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Geochemistry of Arsenic in the Huanghe (Yellow River) and Its Delta Region – A Review of Available Data

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Abstract. Water and suspended sediment samples from the Huanghe and its delta region were analyzed to determine arsenic concentrations. Comparison with the data of previous studies and other world pristine and less disturbed rivers reveals high levels of both dissolved and particulate As in this high turbidity river. Relatively stable distribution along the river course and in delta sediment cores shows that antrhopogenic activities have not altered As concentrations by any significant magnitude since the 1940s. Therefore, high levels of As in the Huanghe should be controlled by natural weathering and lithology. In the estuary, biological removal/regeneration and abiotic events (e.g. remobilization) have been identified to cause the active (non-conservative) As distributions. With the limited data set of the present study, the abiotic and biological contributions cannot be assessed accurately, however.

Key words: arsenic, dissolved and particulate concentrations, Huanghe (Yellow River), estuary, Bohai.

1. Introduction

Arsenic has been widely used in both industry and agriculture (e.g. plastics, glass, herbicides/pesticides, etc.). Mining, metallurgy, and combustion could also release a certain amount of As into the atmospheric and aquatic environments. Due to its ability to participate in metabolism, As is nearly ubiquitous in the biosphere (Underwood, 1977). In aquatic ecosystems (river, lake, sea, etc.), the similar distribution of As to phosphate (e.g. PO_4^{-3}) indicates that As is involved in consumption and regeneration of nutrient elements (cf. Seyler *et al.*, 1989). High levels of both dissolved and particulate As concentrations have been reported from polluted European and North American rivers (Tejo: Andreae *et al.*, 1983; Rhine: Van der Sloot *et al.*, 1985; Rhône: Seyler and Martin, 1990), whereas low concentrations of dissolved As cited in the literature are mostly from the pristine and/or less disturbed rivers (e.g. Krka: Seyler and Martin, 1991; Lena: Martin *et al.*, 1993a). Arsenic distribution in some major Chinese estuaries (Huanghe and Changjiang) has recently been evaluated under Sino-French joint study programs (Huang *et al.*, 1988; Elbaz-Poulichet *et al.*, 1990; Zhang *et al.*, 1990a). However, questions are raised when one reexamines the geochemistry of arsenic in large Chinese river-estuary systems, such as:

(1) Are the high levels of As in these rivers due to pollution?
(2) What is the distribution pattern of As in the river from the upper reaches to the mouth?
(3) Has the budget of As been remarkably changed by anthropogenic activities?

Here are reported the results for arsenic from several expeditions in combination with the data of previous studies in order to integrate the arsenic geochemistry in the Huanghe (Yellow River) and its delta region, the most turbid large river/estuary in the world. The available data sets are incomplete in various respects and do not permit a fully quantitative interpretation, but some tentative conclusions and comparison of arsenic behavior with that observed in other rivers and/or estuaries of the world have been obtained.

2. The Huanghe Drainage Basin

To understand the control of weathering and erosion on the riverine arsenic levels, a short description on physical and geological characteristics of the drainage basin would be helpful. The Huanghe drainage basin is principally developed over the old Sino-Korean Shield, which was formed between the Archaeozoic Era (Ar) and the Proterozoic Era (Pt). The cover strata are composed of sedimentary rocks from the Palaeozoic (Pz) to Cenozoic (Kz) Eras. The geology of the watersheds encompasses a broad range of tectonic series, ranging from the oldest metamorphic rocks to modern fluvial-lacustrine sediments (Figure 1). Schist, gneiss, marble, magmatite, and metamorphosed volcanic and detrital rocks of the old basement are scattered in the south and north/northwest of the drainage area with an average age of 1.5–2.5 $\times 10^9$ yr. Carbonates (E–O), coal series (C–P, J) and petroclastic rocks (T–K) from the Palaeozoic to Mesozoic eras occur in high lands and deep valleys along the river course. The red series of Cretaceous and Tertiary periods with intercalated beds of gypsum were reported to be exposed in the upper and middle reaches. The igneous rocks scatters in the watersheds, most of which are old granites $(\gamma_2 - \gamma_2)$. In the middle reaches of the Huanghe, Quaternary loess deposits cover an area of ca. 0.3×10^5 km^2, some 40% of the total catchment areas (Figure 1). The Quaternary loess deposits in the Huanghe drainage basin are characterized by fragile structures, low resistance to erosion, columnar jointing, and poor vegetation. The soil loss is quite intense over the loess-covered region where the physical denudation averages 3.5×10^6 kg km^{-2} yr^{-1} and may reach 25.0×10^6 kg km^{-2} yr^{-1} (Zhang *et al.*, 1990b). This makes loess the most important sediment source to the Huanghe, ca. 90% of riverine sediment loads are delivered from this region. Although some conflict still remains, the general opinion on loess accumulation is that it is wind deposition in origin and developed under cold and arid climate conditions (glacial epoch), while palaeosoil intercalated beds

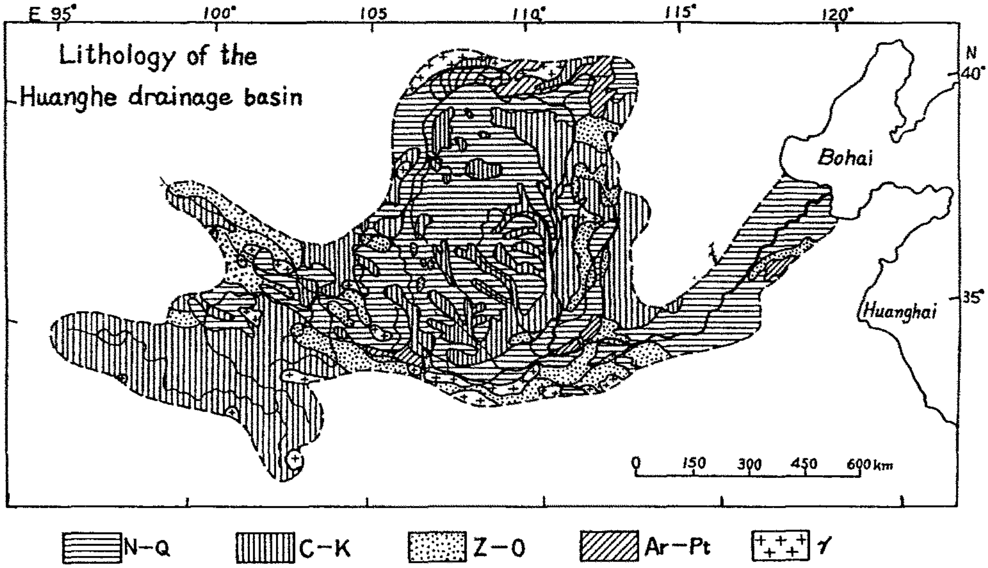

Fig. 1. Geology of the Huanghe watersheds, with major petrology and tectonic series. See the text for lithology description. Legend: N–Q: unsolidified/undiagenetic sediments of Cenozoic era, including loess in the middle reaches and fluvial deposits in the lower course. C–K: detrital rocks of late Palaeozoic (C–P) to Mesozoic (T–K) eras, including coal-bearing formation and red-bed series. Z–O: Carbonates of late Proterozoic (Z) and early Palaeozoic (E–O) eras. Ar–Pt: metamorphic rocks of Archaeozoic (Ar) and early Proterozoic (Pt_1–Pt_2) Eras. γ: granite series.

are indicative of warm and humid climates (interglacial period). Mineralogical evidence has shown that quartz, feldspar, and micas are the most common detrital components with 10–20% of carbonates in addition. Heavy minerals accounts for 5–10% in which magnetitite, hematite, pyroxene, hornblende, ilmenite, garnet, apatite, and zircon, etc., have been found. From such a mineral assemblage, one may expect that the source materials of loess are mainly developed from neutral and acid igneous rocks in origin which have weathered under cold and arid climates. In the clay-size fraction, illite accounts for 40–60%, kaolinite represents 15–20%, smectite occupies ca. 10%, and chlorite plus vermiculite is 5–10%.

With a drainage area of 752 400 km^2, the Huanghe rises in the Qinghai-Tibet Plateau at an altitude of 4500–5000 m. It drains in a region of temperate and semi-arid climate zones from the Northern Hemisphere, with 80% of the annual atmospheric precipitation (500–600 mm) occurring in June–August each year. The river carries seawards 1.1×10^{12} kg yr^{-1} of suspended sediments, second only to the Ganges/Brahmaputra systems, corresponding to a freshwater discharge of 41.0×10^9 m^3 yr^{-1}. Historically, large variations of both annual water ($9.1 - 97.3 \times 10^9$ m^3 yr^{-1}) and sediment ($0.2 - 2.1 \times 10^{12}$ kg yr^{-1}) loads were observed in the Huanghe. Suspended sediment concentrations average $20 - 50 \times 10^3$ mg l^{-1} in the middle and lower parts of the river, while much higher values, up to $0.5 - 1.0 \times 10^6$

mg l^{-1}, have been found in some tributaries in floods. Consequently, the seawards amount of suspended matter from the Huanghe alone represents ca. 10–15% of the total world riverine sediment loads (Zhang *et al.*, 1990b).

3. Sample Collection and Analysis

The expeditions to the Huanghe and adjacent coastal areas were undertaken in May and August 1985 and in August 1986 (Figure 2 and 3). Data of previous studies were also screened from the literature and combined with the present work to give an historical overview of arsenic geochemistry in this large and high-turbidity system (cf. CHRPM and GDBU, 1980; Qu *et al.*, 1984; Huang, 1986; Ma *et al.*, 1986; Huang *et al.*, 1988; Li *et al.*, 1991). On the whole, the Huanghe is not open to navigation. Water depth of the river is often less than 2 m and the main channel changes frequently especially close to the river mouth, due to heavy deposition of suspended matter. Selection of sample sites, therefore, depends mostly upon conditions of land traffic and an accessible path to the river channel. Samples were collected in mid-channel by placing an acid-cleaned 2 l polyethylene bottle in a plastic holder attached to the end of a fibreglass reinforced plastic pole (5 m bottle-pole system). The bottle was immersed while upside down below the water surface (0–50 cm) on the upstream side of the boat, inverted and allowed to fill. Occasionally, when the boat was not available, samples were taken directly with the 5 m bottle-pole system in the river. Sampling stations were chosen to avoid nearby tributaries and any apparent sources of pollution (Figure 2). Samples from the Weihe (J6), one of the Jamor tributaries in the watersheds, were also taken just before it joins the Huanghe. Under arduous field working conditions, water samples were filtered in situ (in the field within a clean plastic cover) with a closed plastic Syringe-Swinnex system (Millipore Co.) through acid-cleaned Nucleopore filters (Polycarbonate with a pore size of 0.4 μm). The Syringe-Swinnex system is directly connected to a precleaned 250 ml polyethylene bottle. Filters were changed or removed only in the laboratory under clean conditions. After filtration, the filtrates were acidified to pH = 2 with HCl (Merk Suprapur Co.) and kept at ~ 4°C, the swinnex with filters were preserved in an ice box until returned to the laboratory. Water samples from the estuarine region were obtained with a 5 l Go-flo sampler on board the research vessels. The samples were immediately filtered through 0.4 μm Nucleopore filters within a clean bench (class 100) on board. Both acidified filtrates and suspended matter samples were reserved at ~ 0–4°C in an ice box until analysis.

In the laboratory, dissolved arsenic was determined with hydride generation/atomic absorption spectrometry (Andreae, 1977; Seyler, 1985). Arsenate was transformed to arsenite with KI in acid medium (HCl). Arsenite was then reduced by sodium borohydride in a closed system and the arsine formed was purged into a quartz furnace of PE-3030/MHS-10 (Perkin-Elmer Co.) combination. The results give the concentrations of total dissolved arsenic. Reduction with KI may not

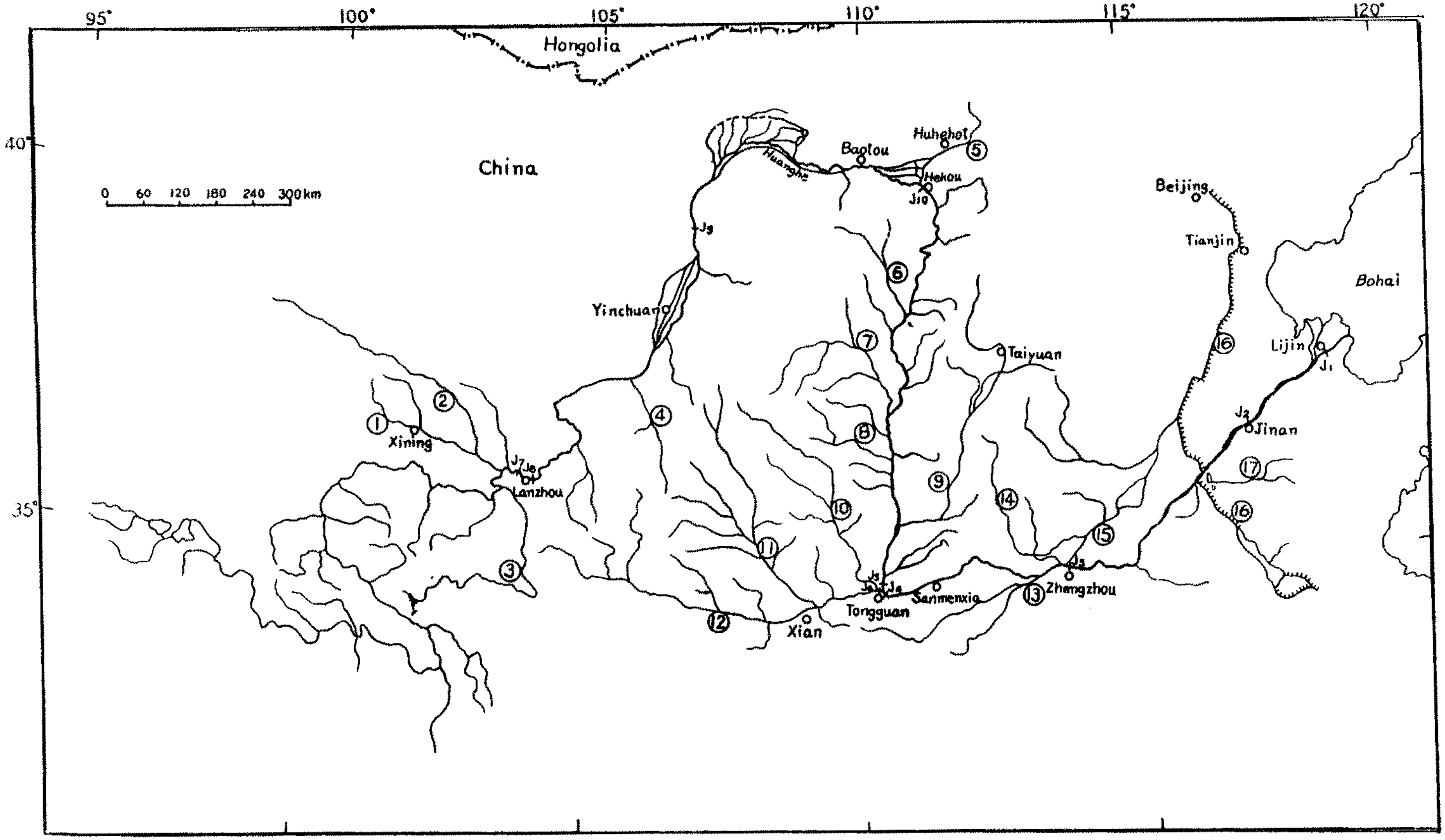

Fig. 2. Drainage basin of the Huanghe. It shows the major tributaries and sample locations (J1–J10). (1) Huangshui; (2) Datonghe; (3) Taohe; (4) Qingshuihe; (5) Daheihe; (6) Kuyiehe; (7) Wudinghe; (8) Yianhe; (9) Fenhe; (10) Luohe; (11) Jinghe; (12) Weihe; (13) Yiluohe; (14) Xinhe; (15) Weihe; (16) Dayunhe; (17) Dawenhe.

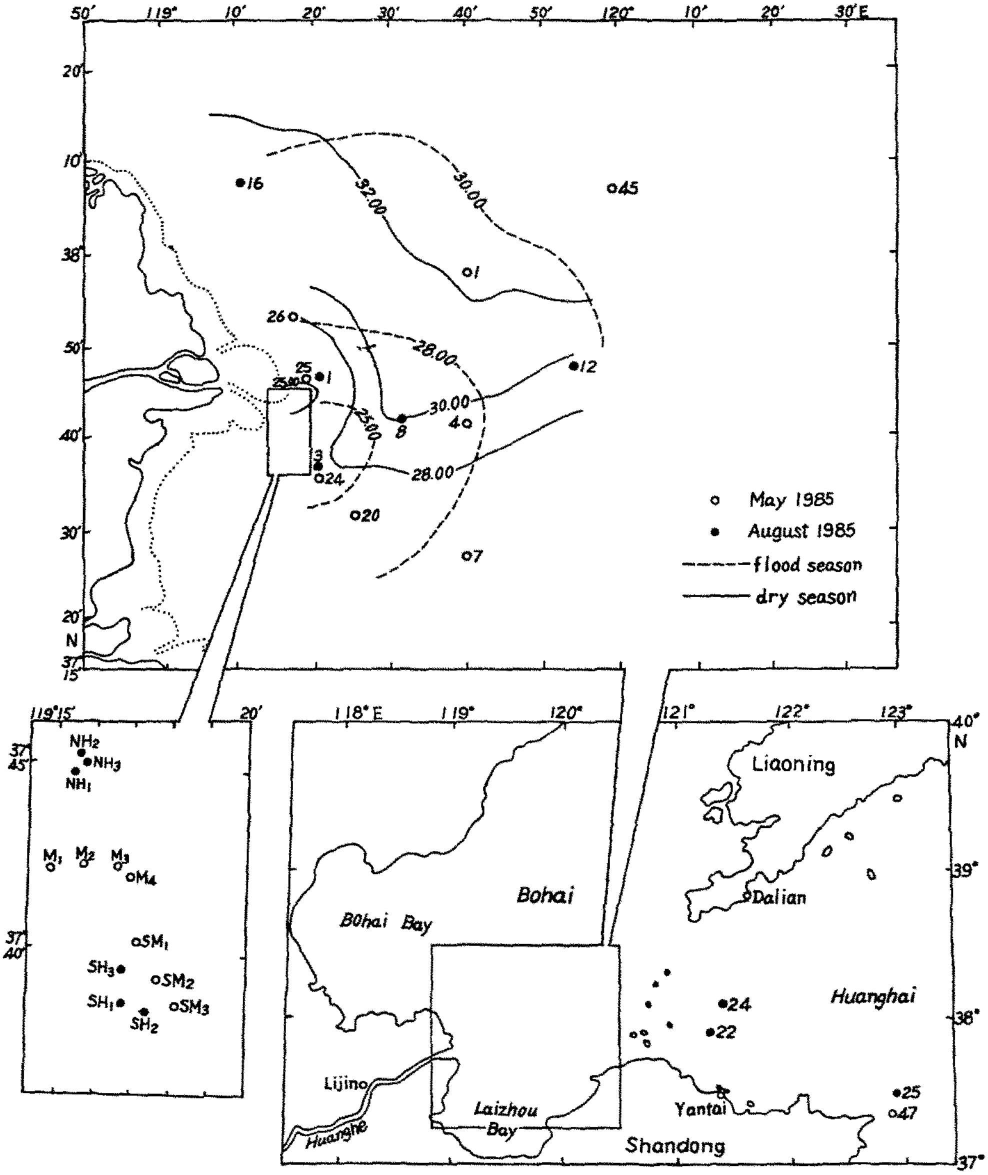

Fig. 3. Map of the Huanghe estuary and Bohai. It shows sampling sites of two consecutive cruises, (May and August 1985). The dashed lines in the South Bohai shows the salinity distributions in flood seasons (summer and fall), solid lines demonstrate isolines of salinity in dry seasons (winter and spring).

quantitatively convert the methylarsenic species into arsenite. The methylarsenicals can be converted to the methylarsenic hydrides with the present procedure, but they may not be efficiently detected unless the system was optimized for them. At any rate, there is usually only a small fraction of dissolved arsenic in the riverine environment (M.O. Andreae, personal communication). Suspended sediments were digested with HF–HNO_3–$HClO_4$ in an airproof Teflon system. The solutions were then analysed with a PE-3030/MHS-10 combination to determine particulate arsenic concentrations. The detection limits of dissolved and particulate arsenic are 0.25 nM and 0.05 μg g^{-1}, respectively. The precision and accuracy of As determinations were monitored through repeated analysis of Canadian NASS-1, SLRS-1 and MESS-1 standards. The results showed satisfied recoveries with differences between our laboratory data and the recommended values $\leq$5–10% for dissolved ($n = 16$) and $\leq$5% for particulate ($n = 6$) arsenic, respectively. Presumably, digestion with HF–HNO_3–$HClO_4$ in determination of particulate phases may suffer from some loss of arsenic, owing to the low vaporising temperature of arsenic compounds (e.g. 60°C for AsF_3). The satisfactory recovery of standard determinations (MESS-1) convinces one of the reliability of particulate arsenic data in this study, however. This also indicates that the loss of arsenic (if there is some loss) with acid digestion is negligible. Nitrate, PO_4^{-3} and dissolved SiO_2 were determined with colormetry. For the determination of aluminium, 50 mg of suspended sediments was melted with NaOH at 600°C for 10 h, samples were then extracted with hot distilled water, and Al in solution was determined by titration with Zn^{+2} after complexing by EDTA (Huang *et al.*, 1992). The method shows an associated error of <1.5% and detection limit of 5×10^{-3} (i.e. 0.5%) for Al determination. All apparatus and laboratory wares (e.g. bottle, syringe/swinnex and plastic dishes and flasks, etc.) for sample collection and pretreatment were first washed with detergent and rinsed thoroughly with distilled water, they were immersed in dilute HNO_3 (1:5) and then in HCl (1:5) for one to two weeks. Finally, the wares were rinsed with Milli-Q water (18 MΩ – cm at 25°C, Millipore Co.) before use. The Nucleopore filters were first immersed in HCl (1:5 GR) for one week and washed thoroughly with Milli-Q water until pH ~ 7.

4. Results

4.1. DISSOLVED SPECIES

Due to very difficult field conditions, the water samples could not be kept frozen. Speciation changes of arsenic may take place, and the dissolved arsenic data should present the total dissolved phases. Table I shows the concentrations of dissolved arsenic in the Huanghe in the 1986 cruise. Water discharge was 1000–2000 $m^3\ s^{-1}$ in the river, some 80% of the average from long-term observations (1500–3000 $m^3\ s^{-1}$). Dissolved arsenic levels ranged from 19–20 nM at upstream stations [Lanzhou (J7 and J8)] to 31–32 nM in the middle and lower reaches [Tongguan (J4 and J5) and Zhengzhou (J3)]. It is evident that lower values of arsenic occur in the upper reaches, whereas dissolved arsenic keeps rather high and constant values (26.5–31.5 nM), as expressed by an average of 28.6 nM ($\sigma x/\bar{X} \pm 6.4\%$) when the Huanghe drains the Quaternary Loess Plateau in the middle of the drainage basin. High levels (28.0–31.0 nM) of dissolved arsenic have also been found at the river mouth. An increase of silica from 0.20 to 0.50 mM, along with a decrease of SO_4^{-2} from 1.7 to 0.65 mM were observed down the river course. The pH values varied between 8.00 and 8.40 and show a downstream increase in the Huanghe (unpublished data). Hence, loess has a significant impact upon the dissolved arsenic levels in the Huanghe. Samples from the Weihe (J6), which drains entirely into the loess covered area, have a dissolved arsenic concentration of 26.6 nM, very close to the values of the main course in this region (e.g. J4 and J10). The Weihe is ca. 0.3–0.4 pH units more and acidic than the Huanghe at the upstream stations and has a higher suspended load. These differences may lead to some adsorption of anions and desorption of cations when the more acidic and sediment-rich waters of the Weihe join the main course. Therefore, dissolved arsenic may not be necessarily conservative upon mixing (cf. Shiller and Boyle, 1987; Zhang and Huang, 1993). Differences in dissolved arsenic concentrations between the upper stream (J7 and J8) and lower reaches have been reported in previous studies (Huang, 1986 and references within). Presumably, an increase of dissolved arsenic levels in the lower part of river course results from the high levels of arsenic in the loess and serious weathering (e.g. decomposition of minerals) and erosion (e.g. physical volume removed from the basin) over the Loess Plateau, since the loess covered area supplies ca. 40% of the river water and 90% of the sediment loads (Zhang *et al.*, 1990b). Samples J3 and J8 were collected downstream from two large cities: Lanzhou (petrochemical industry) and Zhengzhou (chemical and textile industry) each with a population $> 5 \times 10^6$. These stations show somewhat higher but not significantly different concentrations (within $\bar{X} \pm 2\sigma x$) for dissolved arsenic compared to the values from the other stations (e.g. up and downstream).

Speciations of dissolved arsenic in the Huanghe remain unknown. In this study, there have been no possibilities to determine arsenite (As III) and methylated arsenic compound (mono-, di- and trimethylated arsenic) species. Although the filtered and acidified samples should have been suitable for the determination of methylarsenicals, the laboratory apparatus (e.g. PE-3030/MHS-10 combination) was not optimized for their recovery. Also, the transform of As (III) to As (V) might take place during sample storage. However, field measurements show pH and Eh values of 8.00–8.40 and 310–350 mv, respectively (Huang, 1986 and our unpublished data). It can be expected, therefore, that As (V) should be the predominant species in the Huanghe.

Table II presents the dissolved major ion compositions of the Huanghe. Data in Table II are from long-term observations (e.g. 30–40 years) and provide information about what the river does as a whole from the upper to lower reaches. Obviously, abundant dissolved major ion levels in the river most likely result from serious weathering and erosion (e.g. carbonates and salts) over the drainage

TABLE I. Concentrations of nutrient elements (PO_4^{-3}; μM, NO_3^- and SiO_2: mM), dissolved (nM) and particulate (μg g^{-1}) As, Al (%) and pH values of the Huanghe in the August 1986 cruise. See Figure 2 for sample locations.

Station	pH	NO_3^{-1} (mM)	PO_4^{-3} (μM)	SiO_2 (mM)	Dissolved As (nM)	Particulate As (μg g^{-1})	Al (%)
J1	8.26	0.17	0.50	0.35	28.8	19.7	8.3
J2	8.18	0.08	0.49	0.44	27.6	18.9	8.4
J3	8.34	0.15	0.25	0.25	31.0	20.3	8.2
J4	8.00	0.11	0.38	0.35	26.4	18.2	7.7
J5	8.37	0.14	0.34	0.29	31.5		
J6	8.01	0.27	0.47	0.49	26.6	19.4	9.4
J10	8.30	0.08	0.28	0.20	27.5	20.8	8.0
J9	8.39	0.06	0.63	0.19	30.0	12.6	7.1
J8	8.14	0.08	0.24	0.20	19.6	24.6	8.8
J7	8.06	0.07	0.06	0.20	19.2	22.0	9.8

areas, which maintain elevated pH values. Again, dissolved major ion concentrations in the Huanghe is ca. a factor of five to one order to magnitude higher than those from other large world systems (e.g. Amazon, Zaire, Orinoco, Changjiang, and Ganges/Brahmaputra, etc.) (Zhang *et al.*, 1990c). It has been estimated that dissolved trace elements show positive correlations with silica in the Huanghe, which emphasizes, by contrast to the polluted systems, the significance of weathering on the riverine element budgets (Zhang and Huang, 1993). It is evident that elevated major element levels are sustained mainly by dissolution of inorganic salts and/or carbonates, and trace elements may be closely related to the alumino-silicates during the weathering (Zhang and Huang, 1993). Covariations of dissolved arsenic with nutrient salts (e.g. PO_4^{-3}) have been reported (Seyler *et al.*, 1989). In the Huanghe, dissolved arsenic shows somewhat covariations with phosphate ($\gamma = 0.59$), but correlations between As and nitrate ($\gamma = 0.29$) and dissolved silica ($\gamma = 0.23$) were quite weak. This implies that use of nutrients in agriculture (e.g. chemical fertilizers) may not necessarily have a considerable impact upon the budget of dissolved arsenic in this high turbidity river. Other processes (e.g. weathering) should be taken into account when addressing arsenic chemistry in the Huange, however.

4.2. PARTICULATE As

Arsenic concentrations in suspended sediments of the Huanghe fall in the range of ca. 12–25 μg g^{-1} with an average of 19.6 ± 3.3 μg g^{-1} ($\bar{X} \pm \sigma x$) (Table I). Longitudinal trends of particulate As distribution is still not clear, although variations in As concentrations in suspended sediments may reach a factor of two in the river. Samples J3 and J8 have higher particulate As levels compared to both up and

TABLE II. Dissolved major ion compositions (mg l^{-1}) of the Huanghe from the upper reaches to the river mouth. Data are from the Yellow River Conservancy Commission (1980).

Station	pH	Ca^{+2}	Mg^{+2}	$Na^+ + K^+$	Cl^-	SO_4^{-2}	CO_3^{-2}	HCO_3^-
Lanzhou	8.1	51.3	15.4	28.3	27.3	44.3	4.6	190
Hekou	7.9	50.9	25.5	42.3	67.5	44.4	3.6	206
Sanmenxia	8.0	43.4	21.2	75.0	50.3	93.0	5.7	209
Jinan	7.9	42.0	17.7	58.5	46.9	71.7	3.5	182

downstream stations, they are within $\bar{X} \pm 2\sigma x$, however. Examination of the data in Table I reveals close correlations between As and Al in the suspended matter of the Huanghe ($\gamma = 0.68$), which indicates the influences of grain-size variations upon As distribution in riverine sediments. Arsenic concentrations of loess over the Huanghe drainage basin ranges from 5 to 24 μg g^{-1} with an average of 10.4 μg g^{-1} ($n = 22$) [Commission of the Huanghe Resources Protection and Management (CHRPM) and Geography Department of Beijing University (GDBU), 1980]. More recently, Tian and coworkers (1991) provided an average arsenic concentration of 12.7 μg g^{-1} based on the samples from 60–70 soil sections over the whole Loess Plateau. These values are 40% higher than the background of As (median: 9.2 μg g^{-1}) in Chinese soils (data from 4100 soil sections) (Wei *et al.*, 1991). Bottom sediments from the main channel show As concentrations of 4–10 μg g^{-1}, much lower than the suspended matter does (Huang, 1986). Previous studies attributed lower As concentrations in bottom sediments to the higher content of coarse particles, because the fine sediment fractions (<2 μm) may contain 24 μg g^{-1} of As in comparison to 8.4 μg g^{-1} in coarse fractions (CHRPM and GDBU, 1980). Also, arsenic concentrations increase with higher fine particle fractions (<2 μm) in bulk sediments, which was observed in both loess and riverine sediments (CHRPM and GDBU, 1980). It can be concluded that the variability of particulate arsenic in the Huanghe is, at least in part, related to the grain-size variations for both suspended and bottom sediments.

Enrichment factors (EF), that is the ratio of As to Al in the riverine sediments [$(As/Al)_{pm}$] (pm: riverine suspended matter) to that of source materials [$(As/Al)_{fr}$] (fr: fresh rock or soil), are widely used to identify pollution impact because the concentration of Al in weathering products (e.g. soils) and their parent materials are comparable. It is often difficult, however, to determine the representative [$(As/Al)_{fr}$] values for a vast watersheds as the Huanghe drainage basin, even though the sediment origin of the Huanghe is quite unique (i.e. loess). Compositions of bed rock and/or soil are highly variable from place to place, depending upon the lithology, geotectonics and weathering. The As/Al ratios of loess was used as [$(As/Al)_{fr}$] in this study, since loess supplies ca. 90% of riverine sediment loads. The EF values of As in the Huanghe suspended sediments range from 0.97 to 1.53 with an average of 1.28 ± 0.15 ($\bar{X} \pm \sigma x$). Taking into account a variation of 20–

25% associated with As concentrations in loess (As levels in riverine suspended sediments are somewhat higher than in loess). If the EF values are supposed to be ca. 1.0, the dependence of the element concentrations upon grain-size/mineralogy of river sediments should be identical to that of source materials for both As and Al. The sorting effect in weathering and transport can be expected to be negligible, which implies that variations of grain-size and/or mineralogy in the weathering and transport processes have the same effect on the levels of both As and Al. It seems that this is not the case for the Huanghe, however. Otherwise, [$(\text{As/Al})_{\text{pm}}$] values would be either higher or lower than [$(\text{As/Al})_{\text{fr}}$] simply due to the differences in grain-size and/or mineral compositions, rather than anthropogenic activities (Huang *et al.*, 1992). It is very difficult to verify this hypothesis with limited data sets at the present stage, however.

4.3. COMPARISON WITH OTHER WORLD RIVERS

Table III tabulates arsenic concentrations from some of the world's rivers, which are picked up from previously published data sets in the literature. Considering the dissolved As, the Huanghe has higher levels than those from pristine (Krka, Yakushima and Lena) and/or less disturbed (Changjiang and Yukon, etc.) riverine systems, but close to or even higher than some polluted European and North American and East Asian rivers (e.g. Gironde, Loire, Tama, etc.) and world average in addition. Much higher values have been reported from highly disturbed European rivers such as the Tejo, Rhine, Schelde and Tamar (Table III). Nevertheless, dissolved arsenic concentrations of the Huanghe are lower than the previously estimated European river average (46 nM: Andreae and Froelich, 1984). Moreover, the differences in dissolved arsenic concentrations from pristine rivers are quite significant, which indicates the effect of local lithology upon the As in surface waters. As an example, the Krka drains a carbonate enriched region, whereas rivers of the Yakushima Island are developed over granites. It can be expected that dissolved As in the Yakushima river (2.8 nM) are higher than in the Krka (1.7 nM), and the ratio of As between these two rivers (1.65: Yakushima/Krka) is identical to that of average granite to carbonate rations (1.5–1.9) for arsenic (Institute of Geochemistry, 1981; Tanizaki and Nagatsuka, 1983; Seyler and Martin, 1991).

With respect to particulate As, concentrations in the Huanghe are higher than those from large and less disturbed rivers (e.g. Changjiang, Parana, and Niger, etc.) and U.S. riverine sediments, and can be a factor of 4–5 greater than the world average. Polluted European rivers (Gironde, Loire and Tejo, etc.) may show even higher particulate As levels than the Huanghe does (Table III). Again, the comparison above emphasizes that riverine particulate As levels can be affected by the lithology of the drainage basin combined with the pollution input.

Clearly, element concentrations in the river are highly variable, depending upon the water discharge and sediment load. Compared with dissolved phases, particulate arsenic concentrations may be more closely related to the lithology and

TABLE III. Comparison of dissolved (nM) and particulate (μg g^{-1}) As levels between the Huanghe and other rivers of the world. Note that elevated As concentrations were observed from polluted rivers in Europe and North America, whereas pristine rivers have low As values. World averages of As are also given for comparison.

River	As (dis) (nm)	As (par) (μg g^{-1})	References
Huanghe	28.7	19.6	This study
Changjiang	10.6	13.8	Elbaz-Poulichet *et al.* (1990), Zhang *et al.* (1990a)
Peace	16.5		Froelich *et al.* (1985)
Schelde	40		Andreae and Andreae (1989)
Yakushima	2.8		Tanizaki and Nagatsuka (1983)
Susquehanna	3.9		Sanders (1985)
Rhine	10–100		Van der Sloot *et al.* (1985)
Tama	8.3	2.9	Tanizaki *et al.* (1985)
Langat	201	18.4	Sarmani (1989)
Rhône	20–50	9.6–23	Seyler and Martin (1990) and unpublished data
Gironde	8.8–18.1	30–35	Seyler and Martin (1990)
Loire	20.5–40	40	Seyler and Martin (1990)
Krka	1.7		Seyler and Martin (1991)
Savannah	2.8		Byrd (1988)
Tamar	50–70		Knox *et al.* (1984)
Elbe	85.5		Andreae and Froelich (1984)
Tejo	55–68	54.6	Andreae *et al.* (1983); Andreae and Froelich (1984)
Yukon	6.41		Andreae and Froelich (1984)
St. Lawrence	7.15		Andreae and Froelich (1984)
Niger		4.1	Ndiokwere (1984)
Menominee		4.1	Brannon and Patrick (1987)
Detroit		11.4	Brannon and Patrick (1987)
Seine		9.4	Thomas and Martin (1982)
Parana		13.8	Thomas and Martin (1982)
Lena	2		Martin *et al.* (1993a)
European mean	46		Andreae and Froelich (1984)
U.S. rivers		7.1	Horowitz *et al.* (1989)
World average	22.7	5	Martin and Windom (1991)

weathering/erosion features over the watersheds, especially in those receiving very limited pollution drainage (Berner and Berner, 1987). In polluted river systems, arsenic concentrations could be one to two orders of magnitude higher compared to the source materials (e.g. soil). Taking the Xiangjiang as an example, which is one of the major tributaries of the Changjiang, Cui and Liu (1988) reported As levels of 10–100 μg g^{-1} in sediments (bottom + suspended sediments) and 50–500 nM in river water. Our previous studies provided values of As of 12–14 μg g^{-1} in suspended sediments and 10–15 nM in dissolved phases from the Changjiang close to the river mouth, however (Elbaz-Poulichet *et al.*, 1990; Zhang *et al.*, 1990a).

TABLE IV. Concentrations of As in dissolved (nM) and solid (μg g^{-1}) phases of the Huanghe reported from previous studies.

Cruise	Location	Water discharge (m^3 s^{-1})	As (dis) (nM)	As (par) (μg g^{-1})	References
1980	Jinan (J2)			12.2	Que *et al.* (1984)
1985	Kenli (J1)	1100	26.8	11.7	Huang *et al.* (1988)
1985	Kenli (J1)	2200	27.1	14.4	Huang *et al.* (1988)
1984	Kenli (J1)		24.7	15.2	Lie *et al.* (1991)
1977	whole river		56.5	6.9	Huang (1986)
1986	whole river	1000–2000	28.7	19.6	This study

4.4. PREVIOUS STUDIES

Studies of As in the Huanghe date from the 1970s and 1980s in the literature. Table IV compares previously published As data on the Huanghe since the 1980s. Concentrations of As in these studies were determined with hydride generation/atomic absorption spectrometry, INAA (instrumental neutron activation analysis) and DDC-Ag (silver diethyldithiocarbamate) colormetry (Huang, 1986; Huang *et al.*, 1988; Zhang *et al.*, 1990a; Li *et al.*, 1991).

It is obvious from Table IV that dissolved arsenic concentrations of the present study are quite similar to those of our 1985 cruises (Huang *et al.*, 1988; Li and coworker, 1991). These studies provide mean dissolved As values of 26.8 ± 1.4 nM [$\bar{X} \pm 3\sigma x$ (range: 24.7–28.7 nM)] in the Huanghe. Higher values of Huang and coworkers (Huang, 1986) are most likely due to the uncertainties associated with sample collection and analysis (DDC-Ag method). Huang and coworkers (Huang, 1986) reported dissolved As values from 'decanted' rather than filtered water samples, and their 'dissolved arsenic concentrations' should include contributions from fine particles that remained in suspension (Table IV). Also, 10–50 nM of arsenic in the riverine water samples is close to the detection limit of the DDC-Ag colormetry method.

The particulate arsenic data (12–25 μg g^{-1}) of this study are relatively high compared to the previously reported values (Table IV). Arithmetic average of the data in Table IV provides particulate As values of 11.7–19.6 μg g^{-1} with an average of 14.6 ± 2.8 ($\bar{X} \pm 3\sigma x$) μg g^{-1} [data of Huang (1986) were not included, since they were from analyses of bottom sediments]. Differences in As concentrations may partly result from the alck of intercalibration of chemical analysis. In the foregoing studies, As in suspended sediments were determined with either INAA (Huang *et al.*, 1988) or DDC-Ag (Ma *et al.*, 1986; Li *et al.*, 1991) methods. Although the As data of INAA were obtained against satisfied analyses of the IAEA SDN 1/2 standard, the DDC-Ag method might give either an over or underestimation of As in solid phases (Zhang, 1988). Again, variabilities of grain-size compositions and mineralogy in time and space may alter the observed As levels in the river. For example, data of CHRPM and GDBU (1980) show the covariations of As with clays in the loess and riverine sediments, which can be described as

$$\text{As} = 6.63 + 0.38 \times \text{ [clay content of river sediments in \%]}, \tag{1}$$
$$\gamma = 0.90 (n = 41)\ (n\text{: number of samples});$$
$$\text{As} = 7.25 + 0.19 \times \text{ [clay content of loess in \%]}, \tag{2}$$
$$\gamma = 0.29 (n = 61)\ (n\text{: number of samples}).$$

The correlation of As with clay-size fraction [e.g. Equations (1) and (2)] highlights the influences of grain-size compositions relative to hydrodynamic conditions upon the observed As concentrations. Evidently, arsenic concentrations increase with higher fine particle contents. It can be expected that differences in sedimentary regimes between dry and flood periods may affect riverine arsenic levels, since the suspended matter is highly variable in both amount and composition. Our previous studies have shown that most of the suspended sediment in flood seasons is from surface erosion due to heavy rainfall in the watersheds, whereas resuspension of bottom sediments makes important contributions to the riverine suspended matter in dry seasons. Consequently, suspended matter in flood seasons is expected to have higher arsenic concentrations than in dry seasons, as shown by the data of the 1985 cruises (Table IV). Huang and coworkers (1986) determined As concentrations in bottom sediments at 13 stations from the river mouth to the upper course and provided a mean value of 6.9 ± 1.6 μg g^{-1} (Table IV). It remains unclear that the covariations of arsenic with water and sediment discharges between individual expeditions may not necessarily be the same. The data of Huang and coworkers (1988) are from samples taken at the river mouth corresponding to suspended sediment concentrations of 10–25 g l^{-1}, concentrations of As in the 1980 and 1984 cruises were from the samples taken at Jinan (J2) and Lijin (between J1 and J2), respectively, with water discharge and sediment content unknown (Qu *et al.*, 1984; Ma *et al.*, 1986; Li *et al.*, 1991). It can be concluded, therefore, that variabilities of water and sediment loads should have significant impact upon As concentrations in the Huanghe.

The differences in As-particles (e.g. clays) covariations between loess and riverine sediments in Equations (1) and (2) most likely results from the variability of mineralogy and grain-size compositions. The variations of grain-size and mineral compositions may occur during weathering and erosion and transport as well, although at present a quantitative estimation is difficult to reach. Riverine suspended matter contains somewhat more fine materials (25–55%) than the loess does (10–20%). Content of quarz and feldspar averages 50–60% and 30–40% in loess, whereas in the riverine sediments quarz is <20–30% and micas accounts for 60–70% (Huang *et al.*, 1992). Moreover, feldspar and micas in the suspended sediments can be much more abundant than quartz, consistent with the higher Al and Fe levels found from the riverine suspended matter in the region (Qu and Yan, 1989). Comparison of clay compositions reveals that riverine sediments contains higher proportions of illite, smectite and chlorite/vermiculite, whereas loess has more abundant kaolinite (Huang *et al.*, 1992).

4.5. DELTA REGION

It has been shown that arsenic distribution is fairly conservative in pristine estuaries and/or estuaries receiving little anthropogenic input (Seyler, 1985 and references therein). Arsenic in polluted estuaries shows considerable deviations from the theoretical dilution curve (Seyler and Martin, 1990). In the Huanghe estuary, dissolved arsenic has different distribution patterns between low and high water stage cruises. These distribution features were observed in four consecutive cruises between 1984 and 1985 (Ma *et al.*, 1986; Huang *et al.*, 1988; Li *et al.*, 1991). To examine in more detail the arsenic distribution in the Huanghe estuary and adjacent coastal areas, concentrations of As from four consecutive cruises from May 1984 to August 1985 were plotted against chlorinity, which corresponds to the dry season/low water stage (May) and the flood season/high water stage (August), respectively (Figure 4). At low water stage conditions, dissolved arsenic distribution showed a mixing model of two sections with three end-members (Figure 4). Dissolved arsenic is quasiconservative in the upper estuarine mixing zone until a chlorinity of ca. 15‰, the second mixing takes place between As-depleted waters from the South Bohai (Laizhou Bay) and As-enriched waters of the Central Bohai in high chlorinity areas (chlorinity: 14–18‰). Concentrations of As in the South Bohai in May 1985 were twice as high as those of the May 1984 cruises (riverine arsenic levels kept rather constant during these two expeditions). Clearly, if the three end-member mixing model is invoked, one should make sure that a table with estuarine data has to be included and sampling sites along with the end-member values as shown in Figure 4. At high water stage conditions, dissolved arsenic shows exclusively nonconservative distributions in both the August 1984 and August 1985 cruises, and the arsenic depleted water masses in South Bohai were not observed (Figure 4). The convex features of dissolved arsenic in the mixing zone suggests that remobilization is a predominant process affecting arsenic distributions in the Huanghe estuary, which may add ca. 10–30% to the riverine arsenic budget to the sea depending upon water and sediment loads. In high chlorinity regions (Central Bohai), concentrations of dissolved arsenic were identical to those in low-water stage cruises (~20 nM). Values of 27.5–32.5 nM for dissolved As were observed, well above the mixing curves within data resolutions. These high concentrations occurred in high chlorinity areas during the August 1984 cruise, for reasons unknown. One should examine these high As values in the view of local and/or regional sources, because the 27.5–32.5 nM for dissolved As is also higher than 20–25 nM for the typical shelf waters (e.g. Kuroshio Current). It is most likely that such high concentrations of dissolved As are from local pollutant drainages, because the samples were collected in shallow water areas (water depth < 10 m) at the south of Laizhou Bay (Li *et al.*, 1991). Obviously, the nonconservative behavior of a chemical species in the estuary can only be deduced from the curvature in the species/chlorinity plot rather than the total dissolved concentrations, if the concentration in the riverine end-member has remained constant. Observations at the river mouth showed seasonal variations of dissolved arsenic from the Huanghe: values of As in the flood stage (August–December) may be 100–150% those of the dry season (January–May) in 1984–1985, even though the samples were analyzed with the iron hydroxide coprecipitation/DDC-Ag method and showed some scatters (Li *et al.*, 1991). Lower dissolved arsenic values than those predicted from the dillution curve for samples from the South Bohai in the dry season cruises were attributed to the contribution from the 'old water mass' with low arsenic concentrations in these regions (Zhang, 1988). The distributions of salinities showed accumulations of riverine effluents in the southern part of Laizhou Bay during the low water stage (e.g. winter) and a northeastward movement of the fresh water mass in the high-water stage (e.g. summer), which suggests a longer water residence time in dry periods than in flood periods (Figure 3). Stable oxygen isotope data provided evidence of 'old water mass' in the South Bohai (Laizhou Bay) with residence times varying from 2 months during the flood period to 3–4 months in the dry seasons (Zhang *et al.*, 1990d). In the 'old water mass' occupied area, we did observe a high density of phytoplankton (1.0–10 × 10^6 cells m^{-3}) and zooplantkon (500–1000 numbers m^{-3}) during low water stage cruises. During the high water stage cruises, the 'old water mass' were renewed and removed from the South Bohai (Laizhou Bay), and the differences in phytoplankton/zooplankton compositions suggests that the 'old water mass' has been replaced in summer and autumn. It can be expected, therefore, that the deficits of dissolved arsenic in the May 1984 and 1985 cruises most likely results from (1) lower riverine concentrations in the winter (10–15 nM) than in the summer (25–30 nM) which induced a depletion in As at high salinity areas, and (2) biological accumulation/uptake which may scavenge arsenic from the dissolved phase and induce somewhat higher absolute concentrations of particulate phases and organic carbon in the South Bohai (Zhang, 1988). Furthermore, the longer the residence time in the dry season (winter and spring), the lower the As concentration remaining in the Laizhou Bay, as identified in the May 1984 and 1985 cruises.

Both quasi-conservative (three end-members mixing) and active (nonconservative) distributions of dissolved arsenic were found in the Huanghe estuary, depending upon the season and water stage (Figure 4). Four consecutive field surveys were undertaken in dry and flood seasons, and 1984 observations were confirmed by two consecutive observations in 1985. It is evident that the data of the 1985 cruises differ from those in 1984 in higher estuarine end-member values in the dry season and more pronounced estuarine maximum in the flood season. The estuarine end-member in May 1985 was roughly a factor of two (ca. 10 nM) higher than that of the May 1984 cruise, corresponding to an estuarine maximum in August 1985 which is ca. 10 nM higher than that of the August 1984 cruise. Taking into account a flushing time of several months in South Bohai (Laizhou

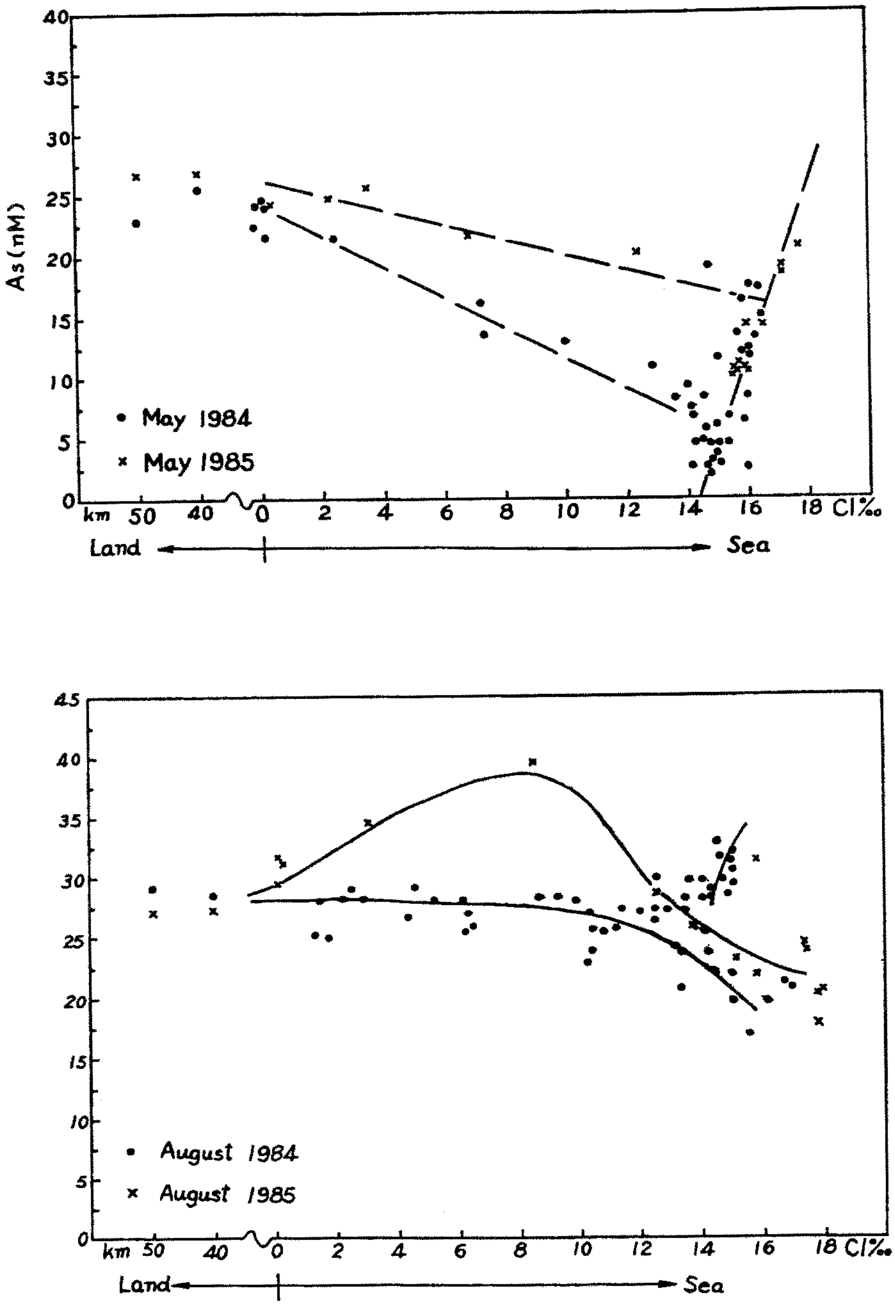

Fig. 4. Plots of dissolved arsenic concentrations against chlorinity in the Huanghe estuary. The expeditions were undertaken in both low (May 1984 and 1985) and high (August 1984 and 1985) water stages. See the text for the detail.

Bay), a seasonal evolution of dissolved arsenic can be expected to take place in the region. Briefly, water residence time in the South Bohai is ca. 4–5 months at the low-water stage (winter), and the estuarine 'old water mass' has lower arsenic levels which induce a mixing model of three end-members in the spring. The lower values of dissolved arsenic in the 'old water mass' results from either estuarine scavenging/biological uptake or variations of riverine end-member (lower freshwater end-member in dry season) or both. During the flood seasons (summer and fall), water residence time decreased to ca. 2 months. An increase of water discharge replaces the 'old water mass' with relatively higher arsenic concentrations, and remobilization and/or regeneration associated with solid phases (suspended and bottom sediments) is much more significant, due to higher reverine suspended matter loads. It appears that the whole process of replenishment takes place within several months, and that seasonal evolution of arsenic in 1985 was substantially identical to that of 1984, except the higher levels (ca. 10 nM) of arsenic in the South Bohai for both dry and flood seasons.

During the high water stage cruises, remobilization of arsenic took place in both low and high salinity regions (Huang *et al.*, 1988; Li *et al.*, 1991). The excess As relative to the theoretical dilution curve is attributed to the desorption of As from riverine sediments in the upper estuary (low salinity region) and/or regeneration from bottom sediments in the lower estuary (South Bohai) due to the redox cycle of Fe–Mn oxides/hydroxides and decomposition of organic materials in the coastal zone (water depth: <15–20 m). Dissolved As has a positive correlation with phosphate (PO_4^{-3}) and dissolved organic carbon (DOC) in the Huanghe estuary (Figure 5), which suggests the affinity of As with biota and the involvement of arsenic in cycles (regeneration/uptake) of nutrient elements. It seems that active (nonconservative) distribution of dissolved As has no significant impact on the particulate As in the estuary. Trace element-nutrient covariations in the estuary has been demonstrated by Windom and coworkers, who showed close correlations between nutrients and some trace metals and, hence, suggested the regeneration of metals along with decomposition of organic matter and nutrient cycles (Windom *et al.*, 1991). It should be kept in mind, however, that with any statistics, a relationship may or may not be realistic, even if a high percentage of the variability can be explained by a correlation. Considering the correlation coefficients, e.g. $\gamma = 0.6 - 0.7$ in Figure 5, one may expect that about 40–50% of the variations can be attributed to processes involving DOC and/or phosphate, assuming that there are some real relationships. Patterns of As–PO_4^{-3} and As–DOC relationships are quite different between low and high-water stages, indicating the different mechanisms taking place in the Huanghe estuary. Under high-water stage conditions (August 1985), DOC and PO_4^{-3} and dissolved As have shown broad estuarine maxima at chlorinity of 5–10‰. The estimated estuarine release based on element-chlorinity relations are 15% for DOC (0.3–0.4 mg l^{-1}), 45% for PO_4^{-3} (0.2 μM) and ~30% for As (9.8 nM). The slopes as As–DOC and As–PO_4^{-3} curves during high discharge conditions are 4.12 and 20.53, respectively. These values should be similar to As/DOC and As/PO_4^{-3} ratios of organic materials (e.g. plankton), if one assumes that the estuarine maxima of As is caused by regeneration from degrading organic matter (Windom *et al.*, 1991 and references within). Otherwise, the $\Delta As/\Delta PO_4^{-3}$ ratio may approach the corresponding values of loess (~8.96). However, DOC displays a pattern of some removal in the low chlorinity area (chlorinity: <5‰) in high-water stage cruises. Laboratory modeling shows abiotic release of phosphate from the solid phases along with a mixing of riverine and marine waters (unpublished data). Under low-water discharge conditions, phosphate displays rather a conservative distribution and DOC has an estuarine removal of 28% (~1.0 mg l^{-1}). The As–PO_4^{-3} correlation becomes worse, whereas that of As–DOC is better compared to the high-water stage cruises (Figure 5). Examination of the data reveals that the 'old water mass' from the South Bohai has lower (ca. 5–8 nM) As concentrations, which leads to a removal of 20% (~5.4 nM) of As in the estuary, presumably due to the biological uptake (Zhang, 1988). It is premature at present to simply attribute apparent As–DOC and As–PO_4^{-3} relations to either biologic release/uptake or regeneration along with cycling of nutrient elements by degradation of organic materials. Abiotic processes (e.g. adsorption/precipitation and redox change, etc.) may affect As distributions in the Huanghe estuary. It seems that in-situ bioproduction does not contribute significantly to the estuarine organic matter pool, owing to very high turbidity within the riverine effluent plume. Instead, terrestrial materials and/or marine biota are the major sources. Due to the extremely high suspended sediment load of the Huanghe, desorption of 5–10% from particulate phases may introduce a concentration of 10–15 nM for dissolved As in the mixing zone (Zhang, 1988). Figure 5 indicates a covariations of As concentrations with biological uptake/release of PO_4^{-3} and organic carbon by degradation of organic matter in the estuary. The estuarine mixing processes, imposed by biogenic consumption/regeneration, should be more rapid during floods than in dry seasons, owing to a much shorter water residence time under high-water stage conditions. The swimming and benthic faunas (fish and benthos) from the Huanghe and adjacent coastal areas may concentrate As from the ambient environment (water column and bottom sediment) at a significant level, and have an As enrichment factor to 10^3–10^4 relative to ambient sea water (Li *et al.*, 1991). Obviously, As can be enriched in the organisms and transferred along the marine food chains. The high concentrations of As in swimming and benthic faunas of the region provides strong evidence that As cycles in the Huanghe estuary and adjacent coastal areas can be complicated by the in-situ ecosystems. Values in Figure 6 vary between 0.9 and 23.1 $\mu g\ g^{-1}$, which are relatively high compared to As levels in algae (0.4–1.0 $\mu g\ g^{-1}$) and fish (2.0 ± 0.8 $\mu g\ g^{-1}$) from unpolluted areas (Underwood, 1977; Sanders and Osman, 1985).

Sediment core samples taken from the delta region show vertical profiles of As in coarse (0.001–0.05 mm) and fine (<0.001 mm) fractions and bulk sediment (Figure 7) (CHRPM and GDBU, 1980). These core samples were collected from the delta region (above sea level) and analyzed to determine arsenic concentrations

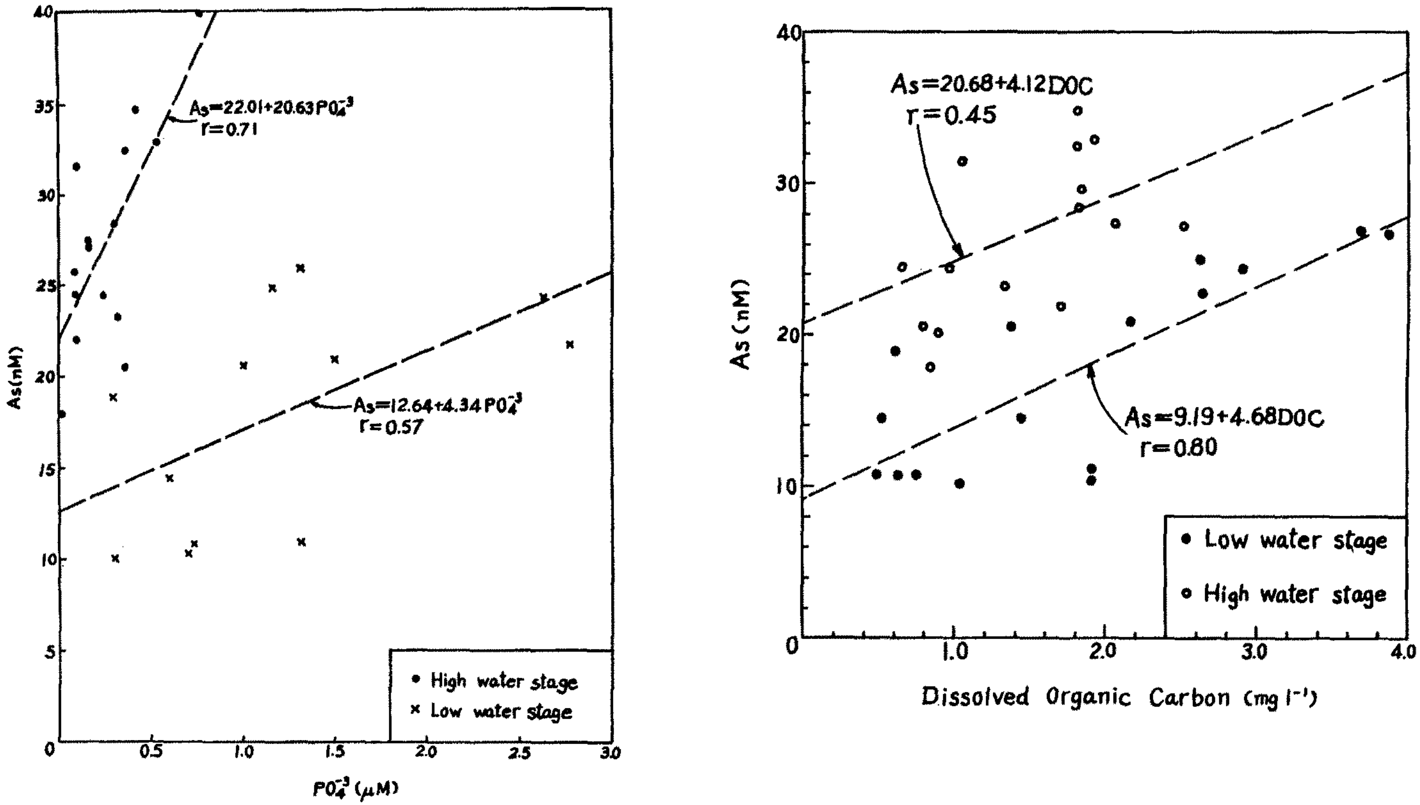

Fig. 5. Dissolved arsenic (nM) vs. phosphate (μM) (left) and DOC (mg l^{-1}) (right) for the Huanghe estuary during low water (May 1985) and high water (August 1985) discharge conditions. Dotted lines represent linear regression curves (γ: correlation coefficient).

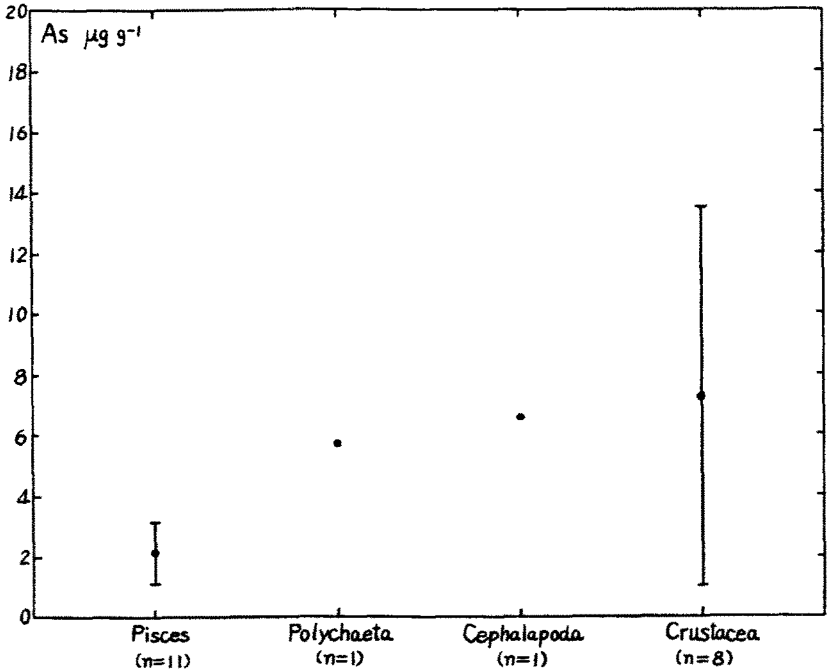

Fig. 6. Concentrations (μg g^{-1} of dry weight) of As for marine animals from the Huanghe estuary and adjacent coastal areas (data are from Li *et al.*, 1991). The enrichment factors of 10^3–10^4 relative to ambient seawaters clearly demonstrate that arsenic can be accumulated in both swimming and benthic faunas and transferred along the food chains.

in different grain-size fractions. The deposition rates at the delta region was estimated by both isotopic (^{210}Pb) and sedimentary structure methods (cf. CHRPM and GDBU, 1980; Huang, 1986). It is most likely that arsenic has shown somewhat constant distributions in core sediments since the 1940s, which suggests that industralization over the drainage basin had a negligible impact upon reverine As budgets over the last 40–50 years. The deposition rate in the Huanghe delta region is highly variable (10–100 cm yr^{-1}), depending upon the sample locations. It seems most likely that deposition in this region is very episodic and localized, with sediment deposition rates varying in time and space. Moreover, both seasonal and interannual cycles were observed from the core samples (Kang *et al.*, 1988). Arsenic in fine sediment fractions averages 24.0 ± 5.1 μg g^{-1} (n = 38), which is a factor of three higher than that for coarse sediment fractions (8.4 ± 2.5 μg g^{-1}) (n = 11). Sequential extraction methods (0.2 M calcium oxalate + 0.1 M oxalic acid) may extract 10–30% of As from bottom sediments of which ca. 60% is associated with Fe–Mn oxides/hydroxides (Ma *et al.*, 1986; Li *et al.*, 1991). Previous studies reported that ca. 5–10% of As in loess and riverine sediments is soluble and 20–30% of As is combined with carbonates (CHRPM and GDBU, 1980; Huang, 1986). Again, As in a 1.0 M HCl extractable fraction of estuarine

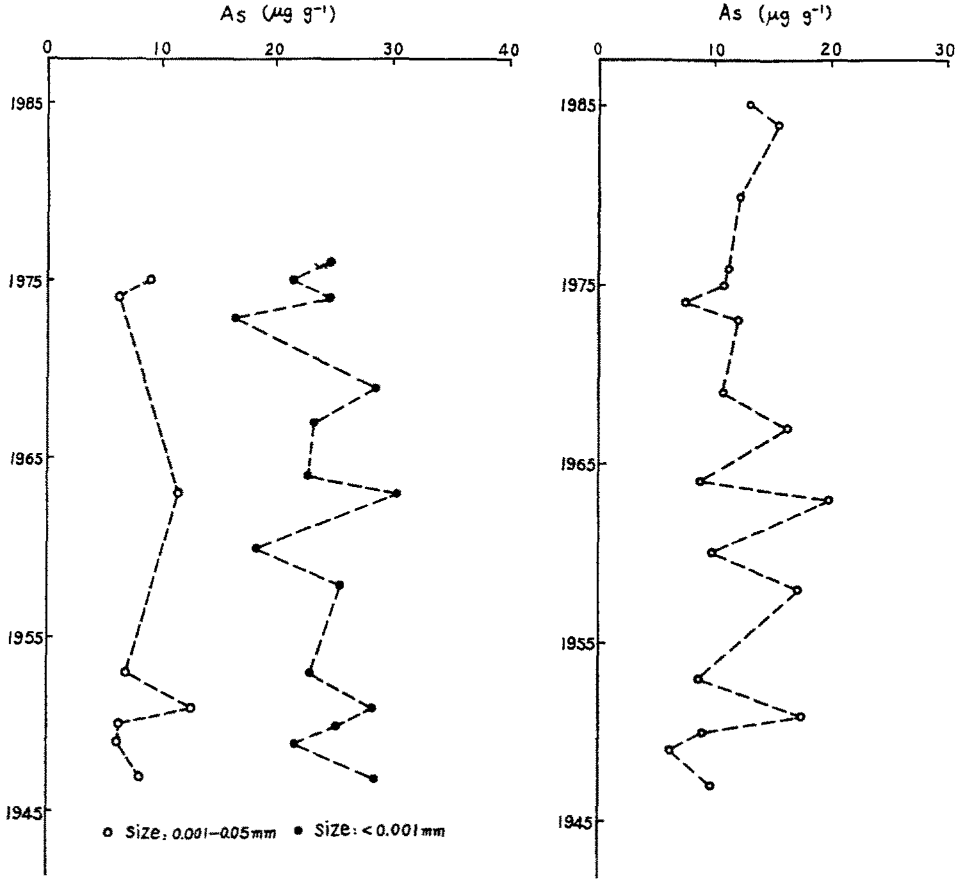

Fig. 7. Vertical profiles of As (μg g^{-1}) from delta sediments of the Huanghe. The figures show As in coarse (0.001–0.05 mm) and fine (<0.001 mm) sediment fractions (left) and bulk sediments (right) (data are from CHRPM and GDBU, 1980, and our unpublished work).

sediments show close correlations with the content of fine sediments (<16 μm) and/or specific surface of bulk sediments (Gao *et al.*, 1991a,b). From these results, one may expect that remobilization of As associated with solid phases may take place in the Huanghe estuary through either desorption at the fresh-saline water interface or redox cycles of Fe–Mn oxides/hydroxides in bottom sediments or both. Due to the high suspended sediment contents in the river course and effluent plume and frequent resuspension of bottom sediments in the estuary, remobilization of As may not necessarily change the distribution pattern of As in the solid phase but would alter dissolved As regimes (e.g. budget) over the delta region (Huang *et al.*, 1988; Zhang, 1988).

Relatively stable distributions of particulate As occur in the Huanghe estuary within data resolutions, especially when absolute As concentrations are normalized to scandium (Sc), which suggests a limited contribution of biota to As in solid phases, and sedimentary dynamics in predominent mechanisms affecting particulate As behavior in the estuary (Figure 8) (Huang *et al.*, 1988; Zhang, 1988). Given the often suggested mechanism of As removal by coprecipitation with Fe, one may expect some correlation between these two elements in the solid phases. Figure 9 plots As against Fe for riverine samples and samples from the Huanghe estuary, which indicates an increase of As with higher Fe in suspended matter. However, dissolved Fe shows an estuarine maximum in the mixing zones (chlorinity: $\leq 15‰$) during both low and high-water stages, particulate Fe shows a stable distributions in the estuary. Also, Fe has a positive correlation with Al in sediments (Zhang, 1988). It can be concluded, therefore, that both Fe and As may increase with higher fine-size fractions (e.g. clay) in sediments, and coprecipitation of As with Fe is negligible in the Huanghe estuarine mixing processes, taking into account the remobilizations of Fe in both low and high-water stage conditions. Small differences in As concentrations could be considerably reduced when As is normalized to Sc. Values of As/Sc in suspended sediments from the estuary (up to salinity = 32.50) averages 0.94 ± 17% ($n = 9$) in low ater and 0.97 ± 14% ($N = 12$) during high water discharge conditions (Zhang, 1988). Indeed, particulate organic carbon (POC) averaged 0.4–0.5% in the river and ranged from 0.5% to 3–4% within the effluent plume in the estuary (unpublished data), which is generally low compared with other Chinese river/estuary systems such as the Changjiang (Cauwet, 1990). Hence, the mass balance of particulate As could be estimated with the product of riverine arsenic concentrations and sediment load, which would give a steady-state seaward transport (31.6×10^6 kg yr^{-1}) of particulate As from the Huange. Seasonal and/or internannual varations in As levels related to grain-size and/or mineralogy may alter As regimes in the Huanghe estuary, however.

5. Discussion

5.1. POLLUTION AND WEATHERING OVER THE DRAINAGE BASIN

As mentioned above, the Huanghe shows relatively high As concentrations in both dissolved and solid phases. Extensive deposition of suspended materials (ca. 0.5 $\times 10^{12}$ kg yr^{-1}) takes place in the lower reaches over a distance of 800–1000 km, which results in an elevation of river bed 5–10 m above the alluvial plains on both sides (Zhang *et al.*, 1990b). Pollution drainages from point sources into the tributaries in the upper and middle reaches are frequently reported, whereas direct input of pollutants into the lower reaches is very limited. Samples taken downstream of the large industrial centers and/or high population areas in the upper and middle reaches (e.g. J3 and J8) have dissolved and particulate As concentrations that is 100-115% for those from upstream stations, but high values were not found at downstream sampling sites. It can be expected that due to enormous turbidity, high pH values (8.00–8.40) and/or abundant water discharge, any pollutants from point sources would be rapidly diluted in the Huanghe. China is an agricultural coun-

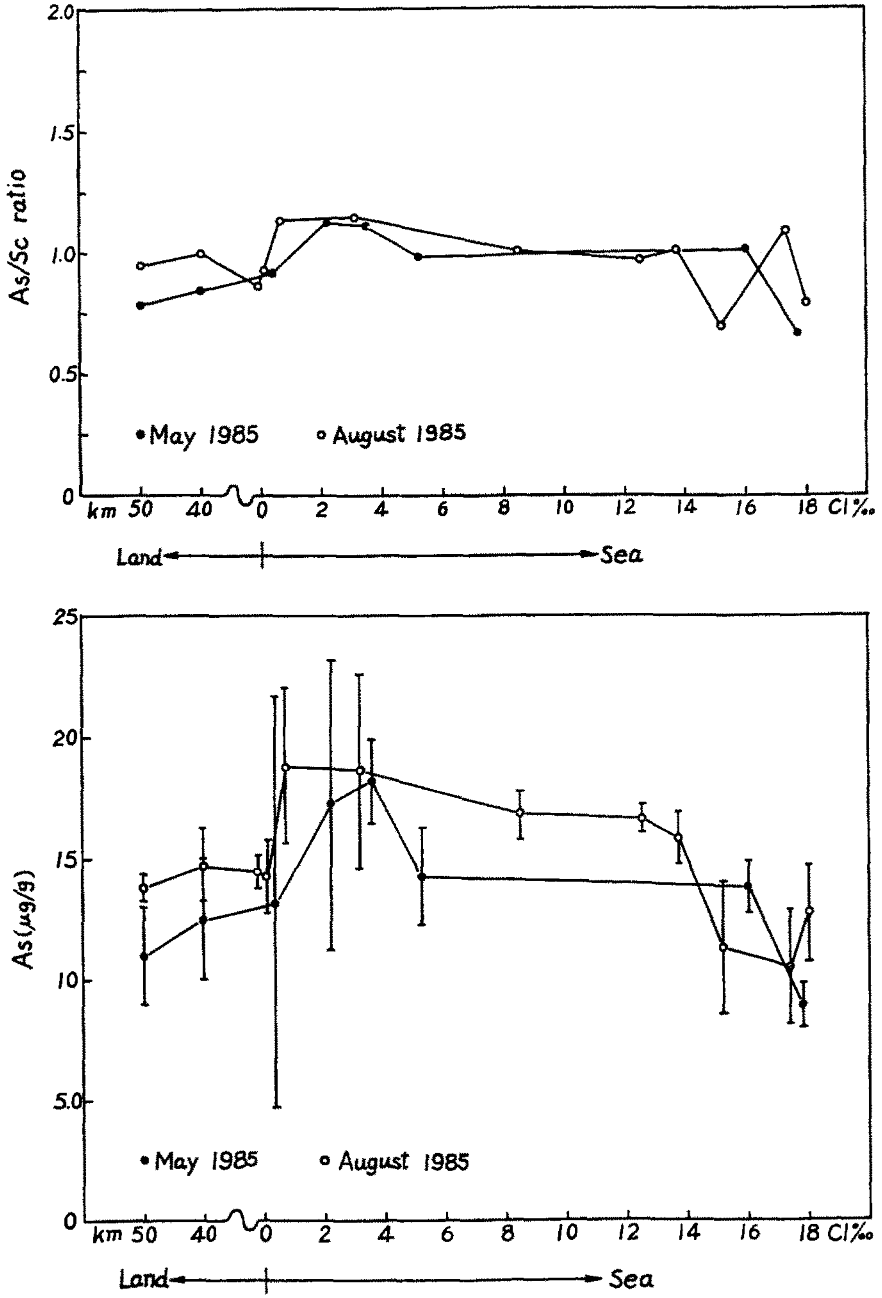

Fig. 8. Particulate As in the Huanghe estuary. Note that As shows relatively stable distributions within data resolutions, especially when absolute concentrations were normalized to scandium (Sc). The distribution patterns in the mixing zones during the flood season cruise (August 1985) is the same as that in the dry season cruise (May 1985), except that higher riverine concentrations has been observed in flood periods. The data show the concentrations plus errors (vertical bars) for INAA analyses.

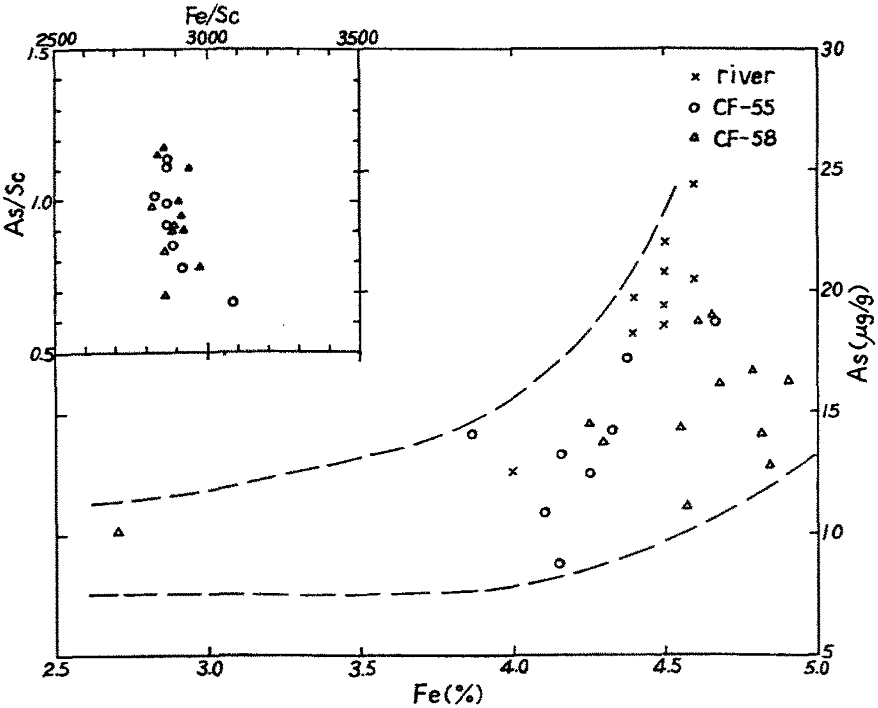

Fig. 9. Plot of As against Fe in suspended matter from the Huanghe and its estuary. Data of Fe are from Zhang (1988) and Huang *et al.* (1992). It shows both absolute concentrations and element to Sc ratios. Note that concentration of As may increase with higher Fe levels in suspended matter, which is true for both riverine and estuarine samples. However, the covariations of As and Fe may not necessarily provide evidence of As coprecipitation with Fe, since both As and Fe increase with higher fine-size fractions in sediments. Values of As/Sc do not indicate any apparent trends against Fe/Sc in the estuary during low and high water stage conditions.

try, crops cultivation is the most important anthropogenic activity. Agricultural use accounts for 80–90% of nationwide water resources consumption (Tang and Zhang, 1989; Zhang *et al.*, 1994a). Use of chemical fertilizers and herbicides/pesticides in cultivation introduce As to the surface soil, which may, in turn, enter the river owing to heavy erosion. Statistical data shows that total As-containing fertilizer/pesticide consumption over the Huanghe drainage area was 0.1–0.2 × 10^6 kg yr^{-1} in the 1970s (CHRPM and GDBU, 1980), which, according to the CHRPM and GDBU reports, has no important effect upon As budgets in the Huanghe. During the 1980s, consumption of As-containing fertilizers/pesticides was estimated to be ca. 0.2–0.4 × 10^6 kg yr^{-1} (unpublished data). If one assumes that arsenic in fertilizers/pesticides is totally removed in subconsequent weathering and erosion, concentrations of dissolved arsenic would be ca. 5 nM higher. It appears that an estimate of 5 nM is the upper limit of arsenic drainage related to agriculture. Several factors should be taken into account before the impact from cultivation upon riverine arsenic budget can be addressed in more detail. Modern cultivation over the Huanghe drainage basin is largely restrained to the regions close to urban areas, whereas traditional cultivation covers most of the drainage areas and 0.2–0.4 × 10^6 kg yr^{-1} might be an overestimate. Also, arsenic in the fertilizers/pesticides may not be necessarily eroded into the river, it can be retained/mineralized in soils and/or uptaken by crops (1–10 × 10^3 kg yr^{-1}). Atmospheric input of arsenic through wet and dry depositions is still unknown. Dissolved arsenic in the river may be eliminated due to the high suspended sediment concentrations and elevated water pH values (pH = 8.00–8.40), which provides abundant sites available for adsorption of cations and favors the precipitation of hydroxides/oxides. At such high pH values ($pH \geq 8.0$), it seems that the particles should be negative charged and not particularly adsorptive for anions (e.g. AsO_3^{-1}). However, the combination of anions (e.g. PO_4^{-3} and AsO_3^{-1}) with solid phases may take place through cations acting as bridges between anion and particles (unpublished data), which is highly dependent on the sediment characteristics (e.g. composition and amount) and As levels in the river. Alternatively, the Quarternary Loess Plateau supplies ca. 90% of suspended sediments and ca. 40% of water loads. Fragile structures and well developed vertical cleavages of loess, and poor vegetation and frequent rain storms in summer and autumn, etc., over the Loess Plateau make the loess quite sensitive to erosion. Traditional ploughing and cultivation may accelerate the soil erosion and induce weathering to a greater depth. The overall landscape of the Loess Plateau can be described as hills and small plains at altitudes between 1000 and 2000 m separated by deeply cut valleys. Cultivation in terraces is widely used in order to reduce surface water and soil loss, and gully erosion, in turn, becomes more significant. A certain amount of riverine sediments is supplied from loess in deep layers rather than from cultivated surface soils (cf. Zhu, 1984). Longitudinal variations of grain-size and mineralogy of suspended sediments were observed in previous studies. Suspended sediments from the middle reaches contain more fine size (<63 μm) and less coarse fractions than samples from the upper reaches. Variations of detrital minerals can be summarized as higher contents of unstable minerals (e.g. calcite, dolomite, hornblende and micas, etc.) relative to stable minerals (e.g. quartz) in the middle reaches compared to the upper stream (Figure 10) (Que and Yan, 1989). Hydrographic and geological information indicates that riverine water in the upper stream is supplied from melt snow and ice, whereas rainfall is the main water source in the middle and lower reaches. In the upper reaches, sandstone and other detrital rocks of Tertiary age supply mainly stable quartz, whereas the Huanghe gains a large amount of unstable minerals and fine sediment fractions (which often have high As levels) when it drains the Loess Plataeau (Que and Yan, 1989; Zhang *et al.*, 1990b). Consequently, dissolved arsenic concentrations increase by 50% owing to weathering in this region (Quaternary Loess Plateau). Moreover, differences in grain-size and mineralogy between loess and Huanghe-suspended sediments occur in that the river sediments contain higher fine size particle fractions and have more abundant micas and feldspar than quartz compared to loess (in which quartz is

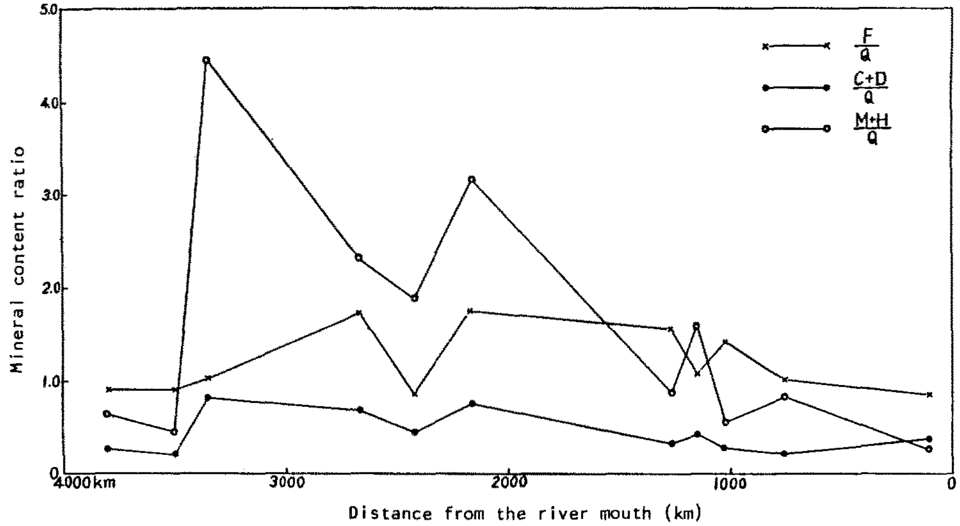

Fig. 10. Ratios of unstable to stable minerals in suspended sediments vs. distance from the river mouth upstream for the Huanghe. Data are from Qu and Yan (1989). Q: quartz; F: feldspar; C: calcite; D: dolomite; M: mica; H: hornblende.

the most important mineral, but replaced by micas and feldspar in river suspended sediments). One may speculate that unstable minerals and fine particles should have higher affinity with As compared to quartz and coarse particles due to their crystal lattice characteristics (e.g. defect and substitution) and high surface to volume ratios. The unstable minerals are natural hosts for As and easily destroyed in weathering. Weathering of unstable minerals can supply higher As than the stable ones do. Therefore, relatively high dissolved and particulate As concentrations in the river should be the product of weathering/erosion and lithology in combination over the drainage basin.

If one neglect the impact of anthropogenic activities on As levels in the river, high concentrations of dissolved As should reflect the relative contributions of atmospheric deposition and weathering. Mobilizations of As relative to Al, that is ratio of dissolved As to Al $[(\mathrm{As/Al})_{\mathrm{di}}]$ (di: dissolved values) to parent materials $[(\mathrm{As/Al})_{\mathrm{fr}}]$ (fr: fresh rock or soil) averaged 2.5×10^3 in our 1985 cruises. This suggests that As is much more easily remobilized relative to Al in weathering/erosion over the Huanghe drainage basin. We use Al as an index, since aluminium is one of the most abundant elements in rocks/soils and is nearly insoluble in weathering. Concentrations of dissolved Al is quite low in natural waters (Martin and Whitfield, 1983). High $[(\mathrm{As/Al})_{\mathrm{di}}]$ to $[(\mathrm{As/Al})_{\mathrm{fr}}]$ ratios indicate that As is readily released from the solid phases and remains at relatively high levels in the dissolved phases in the Huanghe drainage basin.

TABLE V. Comparison of partitioning coefficient (lg Kd) between the Huanghe and some of the world's rivers. Note that As levels of these rivers are highly variable, partitioning coefficients (lg Kd) are somewhat constant (i.e. variations within one order of magnitude), however.

River	lg Kd	References
Huanghe	3.96	This study
Changjiang	4.24	This study
Rhône	4.06	Seyler and Martin (1990) and unpublished data
Loire	4.21	Seyler (1985), Seyler and Martin (1990)
Tejo	4.12	Andreae *et al.* (1983)
Tama	3.67	Tanizaki *et al.* (1985)
World average	3.46	Martin and Whitfield (1983)

5.2. ARSENIC PARTITIONING AND TRANSPORT

The partitioning coefficients (Kd) of As in the river is defined as

$$\mathrm{Kd} = (C_p \times 10^3)/C_w \tag{3}$$

where C_p is the As concentration in solid phases (mg kg^{-1}) and C_w represents dissolved As level (μg kg^{-1}). Table V tabulates Kd values of some world rivers: the Huanghe, Changjiang, Rhône, Loire, Tejo, and Tama. It is obvious from Table V that the Kd values in these less disturbed or even polluted rivers show some similarity: log Kd ranges from 3.7 to 4.2, i.e. within one order of magnitude, if one takes into account the variabilities (i.e. two orders of magnitude) of both dissolved and particulate As concentrations in rivers (Tables III and V). This probably implies the general control of weathering/erosion (e.g. lithology) on element geochemistry over river drainage basins (Huang *et al.*, 1992). In large and less disturbed rivers, trace elements show low levels and similarity in both dissolved and solid phases (Shiller and Boyle, 1985, 1987; Huang *et al.*, 1992; Zhang and Huang, 1993). Data of trace element concentrations from large and less disturbed rivers (Amazon, Zaire, Orinoco, Changjiang, Huanghe, etc.) are close to the background in watersheds, whereas in heavy polluted rivers (e.g. Rhine), element levels may be two orders of magnitude higher. In the laboratory model studies when the trace element spikes to the river water (e.g. pollution) are within two orders of magnitude that of natural levels, the partitioning coefficient (Kd) keeps somewhat constant, further input would considerably reduce the Kd (Trefry *et al.*, 1986; Zhang *et al.*, 1994b).

If the river has suspended sediment concentrations S_i (mg l^{-1}), the proportion of the total concentration (C_t: μg kg^{-1}) in the dissolved (C_w) and particulate (C_p) phases could be estimated from the expression:

$$C_w/C_t = 10^6/(10^6 + \mathrm{Kd} \times S_i) \tag{4}$$

and

$$C_p/C_t = 1000\mathrm{Kd}/(10^6 + \mathrm{Kd} \times S_i) \tag{5}$$

with total percentage transport associated with suspended sediments:

$$1 - C_w/C_t = (\mathrm{Kd} \times S_i)/(10^6 + \mathrm{Kd} \times S_i), \tag{6}$$

$$C_t = C_w + C_p \times (10^{-3} \times S_i). \tag{7}$$

The effect of suspended sediments is to reduce the magnitude of any changes in dissolved arsenic concentration through adsorption (Ball, 1989). The capacity of particles to buffer changes in dissolved As concentrations depends upon the interaction with solid phases and the amount of suspended matter. Taking the Huanghe as an example, concentrations of particulate As in the river water (i.e. in nmol per liter) varied between 200 and 7.50×10^3 nmol l^{-1} in the 1985–1986 cruises, presumably depending on the riverine sediment loads, which can be one to two orders of magnitude higher than those from the Changjiang (Zhang *et al.*, 1990a). In the riverine effluent plumes of Huanghe estuary, concentrations of particulate As in water decreased from 450 to 25 nmol l^{-1} corresponding to the salinity increase upto 20.00–25.00, and values of 1–5 nmol l^{-1} have been found at salinity >30.00 further offshore.

The partitioning coefficient (Kd) in Table V demonstrates the vast/specific capacity of particles to take up arsenic. Since the Kd values in Table V are quite similar, the proportion of the total dissolved As concentrations relies mostly on the suspended sediment contents in the river, as illustrated in Figure 11. Suspended sediment contents of rivers in Table V range from ca. 5–10 mg l^{-1} to 20–30 $\times 10^3$ mg l^{-1}. In Figure 11, the Huanghe may present an extreme case with $C_w/C_t \leq 0.5\%$, i.e. 99.5% of total As being associated with solid phases, whereas in the Tama, $\geq$95% of total As is transported as dissolved species in waters. It can be concluded that with available Kd values and total As concentrations, high turbidity rivers would have relatively lower dissolved As levels and, hence, higher buffer capacity against pollution drainages.

Other interesting evidence for the sensitivity of aquatic systems to changes in dissolved trace elements (e.g. As) comes from the comparison of rivers in Table V. Particles have an important control on the fractionations of As between dissolved and particulate phases. At high particle loads (depending on the particle reactivity with the element and, hence, the Kd), the dissolved phases represent only a minor fraction of the total concentrations. Rivers with high suspended sediment load are, therefore, not sensitive to changes in concentration in dissolved As (e.g. from pollution), since most of the increase of total concentrations is taken up by the particulate phases which tends to act like a buffer. It is extremely difficult to identify an anthropogenic signal merely on the basis of concentration measurements, the fractionation of As between dissolved and particulate phases would dramatically reduce the concentrations in dissolved phases and, hence, bioavailability. In the Huanghe estuary, fresh particles are generated by fluvial and atmospheric inputs, mineralization and primary production, and by resuspension as well. These sources are interbalanced by dissolution and sedimentation, and advection in addition. The

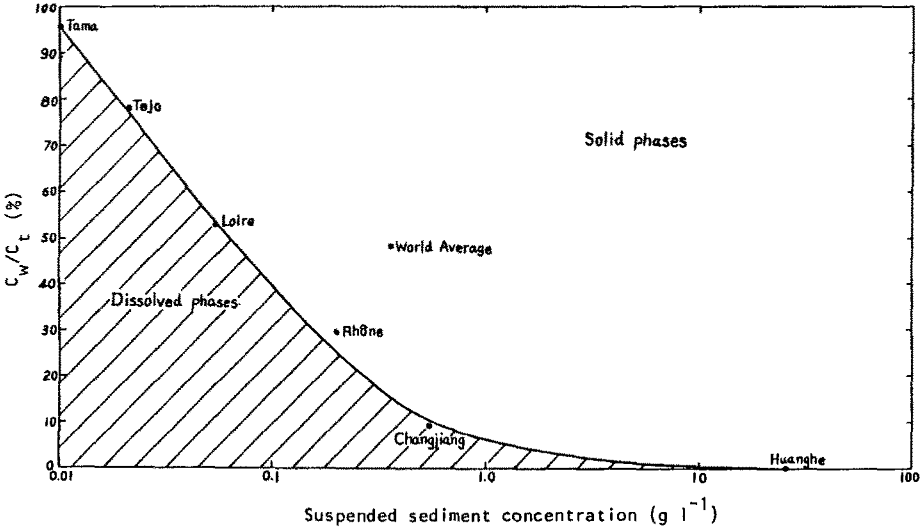

Fig. 11. Proportion of total As concentrations (C_t) as the dissolved species (C_w) vs. amount of riverine suspended matter (S_i) for some world rivers.

effect of these continuous input and outputs in a reservoir is to remove metals from the solution, because the freshwater end-members is higher than the saline waters. Where the primary production is the principal source of particles, As fluxes are closely correlated to those of dissolved and particulate organic carbon (DOC and POC), the net result of the process is to further reduce the magnitude of any change (Ball, 1989). It should be kept in mind, however, that the partitioning coefficient Kd describes transport regimes of arsenic from individual rivers, and the environmental significance of Kd is hardly identified. Partitioning of arsenic between dissolved and particulate sources is likely to be restricted by reaction kinetics. Since no attempt was made to determine the amount of arsenic associated with labile fractions (e.g. adsorbed As) relative to the clastic fraction in particulate phases, further discussion of bioavailability and the impact of anthropogenic activities on arsenic in the Huanghe and its estuary should be limited until new data sets on labile As become available.

Finally, based upon the data available for both dissolved and particulate arsenic, a tentative estimate of seawards transport (e.g. budget) of As can be reached for the Huanghe. Considering the annual average freshwater discharge of 41.0 × 10^9 m^3 and terrigenous sediment load of 1.1 × 10^9 tons, data of this study provide a budget of 1.17 × 10^6 mol yr^{-1} as dissolved and 21.6 × 10^6 kg yr^{-1} associated with particles for arsenic from the Huanghe. These budgets shows the arsenic transport to the river mouth, and from this study, the seawards budgets of arsenic will be greatly modified by the estuarine processes with respect to either abiotic or biotic mechanisms or both. Moreover, about 90% or more of Huanghe sediments are released in the shallow water areas around the river mouth. Thus, the net flux of particulate As from the Huanghe to the Central Bohai should be ca. 10% of that to the river mouth. The extrapolation of nonconservative distributions for arsenic to the freshwater end-member gives an apparent riverine concentration that is a factor of two higher than what has been found in the river itself, and the overall seaward exports of dissolved arsenic can be enhanced by 50–100% (ca. $2.0 - 2.5 \times 10^5$ mol yr^{-1}) by the estuarine mixing processes. Our recent studies has shown that some of the terrigenous sediments discharged by the Huanghe may be carried further offshore to the Northwest Pacific coastal oceans (e.g. Yellow Sea) via nepheloid layers across the Bohai Strait with a net flux of suspended matter of 6×10^9 kg yr^{-1} (Martin *et al.*, 1993b). Detailed examinations of particulate As from the Bohai Strait and North Yellow Sea provided an average value of 19.0 $\mu g\ g^{-1}$, very similar to the freshwater end-members. This suggests that particulate As escaped into the Bohai is further limited by the removal/deposition taking place on the continental shelf with a net flux to the NW Pacific Ocean of 65×10^3 kg yr^{-1} for particulate As. Clearly, the riverine dissolved As flux is small but not negligible compared to particulate As transport. The net flux towards the NW Pacific Ocean of dissolved As can be equal to or even higher than that for particulate As, owing to somewhat complicated biogeochemical processes taking place in the Huanghe estuary and South Bohai.

6. Summary and Problems Remained

Relatively high concentrations of both dissolved and particulate arsenic were observed in the Huanghe compared to other rivers of the world receiving little pollution over the drainage areas. Examination of the data demonstrates that the major processes controlling the As geochemistry in the Huanghe should be the weathering and erosion in watersheds. Indeed, the input of point-source pollution drainage is limited to the upper and middle reaches of the Huanghe catchment basin, due to relatively low industrialization and unique lithology (e.g. loess)/hydrography features (high turbidity). However, the impact from agricultural and domestic activities (nonpoint sources) is much more difficult to quantify and remains unclear. The contribution of As from groundwater and atmospheric deposition is still poorly documented or virtually unknown. With the successive control and management of industrial waste drainages (point-sources), the nonpoint-source pollutions (urban and agricultural practices) will become more significant in the near future. Various potential causes exist for trends in most constituents. For example, changes in fertilizer use, atmospheric deposition and municipal waste treatment can each be identified as the major cause of As trend in specific basins (Smith *et al.*, 1987). High levels of As in the Huanghe is most likely due to the elevated background of source materials (e.g. loess) and remobilizations of As in weathering/erosion (with the mean denudation modulus of 1.4×10^6 kg km^{-2} yr^{-1}) over the whole drainage basin. Comparison of As concentrations between the Huanghe and other rivers of the world reveals some homogeneity of partitioning coefficients (Kd) in spite of the high variabilities of As concentrations and water/sediment loads between individual rivers. Abundant suspended particles and high pH values in the Huanghe can reduce any pollution associated dissolved element concentration changes through adsorption and/or precipitation of hydroxides/oxides. River suspended particles could reduce changes of dissolved As concentration, hence buffer the pollution and decrease the bioavailability of As in aquatic environments. In the estuary, particulate As showed stable distributions against chlorinity, especially when absolute concentrations were normalized to Sc. Dissolved As can be either remobilized or removed in the mixing zone, depending upon the freshwater and sediment discharges. Bottom sediment records show relatively stable distributions of As over the last 40–50 years, which suggests that economic advances over the drainage basin since the 1940s has not dramatically biased/increased the arsenic budget to the delta region. However, the high affinity of As for fine sediment fractions (e.g. clay) and active distributions of dissolved As suggests that potential remobilizations of As can be expected to occur in the estuary and delta region, which is what we have observed in previous estuarine studies.

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