the National Sanitary Standard for drinking water (GB5749-85), while the supplied water is within the safe limit.

The China Geological Survey has set the seawater intrusion standards by Cl^- of 250 mg/L, Br^- of 0.55 mg/L, and TDS of 1.0 mg/L (Wang *et al.* 2015). The supplied water was characterized by non-intrusion. The average Cl^-, Br^-, and TDS levels in local groundwater were 454 mg/L, 0.86 mg/L, and 1.41 mg/L respectively. All the local villages (except Xujiazhuang, Lvjiazhuang, and Fu'an) had groundwater out of the standards. Moreover, the Cl^-, Br^-, and TDS levels in Xujiazhuang, Lvjiazhuang, and Fu'an villages were obviously higher than those in Liujia and Bajia villages, also indicating the slight mixing of seawater in the three villages. Compared with the supplied water, the local groundwater was higher in pH, TDS, HCO_3^-, Cl^-, Br^-, SO_4^{2-}, Na^+, and K^+ levels and lower in Ca^{2+} levels because of seawater intrusion.

Table 1 | Geochemical properties in local groundwater and supplied water[a]

		F	pH	Ec	TDS	HCO_3^-	Cl^-	Br^-
Local water	Range	0.7–9.9	7.3–8.3	1.21–4.67	0.6–2.28	3.9–12.13	81–879	0.25–1.73
	Mean	2.3	7.7	2.89	1.41	7.97	454	0.86
Supplied water	Range	0.4–0.5	7.3–7.5	1.03–1.04	0.52–0.52	3.57–3.88	107–107	0.15–0.16
	Mean	0.5	7.4	1.04	0.52	3.73	107	0.16
		SO_4^{2-}	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	
Local water	Range	78–624	0.004–0.162	91–634	4.4–96.5	4.5–103.9	2.3–62.7	
	Mean	338	0.04	390	31.1	58.25	35.6	
Supplied water	Range	90–90	0.005–0.005	44–44	1.2–1.2	20.2–20.7	82.8–83.6	
	Mean	90	0.005	44	1.2	20.45	83.2	

[a]unit in mg/L except pH.

Fluoride-leaching ability of aquifer sediments

The fluoride-leaching of aquifer sediments under different mixture ratios of seawater or brine water is quite different (Figures 3 and 4). There is no obvious tendency that leached fluoride increases with contact time since 8 h, and the reason may be that the fluoride-leaching has attained an equilibrium state. Meanwhile, the leached fluoride fluctuates over contact time, and this may be because of the complex processes, such as the dissolution, adsorption, or complexation of fluoride-bearing minerals

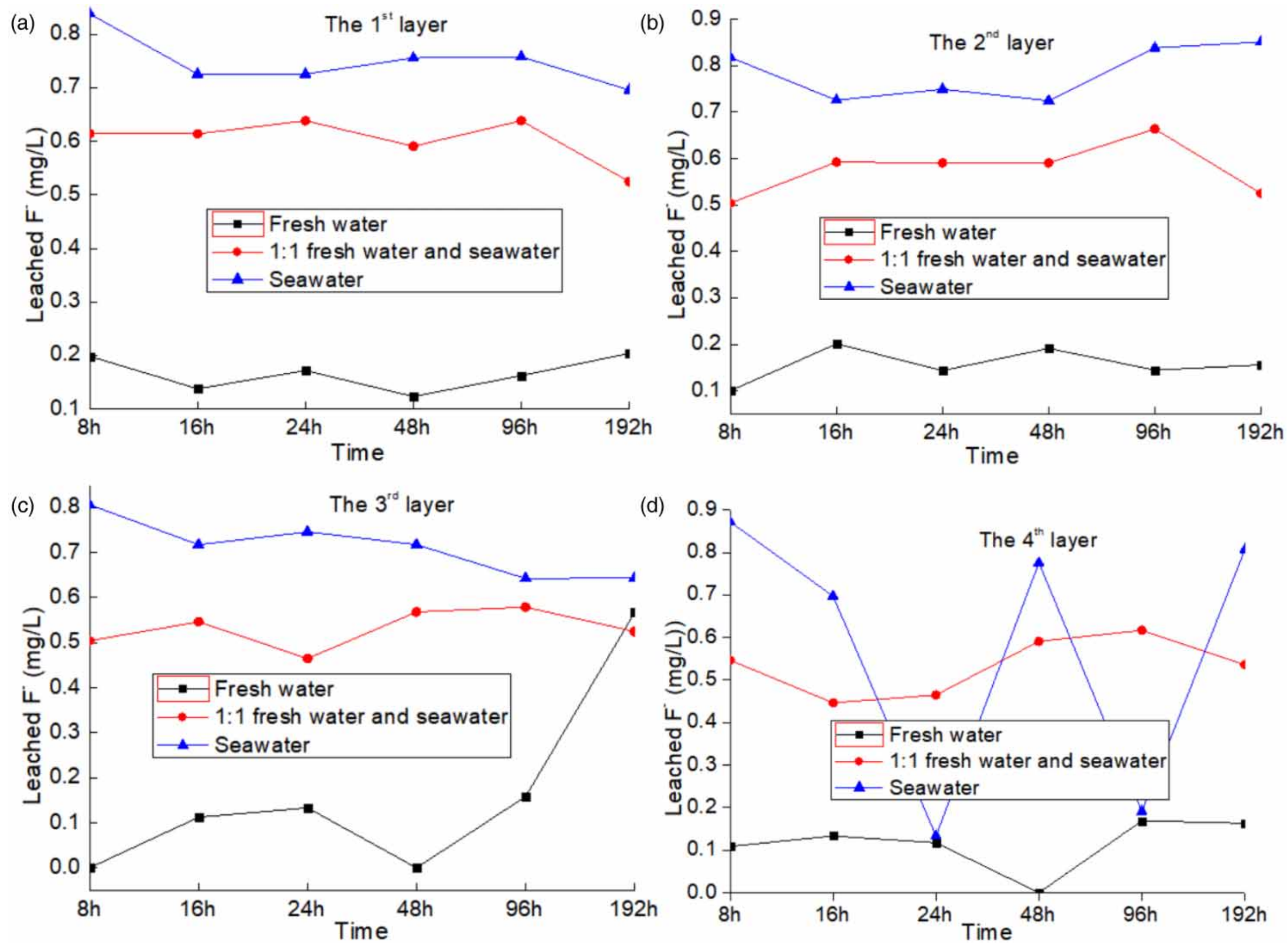

Figure 3 | Leached fluoride from sediments in four aquifers under different mixtures of seawater.

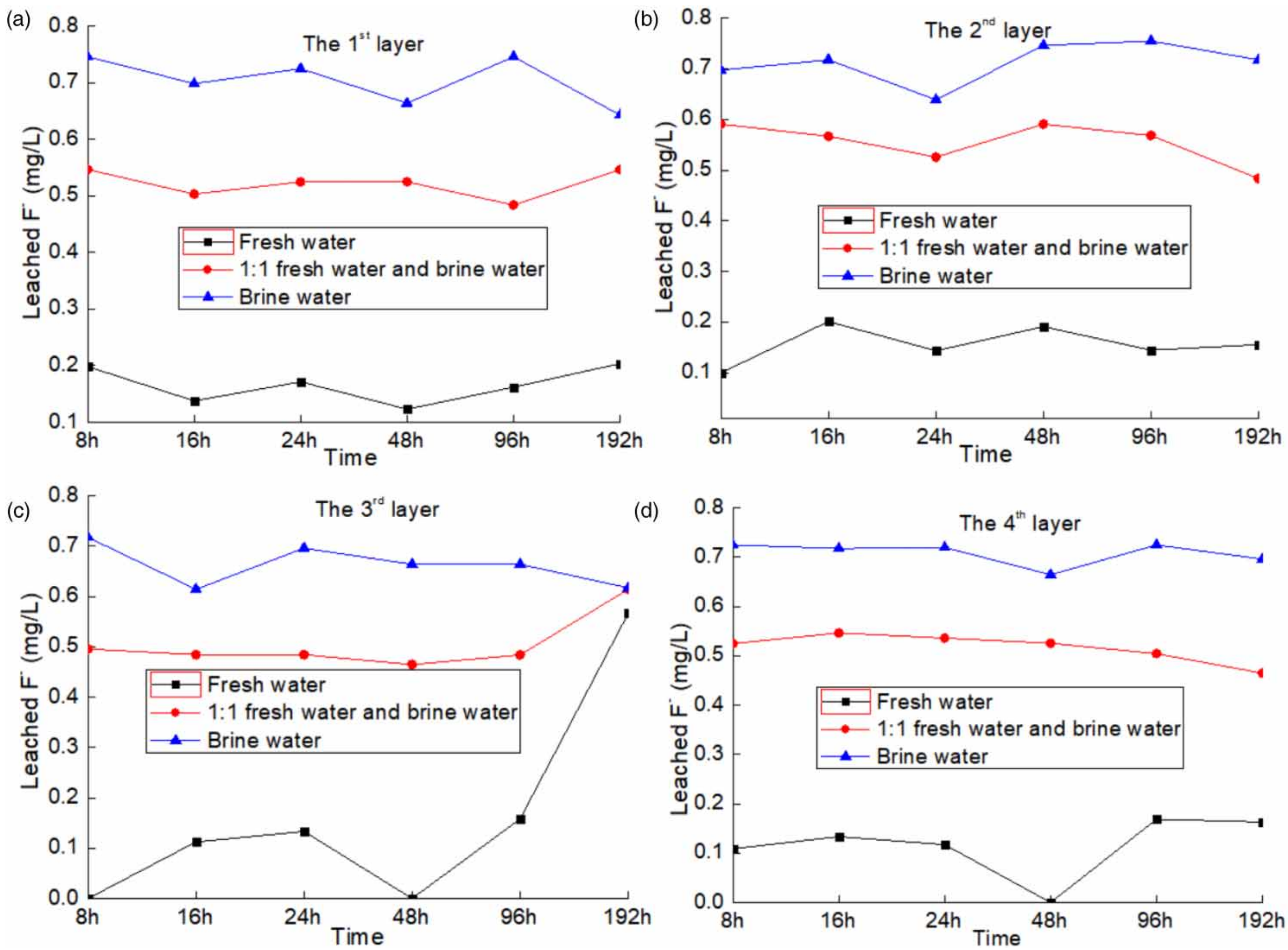

Figure 4 | Leached fluoride from sediments in four aquifers under different mixtures of brine water.

(Chen *et al.* 2019). But the fluoride-leaching from sediments in the four aquifers shows general order as follows: seawater > 1:1 freshwater and seawater > freshwater, and brine water > 1:1 freshwater and brine water > freshwater, except those at 24 and 96 h of sediment in the fourth layer (Figure 3(d)). Such results directly confirm that seawater (brine water) intrusion promotes sediment fluoride-leaching ability.

The fluoride leaching-ability shows increasing tendency with higher $NaHCO_3$ level and lower $CaCl_2$ level in the four aquifers (Figure 5). Also, more fluoride is leached by 1 mol/L NaCl than by 0.1 mol/L NaCl except at 192 h in the 2nd layer (Figure 5(b)) and the 4th layer (Figure 5(d)). All these confirm that high Na^+ and HCO_3^- and low Ca^{2+} can promote fluoride-leaching from rocks or soils.

DISCUSSION

Fluoride-rich groundwater is frequently recorded along coastal plains, and its forming factors are also discussed. Although seawater intrusion results in high Na^+, Cl^-, TDS, pH, and HCO_3^{2-} and low Ca^{2+}, it has not been noticed when enrichment mechanisms of groundwater fluoride are discussed along coastal plains.

Groundwater Na^+ increases because more Na^+ mixes when seawater intrudes. While groundwater Ca^{2+} generally decreases because of the alkaline conditions, $CaCO_3$ precipitation and Na-Ca cation exchange (Gao *et al.* 2007; Wang *et al.* 2015; Chen *et al.* 2020b). The geochemical characteristics of high Na^+ and low Ca^{2+} can greatly promote fluoride-leaching from soil or rock because of the following reasons: First, the Na-F combination is prior to Ca-F or Mg-F combination. Second, the NaF solubility is remarkably higher than CaF_2 or MgF_2 (Chae *et al.* 2007; Chen *et al.* 2012, 2019, 2020b). Meanwhile, the fluoride levels in groundwater are restricted by Ca^{2+} levels because of the low CaF_2 solubility, and Ca^{2+}-F^- negative

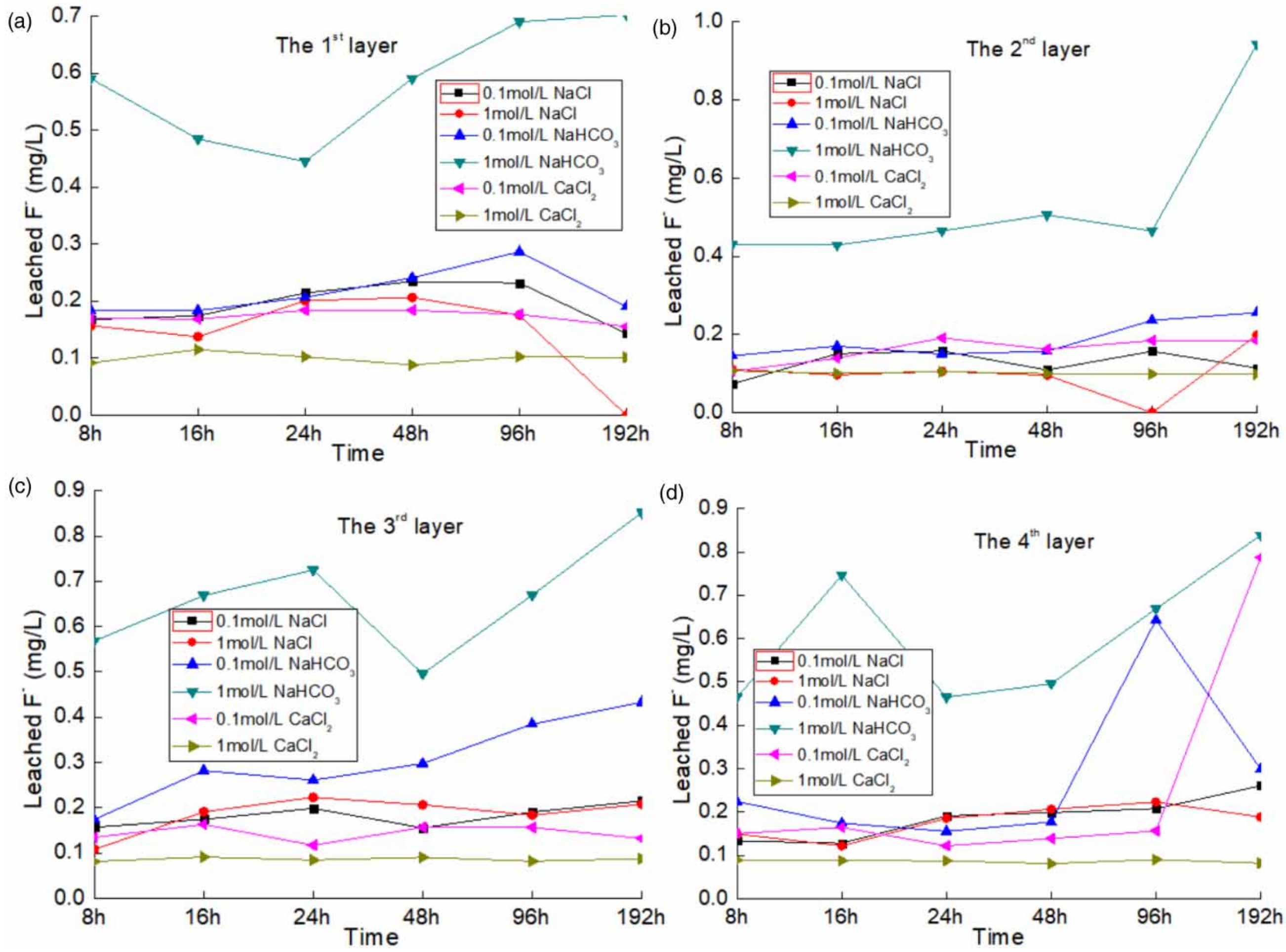

Figure 5 | Leached fluoride from sediments in four aquifers under different laboratory solutions.

relationship in groundwater is commonly observed and documented (Ozsvath 2009; Wang *et al.* 2015). The leached fluoride from rock (soil) and groundwater fluoride levels are also proved to increase with Na^+ increasing and Ca^{2+} decreasing by field investigations or simulation experiments (Krainov & Zakutin 1994; Gao *et al.* 2007). Our works also observed that the fluoride-leaching from aquifer sediments increased with an increase in NaCl, $NaHCO_3$ levels and a decrease in $CaCl_2$ levels, which was in agreement with these previous observations.

The following reactions occur when Na^+ and HCO_3^- ions enrich groundwater:

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2$$

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$$

This process makes more CaF_2 dissolve and is considered to be the important factor influencing groundwater fluoride level (Rao & Devadas 2003). Our simulation also observes that fluoride-leaching ability is promoted with higher levels of $NaHCO_3$ solutions, and HCO_3^- in the local groundwater also shows higher levels than in the supplied water.

OH^- and F^- have similar charge and radium, and can substitute for each other (Chen *et al.* 2012; Wang *et al.* 2015). OH^- in groundwater often enters into the sediment and sediment F^- leaches under alkaline conditions, and groundwater fluoride levels are also observed to be positively correlated with pH (Rezaei *et al.* 2017; Singh *et al.* 2018). Thus, the high pH caused by seawater intrusion improves fluoride-leaching from sediments. Actually, the pH in the local groundwater also shows higher levels than in the supplied water, which may be one of the reasons for its higher fluoride levels.

In addition, the high salinity, TDS, conductivity and harness due to seawater intrusion are benefit for the fluoride-leaching from the sediment/rocks and fluoride-enrichment in groundwater (Gao *et al.* 2007; Chen *et al.* 2014, 2020a).

Multiply researchers have stated high fluoride groundwater is strongly associated with alkaline and soft environments, which are enriched in Na^{+} and depleted in Ca^{2+} (Ozsvath 2009; Wang *et al.* 2015; Chen *et al.* 2019). Although there are no direct proofs detailing the effect of seawater intrusion on groundwater fluoride levels yet, the salt intrusion, which is similar to seawater intrusion, has been documented to be an important dynamic in improving the fluoride-leaching and evaluate groundwater fluoride levels in Nagar Parker, Sindh province of Pakistan (Tahir *et al.* 2009) and Yuncheng, Shanxi province of China (Gao *et al.* 2007) by field investigation and indoor experiments. So seawater intrusion, a common process along coastal areas, should be noticed and may be a possible dynamic of fluorosis.

CONCLUSIONS

Fluoride levels in groundwater and sediments in a seawater intrusion and fluorosis area of Buzhuang Town were investigated. The local groundwater was characterized by high fluoride levels and seawater intrusion. The sediment fluoride levels were confirmed to be equal to or lower than average sediment fluoride levels in China and Shandong province, and the fluoride levels in aquifer sediments were obviously lower than those in other layers. The sediment fluoride levels themselves cannot explain the high-fluoride groundwater, while the strong fluoride-leaching was an important cause of high-fluoride groundwater. Simulation experiments confirm fluoride-leaching of aquifer sediments increased with the increasing of seawater mixing ratios and NaCl or $NaHCO_3$ levels, but with the decreasing of $CaCl_2$ levels. The high Na^{+} and HCO_3^{-} levels and low Ca^{2+} levels because of seawater intrusion promoted sediment fluoride-leaching. Seawater intrusion should be the important factor affecting groundwater fluoride levels along coastal plains.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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