SEASONAL VARIATION OF HEAVY METALS IN *MYTILUS EDULIS*, *FUCUS VESICULOSUS* AND SEDIMENT FROM THE SHANNON ESTUARY

Caitríona O'Leary and John Breen

ABSTRACT

Samples of *Mytilus edulis*, together with samples of sediment and *Fucus vesiculosus*, were taken monthly from each of five shores on the south coast of the Shannon Estuary from March 1992 to December 1993 inclusive. Samples were digested individually and the levels of iron, zinc, manganese, cobalt, chromium and copper were determined using atomic absorption spectrophotometry. Levels of metals were lower than previously published values from Irish east coast estuaries, including Dublin, except for a few high levels in *M. edulis*, which did not persist in the tissues and were probably lost through excretion, spawning or detoxification. Of the metals analysed iron showed the highest levels. This was attributed in part to the background levels of iron in sediment. On some occasions high metal levels in sediment did not lead to higher levels either in *F. vesiculosus* or in *M. edulis*, suggesting that metals in *M. edulis* may come from other sources, including anthropogenic inputs, in the estuary. On an international scale the levels in *M. edulis* of the six metals studied were relatively low in the Shannon Estuary. The longer-term monthly sampling regime followed in this study is important since it shows that occasional high levels, which may be detected by once-off studies, are not always maintained.

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INTRODUCTION

The Shannon Estuary (Fig. 1), the largest in Ireland, extends over 100km from the seaward boundary to the upper limit of the tides. The River Shannon drains into the estuary from the east. The mean annual rainfall in the area is *c.* 1000–1200mm (Rohan 1986). The estuary is widest (4km) opposite Kilrush and narrowest (0.8km) at Tarbert Race, which divides the estuary into an upper and a lower part. The high-volume flow of water in the Shannon Estuary reduces pollution load problems, and effluent disposal problems should be minimal (see, e.g. O'Gara *et al.* 1990). The estuary has important amenity and fishing values. As vast mud banks are exposed at low tide, the estuary is one of the most significant wetlands in Europe for feeding birds (Gooders 1988).

In recent years the Shannon Estuary has been the subject of a series of hydrographic, economic and recreational studies (Anon. 1983a,b,c). These studies focused on the resources of the estuary and its potential to accommodate a range of activities. Data on metal levels in the Shannon Estuary were included in a number of general studies of Irish estuaries (Nixon *et al.* 1991; O'Sullivan *et al.* 1991; Wilson and Elkaim 1991). However, such once-off studies can miss short-lived peaks of metal levels. There are no previous longer-term studies of metal levels in the estuary.

Like in many estuaries, there is a net inflow of sea water near the bottom and a net outflow of freshwater on the surface of the Shannon Estuary (O'Gara *et al.* 1990). This is an important factor as bioaccumulation of metals by invertebrates was shown by Amiard-Triquet *et al.* (1991) to be dependent on salinity levels. Thermal stratification is evident in the lower estuary in summer, salinity stratification occurs throughout the estuary and the levels of suspended matter in the estuary are generally high (O'Gara *et al.* 1990). In a framework for the maritime development of the estuary (Anon. 1983c), the Shannon Free Airport Development Company proposed using the mouth of the estuary beyond Tarbert for heavy industry. The estuary has a busy port at Foynes and its industries include a major aluminium smelter at Aughinish 3km upstream of Foynes.

Reliable indicators of existing heavy-metal levels in the estuary are needed to allow comparison with levels reported elsewhere and to provide a baseline should further industrial development take place. Seaweeds, including *Fucus vesiculosus*, have frequently been used as indicators of heavy-

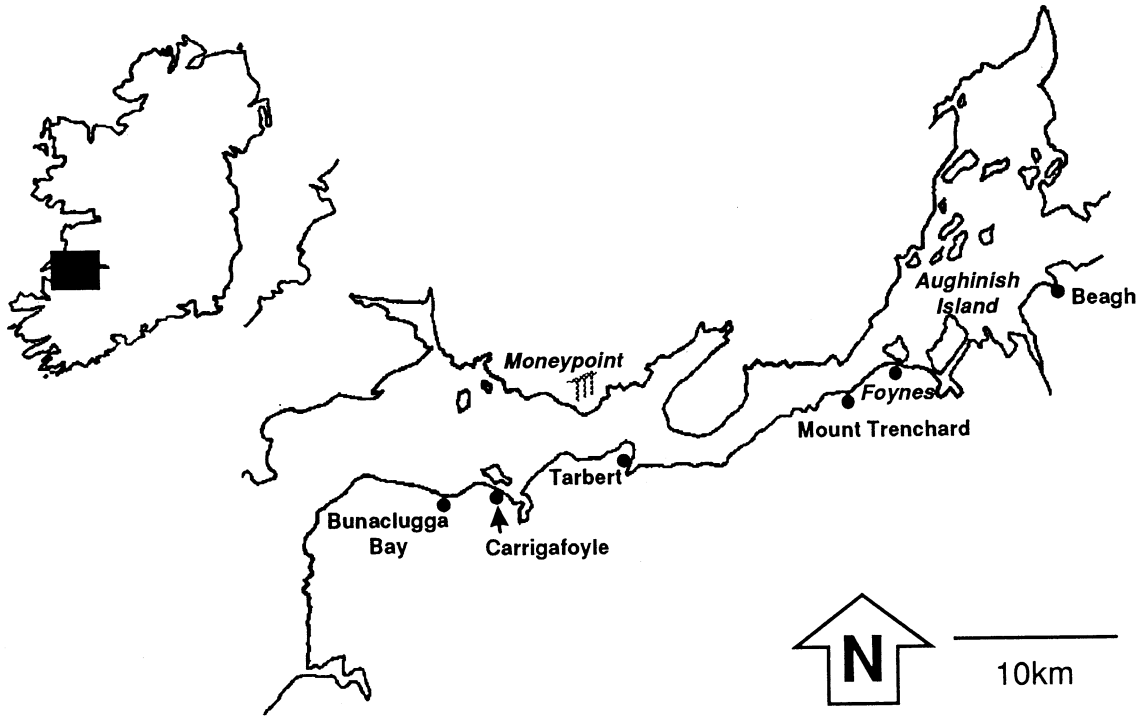

Fig. 1—Map of Ireland showing the location of the Shannon Estuary, and a detailed map of the estuary showing the sites mentioned in the text.

metal pollution (e.g. Bryan 1983; Bryan and Gibbs 1983; Forsberg *et al.* 1988) as have estuarine sediments (Bryan *et al.* 1980; Cantillo and O'Connor 1992; Alam and Sadiq 1993; Rowlatt and Lovell 1994). Many authors (see reviews by Phillips 1976; Goldberg *et al.* 1978; Bryan *et al.* 1980) have proposed using the filter-feeding bivalve mussel *Mytilus edulis* to indicate possible contamination because it can bioaccumulate heavy metals, and this is the approach followed during the present study (O'Leary 1995).

As a euryhaline species, *M. edulis* is widely distributed in the Shannon Estuary. A steady decrease in mussel population is apparent from the mouth of the estuary eastwards and its upper limit is *c.* 10km west of Limerick. *Fucus vesiculosus* has an upper limit in the estuary *c.* 8km west of Limerick. These distributions are adequate to provide a number of comparable sites for analysis.

Not all metals in sediments are available for bioaccumulation; they may come from the organic or particulate fractions of the sediment. Analysis of metals in sediments in conjunction with those in mussels and seaweed can suggest the origin of the metals (e.g. anthropogenic, natural bedrock, organic or particulate matter). The source of metals in sediments—the organic fraction or particulate fraction—can be investigated by 'normalising' the data. This is done by graphing individual metal levels using as independent variables the organic matter (as an indicator of the organic fraction) and Fe (as an indicator of the particulate fraction). If the independent variable is shown to be a reasonable predictor of the levels of any metal this is evidence of an organic fraction or particulate fraction source for that metal (see Wilson *et al.* 1986). The aims of this study were: (i) to provide a longer-term monthly study of the heavy-metal levels of *M. edulis*, *F. vesiculosus* and sediment from the Shannon Estuary; (ii) to establish monthly patterns, if any, of metal bioaccumulation in relation to site variability; and (iii) to attempt to attribute metal levels in the estuary to particulate or organic fractions.

METHODS

SAMPLING AND PREPARATION

Site locations and descriptions are provided in Fig. 1 and Table 1. Samples of *M. edulis*, *F. vesiculosus* and sediment were collected each month from March 1992 to December 1993 at Beagh, Mount Trenchard, Tarbert, Carrigafoyle and Bunaclugga Bay. At Tarbert a few large mussel specimens corresponded to *M. galloprovincialis* using morphological characters (Barrett and Yonge 1958), but those at all other sites corresponded to *M. edulis*. Since Gosling (1984) considered *M. galloprovincialis* to be a variant of *M. edulis*, based on morphological and biochemical criteria, all our specimens are taken to be *M. edulis*.

In *M. edulis* a sample consisted of fifteen individual specimens from each site. Samples of *M. edulis* were collected from the lower shores using low spring tide as a reference. This precaution should eliminate possible variability between mussels from different levels on the shore (Seed 1980). Boyden (1974; 1977) showed that small mussels may exhibit high metal levels and larger mussels may have lower metal levels, possibly owing to maturity, increased dry weight and spawning. It was reported that the environmental level of metals was not the only factor affecting the metal content of mussels and both size and season markedly affect this parameter. Deceptive results can be obtained by investigating a single size of mussel. Consequently samples of different shell size were collected to allow for any age variability with respect to bioaccumulation (Borchardt *et al*. 1989). The samples were washed in sea water to remove sediment, and epiphytes and epifauna were removed. The samples were then placed in a container of clean sea water at 4°C for 5 days to allow for depuration. These preparatory techniques broadly follow the procedures of Bryan *et al*. (1980) and Söderlund *et al*. (1988). The samples were then held in lightweight polythene bags in a freezer (−18°C) until analysis.

Samples of *F. vesiculosus* (identified using Hiscock 1979) were collected as close to the *M. edulis* samples as possible. Immature frond tips of current year's growth were collected to allow for the standardisation of the sample as recommended by Söderlund *et al*. (1988). On each sampling occasion, *F. vesiculosus* tips were collected from two or three plants and pooled for analysis. All *F. vesiculosus* samples were washed three times: in sea water, in distilled water and in sea water again. The samples were then scrubbed in sea water using a nylon brush, rinsed in distilled water and rinsed in sea water. All epifauna were removed. The samples were air-dried at room temperature for 3–4 days before storage in lightweight polythene bags until analysis.

At each site three 50-mm deep surface sediment samples were collected adjacent to where the *M. edulis* and *F. vesiculosus* were sampled. These samples were pooled and air-dried at room temperature for 2–3 weeks. After 1 week the samples were crumbled by hand to aid drying. When dry the samples were sorted by hand to remove large gravel, algae and invertebrates, dry-sieved to obtain a particle size of $<63\mu m$ diameter (Holme and McIntyre 1971) and stored dry until analysis. The combustible organic matter content of the sediments was obtained by loss on ignition at 450°C for 8 hours (Holme and McIntyre 1971) using samples of approximately 1g of sediment weighed to an accuracy of 0.1mg on an analytical balance.

SAMPLE ANALYSES

Before use all glassware and plastic containers were treated in accordance with the regime proposed by Greenberg *et al*. (1989). They were soaked in detergent for 12 hours and on removal

Table 1—Study sites on the Shannon Estuary with shore description, Irish grid reference and a subjective sediment rating (S.R.) based on the visual assessment of silt content: +++++ for sediment deposits that are very high in silt and low in gravel; then with increasing gravel −++++, −−+++, −−−++, −−−−+.

Site	*Grid reference*	*S.R.*	*Physical description*
Bunaclugga Bay	Q95 47	−−−−+	Shingle beach; little gradient; zonation poor. *Mytilus edulis* sitting on gravel surface.
Carrigafoyle	Q99 47	−−−++	Sheltered mud-flat between Ballylongford Bay and Carrig Island. *Mytilus edulis* in mud.
Tarbert	R11 46	−−+++	Sheltered mud-flat 300m from power plant and ferry pier; subject to tidal currents. *Mytilus edulis* in mud.
Mount Trenchard	R12 51	−++++	Semi-exposed and subject to tidal currents; steep gradient; mud silty. Outcrops of rock with *Mytilus edulis* attached.
Beagh	R14 56	+++++	Sheltered rock outcrops near Beagh Castle. *Mytilus edulis* under rock crevices.

washed in detergent, rinsed in distilled water and finally acid-rinsed in approximately 50% nitric acid for 3 days before first usage. Between digestions glassware was treated similarly except that acid rinsing was restricted to overnight.

The treatment of *M. edulis* samples is also based on Greenberg *et al.* (1989). Before analysis *M. edulis* samples were removed from the freezer and allowed to thaw overnight. Each sample was placed on its side and allowed to drain for 5 minutes. Total animal weight was obtained (all weights to 0.1mg). For each sample the soft body tissues were removed from the shell and placed in a pre-weighed crucible. Wet weight was obtained. The soft body tissues were then dried individually in an oven at 65°C for 20 hours and dry weights calculated.

For metal analysis a dry-weight nitric acid digestion was used following Greenberg *et al.* (1989). A known weight of sample was placed in a digestion tube and 5ml of 68% nitric acid was added. A glass marble was placed on the top of each digestion tube. Samples were allowed to digest at room temperature for 17 hours to reduce frothing. The digestion tubes were then placed on a preheated block at 120°C. The heat was increased to 180°C and digestion was continued for 3 hours. The glass marbles were removed when each solution was a clear straw colour (with a red precipitate in the case of sediments), and the nitric acid was allowed to evaporate until approximately 1ml remained. The digestion tubes were removed from the metal block and 1ml of purified water and 1ml of nitric acid were added to each digestion tube before filtration through Whatman No. 1 (11cm) filter paper. The boiling tube was then rinsed with de-ionised water and this was filtered with the sample also. Samples were brought up to volume using de-ionised water and stored in acid-rinsed plastic containers (Starsted, Wexford) until analysis.

The samples were then analysed for iron (Fe), zinc (Zn), manganese (Mn), chromium (Cr), cobalt (Co) and copper (Cu) using a Varian atomic absorption spectrophotometer (AAS). Quality control of metal analysis was performed using destruction blanks and standard dried copepod reference material (MAA1/TM supplied by the International Atomic Energy Agency, Austria). The percentage recovery for all metals was in good agreement with the certified values (90–98%). All sample readings with an AAS percentage relative standard deviation (replicate of three) of below 10% were used in the statistical analyses. Values below the detection limit of the AAS are reported as zero values. The optimum working ranges for the metals studied were as follows: Co (3.0–12.0μg ml^{-1}), Cr (2.0–8.0μg ml^{-1}), Cu (2.0–8.0μg ml^{-1}), Fe (2.5–10.0μg ml^{-1}), Mn (1.0–4.0μg ml^{-1}), Zn (0.4–1.6μg ml^{-1}).

DATA ANALYSIS

All data were transformed to natural logarithms, $\log_e (x + 1)$, before analysis (Stronkhorst 1992; Jorgensen and Pedersen 1994; O'Leary 1995; O'Leary and Breen 1997). Analysis of variance (ANOVA) was carried out to compare the levels of metals on different shores and at different dates using SPSS for Windows (Norušis 1993). All the graphs in this paper are based on untransformed data.

RESULTS

MYTILUS EDULIS

Figure 2 shows the mean levels of heavy metals in *M. edulis* from four representative sites on the south coast of the Shannon Estuary. Note that scales of the metal axes differ between metals but are similar between shores. When the rate of uptake differs from the rate of excretion, *M. edulis* becomes a net accumulator ('bioaccumulator') or net loser of heavy metals. The graphs show similar trends of bioaccumulation for all metals at all sites. The order of magnitude of bioaccumulation of the metals at all sites showed a similar pattern of Fe > Mn > Zn > Cu > Cr > Co. Levels of Cu were low at all sites except during March 1992. The graphs also show that, in many instances, the observed levels remained quite constant over the study period. However, variation did occur from one month to the next and between years and this was consistent between the five sites sampled.

There were obvious patterns of bioaccumulation of Co on at least two occasions during the study period: March–May 1992 and March–May 1993. This occurred at all sites and was followed by losses in the following months. Levels of Cr tended to be uniformly low, but there were a few occasions with enhanced levels at all sites (e.g. June–July 1993). Copper levels were consistently low except for a single high level at all sites in May 1992. Levels of Mn were also consistently low except for a few scattered higher levels at some of the sites in summer 1992. The levels of Fe were considerably higher than those of the other metals studied at all the sites and the highest levels of Fe were at Beagh. Generally the levels of Zn were intermediate in value; however, on a few occasions (early in 1993) elevated levels of Zn were noted, and low levels occurred at all sites in April 1992 and at two sites in May 1993.

The appendix gives the means, standard error and results of ANOVA analysis for each month. Zero values in this table indicate levels below the detection limit. When significant results were obtained ($P < 0.05$), Duncan's *a posteriori* tests were performed to compare the means of the different shores.

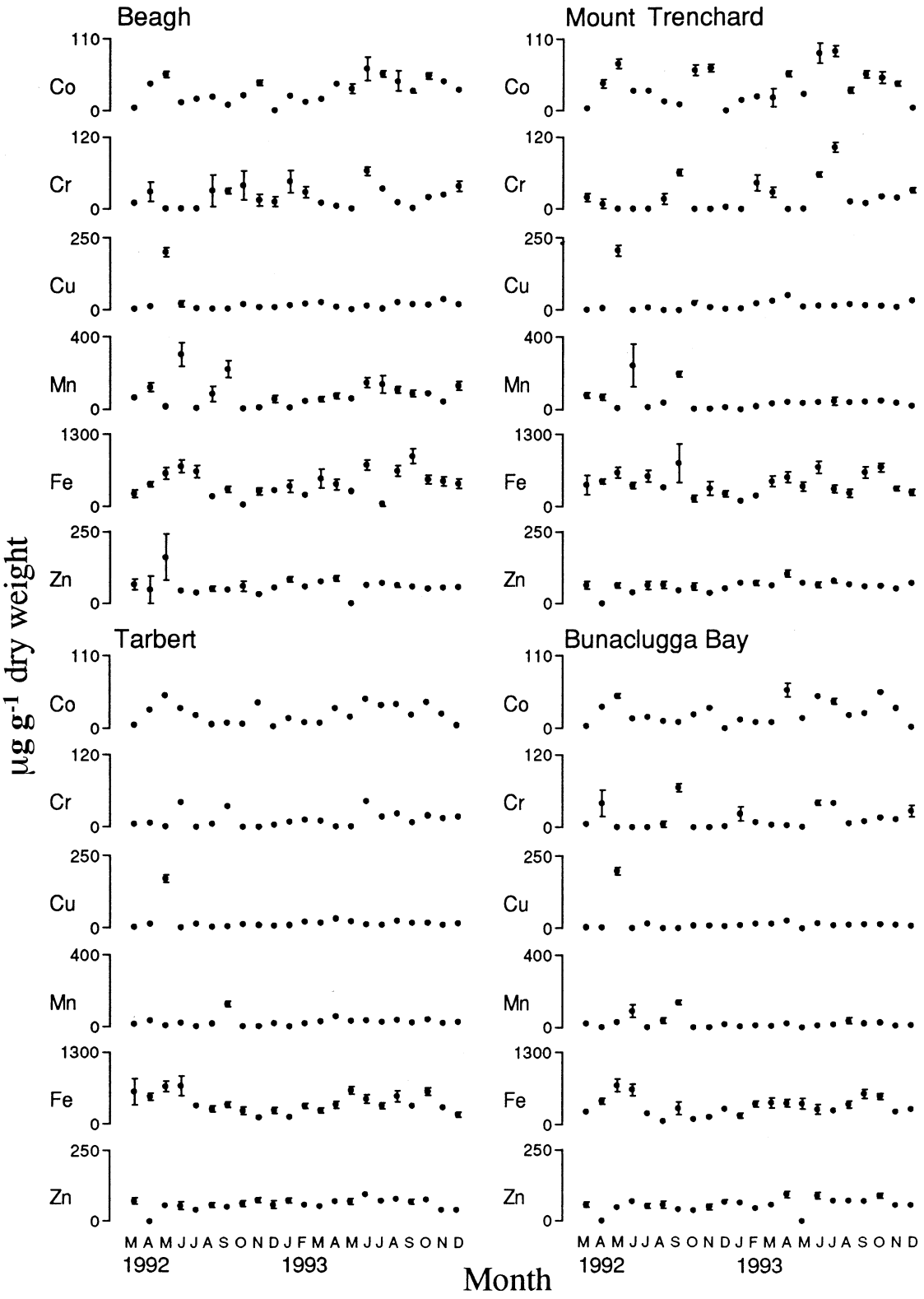

Fig. 2—Levels of Co, Cr, Cu, Mn, Fe and Zn (µg g^{-1} dry weight, mean ± S.E.) in *M. edulis* from four sites on the Shannon Estuary, March 1992–December 1993.

Some trends can be seen in the appendix. For Fe and Zn significant differences between sites seem more common in the summer months. Beagh [b] and Mount Trenchard [t] were fre-

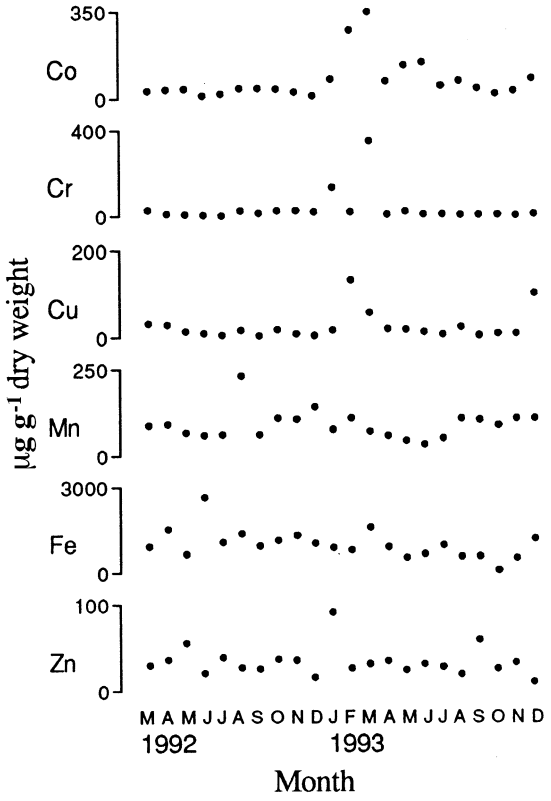

Fig. 3—Levels of Co, Cr, Cu, Mn, Fe and Zn (µg g^{-1} dry weight) in *F. vesiculosus* from Bunaclugga Bay, March 1992–December 1993.

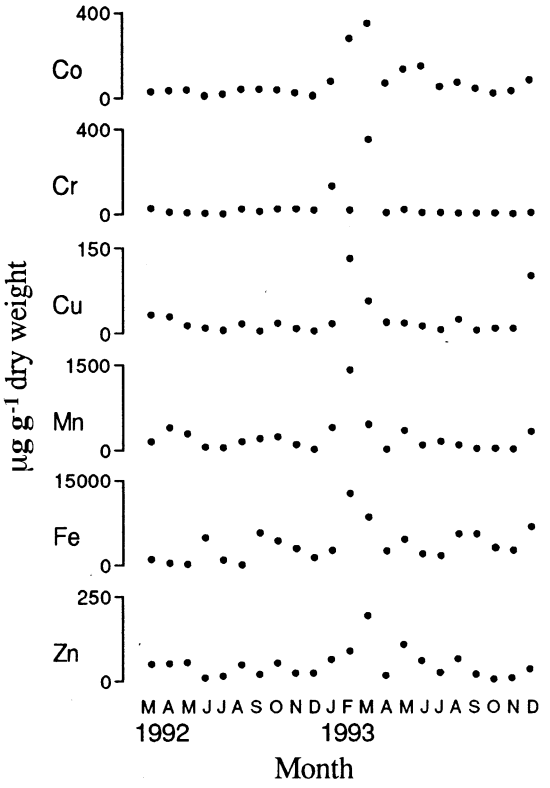

Fig. 4—Levels of Co, Cr, Cu, Mn, Fe and Zn (µg g^{-1} dry weight) in sediment from Bunaclugga Bay, March 1992–December 1993.

quently grouped together. This suggests similar levels for the metals studied at these two sites. Similarly the levels from Bunaclugga Bay [d] were significantly different from the levels of the other groups on many occasions.

FUCUS VESICULOSUS

Since levels of metals in *F. vesiculosus* were similar at all sites, only the data from Bunaclugga Bay have been presented (Fig. 3). Trends between months were similar except for an occasional difference (e.g. Mn in August 1992). There was a noticeable increase in Cu, Cr and Co at Bunaclugga Bay in February/March 1993.

SEDIMENT

The metal levels in sediment at all sites were also similar and only those for Bunaclugga Bay are given (Fig. 4). The order of magnitude of the sediment metal levels at this shore was Fe > Mn > Cr/Co > Zn > Cu. The levels of Fe in the sediments were considerably higher than those of the other metals studied. The percentage loss on ignition (organic matter) in the sediments at all five sites is shown in Fig. 5. Organic matter values were low (*c.* 10%) with a few exceptions.

In order to investigate whether the metals were based in the organic or particulate fractions of the sediment, scatter diagrams of the metal values were plotted against the percentage loss on ignition (organic matter) and against the percentage Fe (Fig. 6a and b). Examination of these graphs reveals a trend of increasing metal levels associated with percentage Fe (Fig. 6b) rather than with percentage loss on ignition. This is discussed below.

MYTILUS EDULIS, *FUCUS VESICULOSUS* AND SEDIMENT

Comparing the levels of the heavy metals in the *F. vesiculosus* and sediment samples with the corresponding metal levels in *M. edulis* shows that increased metal levels in sediment generally did not lead to similar increases in *M. edulis*.

Localised activity at Bunaclugga Bay, associated with nearby road-building at the beginning of 1993, was the probable cause of high levels of Cr and Fe in *M. edulis* around this period. Corresponding increases in the Cu, Cr, and Co levels in *F. vesiculosus* and in all metal levels in sediment were also noted at this time. By June 1993 the levels in the sediment and *F. vesiculosus* samples had returned to their pre-disturbance levels, whereas those in *M. edulis* had not fully recovered.

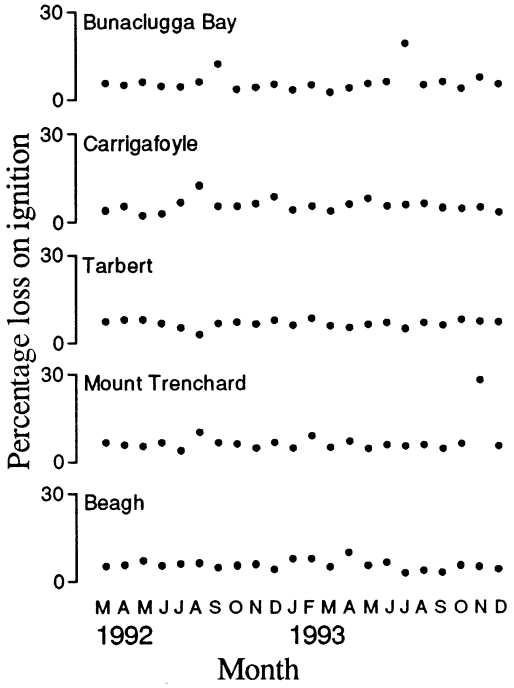

Fig. 5—Percentage loss on ignition (organic matter) in sediments from five sites on the Shannon Estuary, March 1992–December 1993.

On some sampling dates increases in metal levels in sediment and *F. vesiculosus* were not accompanied by similar increases in *M. edulis*. For example, Cu increased in sediment and *F. vesiculosus* in December 1993 and July 1992 but not in *M. edulis*. On other occasions increases were observed in sediment and in *M. edulis* but not in *F. vesiculosus*, e.g. levels of Fe at Tarbert in April 1992 showed increases in sediment and in *M. edulis* but a decrease in *F. vesiculosus*. A similar pattern was observed for Mn at Tarbert during September 1992. At Carrigafoyle in July 1992 Co and Cr levels in the *F. vesiculosus* increased with no corresponding increase in *M. edulis* or sediment. Increased metal levels in sediment, *F. vesiculosus* and *M. edulis* were also observed at the same site, during the same period, e.g. Zn levels at Mount Trenchard in April 1992 and again in April 1993.

DISCUSSION

LONGER-TERM SAMPLING OF *MYTILUS EDULIS*

A number of authors (see Borchardt *et al.* 1988) have suggested that the analysis of heavy metals in bioindicators such as *M. edulis* should be based on more than one sampling date or period to account for the variability found in the results. Borchardt *et al.* (1988) suggested that seasonal variations of metal levels in *M. edulis* follow a sinusoidal curve. Their logic is as follows: the growth period in late spring/early summer causes rapid increases in biomass, which results in lower metal levels when they are expressed in relation to this increased biomass. If these data are then used as a baseline, increases in metal levels observed in summer can appear to be enhanced. Expressed graphically, such levels appear as a sinusoidal curve. If such curves exist, they may be metal specific, as different metals are known to be bioaccumulated at different rates (Phillips 1980; Phillips and Rainbow 1994). The rate of accumulation and the ability of the mussels to detoxify particular metals also differ greatly (Rainbow *et al.* 1990). The estuarine environment is not static. The levels of metals present are dependent on the anthropogenic input into the estuary. This would disrupt a sinusoidal curve pattern.

The results from the present study suggest that seasonal variation of heavy-metal levels in *M. edulis* from the Shannon Estuary was irregular and did not follow sinusoidal curves (Borchardt *et al.* 1988). The levels of Co, which showed seasonal peaks from March to May in both years, are a possible exception.

Uptake and loss of metals are also affected by spawning. According to Rainbow *et al.* (1990), invertebrates regulating the body-tissue levels of a metal resort to accumulation if the regulation process breaks down. This is generally carried out by detoxification and storage. If these metals are stored in the gonad tissue they may be lost from the tissue during spawning. Separate observations (O'Leary 1995) suggest spawning dates for *M. edulis* in the Shannon Estuary between June and July in 1993. Thus some of the changes in metal levels in the tissues of *M. edulis* can be attributed to spawning and not to anthropogenic influences.

Although exposure, assessed subjectively by the presence of mud, other substrate, aspect and slope, differed between sites (Table 1), the metal levels in *M. edulis* acted similarly at all the sites with respect to uptake and bioaccumulation. This suggests that metal levels are low and are not interfering with the normal metabolic processes of *M. edulis* (Anderlini 1992; Vazquez *et al.* 1993).

Notable variation was found between the study sites, but the overall pattern was constant at all sites. The order of magnitude of accumulation at all sites was Fe > Mn > Zn > Cu > Cr > Co. Levels of Fe in the sediments were high, but Fe occurs naturally in the environment and may come from background levels in the sediments. This is further discussed below.

COMPARISONS WITH OTHER SITES

Compared to elsewhere in Ireland metal levels in the Shannon Estuary are low, except for occa-

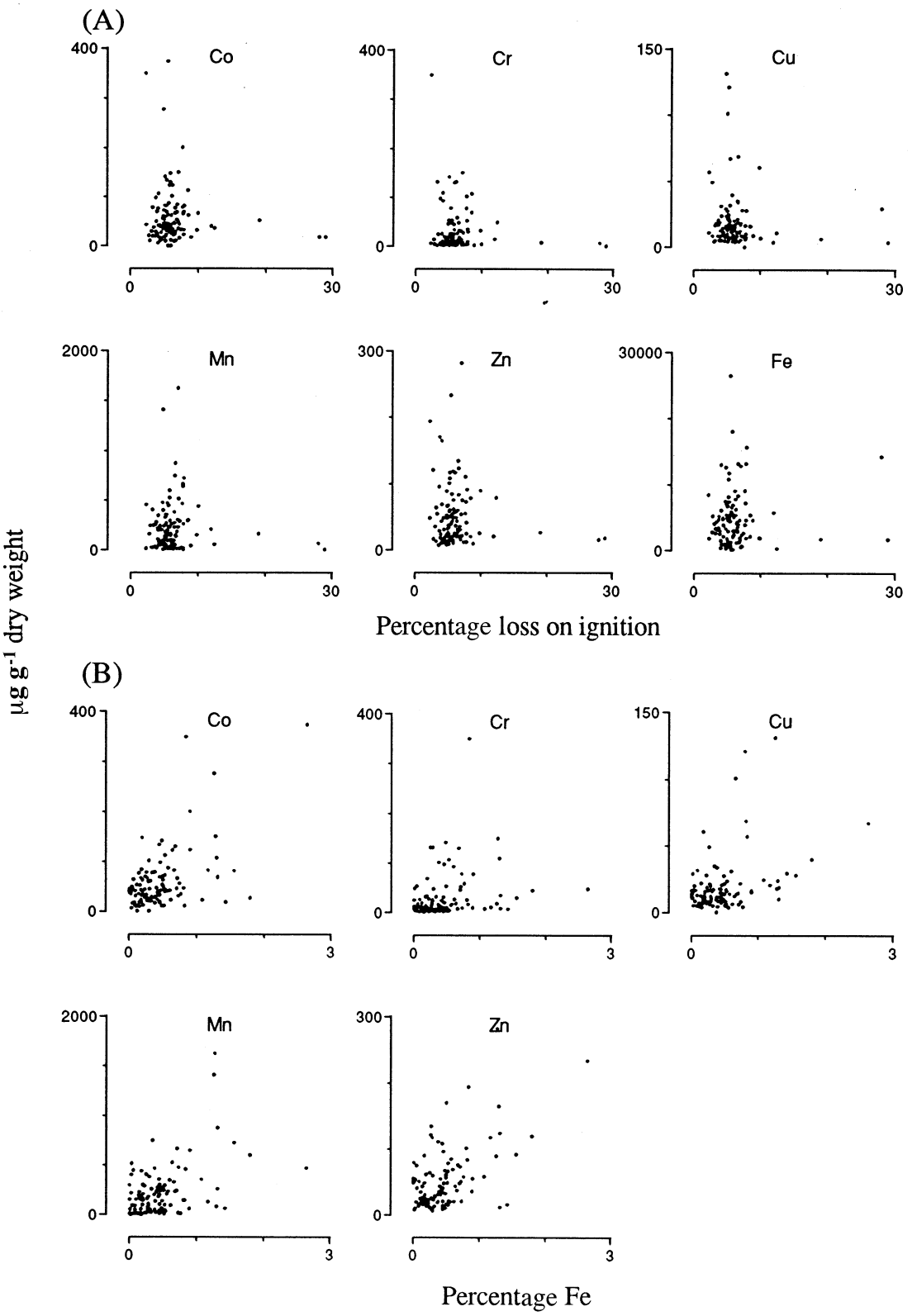

Fig. 6—Scatter diagrams of (A) Co, Cr, Cu, Mn, Zn and Fe levels (μg g^{-1} dry weight) plotted against percentage organic matter and (B) Co, Cr, Cu, Mn and Zn levels (μg g^{-1} dry weight) plotted against percentage Fe.

sional high levels that did not persist. Comparisons between estuaries are difficult because of the inherent differences between estuaries (Wilson and Elkaim 1991). Metal levels that originate from

natural processes such as erosion and flocculation of metals (Sholokovitz 1978; Wilson *et al.* 1986; Din 1992) may cause elevated levels in sediments and biota unrelated to anthropogenic sources. Nevertheless comparisons were made, a number of them with the work of O'Sullivan *et al.* (1991), who provided results for mussels, referenced to wet weight, which we have converted to dry weight using the '% dry weight' given in their Table 1.

Chromium levels in *M. edulis* were regularly higher in the Shannon Estuary than values found in studies elsewhere in Ireland, viz. *maximum* values given by O'Sullivan *et al.* (1991) for the Boyne Estuary (12.92μg g^{-1}), Dublin Bay (4.46μg g^{-1}) and Wexford Harbour (8.83μg g^{-1}), and *mean* values given by Wilson (1980) for Dundalk (10.3μg g^{-1}), Drogheda (8.6μg g^{-1}), Malahide (0.5μg g^{-1}), Dublin (3.7μg g^{-1}) and Arklow (2.7μg g^{-1}) and by Berrow (1991) for Cork Harbour (4–8μg g^{-1}). The fact that these levels do not persist is evidence of bioaccumulation and of the ability of *M. edulis* to remove Cr from its tissues, as a number of levels below the detection limit of the AAS were also noted throughout the sampling period.

With the exception of a few data in the appendix, Zn levels in the Shannon Estuary were lower than on the east coast of Ireland (Wilson 1980) and in Carlingford Lough (Manga and Hughes 1981), and considerably lower than in Cork Harbour (Berrow 1991). On all occasions levels were lower than the maximum levels given by O'Sullivan *et al.* (1991) for Dublin Bay (161.08μg g^{-1}), the Boyne estuary (165.17μg g^{-1}) and Cork Harbour (233.07μg g^{-1}), but comparable to those for Wexford Harbour (84.24μg g^{-1}). On almost all occasions the Zn levels from this study were lower than the once-off level given by O'Sullivan *et al.* (1991) for the Shannon Estuary (102.77μg g^{-1}).

Levels of Cu in the Shannon Estuary were slightly higher than at Dundalk, Drogheda, Malahide, Dublin and Wicklow, and considerably lower than at Arklow (Wilson 1980). Levels were slightly higher on a number of occasions in the present study than levels reported by O'Sullivan *et al.* (1991) for the Boyne Estuary (14.10μg g^{-1}), Dublin Bay (8.65μg g^{-1}), Waterford Harbour (21.3μg g^{-1}), Cork Harbour (9.37μg g^{-1}), Shannon Estuary (6.59μg g^{-1}) and by Manga and Hughes (1981) for Carlingford Lough. However, levels were lower on almost all occasions than the Cork Harbour values (23–29μg g^{-1}) reported by Berrow (1991).

Manganese levels reported in east coast estuaries are in the range 11.0–43.3μg g^{-1} (Wilson 1980). Levels in the present study were higher than these on a number of occasions, but did not persist: they sometimes reached levels reported from Carlingford Lough (116–490μg g^{-1}) by Manga and Hughes (1981).

Levels of Fe for the Shannon Estuary occasionally exceeded those for east coast sites: 343–616μg g^{-1} (Wilson 1980). While noteworthy, these values are not of concern as they did not persist, but they do point to repeated accumulation and loss throughout the study.

The International Council for the Exploration of the Sea (ICES) studied metal levels in fish and shellfish in sixteen countries around the North Atlantic and Baltic (Anon. 1988). Three of the metals covered in that report were included in the present study. For Zn ICES reported values of 47–410μg g^{-1}. All but four of the monthly/site Zn values for the Shannon Estuary reported here were less than 100μg g^{-1}; about one-third of the values were <47μg g^{-1} and some zero values occurred. The ICES report gave values for Cu of 4.2–163μg g^{-1}. Most of the values reported here were <20μg g^{-1}, except for May 1992, when elevated values of 114–205μg g^{-1} were obtained at all five sites. It is worth noting that very low values were obtained at all sites in the months immediately before and after this event. This suggests that there was a flush of Cu through the estuary at that time. It is interesting that the persistence of Cu in the tissues was so short-lived. The ICES report gave values for Cr of 0.15–8.5μg g^{-1}. Many of the Cr levels reported here, with a maximum of 82.3μg g^{-1}, are much higher than the maximum value reported by ICES, and the values were higher during the second year of the study. However, many of the high levels were followed by very low levels in the following month, which suggests that there are regular flushes of Cr through the estuary.

LEVELS IN *FUCUS VESICULOSUS* AND SEDIMENT

In addition to anthropogenic inputs, metals may also come from natural erosion. The problem of naturally occurring background levels in sediment, seaweed and biota was discussed by Berkman and Nigro (1992), Kureishy *et al.* (1993), Petri and Zauke (1993) and Zauke and Petri (1993). Consequently, sediment and *F. vesiculosus* were included in this study to allow comparisons.

Metal levels in *F. vesiculosus* did not vary greatly between sites, although there was a marked seasonal variation. Consequently time of year must be taken into account when comparing heavy-metal levels reported from *F. vesiculosus*.

MYTILUS EDULIS, *FUCUS VESICULOSUS* AND SEDIMENT

On the same sampling occasion, the metal levels in *M. edulis* and *F. vesiculosus* were different, although comparable ranges were found for all except Fe and only the monthly patterns differed, which may suggest different accumulation rates between seaweeds and mussels. However, Fe levels were higher in *F. vesiculosus* than in *M. edulis*. This may indicate different sources of Fe in these two species, as seaweeds absorb metals from the surrounding environment and *M. edulis* uptake is primarily through filter-feeding.

Metal levels in *M. edulis*, *F. vesiculosus* and sediment varied little between sites except for the occasional high level. It is interesting to note that high levels of a number of the metals in both sediment and *F. vesiculosus*, but not in *M. edulis*, at Bunaclugga Bay in early 1993 coincided with the disturbance caused by adjacent road-building. The variations of metal levels in sediment and in *M. edulis* found in this study suggest that on some occasions metals of sediment origin were released and bioaccumulated by *M. edulis*. The investigation involving comparison of metal levels normalised by organic matter or Fe (Fig. 6) suggested that not all the Fe in the sediment is available for bioaccumulation by *M. edulis*. The scatter diagrams of metal levels plotted with the percentage Fe and with percentage loss on ignition (organic matter) showed a trend of increasing metal levels with Fe but not with the organic matter, which suggests that the metals came from the particulate rather than the organic fraction of the sediment. This was most obvious in the case of Zn and was also evident in the case of Cu, Co and Mn (Fig. 6b).

Some high Fe levels were noted in the sediment samples, including a level of 26,466μg g^{-1} (=2.65%) at Carrigafoyle in June 1993. These levels did not appear to persist. High levels of Fe are known to occur in sediment, and a proportion of Fe in sediment may be due to natural erosion (Boggs 1987). The Fe levels in the Shannon Estuary sediments were high, though of similar magnitude to those reported from the Plymouth area of Britain (Bryan *et al.* 1980). The order of magnitude of levels of metals in the sediment in general was as follows: Fe > Mn > Cr/Co > Zn > Cu. The levels of Fe in *M. edulis* were considerably lower than those in sediment.

CONCLUSIONS

Monthly sampling allows a comprehensive description of the metal levels of Fe, Mn, Cr, Co, Zn and Cu in *M. edulis*, *F. vesiculosus* and sediments in the Shannon Estuary. Overall the results for Mn, Co, Zn and Cu are lower than values published for other Irish sites. The values for Cr are higher than at other Irish sites and suggest regular flushes of Cr through the estuary. The levels of Fe were high, especially in sediments, though of similar magnitude to those published in Britain. Fluctuations in metal levels in *M. edulis* suggest accumulation followed by losses.

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APPENDIX

Means ($\bar{x}$) and standard errors (S.E.) of Fe, Zn, Co, Cu, Cr and Mn in *Mytilus edulis* 1992–3 at five sites on the Shannon Estuary (b = Beagh, m = Mount Trenchard, t = Tarbert, c = Carrigafoyle, d = Bunaclugga Bay), compared, using ANOVA (A), with Duncan's *a posteriori* test. Sites not significantly different from each other ($P < 0.05$) are enclosed in brackets. Means of groups separated from each other by square brackets are significantly different, whereas groups enclosed in square brackets are not. For example, for Fe in March 1992, t[bm] indicates that the Fe levels at Tarbert [t] were significantly different ($P < 0.05$) from those at Beagh [b] and Mount Trenchard [m], whereas the means of the levels at Beagh and Mount Trenchard were not significantly different from each other. Sites do not differ unless mean values are followed by site letters (of significantly different sites).

Month	*Site*	*Fe*			*Zn*			*Cu*		
		$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*
1992										
March	b	226.78	71.41	b[t]	66.05	19.14		1.88	0.61	b[mc][d]
	m	387.91	170.39	m[t]	64.48	13.96		0	0	m[btd]
	t	582.07	239.10	t[bm]	73.02	12.19		2.13	0.68	t[mc]
	c	338.59	44.73		83.91	9.81		0.67	0.48	c[btd]
	d	233.65	30.19		57.00	9.34		3.25	0.65	d[bmc]
April	b	397.75	43.95		47.60	47.60		11.00	1.89	b[cdm]
	m	453.43	43.51		0	0		6.98	2.54	m[bt]
	t	492.00	64.81		0	0		12.70	1.54	t[cdm]
	c	476.28	46.19		0	0		2.60	0.85	c[bt]
	d	423.38	56.33		0	0		2.83	0.91	d[bt]
May	b	596.40	108.22		161.20	79.59		199.00	15.46	b[c]
	m	610.68	95.21		63.22	8.71		205.00	18.83	m[c]
	t	677.38	98.93		56.52	5.85		170.00	13.29	t[c]
	c	514.28	89.91		75.79	16.47		114.00	7.89	c[bmtd]
	d	713.62	114.48		48.08	5.09		199.00	13.69	d[c]
June	b	722.86	118.69		44.62	3.31	b[d]	19.30	10.78	b[mtcd]
	m	380.39	58.29		38.85	2.50	m[d]	0.66	0.23	m[b]
	t	689.59	178.16		55.08	14.39	t[d]	0	0	t[b]
	c	556.47	122.71		45.63	6.02	c[d]	0	0	c[b]
	d	631.97	107.79		69.70	3.64	d[bmtc]	0.48	0.21	d[b]
July	b	628.29	113.69	b[d]	37.68	4.26	b[mc]	4.74	0.96	b[tcd]
	m	547.61	108.02	m[d]	63.96	14.25	m[b]	9.77	3.57	m[tcd]
	t	327.64	29.46		40.95	4.95	t[c]	14.00	1.14	t[bm]
	c	382.12	47.04		76.67	12.16	c[bt]	13.90	1.79	c[bm]
	d	210.21	22.11	d[bm]	52.75	8.35		15.70	0.98	d[bm]

APPENDIX—(continued)

Month	*Site*	*Fe*			*Zn*			*Cu*		
		$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*
Aug.	b	176.58	39.00	b[d][mtc]	50.47	8.99		1.78	1.11	
	m	342.36	35.07	m[bd]	66.03	12.54		0.72	0.44	m[t]
	t	269.32	52.91	t[bd]	58.10	9.17		2.33	0.66	t[md]
	c	287.45	31.68	c[bd]	80.91	10.15		1.54	0.67	c[d]
	d	68.47	11.30	d[bmtc]	57.16	13.06		0	0	d[tc]
Sept.	b	304.40	55.90		47.44	5.98		2.34	0.58	b[mc]
	m	781.44	345.47		46.80	5.00		0.26	0.18	m[bt]
	t	345.79	52.36		50.74	3.98		3.85	0.66	t[mcd]
	c	281.90	49.08		64.90	9.88		0.75	0.42	c[bt]
	d	300.01	114.58		41.81	2.00		1.20	0.43	d[t]
Oct.	b	27.31	11.06	b[tcd]	59.85	17.87		17.80	2.41	
	m	141.80	59.55	m[tc]	59.64	12.42		26.20	8.33	m[c]
	t	239.26	66.16	t[bm]	62.92	10.88		10.90	1.80	t[c]
	c	201.66	40.18	c[bm]	51.56	9.63		26.90	2.21	c[mtd]
	d	101.05	20.89	d[b]	38.13	7.68		10.00	1.46	d[c]
Nov.	b	266.27	64.51	b[t]	32.43	4.60		8.36	1.04	b[c]
	m	326.78	125.23	m[t]	37.12	7.08		11.00	1.14	
	t	113.88	32.29	t[bm]	75.57	9.46		8.95	1.90	t[c]
	c	149.85	34.81		51.57	11.58		13.80	1.66	c[bt]
	d	145.39	31.94		50.29	10.65		9.68	1.12	
Dec.	b	291.75	38.32		54.18	5.86		8.04	0.81	
	m	229.08	55.31		53.85	6.85		5.06	0.71	
	t	243.44	53.82		58.81	14.54		6.59	1.04	
	c	244.48	23.34		73.09	6.38		8.71	1.22	
	d	290.38	34.49		68.09	8.03		7.16	0.69	
1993										
Jan.	b	360.35	106.50		84.40	9.29		14.60	2.22	
	m	99.98	17.43	m[cb]	71.76	6.23		8.42	0.93	
	t	125.41	22.94		73.23	8.63		8.70	0.91	
	c	170.93	30.57	c[m]	107.70	7.71		19.70	11.08	
	d	166.56	44.78		65.82	5.95		11.30	2.91	
Feb.	b	209.78	34.26	b[tcd]	59.50	3.87	b[d]	19.20	1.66	b[c][m]
	m	193.27	36.51	m[tcd]	72.60	8.85	m[d]	25.30	1.46	m[btcd]
	t	324.15	44.38	t[mb]	57.57	4.81	t[d]	20.10	2.22	t[c][m]
	c	402.59	48.57	c[mb]	92.56	4.86	c[d]	11.80	1.21	c[bmtd]
	d	380.62	57.72	d[mb]	46.79	7.34	d[bmtc]	17.00	1.08	d[c][m]
March	b	504.28	170.10		76.44	4.17	m[t][c]	25.50	1.42	b[tcd][m]
	m	454.42	99.53		63.78	4.62	b[td]	33.60	2.12	m[btcd]
	t	245.93	43.53		53.23	7.64	t[bmc]	15.80	2.18	t[bm]
	c	399.39	84.85		90.57	5.51	c[mtd]	14.30	1.55	c[bm]
	d	401.73	91.91		57.62	4.74	d[bc]	16.70	1.27	d[bm]
April	b	395.31	97.91		87.26	9.04		9.62	4.24	b[mtcd]
	m	529.83	90.73		105.00	12.20		53.20	3.61	m[btd]
	t	341.68	67.01		69.76	6.95		31.40	2.94	t[b][mc]
	c	324.08	66.87		90.73	8.67		54.80	5.24	c[btd]
	d	391.17	68.57		94.58	11.70		26.40	3.13	d[b][mc]
May	b	276.88	39.88		0	0	b[mtc]	0	0	b[mtc]
	m	363.15	82.95		73.13	6.57	m[bd]	15.30	1.25	m[bd][c]
	t	605.96	63.13		69.86	9.91	t[bd][c]	21.90	6.24	t[bd][c]

APPENDIX—(continued)

Month	*Site*	*Fe*			*Zn*			*Cu*		
		$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*
	c	593.56	105.30		94.23	6.78	c[btd]	27.50	3.08	c[bmtd]
	d	383.29	95.54		0	0	d[mtc]	0	0	d[mtc]
June	b	747.70	93.21	b[td]	63.90	5.07	b[tc]	13.20	2.14	b[mcd]
	m	710.04	109.30	m[d]	66.44	10.00	m[tcd]	19.00	1.22	m[bt]
	t	449.84	81.01	t[d][cb]	95.33	6.90	t[mb]	11.90	0.78	t[mcd]
	c	716.80	123.40	c[td]	110.80	13.10	c[bm]	16.90	1.62	c[bt]
	d	280.46	86.16	d[bmtc]	90.78	11.90	d[m]	17.30	1.73	d[bt]
July	b	444.51	52.09		71.55	6.53		3.04	0.77	b[c][mtd]
	m	317.05	67.31		80.32	8.12		17.90	1.68	m[btcd]
	t	323.98	55.76		72.42	4.93		10.30	0.85	t[bc][m]
	c	301.91	64.60		67.72	6.25		0.76	0.23	c[bmtd]
	d	263.92	32.46		72.63	6.12		10.80	2.66	d[bc][m]
Aug.	b	640.43	97.88	b[mcd]	63.93	8.02		25.40	1.82	b[cd]
	m	240.10	75.76	m[btcd]	67.23	7.74		23.00	1.96	m[cd]
	t	500.42	104.10	t[m]	78.47	6.36		23.20	1.93	t[cd]
	c	340.54	27.16	c[m][b]	83.46	8.40		14.00	1.22	c[bmt]
	d	370.90	66.93	d[m][b]	73.86	5.49		13.40	1.61	d[bmt]
Sept.	b	906.62	133.50		58.07	4.97		18.20	1.62	
	m	618.93	101.60		60.46	5.73		19.90	1.48	
	t	325.18	29.91		70.56	8.97		15.70	1.74	
	c	302.71	46.69		69.91	8.68		14.70	1.37	
	d	562.88	82.55		70.46	6.75		15.60	1.48	
Oct.	b	484.50	81.11		50.67	5.55	b[mtcd]	15.70	1.64	
	m	706.80	79.14		61.89	3.76	m[b][d]	18.40	2.05	m[c]
	t	587.83	70.58		76.90	6.88	t[b]	17.40	1.48	t[c]
	c	421.22	28.67		70.41	5.24	c[b]	12.20	0.57	c[mt]
	d	517.23	58.70		90.43	8.68	d[bm]	14.60	1.05	
Nov.	b	452.84	83.28		55.52	6.08	b[t]	35.20	2.61	b[mtcd]
	m	325.98	44.42		52.89	7.37	m[c]	15.50	1.10	m[t][b]
	t	297.36	35.26		40.10	4.58	t[bdc]	10.50	0.82	t[bmcd]
	c	320.96	35.93		78.93	5.37	c[bmtc]	19.10	1.76	c[td][b]
	d	247.14	36.33		56.51	5.85	d[t][c]	13.40	1.03	d[t][c]
Dec.	b	412.22	84.21		57.04	4.28	b[tc]	17.90	1.37	b[d][m]
	m	261.11	56.43		73.14	6.51	m[tc]	37.60	4.88	m[btcd]
	t	351.28	44.81		40.56	4.47	t[bmd]	14.40	1.45	t[d][m]
	c	265.35	30.11		43.64	8.38	c[bmd]	13.70	1.67	c[d][m]
	d	285.94	40.78		56.25	4.83	d[tc]	9.49	1.12	d[bmtc]

APPENDIX—(continued)

Month	*Site*	*Co*			*Cr*			*Mn*		
		$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*
1992										
March	b	3.94	0.59		9.74	1.23		64.50	11.45	b[tcd]
	m	3.46	0.98	m[t]	18.89	6.59		79.20	16.64	m[tcd]
	t	5.25	0.63	t[mc]	12.44	1.33		15.10	2.85	t[c][bmd]
	c	3.08	0.62	c[t]	16.25	2.21		1.13	0.77	c[bmtd]
	d	3.73	0.31		5.97	0.35		23.00	3.56	d[ct][bm]
April	b	41.13	3.09	b[tc]	28.38	16.06	b[m]	122.00	24.17	b[mtcd]
	m	41.95	6.70	m[t]	8.51	7.76	m[bc]	70.40	16.80	m[cd][b]
	t	27.95	2.59	t[bm]	6.99	4.96		36.90	6.79	t[c][b]
	c	32.37	7.12	c[b]	32.58	19.85	c[m]	7.69	1.33	c[bmtd]
	d	32.61	3.05		39.63	21.47		31.30	4.40	d[c][bm]
May	b	56.24	4.64		0	0	b[c]	14.90	2.75	
	m	72.49	7.37	m[td]	0.56	0.56	m[c]	9.09	0.87	
	t	50.16	3.49	t[cm]	0.64	0.25	t[c]	7.20	0.77	t[d]
	c	67.48	5.09	c[td]	3.14	1.36	c[bmtd]	8.26	1.17	c[d]
	d	49.54	3.74	d[mc]	0	0	d[c]	29.70	10.89	d[tc]
June	b	13.10	1.02	b[mtc]	0	0	b[tc]	303.00	65.33	b[mtcd]
	m	30.35	1.21	m[bd][c]	0	0	m[tc]	246.00	118.21	m[tc][b]
	t	30.37	2.83	t[bd][c]	40.24	10.68	t[bmd][c]	22.50	5.12	t[dmb]
	c	45.66	3.18	c[bmtd]	69.40	4.17	c[bmtd]	24.70	5.27	c[bmd]
	d	15.08	1.22	d[mtc]	0	0	d[tc]	94.00	35.52	d[tc][b]
July	b	17.83	1.96	b[mc]	0	0		6.24	1.02	b[cd]
	m	30.62	1.71	m[btd]	0	0		13.10	3.82	m[tcd]
	t	19.85	1.42	t[mc]	0	0		3.09	0.47	t[d][m]
	c	31.99	1.68	c[btd]	0	0		4.39	1.72	c[bm][d]
	d	17.68	1.02	d[mc]	0	0		1.36	0.64	d[bmtc]
Aug.	b	21.13	2.45	b[mtd]	29.94	26.36		83.60	42.83	
	m	14.08	0.80	m[t][b]	16.92	9.22		38.90	7.16	
	t	6.25	0.70	t[bmcd]	4.78	3.42	t[c]	18.00	3.44	
	c	18.80	2.21	c[td]	9.28	2.12	c[td]	37.00	15.06	
	d	11.51	1.04	d[t][cb]	5.36	5.36	d[c]	39.90	15.55	
Sept.	b	8.96	1.08	b[c]	29.54	26.36	b[mcd]	221.00	47.39	b[t]
	m	9.67	0.70	m[c]	60.98	9.22	m[bt]	199.00	16.58	m[td]
	t	7.86	0.68	t[c]	33.43	3.21	t[mcd]	126.00	15.06	t[bmc]
	c	15.35	1.11	c[bmtd]	82.30	5.43	c[bt]	197.00	13.99	c[td]
	d	9.88	1.03	d[c]	65.71	7.11	d[bt]	142.00	13.39	d[mc]
Oct.	b	23.69	2.24	b[t][mc]	38.84	24.12	b[mtcd]	4.49	0.56	b[td]
	m	62.73	8.22	m[btd]	0	0	m[b]	5.33	0.78	m[td]
	t	6.64	1.10	t[bmcd]	0	0	t[b]	2.12	0.20	t[bmc]
	c	60.39	2.99	c[btd]	0	0	c[b]	5.90	1.35	c[td]
	d	21.23	1.71	d[t][mc]	0	0	d[b]	2.60	0.35	d[bmc]
Nov.	b	43.37	4.29	b[cd][m]	14.48	9.99	b[c]	7.99	4.90	
	m	65.38	5.94	m[btcd]	0	0	m[c]	5.32	2.93	
	t	39.23	3.33	t[c][m]	0	0	t[c]	2.75	0.38	
	c	29.31	3.22	c[bmt]	81.13	27.31	c[bmtd]	2.35	0.45	
	d	31.46	2.73	d[bm]	0	0	d[c]	1.57	0.29	

APPENDIX—(continued)

Month	*Site*	*Co*			*Cr*			*Mn*		
		$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*
Dec.	b	0	0		11.90	8.10		55.90	18.43	b[mtcd]
	m	0	0		3.66	0.95		12.90	2.63	m[b]
	t	2.74	2.74		2.96	0.70		19.30	4.38	t[b]
	c	0	0		6.03	1.29		14.40	1.98	c[b]
	d	0	0		1.91	0.65		18.90	4.46	d[b]
1993										
Jan.	b	23.10	2.52	b[mtd]	45.08	18.47	b[mtcd]	7.40	3.83	b[c]
	m	16.36	1.30	m[bc]	0	0	m[db]	1.61	0.32	
	t	14.82	1.70	t[bc]	7.88	5.37	t[b]	2.71	0.59	t[c]
	c	20.80	1.94	c[mtd]	0	0	c[db]	0.61	0.33	c[tb]
	d	13.65	0.73	d[bc]	22.94	11.66	d[mc][b]	7.69	4.17	
Feb.	b	13.29	1.75	b[tc][m]	27.49	9.53	b[tcd][m]	45.30	9.13	b[mtcd]
	m	21.75	2.12	m[btcd]	44.14	12.79	m[btcd]	20.90	3.50	m[b]
	t	8.73	1.46	t[bm]	11.50	1.32	t[bm]	18.60	3.64	t[b]
	c	7.98	0.95	c[bm]	11.18	0.70	c[bm]	11.60	1.45	c[b]
	d	9.08	0.43	d[m]	9.45	0.69	d[bm]	14.20	1.68	d[b]
March	b	17.96	3.26	b[mt]	9.72	0.66	b[d][mc]	55.10	15.00	
	m	20.41	14.10	m[bcd]	28.09	8.52	m[btd]	36.20	9.95	
	t	7.77	1.05	t[bc]	10.10	3.87	t[mc]	30.80	5.88	
	c	28.26	12.90	c[mtd]	21.51	5.87	c[btd]	15.50	4.91	
	d	9.18	0.82	d[m][c]	4.78	0.41	d[bmc]	10.30	3.54	
April	b	41.44	3.03	b[t]	4.99	1.25	b[mtc]	75.10	15.40	b[cd]
	m	57.25	4.51	m[t]	0.16	0.16	m[bcd]	45.10	8.57	m[c]
	t	30.38	3.66	t[bmcd]	0.68	0.23	t[bcd]	57.40	10.00	t[c]
	c	39.76	2.86	c[t]	1.47	0.17	c[mt][bd]	16.40	2.84	c[bmt]
	d	58.63	10.70	d[t]	3.66	0.48	d[mtc]	26.00	3.81	d[b]
May	b	33.99	7.22	b[td]	0.06	0.04	b[mtd]	58.40	9.99	b[tcd]
	m	26.10	3.01	m[td]	1.54	0.34	m[bc]	39.50	5.56	m[cd]
	t	17.21	1.55	t[bmc]	0.93	0.18	t[bc]	32.30	4.93	t[d][b]
	c	33.87	3.07	c[td]	0.34	0.14	c[mtd]	24.90	4.05	c[d][bm]
	d	15.45	1.08	d[bmc]	1.52	0.42	d[bc]	1.59	0.17	d[bmtc]
June	b	64.58	10.10	b[m]	62.75	6.89	b[dt][c]	148.00	27.10	b[mtcd]
	m	88.96	14.80	m[btcd]	58.21	4.02	m[td][c]	43.90	5.27	m[d][b]
	t	44.93	4.49	t[m]	42.16	1.86	t[bmc]	34.90	5.01	t[d][b]
	c	56.08	4.18	c[m]	80.17	8.16	c[bmtd]	34.60	2.32	c[d][b]
	d	49.21	3.74	d[m]	40.82	4.19	d[bmc]	14.00	1.59	d[bmtc]
July	b	56.58	4.40	b[tcd][m]	33.61	3.32	b[t][mcd]	138.00	47.60	b[mtcd]
	m	92.16	7.86	m[btcd]	103.00	7.84	m[btdc]	49.80	22.20	m[c][b]
	t	34.98	2.72	t[bm]	17.08	1.22	t[bmcd]	26.20	2.45	t[c][b]
	c	37.15	2.28	c[bm]	52.10	3.31	c[btd][m]	11.50	2.54	c[bmt]
	d	41.71	4.16	d[bm]	40.70	2.77	d[bt][mc]	19.20	2.11	d[b]
Aug.	b	45.59	15.50		11.17	1.72		108.00	17.70	b[mtcd]
	m	31.79	4.51		13.63	2.70		46.00	7.76	m[c]
	t	36.99	3.76		22.00	8.69		38.40	7.28	t[c]
	c	49.81	14.40		13.18	1.19		13.20	2.41	c[bmt]
	d	20.11	2.50		7.49	0.80		40.80	18.10	d[b]

APPENDIX—(continued)

Month	*Site*	*Co*			*Cr*			*Mn*		
		$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*	$\bar{x}$	*S.E.*	*A*
Sept.	b	30.70	3.59	b[t][mc]	12.07	0.79	b[t]	87.30	18.50	b[mtcd]
	m	56.77	5.24	m[btd]	10.77	0.97	m[c]	47.30	8.27	m[c][b]
	t	20.31	2.04	t[bmc]	7.81	0.79	t[bc]	26.00	4.57	t[c][b]
	c	55.03	3.99	c[btd]	25.61	7.10	c[bmtd]	30.20	9.78	c[bmtd]
	d	23.32	2.97	d[cm]	10.60	1.41	d[c]	27.20	4.09	d[c][b]
Oct.	b	53.84	4.87	b[t]	18.95	1.61		88.20	11.00	
	m	51.55	8.92		21.60	2.07		53.70	7.14	
	t	39.38	3.48	t[bd]	18.75	1.69		39.80	5.62	
	c	42.81	1.38		17.55	0.44		21.10	2.26	
	d	55.40	3.39	d[t]	16.80	1.13		32.40	8.43	
Nov.	b	45.53	2.80	b[td]	23.26	1.54	b[td]	42.90	5.30	b[mtcd]
	m	43.02	3.74	m[td]	20.42	1.61	m[td]	43.00	9.03	m[cd][b]
	t	21.99	1.97	t[bmcd]	14.44	2.08	t[bmc]	22.50	4.88	t[c][b]
	c	39.85	2.73	c[td]	19.74	1.17	c[td]	16.80	4.07	c[bmt]
	d	31.78	2.81	d[t][bmc]	14.01	1.08	d[bmc]	14.30	3.08	d[bm]
Dec.	b	10.77	1.11	b[mtcd]	37.84	8.55	b[tcd]	131.00	24.50	b[mtcd]
	m	5.14	1.29	m[d][b]	32.56	4.22	m[tcd]	25.30	4.60	m[c][b]
	t	4.60	0.65	t[d][b]	17.20	2.20	t[bm]	27.10	3.54	t[cd][b]
	c	6.38	0.44	c[d][b]	19.93	1.10	c[bm]	8.32	1.30	c[bmt]
	d	2.20	0.49	d[bmtc]	27.67	8.98	d[bm]	16.10	3.42	d[bt]