

ARSENIC IN U.K. ESTUARINE SEDIMENTS AND ITS AVAILABILITY TO BENTHIC ORGANISMS

W. J. LANGSTON

The Laboratory, Marine Biological Association, Citadel Hill, Plymouth

(Figs. 1–7)

Arsenic concentrations in estuarine sediments from England and Wales range over three orders of magnitude. The highest concentrations, up to 2500 $\mu\text{g/g}$, occur in the sediments of estuaries in south west England associated with past or present metalliferous mining activity. Strong correlations exist between arsenic and iron in 1 N-HCl extracts of different estuarine sediments. The As/Fe ratio in those estuaries not contaminated with mine wastes is 11×10^{-4} , increasing to 190×10^{-4} in metalliferous sediments.

The highest arsenic concentrations in organisms, almost 200 $\mu\text{g/g}$, are found at those sites in estuaries where high As/Fe ratios exist in the sediment. Concentrations of arsenic in estuarine organisms correlate more significantly with the As/Fe ratio in sediments than arsenic levels alone. This is most evident in the bivalve *Scrobicularia plana* (da Costa) where the proportion of readily extractable (1 N-HCl) Fe in sediments mediates the availability of As in a predictable way. Other factors, important in the selection of *Scrobicularia* as an indicator of available arsenic in sediments, such as tissue distribution and the effect of size/age on arsenic content, are discussed.

INTRODUCTION

Several forms of arsenic, such as arsenite and arsines, are known to be toxic to a variety of organisms (Ferguson & Gavis, 1972) and are possibly carcinogenic (Neubauer, 1947). Sodium arsenite is used in aquatic systems as a herbicide, while organic arsenicals are used as herbicides and insecticides in a wide variety of agricultural applications and may be extremely persistent (Foley *et al.* 1978; Ferguson & Gavis, 1972). Although high levels of arsenite are occasionally present in fresh water samples (Klumpp & Peterson, 1979), the majority of arsenic in seawater is in the relatively harmless form of arsenate (Andreae, 1978) and is thus not considered such a potentially hazardous element as mercury, cadmium or lead. Extremely high arsenic concentrations have, however, been reported in waters and sediments receiving drainage from metalliferous mining areas (Penrose, Black & Hayward, 1975; Aston *et al.* 1975). The south-west of England has been a centre for such activity since pre-Roman times and not until the late nineteenth century did the production of arsenic begin to decline (Dines, 1956).

Experimental studies have shown that arsenic can be accumulated from contaminated water and food by a number of marine organisms including phytoplankton, shrimp and mussels (Fowler & Ünlü, 1978; Ünlü & Fowler, 1979). There is some evidence linking high levels in marine organisms with environmental levels (Penrose *et al.* 1975; Klumpp & Peterson, 1979) but few data are available of direct relationships. The purpose of this paper is to present evidence of relationships between environmental (sediment) arsenic and that occurring in selected organisms from estuaries in England and Wales. The importance of iron in determining the distribution and availability of arsenic is considered.

MATERIALS AND METHODS

Sediments, *Fucus vesiculosus*, *Nereis (Hediste) diversicolor* (O. F. Müller) and *Scrobicularia plana* were collected, with other common species where available, from a number of estuaries in England and Wales (Table 1, Fig. 1). Oxidized surface sediments were sieved through a 100 μm -polythene mesh and a 2 ml wet sample extracted with 1 N-hydrochloric acid or 25 % acetic acid to provide a nominal value of 'biologically available' metal (Luoma & Bryan, 1978). A 3 ml substample was refluxed with concentrated nitric acid (Analar) for 2 h to provide a 'total' extract.

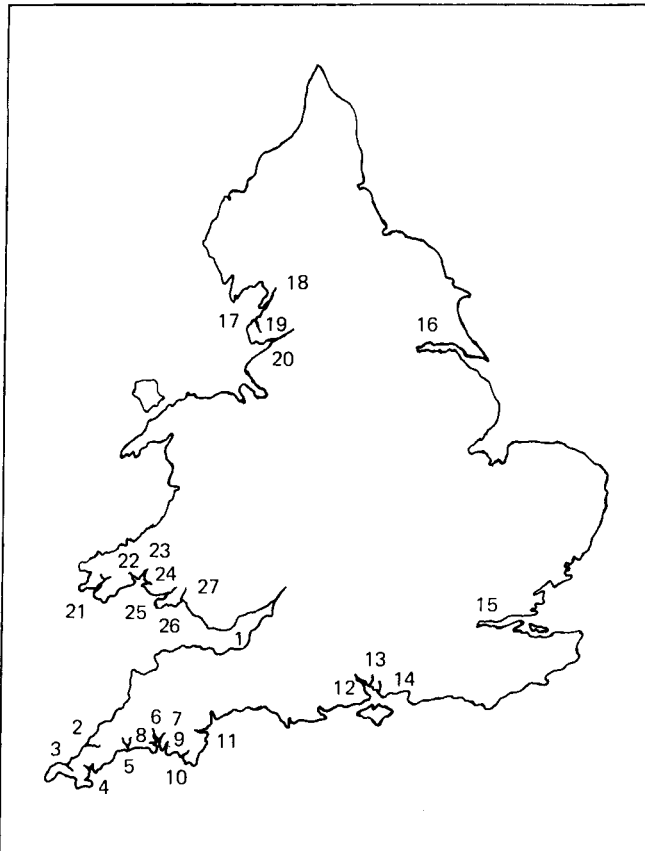


Fig. 1. Estuaries sampled. (1) Severn and Bristol Channel, (2) Gannel, (3) Hayle, (4) Restronguet Creek, Fal, (5) Looe, (6) Tamar, (7) Tavy, (8) Lynher, (9) Plym, (10) Avon, (11) Teign, (12) Test, (13) Itchen, (14) Hamble, (15) Thames, (16) Humber, (17) Morecambe Bay, (18) Lune, (19) Wyre, (20) Ribble, (21) Cleddau, (22) Taf, (23) Tywi, (24) Gwendraeth, (25) Loughor, (26) Swansea Bay, (27) Neath.

Seaweed was washed and subsamples from behind the growing tips of several plants pooled and finely chopped. *Scrobicularia* and *Nereis* were collected from the middle of their vertical ranges and held in 50 % sea water for 7 days. Worms were held in acid-washed sand to aid depuration (Bryan & Hummerstone, 1973). Usually six *Scrobicularia* of approximately 4 cm and up to 30 *Nereis* were pooled and homogenized (Silverson Machines Ltd). Subsamples of weed (1–3 g) or homogenized tissue (up to 10 g depending on water content) were mixed with 15 ml ashing slurry and dry ashed at 500 °C in a muffle furnace (after Penrose *et al.* 1975). After cooling, the residues were dissolved in 25 ml distilled hydrochloric acid and made up to 50 ml with distilled water so that final solutions were approximately 3 N-HCl.

Arsenic was determined by flameless atomic absorption using a Varian-Techtron AA4 spectrophotometer. Arsine, generated by reaction of 5 ml 5% sodium borohydride (Ventron) with up to 0.5 ml sample in a total of 4 ml 3 N-HCl, was collected in a liquid-nitrogen trap and volatilized into a Perkin Elmer HGA 70 graphite furnace heated to 2500 °C. Iron in 1 N-HCl sediment extracts was measured by flame atomic absorption spectrophotometry (Perkin Elmer 603).

RESULTS

Analytical method

The reproducibility and detection limit, based on the analysis of seven 100 nanogram standards and blanks, was 2.7% and 1.1 ng respectively. Response was linear over the range used (0–200 ng) and interferences from other metals negligible. Preliminary investigations with wet ashing methods using mixtures of nitric and sulphuric acids gave adequate recovery of inorganic arsenic but incomplete recovery of organoarsenicals. The dry ashing procedure used in the present study resulted in recoveries of 106 ± 6 , 95 ± 9 and $94 \pm 14\%$ for inorganic arsenic (as arsenic trichloride), dimethylarsenic acid and arsanilic acid respectively. Six analyses of fish flour containing 10 µg/g As (ICES 3rd Intercalibration Exercise) produced a mean value of 10.5 ± 0.3 µg/g.

Arsenic in sediments

Total (nitric acid extractable) arsenic concentrations in estuarine sediments have been measured ranging from 2 µg/g in Morecambe Bay to 2500 µg/g in Restronguet Creek, a

Table 1. Ranges of arsenic concentrations in sediments (total), *Fucus vesiculosus*, *Nereis diversicolor* and *Scrobicularia plana*

Estuary	Sites	Date	As concentration (µg/g dry wt.)				
			Sediment	<i>Fucus</i>	<i>Nereis</i>	<i>Scrobicularia</i>	
South-west England							
Severn and Bristol Channel	21	Nov. 78	7–12	13–28	5.9–16	13–26	
Gannel	2	Sept. 79	110–230	—	21	98	
Hayle	2	Sept. 79	550–950	138	73–83	97–106	
Restronguet Creek, Fal	8	April 78– April 79	120–2500	63–160	58–87	160–190	
Looe	10	April 79	7–16	—	—	—	
Tamar, Tavy, Lynher	13	June 79	42–131	38–60	10–20	28–65	
Plym	2	Nov. 78	41–43	—	—	26–28	
Avon (Devon)	1	Feb. 79	13	17	7.8	23	
Teign	6	May 78	12–74	23–53	8–15	21–37	
Rest of England and Wales							
Southampton Water (Test, Itchen, Hamble)	8	April 78	5–28	14–34	6–14	8–25	
Thames	5	Nov. 77	4–6	11–18	—	16–17	
Humber	14	May 78	18–94	26–34	13–27	28	
N.W. England (Morecambe Bay, Lune, Wyre, Ribble)	12	Sept. 78	2–11	21–24	7.6–20	13–24	
S. Wales (Cleddau, Taf, Tywi, Gwendraeth, Loughor, Swansea Bay, Neath)	27	Oct. 78, May 79	3–24	14–55	4–18	5–25	

branch of the Fal Estuary (Table 1). Although nitric acid does not attack arsenic tightly held in lattice positions of siliceous minerals, comparison with ammonium iodide fusion and hydrofluoric acid treatments suggest almost all the arsenic is removed. The 'biologically available' arsenic removed by 1 N-HCl and 25% HAc amounted to 60% (range 27–93) and 22% (8–36) of the total respectively.

Estuarine sediments most enriched in arsenic are those receiving drainage from former mining areas, although locally elevated concentrations do occur in other estuaries as a result of industrial inputs.

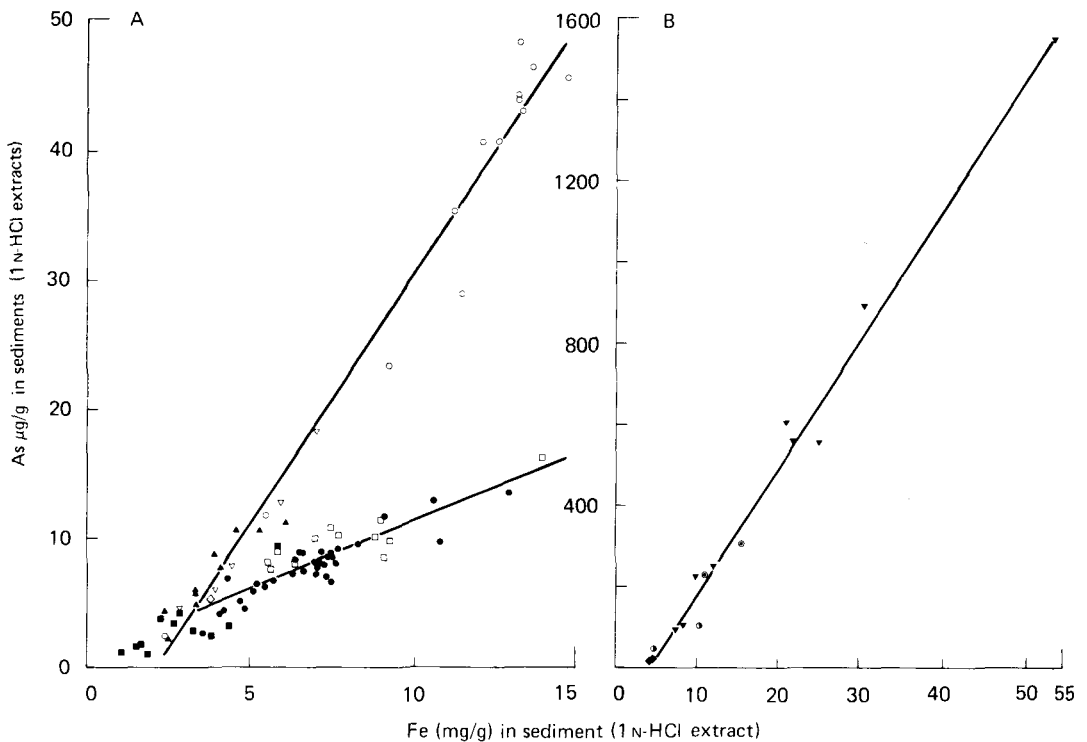


Fig. 2. Correlation between arsenic and iron in sediments (1 N-hydrochloric acid extracts). (A) N.W. England (■). Severn and S. Wales Estuaries 1978 (●) and 1979 (□). Equation is $\text{As sediment} = 1.05 \text{ Fe sediment} + 0.7943$ ($n = 45, r^2 = 0.8012$). For the Looe (▲), Tamar (○), Teign (▽) and Avon (◇) Estuaries the equation is $\text{As sediment} = 3.83 \text{ Fe sediment} - 6.44$ ($n = 24, r^2 = 0.9663$). (B) Plym (◆), Gannel (●), Hayle (○) and Restronguet Creek/Fal (▼) Estuaries. Equation is $\text{As sediment} = 31.27 \text{ Fe sediment} - 124.78$ ($n = 15, r^2 = 0.9885$).

In an attempt to determine which factors, if any, might influence the distribution and availability of arsenic in sediments, relationships between arsenic and iron in extracts were considered together with total organic carbon (estimated by ashing sediments at 400 °C). Highly significant correlations exist between arsenic and iron in 1 N-hydrochloric acid extracts and all but one suite of estuarine sediments in this study can be categorized by one of the three relationships shown in Fig. 2. In metalliferous mining areas of south-west England arsenic and iron might be expected to be connected as the

principal ore of arsenic worked is arsenopyrite, FeAsS (Dewey, 1920). It is also known that iron precipitates rapidly as ferric hydroxide upon contact with seawater and that arsenate is actively scavenged by ferric hydroxide (Crecelius, Bothner & Carpenter, 1975). Coprecipitation of arsenate with iron should therefore occur in estuaries.

The steep slope (31.27) of Restronguet Creek, Hayle, Gannel and Plym sediments, all associated with old mine drainage, indicates a different arsenic-iron relationship to that of the North West England, Severn and South Wales Estuaries (slope 1.05, Fig. 2). An intermediate relationship exists in sediments of the Looe, Tamar, Teign and Avon Estuaries (slope = 3.83). Humber sediments are not uniform with respect to their As/Fe ratios due to a significant input of arsenic from an ore refinery. A concentration of 480 $\mu\text{g/l}$ As was measured leaving an effluent pipe decreasing to 121 $\mu\text{g/l}$ (total) in the estuary water nearby. The distribution of arsenic and As/Fe ratios in Humber sediments in relation to this input is shown in Fig. 3.

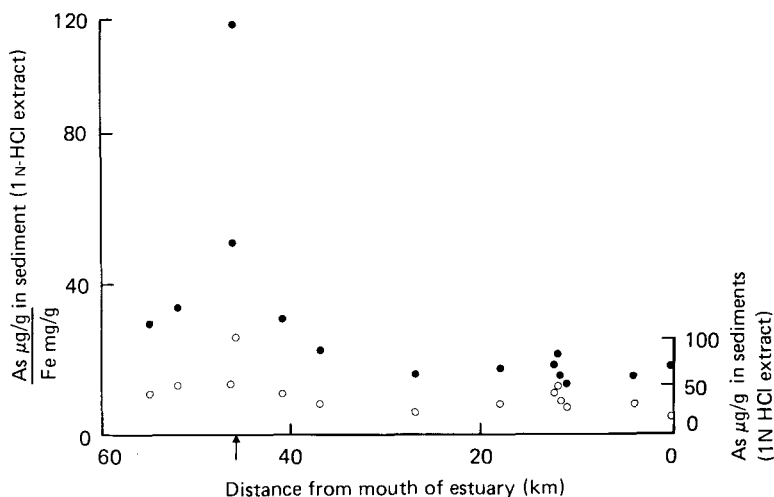


Fig. 3. Distribution of arsenic (○) and As/Fe ratios (●) in 1 N-HCl extracts of Humber sediments. Arrow indicates point of discharge of metal refinery effluent.

Arsenic in biota – choice of indicator species

Several members of estuarine communities were collected from the same site, where present, to determine which species were the best indicators of arsenic contamination. *Scrobicularia* consistently concentrates arsenic to a higher level than other species as indicated by the ratios shown in Table 2, and is of suitable size and widespread distribution to be considered a good indicator species. In highly contaminated estuaries such as Restronguet Creek the concentration of arsenic in *Scrobicularia* is increased relative to other species (Table 2) adding further to the value of this infaunal bivalve as an indicator of biologically available arsenic in sediments.

Table 2. Ratios (*As Scrobicularia*)/(*As sediment, other organisms*) from contaminated and uncontaminated estuaries

Total sediment conc. ($\mu\text{g/g}$)	Sediment	<i>Nereis diversicolor</i>	<i>Fucus vesiculosus</i>	<i>Mytilus edulis</i>	<i>Cerastoderma edule</i>	<i>Macoma balthica</i>	<i>Littorina littorea</i>	<i>Littorina obtusata</i>	<i>Littorina saxatilis</i>
Estuary: Severn/S. Wales									
13 (9.7-18)*	1.49	1.72	0.93	1.82	1.62	1.09	1.18	1.05	2.81
Estuary: Restronguet Creek									
1500 (1400-1600)	0.16	3.07	2.19	—	—	—	3.5	2.9	3.07

* Figures in parentheses indicate range of sediment concentrations.

Arsenic in *Scrobicularia*

Influence of age and size

Three *Scrobicularia* populations from the Gannel, Tamar and Loughor Estuaries have been selected to illustrate the variation that may occur in the relationship between size, age and arsenic tissue burden (Figs. 4, 5). The ages of *Scrobicularia* were determined from their lengths using the Ford-Walford plot (Hughes, 1970).

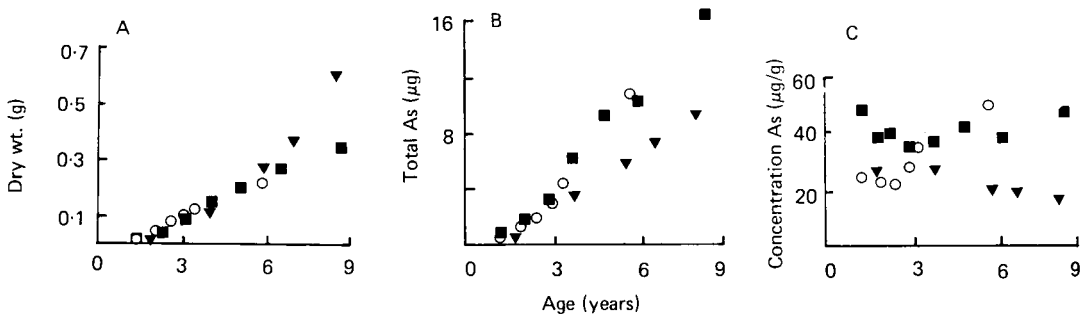


Fig. 4. (A) Relationship between age and dry weight. (B) Age and total arsenic content. (C) Age and arsenic concentration in *Scrobicularia plana* from the Tamar (■), Gannel (○) and Loughor (▼) Estuaries.

The growth rates (increases in dry weight with age) of the three populations are different from each other (Fig. 4A). Growth in Gannel *Scrobicularia* slows gradually with age while the reverse is true of Loughor animals. The increase in weight of Tamar animals is maintained at a constant rate through life.

The total arsenic burden in *Scrobicularia* increases with age in all three populations (Fig. 4B); however, the relationship between tissue concentration and age depends upon the rate at which arsenic is assimilated in relation to the growth of the animal (Fig. 4C). Tamar *Scrobicularia* accumulate arsenic and grow at relatively similar rates so that concentration does not change significantly with increasing age. Loughor animals accumulate arsenic at a constant rate but growth is more rapid in older individuals and tissue concentrations decrease slightly with age. There is a trend for growth to slow down

and total arsenic accumulation to accelerate with age in Gannel animals resulting in a more obvious increase in tissue concentration in animals more than 2 years old.

The relationships of size (shell length), arsenic concentration and dry weight are plotted on logarithmic scales in Fig. 5. Tissue concentration can be related to body weight using the equation $\log_{10} \text{conc} = b \log_{10} \text{weight} + \log_{10} a$, for animals greater than 0.02 g dry wt (Fig. 5B). Values of b (slope) are 0.5734, -0.3606 and 0.0653, indicating arsenic concentration increases, decreases and is independent of size in Gannel, Loughor and Tamar populations respectively (Fig. 5B). Relationships between arsenic and other metals in *Scrobicularia* tissues are, at present, obscure. Like arsenic, concentrations of silver, cadmium, cobalt, copper, nickel, lead and zinc increased with size in Gannel animals (Bryan & Hummerstone, 1978). However, of ten metals analysed, only iron resembles arsenic in being independent of size in Tamar *Scrobicularia* (Bryan & Uysal, 1978).

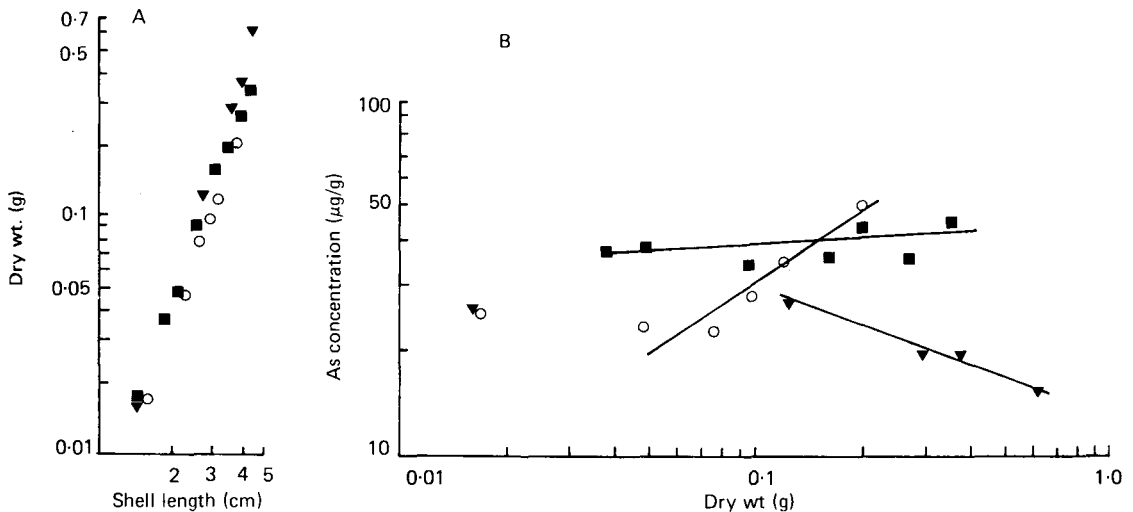


Fig. 5. (A) Relationship between shell length and dry weight of whole soft parts in *Scrobicularia plana*. Equations of lines are $\log_{10} \text{dry weight} = 2.8003 \text{ shell length} - 2.3255$ for Gannel animals (\circ), $\log_{10} \text{dry weight} = 3.1241 \log_{10} \text{shell length} - 2.2805$ for Loughor animals (\blacktriangledown) and $\log_{10} \text{dry weight} = 2.6729 \log_{10} \text{shell length} - 2.1663$ for Tamar animals (\blacksquare). (B) Relationship between dry weight and arsenic concentration in *Scrobicularia plana*. Equations (for animals larger than 0.02 g dry wt) are $\log_{10} \text{As concentrations} = 0.5734 \log_{10} \text{weight} + 2.066$ for Gannel animals, $\log_{10} \text{As concentrations} = -0.3606 \log_{10} \text{weight} + 1.1177$ for Loughor animals, $\log_{10} \text{As concentration} = 0.0653 \log_{10} \text{weight} + 1.6588$ for Tamar animals (symbols same as Fig. 4).

The differences in arsenic/age relationships in the three populations studied is unlikely to be due to differences in contamination, as concentrations in all three are comparable. Further evidence of the importance of growth rate and condition are shown in Fig. 5B. Differences in condition between populations are greatest in larger animals, corresponding to the most significant differences in arsenic concentrations.

Tissue distribution

Two *Scrobicularia* populations, from the Hayle and Tamar Estuaries, show almost identical trends in the partitioning of arsenic between tissues, despite differences in total metal concentration (Table 3).

Table 3. *Distribution of arsenic in tissues of Scrobicularia plana* ($\mu\text{g/g dry wt}$)*

Estuary	Whole animal	Digestive gland	Mantle and siphons	Gonadial foot	Muscular foot	Adductor muscle	Gills
Hayle	87	137 (35)	97 (35)	88 (11)	55 (6)	52 (5)	152 (9)
Tamar	38	56 (36)	65 (39)	53 (9)	55 (5)	36 (5)	48 (6)

* Figures in parentheses are percentages of total As burden

More than one third of the total body arsenic resides in the digestive gland – a similar distribution to that found for copper and silver in the digestive gland of Tamar *Scrobicularia* (Bryan & Uysal, 1978). That this organ, which accounts for one quarter of the total dry weight, should account for a greater proportion of the total arsenic is a direct indication of uptake from ingested sediments, although uptake from solution cannot be discounted. More conclusive evidence of the importance of sediment uptake is available for cadmium, cobalt, chromium, nickel, lead and zinc, as generally more than three-quarters of these metals is found in the digestive gland (Bryan & Uysal, 1978).

Availability of arsenic in sediments to Scrobicularia plana

The concentration of arsenic in sediments is of prime importance in determining tissue concentrations in *Scrobicularia plana*. Generally, the levels in these animals reflect total arsenic in sediments (Table 1) and also that extracted by dilute acids. However, preliminary data indicated that relationships between tissue levels and sediment extracts alone were not directly proportional, though weak acid extracts, particularly 1 N hydrochloric were better indicators of available arsenic than concentrated nitric. Hydrochloric acid extractable iron was examined as a possible controlling factor in this relationship in view of the associations between iron and arsenic described elsewhere in this paper, and also of its role in determining the biological availability of lead (Luoma & Bryan, 1978). When arsenic in bivalves was plotted against the arsenic/iron ratio in 1 N-HCl sediment extracts significant correlations were obtained using linear ($r^2 = 0.93$) and logarithmic ($r^2 = 0.82$) scales. The result of the logarithmic plot is shown in Fig. 6. Less-significant correlations ($r^2 = 0.64$) were obtained between tissue and sediment concentrations by exclusion of iron from regression equations (legend Fig. 6).

Additional samples were collected at seven different sites in the Tamar and Fal Estuaries to assess the value of the above relationship in predicting arsenic levels in *Scrobicularia*. Using the linear regression equation

As tissue concentration = $6.765 \text{ As}(\mu\text{g/g})/\text{Fe}(\text{mg/g}) \text{ sediment (HCl)} + 11.239$,
 the error between predicted and observed values in animals was $17.5 \pm 12.4\%$. The error in predicted values using the regression equation
 $\log_{10} \text{ As tissue concentration} = 0.6767 \log_{10} \text{ As}(\mu\text{g/g})/\text{Fe}(\text{mg/g}) \text{ sediment (HCl)} + 1.2121$
 was marginally higher ($22 \pm 18\%$).

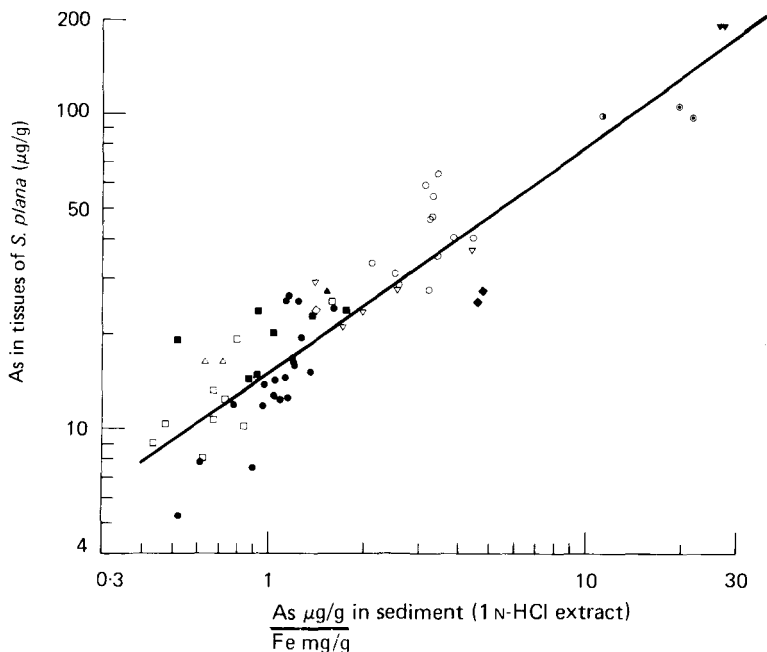


Fig. 6. Relationship between concentration of arsenic in *Scrobicularia* and As/Fe ratio in 1 N-HCl sediment extracts. Equation is $\log_{10} \text{As } Scrobicularia = 0.6767 \log_{10} \text{As/Fe sediment} + 1.212$ $n = 75, r^2 = 0.82$. Except for Thames (Δ), Humber (\blacktriangle) and Southampton (\square) *Scrobicularia*, symbols for different estuaries are the same as Fig. 2. [The relationship between arsenic in *Scrobicularia* and sediment is $\log_{10} \text{As } Scrobicularia = 0.4363 \log_{10} \text{As sediment} + 0.8875$ ($n = 75, r^2 = 0.64$).]

Availability of arsenic in sediments to Nereis diversicolor and Fucus vesiculosus

The polychaete *Nereis diversicolor* and seaweed *Fucus vesiculosus* are commonly found in estuaries and may be considered candidates for use as biological indicators of arsenic contamination. Arsenic levels in these species generally reflect sediment concentrations (Table 1), however, correlations between tissue concentrations and As/Fe ratios in sediments were poor (*Fucus* $r^2 = 0.6159$, *Nereis* $r^2 = 0.5524$) in contrast to *Scrobicularia* (Fig. 7). Consequently, predictions of available arsenic in *Nereis* and *Fucus* from sediments are tenuous. Removing iron from these equations, described in the legend of Fig. 7, does not significantly alter the relationship between arsenic in *Fucus* or *Nereis* and sediments and it may be that other factors such as water concentration, phosphate competition or the ability to regulate arsenic may be more important than iron in determining the availability of this metal. Organic matter – arsenic associations do exist in estuaries (Waslenchuk & Windom, 1978) but no evidence was found of total organic carbon influence upon arsenic occurrence and availability in this study.

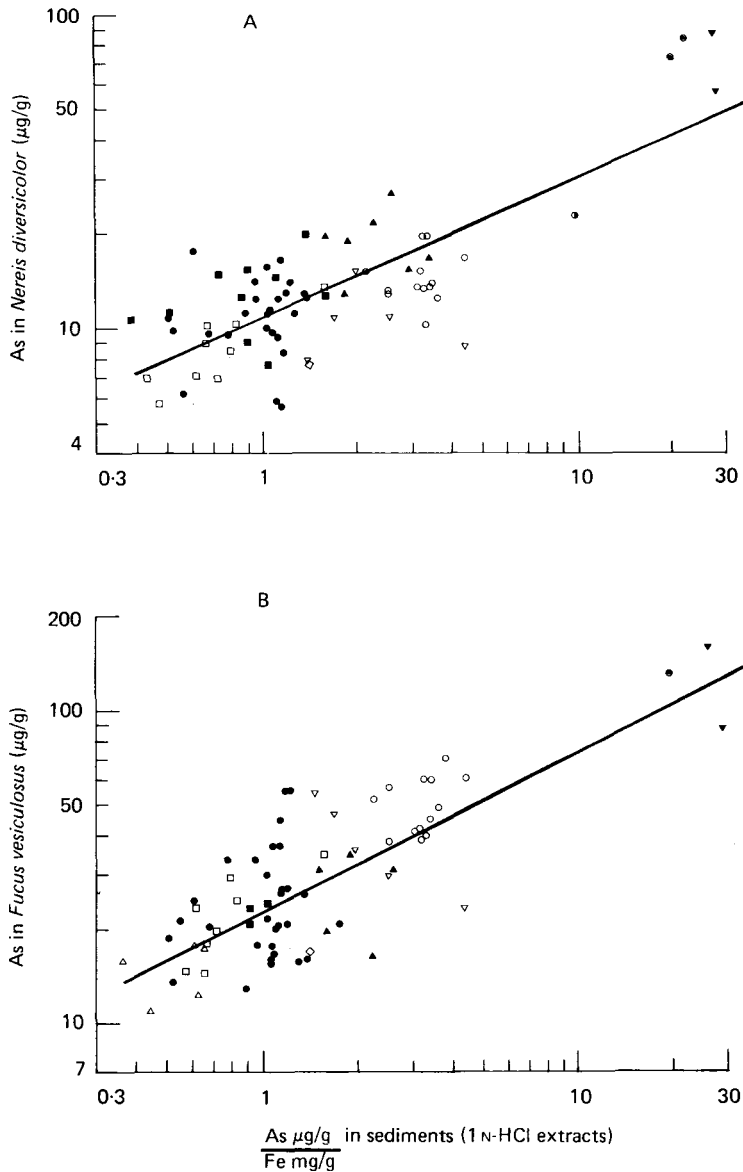


Fig. 7. (A) Relationship between concentration of arsenic in *Nereis diversicolor* and As/Fe ratio in 1 N-HCl sediment extracts. Equation is $\log_{10} \text{As } Nereis = 0.4546 \log_{10} \text{As/Fe sediment} + 1.0249$ ($n = 82$, $r^2 = 0.5524$). [Without iron, equation is $\log_{10} \text{As } Nereis = 0.2804 \log_{10} \text{As sediment} + 0.8038$ ($n = 82$, $r^2 = 0.44$).] (B) Relationship between concentration of arsenic in *Fucus vesiculosus* and As/Fe ratio in 1 N-HCl sediment extracts. Equation is $\log_{10} \text{As } Fucus = 0.4952 \log_{10} \text{As/Fe sediment} + 1.3766$ ($n = 82$, $r^2 = 0.6159$). Symbols as in Fig. 6. [Without iron, equation is $\log_{10} \text{As } Fucus = 0.302 \log_{10} \text{As sediment} + 1.13$ ($n = 82$, $r^2 = 0.52$).]

DISCUSSION

Arsenic has been measured in estuarine sediments ranging over three orders of magnitude, with the highest values occurring in areas of metalliferous mining activity in the south-west of England. Aston *et al.* (1975) found similar distributions of arsenic in a semiquantitative study of freshwater streams where the occurrence in sediments reflected the contamination of overlying waters. The most probable source of arsenic in these waters was considered to be from dissolution of arsenic ores.

Enhanced concentrations of arsenic have been measured in estuarine sediments as a result of industrial discharge, as in the Humber Estuary, though any significant effect of such sources seems to be localized. The major influence of arsenic-bearing drainage from abandoned mine workings on marine sediments in Newfoundland was also reported to be extremely localized (Penrose *et al.* 1975). This contrasts to a more widespread distribution of contaminated sediments within the estuaries associated with mine workings, found in the present study.

Arsenic usually enters estuaries in particulate form, from weathering of ores such as arsenopyrite (FeAsS), and as arsenite and arsenate ions which may be scavenged by hydrated iron oxides in estuarine sediments (Ferguson & Gavis, 1972; Crecelius *et al.* 1975). Strong correlations exist between 1 N-HCl extractable iron and arsenic in estuarine sediments, the precise nature of which is determined by the degree of mineralization in the surrounding watershed. In estuaries associated with arsenopyrite lodes, such as Restronguet Creek and Hayle the As/Fe ratio approaches 190×10^{-4} in contrast to a ratio of 32×10^{-4} in other estuaries in the south-west and 11×10^{-4} in estuaries not associated with metalliferous mines. Comparable figures for North Atlantic sediments are reported by Neal, Elderfield & Chester (1979) and for ferromanganese nodules by Calvert & Price (1977). The 'authigenic' (readily extractable) As/Fe ratio in most deep sea sediments is identical to that found in uncontaminated estuaries in the present study and arsenic is believed to be of sea-water origin. The As/Fe ratio increases to 20–50 $\times 10^{-4}$ in metalliferous deep-sea sediments and nodules.

Ratios of As/Fe in Humber sediments ranged from 13×10^{-4} to 119×10^{-4} , depending on their proximity to an aqueous industrial input. The highest of these ratios is comparable to that found in estuaries such as Restronguet Creek and suggests that arsenic in sediments from these estuaries could also be largely derived from an aqueous source, such as adit drainage. Elevated levels of dissolved arsenic, up to 121 $\mu\text{g/l}$, have been measured in the Carnon River which receives water from the County Adit, an extensive underground drainage system, before entering Restronguet Creek.

Similar variations in the lead-iron relationships in sediments have been used to characterize those estuaries receiving wastes from old lead mines (Luoma & Bryan, 1978).

Arsenic may be over-emphasized as a potentially toxic agent when compared with some other metals. Many marine animals can convert arsenic to a stable organic form such as arsenocholine avoiding possible harmful effects (Lunde, 1977; Irgolic *et al.* 1977). Nevertheless it is important to know to what extent arsenic is accumulated in living organisms and which are the controlling factors; only then can potentially damaging situations be recognized.

The concentration of arsenic in 1 N-HCl sediment extracts is important in determining

the degree of contamination in the deposit feeding bivalve *Scrobicularia plana*. However, it is the amount of similarly extractable iron in sediments which influences the availability of arsenic in a predictable way. Using equations described above, reasonable estimates of biologically available arsenic can be derived by measurement of metals in sediment extracts from sites where suitable organisms are not present.

Although iron has been implicated as the major influence on availability of arsenic to *Scrobicularia*, and has been similarly reported as controlling the availability of lead (Luoma & Bryan, 1978), other controlling factors cannot be discounted for other estuaries.

Concentrations of arsenic in *Scrobicularia* from Restronguet Creek are higher than for most other species reported in the literature even from contaminated areas (Penrose *et al.* 1975; Klumpp & Peterson, 1979) and are clearly good indicators of estuarine contamination. In addition to evidence from arsenic tissue distribution, the significant sediment – *Scrobicularia* relationship described above supports the view that particulate arsenic is the most important source of metal to these bivalves, although some absorption from solution cannot be discounted.

Size is not such an important factor controlling arsenic concentration in *Scrobicularia* compared with other metals (Bryan & Uysal, 1978) except perhaps in populations in poor condition or where growth is slow. When comparing populations, however, it may be more reliable to avoid animals at extreme ends of the size range.

Thanks are due to Dr G. W. Bryan for helpful discussions and to Mrs J. Sleep, Mr L. Hummerstone, and Mr G. Burt for their assistance with this work which was supported by the Department of the Environment under Contract DGR 480/51.

REFERENCES

- ANDREAE, M. O., 1978. Distribution and speciation of arsenic in natural waters and some marine algae. *Deep-Sea Research*, **25**, 391–402.
- ASTON, S. R., THORNTON, I., WEBB, J. S., MILFORD, B. L. & PURVES, J. B., 1975. Arsenic in stream sediments and waters of South West England. *Science of the Total Environment*, **4**, 347–358.
- BRYAN, G. W. & HUMMERSTONE, L. G., 1973. Adaptation of the polychaete *Nereis diversicolor* to manganese in estuarine sediments. *Journal of the Marine Biological Association of the United Kingdom*, **53**, 859–872.
- BRYAN, G. W. & HUMMERSTONE, L. G., 1978. Heavy metals in the burrowing bivalve *Scrobicularia plana* from contaminated and uncontaminated estuaries. *Journal of the Marine Biological Association of the United Kingdom*, **58**, 401–419.
- BRYAN, G. W. & UYSAL, H., 1978. Heavy metals in the burrowing bivalve *Scrobicularia plana* from the Tamar Estuary in relation to environmental levels. *Journal of the Marine Biological Association of the United Kingdom*, **58**, 89–108.
- CALVERT, S. E. & PRICE, N. B., 1977. Geochemical variation in ferromanganese nodules and associated sediments from the Pacific Ocean. *Marine Chemistry*, **5**, 43–74.
- CRECELIOUS, E. A., BOTHNER, M. H. & CARPENTER, R., 1975. Geochemistries of arsenic, antimony, mercury and related elements in sediments of Puget Sound. *Environmental Science and Technology*, **9**, 325–333.
- DEWEY, H., 1920. Arsenic and antimony ores. *Memoirs of the Geological Survey. Special Reports on the Mineral Resources of Great Britain*, **15**, 59 pp.
- DINES, H. G., 1956. *The Metalliferous Mining Region of South-West England*, vol. 2. 795 pp. London: H.M. Stationery Office.
- FERGUSON, J. F. & GAVIS, J., 1972. A review of the arsenic cycle in natural waters. *Water Research*, **6**, 1259–1274.
- FOLEY, R. E., SPOTILA, J. R., GIESY, J. P. & WALL, C. H., 1978. Arsenic concentrations in water and fish from Chautaugua Lake, New York. *Environmental Biology of Fishes*, **3**, 361–367.

- FOWLER, S. W. & ÜNLÜ, M. Y., 1978. Factors affecting bioaccumulation and elimination of arsenic in the shrimp *Lysomata seticaudata*. *Chemosphere*, **7**, 711-720.
- HUGHES, R. N., 1970. Population dynamics of the bivalve *Scrobicularia plana* (da Costa) on an intertidal mudflat in North Wales. *Journal of Animal Ecology*, **39**, 333-356.
- IRGOLIC, K. J., WOOLSON, E. A., STOCKTON, R. A., NEWMAN, R. D., BOTTINO, N. R., ZINGARO, R. A., KEARNEY, P. C., PYLES, R. A., MAEDA, S., MCSHANE, W. J. & COX, E. R., 1977. Characterization of arsenic compounds formed by *Daphnia magna* and *Tetraselmis chuii* from inorganic arsenate. *Environmental Health Perspectives*, **19**, 61-66.
- KLUMPP, D. W. & PETERSON, P. J., 1979. Arsenic and other trace elements in the waters and organisms of an estuary in S. W. England. *Environmental Pollution*, **19**, 11-20.
- LUNDE, G., 1977. Occurrence and transformation of arsenic in the marine environment. *Environmental Health Perspective*, **19**, 47-52.
- LUOMA, S. N. & BRYAN, G. W., 1978. Factors controlling the availability of sediment-bound lead to the estuarine bivalve *Scrobicularia plana*. *Journal of the Marine Biological Association of the United Kingdom*, **58**, 793-802.
- NEAL, C., ELDERFIELD, H. & CHESTER, R., 1979. Arsenic in sediments of the North Atlantic Ocean and the Eastern Mediterranean Sea. *Marine Chemistry*, **7**, 207-219.
- NEUBAUER, O., 1947. Arsenical cancer: a review. *British Journal of Cancer*, **1**, 192-251.
- PENROSE, W. R., BLACK, R. & HAYWARD, M. J., 1975. Limited arsenic dispersion in sea water, sediments, and biota near a continuous source. *Journal of the Fisheries Research Board of Canada*, **32**, 1275-1281.
- ÜNLÜ, M. Y. & FOWLER, S. W., 1979. Factors affecting the flux of arsenic through the mussel *Mytilus galloprovincialis*. *Marine Biology*, **51**, 209-219.
- WASLENCHUK, D. G., & WINDOM, H. L., 1978. Factors controlling the estuarine chemistry of arsenic. *Estuarine and Coastal Marine Science*, **7**, 455-464.