ASSESSMENT OF ARSENIC CONTAMINATION IN THE RED RIVER: HIGH RESOLUTION MONITORING COUPLED WITH SPATIAL ANALYSIS BY GIS

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ABSTRACT

The Red River (China/Vietnam, A = 155 000 km^2) is a typical humid tropics river originating from the mountainous area of Yunan Province in China. Based on two sampling campaigns covering the whole Vietnamese watershed in 40 sites at low and high water levels during 2009, the seasonal and spatial variations of As concentrations in dissolved and particulate phases were determined. The dissolved As concentrations in rainy season were relatively lower than in dry season, suggesting the dilution effect of less arsenic-contaminated water. In contract, the particulate As concentrations during low water level were clearly lower than that during high water level, demonstrating a change phenomenon in As source(s) with hydrology. In addition, in order to assess spatial distribution of the As contamination in the Red River watershed and localize geochemical anomalies, multidimensional statistical analyses combined with As maps generated by GIS tool were used. The results showed that the highest As concentrations are originated from the upstream catchment and strongly decrease from upstream to downstream. Finally, the comparison between dissolved As concentrations from the Red River watershed and the national technical regulation on surface water (QCVN 08:2008/BTNMT) indicated that the quality of water in the Vietnamese Red River watershed can be classified as poor quality in the upstream part and as mediocre quality in the downstream part.

Keywords: Red River, Vietnam, As concentrations, anomaly, water quality, GIS.

1. INTRODUCTION

Arsenic buildup in the environment is of increasing concern due to its high toxicity and increasingly widespread occurrence [1, 2]. It is ubiquitous in nature (i.e. freshwater; seawater; soil, atmosphere, biosphere) and elevated levels have resulted from both natural and anthropogenic sources [3, 4, 5, 6]. Since several centuries, huge amounts of arsenic have been introduced into the environment by anthropogenic activities such as mining, combustion of fossil fuels or agriculture [3, 4]. Arsenic has become a major environmental and human-health preoccupation. In the South Asia, many researches have focused on As level because of within the deltas in this area, widespread consumption of groundwater containing dangerous levels of As adversely impacts tens of millions of people in Bangladesh, India, Cambodia, and Vietnam [7, 8]. Stream sediments integrate geochemical signals from the watershed upstream of the sampling site and they are commonly used in environmental studies to evaluate concentrations of chemical elements in soils over wide areas and to identity possible sources of anomalies such as ore deposits (geochemical exploration) or anthropogenic sources [5, 9, 10].

The Red River (Fig. 1), drainage in Himalaya, is the one of largest rivers in the South-East Asia and contributes significantly to the global sediment budget and water discharge to the ocean [11, 12]. Much research has been done on the contamination of heavy metals in the ground water, sediment and soil in the Red River Delta in Vietnam [8, 13, 14]. The metallic contamination has posed a serious health threat to millions of people living in this area, especially As. Dissolved arsenic concentrations in drinking water wells in this region can exceed 3050 µg/l [7], i.e. more than 300 times the national technical regulation on surface water of 10 µg/l (QCVN 08:2008/BTNMT). The groundwater arsenic pollution seems to be of natural origin and caused by reductive dissolution of arsenic-bearing iron phases buried in aquifers [7]. However, the rapid intensification of industrial activities including copper and lead casting, phosphorous fertilizer production, chemical manufacturing, etc. have been indicated to have introduced heavy metals into water and soil systems of the Red River basin [16].

N°	Lat	Long
1 (LC)	22°30,063	103°58,155
2	22°31,127	104°60,034
3	22°10,936	104°15,067
4	22°10,254	104°21,288
5 (PT)	21°41,656	104°52,200
6 (Da)	20°46,460	105°19,510
7	21°03,093	104°42,655
8	21°28,543	104°02,050
9	21°26.247	104°03.030
10	21°37,057	103°55,198
11	21°39,795	103°36,890
12	21°47.377	103°18.074
13	22°06,242	103°05,974
14	22°00,709	103°10,531
15	22°21,652	102°46,894
16	22°24,474	102°42,492
17	22°33,799	103°16,019
18	22°32,895	103°16,759
19 (Lo)	2[illegible]°25,921	105°21,054
20	21°38,579	105°10,595
21	22°06,715	104°41,888
22	22°32,754	104°21,300
23	21°35,347	105°24,555
24	22°06,267	105°32,825
25	21°49,171	105°13,173
26	22°02,027	105°07,006
27	22°27,638	104°40,803
28	22°50,689	104°53,685
29	23°04,888	105°04,159
30	23°06,500	104°54,961
31	22°07,654	105°16,348
32	22°07,507	105°16,214
33	22°12,061	105°19,766
34	22°27,178	105°43,446
35	22°38,761	105°15,373
36	22°44,322	105°24,307
37	23°02,269	105°25,234
38	22°56,583	105°40,204
39	22°56,342	105°32,329
40 (ST)	21°09,223	105°30,337

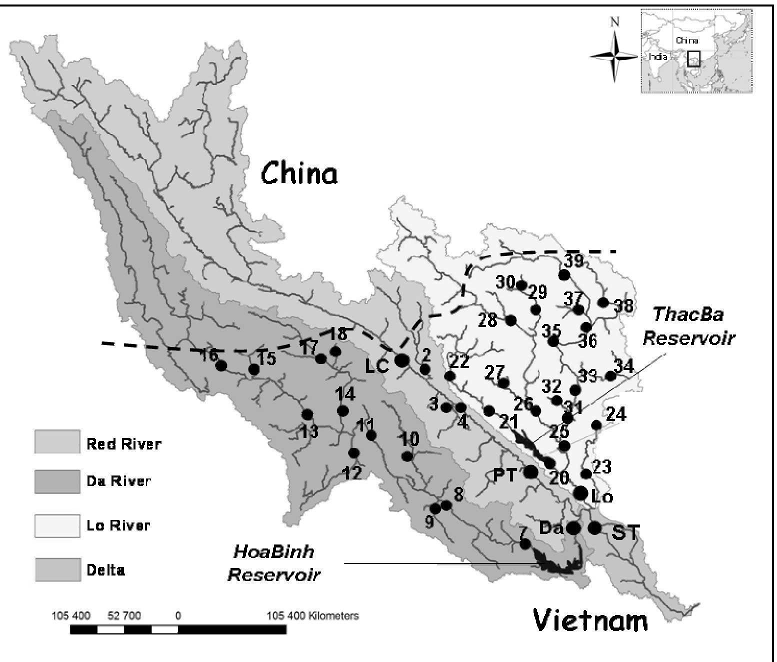

Figure 1. Description of the Red River watershed and sampling strategy: location of study sites during two spatial sampling campaigns (black points) and the sampling site coordinates. The black dotted represents the China/Vietnam frontier.

Despite the known arsenic pollution affecting the groundwater in the Red River Delta, little information is available on particulate and dissolved arsenic concentrations in the fluvial system, especially in the upstream part causing conditions of access to sites [11, 12]. This paper presents the data of particulate and dissolved arsenic concentrations obtained from 40 points throughout the Red River basin in Vietnamese part in two contrasting hydrological conditions during 2009: high and low water levels. The objectives of this study are to: (i) determine seasonal and spatial As concentration variations; (ii) localize As anomalies in the Red River watershed and (iii) characterize water quality in term of dissolved As.

2. MATERIALS AND METHODS

2.1. Area descriptions

The Red River system has a total watershed area of 169,000 km², 50.3 % of which in Vietnam, 48.8 % is situated in China and 0.9 % is situated in Laos and includes a fertile and densely populated delta plain (14,000 km²; Fig. 1). The Red River originates from the mountainous area of Yunnan Province in China, flows 1200 km south-eastward and then flows through seven Vietnamese provinces before flowing into the Gulf of Tonkin in the South China Sea. The red laterite soils are abundant in this mountainous area and give the river its characteristic color. The main tributaries of the Red River are the Da River, on the right bank, and the Lo River, on the left bank. The Da River has its source in the Yunnan Province, near to that of the upstream Red River, at an elevation > 2000m.

The Red River basin is characterized by two distinct seasons: the rainy season from May to October and the dry season from November to April, due to the South West monsoon in summer and the North East monsoon in winter, respectively. The rainy season is warm and very humid, with mean temperatures ranging from 27 °C to 29 °C whereas the dry season is cool and dry with mean monthly temperatures ranging from 16 °C to 21 °C (Fig. 2). The average annual rainfall in the Red River System is 1600 mm, with 85 % - 95 % of this falling during the summer season.

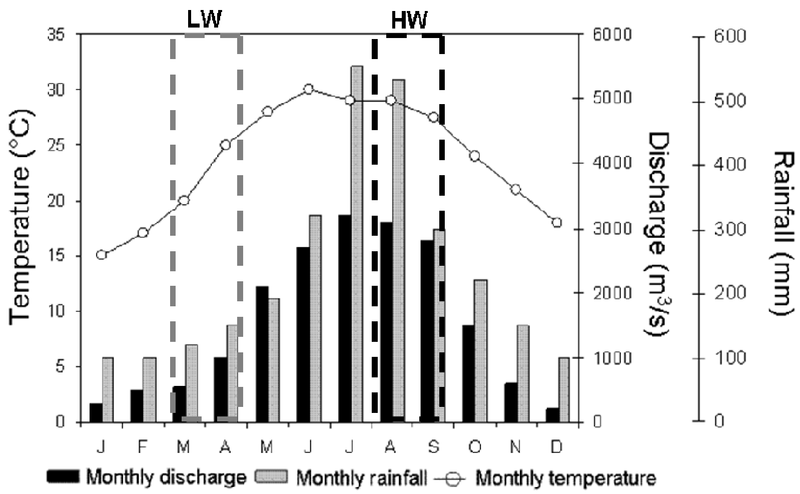

Figure 2. Description of monthly averages of temperature, water discharge and rainfall of the Red River. LW, HW: sampling spatial campaign at low and high water levels. (Source: [11]).

2.2. Data and methodology

Sampling frequency: During 2009, sampling campaigns were performed at 40 points throughout the Vietnamese parts of the Red River watershed in two contrasting hydrological conditions: low water discharge in Mars – April 2009 (dry season) and medium to high water discharge in August - September 2009 (rainy season; Fig. 1 and 2). The coordinates of the sampling location were recorded with a differential GPS. At each site, the dissolved, stream sediment samples were measured (Fig. 1). The coordinates of the sampling sites were listed in figure 1.

Sampling and Sample treatment: Water was manually sampled for dissolved trace metal analysis at 2m from the riverbank and 50cm depth by one – liter acid pre-cleaned poly-propylene bottle previously rinsed with river water. Homogenized sample aliquots were filtered on site using 0.2µm Sartorius® cellulose acetate filters. Filtrates were collected in 14cc polypropylene tube, previously decontaminated and thoroughly rinsed with the filtrate, acidified (HNO_3 super pure grade; 1 : 1000) and stored at 4 °C until analysis [18].

Stream sediment samples were manually collected using a plastic spatula, consisting of the uppermost 1cm of sediment from several recent depositional pockets within a distance of twenty five meters. Stream sediment samples were sieved (<63 µm; nylon sieves) to remove coarse material which was obviously not representative of typical grain size of suspended particulate matter [5, 9].

Sample analyses: - Particulate phase digestion: Representative sub-samples (~30 mg of dry, powdered and homogenized material) were digested in closed Teflon reactor (Savillex®) on a heating plate (110 °C in 2 h) using 750 µl HCl (12 N, super pure), 250 µl HNO_3 (14 M, super pure) and 2 ml HF (22 M, super pure). After complete cooling, the digested solution was evaporation to dryness. Each sample was brought to 10 ml using 150µl HNO_3 (14M super pure and double deionized (milli-Q®) water [18, 20].

- Total dissolved and total particulate metal concentration analyses: Dissolved and particulate metals were measured using ICP-MS (X7 THERMO) with external calibration. After each beach of five samples, a calibration blank and one calibration standard were measured to control potential sensitivity variations. The analytical methods employed were continuously quality checked by analysis of certified reference sediments (NCS DC 78301 and LGC 6178) and river water (SRLS4, SRLS5 and TMRAIN). Accuracy was within 5 % of the certified values and the analytical error (relative standard deviation) was generally better than 5 % (relative standard deviation) for concentration 10 times higher than detection limits.

- GIS Arsenic distribution analysis: In this study, we used Geographic Information System (GIS; Mapinfo) to treat Topographical, geological data and metal/metalloid concentrations. According to the coordinates of the sampling locations of 40 sites in the hydrological network during two specific campaigns, the limits and areas of the respective drainage basins have been extracted. Arsenic concentrations were considered as generally representative of the watershed area upstream from the sampling point.

3. RESULTS AND DISCUSSION

3.1. Variability of dissolved and particulate As concentrations

The summary of the statistical parameters (including the arithmetic mean, median, 10- and 90-centiles, minimum and maximum) describes variability of dissolved As concentrations measured during high and low water levels from 40 sampling sites in the Vietnamese part of the

Red River watershed showing strong spatial variations (Fig. 3). In low water level, the dissolved As concentrations varied between 0.11 and 20.4 µg/l and its values varied between 0.08 and 14.1 µg/l in high water condition (Fig. 2). The average dissolved As concentrations were 2.86 µg/l and 3.45 µg/l in high water and low water levels, respectively, showing the slight diminution of dissolved As concentrations in high water condition due to the dilution effect. This dilution phenomenon of dissolved metal concentrations by water discharge was observed in many rivers in the world such the Mekong [16], the Yellow [21], the Garonne [4], the Amazone [18] or the Mississippi [19].

Concerning to the As concentrations in the <63µm fraction of the stream sediments from 40 points in the Red River watershed, As concentrations ranged between 2.46 and 612 mg/kg (average value of 79.8 mg/kg) in high water level and between 0.71 and 510 mg/kg (average value of 58.2 mg/kg) in low water level. We noted that the As concentrations in the Red River watershed were strongly higher than the world average value (36 mg/kg) established by Viers et al. (2009, [20]), even the hydrological conditions (Fig. 3).

In addition, it's very interesting to note that the As concentrations in < 63 µm fraction during dry season were clearly lower than that during rainy season. Generally, particulate metal concentrations in sediment tend to decrease with increasing water discharges due to erosion of less contaminated sediments (alluvial floor of the channel and bank deposits) and/or a higher percentage of relatively coarse material and have been reported for medium scale watersheds. In contrast, increasing particulate concentrations during rainy seasons compared to dry season is more typical for small watersheds with important point sources such as mining tailings [5]. For the case of the Red River, the results suggest a change in punctual As source(s) with hydrology in rainy season (e.g. mining/industrial point sources located along the Red River basin and/or plain erosion).

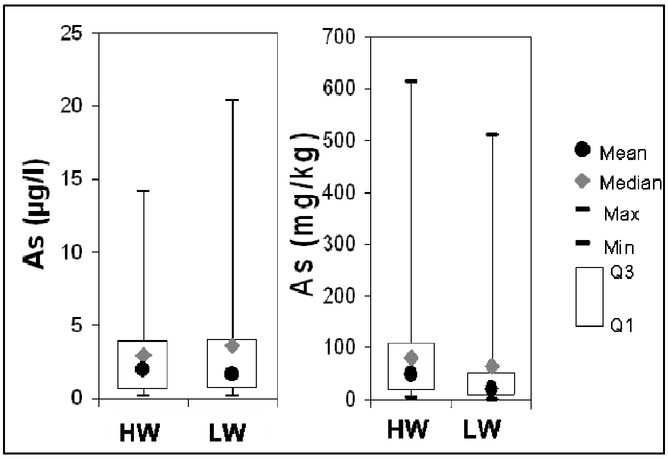

Figure 3. Box plots of As concentrations of the Red River in two specific campaigns during low and high waters (HW and LW) in 2009.

3.2. Spatial distribution analysis assisted by GIS tool

In order to determine As sources and identify the spatial distribution of As concentrations in the Red River basin, the As concentrations obtained from 40 sites in the whole Red River watershed were used to establish the maps assisted by GIS tool. For purposes of comparison, the measured concentrations ranges were separated into five classes. Each class represents concentration ranges <1, 1-2, 2-5, 5-10 and >10 times that of world average (noted Bn) established by Viers et al. 2009 (Fig. 4).

The figure 4 show that the high arsenic anomalies (in dissolved and particulate phases) are observed in the upstream Red River in both high and low water levels and may be due to natural and/or anthropogenic sources in upstream part (14, 15, 16, 17]). Furthermore, the study by Dang et al. (2011, [21]) on mineralogical in-situ characterization of particle in mining-impacted stream sediment allowed to identify the main As carrier phases and understand their fate on As mobility in the studied system. The results obtained showed that the main As-bearing phase is highly hydrated/hydroxyled products with variables (As, Fe) composition (fermihydrite-type; [21]). This massive health crisis is the product of a confluence of processes initiated by the erosion of As-bearing minerals in the Himalaya, transport of sediments containing As-bearing iron oxides down the Red River systems, and deposition as deltaic sediments.

Finally, we noted that the As concentrations in both dissolved and < 63µm fractions in high and low water conditions decrease from upstream to downstream, suggesting the dilution effect by water (dissolved phase) and by sediment (sediment phase) due to erosion of less contaminated sediments in the more downstream parts of the watershed. These results show that the highest As concentrations are originated from the upper Red River System. Future research efforts need to characterize water quality (e.g. As in dissolved and particulate phases) with a high temporal and spatial resolutions) in Chinese part as well their speciation (carrier phases) in order to determine the natural and/or anthropogenic sources and evaluate bioavailability and eco-toxicological potential.

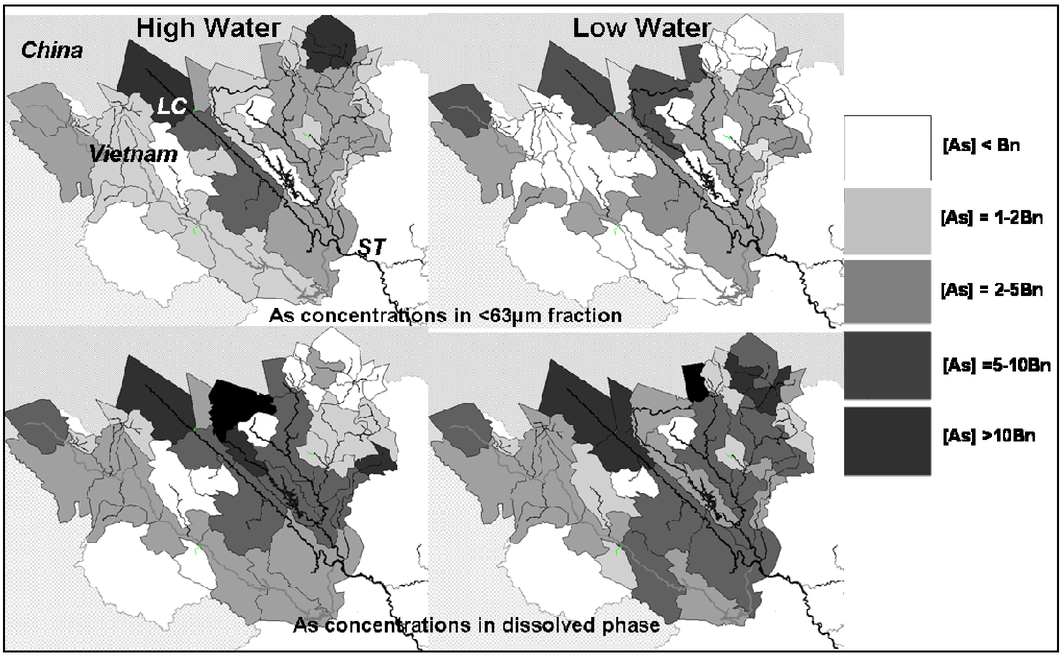

Figure 4. Spatial distribution of As concentrations in the Red River basin in sediment (< 63 µm)) and in water (dissolved < 0.2 µm).

3.3. Estimation of water quality

In general, the water sources of the Red River in Vietnam are not only significantly used for industries and irrigation but also for domestic demand, particularly in country-village (Le et al., 2005). In order to evaluate the water quality of the Red River basin, the dissolved Arsenic concentrations in the Red River watershed were compared to the national technical regulation on surface water (QCVN 08:2008/BTNMT; [As] = 10 µg/l). Based on this regulation, dissolved As concentrations from the 40 points throughout the Red River basin in Vietnamese part were subdivided in four classes: i) [As] < 5 µg/l, ii) [As] = 5-10µg/l, (iii) [As] = 10 - 15 µg/l and (iv) [As] > 15 µg/l. The results are presented as GIS-based maps in Figure 5 for high and low water seasons.

The figure 5 shows that dissolved Arsenic concentrations exceeded the Vietnamese limit values of 10µg/l (QCVN08:2008/BTNMT) in the upstream part of the Red River in both high and low water levels but also in the Da and Lo Rivers in low water level. The results of this survey reveal that several million people of the Red River basin are exposed to a risk of chronic arsenic poisoning, particularly in the high mountain region where surface water is used without treatment for life activities. Thus, the management of water quality in the Red River watershed is very important and must be carried out in an integrated and holistic manner, acknowledging that all elements of the environment are interrelated.

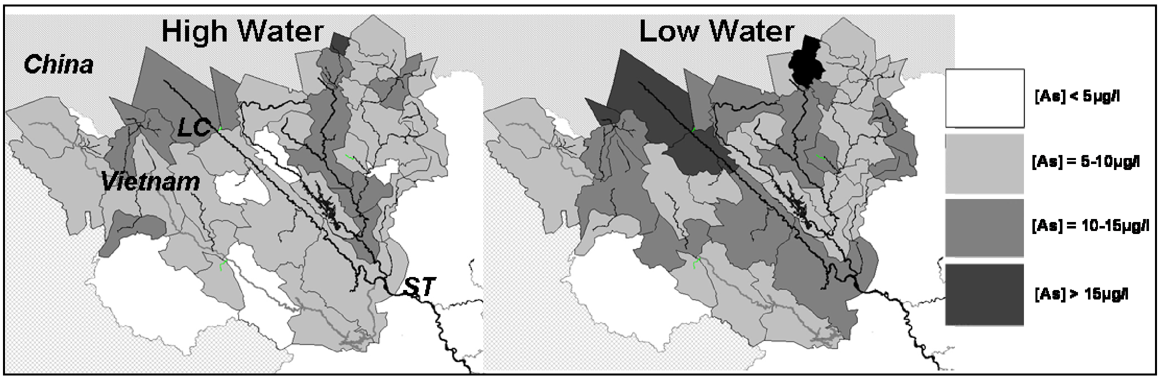

Figure 5. Spatial distribution of dissolved Arsenic contamination levels based on the national technical regulation on surface water (QCVN08:2008/BTNMT).

4. CONCLUDING REMARKS

The main results of the seasonal and spatial variations of the dissolved and particulate As concentrations in the Red River system in Vietnamese parts showed that:

- The dissolved As concentrations in high water level were relatively lower than in low water level, showing the dilution effect by water discharge. In contract, the particulate As concentrations during low water level were clearly lower than that during high water level, suggesting a change phenomenon in As source(s) with hydrology on As concentrations in the Red River watershed in Vietnamese part.

- The highest As concentration anomalies are located in the upstream catchment (in China) and strongly decrease from upstream to downstream.

- Concerning to the water quality in term of dissolved As, the quality of water in the Vietnamese Red River watershed can be classified as poor quality in the upstream part and as mediocre quality in the downstream part.

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TÓM TẮT

ĐÁNH GIÁ Ô NHIỄM ARSEN TRÊN LƯU VỰC SÔNG HỒNG: QUAN TRẮC TẦN SUẤT CAO KẾT HỢP VỚI PHÂN TÍCH KHÔNG GIAN GIS

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Dựa trên các kết quả hàm lượng kim loại asen (dạng hòa tan và lơ lửng) thu được từ hai đợt lấy mẫu 40 điểm trên toàn lưu vực sông Hồng ở Việt Nam vào mùa khô và mùa mưa trong năm 2009, sự biến đổi theo mùa và theo không gian hàm lượng As trên lưu vực sông Hồng đã được xác định. Các kết quả chỉ ra rằng nếu hàm lượng As hòa tan đo được trong mùa mưa thấp hơn trong mùa khô do hiện tượng pha loãng bởi nước mưa thì ngược lại, hàm lượng As lơ lửng trong mùa mưa lại cao hơn nhiều trong mùa khô cho thấy sự thay đổi các nguồn As lơ lửng trong nước sông Hồng theo điều kiện thủy văn. Hơn thế, để xác định được sự phân bố theo không gian và các điểm dị thường (anomaly) hàm lượng As trên toàn bộ lưu vực sông Hồng tại Việt Nam, chúng tôi đã sử dụng phân tích thống kê đa chiều kết hợp bản đồ bằng công cụ GIS. Theo đó, hàm lượng As cao nhất đo được phân bố trên thượng lưu các sông và chúng giảm mạnh về phía hạ lưu. Điều đó cho thấy nguồn gốc kim loại As trong nước sông Hồng là từ thượng lưu tại Trung Quốc. Cuối cùng, sự so sánh giữa hàm lượng As hòa tan thu được trên toàn lưu vực sông Hồng với quy chuẩn kĩ thuật quốc gia về chất lượng nước mặt (QCVN 08:2008/BTNMT) chỉ ra rằng chất lượng nước (xét theo chỉ tiêu As hòa tan) tại vùng thượng lưu tương đối xấu và ở mức trung bình tại vùng hạ lưu.

Từ khóa: Sông Hồng, Việt Nam, nồng độ As, dị thường, chất lượng nước.