INTERNATIONAL COUNCIL FOR THE EXPLORATION OF THE SEA.

C.M. 1993/E:28
Marine Environmental Quality Committee/
Ref.Theme Session Q.

SURFACE MICROLAYER CONTAMINATION AND TOXICITY IN THE NORTH SEA AND PLYMOUTH NEAR-SHORE WATERS.

J.J.CLEARY,I.R.B.MCFADZEN AND L.D.PETERS.

NERC Plymouth Marine Laboratory, Prospect Place, West Hoe, Plymouth, PL1 3DH., U.K.

ABSTRACT

A variety of chemical contaminants accumulate in the surface microlayer at concentrations sometimes orders of magnitude greater than in subsurface waters.Biota resident in the surface waters whether permanent,(the neuston),or temporary,(eg. eggs and larvae of fish and crustaceans),may therefore be exposed to much greater concentrations of toxicants than biota resident in the subsurface.Also organisms resident in the littoral may be exposed to microlayer deposited by the ebbing tide.To determine the extent to which the surface microlayer is toxic to these early life stages,water samples were collected and tested for toxicity using larval bioassay.Cryopreserved veliger larvae of the Manila clam (Tapes philippinarum) and Pacific oyster (Crassostrea gigas) and yolk sac turbot larvae (Scophthalmus maximus) were used to assess the toxicity of North Sea (German Bight) and Plymouth near-shore waters respectively.Chemical analyses revealed enhanced levels of metals (Cu,Pb),organotins and polyaromatic hydrocarbons in the surface microlayer compared with near-surface bulk seawater (0.5m).Bioassay results indicated greater toxicity in the microlayer than subsurface,and strong correlation between chemical contaminants and larval toxicity.

Microlayer studies provide a useful input to environmental assessment,and indicate that the potential effects of contaminants at the sea surface may pose a serious threat to larval survival and fisheries recruitment.

INTRODUCTION

The world's oceans cover 70% of the earth's surface.The sea-surface microlayer which occurs at the air-sea interface is the region through which all gaseous and particulate matter must pass when exchanging between the atmosphere and the ocean.The surface microlayer is not a clearly defined slice of water since microlayer thickness varies with the sampling device used (Garrett & Duce,1980). It is composed of lipids and other macromolecular components such as polysaccharides,proteins and fatty acids, and has the capacity to accumulate enhanced concentrations of chemicals compared to subsurface water (Garrett,1967;Baier et al.,1974).

The sea surface is an important concentration point for both natural biogenic organic films and for organic and metal contaminants (Hardy,1982).Compared to the bulk water only a few centimetres deep,the sea-surface microlayer often contains highly enriched concentrations of both natural and anthropogenic chemicals including polychlorinated biphenyls (PCB's),polyaromatic hydrocarbons (PAAH's),and potentially toxic trace metals (eg.Cu,Pb) and organometals such as TBT,(Hardy et al.,1985a,1987, 1990; Cleary,1991;Hardy and Cleary,1992).

The sea surface is also a biologically active interface inhabited by high densities of micro-organisms (bacterioneuston and phytoneuston), small crustaceans and the eggs and larvae of fish and shellfish (zooneuston) (Hardy,1982).Pelagic fish eggs can concentrate at the surface by floatation due to their high lipid content and positive buoyancy,and fish eggs, larvae and fry can remain in the surface layer even in waves 3-6 feet high (Zaitsev,1971).Biota resident at the surface may therefore be exposed to the higher toxicant concentrations existing in the surface microlayer and suffer greater deleterious effects than biota resident in subsurface waters.

Demersal fish eggs deposited intertidally, and other organisms resident in the littoral zone,may also have extensive contact with the microlayer during the ebbing tide when they are exposed to the sea surface as the tide recedes.The nature of exposure for littoral organisms,particularly those that graze on surfaces on which the microlayer may be deposited,is very different and may be substantially higher than for organisms in subsurface waters.

The possibility therefore exists that toxicant accumulation in the surface microlayer could have serious detrimental effects on the recruitment and survival of both pneustonic and demersal populations.

In this paper we describe some of our studies on microlayer toxicity.The purpose of these studies was to quantify toxicants that accumulate in the surface microlayer and to assess its biological impact by determining pathological effects in larvae of marine organisms.Simple experimental bioassay systems were used on water samples from the North Sea and from sites near Plymouth in Southwest England.Chemical analyses were carried out on the same samples to determine toxicant concentrations.

MATERIALS AND METHODS

Sample collection.

i) North Sea samples were collected during a cruise of the RV Valdivia in March 1990 along a transect in the German Bight (Fig.1).To avoid contamination from the ship,samples were collected from a small inflatable boat about 300 metres upwind of the ship.Microlayer samples were collected using stainless steel and nylon mesh Garrett screens for organic and metal analysis respectively, (Cleary & Stebbing ,1987).Garrett screens collect the top 200-400 microns of the surface microlayer (Garrett,1965).Near-surface bulk water samples were collected by opening a bottle 0.5 m below the surface.For trace metal analyses samples were collected in acid cleaned bottles ; for organotins and bioassay, bottles were acid cleaned and solvent rinsed prior to sampling (Hardy & Cleary,1992).

ii) Samples from sites near Plymouth (Fig.1) were collected using an automated rotating glass cylinder microlayer sampler which collects the top 50-100 microns of the surface microlayer (Carlson et al., 1988).This differs from conventional rotating drum microlayer samplers which are oriented normal to the direction of travel (Harvey,1966;Daumas et al.,1976;Sodergren,1987;Hardy et al., 1988).The glass cylinder is oriented parallel to the direction of travel,and avoids the problem of materials accumulating ahead of the drum as it is towed through the water. Adsorbed microlayer was transferred from the glass drum surface by a windscreen wiper assembly into a reservoir and pumped directly into glass bottles,cleaned as before. Garrett screen and subsurface samples were collected in the usual manner.

Chemical analyses.

The North Sea samples were extracted on board ship for subsequent analysis in the laboratory.For organotins a 2 l water sample was acidified with 50 ml of glacial acetic acid and extracted with 25 ml of toluene by mixing on a platform shaker for 15 min.The sample was transferred to a separatory funnel and the lower aqueous layer discarded.The toluene extract was stored in a glass vial in a freezer until analysis.Where necessary extracts were preconcentrated before analysing for organotins.Aliquots were treated with 1M sodium hydroxide and reanalysed to determine tributyltin (Cleary,1991).

Trace metals were removed from seawater by solvent extraction (Danielsson et al.,1982).Metal carbamate complexes were extracted from seawater (buffered to pH 5) with ammonium pyrollidine dithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC) into 1,1,2-trichloro-1,2,2-trifluoroethane (Freon TF) and back-extracted into 0.3 M nitric acid for analysis by graphite furnace atomic absorption spectrophotometry.

Polyaromatic hydrocarbons were determined by shaking 1 l water samples with 10 ml hexane in sealed glass sampling bottles for 10 min on a platform shaker.The hexane was transferred by pipette into glass storage vials and analysed by UV fluorescence spectroscopy (Law et al.,1988).

Toxicity tests.

Bioassays were performed on the North Sea samples on board the RV Valdivia using cryopreserved oyster (Crassostrea gigas) and clam (Tapes philippinarum) veliger larvae.(For details of this technique see McFadzen,1992).Three hundred larvae per replicate were used,and exposed to the water samples at the incubation temperature of 20 degrees Centigrade for 48 hours.Each vial was then treated with 4% buffered formalin to preserve the larvae for subsequent analysis.Microscopic examination of larvae was conducted at random with survival assessed as the number of viable larvae observed in the first 50 encountered.

Bioassays carried out at Plymouth Marine Laboratory on water samples taken locally used turbot larvae (Scophthalmus maximus) obtained from Golden Sea Produce,Hunterston,Scotland.Static exposure tests,in triplicate, were carried out at 15 degrees Centigrade using a 12 hour light/12 hour dark regime.Three day old larvae were added to the samples (100 larvae /250 ml) and mortalities determined at 24 hour intervals by microscopic examination for the absence of a heart-beat.Toxicity exposure results were compared to control seawater from a clean offshore site.

RESULTS

a) In the German Bight area of the North Sea concentrations of copper,lead,organotin and tributyltin were greater in the microlayer than in near-surface bulkwater at all stations (Fig.2).Enhancement was more marked for organotins than for trace metals,and mean enrichment factors (microlayer concentration / 0.5m subsurface water concentration) were 2.3 (Pb),5.0 (Cu),6.3 (TBT) and 9.8 (organotins).Maximum concentrations occurred at near-shore sites and declined with distance from the land in both the surface microlayer and near-surface bulkwater.The larval bioassay showed a similar trend.The survival of clam larvae exposed to both microlayer and subsurface water increased with distance offshore,and larvae exposed to the surface microlayer showed significantly greater toxicity than those exposed to bulkwater (Fig.3).Oyster larvae also showed the greatest toxicity at the nearshore site in both the microlayer and bulkwater,and declined with distance from the coast (Fig.3).Clam larvae were more sensitive than oyster larvae to microlayer samples,but both showed a similar response to bulkwater samples.

A significant relationship was evident between biological and chemical toxicity.The correlation between larval toxicity and chemical contaminants was more marked with clam than oyster.Survival of clam larvae decreased with increasing concentrations of Cu,Pb,TBT and organotin (Fig.4) in both microlayer and bulkwater.No correlation was evident between oyster larval survival and TBT or organotin concentration,but a positive relationship was found with Cu and Pb (Fig.5).

b) In the Plymouth study, microlayer and bulkwater samples collected near Plymouth were analysed for polyaromatic hydrocarbons (PAH's),widespread contaminants identified in other microlayer studies (Cross et al.,1987;Hardy et al., 1987;Word et al., 1987 and shown to effect the growth of microlayer phytoneuston (Riznyk et al.,1987).They were tested for toxicity using turbot larvae,a species used at PML for toxicity studies.Enhanced microlayer concentrations of total PAH's occurred at the 4 sites sampled,Sutton marina, Looe ,Devonport and Plymouth Sound (Fig.6). Enrichment ratios were 742, 34, 2.7 and 1.2 respectively. Larval mortality followed a similar trend with greater mortality in the microlayer than subsurface (Fig.6).Mortality in the microlayer screen samples was intermediate between microlayer drum and 0.5 metre subsurface,consistent with the greater thickness of microlayer sampled with the screen (200-400um) compared with the glass drum (50-100 um) (Fig.7).The strong correlation between larval mortality and PAH concentration (Fig.8) shows that a significant relationship exists between biological response and contaminant concentration.

DISCUSSION

Consistent features of these microlayer studies are:- i) the ability of the surface microlayer to accumulate a range of chemical contaminants eg.metals,organometals and organic compounds; ii) the greater toxicity shown by the microlayer exposed to different species of marine organism; iii) the

significant correlations between contaminant concentration and toxicity.

Although such correlations do not prove cause and effect,it is clear that the microlayer is more toxic than subsurface water,and can accumulate chemical contaminants to levels which exceed accepted water quality criteria.For example microlayer concentrations of TBT and Cu exceed both the U.K.EQS value of 2 ng TBT/l and the U.S.EPA chronic water quality limit of 2.9 ug Cu/l.

Clearly,microlayer contamination is a potential threat to neustonic,pelagic and demersal organisms,particularly to the early life stages when organisms are most vulnerable.The reasons for the high incidence (5-26%) of embryo abnormality found in cod,whiting and plaice from the North Sea (Dethlefsen et al.,1985),and the even higher malformation rates (26-44%) in North Sea plaice,flounder and dab found by Cameron et al.,(1992),have not been identified, but suspicion falls on the surface microlayer.It seems likely that the surface microlayer could have a strong influence on fisheries survival and recruitment.

ACKNOWLEDGEMENTS

These studies formed part of the PML research programme on microlayer toxicity and part of the Bremerhaven Workshop on biological effects of contaminants in the North Sea. Funding,in part,was from the U.K. Department of the Environment,PECD 7/7/359.

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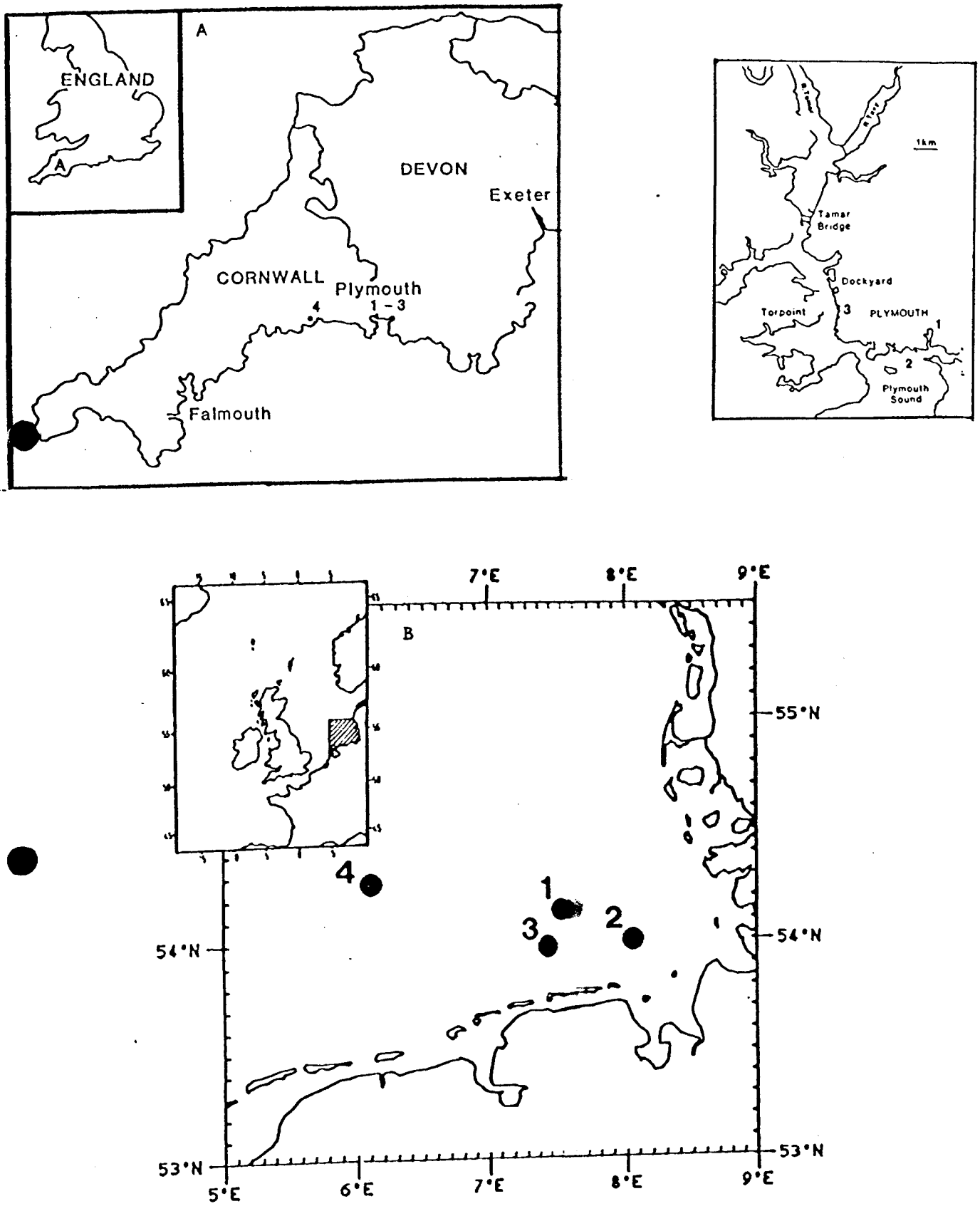


Fig.1.Sampling sites: A) near Plymouth in southwest England,1) Sutton marina,2) Plymouth Sound,3) Devonport,4) Looe and B) in the German Bight.

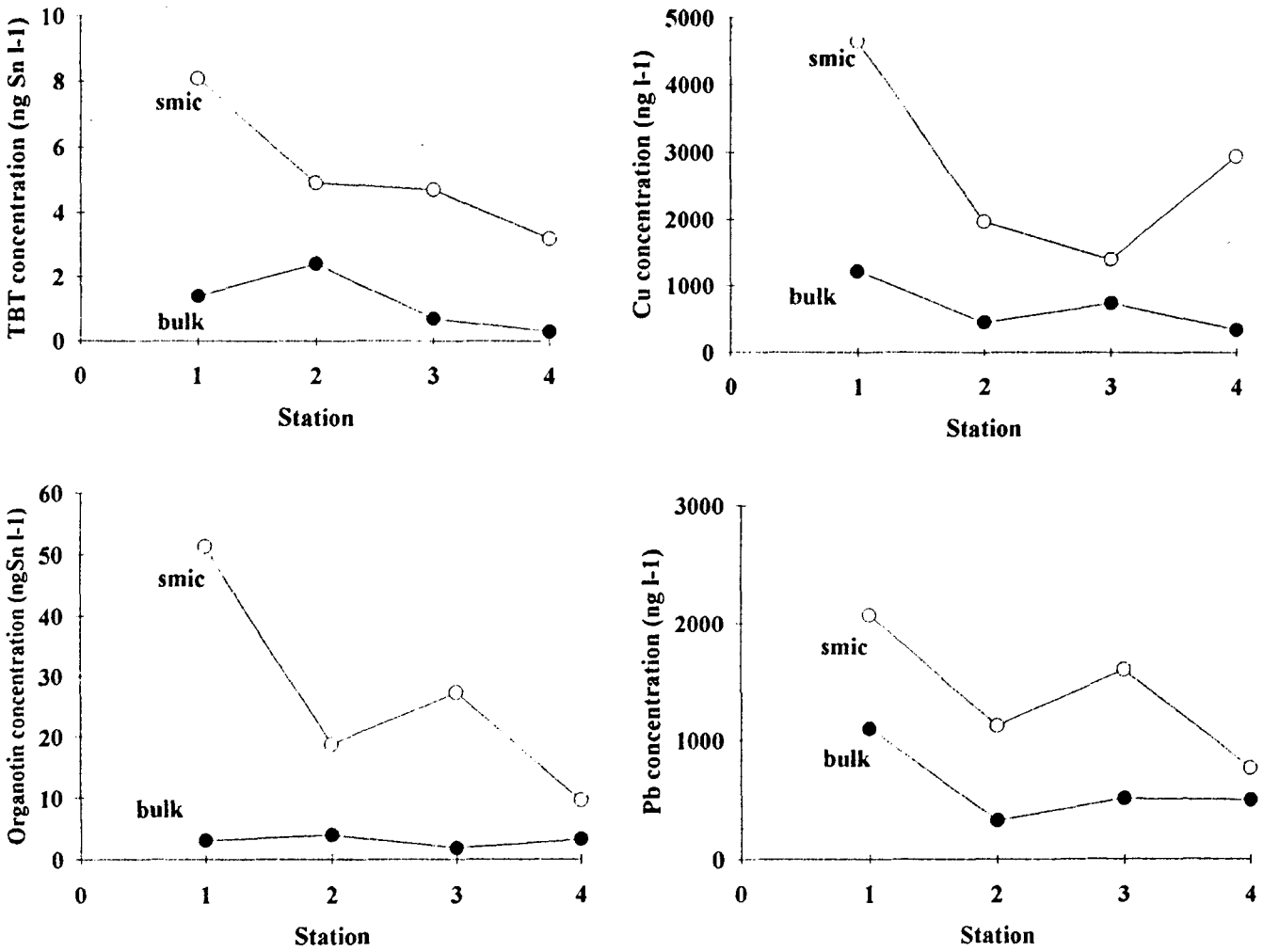


Fig. 2 Contaminant concentrations in the surface microlayer and bulkwater (0.5m subsurface) in the German Bight in March 1990

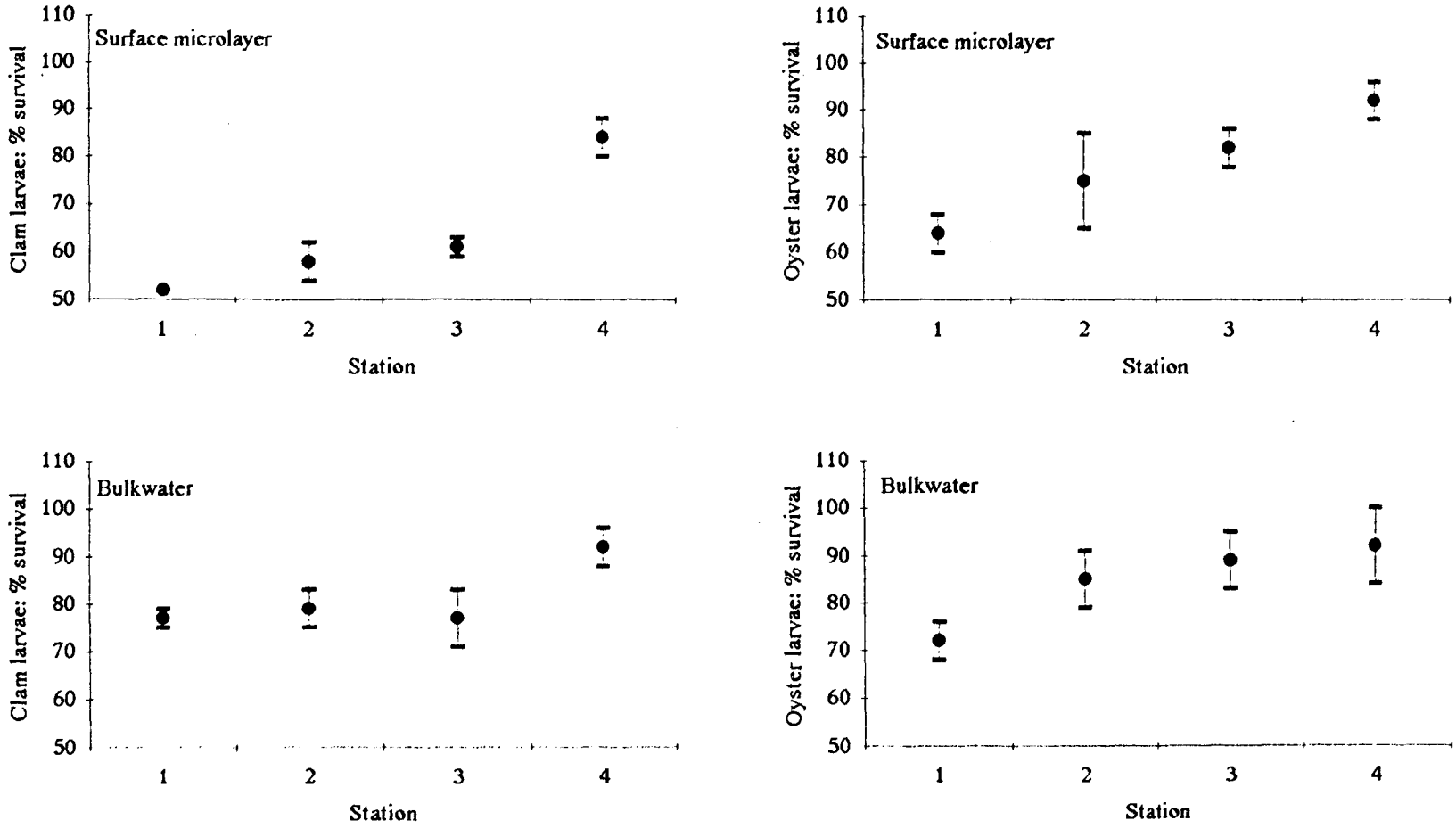


Fig. 3 Toxic responses of clam larvae (Tapes philippinarum) and oyster larvae (Crassostrea gigas) to surface microlayer and bulkwater (0.5m subsurface) from the German Bight

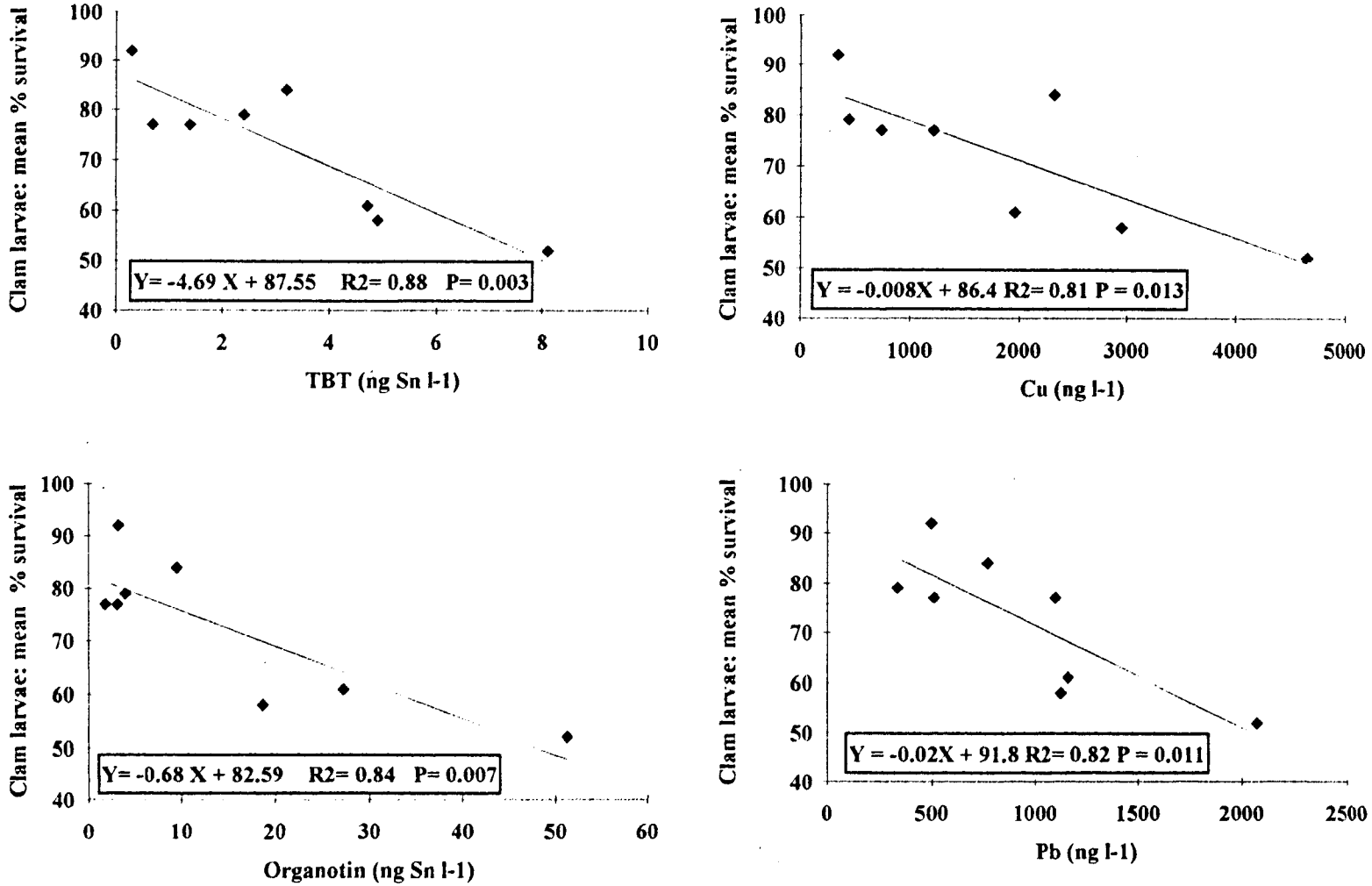


Fig.4 Relationship between contaminant concentrations in surface microlayer and bulkwater (0.5m subsurface) and survival of clam larvae (Tapes philippinarum)

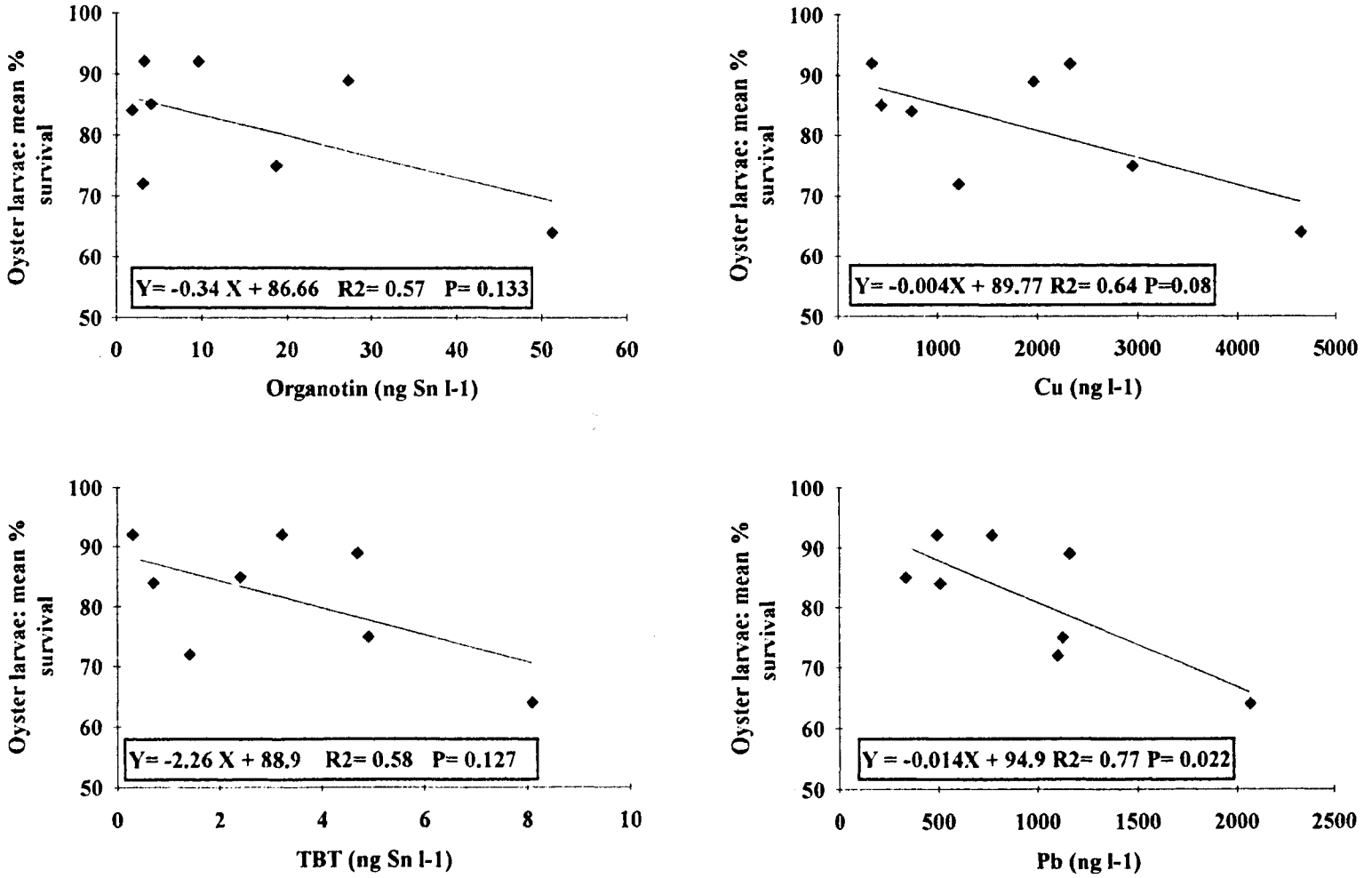
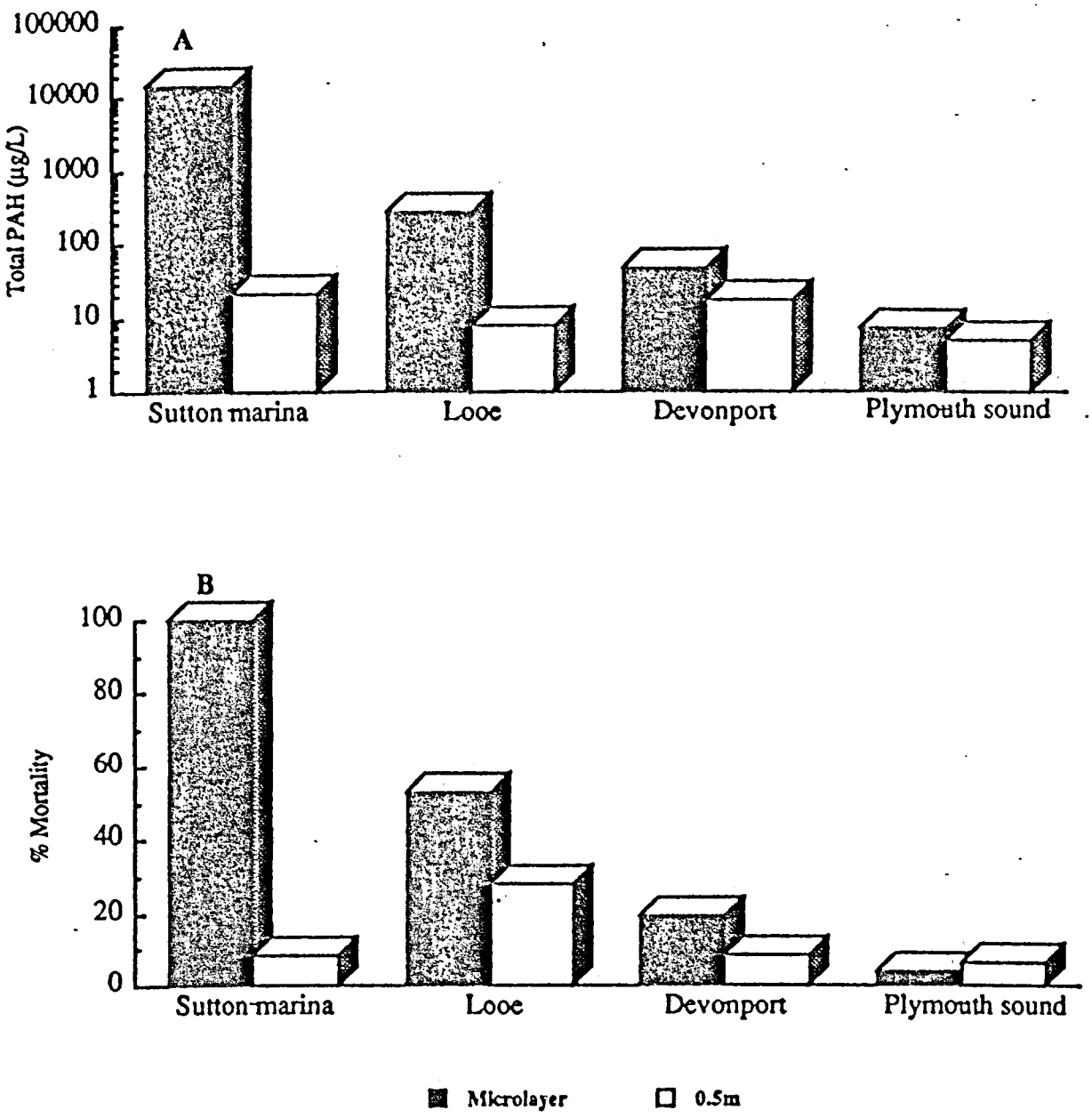


Fig.5 Relationship between contaminant concentrations in surface microlayer and bulkwater (0.5m subsurface) and survival of oyster larvae (Crassostrea gigas)



A. Total PAH levels in microlayer and 0.5m samples, at 4 sites near Plymouth.
B. Mortality responses in turbot larvae after exposure to the above samples for 96 hours.

FIG. 6.

Comparison between the effects of microlayer (drum and screen), 0.5m and control sea water samples from 4 sites near Plymouth, using a turbot larvae bioassay.

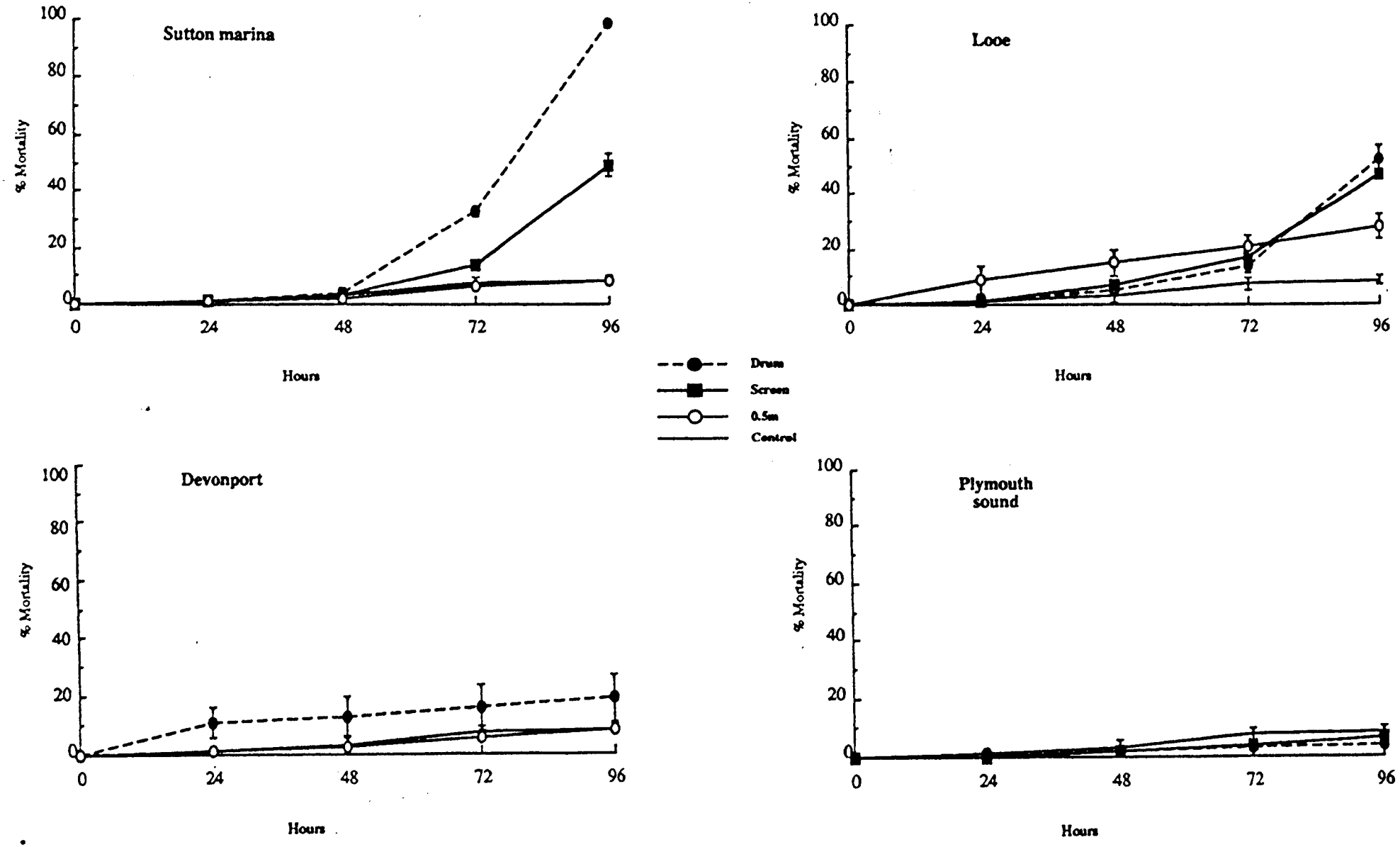


FIG. 7.

Correlation between total PAH (µg/L) and percentage mortality of turbot (*Sc. maximus*) larvae exposed for 96 hours.

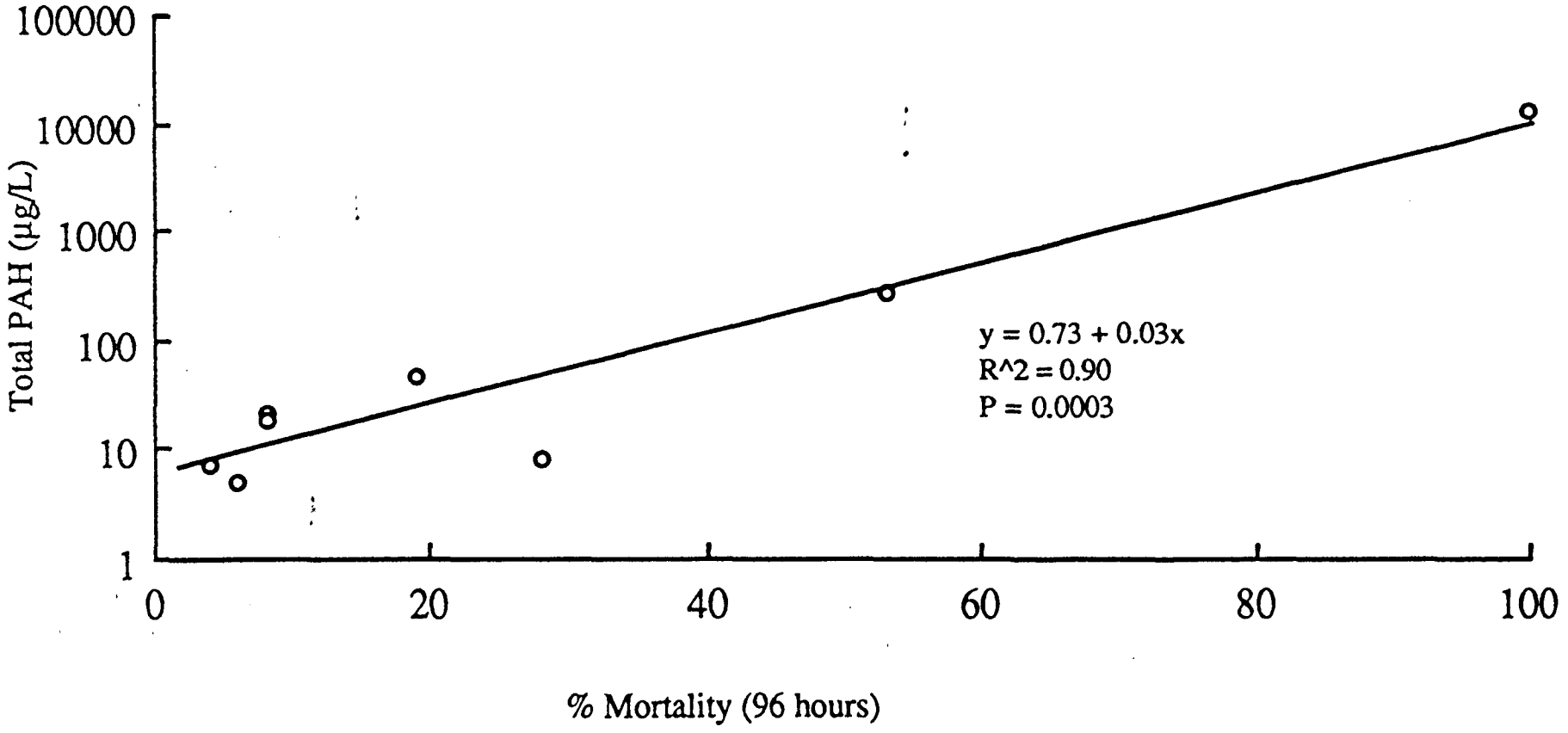


FIG. 8.