

Zinc in Estuaries

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R&D Note 390

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National Rivers Authority

ZINC IN ESTUARIES

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CONTENTS

Page

LIST OF TABLES

iii

LIST OF FIGURES

iii

SUMMARY

1

1. BACKGROUND AND PROJECT PLAN

3

1.1 Background

3

1.2 Summary of Objectives

3

1.3 Project Plan

3

2. MONITORING OF MARINAS

5

2.1 Use of Zinc Anodes

5

2.2 Monitoring Sites

5

2.3 Procedures Used By NRA for Sampling and Analysis

5

3. WRc MONITORING

7

3.1 Sampling sites

7

3.2 Sampling and Filtration

7

3.3 Analysis

8

4. RESULTS AND DISCUSSION

9

4.1 Dissolved Zinc Concentrations

9

4.2 Sediment Zinc Concentrations

17

4.3 Zinc Budgets

22

4.4 Investigation into sources of zinc contamination

26

4.5 Isotope Ratio Studies

28

5. CONCLUSIONS

29

5.1 Sources of Zinc in Estuaries

29

5.2 EQS Exceedances

29

6. RECOMMENDATIONS

31

6.1 Zinc in Estuaries

31

6.2 Monitoring

31

REFERENCES

35

CONTENTS (Continued)

Page

APPENDICES

A	DISSOLVED ZINC CONCENTRATIONS	37
B	PHYSICAL PARAMETERS FOR ROUTINE SAMPLING	39
C	ANALYTICAL METHODOLOGY	45

9

LIST OF TABLES

	Page
4.1 Concentrations of dissolved zinc in a single harbour	13
4.2 Zinc in Sediments	21
4.3 Sources of zinc contamination during filtration	27

LIST OF FIGURES

4.1 Dissolved Zinc in Poole Harbour	11
4.2 Dissolved Zinc in Orwell/Deben Estuaries	15
4.3 Dissolved Zinc in marinas around the South and East coast of England	19
4.4 Depth Profile in Water	23
4.5 Depth Profile in Sediment	24

SUMMARY

Concentrations of dissolved zinc close to or above the Environmental Quality Standard (EQS) of $40 \mu\text{g l}^{-1}$ have been observed in marinas and estuarine waters. Baseline zinc levels in uncontaminated coastal water are typically in the range 0.5 to $2 \mu\text{g l}^{-1}$. The concentrations reported in routine monitoring undertaken by NRA have been considerably higher than this. It has been proposed that dissolution of sacrificial zinc anodes used in marinas and on leisure boats might cause increased levels of zinc at some locations.

This project has the aim of investigating the sources of zinc contamination in estuaries and of providing an indication of how elevated levels might arise and how they can be controlled. In particular, the project was intended to assess the contribution of zinc anodes to concentrations of the metal in marinas and coastal waters.

This work shows that the increase in zinc levels in estuaries due to anode use is likely to be small in relation to the current Environmental Quality Standard. Nevertheless, sacrificial anodes can be expected to lead to measurable increases in concentrations of dissolved zinc in marinas and, to a lesser extent, in nearby estuary areas.

Zinc from anodes is released initially into the dissolved phase. The rate of adsorption to finely divided particulate matter is sufficiently fast to ensure that a large proportion of the metal is transferred relatively quickly from solution to suspended sediments. The division between the contaminated sediment which remains in the marina and that which leaves the marina on the outgoing tide will depend on local conditions (e.g. suspended sediment levels and whether or not the marina is enclosed).

The local increase in concentrations of dissolved zinc near open marinas may be between 2 and $5 \mu\text{g l}^{-1}$. In enclosed marinas, this increase can be as large as $15 \mu\text{g l}^{-1}$. Whilst it is necessary to continue to monitor concentrations of dissolved zinc in estuaries, more attention might need to be paid to concentrations of the metal in sediments, particularly in the vicinity of marinas.

Recommendations are made concerning steps which might be taken to improve the quality of sample collection and filtration for trace metal monitoring. These include: provision of guidance on control of contamination, adoption of a common approach to sample filtration and more widespread use of field blanks.

1. BACKGROUND AND PROJECT PLAN

1.1 Background

Concentrations of dissolved zinc close to or above the Environmental Quality Standard $40 \mu\text{g l}^{-1}$ have been observed in marinas and estuarine waters. Baseline zinc levels in uncontaminated coastal water are typically in the range 0.5 to $2 \mu\text{g l}^{-1}$. The concentrations reported in routine monitoring undertaken by NRA have been considerably higher than this.

In some areas, elevated concentrations can be accounted for by natural inputs of the metal from mineralised catchments or by specific industrial discharges. However, in the majority of locations, high zinc concentrations are not associated with any readily identifiable source of the metal. It has been proposed that dissolution of sacrificial zinc anodes used in marinas and on leisure boats might make a substantial contribution to zinc levels at some locations.

1.2 Summary of Objectives

To investigate sources of zinc contamination in estuaries and provide an indication of how elevated levels can arise and how they might be controlled.

To assess contribution of zinc anodes to concentrations of the metal in marinas and coastal waters.

1.3 Project Plan

1. In collaboration with NRA, to identify sites where studies may be carried out. Locations where elevated zinc levels have been reported will be chosen for intensive monitoring. A further site, where contamination is low, will be used as a control.
2. To assess the quantities of zinc used for electrolytic protection in marinas, the rate of dissolution and estimation of the extent to which zinc released in this way is flushed from the estuaries concerned. This will involve sampling of waters and sediments from a number of relevant locations, so that the extent of contamination can be established.
3. To monitor zinc concentrations at the three sites to establish any seasonal changes which might be linked to activity in marinas. Sediments would also be analysed as an indication of the accumulation of zinc.
4. To produce recommendations regarding the use of zinc anodes and their impact on metal concentrations in estuaries.

2. MONITORING OF MARINAS

2.1 Use of Zinc Anodes

When metallic zinc is connected to iron or steel and both metals are immersed in water, an electrochemical cell is established in which zinc becomes the anode (positively charged) and iron the cathode (negatively charged). The overall effect of this is to reduce the tendency for the iron to be subject to corrosion. This is the principle of cathodic protection which is used widely to protect iron structures in contact with water. Cathodic protection is usually employed in conjunction with other anti corrosion measures, e.g. painting. The anode of the cell is corroded rapidly and, if the protective effect on the iron is to be maintained, must be replaced before it dissolves entirely.

In marine applications of the technique, zinc anodes are bolted either to the hull of the boat (if it is constructed of steel rather than fibreglass), or to the propeller shaft. Although the quantity of zinc used on yachts and in marinas is small in relation to that applied to larger ships, leisure applications of zinc anodes could be important localised sources of zinc contamination. In estuaries or harbours where exchange of water is restricted, the zinc released by anodic dissolution could build up to reach significant concentrations.

2.2 Monitoring Sites

Three sites were chosen for routine monitoring. These were two locations where levels higher than the EQS had been reported - Poole Harbour and the Orwell estuary - and one site where there was less boating activity - the Deben estuary. Sampling positions at these locations were chosen to assess contamination in or near to marinas and (where possible) more remote positions where levels of zinc might be considered to represent the local background.

These sites were sampled on four occasions throughout the summer (boating) season and once in the winter when a large proportion of yachts had been removed from the water.

Single samples were also collected from other locations in order to provide comparative data. These sites were at Plymouth, Torquay, Chichester Harbour, and the Blackwater and Crouch estuaries.

2.3 Procedures Used By NRA for Sampling and Analysis

The determination of trace metal concentrations in environmental samples can be subject to a wide range of analytical and sampling errors. Many studies of the accuracy of environmental data have concluded that contamination during sampling and poor control over analysis have been responsible for large errors.

Attempts to determine the concentrations of trace metals in seawater over the past twenty years has been characterised by an apparent downward trend as contamination has been controlled and methodology has been improved.

2.3.1 Sampling

The approach adopted for the collection and filtration of samples for the determination of trace metals in estuarine samples was investigated for the two NRA Regions concerned (South West/Wessex and Anglian). Staff experienced in trace metal environmental work do not usually undertake sample collection. Sampling is carried out by pollution control staff or by other staff who are involved in on-site work.

The approaches to sampling and the equipment used were different in the two Regions. Past problems of contamination during sample collection had been recognised in South West/Wessex Region. Laboratory staff had tested the filtration equipment and issued guidance to sampling staff. There were plans to issue field blanks as a demonstration of control over contamination.

Syringes, filter apparatus and protocols were obtained from both Regions. These were tested for potential contamination by filtering and analysing aliquots of sea water, deionised water and acidified deionised water. Another type of filter was also tested.

2.3.2 Analytical Accuracy

The National Laboratory Service of the NRA has set up its own programme of quality control for analytical techniques. This programme is now well established and capable of ensuring adequate control over analytical error. However, earlier analytical data for zinc in saline samples which were obtained using techniques developed for river water analysis may have been subject to bias. In particular, determinations using methods based on flame atomic absorption require special attention when used for saline samples. Such methods can be used satisfactorily provided steps are taken to achieve the required limit of detection (by preconcentration) and to control the effects of the salt matrix (by removing it or by adequate calibration procedures). The method of analysis used by WRC is given in Appendix C.

3. WRc MONITORING

3.1 Sampling sites

Sampling sites are identified below.

Sample site	Map reference
Poole Harbour	
Cobbs Quay Marina	SY 994919
Salterns Marina	SZ 036896
Rockley Park	SY 983905
Poole Bridge (A350)	SZ 007903
Brands Bay	SZ 023853
Shell Bay	SZ 038865
Orwell/Deben Estuary	
Felixstowe Beach	TM 293328
Levington Marina	TM 247380
Shotley Marina	TM 252340
Woolverstone Marina	TM 194392
Pin Mill	TM 207380
Waldringfield (Deben)	TM 286446

The sites offered the opportunity to compare several marinas with other sites where the boat density was much lower. At Salterns Marina in Poole and Shotley Marina in the Orwell Estuary, samples were collected from inside and outside the marina.

To provide comparative data, single samples were taken inside and outside marinas in Plymouth, Torquay, Burnham on Crouch, Chichester Harbour and the Blackwater Estuary.

3.2 Sampling and Filtration

Surface samples were collected in 2 litre polyethylene bottles (Nalgene) and filtered at the sampling site. Filtration was carried out under positive pressure using Nalgene 250 ml polycarbonate filter units containing 0.45 μm Millipore cellulose acetate filter membranes. The units and filters were pre-leached and rinsed at the laboratory by filtration of 100 ml of 10% nitric acid followed by two 250 ml portions of deionised water. The units, each complete with its filter membrane, were stored in polythene bags. After filtering the seawater samples, filtrate was decanted into 250 ml polyethylene bottles (washed with 10% nitric acid and rinsed with deionised water) and preserved with 2 ml l⁻¹ nitric acid (Merck AristaR).

Field blank filtrations were carried out on each sampling exercise (approximately 20% of filtrations were field blanks).

3.3 Analysis

Samples were analysed using the solvent extraction flame atomic absorption method described in Appendix C.

A colorimetric technique was developed to determine dissolved zinc in the field. This was useful in the selection of sampling sites and might be of use to NRA in follow-up investigations of zinc contamination. The method is described in Appendix C.

4. RESULTS AND DISCUSSION

4.1 Dissolved Zinc Concentrations

The concentrations of dissolved zinc should be viewed in relation to two guide values. The first is the zinc concentration regarded as typical of relatively uncontaminated coastal water. This is approximately $0.5 \mu\text{g l}^{-1}$ (Tappin *et al* 1993). The extent of contamination by discharges etc. can be assessed with reference to this background concentration. The second important reference concentration is the EQS value of $40 \mu\text{g l}^{-1}$. Concentrations higher than this value are usually taken to warrant remedial action to control pollution.

- Zinc data from each site and background information (temperature, salinity and time of sampling) are presented in Appendices A and B, respectively. These results are discussed below.

(a) Poole Harbour

Results are summarised in Figure 4.1. The control (non-marina) sites of Brands Bay and Rockley Park, both of which are inside the harbour, provided samples of mean zinc concentration of 2.3 and $2.0 \mu\text{g l}^{-1}$, respectively. This is marginally higher than that found outside the harbour at Shell Bay ($1.7 \mu\text{g l}^{-1}$). These values are only slightly higher than the baseline level.

The shape of Poole Harbour with its narrow entrance and relatively long and narrow channel is responsible for its poor tidal flushing characteristics. Estimates of the tidal prism (the ratio of the difference in water volume between high and low tide to the water volume at high tide in the basin) vary between 0.35 and 0.45 (Falconer 1986 and 1984, respectively). This means that elevated zinc concentrations in the harbour might be expected. This is borne out by observations made around the Harbour. At the A350 Poole Bridge site the mean level was $4.3 \mu\text{g l}^{-1}$. This site was at the entrance to Holes Bay, a land-locked sub-system in the Poole Harbour which receives a number of discharges including the effluent from Poole sewage treatment works. Sewage effluent has been identified as a contributor to zinc levels in rivers and estuaries. Concentrations of $30-50 \mu\text{g l}^{-1}$ are typical.

In the two marinas (Cobbs Quay and Salterns), dissolved zinc concentrations were higher than those seen in the outer harbour. Mean levels for Cobbs Quay and Salterns Marinas were 13.7 and $10.7 \mu\text{g l}^{-1}$ respectively. It is worth noting that these levels are still well below the EQS value. The range of concentrations were from 6 to $21 \mu\text{g l}^{-1}$ (Cobbs) and 6 to $16 \mu\text{g l}^{-1}$ (Salterns). This variation is likely to have arisen from sampling at different tidal states. A comparison of five samples taken from different parts of Salterns Marina in January 1995 showed a concentration gradient that tended to increase as the boat density increased (Table 4.1).

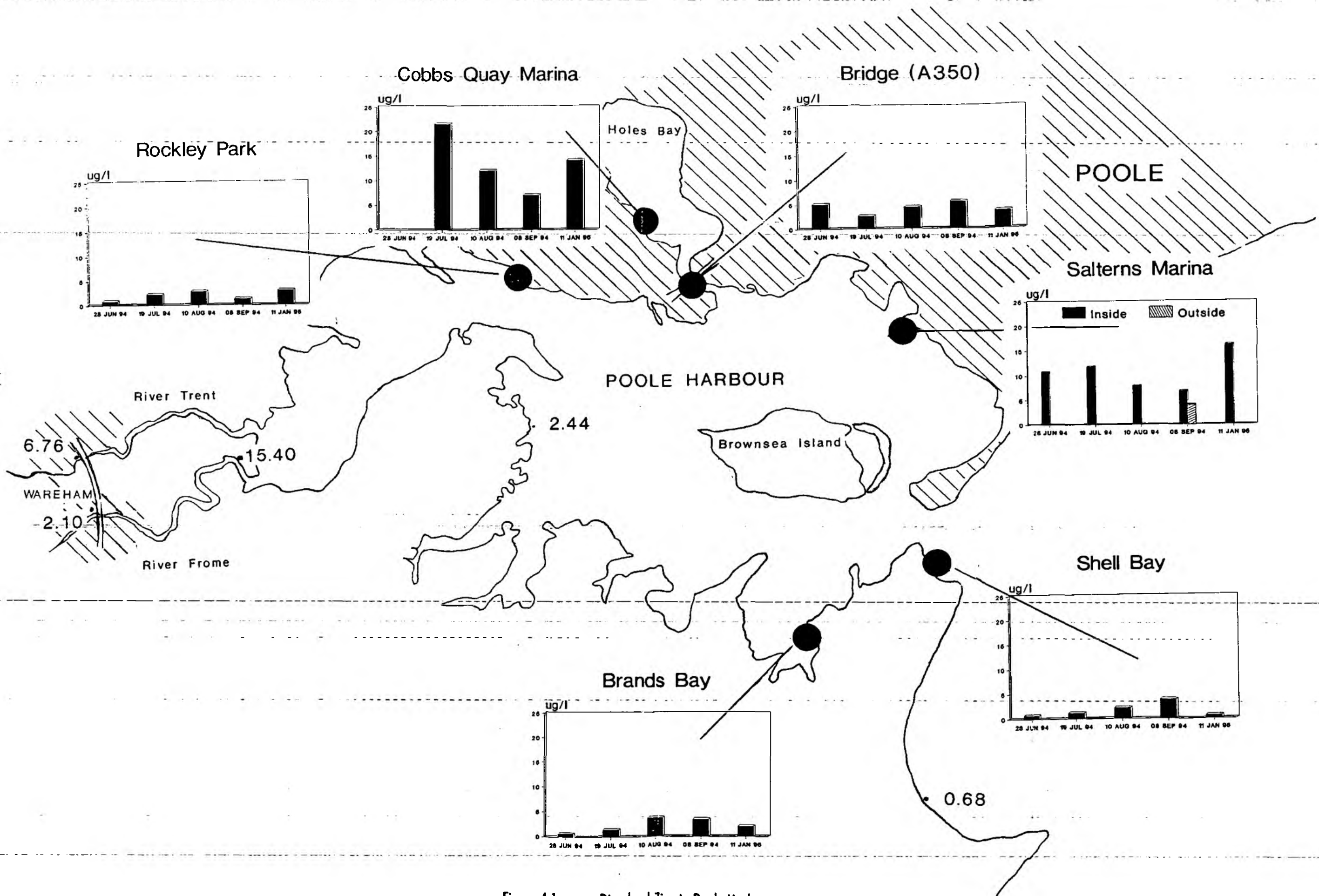


Figure 4.1 Dissolved Zinc in Poole Harbour

Table 4.1 Concentrations of dissolved zinc in a single harbour

Site	Zn ($\mu\text{g l}^{-1}$)				
	I	II	III	IV	V
Salterns Marina (11/1/95)	13.20	14.91	15.74	16.34	21.22
Shotley Marina (19/1/95)	21.05	22.29	22.96	22.20	23.05

(b) Orwell/Deben Estuary

A wide range of dissolved zinc concentrations were measured in the Orwell Estuary (Figure 4.2). At the riverine end member in Ipswich itself, concentrations as high as $379 \mu\text{g l}^{-1}$ were measured. Rapid dilution occurred such that at Wherstead (4 km downstream) levels were reduced to a value of $9.06 \mu\text{g l}^{-1}$.

Three marinas on the estuary were examined. Woolverstone Marina is sited approximately 3 km downstream of the Orwell Bridge and is open to the main flow of the estuary. Zinc dissolved from anodes on yachts is likely to be dispersed rapidly. This expectation was confirmed by a mean measured zinc concentration of $5.0 \mu\text{g l}^{-1}$. This was not significantly higher than levels measured at Pin Mill (mean = $4.8 \mu\text{g l}^{-1}$), down river from Woolverstone and where boat density was comparatively low.

Levington Marina (ca. 8 km downstream from the Orwell Bridge), is a natural inlet that has been enclosed and used to moor yachts. The mean dissolved zinc concentration of $6.1 \mu\text{g l}^{-1}$ is a small increase compared with the nearby control site at Pin Mill.

Shotley Marina is a fully enclosed concrete basin marina with lock gates to allow entry and exit at all states of the tide. The mean zinc level in the marina was $13.1 \mu\text{g l}^{-1}$, compared with only $5.4 \mu\text{g l}^{-1}$ directly outside the lock gates. As noted before, this concentration is well below the EQS. Given that there are few other substantial sources of zinc to the waters of the marina, this concentration might be attributed to anode use. Zinc levels for 5 different points sampled in the marina in January 1995 showed no significant difference suggesting that the water present in the marina is better mixed than that at Salterns Marina (Table 4.1).

Samples taken from Felixstowe beach were of mean concentration of $3.1 \mu\text{g l}^{-1}$. This reflected the influence of the nearby port and the estuaries of the Orwell and Stour. Samples taken from Waldringfield on the Deben Estuary which was chosen as a control site were, as expected, low in zinc (mean = $2.3 \mu\text{g l}^{-1}$).

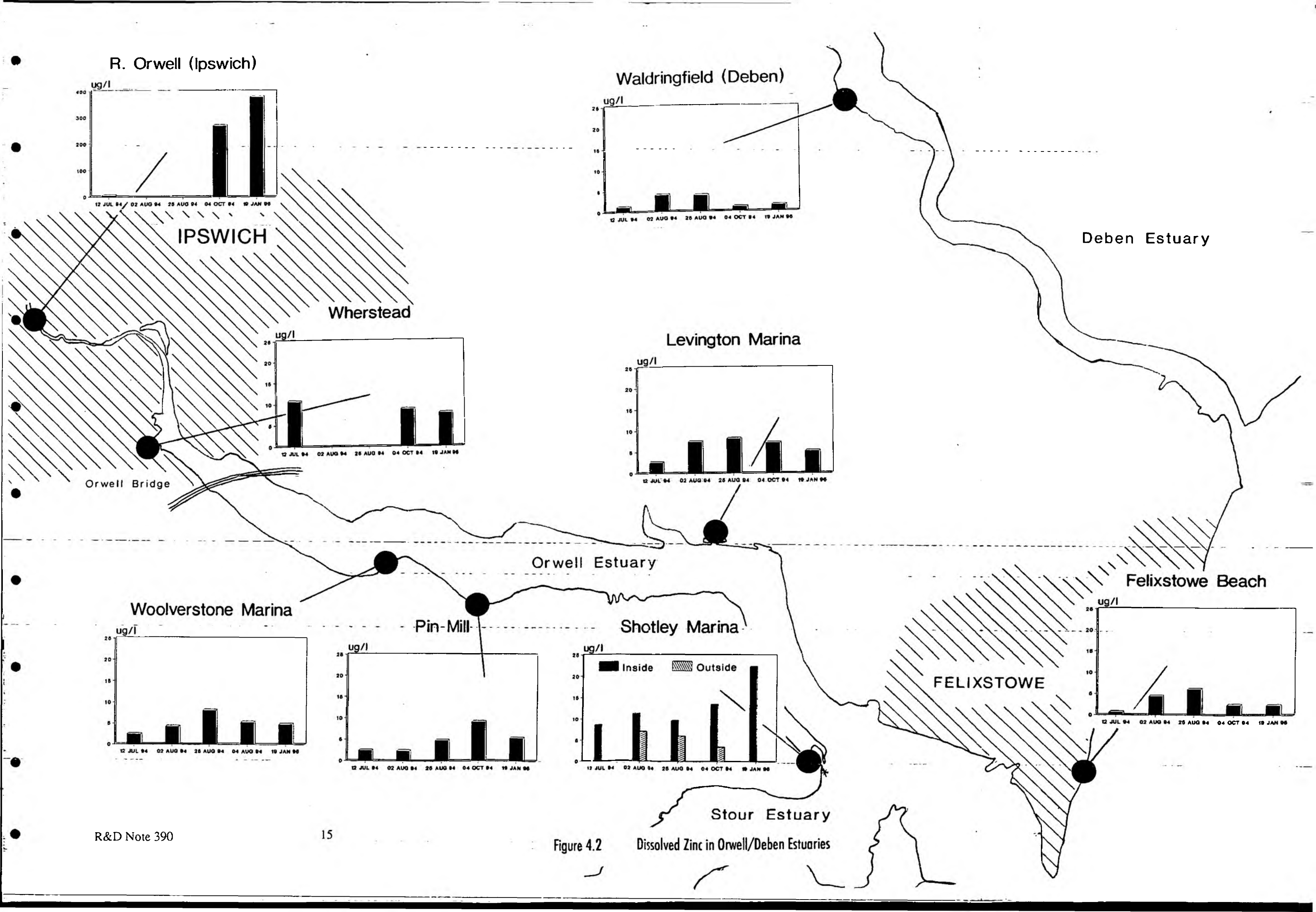
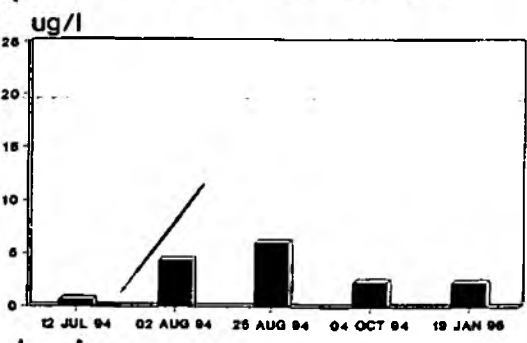
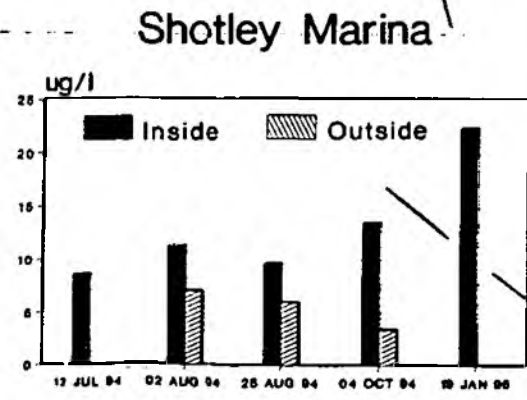
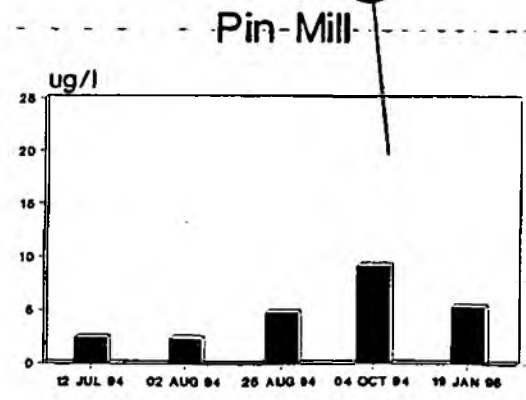
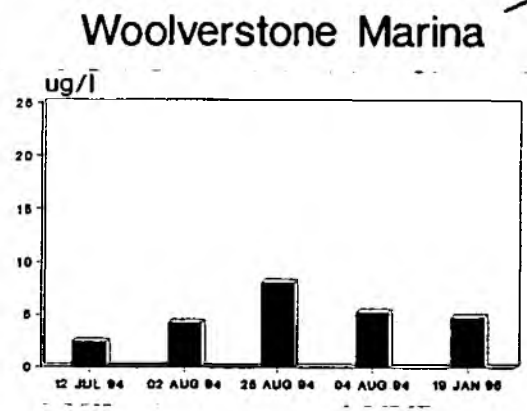
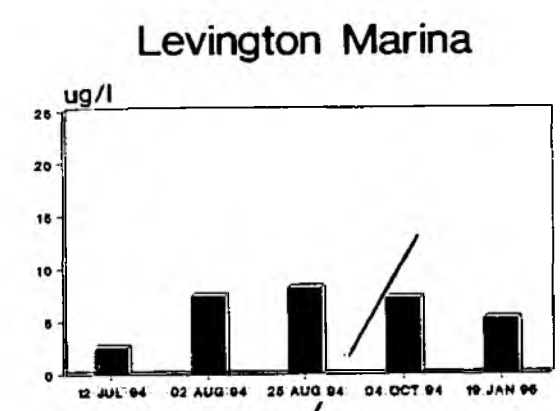
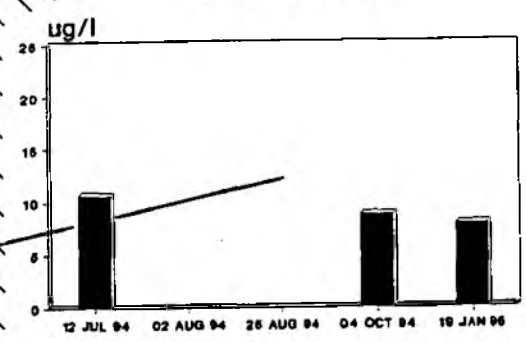
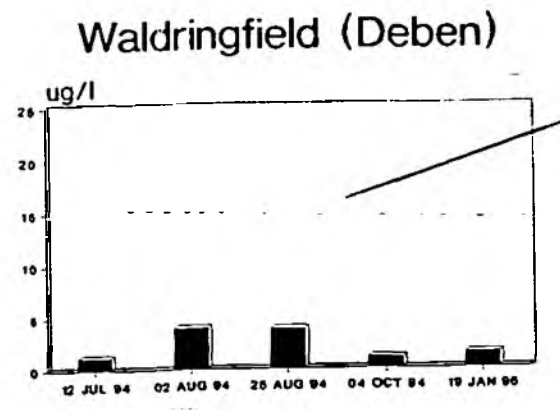
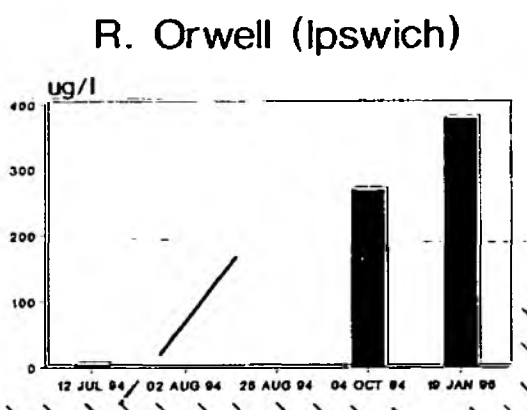


Figure 4.2 Dissolved Zinc in Orwell/Deben Estuaries

(c) Other sites

The other sites sampled showed zinc concentrations similar to those at Poole and in the Orwell (Figure 4.3). Sutton Marina in Plymouth, an enclosed marina with lock gates showed an increase in zinc concentration of around $12.5 \mu\text{g l}^{-1}$ with respect to water collected outside the marina. Higher levels were also obtained from Torquay and Burnham (Crouch Estuary, Essex) marinas. Zinc values in poorly flushed Chichester harbour were similar to those in Poole Harbour. Values inside and outside the marina were 17.3 and $3.7 \mu\text{g l}^{-1}$ respectively.

4.2 Sediment Zinc Concentrations

Sediment samples were taken inside and outside each marina. Concentrations of zinc are provided as total concentrations and as a concentration expressed in relation to the $<63 \mu\text{m}$ fraction of the sample. This second approach provides a more reliable assessment of contamination because the varying effect of dilution with different quantities of larger particles (sand) is removed. Trace metals such as zinc tend to be associated with the $<63 \mu\text{m}$ fraction (Taylor 1986, Bloom and Creclius 1987), so normalisation with respect to this particle size fraction will produce a clearer view of contamination levels and likely biological effects.

Zinc concentrations in sediments are shown in Table 4.2

Sediment zinc concentrations are markedly higher in marinas than outside. Levels for enclosed marinas were typically $200-300 \mu\text{g g}^{-1}$ compared with only *ca.* $100 \mu\text{g g}^{-1}$ in control sediments. The use of anodes is probably the principal source of this enhancement.

There was little difference between samples taken in summer and winter. Sediment zinc concentrations in Salterns Marina (January 1995) were highest at the point furthest away from the marina entrance. Levels showed little variation across the marina ($169 - 178 \mu\text{g g}^{-1}$). These differences reflected the fact that on each tide relatively clean sediment enters the marina from Poole Harbour. Similar concentrations and patterns were observed in Shotley Marina with concentrations increasing away from the lock gates towards the centre of the marina (127 to $252 \mu\text{g g}^{-1}$).

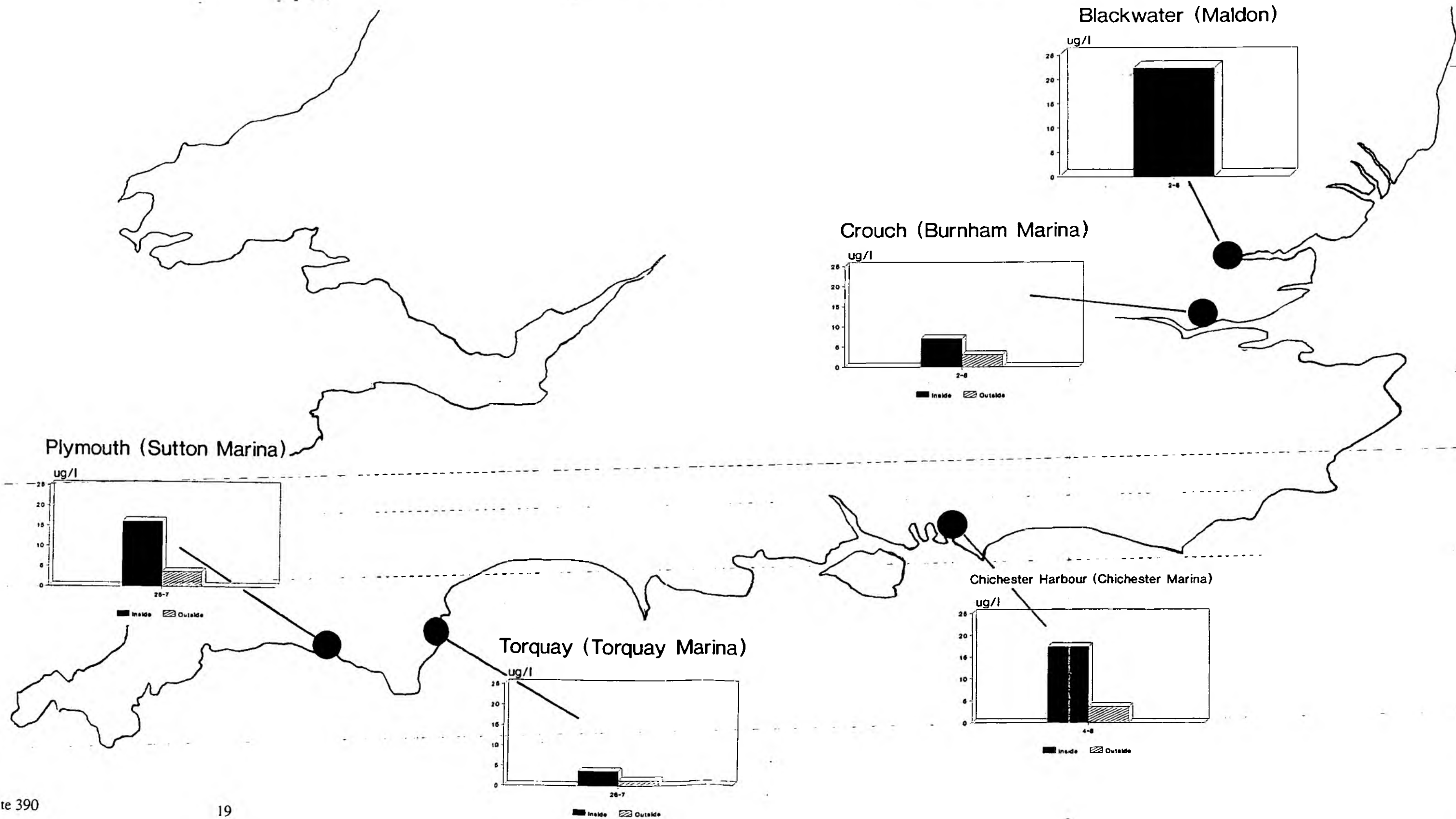


Figure 4.3 Dissolved Zinc in marinas around the South and East coast of England

Table 4.2

Zinc in Sediments

Sample	Zn ($\mu\text{g g}^{-1}$)	Zinc Concentration	
		Normalised* ($\mu\text{g g}^{-1}$)	Percentage sediment <63 μm
Poole Harbour			
Cobbs Quay Marina (19/7/94)	192.6	192.6	>99.9
Cobbs Quay Marina (11/1/95)	161.4	161.4	>99.9
Salterns Marina (28/6/94)	247.8	265.5	93.3
Salterns Marina (11/1/95) I	230.8	241.4	95.6
II	218.4	243.6	89.7
III	168.9	182.6	92.5
IV	176.5	198.7	88.8
V	178.4	186.9	95.4
Brands Bay (28/6/94)	27.9	157.4	17.8
Rockley Park (11/1/95)	69.9	173.2	40.4
Arne (28/6/94)	26.0	205.5	12.6
Orwell/Deben Estuary			
Shotley Marina (12/7/94)	262.5	262.5	>99.9
(19/1/95) I	137.2	144.9	94.7
II	127.2	149.6	85.1
III	132.8	138.8	95.7
IV	197.6	204.7	96.5
V	251.5	258.2	97.4
(Outside, 12/7/94)	71.8	101.1	71.0
Woolverston Marina (12/7/94)	125.9	127.2	99.0
(19/1/95)	127.2	128.1	99.3
Levington Marina (12/7/94)	127.9	127.9	>99.9
(19/1/95)	112.4	112.4	>99.9
Pin Mill	98.3	223.7	44.0
Orwell Bridge	25.6	170.6	15.0
Waldringfield (Deben) (12/7/94)	94.0	106.6	88.2
(19/1/95)	138.6	169.4	81.8
Crouch			
Burnham Marina	118.2	118.2	>99.9
(Outside)	77.5	106.7	72.6
Blackwater			
Maldon	165.8	171.2	96.9
Plymouth			
Sutton Marina	281.4	313.9	89.7
Torquay			
Torquay Marina	127.1	278.7	45.6

* Normalised to <63 μm fraction of sediment

Depth profiles of dissolved zinc in the water column in Salterns Marina and for total zinc the associated sediment are given in Figures 4.3 and 4.4. In the water column, the reduction in dissolved metal with depth can be explained by adsorption to sediments. Although periodic dredging of the marina will have caused a significant disruption of the sediment a slight sub-surface maximum in zinc concentration was observed typical of trace metal profiles. Trace metal behaviour in sediments can be summarised as (a) sedimentation and precipitation of dissolved metal as sulphide at the anoxic boundary near to the sediment surface; (b) re-dissolution in lower layers of sediments (as the sediment is compacted and under the influence of chemical processes e.g. formation of soluble polysulphides); (c) upward diffusion of re-dissolved zinc; and (d) re-precipitation of the metal at the surface (as sulphide or by coprecipitation with iron sulphides). These processes tend to produce the type of profile which was observed.

Estimates of safe concentrations of zinc in sediment have been derived from partitioning experiments (e.g. 75 and 100 $\mu\text{g g}^{-1}$, Pavlou and Weston 1983). Such estimates are likely to form the basis of Sediment Quality Standards which may be adopted by the UK.

4.3 Zinc Budgets

The following Information on anode use was obtained for Salterns Marina in Poole Harbour.

Average No. of yachts	= 260
0.29 Kg Zn dissolved per yacht per year	= 74.3 Kg Zn dissolved from yachts per year
No. of anodes in marina	= 720
2.4 Kg Zn dissolved per anode per year	= 1728 Kg Zn dissolved from marina per year
TOTAL Zn dissolved from anodes per year	= 1802.3 kg per year
	= 4.94 kg day ⁻¹
	= <u>2.47 Kg per tide</u>
Volume of water at low tide	= 46500 m ³
Volume of water at high tide	= 108500 m ³
Flushing volume of marina	= <u>62000 m³ per tide</u>

DISSOLVED SYSTEM

Mean aqueous concentration of Zn in marina	= 10.7 $\mu\text{g l}^{-1}$
Mean aqueous concentration of Zn outside marina	= 2.00 $\mu\text{g l}^{-1}$

Assuming 62000 m³ of 'clean' seawater mixes with 46500 m³ water remaining in the marina at low water, then that low water volume must contain 22.3 $\mu\text{g l}^{-1}$ of zinc to maintain a zinc level of 10.7 $\mu\text{g l}^{-1}$ at high water. Therefore 11.6 $\mu\text{g l}^{-1}$ of dissolved zinc is required to dissolve into the low water volume each tide to elevate the concentration to 22.3 $\mu\text{g l}^{-1}$ ready for the next tidal cycle.

Therefore 11.6 $\mu\text{g l}^{-1}$ x 45600 m³ = 0.54 kg required from anodes

Water Depth (m)

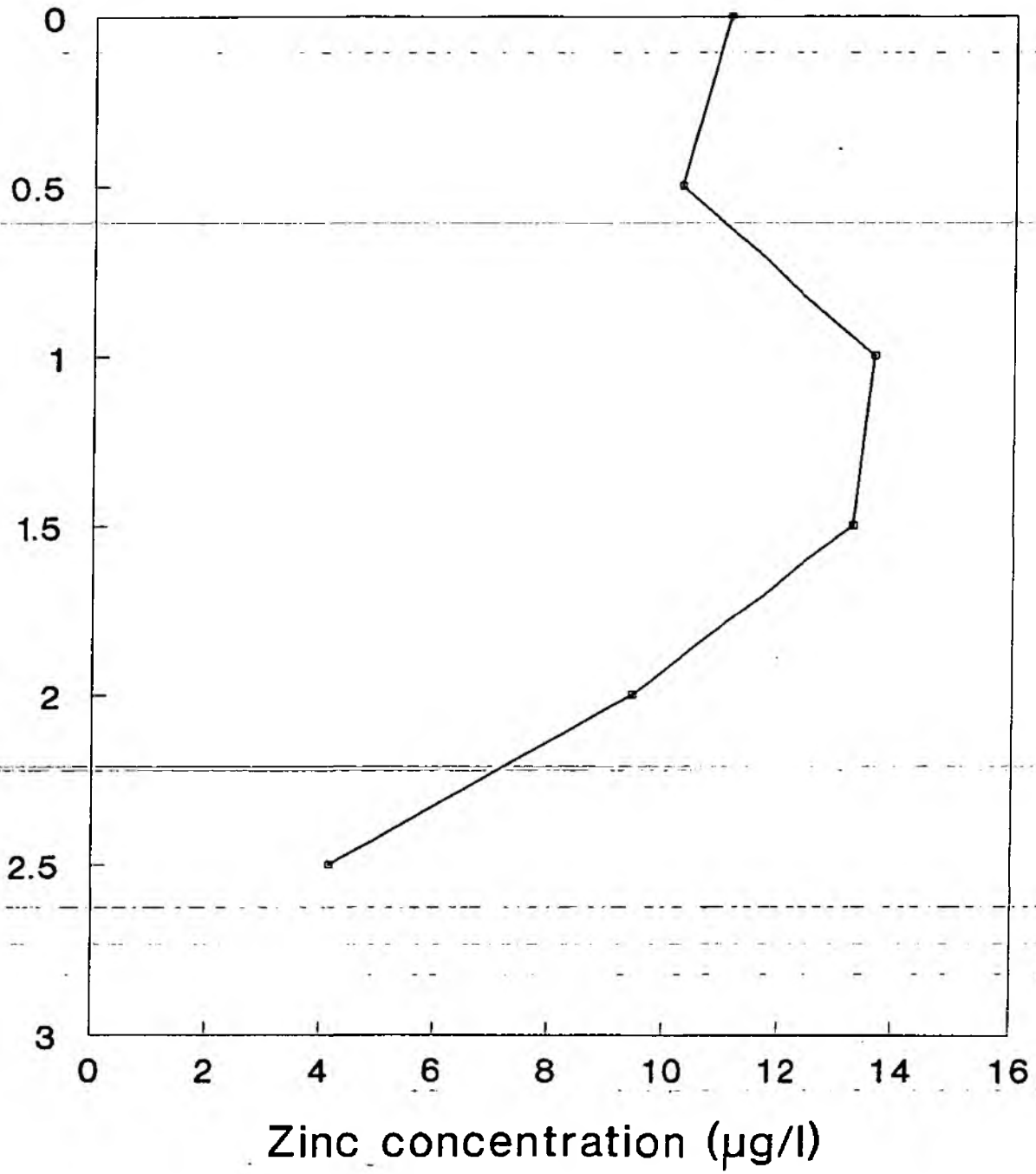


Figure 4.4 Depth Profile in Water

Sediment Depth (cm)

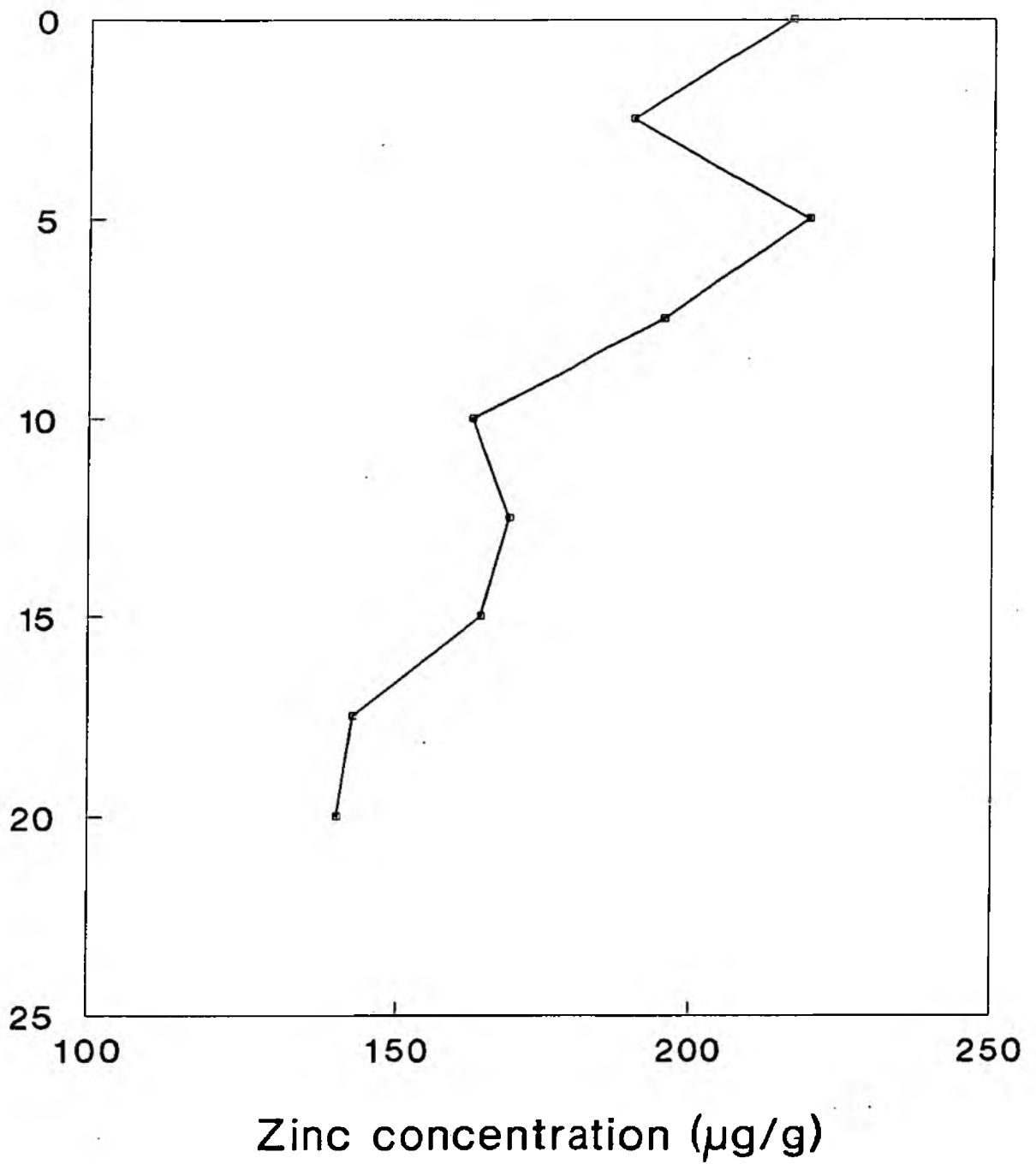


Figure 4.5 Depth Profile in Sediment

PARTICULATE SYSTEM

Therefore $2.47 - 0.54 = 1.93$ kg of zinc per tide must be accounted for through transportation on the solids.

Suspended solids outside the marina

(Rockley, Brands Bay) = 45.8 mg l^{-1}

Suspended solids inside the marina = 8.1 mg l^{-1}

Suspended solids lost to marina sediment = 37.7 mg l^{-1}

$$= 62000 \text{ m}^3 \times 37.7 \text{ mg l}^{-1}$$

$$= 2337.4 \text{ kg per tide}$$

Mean Zn content in marina sediment = 205.3 mg kg^{-1}

Zn content in typical 'control' sediment with fraction
> $53 \mu\text{m}$ (Waldringfield + Pin Mill) = 103.4 mg kg^{-1}

Enhancement in marina = 101.9 mg kg^{-1}

Therefore amount of zinc required to raise the concn. by 101.9 mg kg^{-1} for 2337.4 kg of sediment per tide

$$= 0.23 \text{ kg of Zn}$$

(Therefore $1.93 - 0.23 = 1.7$ kg of zinc must leave the marina on suspended solids with the ebbing tide.)

This quantity is unrealistically large in relation to the amount and metal content of suspended material in the harbour $< 100 \mu\text{g g}^{-1}$ for 8 mg l^{-1} suspended solids $\times 62000 \text{ m}^3 = < 0.05 \text{ kg}$ of Zn per tide). The discrepancy is probably accounted for by the fact that anodes do not dissolve completely before they are replaced, in addition to the following assumptions:

- (a) flushing volume does not include that present at low water
- (b) water present in the marina is well mixed
- (c) average tidal volume used, therefore the double high water, spring and neap tides are averaged out
- (d) that the yachts are present in the marina 24 hours a day
- (e) seasonal variations are ignored

The above estimates indicate that the increase in zinc concentration in Salterns Marina can be attributed to dissolution of anodes. Yachts appear to only contribute a small proportion of the total (4% in this case).

Similar estimates have been made for the dissolution of Zinc from anodes at Shotley Marina (307 kg of Zn used by yachts and 407 kg of Zn used by marina, Shotley Marina *pers. comm*). Less zinc is used by the marina as it is mainly a concrete construction

4.4 Investigation into sources of zinc contamination

Data from the above surveys revealed no concentrations of dissolved zinc greater than $20 \mu\text{g L}^{-1}$. Since this was lower than many values reported by NRA, potential sources of contamination during filtration were investigated.

Filters, syringes and procedures were obtained from the two NRA regions concerned: South West/Wessex and Anglian. Another brand of disposable filters (Acrodisk) was also examined. The following equipment was tested for possible contamination.

Source

Anglian	Becton and Dickinson 60 ml Plastipak syringe.
Region	Gelman Sciences disposable filters $0.45 \mu\text{m}$ - unwashed.
South Western	Terumo Sterile ribbon-packed disposable syringes.
Region	Millipore filtration apparatus and $0.45 \mu\text{m}$ Millipore cellulose acetate filters - all of which were acid washed before use.
WRc	Acid washed Terumo 60 ml syringe Acrodisk $0.45 \mu\text{m}$ disposable filters - unwashed
WRc filters (used in this study)	Acid washed, DIW rinsed 250 ml Nalgene filter units. Millipore $0.45 \mu\text{m}$ cellulose acetate filters acid washed and DIW rinsed.

Sixty ml of seawater was drawn into unwashed syringes and dispensed into a polyethylene sample bottle, after 30s. This procedure was repeated, successively, with 60 ml of deionised water and 60 ml of 2% nitric acid. The syringes were then acid washed using 60 ml of 10% nitric acid and rinsed with two portions of deionised water. Finally, a further 60 ml of deionised water was filtered and retained.

The filters were tested in the same way - the cleaning procedures specified in the above table were carried out and successive 60 ml portions of seawater, deionised water and 2% acid were passed through the filter. The filter was then treated with 10% nitric acid, rinsed with deionised water and a 60 ml portion of deionised water was filtered and retained. The solutions were all flushed through the filters using syringes that had been acid washed before use.

For all investigations, blank (unfiltered and not in contact with the syringe) portions of sea water, deionised water and 2% acid were analysed for comparison purposes. The data were analysed statistically to test the significance of any differences between the test solutions and the blank samples (Table 4.3).

Table 4.3 Sources of zinc contamination during filtration

Sample	Difference between sample and blank ($\mu\text{g l}^{-1}$)	n*	s.d. (pooled) ($\mu\text{g l}^{-1}$)	t(calc)	t(0.05)	Signif? at 95% level
Anglian NRA						
Plastipak syringe:						
Seawater	+0.38	1	-	-	-	-
DIW	+1.59	1	-	-	-	-
2% Acid	+9.23	1	-	-	-	-
'Clean DIW'	+0.25	1	-	-	-	-
Filters:						
Seawater	+4.72	6	0.76	6.24	2.37	YES
DIW	+4.02	6	0.47	8.60	2.37	YES
2% Acid	+5.04	6	1.30	3.88	2.37	YES
'Clean DIW'	+0.43	6	0.62	0.69	2.37	NO
South Western NRA						
Terumo syringe:						
Seawater	+1.55	3	0.32	4.84	2.78	YES
DIW	+1.10	3	0.20	5.62	2.78	YES
2% Acid	+5.16	3	0.29	17.52	2.78	YES
'Clean DIW'	+0.26	3	0.83	0.32	2.78	NO
Filters:						
Seawater	-0.49	3	0.92	0.53	2.78	NO
DIW	+0.06	3	1.09	0.06	2.78	NO
2% Acid	+0.30	3	0.50	0.59	2.78	NO
'Clean DIW'						
Acrodisk filters:						
Seawater	-1.27	4	0.62	2.05	2.57	NO
DIW	+0.28	4	1.95	0.14	2.57	NO
2% Acid	-0.95	4	1.02	0.92	2.57	NO
'Clean DIW'	+0.45	4	1.72	0.26	2.57	NO
WRc Field blanks:						
DIW	-0.10	20	0.18	0.57	2.09	NO

* n = number of replicate filtrations

sd is the standard error of the mean difference between test samples and blanks
t(calc) and t(0.05) are calculated and tabular values of the Student's "t" statistic

For the syringes it was shown that 2% nitric acid was capable of releasing zinc equivalent to a sample concentration of *ca.* 5 to 9 $\mu\text{g l}^{-1}$. For seawater and deionised water the syringes contributed a small (but statistically significant at the 0.05 probability level) quantity of zinc (*ca.* 1 $\mu\text{g l}^{-1}$). Using the acid washing procedure there was no significant increase in concentration due to filtration.

The Anglian NRA filtration procedure (unwashed disposable filters) introduced as much as 5 $\mu\text{g l}^{-1}$ of zinc to the water samples. This was reduced to a negligible quantity by acid washing.

The unwashed Acrodisk filters were shown to be zinc-free for all of the solutions passed through them. These filters may not be suitable for general use because of their small size and sample capacity. However, this test illustrates that there are types of filter which might be used without washing. The contamination introduced by the larger-scale WRC procedure was shown to be small and of no statistical significance ($p=0.05$).

In conclusion, the procedure that introduced the most contamination, using unwashed syringes and filters, could lead to an increase in zinc concentration of up to *ca.* 6.5 $\mu\text{g l}^{-1}$. Acid washing or using a "cleaner" (tested) brand of filters could reduce contamination to a negligible amount.

The increase in sample concentration attributable to contamination during filtration, whilst being potentially important does not account for the larger discrepancies between NRA data and those reported here. The apparent exceedances of the EQS value may contain a contribution from filtration but other sources of error need to be sought. These are: analytical errors caused by the use of inappropriate techniques or calibration procedures and other sources of contamination during sample collection.

4.5 Isotope Ratio Studies

The value of using differences in the abundance of naturally occurring isotopes of zinc for the identification of the sources of contamination was examined. Samples of zinc from anodes, from marina water, and from marina sediments were compared with "natural zinc" in water and sediment samples from a mineralised area in Derbyshire. No differences in isotope ratios were detectable.

5. CONCLUSIONS

5.1 Sources of Zinc in Estuaries

Zinc is the most widely distributed of the six trace metals monitored routinely in the environment. It is a constituent of a range of commercial and household products and of various industrial effluents. Thus, the majority of discharges to rivers and estuaries, including sewage effluents, are likely to be responsible for increases in zinc concentration.

This work demonstrates that the contribution of anodes to elevated zinc levels in estuaries is likely to be small in relation to the current Environmental Quality Standard. Nevertheless, sacrificial anodes can be expected to lead to measurable increases in concentrations of dissolved zinc in marinas and, to a lesser extent, in nearby estuary areas.

Zinc from anodes is released initially into the dissolved phase. The rate of adsorption to finely divided particulate matter is sufficiently fast to ensure that a large proportion of the metal is transferred relatively quickly from solution to suspended sediments. The division between the contaminated sediment which remains in the marina and that which leaves the marina on the outgoing tide will depend on local conditions (for example, suspended sediment levels and whether or not the marina is enclosed).

Results reported here suggest that the local increase in concentrations of dissolved zinc caused by open marinas may be between 2 and 5 $\mu\text{g l}^{-1}$. In enclosed marinas, this increase might be as large as 15 $\mu\text{g l}^{-1}$.

5.2 EQS Exceedances

The concentrations of dissolved zinc reported by NRA over the past few years have been higher than those measured in this programme of intensive monitoring. It is not possible to be certain why routine monitoring data have been subject to positive bias. Three explanations are likely: (i) contamination during sample collection; (ii) contamination during filtration; and (iii) analytical bias.

The first source of bias is difficult to assess - it depends on actions carried out at the time of sampling. In future, improved control over sample collection can be established, see below. The second source of error has been assessed directly in this study. It is likely that contamination during filtration has contributed to positive bias, but that it is not the sole source of systematic error. Considerable progress has been made in controlling analytical error in the determination of trace metals in saline samples. AQC measures adopted in NRA laboratories have addressed bias and limit of detection requirements for zinc and other metals, so analytical errors are less likely to be a source of bias.

6. RECOMMENDATIONS

6.1 Zinc in Estuaries

Whilst it is necessary to continue to monitor concentrations of dissolved zinc in estuaries, more attention might need to be paid to concentrations of the metal in sediments, particularly in the vicinity of marinas.

6.2 Monitoring

The need to control contamination during sampling should be emphasised to personnel responsible for the collection of environmental samples. Different approaches need to be adopted to the collection of samples for different purposes (e.g. trace metals, microbiology, trace organics). Few sampling staff are experienced in all the required disciplines, so some form of standardised training or guidance on the key issues relating to sampling should be considered.

A common approach to the selection, testing and pretreatment of sample filtration equipment should be adopted. There is no need for the same equipment to be used in all NRA Regions. However, it is important that the procedures and equipment have been shown to be capable of meeting predefined criteria for control over contamination.

A system of routine checks on sampling and filtration should be established. This can be achieved by instituting a system of field blank checks.

Current measures to control and demonstrate the accuracy of analysis should be maintained.

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REFERENCES

Bloom, N.S. and Crecelius, E.A. (1987) Distribution of silver, mercury, lead, copper and cadmium in central Puget Sound sediments. *Marine Chemistry*, **21**, 377-390.

Falconer R.A. (1984) Temperature distributions in tidal flow field. *Journal of Environmental Engineering*, **110**, 6, 1099-1116.

Falconer R.A. (1986) Water quality simulation study of a natural harbour. *Journal of Waterway, Port, Coastal and Ocean Engineering*, **112**, 1, 15-34.

Pavlou S.P. and Weston D.P. (1983) Initial evaluation of alternatives for development of sediment related criteria for toxic contaminants in marine waters (Puget Sound). Phase I. Development of conceptual framework. Prepared by JRB Associates for the USA Environmental Protection Agency under EPA Contract No. 68-01-6388.

Tappin A.D., Hydes D.J., Burton J.D. and Statham P.J. (1993) Concentrations, distributions and seasonal variability of dissolved Cd, Co, Cu, Mn, Ni, Pb and Zn in the English Channel. *Continental Shelf Research*, **13**, 8/9, 941-969.

Taylor D. (1986) Changes in the distribution patterns of trace metals in sediments of the Mersey Estuary in the last decade (1974-83) *The Science of the Total Environment*, **49**, 257-295.

APPENDIX A

DISSOLVED ZINC CONCENTRATIONS

Table A1 Data for Dissolved Zinc for Routine Monitoring (all concentrations in $\mu\text{g l}^{-1}$)

	Date				
	28/06/94	19/07/94	10/08/94	08/09/94	11/01/95
Poole Harbour					
Cobbs Quay Marina	-	21.52	11.99	6.97	14.18
Salterns Marina (in) ^a	10.77	11.85	7.96	6.85	16.28 ^b
Salterns Marine (out)	-	-	-	3.98	-
A350 Bridge	5.03	2.58	4.40	5.60	3.69
Rockley Park	0.80	2.19	2.79	1.26	2.98
Shell Bay	0.68 ^c	1.16	2.15	3.88	0.66
Brands Bay	0.56	1.42	3.75	3.53	2.05
Arne	2.44	-	-	-	-
R.Frome	2.10	-	-	-	9.06
R.Frome (estuary)	15.40	-	-	-	-
R.Piddle	6.76	-	-	-	7.56
	12/07/94	02/08/94	25/08/94	04/10/94	19/01/95
Orwell Estuary (Suffolk)					
R.Orwell (Ipswich)	5.01	-	-	269.4	378.7
Wherstead	10.61	-	-	8.74	7.83
Woolverstone Marina	2.42	4.27	8.07	5.27	4.76
Pin Mill	2.42	2.34	4.78	9.15	5.33
Levington Marina	2.53	7.42	8.14	7.18	5.23
Shotley Marina (in)	8.63	11.25	9.66	13.45	22.33
Shotley Marina (out)	-	6.98	5.95	3.37	-
Felixstowe Port	0.73	-	-	-	-
Felixstowe Beach	0.62	4.38	6.01	2.33	2.30
Deben Estuary (Suffolk)					
Waldringfield	1.16	3.95	3.82	1.00	1.41
Deben Mouth	1.16	-	-	-	-

Table A1 Continued

	26/07/94	Date 02/08/94	04/08/94
South West			
Sutton Marina (Plymouth)	16.17		
Sutton Marina (out)	3.65		
Torquay Marina	3.65		
Torquay Harbour	6.52		
Torquay Marine (out)	1.30		
Maldon (Blackwater)		22.29	
Burnham Marina (Crouch)		6.98	
Burnham Marina (out)		3.02	
Chichester Harbour (Bosham)			3.69
Chichester Harbour (Dell Quay)			3.60
Chichester Marina			17.31

^a "in" and "out" refer to samples taken from inside and outside the marina

^b Mean of five samples taken inside marina

^c Sample taken at Studland Bay

APPENDIX B PHYSICAL PARAMETERS FOR ROUTINE SAMPLING

Table B1 Data for Poole Harbour Routine Monitoring.

Poole Harbour	Date				
	28/06/94	19/07/94	10/08/94	08/09/94	11/01/95
High Tide (Portland)	10.58	09.16	09.44	09.22	09.26
Cobbs Quay Marina					
Temperature (°C)	-	20.0	20.0	16.9	8.0
Salinity (ppt)	-	30.5	30.1	31.2	29.4
Time	-	09.50	15.00	08.40	09.30
Suspended Solids (mg l ⁻¹)	-	30.6	23.4	50.2	46.4
Salterns Marina (in)^a					
Temperature (°C)	-	22.5	19.5	16.2	7.8
Salinity (ppt)	-	34.9	34.2	34.1	32.1
Time	10.00	15.45	10.45	09.50	10.00
Suspended Solids (mg l ⁻¹)	32.7	60.0	23.4	41.4	16.8
Salterns Marine (out)					
Temperature (°C)	-	-	-	16.4	-
Salinity (ppt)	-	-	-	33.8	-
Time	-	-	-	09.50	-
Suspended Solids (mg l ⁻¹)	-	-	-	40.6	-
A350 Bridge					
Temperature (°C)	-	-	21.5	16.8	10.6
Salinity (ppt)	-	34.0	33.5	33.4	32.0
Time	08.30	09.05	15.45	09.30	08.35
Suspended Solids (mg l ⁻¹)	40.7	41.0	21.2	47.4	43.8
Rockley Park					
Temperature (°C)	-	20.4	19.8	16.9	9.0
Salinity (ppt)	-	30.5	31.4	32.1	32.1
Time	09.00	09.05	14.45	09.00	08.45
Suspended Solids (mg l ⁻¹)	63.1	16.0	22.4	81.8	52.7

Table B1

Continued

	Date				
	28/06/94	19/07/94	10/08/94	08/09/94	11/01/95
Shell Bay					
Temperature (°C)	-	25.0	19.0	18.2	9.4
Salinity (ppt)	-	35.4	35.6	36.1	33.3
Time	12.00	12.15	11.50	10.50	11.45
Suspended Solids (mg l ⁻¹)	48.3	23.2	28.2	31.6	69.9
Brands Bay					
Temperature (°C)	-	20.4	19.3	16.6	7.8
Salinity (ppt)	-	30.5	34.5	33.0	30.4
Time	09.00	09.05	12.05	11.15	12.05
Suspended Solids (mg l ⁻¹)	35.7	56.2	35.2	42.4	52.9
Arne					
Temperature (°C)	-	-	-	-	-
Salinity (ppt)	-	-	-	-	-
Time	15.00	-	-	-	-
Suspended Solids (mg l ⁻¹)	429.9	-	-	-	-
R.Frome					
Temperature (°C)	-	-	-	-	8.8
Salinity (ppt)	-	-	-	-	0.6
Time	16.30	-	-	-	13.40
Suspended Solids (mg l ⁻¹)	6.3	-	-	-	29.9
R.Frome (estuary)					
Time	16.00	-	-	-	-
Suspended Solids (mg l ⁻¹)	34.7	-	-	-	-
R.Piddle					
Temperature (°C)	-	-	-	-	8.6
Salinity (ppt)	-	-	-	-	0.8
Time	16.45	-	-	-	13.50
Suspended Solids (mg l ⁻¹)	10.7	-	-	-	25.2

Table B2 Data for Orwell Estuary Routine Monitoring

	Date				
	12/07/94	02/08/94	25/08/94	04/10/94	19/01/95
High Tide (Harwich)	08.19	08.00	08.24	11.40	ca. 13.00
Orwell Estuary (Suffolk)					
R.Orwell (Ipswich)					
Temperature (°C)	-	-	-	11.8	6.2
Salinity (ppt)	-	-	-	17.3	1.4
Time	14.15	-	-	10.00	11.40
Suspended solids (mg l ⁻¹)	58.6	-	-	78.1	16.8
Wherstead					
Temperature (°C)	-	-	-	11.8	5.6
Salinity (ppt)	-	-	-	31.4	15.7
Time	14.00	-	-	10.30	11.20
Suspended Solids (mg l ⁻¹)	17.6	-	-	33.8	63.2
Woolverstone Marina					
Temperature (°C)	-	23.1	18.4	12.8	6.0
Salinity (ppt)	-	33.3	33.7	33.9	30.6
Time	15.00	11.20	09.50	12.00	10.45
Suspended Solids (mg l ⁻¹)	15.6	43.4	62.1	-	68.0
Pin Mill					
Temperature (°C)	-	22.5	18.6	12.8	5.5
Salinity (ppt)	-	32.8	33.6	32.4	31.0
Time	15.30	11.35	10.15	11.45	10.30
Suspended Solids (mg l ⁻¹)	29.8	68.8	-	-	400.0
Levington Marina					
Temperature (°C)	-	22.0	18.0	12.4	5.6
Salinity (ppt)	-	34.6	34.6	34.8	32.7
Time	13.15	09.35	09.00	13.00	12.45
Suspended Solids (mg l ⁻¹)	36.2	46.4	48.2	38.6	84.2

Table B2 Continued

	Date				
	12/07/94	02/08/94	25/08/94	04/10/94	19/01/95
Shotley Marina (out)					
Temperature (°C)	-	22.0	18.0	13.2	-
Salinity (ppt)	-	35.0	35.2	35.3	-
Time	-	12.25	10.40	11.15	-
Suspended Solids (mg l ⁻¹)	-	51.0	190.0	-	-
Felixstowe Port					
Temperature (°C)	-	-	-	-	-
Salinity (ppt)	-	-	-	-	-
Time	09.45	-	-	-	-
Suspended Solids (mg l ⁻¹)	71.6	-	-	-	-
Felixstowe Beach					
Temperature (°C)	-	21.7	18.0	13.2	6.0
Salinity (ppt)	-	35.1	35.8	35.7	35.5
Time	09.30	09.15	08.40	14.25	15.00
Suspended Solids (mg l ⁻¹)	47.2	64.6	102.4	-	273.8
Deben Estuary (Suffolk)					
Waldringfield					
Temperature (°C)	-	22.0	18.0	13.0	5.5
Salinity (ppt)	-	33.5	32.0	32.0	29.5
Time	11.00	09.55	09.25	15.05	12.20
Suspended Solids (mg l ⁻¹)	48.4	50.8	66.8	-	109.4
Deben Mouth					
Temperature (°C)	-	-	-	-	-
Salinity (ppt)	-	-	-	-	-
Time	10.15	-	-	-	-
Suspended Solids (mg l ⁻¹)	30.4	-	-	-	-

Table B3

Data for Other Sampling Sites

	Date	26/07/94
High Tide		12.00
Sutton Marina (Plymouth)		
Temperature (°C)		18.7
Salinity (ppt)		35.4
Time		09.50
Suspended Solids (mg l ⁻¹)		41.6
Outside Marina		
Temperature (°C)		18.0
Salinity (ppt)		35.3
Time		10.30
Suspended Solids (mg l ⁻¹)		47.8
Torquay Beach		
Temperature (°C)		19.0
Salinity (ppt)		36.0
Time		12.00
Suspended Solids (mg l ⁻¹)		45.0
Torquay Marina		
Temperature (°C)		19.0
Salinity (ppt)		36.0
Time		12.30
Suspended Solids (mg l ⁻¹)		43.6
Torquay Harbour		
Temperature (°C)		19.0
Salinity (ppt)		34.7
Time		13.00
Suspended Solids (mg l ⁻¹)		42.0

Table B3 Continued

	Date	
	02/08/94	04/08/94
High Tide	08.00	
Maldon (Blackwater)		
Temperature (°C)	24.0	
Salinity (ppt)	4.2	
Time	15.15	
Suspended Solids (mg l ⁻¹)	46.8	
Burnham Marina (Crouch)		
Temperature (°C)	23.5	
Salinity (ppt)	35.2	
Time	16.10	
Suspended Solids (mg l ⁻¹)	61.0	
Crouch Estuary		
Temperature (°C)	23.8	
Salinity (ppt)	35.3	
Time	16.00	
Suspended Solids (mg l ⁻¹)	47.2	
Dell Quay (Chichester Harbour)		
Temperature (°C)		21.2
Salinity (ppt)		32.4
Time		12.30
Suspended Solids (mg l ⁻¹)		32.2
Chichester Marina		
Temperature (°C)		21.2
Salinity (ppt)		33.6
Time		13.00
Suspended Solids (mg l ⁻¹)		18.2
Bosham (Chichester Harbour)		
Temperature (°C)		-
Salinity (ppt)		-
Time	13.35	
Suspended Solids (mg l ⁻¹)	19.2	

APPENDIX C

ANALYTICAL METHODOLOGY

C1 SOLVENT EXTRACTION FOR THE DETERMINATION OF ZINC IN SALINE SAMPLES

All water used was deionised and all chemicals were of Reagent Grade unless stated. All apparatus was pre-soaked in 5% v/v nitric acid and rinsed before use.

The analytical reagent was prepared by dissolving 1.0 (± 0.01 g) of ammonium pyrrolidine dithiocarbamate (APDC; Sigma Chemicals) and 5.3 (± 0.1 g) of sodium hydrogen carbonate (Merck) in 500 ml of deionised water. This reagent was then decanted into a clean polythene bottle and purified by shaking with 20ml (± 1 ml) 1,1,1 Trichloroethane (Merck AristaR or equivalent) for 5 minutes. Methyl-isobutyl ketone (MIBK) - Merck SpectrosoL or equivalent Standards were prepared by diluting Merck SpectrosoL (1000 mg l^{-1}) standards with deionised water containing 2 ml l^{-1} of nitric acid.

The extractions were performed in 100 ml polypropylene volumetric flasks. Extractions were carried out in batches of 24 samples. These comprised 12 samples, 2 blanks, 4 standard solutions in deionised water (12.5 , 25.0 , 37.5 , and $50.0 \text{ } \mu\text{g l}^{-1}$), 2 spiked seawater controls ($10 \text{ } \mu\text{g l}^{-1}$), 2 spiked deionised water samples of low concentration ($5 \text{ } \mu\text{g l}^{-1}$) and two deionised water samples spiked at a higher concentration ($20 \text{ } \mu\text{g l}^{-1}$).

Aliquots ($60 \text{ g } \pm 0.2 \text{ g}$) of sample were decanted into 100 ml volumetric flasks. (Weighing the samples directly into the flasks avoided unnecessary transfer of the sample into the flask via a measuring cylinder, hence reducing the possibility of contamination.) Fifteen ml of the reagent was added followed by ml of the MIBK. The flasks were then shaken for 5 minutes. Deionised water was added to the flasks to bring the MIBK up into the neck of the flask to facilitate aspiration into the flame AAS instrument.

The Analytical Quality Control (AQC) samples were used to plot control charts and to provide performance data as recommended by WRc and approved by NRA. AQC data are shown below.

Precision Results for the determination of Zinc

BATCH	Blank	Low Standard	High Standard	Control Sample
1	0.50	5.500	19.670	10.800
	0.250	5.500	19.830	9.830
2	0.610	4.770	20.320	9.280
	0.200	4.900	20.880	9.150
3	0.630	5.480	19.170	10.170
	0.310	5.740	20.350	9.650
4	0.390	4.470	18.080	12.250
	0.580	4.470	17.890	9.330

BATCH	Blank	Low Standard	High Standard	Control Sample
5	0.930 0.780	5.830 5.210	19.580 18.540	7.710 8.960
6	0.450 0.340	5.280 4.940	22.950 18.620	10.560 9.030
7	0.320 0.290	5.890 5.740	21.510 21.150	10.350 10.710
8	0.200 0.310	4.910 4.810	20.250 20.880	10.150 9.540
9	0.300 0.350	5.380 5.470	19.820 19.840	9.270 11.090
10	0.230 0.360	5.200 5.400	19.200 19.500	9.100 9.400
11	0.420 0.450	5.390 5.630	19.840 19.780	9.690 9.850
12	1.260 1.450	4.800 5.200	20.100 20.430	10.840 10.410
13	1.200 1.450	4.510 5.080	19.810 19.700	9.300 9.300
	Blank	Low	High	Control
MEAN	0.560000	5.211540	19.911200	9.835380
M1	0.283767	0.314595	1.440570	0.940496
M0	0.020600	0.046446	0.859219	0.683562
F VALUE	13.77510	6.77333	1.67660	1.37588
SIGNIF	**	**	N.S.	N.S.
SW	0.143270	0.2155140	0.9269410	0.8267780
SB		0.3661620	0.5391420	0.3584230
ST		0.4248770	1.0723300	0.9011260
F 0.05	1.72	1.67	1.55	1.54
CALC f		0.1805	1.1499	0.8120
DEG F		15	23	24
OK?		PASS	PASS	PASS

Limit of detection..... 0.718948 $\mu\text{g l}^{-1}$

Precision target 1 $\mu\text{g l}^{-1}$ or 5% of concentration

Recovery Data

(1) Recovery for low spike

Concentration of standard used for spiking	10 mg l ⁻¹
Volume of standard solution	30 µls
Volume of water used	60 mls

Grand Mean Recovery.....	4.6515
Std. Devn. of mean recoveries.....	.62
95% C.L. on Grand Mean Recovery.....	±.306

Expected Recovery.....	4.997
% Recovery	93.08
Second chance at spiking recovery.....	PASS
Best Possible % Recovery	99.2152

(2) Recovery for high spike

Concentration of standard used for spiking	10 mg l ⁻¹
Volume of standard solution	120 µls
Volume of water used	60 mls

Grand Mean Recovery.....	19.3512
Std. Devn. of mean recoveries.....	.975197
95% C.L. on Grand Mean Recovery.....	±.481979

Expected Recovery.....	19.959
% Recovery	96.9547; PASS

C2 Field Technique for the Determination of Zinc

Reagents

- Dithizone Solution (I) 10 mg dithizone in 100 ml 1,1,1 trichloroethane
- Dithizone Solution (II) 25 ml solution (I) + 225 ml of 1,1,1 trichloroethane
- Sodium thiosulphate (12.5g in 50ml DIW)
- Hydrochloric Acid (2 ml 12M HCl in 100ml DIW)
- Sodium acetate solution (2M)
- Acetic acid solution (25ml concentrated acetic acid in 200ml)
- Acetate buffer (100 ml sodium acetate solution + 100ml acetic acid solution)

The acetate buffer was cleaned by shaking it in a separating funnel with *ca.* 10 ml of 1,1,1 trichloroethane then shaking for 5 minutes, before drawing off the 1,1,1 trichloroethane.

Procedure

50 ml of sample were added to a 125 ml Nalgene polyethylene bottle, followed by 0.4 ml of the dilute hydrochloric acid. The 5 ml of sodium thiosulphate and 5 ml of the dithizone reagent were added. The bottle was shaken for five minutes and the phases allowed to separate. A portion of the trichloroethane phase was transferred (by pipette) into a 2 cm optical cell and its absorbance was determined at 520 nm using a portable colorimeter (Jenways 6051).

A deionised water blank and three standard solutions (10, 20 and 40 $\mu\text{g l}^{-1}$) were included in each batch of analyses.