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Boron isotopes in the Huaihe River, China: An exploration of anthropogenic contamination

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ABSTRACT

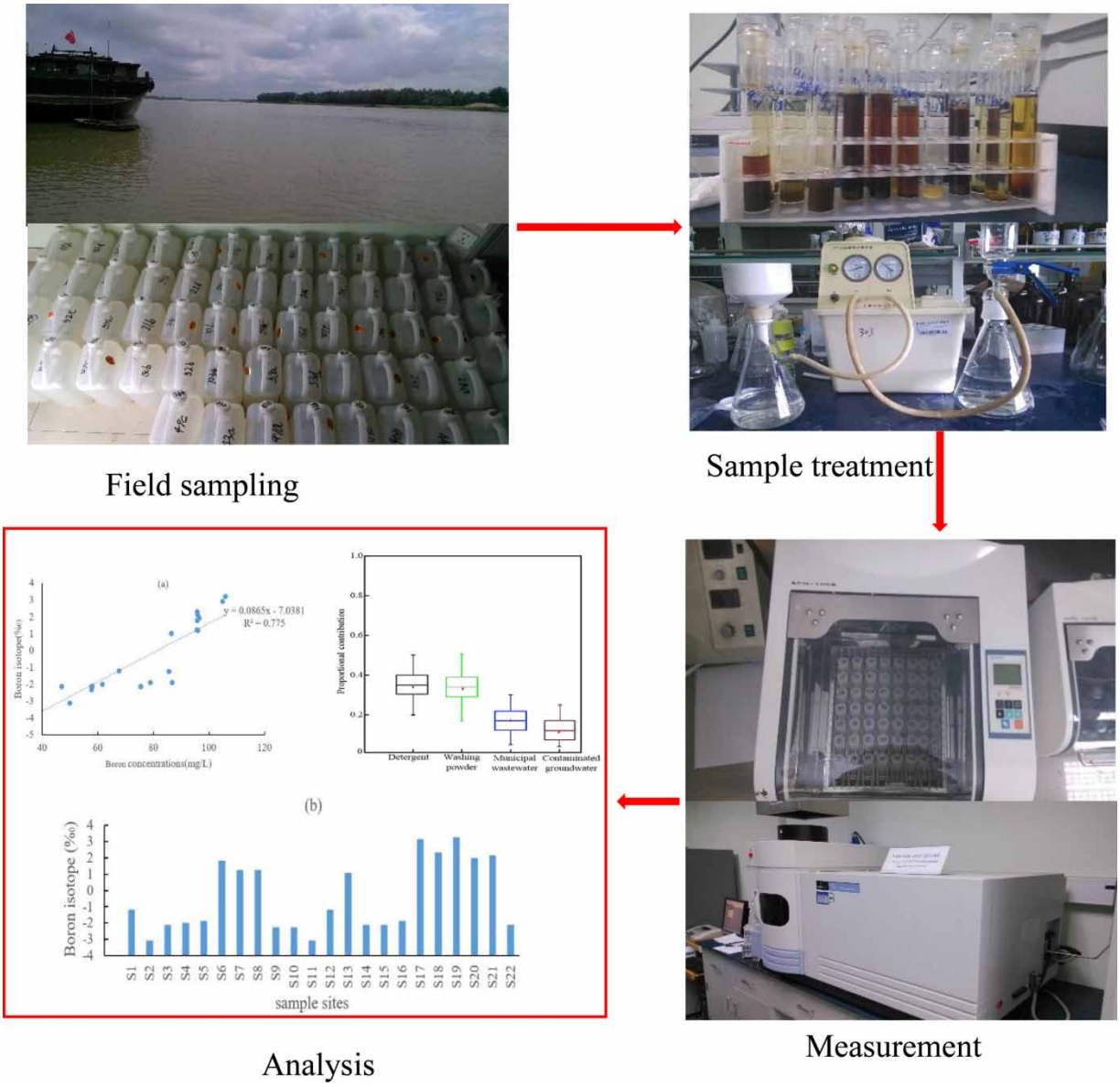
Thirty-four water samples were collected to measure their boron concentrations and δ^{11}B values. The results indicated that the concentrations of boron in the Huaihe River ranged from 37.99 to 105.99 μg/L, much lower than those of groundwater, farmland irrigation water and sewage water. The δ^{11}B values were between −3.12‰ and 3.21‰, with a mean value of −0.44‰. There were obvious variations trend of boron and δ^{11}B between upstream, midstream and downstream. δ^{11}B had a relatively high correlation with pH, boron and chlorine. Boron was positively correlated with EC, Na^+, K^+, F^-, Li^+, As and δ^{11}B, while negatively correlated with $Ca^{2+}$and Mg^{2+} in water. The structural equation model suggested industrial structure, population, economic development and pollution emission had positive effects on boron, whereas industrial structure and pollution emission had positive effects on δ^{11}B. The contents of boron and δ^{11}B showed a slight difference between the farmland, groundwater, sewage treatment plant and the Huaihe River. Hierarchical cluster analysis indicated that the same source was occurred between the Huaihe River and groundwater, between farmland and sewage treatment plant. A stable isotope analysis in R model revealed that detergent provided the greatest proportion of boron sources, followed by washing powder, municipal wastewater and contaminated groundwater.

Key words: boron, boron isotopes, Huaihe River, source

HIGHLIGHTS

- The different water samples were collected to determine the boron and δ11B.
- The correlations between the physical and chemical parameters and boron isotopic were studied.
- A structural equation model was used to analyze the effects of anthropogenic factors.
- Hierarchical cluster analysis was employed to distinguish the source.
- Spatial distribution characteristics of boron and boron isotope were studied.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Boron is a soluble incompatible element, which has two stable isotopes of ^{11}B and ^{10}B, with a ratio of about 4 (Deiana *et al.* 2020). The large relative mass difference between the two isotopes leads to the variation range of boron isotopic composition (denoted by $\delta^{11}B$) from −37‰ to 60‰, but there are specific $\delta^{11}B$ values in the different geochemical reservoirs (Clauer *et al.* 2018). Since the 1980s, people began to apply boron isotope analysis technology into some geochemical fields with the continuous improvement of boron isotope determination methods (Ercolani *et al.* 2019; André *et al.* 2020). Boron isotope has been widely used to solve many problems in the geochemical process, and has achieved fruitful results in the research fields of crust mantle evolution, groundwater, hydrothermal deposits, paleo environmental changes and so on (Guinoiseau *et al.* 2018). In the last 10 years, researchers have successfully used boron isotopes to solve the problem of environmental pollution, especially in tracing the source of water pollutants (Harkness *et al.* 2018) and analyzing boron isotopes with National Institute of Standards and Technology traceable commercial standards for quality control (Nigro *et al.* 2018). Gäbler *et al.* (2007) successfully traced the source, scope and degree of anthropogenic pollutants discharged into surface

water and groundwater in the northern Harz mountains of Germany by boron isotopes content. Tartari & Camusso (1988) found a strong correlation between boron content and soluble total phosphorus and anionic surfactant. Therefore, it was considered that high boron content was related to man-made pollution (Tartari & Camusso 1988; Ercolani *et al.* 2019). Noireaux *et al.* (2021) have analyzed and compared the average contents of boron with those of chloride and soluble phosphate in British rivers to distinguish two potentially important sources of boron input into the water: atmosphere or sewage. In China, Chetelat *et al.* (2009) have also applied the boron isotope method to the study of seawater intrusion and achieved good results. Anthropogenic activities have led to the aggravation of surface water pollution, the massive discharge of industrial and domestic sewage, farmland irrigation, wastewater reuse, the leaching of solid waste by atmospheric precipitation and the salinization of groundwater have accelerated the deterioration of water quality (Kyei & Hassan 2021; Noireaux *et al.* 2021). Therefore, early identification of pollution sources (natural or artificial pollution) and appropriate monitoring and treatment are one of the important purposes of environmental protection (Galal *et al.* 2021). Due to the complexity of pollution sources and the unknown changes of pollutants in the process of water self- purification, it is difficult for general hydrochemical elements to explain the sources and changes of pollutants (Widory *et al.* 2005). During the flow process, the fluid always has various complex interactions with the surrounding geological bodies, such as ion exchange, volatilization, evaporation, complexation, etc. (Baksheev *et al.* 2018). Most stable isotopes are easily limited and cannot determine the real source of pollutants. However, the chemical characteristics of boron isotopes can provide a new perspective for hydrodynamics (Kyei & Hassan 2021). The $\delta^{11}B$ value changes greatly from nature, and the change of $\delta^{11}B$ value in borate from the pollution source is generally small, that is, they basically keep the original boron isotopic composition in the production process and are different from the boron isotopic background value of the surrounding environment (Deyhle & Kopf 2005). Moreover, boron isotopic is not removed or accumulated in sewage sludge in sewage treatment plant, and the original boron isotopic composition in the wastewater is retained, which makes it a good tracer (Re & Sacchi 2017). Consequently, using boron isotopes as tracers and combined with other information can analyze and identify the pollution sources in aquatic ecosystem.

Huaihe River is one of the seven major rivers in China with a total length of about 1,000 km. It flows through three provinces from the upstream to the downstream including Henan, Anhui and Jiangsu Province, and Anhui is located at the middle reach with a total length of 430 km (Da *et al.* 2018). The average discharge in the upstream, midstream and downstream reaches are 456 m^3/s, 591 m^3/s and 479 m^3/s respectively. The average flow speed in the upstream, midstream and downstream reaches are 0.97 m/s, 1.90 m/s and 1.01 m/s respectively. The relatively high discharge and flow in the middle reaches is mainly due to the inflow of many tributaries into the Huaihe River. In recent years, the Huaihe River was polluted seriously with the development of industry and agriculture (Da *et al.* 2019a). All kinds of domestic wastewater, industrial wastewater, domestic garbage and industrial waste have been dumped into the Huaihe River in the past few decades, which led to complex sources of pollutants in the Huaihe River and tracing the source difficultly. Some previous studies have suggested that increased industrial and domestic wastewater discharges and agriculture garbage along the Huaihe River obviously contributed to the elevated residues of heavy metals, polycyclic aromatic, hydrocarbons and polybrominated diphenyl ethers and organochlorine pesticides in the Huaihe River (Da *et al.* 2019b). Based on the previous findings, the current work is mainly to study the boron concentration and boron isotopic composition in the Huaihe River, to identify the pollution sources by boron isotopic composition in the Huaihe River.

2. MATERIALS AND METHODS

2.1. Field sampling

Twenty-two water samples (water depth = 5 cm) were collected from the Huaihe River of Anhui section in July 2020, using a single layer sampler. Five groundwater samples were collected from the wells of the residents near about 1.5 km along the Huaihe River. Five farmland irrigation water samples were collected near 1 km along the Huaihe River. Two water samples from sewage treatment plant were collected near 4 km the Huaihe River. Special rubber gloves were worn during sampling. The collected water samples were filtered through 0.2 μm cellulose acetate filters *in situ*, the parameters such as pH, conductivity and water temperature were determined using the multi-parameter water quality analyzer, and recorded on the sampling sites. The water samples were put in a polyethylene plastic bottle treated with nitric acid, sealed with paraffin and gauze, and stored in an ice box at −4 °C. The sampling locations were displayed in Figure 1.

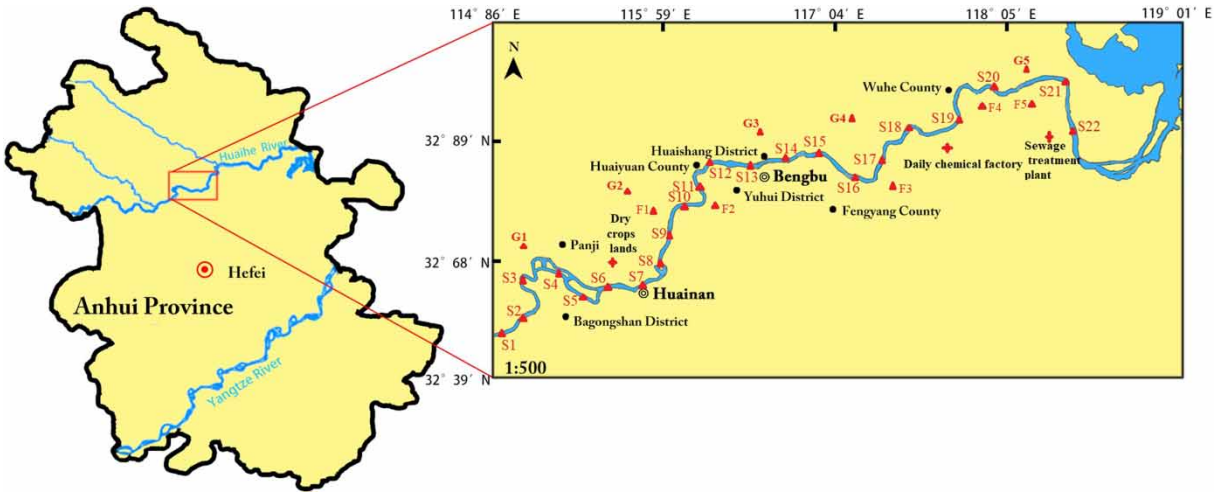


Figure 1 | Locations of sampling points. S1-S22: The sampling sites of the Huaihe River; G1-G5: The sampling sites of Groundwater; F1–F5: The sampling sites of farmland irrigation water.

2.2. Materials

Deionized water was purified by quartz sub-boiling distillation, and then treated with boron-specific resin (Amberlite-743) to remove the boron. High purity hydrochloric acid was prepared from superior pure HCl by an equilibrium method. The boron specific ion exchanger Amberlite IRA 743 (Rohm & Haas, American) was rinsed with 2 mol/L NH_4OH (high-grade pure), 0.1 mol/L HCl and then remove boron impurities with deionized water. The utensils used in the whole experiment process were made of polytetrafluoroethylene and polyethylene. Glassware was not contacted and used to avoid contamination of boron. The thermal ionization mass spectrometer (Phoenix) was from isotope X Company of UK.

2.3. Sample treatment and measurement

Boron in the water samples must be separated in order to eliminate the interference of the other substances to mass spectrometry measuring instruments. A boron-specific ion exchanger resin was used in the separation techniques. The steps of boron separation were as follows: The boron-specific ion exchanger resin was eluted with deionized water and 0.1 mol/L HCH. 50 ml water samples were pumped in the boron-specific ion exchanger resin with 4.6 cm of column height and 0.5 cm of inner diameter. A small amount of anions except boron adsorbed on the column was eluted with 2 mol/L NH_4OH. Finally, boron was eluted with 0.1 mol/L HCl. The eluents were collected, heated at 60 °C on electric heating plate in the fume hood, evaporated near dry for the positive thermal ionization mass spectrometry. A current of 3.0A was added to the Ta belt vacuum belt burning device and the sample baked for 60 minutes to remove the impurities on the Ta belt that affected the determination of boron isotopes. 3 μl graphite and ethanol suspension were coated on the Ta belt. Then we took 2 μL samples on the graphite, slowly increased the current to 1A, and reduced it to zero after drying. We put the samples on the sample tray and load it into the mass spectrometer. The samples were measured after the system was evacuated to 1.0×10^{-7} mbar. The peaks of 89 and 88 were detected by magnetic peak skip scanning. We adjusted the sample current to make the ion current intensity at a 89 peak to reach $1–3 \times 10^{-12}$ A. The ion current intensity of 89 ($^{23}Na_2^{11}B^{16}O_2^+$) and 88 ($^{23}Na_2^{101}B^{16}O_2^+$) were measured by Faraday cup. The determination time was generally 160 min and the ion flow remained stable. The ion current intensity ratios (R89/88) were calculated. After oxygen isotope correction, $^{11}B/^{10}B = R89/88–0.00078$. The boron isotope reference material used in this experiment was NIST 951a. The reference value: $^{11}B/^{10}B = 4.043\ 7 \pm 0.0033$. The variation of boron isotopic composition in the samples can be shown by the $\delta^{11}B$ value. The formula (1) was as follows: $\delta^{11}B = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{standard} - 1] \times 1000$ (Nigro *et al.* 2017).

Refering to the previous literature (Chetelat & Gaillardet 2005), B concentrations were analyzed on a Perkin-Elmer quadrupole ICP-MS Elan 6000 instrument at the Laboratoire de Géochimie of Toulouse. The concentrations of anion including SO_4^{2-}, Cl^-, Br^- and F^- were determined using ion chromatography (Dionex300), and those of the other cations and elements (Ca^{2+}, Mg^{2+}, Na^+, K^+, B, As, Li and Sr) were determined using ICP-AES (IRIS INTRE IIXSP) and ICP-MS instrumentation (Agilent 7500).

2.4. Quality assurance and quality control

To avoid any interference contamination, all plastic containers were precleared with deionized water and HCH before use. A procedural blank was carried out using the identical procedures in every five samples to judge for interferences, and no studied substance was found in the blank samples. All samples were carried out in triplicate to test the relative standard deviations. The relative standard deviations varied within acceptable limits (0.03–0.3%). The method detection limits of boron were on average 20 μ/L.

3. RESULTS AND DISCUSSION

3.1. Contents of boron and boron isotope in the Huaihe River

The contents of boron and boron isotope in the Huaihe River are listed in Table 1. Boron concentrations in the Huaihe River ranged from 37.99 μg/L to 105.99 μg/L, with a mean value of 75.23 μg/L. Boron isotope compositions in the Huaihe River ranged from −3.12‰ to 3.21‰, with a mean value of −0.44‰. Boron concentrations in the Huaihe River were less than the limit of boron concentrations (500 μg/L) in the surface water in China (Zhao & Liu 2010). It was also lower than the boron content (1,200 μg/L) of polluted river waters in Britain and the limit of boron concentrations (1,000 μg/L) in the surface waters in the European Union and Japan (Yu *et al.* 2021). It was reported that the concentrations of boron in the surface water from the United States ranged from 10 to 200 μg/L, with a median value of 76 μg/L (Williams *et al.* 2015). The average concentrations of boron in the surface water from Canada was 160 μg/L (Fernandes *et al.* 2019). Compared with these areas, the boron content in the Huaihe River water was relatively low. The boron concentrations in the Huaihe River were also lower than that in irrigation water (1 mg/L) and the corresponding Drinking Water Standard (0.5 mg/L) recommended by the World Health Organization (André *et al.* 2020). Although the boron content in the Huaihe River differed largely, the boron isotope values were within a relatively small range of −3.12‰ to 3.21‰.

3.2. Spatial distribution characteristics of boron and boron isotope in the Huaihe River

Figure 2 shows that there were obvious variations in the trend of boron and boron isotopes between upstream (site: S1-S7), midstream (site: S8-S16) and downstream (site: S17-S22). The boron concentrations in water samples from upstream, midstream and downstream were all less than the limit for boron concentrations (500 μg/L) in the surface water in China (Quast *et al.* 2006), which indicated that the Huaihe River was not polluted by boron. However, relatively high levels of boron were found in the samples from sites S17–S21, S12 and S13, S6–S8. During our field investigation, we noticed that a daily chemical factory producing cleaning powder with high boron concentration merged into the Huai River, and the sample S17–S21 was just collected very near their intersection. Thus, the boron concentration of S17–S21 may be affected by the recharge of this boron-enriched stream. The sites S12 and S13 are located near the entrance of the two tributaries (Guohe River and Xinhe River) into the Huaihe River. Therefore, boron in industrial and domestic sewage might flow into the Huaihe River through these two tributaries, resulting in the increase in boron concentration at these two points. S6–S8 locate near a lot of dry crops lands, where there is a need to apply a large amount of boron fertilizer in the growth process of crops. Therefore, boron fertilizer applied in agricultural processes may enter the Huaihe River through surface runoff. In addition, the self-purification of the Huaihe River, especially adsorption of boron in river water onto riverbed sediment could also affect the boron concentration (Chetelat & Gaillardet 2005). Boron isotope compositions in the Huaihe River ranged from −3.12‰ to 3.21‰. The relatively high compositions of boron isotope were found in the samples from sites S17–S21, S6–S8 and S13 but S1–S5, S9–12, S14–S16 and S22 are less than zero, which was generally consistent with the change in trend of boron concentration in these sites. The different changes of boron and boron isotopes in the different sites may be related to the velocity of the Huaihe River in addition to the input of external pollution. The Huai River is a winding river, the flow speed is high at the flat sampling sites but low at the bend sampling sites. The exogenous boron was accumulated at the sites with low flow speed, and washed away by the water flow at the sites with high flow speed. Although there was exogenous input of boron from sewage treatment near site S22, the concentrations of boron and boron isotopes at site S22 decreased significantly compared with those at site S21. The reason was that the water flow speed was low at the bend of S21 (0.68 m/s), while the water flow speed was high at the flat of S22 (2.5 m/s). It was noteworthy that the relatively high levels of boron but the relatively low level of B isotopic compositions were observed in S12, S15, S16 and S22. Mao *et al.*(2019) have reported that B isotopic compositions was affected by many factors including anthropogenic contamination, physical and chemical parameters of water and water–rock interactions.

Table 1 | Physical and chemical parameters in the different water samples (in mg/L, except for EC in μS/cm, Cl in μg/L, B in μg/L and $\delta^{11}B$ in ‰)

Sample	Sample sites	pH	EC	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{2-}	SO_4^{2-}	Cl^{-}	CO_3^{2-}	F^{-}	Br^{-}	Sr	Li	As	B	$d^{11}B$
The water from the Huaihe River	S1	7.32	89.1	13.61	2.98	4.76	0.89	6.13	2.31	72.12	1.21	2.91	0.01	0.05	nd	0.01	67.65	−1.21
	S2	7.01	101.2	14.43	1.23	3.58	1.78	2.34	2.45	49.98	1.54	3.76	0.04	0.01	0.02	0.01	49.98	−3.12
	S3	7.08	99.7	15.31	1.88	2.31	1.99	1.54	2.51	59.89	1.11	2.11	nd	0.11	nd	nd	57.81	−2.13
	S4	7.1	106.9	15.39	2.56	3.39	2.11	2.11	2.45	67.12	0.99	1.21	nd	0.09	nd	0.01	61.68	−2.01
	S5	7.34	78.7	14.67	1.98	2.68	2.02	1.31	3.16	76.34	2.11	3.98	0.08	0.12	0.01	nd	78.91	−1.90
	S6	8.01	99.7	18.79	2.34	4.45	3.02	1.99	3.87	87.89	1.10	4.65	0.09	0.33	nd	nd	95.71	1.78
	S7	7.65	106.8	17.89	3.67	4.54	1.23	2.87	3.81	89.90	1.21	6.69	0.01	0.34	nd	nd	95.61	1.23
	S8	7.71	121.9	16.59	3.56	3.59	2.31	1.99	2.18	87.89	2.21	3.54	nd	0.56	0.04	nd	96. 01	1.21
	S9	7.09	109.7	19.98	4.59	3.76	2.15	6.78	1.98	50.01	1.34	4.56	0.07	0.34	0.07	nd	38.21	−2.31
	S10	7.12	105.6	18.54	4.65	2.21	3.21	5.61	2.14	59.02	1.32	2.45	nd	0.12	0.09	nd	57.81	−2.31
	S11	7.05	99.0	21.76	4.67	6.65	4.12	4.56	3.12	45.08	1.98	3.21	0.08	0.12	0.11	0.03	37.99	−3.10
	S12	7.31	89.6	23.68	3.99	2.23	4.82	4.67	3.15	78.91	1.45	3.11	nd	0.13	nd	0.01	85.61	−1.23
	S13	7.61	99.9	21.98	2.77	6.65	5.26	5.12	2.51	78.90	1.12	3.67	0.08	0.34	nd	nd	86.56	1.01
	S14	7.34	100.9	20.95	3.76	4.69	4.28	4.32	2.41	67.98	1.23	5.78	0.01	0.34	nd	nd	46.99	−2.13
	S15	7.21	89.9	19.87	3.79	5.42	3.45	2.13	3.21	67.08	1.44	1.12	0.06	0.56	0.11	nd	75.45	−2.13
	S16	7.22	98.7	18.89	6.56	4.68	2.11	1.34	2.98	78.91	2.35	2.32	0.07	0.12	0.11	0.01	86.75	−1.90
	S17	8.09	101.2	17.67	5.67	3.45	1.99	1.43	3.12	98.95	3.54	3.12	0.08	0.13	0.09	nd	104.89	3.13
	S18	7.82	99.8	19.89	5.07	6.65	1.21	1.41	3.41	96.98	3.11	1.23	0.08	0.32	0.05	nd	95.76	2.31
	S19	8.14	98.7	21.98	4.99	4.53	1.01	1.32	3.29	98.96	1.11	2.31	nd	0.22	0.01	0.02	105.99	3.21
	S20	7.99	89.6	20.98	6.56	4.23	1.09	1.99	3.12	89.56	1.21	2.19	0.01	0.21	0.01	0.01	96.57	1.95
	S21	7.89	88.9	21.81	5.77	4.35	1.11	2.91	3.16	98.89	1.01	1.65	0.01	0.22	nd	0.01	95.98	2.12
	S22	7.12	89.8	22.67	5.87	4.21	1.02	2.89	3.19	78.43	1.01	1.43	0.01	0.13	nd	0.01	58.01	−2.12
Mean		**7.47**	**98.4**	**18.97**	**4.04**	**4.23**	**2.37**	**3.03**	**2.89**	**76.31**	**1.58**	**3.05**	**0.03**	**0.22**	**0.03**	**0.005**	**75.23**	**−0.44**
Groundwater	G1	8.89	123.7	29.98	7.89	4.18	2.11	2.31	2.17	321.45	21.31	3.45	0.19	0.12	0.02	0.01	301.01	14.45
	G2	8.09	120.9	31.21	8.56	5.32	2.19	2.89	3.12	341.32	22.11	5.78	0.16	0.23	0.15	0.02	290.89	13.21
	G3	8.15	114.8	30.98	9.78	5.19	1.23	3.81	4.56	298.19	20.12	8.98	0.75	0.11	0.13	nd	400.81	15.88
	G4	8.11	118.9	29.89	10.89	6.11	1.28	2.87	5.67	356.73	19.89	9.89	0.34	0.34	0.11	nd	410.21	16.21
	G5	8.19	119.8	29.78	11.89	5.12	1.23	3.22	5.89	345.87	23.18	9.98	0.21	0.12	0.06	0.01	309.5	15.31
Mean		**8.29**	**119.62**	**30.37**	**9.80**	**5.184**	**1.61**	**3.02**	**4.28**	**332.71**	**21.32**	**7.62**	**0.33**	**0.18**	**0.09**	**0.008**	**342.48**	**15.01**
Farmland water	F1	8.19	56.12	45.91	3.49	5.32	1.99	3.21	7.91	81.13	13.56	5.76	0.21	0.23	nd	0.01	378.81	15.01
	F2	8.67	43.12	50.93	2.98	4.51	2.31	3.45	6.78	79.12	14.52	4.53	0.01	0.11	nd	0.02	269.97	16.01
	F3	8.45	34.12	65.45	3.76	4.32	2.34	3.21	7.85	67.34	12.54	5.45	0.02	0.34	0.01	0.01	381.12	19.01
	F4	8.69	32.45	56.81	2.34	3.71	3.45	4.67	6.78	58.12	11.31	3.12	0.01	0.12	0.01	0.03	380.34	19.98
	F5	8.56	33.12	66.82	3.11	4.89	4.51	3.56	7.89	56.89	12.31	3.45	0.03	0.34	nd	nd	478.21	14.01
Mean		**8.51**	**39.79**	**57.18**	**3.14**	**4.55**	**2.92**	**3.62**	**7.44**	**68.52**	**14.26**	**4.99**	**0.10**	**0.22**	**0.02**	**0.013**	**377.69**	**16.80**
Water from sewage treatment plant	P1(inflow)	7.89	56.78	23.12	11.98	12.34	3.41	4.56	14.56	345.34	11.34	4.89	0.01	0.21	0.19	0.04	569.34	11.45
	P2 (outflow)	3.04	57.99	19.87	69.89	13.43	2.67	3.45	5.98	332.12	10.98	4.23	0.01	0.32	0.14	0.02	550.21	11.12
Mean		5.47	57.39	21.50	40.94	12.89	3.04	4.01	10.27	338.73	11.16	4.56	0.01	0.265	0.17	0.03	559.78	11.29

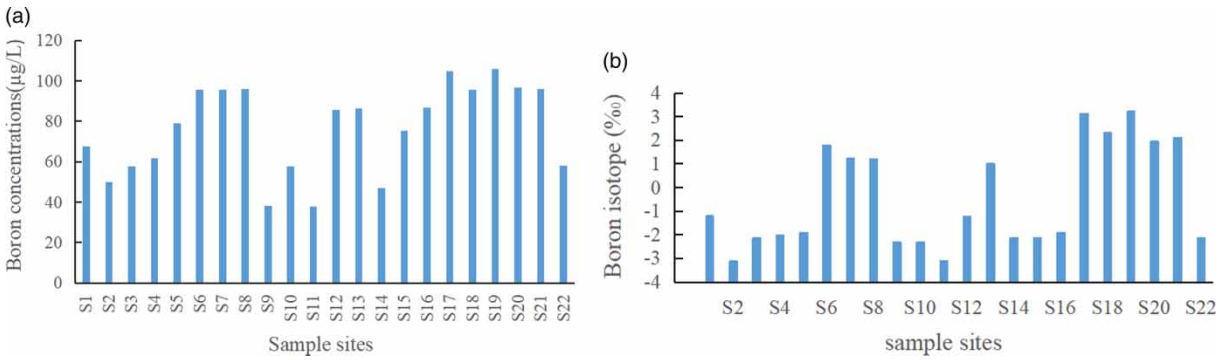


Figure 2 | Spatial distribution characteristics of boron and boron isotope in the Huaihe River .

As seen from Fig. S1, the variation in range of boron isotope in the Huaihe River water was consistent with that in detergent and washing powder. Therefore, it was speculated that the boron in the Huaihe River was from detergent and washing powder, but the real sources still need to be quantified with a stable isotope analysis in R the next section.

3.3. Discussion on influencing factors of boron isotopic composition

In order to explain that boron isotopes compositions were relatively low in samples from the Huaihe River, the correlations between boron isotopes and boron, pH and chlorine were analyzed. As seen in Figure 3(a)–3(c), Boron isotope had a relatively high correlation with pH, boron and chlorine in the Huaihe River, in particular, a high correlation ($R^2 = 0.95$) between boron isotope and pH value was observed. According to previous reports (Chen *et al.* 2008), the boron isotope

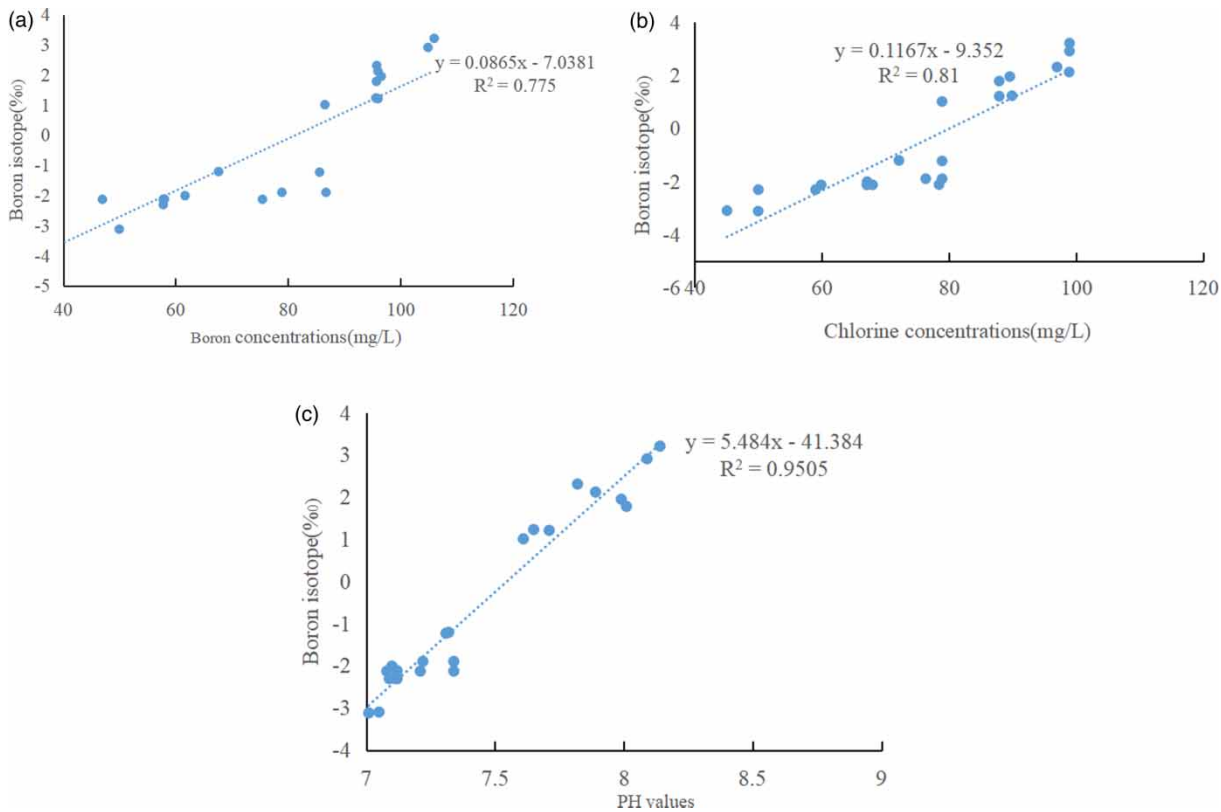


Figure 3 | Boron isotopes vs boron (a), chlorine (b) and pH values (c) in the Huaihe River.

gradually decreased with the increasing pH values, boron mainly existed in the form of $B(OH)_3$ and $B(OH)_4^-$ in the solution. ^{10}B was relatively enriched in $B(OH)_4^-$ and easy to enter the sedimentary fancies, while ^{11}B was relatively enriched in $B(OH)^3$ and retained in the solution. The distribution ratio of $B(OH)_3$ and $B(OH)_4^-$ in the solution was controlled by the pH of the solution (Wei *et al.* 2021). Chlorine concentrations was an important indicator of the salinity of the solution (Li *et al.* 2021). Harkness *et al.* (2018) have shown that ^{10}B is always deposited in the sediment prior to ^{11}B in the solution with high chlorine contents, so ^{11}B was relatively enriched in the solution (Li *et al.* 2016). Therefore, according to the calculation formula (1) for the boron isotope, the boron isotope was higher in the solution enriched by ^{11}B. Therefore, it was not difficult to explain the high correlation between chlorine and boron isotopes in this study. The concentrations of boron were relatively low in this study, but the boron isotopes were high, which may be related to the source of boron.

In order to examine the possible correlation among the measured physical and chemical parameters of water, their correlation coefficients have been calculated and presented in Table 2. It suggested that B was positively correlated with EC, Na^+, K^+, Cl^-, F^-, Li^+, As and boron isotopes, while negatively correlated with Ca^{2+} and Mg^{2+}. The boron isotopes was positively correlated with B, EC, As and pH, but negatively correlated with Ca^{2+} and Mg^{2+}. The significant correlations between boron, boron isotope and EC, Na^+, K^+, Cl^-, F^-, Li and As can probably be attributed to their common origin. The occurrence of HCO_3^- to CO_3^{2-} can cause precipitation of Ca^{2+} and Mg^{2+}. Thus, boron and boron isotopic has negative correlations with Ca and Mg.

To further study the factors influencing the source of B and boron isotopic, a structural equation model (SEM) encompassing 15 anthropogenic factors was used (data collected from http://www.stats.gov.cn) in recent years in Anhui Province. The anthropogenic factors are listed in the Table S1. PCA was used to divide the 15 individual factors into six categories. The categories contained urbanization, population, economic development, industrial structure, pollution emission and transportation volume. The result produced by the SEM is displayed in Figure 4. The hypothetical model agreed with our data: $\chi 2 = 14.4$, $P = 0.23$, d.f. $= 13$, GFI $= 0.71$, AIC $= 62$ and RMSEA $= 0.03$. Industrial structure ($\lambda = 0.97$, $P < 0.001$), population ($\lambda = 0.78$, $P < 0.01$), economic development ($\lambda = 0.79$, $P < 0.001$) and pollution emission ($\lambda = 0.91$, $P < 0.05$) had positive effects on boron, whereas industrial structure ($\lambda = 0.75$, $P < 0.001$), and pollution emission ($\lambda = 0.71$, $P < 0.05$) and boron ($\lambda = 0.82$, $P < 0.05$) had positive effects on the boron isotope. Notably, although population had no direct effects on the boron isotope, it had positive effects on boron.

3.4. Source analysis of boron and boron isotopes

In order to study the pollution source and migration in the Huaihe River, five groundwater samples, five farmland water samples and two sewage samples from the sewage treatment plant around the Huaihe River were also collected. As shown in Table 1 and Figure 5(a) and 5(b), the contents of boron in the different water samples showed the following sequence, i.e., sewage treatment plant > farmland > groundwater > Huaihe River. The contents of boron in the sewage treatment plant were higher than those of the other water samples. In addition, the concentrations of boron did not significantly change in the outflow of the sewage treatment plant compared with those in the inflow of the plant (Table 1), which confirmed the previous results showing that boron was neither eliminated, nor accumulated in the sewage sludge (Coyte *et al.* 2019). Boron isotope compositions in the different water samples showed the following sequence, i.e., farmland > groundwater > sewage treatment plant > Huaihe River. This sequence was slightly different from that of boron contents in all investigated samples. It was reported that boron isotopic composition was controlled by source, adsorption/desorption, mineral precipitation/ decomposition, volatilization and other factors which will produce great differences (Naik *et al.* 2015; Nigro *et al.* 2018). Coyte *et al.* (2019) have also shown that there was no corresponding relationship between boron isotopic composition and boron content. Boron concentrations in the groundwater ranged from 290.89 μg/L to 410.21 μg/L, with a mean value of 342.48 μg/L. Boron isotope concentrations in the groundwater ranged from 13.21‰ to 16.21‰, with a mean value of 15.01‰. The results were similar to those of contaminated ground water from the Dan Region of Israel (boron: 280–580 μg/L, boron isotope: 6.9–18.2‰ (Cary *et al.* 2013). According to the distribution of boron isotopic composition in different media (Fig. S1), the variation in range of boron isotope in polluted groundwater was 5‰ to 25‰. The variation in range of boron isotopes (13.21–16.21‰) in groundwater from this study was within the range, which indicated that the groundwater might been polluted in this study. It was noted that the pH value of the five groundwater samples was greater than 8, indicating that the groundwater was alkaline. The normal pH value of groundwater was about 7.5 (Coyte *et al.* 2019). The relatively high pH value also indicated that the groundwater had been polluted, which was harmful to human health. The relatively high chloride and boron concentrations detected in the groundwater suggested anthropogenic

Table 2 | Spearman's correlation coefficients of water samples from the Huaihe River

	B	EC	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	CO_3^{2-}	F^{-}	Br^{-}	Sr	Li	As	PH	$\delta^{11}B$
B	1																
EC	0.784 **	1															
Ca	−0.915**	0.797**	1														
Mg	−0.843**	0.636**	−0.777**	1													
Na	0.711	0.795	−0.738**	−0.477**	1												
K	0.813**	0.774**	−0.641	−0.132	0.777	1											
HCO_3	0.344**	0.124	0.629**	0.311**	0.838**	0.877	1										
SO_4	0.372	0.623**	0.643	0.429	0.741	0.938**	0.613**	1									
Cl	0.783**	0.216	−0.636**	0.193**	0.629**	0.641	0.638	0.777**	1								
CO_3	0.073	0.275**	0.631*	0.736	0.543	0.729	0.841	0.838	0.715	1							
F	0.919**	0.671*	−0.517	0.638**	0.739**	0.843**	0.729**	0.641**	0.238**	0.775	1						
Br	0.154*	0.731**	−0.638**	0.574	0.639	0.736	0.743*	0.629	0.351	0.168**	0.634	1					
Sr	0.173**	0.723	−0.631	0.638**	0.587**	0.238**	0.636**	0.543*	0.629**	0.641	0.738**	0.173	1				
Li	0.943	0.634**	0.229**	0.641*	0.698*	0.474*	0.638	0.636	0.743**	0.329**	0.363	0.638**	0.617	1			
As	0.875*	0.654	0.613	0.829**	0.541	0.238	0.577	0.738**	0.636	0.146**	0.329**	0.331**	0.738**	0.779	1		
PH	0.149*	0.345*	0.136**	0.643	0.316**	0.311**	0.638**	0.377*	0.638**	0.166	0.043*	0.621*	0.841**	0.638**	0.618	1	
$\delta^{11}B$	0.832**	0.861**	− 0.838*	− 0.796*	0.243	0.129	0.441*	0.438	0.477*	0.238**	0.036**	0.153	0.029*	0.241*	0.752**	0.713**	1

Levels of significance: $^{**}P < 0.01$; $^{*}P < 0.05$.

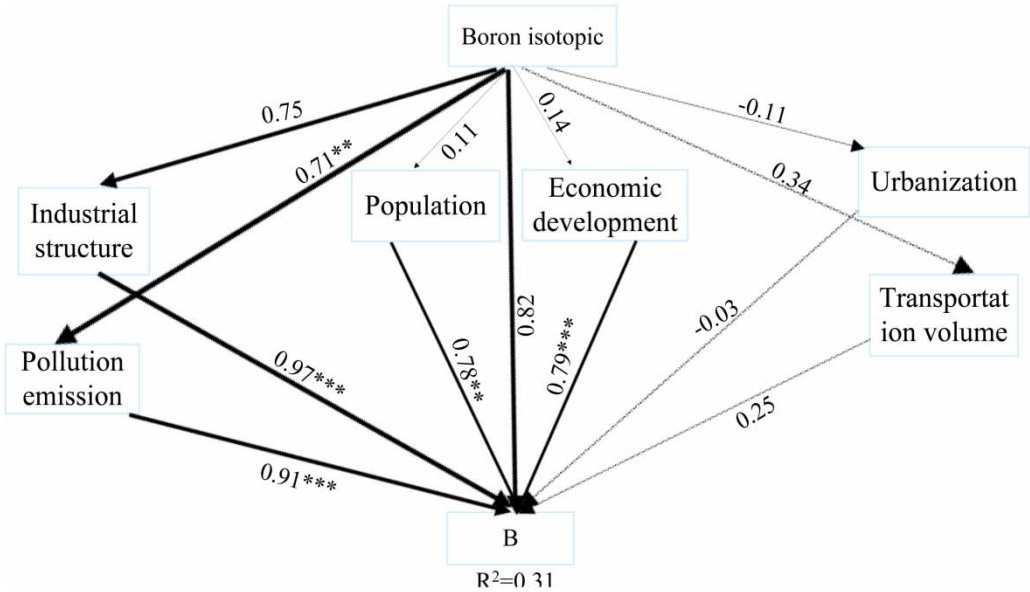


Figure 4 | Structural equation models showing the direct and indirect effects of climate factors and anthropogenic factors on boron isotope. Noted: Numbers adjacent to the arrows are path coefficients and indicative of the effect size of the relationship. Width of solid lines indicates the strength of the path coefficients. Dashed lines indicate nonsignificant relationships. $*P < 0.05$, $**P < 0.01$ and $***P < 0.001$. R^2 represents the proportion of variance explained by the relations in the path model. .

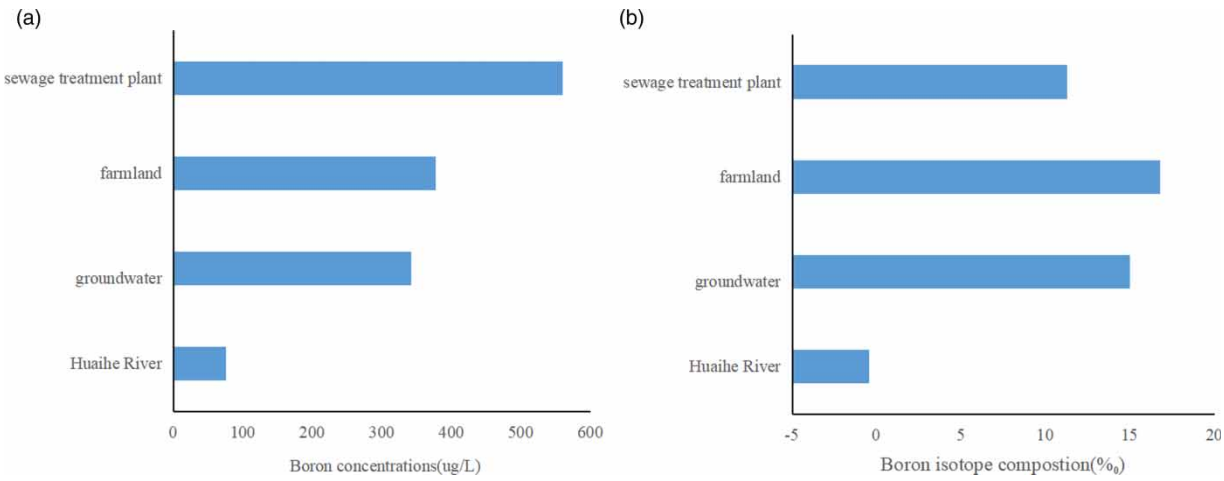


Figure 5 | The contents of boron and boron isotopes in the different water samples.

influences. Nigro *et al.* (2018) suggested that the chlorine concentration in uncontaminated groundwater was less than 50 mg/L (Nigro *et al.* 2018). The chlorine concentration was far more than 50 mg/L in the groundwater from this study. The higher concentrations of chloride and pH value indicated that the groundwater was polluted and salinized generally in this study.

Hierarchical cluster analysis was employed to classify the water samples into two groups, one group contained Huaihe River water and groundwater, the other contained farmland water and the sewage treatment plant. The results indicated that the same source was present between Huaihe River water and groundwater, between farmland water and the sewage treatment plant. From Table 1, it was not difficult to observe that high contents of boron and boron isotopes found both in farmland irrigation water and sewage water.

To quantify proportional contributions of pollution sources, a stable isotope analysis in R called SIAR model was applied to estimate proportional contributions. The mixing model SIAR can be expressed as below (Liu *et al.* 2018):

$$X_{ij} = \sum_{k=1}^{K} P_k(S_{jk} + c_{jk}) + \varepsilon_{ij} \quad (1)$$

X_{ij} represents the value of the isotope j in the sample i; P_k represents the proportion of source k; S_{jk} is the value of the isotope j in the source k; C_{jk} represents the fractionation factor for isotope j in source k; ε_{ij} is the residual error. A detailed description of the mixing model was elaborated in Liu *et al.* (2018).

According to Fig. S1, SIAR was applied to calculate the contribution of five pollution sources: fly ash and waste leachate (F), washing powder (W), detergent (D), municipal wastewater (M) and contaminated groundwater (C). According to the output results of the mixing model (Figure 6), the contribution rates of five boron isotope sources were as follows: detergent (34%) > washing powder (33%) > municipal wastewater (18%) > contaminated groundwater (15%) > fly ash and waste leachate (0%). The result that greater contributions from detergent and washing powder was likely to be due to the more domestic sewage discharged in the Huaihe River. Secondly, municipal wastewater and contaminated groundwater also contributed to the source of water pollution in the Huaihe River. In summary, detergent and washing powder sources were the primary contributors of boron to the Huaihe River.

4. CONCLUSIONS

This study found that the boron content in the Huaihe River water was relatively low and, furthermore, there were obvious variations in trend of boron and boron isotope between upstream, midstream and downstream in the Huaihe River. Boron isotope had a relatively high correlation with pH, boron and chlorine. Boron was positively correlated with EC, Na^+, K^+, Cl^-, F^-, Li^+, As and boron isotope, while negatively correlated with Ca^{2+} and Mg^{2+} in water. A structural equation model suggested that industrial structure, population, economic development and pollution emission had positive effects on boron, whereas industrial structure, pollution emission and boron had positive effects on the boron isotope. The compositions

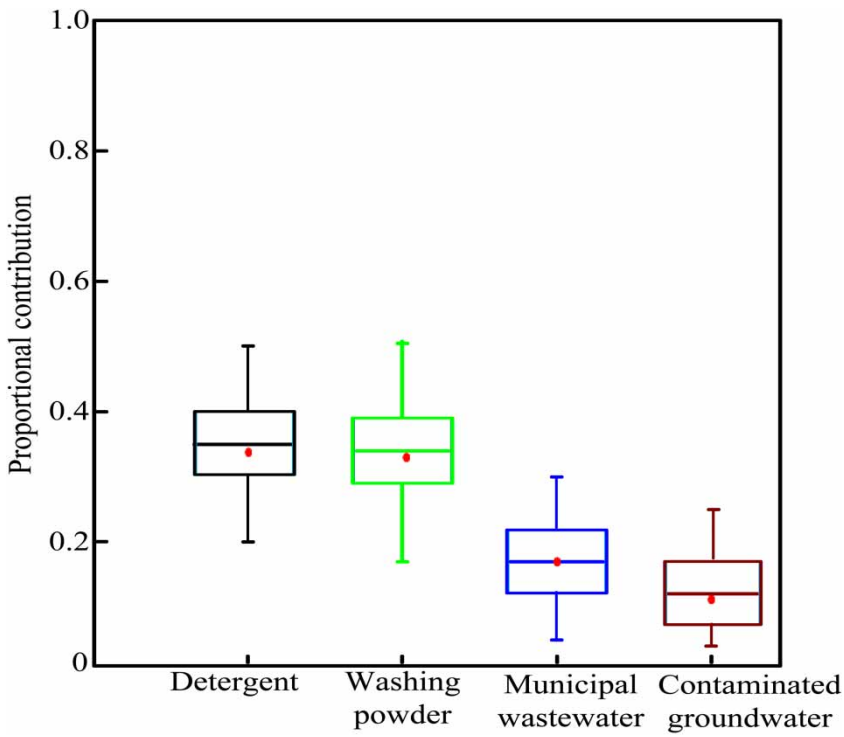


Figure 6 | Proportional contribution of four potential sources of boron for the Huaihe River.

analysis of boron isotope showed a slight difference in the farmland, groundwater, sewage treatment plant and the Huaihe River. Hierarchical cluster analysis indicated that the same source was present between Huaihe River and groundwater, and between farmland and sewage treatment plant. A stable isotope analysis in the R model indicated that boron was derived primarily from detergent and washing powder sources in the Huaihe River.

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DATA AVAILABILITY STATEMENT

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

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