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Simulation of arsenic partitioning in tributaries to drinking water reservoirs

E. Alkhatib · E. Berna

Abstract Arsenic released by bottom sediments was determined by experiments in which the sediments were artificially re-suspended using a particle entrainment simulator (PES) to simulate river conditions. Sediment cores were collected from various tributaries to drinking water reservoirs in Connecticut spiked with arsenic, and run in the PES at simulated bed-flow shear stresses from 0.0 to 0.6 N/m². Under equilibrium conditions, the dissolved fraction of arsenic was found to range from 8.3 to 22.1 µg/l, which in most cases exceeded EPA Maximum Contaminant Level (MCL) of 10 µg/l. Experimental results from these simulations have shown that bed-flow shear stress causes an increased concentration of dissolved arsenic, most notably at shear stresses of 0.4, 0.5, and 0.6 N/m². For the solid phase under equilibrium, the concentrations of arsenic ranged between 71 and 275 mg/kg. The average concentration of arsenic on the solid phase as well as partitioning coefficient values (K_p) were highest at initial shear stress. This was attributed to the higher fraction of colloidal material and finer

organic particles in the suspended solid mixture. Particles of such nature proved to have higher affinity to arsenic. K_p values were determined from PES data and were found to range from 4,687 to 24,090 l/kg. However, on a mass load basis, the amount of arsenic found in suspended sediment increased with the increase of shear stress. Similarly, the amount of arsenic in the solid phase increased significantly for sites with high Volatile Organic Carbon (VOC) content. Because of the influence of Total Suspended Solids (TSS) and VOC concentrations on K_p , the use of the PES is more appropriate in obtaining K_p values that would be found under real stream conditions when compared to the traditional way of measuring K_p using a jar study technique.

Keywords Arsenic · Bottom sediments resuspension · Metals partitioning · River flow simulation

Introduction

Arsenic is a naturally occurring element found throughout the environment in soils, groundwater, bedrock, surface waters, and sediments. In the environment, arsenic is usually found combined with oxygen, chlorine, or sulfur as inorganic arsenic, or with carbon or hydrogen as organic arsenic (ATSDR 2000). Arsenic may enter water through wind-blown dust

or the weathering of arsenic-containing bedrock. In the environment it also has anthropogenic sources such as runoff from roadways, the combustion of arsenic containing coal, and the release of arsenic from pressure treated wood that has been preserved with chromated copper arsenate (Rice et al. 2002). High concentrations of arsenic in sediments and soils are usually due to industrial contaminations and pesticide or herbicide applications (Keon et al. 2001). The United States Environmental Protection Agency (EPA) lists arsenic as a primary drinking water contaminant with a Maximum Contaminant Level (MCL) of 10 $\mu\text{g/l}$, and a Maximum Contaminant Level Goal (MCLG) of 0 mg/l (USEPA 2005a,b).

Arsenic poses a threat to humans, especially in ingestible forms. The primary concerns associated with oral exposure to arsenic are gastrointestinal effects, anemia, liver or kidney damage, and ingestion of inorganic arsenic has been strongly linked to skin, bladder, liver, and lung cancer. Inorganic arsenic is classified by the EPA as a human carcinogen (USEPA 2005a,b), therefore, the potential presence of arsenic in drinking water is a major concern.

Both industrial and pesticide-based arsenic contaminations of sediments have been found worldwide (Keon et al. 2001). In tributaries to drinking water reservoirs, arsenic may be present in the water as a dissolved form, or in the sediments. During wet weather conditions sediments may be stirred up and re-suspended into the water column, carrying arsenic downstream into the reservoirs. Therefore, it is worthwhile to study the sedimentation and stratification of arsenic in drinking water sources.

A study in Virginia found that the increase in streamflow during storms increased the amount of arsenic flowing into the lake being studied (Rice et al. 2002). In a study done on sediments in interstitial waters of the Pacific, arsenic was found in both water and sediments with the highest concentrations being about 60 cm below the sediment surface (Meinrat 1979). Unfortunately, instances of the published studies on the effects of turbulence on arsenic concentration in water are rare. Most studies focused on external sources of arsenic or locations of arsenic contamination in an aquatic environment. That data cannot be directly applied to the movement of arsenic within a water column.

Natural water is well buffered and has stable pH conditions. The general partitioning behavior of arse-

nic in an environment where pH and buffer content is essentially constant can be generally described as:

$$K_p \doteq 10^9(p/m)/C \quad (1)$$

Where, 10^9 is a conversion constant, p is the pollutant concentration on particulates (mg l^{-1}), m is the suspended solids concentration (mg l^{-1}), C is the dissolved pollutant concentration in water phase ($\mu\text{g l}^{-1}$) and K_p is the partition coefficient (l kg^{-1}) (Alkhatib and Weigand 2002). K_p values are typically higher in organic matter (Mackay et al. 1996).

There are many physical and chemical parameters that affect the entrainment of sediments into the water column. These parameters include river flow velocity, mineralogy of the sediment, particle-size distribution of the sediment, and organic content of the sediment (Lee et al. 1981). One method that is used to re-suspend sediments and replicate river turbulence requires a device called a Particle Entrainment Simulator (PES). The PES makes it possible to evaluate the re-suspension of bottom sediment as a function of river-bed flow (Alkhatib and Castor 2000). The PES can be used to suspend sediment particles in a recreated water column. If the sediment contains arsenic it may desorb from the particles and enter the water.

The present study used a PES to determine the release of arsenic into the water column. Different amounts of shear stresses simulating river bed-flows were applied in order to resuspend sediment particles. Arsenic concentrations were determined in both solid and dissolved phases. This method was repeated on six different cores collected from tributaries to drinking water reservoirs in Connecticut, USA, using sediments with different characteristics.

Methodology

Particle entrainment simulator (PES)

The PES, Fig. 1, is a device used to simulate the resuspension of sediments. Although the turbulence created by the PES is very different from that found in rivers and lakes, suspended solids in the PES can be measured and compared to annular flumes. Annular flumes are chambers in which water is allowed to flow over a bed of sediment and they have been used to simulate shear stress, but were often times consum-

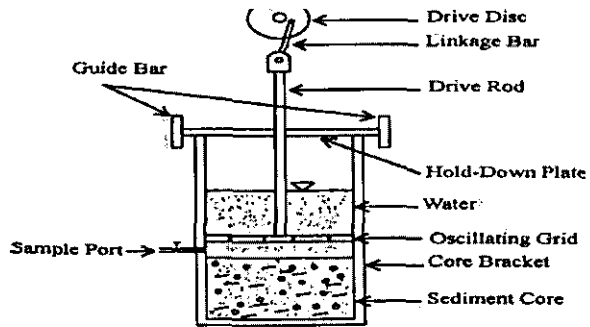


Fig. 1 Particle entrainment simulator (PES)

ing and difficult to use. By direct comparison of flume and PES suspension data it has been possible to find equivalent shear stresses which allow for calibration of the PES at various oscillation speeds. The PES uses an oscillating grid to generate turbulence above sediment that simulates erosive shear stress found in a shear flow. The PES used in this study was constructed using EPA PES specifications and was calibrated prior to the experiment by performing analyses of the same cores with the PES used and with another EPA PES parallel fashion and then comparing the results of the two instruments.

Sample collection and preparation

Sediments were collected from the tributaries to reservoirs in various regions of southern Connecticut. Samples were collected from the top 2–3 in. of sediment and transported back to the lab where they were immediately placed in acrylate cores that were washed with tap water and rinsed with distilled water and trace metal grade nitric acid prior to each use. These cores were 30 cm high and had 12.7 and 11.7 cm internal and external diameters, respectively. These cores also serve as the PES sample holder. A 5–7 cm layer of sediment was placed in the bottom of the core. River water was added to cover it with an extra 5 cm.

A sub-sample of each sediment sample was dried at 105°C until completely dry. Each dried sub sample was then sieved to separate grain size from 14 to 230 mesh (using US standard sieves). Cumulative Frequency Distribution Curves were plotted as a function of grain size. A small portion (2–5 g) of the dry sub-sample was heated in a muffle furnace for 20 min at 550°C in order to determine Volatile Organic Content (VOC) in the sample (AWWA 1999).

Two cores were modified in order to alter their VOC content. Enough sediment was collected from the Mohegan River to make three cores. One core was not altered. The other two were altered so they had 4.3 and 2.9 % VOC and were named Mohegan II and Mohegan III respectively. The VOC values were estimated and then the samples were measured according to the procedure described in standard methods (AWWA 1999).

Sample spiking

Arsenic (III) oxide was selected as the contaminant. Spiked samples were prepared as follows: 350 g of dry, sieved sediment were placed in a 1,000 ml round Nalgene bottle that had been washed with detergent and rinsed with distilled water and trace metal grade nitric acid. Six hundred milliliter of river water was added to the sediment along with 0.100 g Arsenic (III) oxide. The sample was capped and shaken over the next 72 h. This was to ensure even distribution of arsenic on the sediments and to ensure steady state equilibrium conditions.

After equilibration period the spiked sample was introduced to the sediment core. The liquid was decanted into the PES sample holder on top of the unspiked sediment layer. The contaminated sediment was then transferred uniformly to the sample holder in order to leave an even 2.5 cm layer of contaminated sediment. The contaminated sediment was considered sufficient to work with since in prior experiments (Alkhatib and Weigand 2002) breakthrough did not occur to the underlying layer. River water from the site was added to the PES to provide a 15.2 cm layer of overlying water. The height was adjusted so that the oscillating grid reached 5.0 cm above the surface at its lowest point in oscillation. Each sample was allowed to settle for 2 days. The PES was subsequently run using the following oscillations per minute in order to simulate various values of shear stress: 0, 269, 357, 455, 547, and 692 oscillations per minute. These values translate to shear stresses of 0, 0.2, 0.3, 0.4, 0.5, and 0.6 N/m², respectively. At each oscillation rate the PES remained under stress for approximately 15 min to achieve equilibrium. At equilibrium a 50 ml sample was drawn from the sample port into a graduate cylinder while the core was being agitated. To compensate for this withdrawal 50 ml of river water was added.

Each sample was immediately filtered using a Nalgene filter holder with a 250 ml flask. A pre-weighted Millipore isopore membrane filter with 0.6 μm opening was used to separate water and sediment fractions. The filtrate was placed in a 60 ml Nalgene bottle and acidified with 1 ml trace metal grade nitric acid. The sediment containing filters were dried at 105°C for 30 min and then weighed in order to determine dry weight of sediment. The dry filter was then folded, put in a 7 ml screw-top vial and 7 ml of solution containing 2% trace metal grade nitric acid was added to extract arsenic from sediment. All filtrate and filter samples were kept refrigerated until analysis.

Sample analysis

Samples were analyzed using a Buck Scientific Atomic Absorption Spectrometer (AA) model 211VGP equipped with a graphite furnace and auto sampler. The instrument was calibrated using standards prepared in the lab and a continuing midrange standard was run every 10 samples in order to ensure consistency of results.

To each sample, standard matrix modifiers in the forms of magnesium nitrate and palladium nitrate were added in concentrations of 1,000 and 200 mg/l, respectively. Matrix modifiers are used to reduce background interference. Modifiers were added so that they accounted for 10% of each sample to be analyzed. Each sample was analyzed in triplicate.

The AA operation parameters were as follows: initialization at 60°C for 10 s, dry ramp to 200°C for 20 s, dry at 250°C for 5 s, ash ramp to 850°C for 20 s, ash at 850°C for 15 s, auto zero for 3 s, data starts at 850°C, atomize-ramp at 2,300°C for 1.5 s, atomize at 2,250°C for 5 s, burn ramp up to 2,400°C for 1 s, burn at 2,400°C for 1 s, data stops, and cool to 80°C for 10 s.

Results and discussion

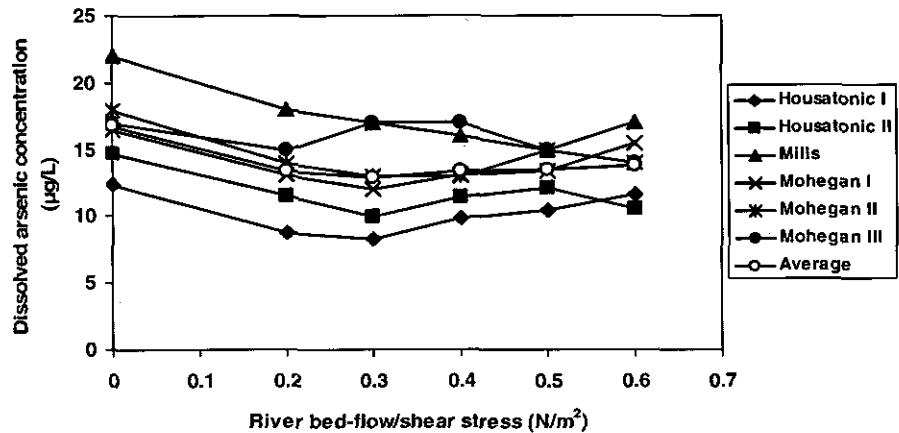
Sediment characteristics

Grain size distribution data obtained from cores were plotted as Cumulative Frequency Distribution Curves (Fetter 2002). Results are shown in Table 1. Sediments from each core were subsequently classified according to the 10th percentile into one of three types: fine sand, fine sand with silt, or silt. The Uniformity Coefficients (C_u) for each core were also calculated by dividing the 60th percentile by the 10th percentile, but no substantial variation was found in the coefficients between cores. For the six cores studied C_u ranged from 2.94 to 3.37. In addition to classifying by grain size, it was possible to classify cores according to VOC content. Four of the cores (Table 1) had VOC between 2.9 and 6.4%. These were considered to contain "high VOC." The other two cores both had VOC of 1.3% and were considered to be "low VOC" cores.

Table 1 Sediment characteristics by site

Site	VOC (%)	Sediment characteristics	Uniformity coefficient (C_u)	d_{10} (mm)	TSS mg/l					
					0.0 N/m ²	0.2 N/m ²	0.3 N/m ²	0.4 N/m ²	0.5 N/m ²	0.6 N/m ²
Housatonic River I	6.4	Fine sand and silt	3.27	0.055	276	1,954	2,224	3,992	4,270	5,886
Housatonic River II	5.8	Fine sand and silt	3.27	0.075	220	1,456	1,808	3,011	4,005	4,896
Mills River	1.3	Fine sand	2.94	0.425	24	98	170	194	218	298
Mohegan River I	1.3	Fine sand	3.22	0.225	26	102	104	232	184	636
Mohegan River II	4.3	Fine sand	3.22	0.225	156	401	672	830	1,650	2,236
Mohegan River III	2.9	Fine sand	3.20	0.225	80	120	186	338	420	890

Fig. 2 Variaton in dissolved arsenic concentration with simulated river-bed flow



Suspended solids

TSS was measured based on samples from each PES run. In Table 1, TSS ranged from 24 to 5,886 mg/l at simulated shear stresses from 0.0 to 0.6 N/m². It was not possible to measure the VOC on the suspended solids as they were collected on polycarbonate filters. We elected not to take an additional sample to measure VOC in order to avoid dilution errors.

Dissolved arsenic

Dissolved arsenic concentration was plotted against simulated shear stress in Fig. 2, and ranges for all runs are presented in Table 2. Analysis of the dissolved fraction of arsenic in all runs ranged from 8.3 to 22.1 µg/l, and in most cases exceeded the EPA MCL standards for drinking water. The dissolved arsenic concentration did not remain constant with varying levels of shear stress, however, a general trend was observed. Among most cores evaluated, there was decrease in the dissolved concentration with the increase of sheer stress to 0.3 N/m² and in some cases to 0.4 N/m². A slight shift in this trend was notable for Mohegan III in which there was an

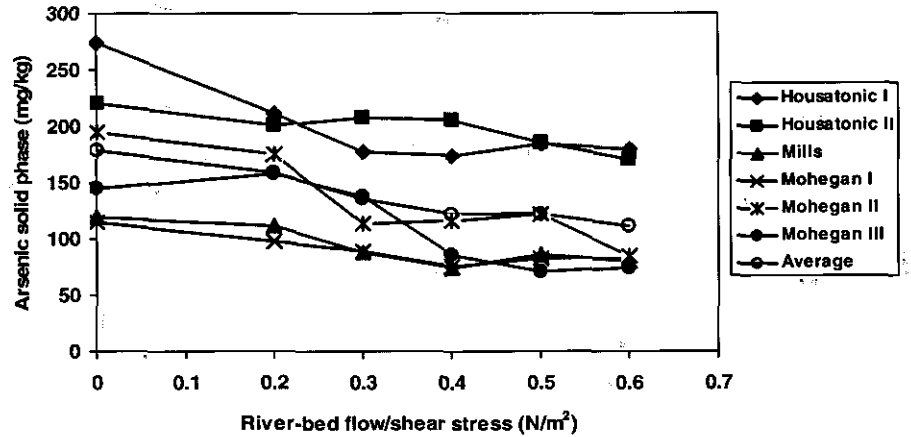
increase in arsenic concentration at stress 0.3 and 0.4 N/m². In spite of this anomaly in Mohegan III, the general trend of decrease still holds for the average of the six cores as shown in Fig. 2. Also, a shift visible in Fig. 2 shows that the three highest shear stresses caused an increase in the concentration of dissolved arsenic. This is especially notable in the case of cores with higher VOC content: Housatonic I, Housatonic II, and Mohegan II, as well as in the overall averages of the six cores. Dissolved arsenic concentration increased in these cases from 0.4 to 0.5 N/m² and then again from 0.5 to 0.6 N/m². The rebound in the concentration at these higher levels of shear stress can be attributed to the more dramatic agitation levels which break deeper into bottom sediments and bring more fine particles in suspension.

It is worthwhile to note the high initial concentrations of dissolved arsenic in the cores before the start and at the low levels of agitation. This is probably due to the sorption of arsenic onto the very small colloidal particles in the water that are smaller than 6 µm (the size of the filter openings in this study). Due to the nature of colloidal particles, there is very high probability that arsenic will sorb onto these colloids at higher rates, causing an increase in the

Table 2 Arsenic K_p values for various sediment samples

Site	K _p (l/kg)	Dissolved arsenic concentration (µg/l)	Arsenic concentration on solid phase (mg/kg)
Housatonic River I	16,071–24,090	8.3–12.4	175–275
Housatonic River II	14,932–21,010	9.9–14.8	171–221
Mills River	4,687–6,222	22.1–15.0	75–120
Mohegan River I	5,290–7,480	10.4–12.9	76–115
Mohegan River II	6,070–12,571	12.1–18.0	85–195
Mohegan River III	4,733–10,532	14.0–17.1	71–158

Fig. 3 Variation of arsenic concentration on solid phase with river-bed flow



initial dissolved fraction concentration. Since they pass through the filter the concentration will be measured as dissolved arsenic.

Arsenic in the solid phase

Arsenic concentrations on the solid phase were plotted against simulated bed-flows as shown in Fig. 3. The ranges of all runs are presented in Table 2. A summary of the concentrations of each core run at each level of stress was averaged and these values were plotted as the average line. There was a clear trend visible through every core. Most of the cores had arsenic concentrations (mg/kg) on the solid phase at the highest river bed-flows of shear stress (6 N/m^2) that were lower than the initial flow conditions. The initial and final solid phase arsenic concentrations for the Housatonic I, Housatonic II, Mills, Mohegan I, Mohegan (II), and Mohegan (III) were; 275–180,

212–158, 120–80, 115–82, 195–85 and 145–75 mg/kg of arsenic respectively and for the overall average was 178–112 mg/kg.

This decrease in arsenic solid phase concentration as river bed-flow increased can be explained by two factors. First, an increase of the proportion of the larger non-organic sediment particles was responsible for a decrease in arsenic content mainly because these particles contained lower arsenic concentration per unit mass. This is supported by the observation that at higher bed-flows, more sandy particles and larger particles in general could be detected in the water. Second, contribution to the arsenic concentration in the solid phase was due to a redistribution of some of the arsenic to the water phase. This redistribution was due to the loss of absorption sites on particles as suspended solid concentrations increased. This resulted in the transfer of contaminants from absorption sites in particle flocs to the water phase, which

Fig. 4 Variation of K_p with simulated river-bed flow

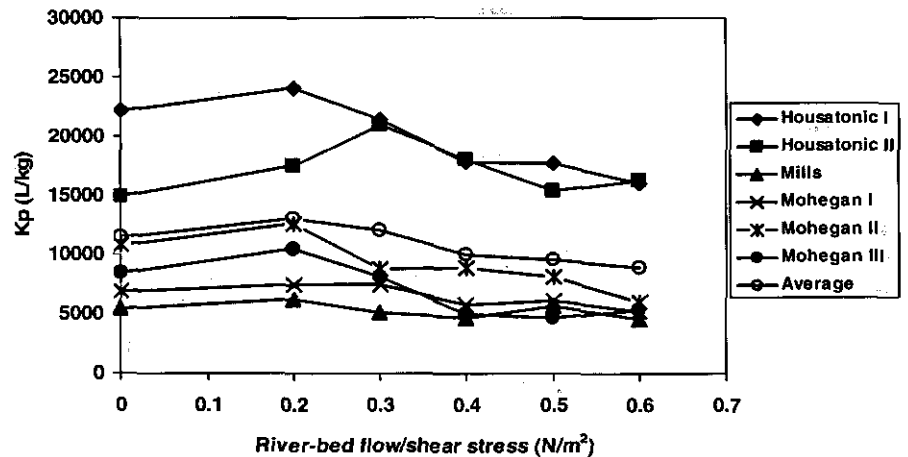
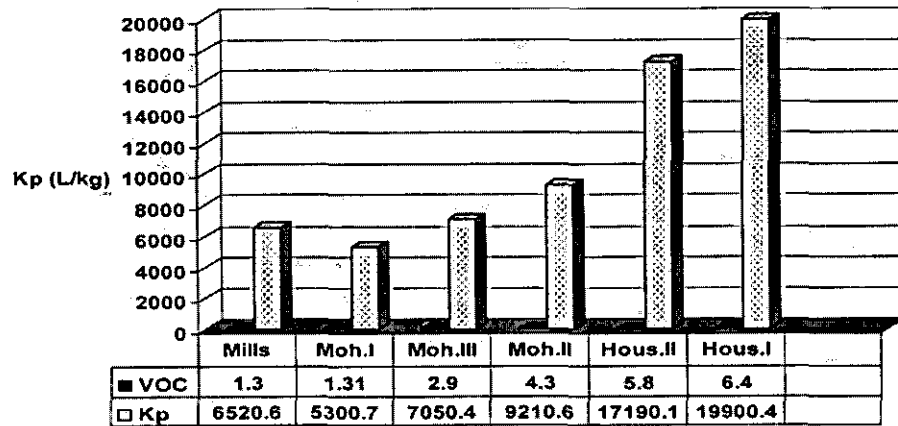


Fig. 5 Average K_p versus percent volatile organic content in the six core sample



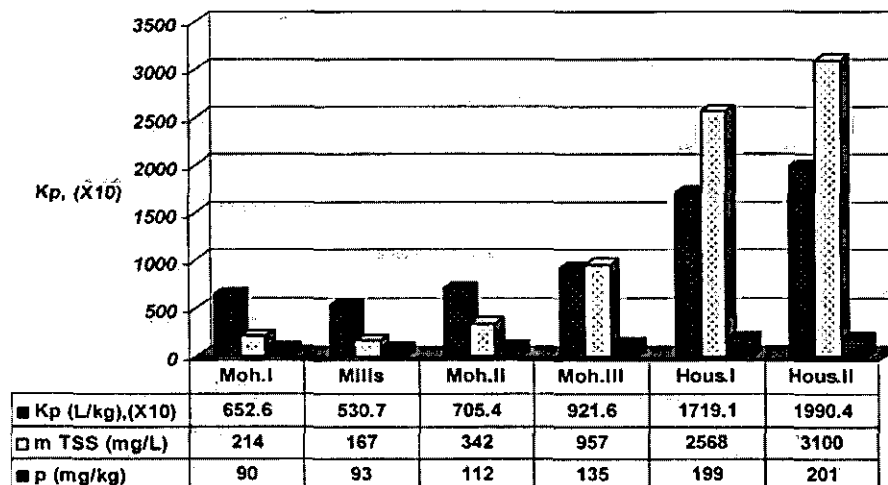
again was supported by the increase in the concentration of dissolved arsenic at higher levels of shear stresses as shown in Fig. 2.

Partition coefficient

Partition coefficients were calculated using Eq. 1, based on particulate and water data for each simulated bed-flow condition. K_p values were plotted against the simulated shear stress for each core in Fig. 4. The visible trend in this relation shows an increase of K_p between shear stresses 0 and 0.2 N/m^2 . The higher values of K_p at the lower stresses is attributed to the high initial fraction of smaller grain size particles and the colloidal material present. Materials of this nature tend to hold a higher concentration of arsenic on the solid phase than larger inorganic particles. The shear stress 0.2 N/m^2 is fairly gentle and only resuspended the very fine portion of the sediment. At higher shear stresses the relation between K_p and river bed-flow

was less obvious. Notable in Fig. 4 is the higher K_p values in Housatonic I and Housatonic II, 19,900 and 17,190 l/kg respectively. These rivers sediments' exhibit high VOC concentrations in the range of 5.8–6.4% compared to the rest of core samples which are all lower than 2.9% VOC. K_p values for the lower content of VOC ranged between 6,520 and 9,210 l/kg. Figure 5 emphasizes the effect of VOC concentration on K_p . A very clear trend showing the increase of the average K_p values with the increase of percent VOC in the sample can be observed. Figure 6 shows the averages of K_p , TSS, and solid phase concentrations of all simulated bed-flows in each sediment core. The graph clearly shows that as the TSS increases, there are also an increase in K_p and an increase in the solid phase concentration. The average of these values incorporates the simulated river bed-flows at high stresses. Under such conditions, both the fine sediment particles impeded deeper in the core, and the larger sand particles will be brought into suspensions.

Fig. 6 Average values of K_p , TSS and solid phase concentration in the six cores evaluated



The ranges of K_p values and arsenic concentrations are shown in Table 2. At lower TSS values, there is a smaller grain size and a higher VOC, which causes the arsenic on the solid phase to be higher. However, on a mass load basis, the amount of arsenic found in the suspended sediment would increase with the increase of river bed-flow.

Conclusion

1. In a simulated river flow under equilibrium conditions of sediment suspension, in most cases the concentrations of the dissolved fraction of arsenic exceeded the EPA MCL set standard of 10 $\mu\text{g/l}$.
2. Significantly higher K_p values were determined under low river-bed flow conditions compared to high river bed-flow conditions, which is attributed primarily to the fine particles size and the organic nature of the suspended solid particles.
3. A positive correlation was observed showing an increase of K_p with the increase of percent VOC in the sediment.
4. As the TSS concentration increases, there is also an increase in K_p values and an increase in arsenic solid phase averages for all simulated bed-flows.
5. K_p values can be beneficial to study arsenic transport in rivers particularly during wet weather conditions, where high bed-flow conditions are generated.
6. Because of the influence of sediment characteristics, VOC, and the dynamic nature of bottom sediment resuspension, the use of the PES is more appropriate in obtaining K_p under real stream conditions than the traditional use of a jar study technique.

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References

- Alkhatib, E., & Castor, K. (2000). Parameters influencing sediment resuspension and link to sorption of inorganic compounds. *Environmental Monitoring and Assessment*, 65, 531–546.
- Alkhatib, E., & Weigand, C. (2002). Parameters affecting partitioning of 6 PCB congeners. *Environmental Monitoring and Assessment*, 78, 1–17.
- ATSDR (2000). *Public health statement for arsenic*. Atlanta, GA: Department of Health and Human Services.
- AWWA (1999). *Standard methods for the examination of water and wastewater*. Denver, CO: American Water Works Association.
- Fetter, C. W. (2002). *Applied hydrology*. New Jersey: Prentice Hall.
- Keon, N. E., Swartz, C. H., Brabandar, D. J., Harvey, C., & Hemond, H. F. (2001). Validation of arsenic sequential extraction method for evaluating mobility in sediments. *Environmental Science & Technology*, 35, 2778–2885.
- Lee, D. Y., Lick, W., & Kang, S. W. (1981). The entrainment and deposition of fine-grained sediments in Lake Erie. *Journal of Great Lakes Research*, 22, 224–233.
- Mackay, D., Shiu, W. Y., & Ching, M. K. (1996). *Illustrated handbook of physical chemical properties and environmental fate for organic chemicals*. New York: Lewis.
- Meinrat, A. (1979). Arsenic speciation in seawater and interstitial waters: The influence of biological-chemical interactions on the chemistry of a trace element. *Limnology and Oceanography*, 24, 440–452.
- Rice, K. C., Conko, K. M., & Hornberger, G. M. (2002). Anthropogenic sources of arsenic and copper to sediments in a Suburban Lake, Northern Virginia. *Environmental Science & Technology*, 36, 4962–4967.
- USEPA. (2005a). Arsenic compounds. Retrieved May, 2006, from <http://www.epa.gov/ttn/atw/hlthef/arsenic>.
- USEPA. (2005b). Arsenic in drinking water. Retrieved July 10, 2006, from <http://www.epa.gov/safewater/arsenic>.