Atmospheric deposition of heavy metals to the Severn Estuary

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Doctor of Philosophy

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This work has not been submitted for any other degree and is the result of the candidate's own investigation.

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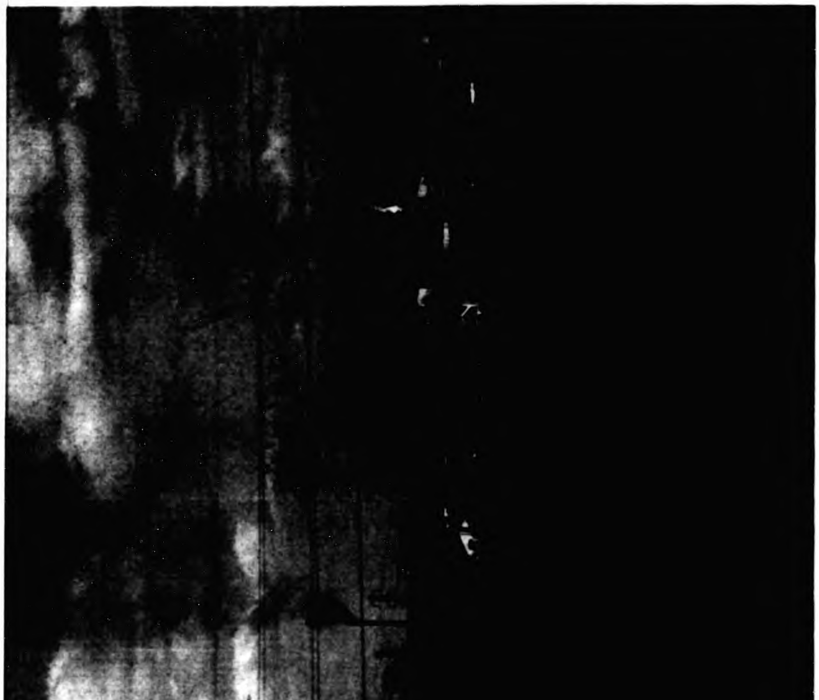

ABSTRACT

The atmospheric inputs to the Severn Estuary of the metals cadmium, copper, chromium, nickel, lead, zinc and aluminium were determined by collecting total deposition samples from eleven sites within and around the estuary. Samples were collected in NILU RS1 total deposition sampling devices biweekly over a period of fifteen months and analysed at Wessex Water Plc's Saltford Laboratory for metal content.

The sodium and chloride content of the samples were also analysed for evidence of incursion of sea-spray to the samples (Maritime Effect) and hence recycling of metals. An array of sampling devices was also placed at Northwick Landfill site to test for this phenomenen.

The total metal input to the Severn Estuary was determined by interpolation (using linear, Log_{10}, Log_e and square root methods) of the point deposition data across the water surface by means of isoplething. The area between isopleths was calculated and a mean metal input derived. On the basis of the data transformations the most reliable estimates for metal inputs ($kgday^{-1}$) were: Cd - 0.84, Cu - 8.64-8.68, Cr - 1.93-1.94, Ni - 2.75-2.80, Pb - 62.8, Zn - 96.07 and Al - 0.31.

In comparison to earlier estimates (1978/9) these results show that there has been considerable decline in aerial metal inputs to the Severn Estuary by one to two orders of magnitude. The decline was attributed to improved methodologies as well as a real decrese in metal inputs. Recent reports have also indicated that the overall water quality of the Severn Estuary has improved.

The Avonmouth area was identified as an important source area for all metals although significant, secondary sources of Cr and Ni appear to exist in the outer estuary that emanated from South Wales.

There was an absence of clear seasonal variation in metal deposition although there was marked fluctuation between sampling periods indicating either variable emission rates or meteorological conditions. The deposition of metals also appeared to be dominated by wet processes.

There was no conclusive evidence for the existence of the Maritime Effect although more research is needed into this phenomenen in the Severn Estuary.

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AERIAL INPUTS OF METALS TO THE SEVERN ESTUARY

1 INTRODUCTION

1.1 Objectives

In 1973 the Severn Estuary Joint Committee (S.E.J.C) was formed and since that date has carried out a series of studies to establish the total inputs of metals to the estuary in conjunction with surface water analysis programmes. The results of these and later studies were reported in the first and second reports of the Severn Estuary Survey and Systems Panels (Welsh Water, 1977; 1980) and later in a special issue of the Marine Pollution Bulletin which summarised current knowledge of the estuary (Owens, 1984; Morris, 1984). These reports indicated that the concentrations of metals in the waters of the Severn Estuary were quite high and that they could not be accounted for by the concentrations in land based discharges alone. Atmospheric inputs were suggested as a possible additional source of metals to the Severn and two investigations were carried out to examine the aerial inputs.

The first study, carried out between October 1978 and September 1979, showed that atmospheric inputs could account for the discrepancy between the overall water quality and the levels in land based inputs. The aerial inputs were estimated to account for 58% of lead, 42% of zinc, 21% of cadmium, 19% of copper and 12% of nickel inputs to the estuary. Carried out between August 1982 and October 1983, the second investigation, using the same

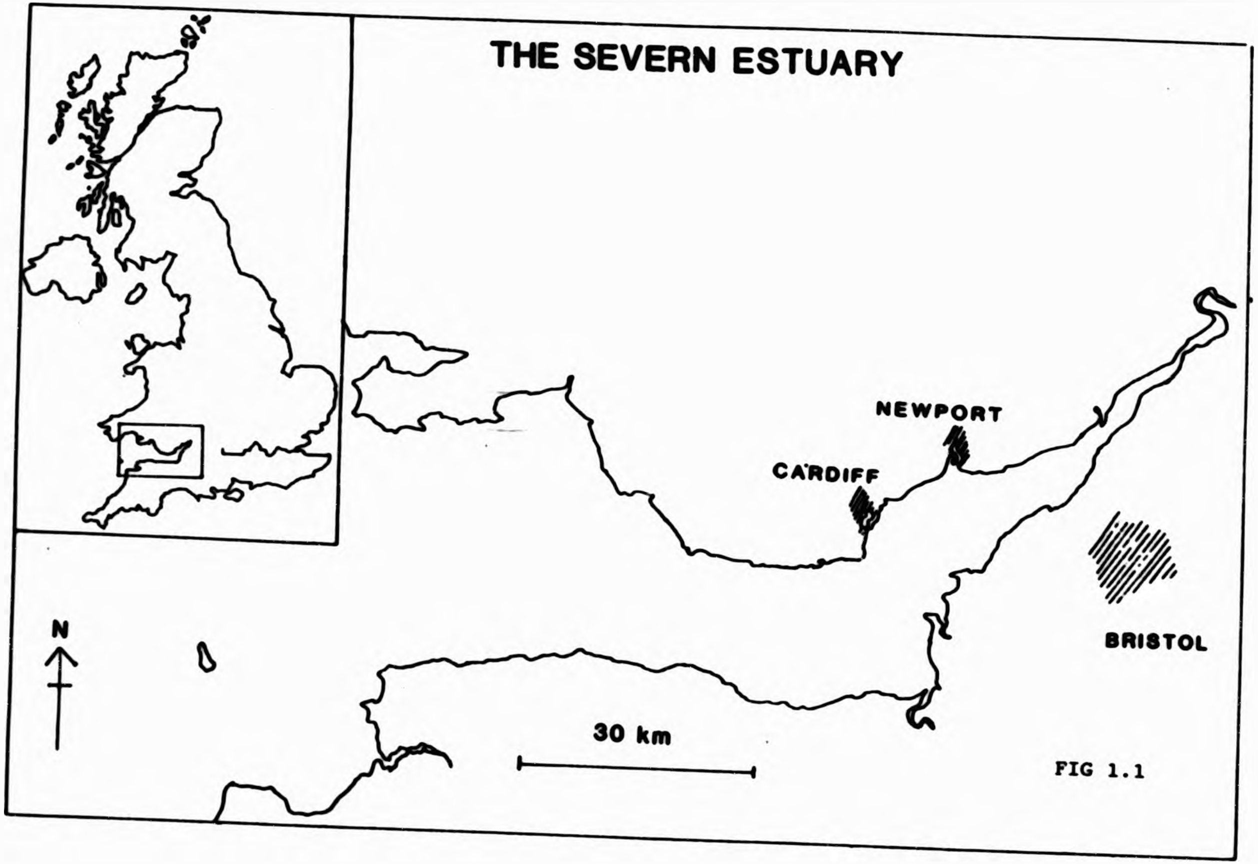


FIG 1.1

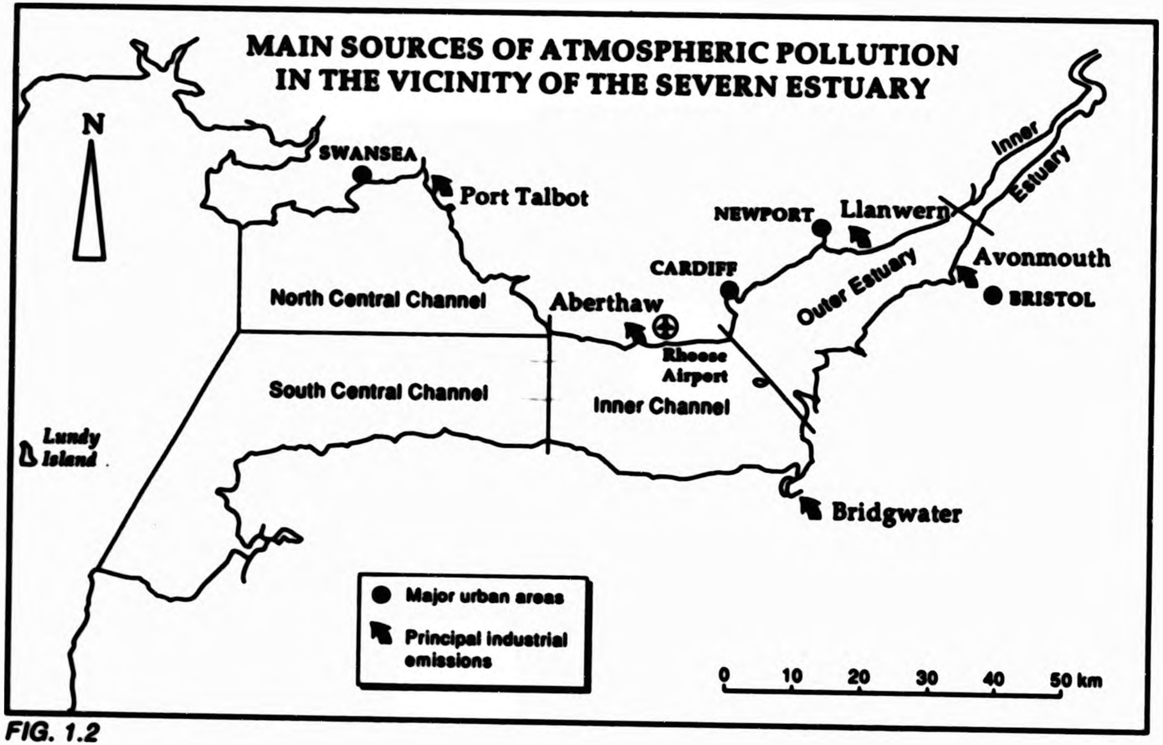

MAIN SOURCES OF ATMOSPHERIC POLLUTION
IN THE VICINITY OF THE SEVERN ESTUARY
N
SWANSEA
Port Talbot
NEWPORT
Llanwern
Inner Estuary
CARDIFF
Avonmouth
BRISTOL
Outer Estuary
North Central Channel
Aberthaw
Rhoose Airport
South Central Channel
Inner Channel
Lundy Island
Bridgwater
Major urban areas
Principal industrial emissions
0
10
20
30
40
50 km

FIG. 1.2

methodology for sample collection and analysis as well as data interpretation, showed that aerial inputs could no longer account for the discrepancy.

In light of the current interest in atmospheric pollution and the problems arising from previous attempts to quantify atmospheric inputs of metals in this region this study aimed to resolve the question of aerial inputs of cadmium, copper, chromium, nickel,lead ,zinc and aluminium to the tidal area of the Severn estuary. This has been achieved by using a re-designed sampling network and improved sampling equipment with an alternative approach to extrapolating the data as well as a consideration of meteorological variables.

1.2 Physical Environmental setting

The Severn Estuary (Fig 1.1) is the largest estuary in Great Britain. Several major rivers drain into it, the largest of which is the Severn itself with an annual discharge of approximately $10^{10}m^3$. This represents about 25% of the freshwater discharge (Morris,1984), the remainder of which comes from many other natural and anthropogenic discharges. The Severn estuary is largely bounded by upland areas in its outer reaches with the hills and valleys of South Wales to the north and Exmoor and the Quantock Hills to the south. The Severn drains a catchment area of 1672km^2 and from its source to the outer reaches of the Bristol Channel is some 180km long (Bassindale, 1943). Large tributaries join the Severn Estuary at Chepstow (River Wye), Newport (River Usk), Avonmouth (River Avon) and Bridgwater (River Parrett) and these have catchment areas of 353, 639, 214 and 222km^2 respectively.

Historically the estuary has been the focus of industrial activity since the industrial revolution with a concentration of mining and smelting activities taking place, particularly in South Wales. Some of these industries "have been attracted to the area by the large capacity of the Severn estuary to disperse and assimilate pollution loads" (Energy, 1981b; reported in Glover (1984)).The area is still a centre of industry providing a constant source of pollutants to the water mass via both land-based runoff and drainage as well as atmospheric deposition. The principal industrial centres are located (Fig. 1.2) at Avonmouth and Severnside, Swansea Bay and Llanwern Steel works in addition to the urban centres of Bristol, Cardiff and Newport. Other minor inputs from point sources include the coal-fired power station at Aberthaw and Bridgwater whilst multiple emissions are discharged by domestic and industrial fuel combustion and vehicle exhausts from the extensive local road network. Although these sources may be individually small their combined pollution load may be a significant contribution to the estuarine waters of the Severn, whether by land based or atmospheric input. It is likely the majority of pollution to the Severn estuary is from local sources but there may some background aerosol input imported from Europe and S. Ireland, for example, via the atmosphere depending on prevailing meteorological conditions.

2 DISPERSAL OF POLLUTANTS WITHIN THE ATMOSPHERE

2.1 Introduction

The volume and concentration of pollutants that arrive at a receptor site are determined largely by the nature of pollutant emissions and the state of the atmosphere at the time of emission. Pollutants are emitted into the atmosphere either from natural sources such as volcanoes and sea spray or anthropogenic sources. The latter includes many forms of industrial processing, releases from combustion engines and the burning of fossil fuels. The fate of emissions will ,initially, be controlled by the physical and chemical nature of the pollutants, the rate, height and duration of release.

Once in the atmosphere the dispersal and removal of pollutants are controlled by prevailing atmospheric conditions. The major atmospheric controls are horizontal wind velocity and turbulence and the thermal stratification of the boundary layer. The atmospheric boundary layer is the thin layer of the atmosphere directly above the earth's surface and is characterised by well developed turbulence that arises from the frictional forces that are created as the atmosphere moves across the uneven and rigid surface Fig. 2.1. The temperature stratification of the boundary layer defines atmospheric stability which may be regarded as the relative tendency of an air mass to move vertically and in a stable atmosphere this movement is restricted (Oke, 1987).

The wind field controls the horizontal dispersion of pollution

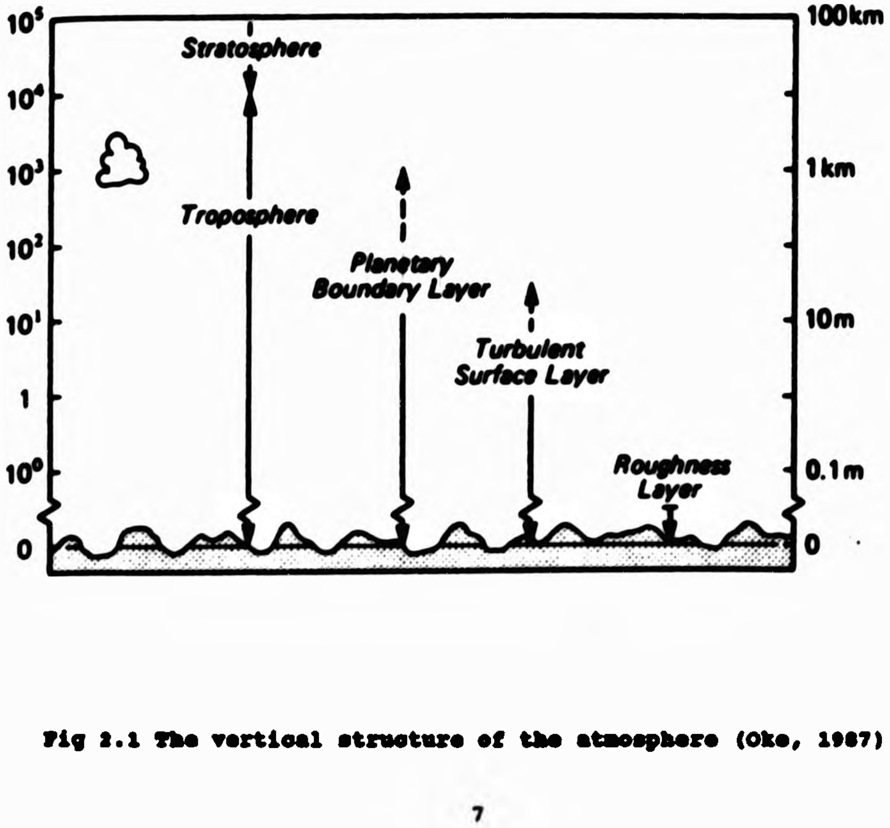


Fig 2.1 The vertical structure of the atmosphere (Oke, 1987)

and its strength will determine the dilution of the emission concentrations received down wind. The wind direction regulates the trajectory taken by pollutants. The interaction of the wind field with the underlying surface will also affect the intensity of mechanical turbulence within the atmosphere.

1.2 Pollution source characteristics

Initially, the characteristics of emissions will determine the fate of effluent into the atmosphere. The physical and chemical nature of effluent are an important factor in dispersal. The physical form of the pollutant whether gaseous, particulate or dissolved will, for example, have an a bearing on its dispersal. The large majority of heavy metals such as Mn, Cr, Zn, and Ni are associated with particulate matter and aerosols but a few (Hg, Se and As) , in their elemental form or as compounds, have sufficiently high vapour pressures to exist in the gaseous state (Schroeder, 1987). If emissions are in a particulate form their dispersal will be controlled by the particle size with large particulates (>10 μm) being removed from the atmosphere very close to source whilst smaller particles will have longer residence times in the atmosphere. The residence time will then be controlled by other emission characteristics such as the height and temperature at which pollutants are emitted and the prevailing meteorological conditions.

The configuration of emission sources including shape, height, duration (whether continuous or episodic) rate and temperature

Table 2.1 Emission source configurations. (After Oke, 1987)

SHAPE	DURATION	HEIGHT	EXAMPLES
POINT	Continuous	Elevated	Chimney stack
		Ground	Bonfire
	Instantaneous	Elevated	Shell burst
		Ground	Explosion
LINE	Continuous	Ground	Motorway, Road
	Instantaneous	Elevated	Crop spray, Vapour Trail
AREA	Continuous	Elevated	City, Stubble burning

of emission will affect the dispersal and eventual removal of pollutants from the atmospheric environment. These configuration elements can be classified into three main types of sources according to shape and are illustrated in Table 2.1.

In terms of anthropogenic sources of pollution the point source chimney stacks are a very important origin with high concentrations of often toxic materials emanating from them. The actual elevation of chimney stacks will determine whether effluent is dispersed in the vicinity of the source by prevailing meteorological elements in the lower atmosphere or whether it is carried much further afield by winds at greater stack heights. An example of the effect of greater emission height is very apparent with acid rain formation in Scandinavia which has been produced by reactions of atmospheric constituents with mainly sulphurous compounds that have originated in Great Britain and the European mainland. If effluent is emitted from chimney stacks at high temperatures the effect will be that the plumes will rise higher in the atmosphere as a result of their elevated buoyancy relative to the ambient air.

The mixing of exhaust fumes from many separate vehicles along major road networks is considered to represent a continuous line source of pollution. A study in Norway indicated that the vertical diffusion of exhaust emissions tended to be greater from cars driving at high speeds (Grønskei, 1988). A city with many industrial and domestic emissions is described as an area source. These definitions hold if a study is carried out on a relatively small regional scale. If a larger continental atmospheric pollution assessment is being made a city may regarded as a point source

2.3 Meteorological controls on dispersal

The principal attributes relevant to dispersal of effluent within the atmospheric environment can be divided into three main meteorological components (Harrison et.al.,1985). These are the vertical structure of the lower atmosphere and horizontal wind speed and direction as well as cloud formation and precipitation mechanisms.

2.3.1 The vertical structure of the atmosphere

Convection in the atmosphere is an important process in the dispersal and diffusion of effluent into a large volume which reduces it's concentration and this is limited by the depth of the mixed layer of the lower atmosphere. In strongly unstable atmospheres with a deep mixed layer such as those experienced under sunny, summer daytime conditions pollutants will be dispersed widely downwind of their emission sources whilst stable conditions, especially combined with a thermal inversion layer restrict vertical mixing and give rise to restricted dispersal and locally high contaminant concentrations.

Stability may be defined as the relative tendency of air to move vertically and is controlled by the vertical temperature structure of the atmosphere. If a volume of air is rising through the atmosphere, neither receiving or emitting heat to the surrounding air it is said to be moving adiabatically. As it becomes more elevated atmospheric pressure decreases and the internal pressure of the air volume becomes greater relative to it's surroundings and it will expand. The only energy available for this expansion is the thermal energy within the rising air so as it rises it becomes cooler. The rate of temperature change, in unsaturated air, with height occurs at a constant value of 9.8°Ckm^{-1} and is known as the **Dry Adiabatic Lapse Rate** (Γ). Eventually, the air will cease to rise and will mix with the surrounding air at that height.

In contrast to the dry adiabatic lapse rate, the actual temperature structure of the lower atmosphere as measured is known as the **Environmental Lapse Rate ELR** and the structure will vary at different levels in response to other meteorological conditions such as wind speed. Stability can be appraised in a dry atmosphere by comparing the ELR against the constant Γ (Fig 2.2). Fig 2.2a shows that the ELR is greater than Γ and is said to be unstable. These conditions may arise near to the ground on warm days when surface heating produces a strong ELR. If air at height z_1 is displaced upwards it's temperature is greater than that of the surrounding air and it will possess buoyancy and continue to rise. The reverse would also be true if the air had been displaced downwards with a continual fall in height.
The reverse case whereby the ELR is less than Γ gives rise to a stable atmosphere is illustrated in Fig 2.2b which shows an

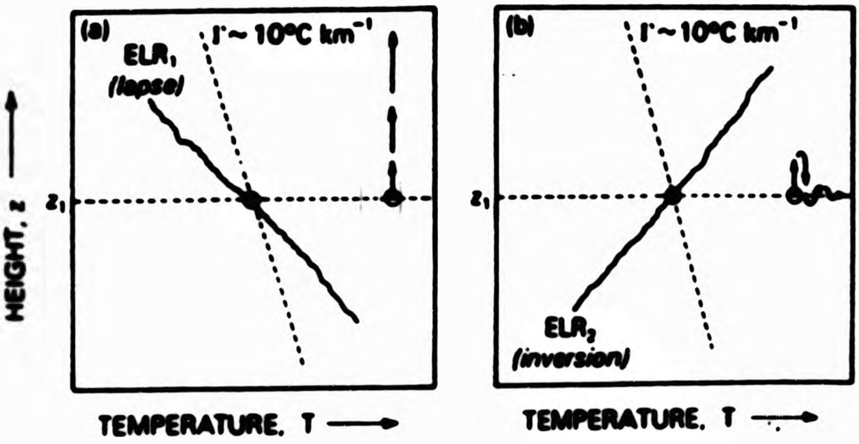


Figure 2.2 Height versus temperature graphs illustrating (a) unstable and (b) stable atmospheres (Oke, 1987).

inversion. An inversion exists where warmer air overlies cooler air. In this example if air was displaced upward from z_1 it would be cooler than its surroundings and tend to sink back to the original height with a downward shift resulting in the air rising back to z_1 as it would be warmer than the ambient air. If the Γ is equal to the ELR the atmosphere is said to be neutral. Any vertical shift would result in the air remaining in it's new position as the temperature of both the air and it's surroundings would be equal. Neutral conditions can occur under cloudy, windy conditions whereby cloud restricts incoming radiation thus minimising the development of horizontal temperature stratification. The wind, by mechanical convection, will aid the production of a uniform temperature stratification.

Stable atmospheres are often associated with thermal inversions and it is these that are very important limiting factors in the dispersal of pollutants within the atmosphere. They are formed by two principal means, either by cooling from below or warming from above. The main mechanism of inversion formation by cooling from below is by radiative cooling. Fig 2.3 shows a generalised form of the air temperature profile in the lowest 150m of the atmosphere at different times of day under sunny conditions.

Profile 1 of Fig. 2.3 shows the idealised temperature profile where a ground based temperature inversion exists that has arisen as a result of long wave surface radiation emission at night. The earth's surface has cooled to a temperature below that of the air above. This causes a downward heat flux from the

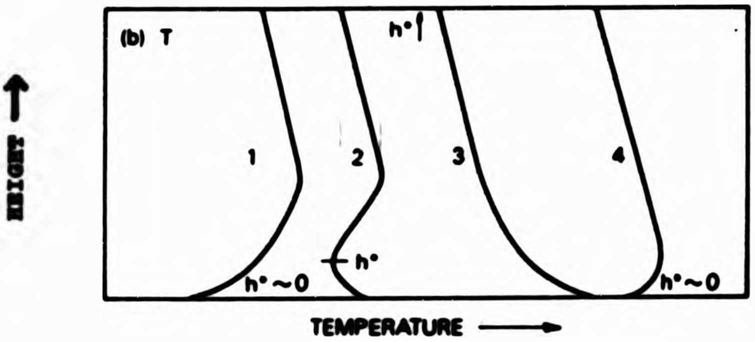


Figure 2.3 Generalised form of the air temperature profile in the lowest 150m of the atmosphere at different times of day with fine weather. Profiles: 1 - Before sunrise, 2 - Just after sunrise, 3 - midday, 4 - Just before sunset.

air above and may extend up to 150m, vertically by sunrise. Profile 2, soon after sunrise, shows conditions in which the radiation budget to the earth is positive and an upward heat flux is generated. This heat is only diffused into the lowest layers of air as further upward movement is restricted by the existing inversion layer. This layer is slowly eroded away by the rising layer of warm air and a shallow mixed layer of air exists up to the height of the remnant inversion layer.

By mid-day (profile 3) the inversion layer is completely eroded and a lapse profile extends up through a deep unstable, mixed layer. Toward sunset the radiation budget becomes negative and a new ground level inversion layer begins to form.

This illustration of the vertical temperature structure throughout a sunny day is idealised and will be modified by other weather conditions, for example cloud cover and strong winds.

Another inversion formation mechanism by cooling occurs by evaporative cooling, for example , in fine weather a rain shower may cool the ground giving rise to a ground based inversion. Similarly, a cool body of water would have this effect.

Inversions formed aloft, by heating from above evolve when cooler air sinks from above and is subject to adiabatic heating. This occurs, commonly, in anticyclonic weather systems, areas of high pressure. A layer of warmer air forms in the vertical temperature column which overlies cooler air below and this layer is described as a subsidence inversion. Subsidence

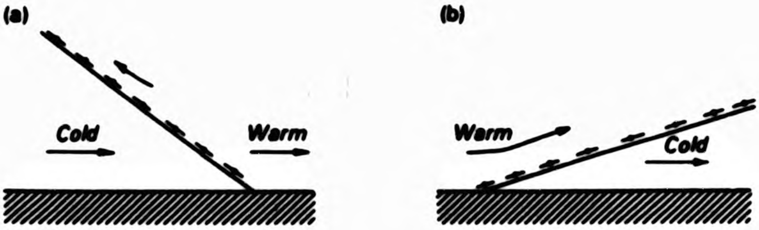


Figure 2.4 Diagrammatic section through (a) a cold front and (b) a warm front.

inversions are generally formed at an approximate height of 2 - 3 km (Shaw and Munn, 1971).A subsidence inversion will effectively cap the underlying mixed layer preventing the dispersal of any pollutants further up into the atmosphere giving rise to a layer of stagnant air below. The concentration of pollutants within this layer may become enhanced if the weather system is particularly slow moving and especially if the inversion height coincides with the height of the surrounding land topography.

Advection inversions are formed at weather fronts where two contrasting air masses meet. If cold air replaces warm air a cold front is produced and the reverse case generates a warm front (Fig 2.4). In both cases the warm air, being less dense, is forced above the colder air mass forming an inversion. Frontal inversions tend to be short lived but a slow moving warm front may restrict vertical mixing for longer periods causing pollutants to be trapped and, locally, high concentrations of contaminants. Atmospheric stability may be enhanced where warm fronts move across valleys filled with cool air thereby giving rise to an inversion layer.

When warm air moves across a cold land surface such a water body the cooling of base of the warm air layer will cause an inversion to form. Inversions may be modified if the air mass in which there is an inversion formed by cooling from below is moved across a warmer surface. As it moves across the land the heating from below erodes the inversion causing it to rise. It will eventually be fully eroded and replaced by a deep, unstable mixed layer in which pollutant dispersal will be more effective. Examples of the effect of thermal inversions on dispersal have been shown by Davidson (1967) and Lawrence (1967). Davidson, in a study of sulphur dioxide as part of the New York Air Pollution Dynamic research programme, showed that the build up of pollution concentration occurred between 200-2500 metres and rapidly decreased above the inversion layer. The maximum concentrations were generally found just below the top of the inversion. Lawrence, in a study of London, showed that the average daily mean concentration of sulphur dioxide for all wind directions was approximately, inversely related to height of the base of the midday inversion. Thus, the mean concentration of sulphur dioxide increased as the height of the inversion base decreased. With very low inversion bases the relationship between height and the rate of concentration increase exceeded the linear rate of change.

2.3.2 Horizontal wind speed and direction

The effect of wind on pollutants, once emitted into the atmosphere, is to diffuse and transport them away from the emission source. Diffusion is promoted by turbulence in the air which is thermally unstable or under the influence of a strong wind shear (Schroeder, 1987). Atmospheric transport results from the circulation of air masses whose driving forces may be global or local in origin. Acting together, these processes disperse atmospheric contaminants to all parts of the planet (Zoller et.al, 1974; Boutron, 1982). If wind eddies are smaller than the size of the pollutant plume the contaminants will be diffused and diluted whilst those eddies that are of greater size will transport pollutants downwind.

Winds will diffuse pollutants in the direction of the wind trajectory and also, by turbulent diffusion, in the cross wind and vertical directions. As wind speed increases pollutants become less concentrated per unit volume. The wind speed will also control the amount of forced convection within the boundary layer that is caused by shearing between air layers and the interaction of the air and land surface beneath (the roughness layer). As the wind speed increases so does the amount of turbulence which results in rapid dilution of plumes by mixing with the ambient air.

Wind direction controls the trajectory of pollution dispersal and, owing to variations about the mean direction of 30 - 40° or more over relatively short periods, will cause the plume width to widen downwind of the emission source. The greater the distance that pollutants are dispersed the more weakly concentrated they will become. More concentrated pollution is seen close to sources, especially if turbulent diffusion is dampened under stable atmospheric conditions.

A large number of emission sources in an area may result in cumulative loading of pollution as a result of wind transport. If the chemical constituents of the combined plumes are particularly reactive this will lead to the formation of secondary pollutants. Such contact, before extensive dilution has occurred, is seen in the formation of acidic sulphate species which result from the heterogeneous oxidation of SO^2 which is catalysed by certain heavy metals (Urone and Schroeder,1969).

Local circulatory systems, such as sea breezes do not tend to disperse pollution in the environment very effectively on a local scale. A sea breeze is formed when coastal land is warmed and the overlying air is warmed and it rapidly expands and at a height of about 2km the pressure begins to rise. This results in air flow seawards at this height and this divergence aloft causes pressure at the land surface to fall as air rises to take its place. The arrival of air above the sea causes a convergence aloft and air subsides below this causing an atmospheric pressure gradient at sea level. It is the development of the surface pressure gradient that causes to the landward flow of air as the sea breeze (White <u>et.al.</u>, 1984). The pressure gradient force operates from sea to land but as a result of Coriolis force the sea breeze may not blow normal to the coastline but will experience a deflection.

Defant (1951) illustrated the effect of Coriolis force and friction on sea breezes along the Massachusetts coastline and demonstrated that the breeze can be deflected as much as 45° away from normal to the coastline. At night a land breeze is formed when cooler land temperatures cause air to subside and diverge at the surface and converge over the sea where the air is forced to rise. The land breeze is generally weaker than the day time sea breeze. As a consequence of this diurnal reversal pollutants in the atmosphere are likely to be recirculated and concentrated, if the emissions are continuous. This type of coastal circulation has been illustrated by Lyons and Ollson (1973) on the shore of Lake Michigan. A balloon was released close to the shore in the morning and it travelled some 4km inland before being convected upward and back out over the Lake and then it moved inland again. By this time the lake breeze had penetrated to 13 km inland and the balloon was carried with it. An example of the effect of sea breezes has been shown in the Los Angeles Basin (Lin and Bland, 1980). Solar heating of the land, especially in valleys, adjacent to the basin produces a sea breeze. In the time that ozone formation occurs the air is carried inland where ozone concentrations may be higher than those areas that emit the original hydrocarbons and oxides of nitrogen that provided the elements for the ozone formation. At night the pollutant flow is reversed but the ozone concentrations are decreased as photochemical reactions cease after sunset.

Wind systems are often modified by local topography and this is an important consideration in the dispersal of pollutants. For example, when an airflow impinges on an upland area the air will be diverted horizontally and vertically by the obstruction. The forced elevation of air passing over a hill and the air layers above causes vertical oscillations of air (lee waves) to be created which may continue for long distance downwind of the obstruction. The consequence of this is that wind speeds may be reduced or increased at several points near the surface of the obstruction. A frequent circumstance is that winds are enhanced at the crest of a hill due to congestion of air flow and again several kilometres in the downwind direction. Lower speeds are seen on the upwind slope of the hill as a consequence of airflow stagnation and, again below the downwind side of the crest, as a result of separation of airflow (McIlveen,1986).

Topographical influences on airflow on airflow are also seen in valley situations whereby a parallel prevailing wind has a channelling effect and raises wind speeds up the valley. Also on sloping ground, local winds may be generated by interaction with solar radiation. When a slope is facing the sun it becomes warmed and, in turn warms the air directly above. This causes vertical expansion of the air and an upslope pressure gradient (Harrison et.al.,1985) which forms an overall upslope **anabatic wind**. The reverse mechanism, nocturnal cooling may generate a downslope **katabatic wind** which tends to be shallower than the anabatic wind. In both types the airflow maximum velocity is usually reached some way above the surface, owing mainly to frictional drag closer to the surface.

Other topographical influences on the wind field occur at coastlines where contrasts in the aerodynamic roughness between land, intertidal sediments and open water surfaces have a pronounced effect on the airflow (Echols and Wagner, 1972). The internal boundary layer adjusts only slowly to the changing physical character of the underlying surface. Boundary layer changes in onshore winds observed over a low coast by Yu and Wagner (1970) indicate that the transition zone between a sea windfield and the airflow over the land may be between 1 and 2 km of the shoreline although the wind flow at a height of 2 m did not appear to reach complete dynamic equilibrium with the underlying surface until it was between 5-12 km inland. The data to establish the limits of the transition zone were obtained by studying the sea breeze on the upper Texas coast in June 1968 and it was found that the wind speed during day and night decreased inland owing to increased frictional dissipation of energy over land as compared to over that water. In terms of dispersal, it is clear that coastal industrial zones will be affected by the transitional nature of the windfield at these sites.

2.3.3 Water in the atmosphere

The presence of water in the atmosphere as cloud droplets, precipitation and fog is important in the study of atmospheric pollution. It is a determining factor in the removal of pollutants, usually by rainfall, from the atmosphere and will therefore limit dispersal. Water vapour condenses or crystallises in the atmosphere as clouds and fog or on the ground as dew or frost. A measure of the humidity in the atmosphere is provided by the difference between the temperature of the air T_a and the dew point T_d which is the temperature at which saturation is reached if air is cooled at a constant pressure and no addition or loss of moisture is incurred. Saturation frequently occurs owing to adiabatic cooling of uplifted air until the dew point for the lower pressure is attained. Further cooling condenses the water vapour and releases the heat of condensation and thus cooling will occur at the saturated-adiabatic lapse rate, where temperature decrease is smaller with height that the Γ.

Table 2.2 Relative particle sizes (Turner, 1971)

Particles	Size (micrometres μ)
Small ions	$<10^{-3}$
Medium ions	10^{-3} to $5*10^{-3}$
Large ions	$5*10^{-3}$ to $2*10^{-1}$
Aitken nuclei	$5*10^{-3}$ to $2*10^{-1}$
Smoke, haze, dust	10^{-1} to 2
Large condensation nuclei	$2*10^{-1}$ to 10
Giant condensation nuclei	10 to 30
Cloud or fog droplets	1 to 100
Drizzle drops	100 to 500
Raindrops	500 - 4000

Table 2.3 Distance at which droplets will evaporate (after Findeisen, 1939)

Radius μ	Fall distance
1	$3.3*10^{-4}$cm
10	3.3cm
100	150m
1000	42km
2500	250km

Clouds are formed when water vapour condenses on suitable condensation nucleii and will occur more rapidly if the particles are large and hygroscopic. The relative sizes of different particles are shown in Table 2.2.

The presence of pollutants in the atmosphere provides a vehicle for cloud condensation and their eventual removal. Before rain is produced from clouds droplets must increase in size so that they have sufficient fall velocity and that evaporation does not occur before the ground is reached. Table 2.3 indicates the distance that water droplets will fall before evaporation.

In terms of dispersal, the presence of water vapour in the atmosphere as fogs can be very limiting. Fogs are usually formed over cool surfaces when air close to the surface becomes slightly supersaturated and produces a layer of cloud in contact with the ground (McIlveen, 1986). They are formed in two main ways; by radiation or advection.

Radiation fogs usually form in shallow layers, a few metres deep when radiation emissions cause surface cooling which, in turn, cools the overlying air to below the dew-point and are frequently seen in the evenings under cloudless and windless conditions. Radiation fogs often form in hollows as they are filled with dense, moist air from adjacent slopes and tend to persist whilst their upper surfaces are cooled by long wave radiation. They are easily dispersed by increased wind and the return of solar heating.

Advection fogs are formed when warm air is cooled to saturation by flowing over a cool surface and may develop to thicknesses of tens of metres. In mid-latitudes, warm, moist air frequently moves over the land in autumn and winter as part of slow moving, synoptic scale weather systems and at these times the land is much cooler than the sea giving rise to advection fog development. Fog is often a result of the combination of advective and radiative formation mechanisms which tend to produce thicker more persistent layers of fog.

The result of fogs on the vertical temperature structure of the atmosphere, on clear nights, is that a temperature inversion is produced at their upper surface. In late autumn and winter the sun may be incapable of removing the fog layers by warming and they will persist until sufficient wind is available, from a changing synoptic situation, for their dispersal by turbulent mixing with the air above.

The implications of fogs for pollutant dispersal are, therefore, important in industrial and urban areas where stacks emit directly into fog layers. High concentrations of pollutants are rapidly built up and may persist for several days, especially in slow moving anticyclonic systems. An example of this was seen in the winter of 1952 in London when fog formed in an anticyclone in combination with continuous emissions of industrial and domestic smoke. This produced a thick 'smog' which resulted in many deaths from respiratory problems (Wise, 1968., Ashby and Anderson, 1981.,Brimblecombe, 1987). This incident led to the eventual Clean Air Act of the 5th July 1956 (Brimblecombe, 1987) and as a result air in British cities has been considerably cleaned up. In combination with this the numbers of foggy days in cities have also decreased indicating that the fog formation was being exacerbated by the presence of condensation nucleii in particulate loaded air (McIlveen,1986).

2.4 Dispersion Mechanisms in the Boundary Layer

2.4.1 Plume Characteristics

When a single plume emits effluent into the atmosphere as an elevated, continuous point source its behaviour in the atmosphere can illustrate the meteorological conditions in operation and, therefore, indicate the potential for dispersal.

The elevation of a stack determines the height of emission and, generally, the higher this is the lower the concentrations at ground level in the vicinity of the stack will be. This is a result of eddy diffusion dilution which will increase with distance. The height of release will be enhanced if effluent discharges at high temperatures and velocities which cause a buoyant uplift before meteorological controls take over. The effective stack height H_s will consist of the actual stack height h_s and the increase in height Δ_h caused by buoyancy such that:

$$H_s = h_s + \Delta_h \qquad (2.1)$$

A typical Gaussian (normally distributed) plume is illustrated, diagrammatically in Fig. 2.5 (after Turner, 1969, Oke 1987). The effective stack height H_s also depends on the diameter of the stack. Once in the atmosphere meteorological controls become effective and the degree of turbulence (stability) in the atmosphere will influence the shape of the plume. A classification of plume shapes, shown in Fig.2.6, was identified by Church (1949) into five main types and another was added by Hewson (1960) which took into account inversions formed aloft.

Looping - This occurs when the ELR is greater than the Γ (Superadiabatic) and large eddies develop in unstable air. High concentrations of pollutants may be deposited at ground level if the topography impinges on the loops. Over long periods diffusion and dilution is very good if unstable conditions persist. Looping occurs under strong solar heating and light winds. Cloudiness prevents unstable conditions from developing.

Coning - Coning occurs when the vertical temperature gradient lies between dry adiabatic and neutral conditions and the atmosphere is slightly stable. The plume is generally cone shaped and will reach the ground at a greater distance than under looping conditions and will form under cloudy and windy conditions, both by day and night. Attempts to model plume dispersion (Fig 2.5) are generally most successful with this type of plume.

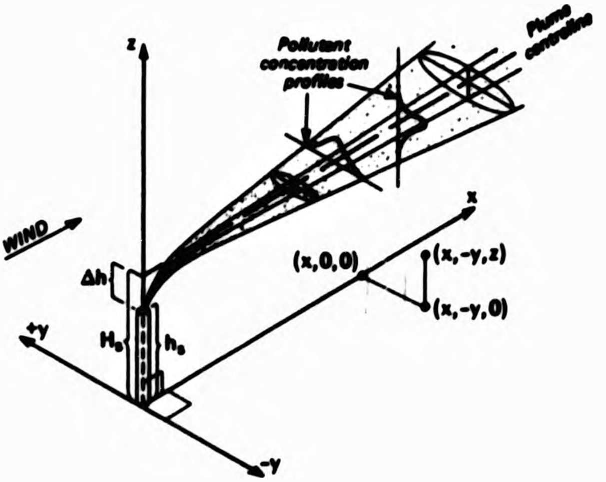


Fig 2.5 A Plume from an elevated point source showing plume rise (Δh) and the Gaussian distribution of pollutant concentrations in the horizontal and vertical. Three dimensional coordinate system used in the Gaussian plume model is also shown. (Oke, 1987)

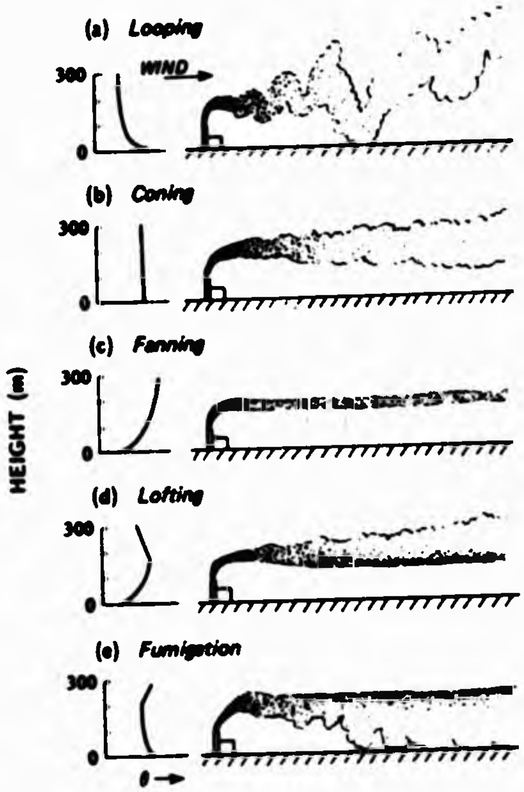


Fig. 2.6 Characteristic plume shapes under different stability conditions. (Oke 1987, after Bierly and Hewson, 1962)

Fanning - Fanning is characteristic of strongly stable atmospheres with vertical suppression of turbulence. Some horizontal mixing occurs and the plume spreads in this direction but not vertically. Plume concentrations tend to be high but little effluent from elevated sources will reach the ground except where the terrain height intercepts the plume or the inversion is broken due to solar heating. The most favourable conditions for fanning are clear skies with light winds and these plumes often develop at night.

Lofting - Lofting occurs where there is a superadiabatic layer above an inversion and is the optimum condition for effluent dispersal. Under these conditions diffusion is rapid in an upward direction but is restricted downward by the inversion layer. Gases do not reach the surface but particulate with high settling velocities may penetrate through the inversion. Lofting occurs in the early evening when a nocturnal radiation inversion builds up from the surface and is more likely to develop under clear skies in open country. As such , lofting is usually a transitional plume category and is replaced by fanning as the inversion layer deepens.

Fumigation - Fumigation is the reverse of Lofting and occurs where an inversion 'lid' above a plume restricts upward dispersal. Below the inversion, unstable conditions are formed by solar heating from below and the turbulence below rapidly carries high effluent concentrations to the ground. Fumigation is promoted by clear skies and light winds and is likely to develop in the summer as a consequence of increased solar heating and especially during the time after sunrise when nocturnally developed inversions are subject to erosion. Under these conditions fumigation may last for 30 minutes or more and simultaneously affect locations many kilometres downwind. (Oke, 1987).

An example of fumigation at Trail, British Columbia was frequently observed when a lead (Pb) and zinc (Zn) smelter released sulphur dioxide (SO_2) into the atmosphere in a mountain valley (Dean etal.1944). Katabatic drainage caused the effluent to travel down the valley below a radiation inversion where little mixing occurred. At sunrise solar heating caused the inversion to erode and resulted in fumigation along the 55km length of the valley.

Fumigation can also occur at coastlines where plumes emit into stable atmospheres at the coast and the effluent is carried inland by sea breezes. Further inland, the plume may encounter a developing unstable layer at which point fumigation will occur.

Trapping - This condition (not illustrated in Fig. 2.6) occurs when an inversion forms aloft, either frontal or by subsidence and a plume will be trapped beneath it. If unstable conditions are found below a coning type plume may develop but dispersal will be limited upwards and effluent concentrations are likely to increase within the plume or at ground level. (Turner, 1971).

2.4.2 Plume Modelling

The pollution concentration profiles shown in Fig. 2.5 exhibit a characteristic 'bell' shape that is described as the Normal or Gaussian distribution. The curve is derived by assuming that the random nature of turbulence causes effluent to mix such that the concentration is distributed bi-normally about the plume's central axis. Thus a normal distribution will be seen in both the x any y planes (Fig 2.5). The mathematical description of the concentration curves can then be used to model plume dispersion (Oke, 1987). Generally, dispersion models used to model dispersion plumes are of a common form in that the concentration at a point downwind of a continuous, single emission are;

a) directly proportional to the rate of emission

b) inversely proportional to the product of the wind speed, the cross wind dispersion and the vertical dispersion. (Pasquill, 1972., Comer,1976)

Equation 2.2 can be used to calculate the concentration of pollution (χ) at any point in a plume using a 3 dimensional coordinate system.

$$\chi_{(x,y,z,H)} = \frac{X}{2\pi\sigma_y\sigma_z\bar{u}} \exp\left[-\frac{y^2}{2\sigma^2_y}\right] * \left\{\exp\left(-\frac{(z-H)^2}{2\sigma^2_z}\right) + \exp\left(-\frac{(z+H)^2}{2\sigma^2_z}\right)\right\} \qquad (2.2)$$

Where:

X = Rate of emission from source (kgs^{-1})

σ_y, σ_z = Horizontal and vertical standard deviations of pollution distribution in the y and z directions (m).

$\bar{u}$ = Mean horizontal wind speed through depth of plume (ms^{-1})

H_e = Effective stack height (eqn 2.1)

(Oke,1987)

The concentration of pollution (χ) is expressed in kgm^{-3}. In this formula it assumed that all effluent remains in the atmosphere and none is deposited. The mathematics can be simplified if all that is required are the concentrations at ground level, plume centreline values at ground level or if the plumes are not elevated by buoyancy within the plume whereby z=0, y=0 and H=0 respectively. This Gaussian plume model will only apply under certain, limiting, conditions, for example, it only holds for continuous emissions from a point source; to almost weightless pollutants (gases and particulate < 20 μm); for time spans of greater than 10 minutes and to distances in the range of hundreds of metres to 10 kilometres downwind. The model can be modified to deal with inversions and topographic restrictions and could be used to cope with the various source configurations shown in Table 2.1. The model is, therefore, restricted in its application in that an isotropic surface is assumed although some modifications can be made for topographic factors. It would be extremely difficult, however, to modify the model to take account of coastlines and the associated changes in the wind field. The model is clearly oversimplified given that variations in meteorological conditions take place rapidly in the atmosphere.

An example of the use of such dispersion models is shown in Fig. 2.7. An explosion in Northern Italy at the Seveso Chemical plant in July 1976 led to emissions of high concentrations of pollutants including dioxin. The ground level concentrations of dioxin are shown with the greatest levels nearest to the source and these decrease and become more dispersed further downwind. In the area close to the plant (zone A) concentrations were so severe that the local population had to be evacuated whilst zone B was subsequently reclaimed. (Fuller, 1977., Elsom, 1987).

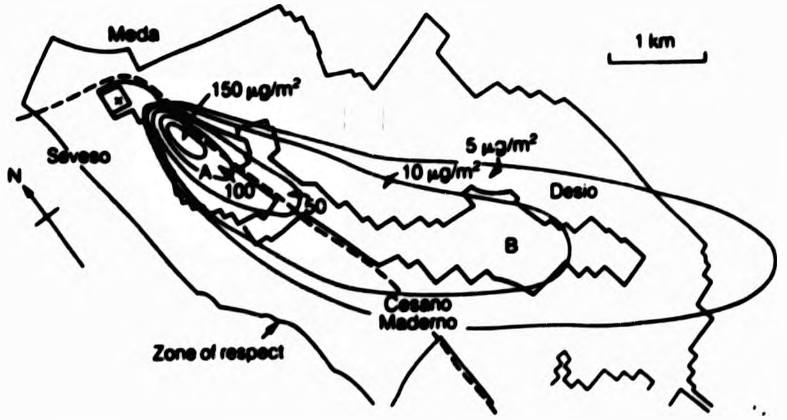


Figure 2.7 Calculated deposition of dioxin in the Seveso area assuming that 2 kg of dioxin were released (Warner, 1979).

2.5 Removal Processes

The residence time of effluent in the atmosphere depends on the physical and chemical nature of pollutants and the removal processes operating upon it. The residence time will be determined by rainfall, the height of injection and the size of particulate with which the effluent is associated (Bowen, 1975). For example, most heavy metals are associated with particulate matter ranging in size from 5nm to 20 μm (Fanaki, 1985). The height at which particulate is found in the atmosphere is also important and the higher it is the longer the material will take to traverse the depth. For instance, particulate in the stratosphere (30-40km) is subject to relatively weak vertical mixing and may take years to be deposited whilst the troposphere (10-17km) experiences strong vertical mixing and the residence time will be in the order of days (Wayne, 1985). The size of particles is also a determining factor in removal whereby fine material <2.5 μm may remain in the atmosphere for days to weeks before removal by rainfall (Bowen ,1979). Coarser material is generally removed more rapidly, with the largest particles being deposited by sedimentation after a few hours (Cutmore and Harrison, 1986). As indicated, there are two main processes by which atmospheric pollutants are removed from the atmosphere; Dry deposition and Wet Deposition.

2.5.1 Dry Deposition

Dry deposition is a continual process and the rate is governed by the concentration of material in the air near to the surface, the aerodynamic resistance of the atmosphere and the surface resistance of deposition. Dry deposition is generally dominant near emission sources (ISO,1986). Dry deposition takes place by three main mechanisms; Gravitational settling, turbulent diffusion and Brownian motion (Yamartino, 1983). It is dominated by larger particles that do not attain rain forming altitudes and is are not efficiently scavenged by precipitation (Cutmore and Harrison, 1986). A means of estimating dry deposition to a land or water surface is the deposition velocity (V_d) which is expressed as:

$$V_d = \frac{\delta M/\delta t}{M} \qquad (2.3)$$

Where:

M = Mass of particles per unit volume ($\mu g l^{-1}$)

$\delta M/\delta t$ = Flux of particles to the surface ($\mu g cm^{-2} s^{-1}$)

V_d is expressed in cms^{-1} (Winchester and Duce, 1977).

The deposition velocity is a function of several factors including the particle size and the properties of the surface to which deposition takes place. Therefore, it is difficult to quantify the V_d for all particles and surfaces (Cutmore and Harrison, 1986). However, an inverse relationship has been demonstrated between deposition velocities of some elements and their enrichment factors (i.e. the extent to which concentrations in the environment exceed those from natural sources) (Cawse, 1985).

The proportion of the total mass of atmospheric particulate removed by dry deposition as opposed to by wet processes has been estimated, with a variety of differing results. For instance, Eriksson (1959-1960) estimated that 50% was removed by dry fluxes whilst Blanchard (1963) and Robinson and Robbins (1971) estimated 23% and 20% respectively.

2.5.2 Wet Deposition

Wet Deposition is an intermittent process and involves both rainout and washout mechanisms of removal. Rainout involves the incorporation of elements into cloud droplets, often acting as condensation nucleii, which are then removed by precipitation. Washout involves the scavenging of elements by falling raindrops below clouds and is less efficient than the process of rainout (Yamartino, 1985).

Wet deposition rates for particles can be estimated by using a scavenging or washout ratio. (Junge, 1963. Schroeder, 1987).

$$W = K\rho/\chi \qquad (2.4)$$

Where:

K = Concentration in surface-level precipitation ($\mu g l^{-1}$)

ρ = Density of air ($1200 g m^{-3}$ at 20°C, 760 mm Hg)

χ = Concentration in surface-level air ($\mu g m^{-3}$) (Junge,1963)

Earlier studies suggest that a general decrease in scavenging ratios are observed as precipitation volumes increase (Lindberg et.al ,1979., Gatz,1977).

The scavenging efficiency of various elements can also be characterised by Washout factors (W) with the equation ;

$$W = \frac{\text{concentration in rain } (\mu g kg^{-1})}{\text{concentration in air } (\mu g kg^{-1})} \qquad (2.5)$$

(Chamberlain, 1960)

If an element has a high washout factor it will be more efficiently scavenged by rainfall (Peirson et.al., 1973).

Rainfall collection efficiency is also dependant on the particle size of trace elements in the atmosphere. For instance, cadmium (Cd) is associated with large aerosols which are efficiently scavenged whereas lead (Pb) has a smaller particle size and is less efficiently scavenged (Lindberg and Turner, 1983).

2.5.3 Occult Precipitation

Another pathway for wet deposition has been identified and is described as occult precipitation (Dollard et.al., 1983). Occult precipitation occurs where vegetation in wind driven cloud, fog or mist intercepts water drops that are not collected efficiently in standard rain gauges (Nagel, 1956). Nagel found that the intensity of fog precipitation was twice that of the mean rainfall measured on Table Mountain. Dollard et.al. measured the concentration of various elements and rate of occult precipitation at Great Dun Fell in Cumbria and found that there was an increase in water collected in areas prone to low cloud by 20% over measurements taken by conventional raingauges alone. Occult precipitation is, therefore, likely to be a significant source of water in areas where orographic cloud cover and advection fogs are common such as upland and coastal areas.

This form of wet deposition is significant for pollution removal as cloud and fogs contain a wide range of elements which are often at concentrations that are higher than those found in rainfall in the same area (Mrose, 1966). The reason for the higher concentrations is likely to be a result of cloud droplets being sampled or impacted at an earlier stage of development than rain drops. As already discussed, pollutant aerosols and particulates act as condensation nuclei and the concentrations of these in cloud and mist will be relatively higher than in rain drops where growth and dilution will have taken place before deposition.

Dollard et.al. measured the concentrations of various elements in fluxes of liquid water collected at a height of 850m collected on Great Dun Fell. They found that the significance of occult precipitation was dependant on drop deposition rate, the chemical concentrations of the water and the frequency and duration of periods of low cloud. The frequency and duration of low cloud at Great Dun Fell was also shown to be dependant on height. Their measurements indicated that conventional raingauges under estimated wet deposition by 15% when compared to the estimates for occult precipitation. It is apparent, then that occult precipitation is a potentially important pathway for pollutant deposition and will be enhanced if emissions are fed directly into wind driven cloud and fog.

Hilly areas have a pronounced effect on rainfall distribution with an increase of rainfall in these areas. Average rainfall in Britain varies from 600 mm over lowland areas of central and eastern England to 4000 mm over Snowdonia and the Lake District (Browning and Hill, 1981). The rain falls at rates of 4-10 mmh^{-1} in upland areas and may be less than 2 mmh^{-1} in low lying and coastal areas. The increase in rate in high ground is referred to as orographic enhancement and can be accounted for in terms of the seeder-feeder mechanism.

Two types of cloud are defined by the seeder-feeder mechanism; the seeder and feeder clouds as shown in figure 2.8. The feeder cloud is the orographic cloud that forms over upland areas at low levels which may be close to saturation. The feeder cloud does not have time to produce raindrops because the cloud may traverse in the hills in western Britain very rapidly in periods of twenty minutes or more. Precipitation falling from higher levels from the pre-existing seeder cloud does not usually grow as it falls through the lowest kilometre of the atmosphere. If, however the rain falling from the seeder cloud passes through the feeder cloud in hilly areas the rainfall rate will intensify during the final stage of the descent.

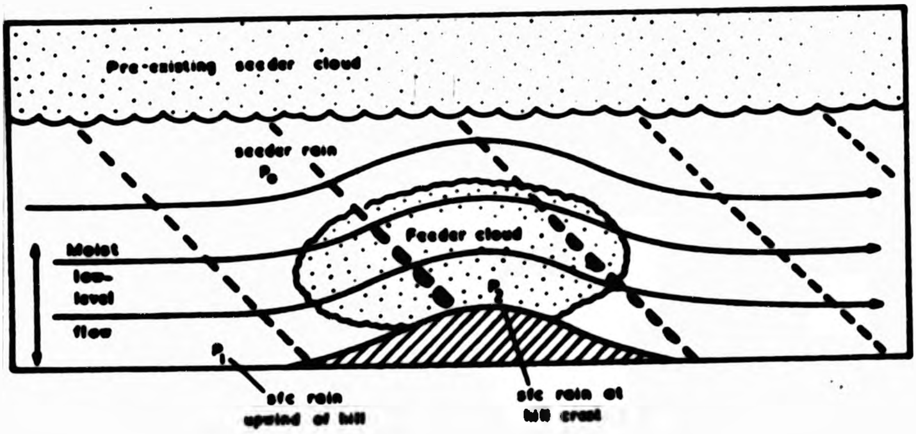


Figure 2.8 Conceptual model illustrating the orographic enhancement of rain (Browning and Hill 1981, after Bergeron)

Browning and Hill estimated that the enhancement for a constant wind speed increases rapidly as the seeding rate increased from 0.0 to 0.5 mmh^{-1} in South Wales. The found that at higher seeding rates the enhancement was more dependant on windspeed and the relative humidity in the lowest kilometre of the atmosphere. A specific example was given whereby rain from a warm front associated with strong low -level winds (230°/29ms^{-1}) crossing the coast of the Severn estuary and continuing over the Glamorgan hills and the Brecon Beacons was studied. Orographic intensification was shown to occur in the lowest kilometre above the hills in contrast with uniform rainfall at comparable levels over the sea surface. With lower wind speeds the low level orographic enhancement over the hilly ground was less distinct.

The sum of both wet and dry deposition is referred to as Total or Bulk deposition or precipitation. The absolute amount of deposition usually varies at a specific location throughout a year as a consequence of seasonal variations in both meteorology and emissions. For example, a seasonal rise in heavy metal emissions may occur during the winter months owing to increased combustion of fossil fuels (Cutmore and Harrison, 1986). Conversely, Lindberg (1982) reported that the highest concentrations of zinc (Zn), Pb and manganese (Mn) were seen in warmer months as a consequence of air stagnation and lower rainfall volumes with little dilution of scavenged material.

2.6 Resuspension and Recycling of atmospheric pollutants

When sampling atmospheric deposition, particularly metal trace elements, it is important to be aware of potentially recycled elements that have been resuspended into the atmosphere. For example, on land-based sites wind blown elements from the surrounding sites may be sampled and at coastal or sea-based sites the incursion of sea spray into samples may occur.

In order to estimate whether elements are enriched over natural sources an enrichment factor (EF) can be calculated. This compares the composition of an aerosol in a crustal or marine area with the composition of the crust or sea beneath to determine how much of the element is attributable to these sources. Enrichment factors are calculated by using a reference element; Aluminium (Al) and Iron (Fe) are indicative of crustally derived material and Sodium (Na) of marine sources. Values of greater than one indicate that the element is enriched (Rahn, 1976).

Recycling of trace elements occurs with the production of sea spray. The passage of bubbles through the sea surface microlayer (50µm thick) concentrates particulate matter and this enhances the chemical composition of sea salt aerosol produced from the water surface (GESAMP, 1980,1985. Hickmott, 1981). Hickmott suggests that bubble bursting is the dominant method of entraining particles into aerosol form at wind speeds of <15ms^{-1} with the shearing of wavecrests by wind and the aerodynamic suction at wavecrests of capillary waves lifting drops into suspension as two minor methods of production. At wind speeds of greater than 15ms^{-1} there is some dispute as to the role of bubble bursting as a method of aerosol production. Hall (1974) estimated that at wind speeds of greater than 30ms^{-1} it was not possible for bubbles to produce more than 20% of the sea salt aerosol flux whilst Wu (1981) suggested that bubble bursting was the major mechanism for spray production even at high velocities.

The sea surface microlayer is enriched in particulate matter with fold enrichments of heavy metals being recorded over bulk sea water (Piotrowicz et.al., 1972. Duce et.al., 1976., 1972., Pierson et.al., 1974., Hoffman and Duce, 1974.). Duce (1975) showed that 50% of particulate metals including Al, Cu, Zn, Ni, Pb, Cr and Cd in Narragansett Bay could be scavenged by bubbles and transported to the air-sea interface. Hardy and Apts (1983) also demonstrated that deposited metals may take 1.5 to 15 hours to traverse the sea-surface microlayer and that enrichment factors of 2 to 100 are seen under light winds.

At a critical wind speed of 8ms^{-1}, particulate enriched material is rapidly formed and may be carried shorewards to be deposited on adjacent coasts and this phenomenon is called the maritime effect.

The maritime effect has been shown to exist as far as 5km inland, based on studies of environmental radioactivity in

Cumbria (Pierson et.al., 1974, 1982. Pattenden et.al., 1987). A series of soil samples from transects taken inland from the Sellafield Nuclear power station were analysed for ^{137}Cs (caesium) and isotopes of plutonium (Pu). The results showed a decrease in Pu concentrations with increasing distance inland that reached baseline levels from weapon fallout at about 5km. The source of the Pu isotopes was largely attributable to the sea. Similarly, Frazier et.al. (1977) measured radioactivity of a lichen in the coastal area of Cotentin, Normandy, France. The data showed a decreasing radioactivity in relation with the distance from the shore. The authors concluded that the observed gradients were a consequence of radionuclide transfer by aerosols from the marine to the terrestrial environment. Cambray et.al. (1985) also illustrated the maritime effect with results from a North Sea gas platform. Concentrations of trace elements in rain were an order of magnitude higher at the gas platform than at two coastal sites. It was presumed that the higher trace element concentrations were a result of the collection of enriched marine spray.

2.7 Atmospheric metal pollution

A number of studies have been carried out in a range of climatic conditions to assess the deposition of metals to both water and land surfaces in relation to direct discharges to water bodies. From these it is clear that the atmosphere is an important medium for the transport of pollution to water surfaces. In a study of emissions in the Lake Michigan area it was found that the atmosphere was a major pathway in which metals entered the Lake. Winchester and Nifong (1971) and Winchester (1972) carried out an emission inventory of the major metals sources to Lake Michigan. They established that the principal sources of metals were the iron and steel industry, coal burning and fuel oil combustion from both domestic and industrial sources, vehicle emissions and cement production. Many metals were studied including Cu, Ni and Zn. They found that the contribution of atmospheric Cu and Ni were comparable to direct discharges but that the atmospheric contribution of Zn was an order of magnitude higher emphasising the importance of this pathway for Zn dispersal. This work was based on simple estimates using the frequency of wind direction from source areas to Lake Michigan and Skibin (1973) later suggested that the use of more sophisticated wind speed data and the incorporation of atmospheric stability would be likely to enhance the estimated atmospheric contribution.

In a study of the New York Bight, comparison was made between atmospheric inputs and direct inputs by rivers, barge dumping, sewage and runoff for selected metals (Duce et.al., 1976). The atmospheric data was collected from a small number of sites and estimations made using a number of assumptions with the resulting data showing that the atmospheric contribution of Pb, Zn, Fe and Cd were 15%, 8%, 5% and 1-2% respectively. The assumptions used were that particulate trace metals were uniformly distributed by turbulent mixing to a height of approximately 1.6 km, that they were advected out over the New

York Bight at a constant wind speed of $5ms^{-1}$ and that they were being removed from the atmosphere at a constant rate proportional to their dry deposition velocity. These assumptions are clearly over-simplified in that wet deposition is an important consideration in atmospheric deposition and that deposition is unlikely to be a continuous process but will vary according to both wind speed and direction as well as stability conditions. The wind speed is also not likely to remain at a constant speed. Despite these assumptions the calculations provided an estimate of the contribution of the atmosphere to the New York Bight although it was clear that direct measurements of deposition to the area were needed.

The authors concluded that the atmosphere was not a major source to the Bight but was significant, nonetheless. With greater distance from the shore it is likely that the atmosphere would become more important. When compared to data from the Southern California Bight (Duce et.al., 1974) the authors found that estimates of dry deposition were comparable but wet deposition was significantly lower in California. This was a result of differing climatic regimes where the New York Bight receives much higher rainfall.

Further comparisons of wet deposition over the winter were made between the Mid-Atlantic coast at Lewes D.E. and the west Atlantic island of Bermuda for various trace metals (Church et.al., 1984). The area is subject to westerly air flow and it was found that the levels of wet deposition of Zn, Pb, Cu, Ni and Cd, amongst others, were greater off the mainland coast than over Bermuda. The authors established that most of the metals were derived from a common source in the eastern U.S.A. and that concentrations were enriched over crustal weathering sources. It was also found, in general, that recycling of trace metals from marine sources was not important with the exceptions of Mn and Vn. A further analysis of this work (Tramontano et.al., 1987) was made on Al between the sites on the basis that Al is an important toxin in aquatic environments (Baker and Schofield, 1982). They found that 50% of the Al flux at both sites was attributable to wet deposition. Two peaks of Al concentrations were seen at Bermuda: one in April which corresponded to spring tilling in the United States and another in July which was possibly a result of the transportation of Saharan dust under easterly wind conditions.

In other studies of Pb to sea water it was thought that high concentrations in the surface waters of the Los Angeles basin were attributable to automobile emissions (Tatsumoto and Patterson, 1963) and that 45% of Pb input to the S. California Bight was deposited via the atmosphere (Patterson and Settle, 1974).

In a review of trace metals in the marine environment (Duce et.al., 1974) it was suggested, with reference to the Bermuda data, that the sources of Pb, Cd, Zn and Cu were from anthropogenic emissions in the U.S. whilst the elements Al, Cr and Ni, amongst others were largely derived from crustal weathering with the marine environment as the principal source for Na, Mg, Ca and K. On the basis of three simple models it was apparent that metal transfer via the atmosphere was an important pathway to oceanic pollution.

Many studies on metal pollution via the atmosphere have been carried out in Europe with particular focus on the water quality of the North Sea. A review and assessment of the current knowledge of atmospheric input of trace metals to the North Sea was prepared by Cutmore and Harrison (1986). For example, an emission inventory of atmospheric sources of pollution was summarised by Pacyna (1989) based on the collation of previous work (Pacyna, 1982, 1984). The author identified various sources of metals in Europe. Combustion processes were the responsible for the majority of Cr, Cu, Zn and Pb with electricity generation accountable for half the total mass of trace elements by combustion of fossil fuels. The majority of thermal power plants are conventional and emit large quantities of Cd, Pb and Zn. Non-ferrous metal production provides the largest emissions of Cd, Cu and Zn by pyrometallurgical processes and emissions from the majority of non-ferrous works existing in 1982 were also estimated (Pacyna and Münch,1988., Pacyna, 1988). From this it was clear that emissions of Cd were associated with Zn and Cu production, Pb emissions were high from works producing Cu, Zn and Pb whilst Zn emissions were primarily associated with Zn production. Other sources identified included the production of iron and steel, cement works , refuse association (particularly for Cd) and combustion of motor fuels which was a principal source for Pb.

In 1982, 76% of Pb emissions were attributable to vehicle emissions in Europe. The introduction of legislation for low lead and lead free oils has contributed to a decrease in Pb emissions. McInnes (1988) in a study of airborne Pb concentrations in the United Kingdom two years before and after the maximum permitted Pb content in petrol was decreased in 1986 (Jan) showed there was a 50% decrease in atmospheric lead concentrations over the pre 1986 levels. A slight increase between 1986 and 1987 was accounted for by the increase in fuel consumption and also severe weather adversely affecting dispersal.

Critchley (1983) identified the main pathways of metals entering the North Sea as the atmosphere and fluvial inputs. This work was based on Norton's (1982) assessments of pollutant pathways and atmospheric deposition was estimated to contribute 28% of Cd, 25% of Cr, 57% of Cu, 44% of Ni, 58% of Pb and 35% of Zn when compared to other inputs. Riverine inputs were also extremely important, especially in the southern North Sea with the rivers Rhine and Meuse major metal pollutant contributors.

Meteorological conditions, particularly wind direction, were also seen to be important at a pollution receptor site; Ostend on the Belgium coast (Kretzchmar and Cosemans, 1979). Daily monitoring of metals including Pb, Zn, Cd, Cu and Cr showed that under easterly and south easterly winds high concentrations were received. North westerly and northerly winds brought very low metal concentrations. These directions were indicative of the source regions of the European industrial mainland and marine airflows. Under certain wind conditions large concentrations of metals were identified as having come from the United Kingdom. Wet deposition of Pb, Cd, Zn and Cu was also seen to be the principal method of deposition to the N Sea (Dedeurwaerder et.al., 1987). Dry deposition was identified as far less important than wet deposition and operated, mainly on larger particles with particulate greater than 7.2μm in diameter responsible for 65% of the dry deposition flux.

Simple model predictions of dispersal and deposition were used to quantify emissions of Cd and Pb in the southern N Sea by van Aalst et.al., (1983a). These showed that predictions for Pb were similar to measured concentrations but those for Cd were much lower than those measured in coastal areas. This was thought to be a result of overestimation of deposition on the basis of rain fall measurements at sea. Concentrations of Cu, Ni, Pb and Zn indicated that the atmosphere was an important pathway for these metals but less important for Cd and Cr when compared to fluvial inputs in coastal areas.

Krell and Roeckner (1988) used long range model simulations for the deposition of Cd and Pb to the N Sea and validated these using measured concentrations of both wet and dry deposition. Their work suggested that the principal emission sources of metals came from the south and western parts of the area and that estimated deposition was considerably lower than that suggested by van Aalst et.al. (op.cit.) and that this was a function of rainfall at sea being considerably lower than at coastal sites.

Similar sources and concentrations of metals in the atmosphere in the southern N Sea were also seen by Dedeurwaerder and Artaxo (1986) and the differences between coastal and marine rainfall were highlighted by van Jaarsveld (1986). When compared to other European countries the U.K was identified as a major contributor of atmospheric pollution of Cd (39%), Cr (57%), Cu (41%), Ni (53%), Pb (60%) and Zn (45%).

Therefore it is clear that the atmosphere is a very important contributor of pollution to water bodies with estimated deposition to land based discharge ratios very similar if not greater (van Aalst, 1988., Chester and Murphy, 1990). A closer examination of the influence of meteorology on atmospheric pollution and pollution studies in the region will be discussed in the following chapter.

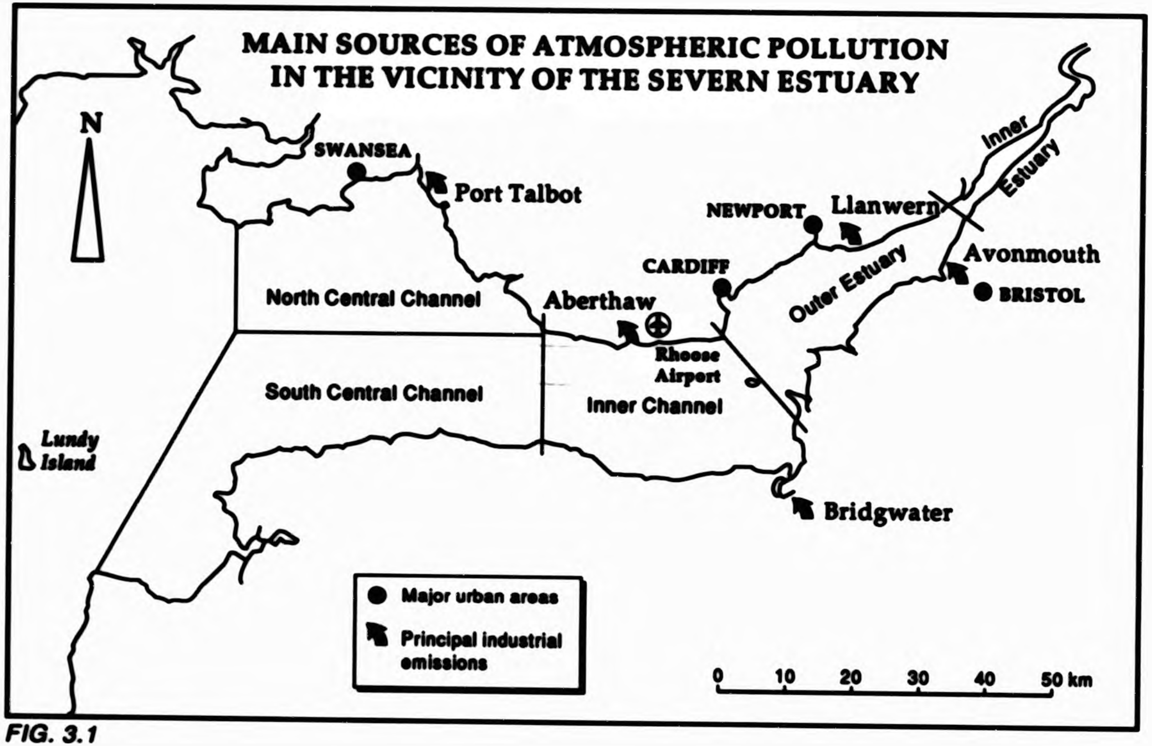
3 DISPERSAL AND DEPOSITION IN THE SEVERN ESTUARY

3.1 Introduction

The Severn estuary, located on the west coast of the British Isles, is bordered by hills both to the north, in South Wales, and the south by the South-West peninsula. This topography combined with the complex meteorology over the estuary and the location of industrial activity on its coastline will have an important effect on the dispersal and deposition of metals.
The northern coastline of the Severn Estuary is mainly bordered by upland areas which rise up gradually from a narrow coastal plain some 5 kilometres wide. A transect from Port Talbot inland in a north easterly direction shows that the land rises from sea-level to 320 m at a distance of 8 km, to 528 m at 20 km and 890m above mean sea level at the highest point in the Brecon Beacons at a distance of 40 km inland. The topography has an important influence on the rainfall in the area with enhanced orographic rainfall seen in the Glamorgan Hills and Brecon Beacons as discussed earlier (section 2.). It is probable that the concentrations of metals and other pollutants emitted from the Swansea Bay industrial complexes is elevated in these areas as a result of the prevailing south westerly winds carrying high pollution loads inland.

To the south of the Severn estuary the coastal area in the western channel rises steeply up onto Exmoor with the land being at a height of 350 m above mean sea-level at a distance of one kilometre inland near Lynmouth. It rises to its highest point at Dunkery Beacon (O.S. Sheet 180, SS 89217) at a height of 519m some seven kilometres inland. Further east, the topography rises up from the coast to the Quantock Hills (310m at 4km inland) and then becomes much flatter and the coast of the Severn Estuary is dominated by the Somerset Levels between Bridgwater and Bristol (Fig 3.1).

Historically the Severn estuary has been the focus of industrial activity since the industrial revolution with a concentration of mining and smelting activities taking place, particularly in south Wales. A sediment core sampled in Swansea Bay, for example, by Clifton and Hamilton (1979) Showed that there had been a steady accumulation of iron, zinc and copper in the accreting sediments which had increased sharply in the second half of the nineteenth century which coincided with the industrialisation of the region. Since then the concentrations of iron and copper had slightly declined but zinc levels had continued to increase and a sharp increase in lead deposition was observed at about 1900 which had continued to increase to the present day. Analysis of the lead indicated that 70-75% originated from coal debris emanating from the local area and the remainder came from industrial wastes from imported ores. Nickel and Zinc concentrations were found to be elevated in the river Tawe its tributary Nant-y-Fendrod by Chubb et.al. (1980) as a result of metal processing activity, both past and present, in the area. The zinc emanated from the waste tips of a zinc smelter in the lower Swansea Valley which closed in 1971 and the



MAIN SOURCES OF ATMOSPHERIC POLLUTION IN THE VICINITY OF THE SEVERN ESTUARY

FIG. 3.1

nickel works still operates at present (Goodman, 1979).

The area is still a centre of industry providing a constant source of pollution to the water body via both land-based discharges as well as atmospheric emissions. The principal industrial centres in operation at present are located (Fig. 3.1) at Avonmouth and Severnside, Swansea Bay and Llanwern Steel works in addition to the urban centres of Bristol, Cardiff and Newport. The Avonmouth area is a particularly important source of Cd, Cu, Pb and Zn (Davis and Clayton, 1985). Other minor inputs from point sources include the coal-fired power station at Aberthaw as well as Bridgwater whilst multiple emissions are discharged by domestic and industrial fuel combustion and vehicle exhausts from the extensive local road network. Although these sources may be individually small their combined pollution load may be a significant contribution to the estuarine waters of the Severn, whether by land based or atmospheric input. It is likely the majority of pollution to the Severn estuary is from local sources but there may some background aerosol input imported from Europe and S. Ireland, for example, via the atmosphere depending on prevailing meteorological conditions.

3.2 Meteorology in the Severn Estuary - Implications for Dispersal and Deposition

Meteorological variation over the Severn Estuary is complex and results from a combination of locally modified mesoscale atmospheric systems and systems developed within its immediate environs. The most important considerations of the meteorology over the Severn, in terms of pollutant dispersal and deposition are the vertical structure of the atmosphere, the wind direction associated with the flow of air masses across the area and the frequency of rainfall.

3.2.1 Stability

In an unstable atmosphere with strong turbulent mixing effluent emitted to the Severn estuary will be dispersed through a deep layer above the surface. Turbulent instability is a characteristic of some air masses such as Polar Maritime which is the most frequently occurring air mass to the British Isles. Polar Maritime air is associated with cool weather with clear spells and heavy showers (Barry and Chorley, 1971) which will also affect dispersal and deposition of atmospheric pollution within the Severn.

Turbulence is also induced by thermal and mechanical interaction with the underlying surface. The topography of the land around the Severn estuary is such that the hills to the north and south encourage deep vertical mixing in onshore flow and emissions from coastal areas may be carried some distance inland. Where airflow occurs over cool estuarine waters there is a greater degree of stability induced in the lower atmosphere and vertical mixing is suppressed. In contrast, the very high tidal range of the Severn (10m at Avonmouth) results in large areas of intertidal sediments being exposed at low tide which, if subject to solar heating, will induce boundary layer instability and enhance effluent mixing.

Stable atmospheres, particularly with temperature inversions, restrict vertical mixing. Under these conditions large stagnant pools of cool air may form over the estuary and the coast as the land cools at night. The majority of industrial sources to the Severn are located in coastal areas and stable conditions are likely to lead to locally high concentrations of pollution. Katabatic airflows from further inland, for example from the South Wales valleys may enhance the stability by bringing more cool air over the estuary. There may also be local fumigation of coastal plumes. Industrial decline has tended to reduce the levels of inputs from this source.

Southerly and easterly airflows are generally the most stable and may be associated with near-surface or elevated inversions. This was demonstrated by Belasco (1952) who observed negative lapse rates under Tropical continental air masses flowing from the south-east or east in the lowest kilometre of the atmosphere during the winter months. The airflows associated with these flows are generally Continental Tropical or Continental Polar and are rarely experienced in the British Isles. The Continental Tropical air mass, when it does occur, is more frequently experienced during the winter and stability is intensified by cooling from below as the air mass passes over the European mainland and Britain (White et.al., 1984). Trapping and entrainment of emissions from stacks may occur under these conditions. There is a greater frequency of stable atmospheres in late winter when land and sea temperatures are low. Although such conditions are less frequent than more unstable westerly flows they may result in episodes of much higher concentrations of pollutants in the lower atmosphere.

3.2.2 Wind speed and direction

The Severn Estuary receives airflow from all directions of the compass but has a predominantly westerly regime (Harrison et.al. 1985). This is seen in Fig 3.2, showing average wind direction and mean wind speed for the Scilly Isles which are located at the south-western approaches to the estuary. It is also clear that the strongest winds are experienced from westerly directions. Estuaries tend to funnel airflow (Harrison, 1988) which in the case of the Severn accentuates south-westerly flows. The irregular coastline of the Severn Estuary modifies the distribution of wind flow which results in differences between the inner estuary and the Bristol channel. There is, for example, a well defined difference between Penmaen, on the Gower Peninsula and Rhoose airport. While winds are from between south-west and north-west for 80% of the time at both sites, Penmaen experiences higher frequencies from the north-west than does Rhoose. This is accounted for by the topography in the vicinity of the stations (Welsh Office 1975). Westerly winds tend to be associated with higher mean wind speeds than easterlies, and have a much higher sodium chloride concentration, but generally carry lower pollution loads. In contrast, the less frequent offshore easterly winds tend to be more stable and may carry much higher pollution loads. On hot summer days, however, unstable conditions may be induced by the heating of the land. Easterly flows will also be constrained by the coastal topography and this will cause pollution loads to be deposited in the estuarine waters.

3.2.3 Clouds and Precipitation

Stable atmospheres are associated with thin cloud layers which may take the form of uniform stratus clouds or fogs. Water droplets in this low cloud and fog provide a medium for the accumulation of particulate and dissolved pollution. Stacks emitting into sea and radiation fogs will result in enhanced local deposition near industrial areas. Effluent plumes also feed directly into low stratiform clouds which release moisture to precipitation and once a plume is entrained in these clouds the pollutants may be carried over long distances before they are deposited. Cyclonic weather systems are modified by orographic effects which not only intensify precipitation but also increase the length of time over which it falls. Because of obvious observation difficulties there are few accurate precipitation records for tidal areas but records from Flat Holm appear to suggest that 24-hour falls are similar to those over the nearby coastal plain. It is likely that tidal water movements may also exert some influence on rainfall amount and intensity (Vugts,1987) although this has not been established for the Severn estuary.

3.2.4 Pollutant Trajectory - Potential Sources

A closer examination of wind direction gives an indication of the potential sources of atmospheric metal pollution from both local sources and further afield. Figure 3.2 shows the average wind directions for both winter and summer and the yearly averages. In January the (most) predominant wind directions are westerly and west-north-westerly and these are associated with the strongest wind speeds. The air masses that are responsible for these wind are Polar Maritime and the pollution loads that

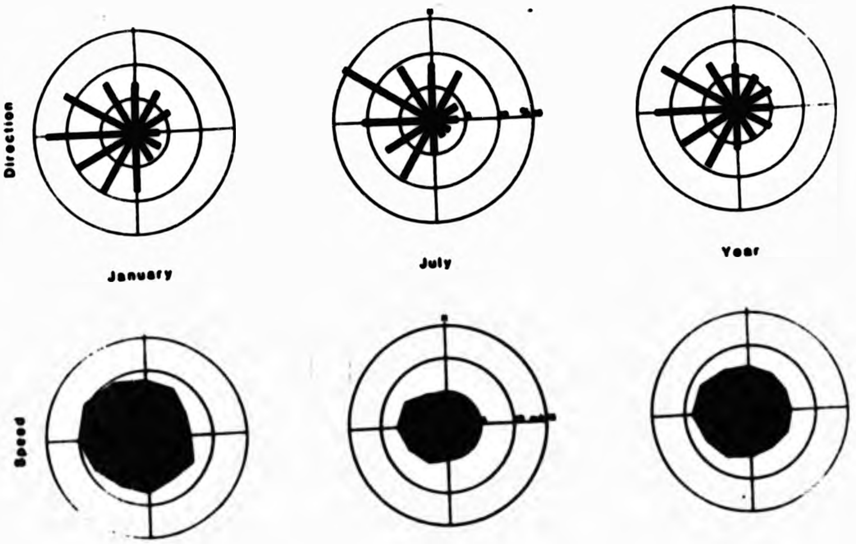


Fig. 3.2 Wind direction and mean wind speed for the Scilly Isles
(Source: Harrison *et.al.*,1985)

these import from the Atlantic are likely to be low although some metals may be brought in from North America. These metals are likely to be very fine particulates or in a dissolved form. It is possible that metals may be carried from emissions from the oil installations at Bantry Bay (450km from centre of the Severn) in south-west Ireland and Milford Haven (125km) in south west Wales. The distances involved suggest that the most important method of deposition from these sources will be by wet methods as dry deposition is associated with larger particles that fall out very close to source. Small particles and gases will, however, remain in the atmosphere for much longer periods and may be added to by wind blown dust resuspended from the ground. Particulates will be incorporated into the masses in clouds and deposition will take place by rainout.

Closer to the Severn estuary emissions in the Swansea Bay area from oil installations, iron and steel works and smelting activity will be transported to the estuarine waters. There is also a possibility of wind blown dust from smelting tips being resuspended and included in the atmospheric load (Welsh office, 1975). Deposition is likely to take place by both wet and dry mechanisms although the waters closest to source will have a greater dry deposition element. In the summer months WNW winds are the most common and the same sources are likely to influence deposition to the Severn but their effect will probably be diminished as a result of reduced rainfall at this time. The most important sources are therefore, going to be localised coastal emissions.

The most frequent winds experienced after the W, WNW winds come from the SW in both winter and summer. The air mass associated with these is Tropical Maritime which brings mild, grey and cloudy weather conditions. Fog and drizzle is a feature of this type of air mass which has important implications for deposition and dispersal of metal pollution locally. The air mass originates in the sub-tropical North Atlantic and is therefore unlikely to carry a heavy pollution load from further afield. It might, however, have an influence on maritime resuspension of metals from the sea surface microlayer and carry high sodium loads.

Southerly winds are relatively high in the winter and are often a result of Continental Tropical airflows which as stated are associated with stable conditions at this time of year and are likely to enhance deposition to the Severn as a result of dampened vertical mixing. The air mass passes over the European mainland and industrial zones in France and may carry metals with it although much of the large particulate will have fallen out before reaching the Severn estuary. The air mass is not generally associated with wet weather so the influence of wet deposition will be limited. Taken on a yearly basis southerly and south-westerly airflows are very rare but their influence on local emissions and deposition to the Severn estuary may be marked.

Polar Continental air masses are associated with easterly flows and are experienced even more rarely across the Severn estuary but again the effects of stability on local deposition will be enhanced particularly from the Avonmouth and Severnside industrial area. These winds are relatively dry so the influence of wet deposition of metals imported from the east of England and N. Europe will be slight as dry deposition will cause the majority of particulate material to be removed before reaching the Severn.

Maritime Arctic and Continental Arctic air masses from the north and north-east occur with similar frequency in both summer and winter but are not as frequent as westerly air masses while being more common than easterly and southerly conditions. Maritime Arctic air masses originate in the Arctic Ocean. They are unstable and humid bringing heavy showers to Great Britain, often as snow. Pollutant loads will be scavenged by clouds as the air mass passes over Britain. The trajectories taken are not likely to import much pollution to the Severn as the principal industrial zones in the U.K. are to the north-west. By contrast NE winds from cold, dry Continental Arctic masses pass across the major industrial areas including the NE coast (≈400km), Manchester and surroundings (≈300km) and the Midlands (150-200km). The importance of particulate and dissolved metal deposition from these sources will be diminished as consequence of the dry air but gaseous pollutants may well be brought to the estuary.

This examination of wind direction, therefore, emphasises the importance of local sources of metals to the Severn and although, infrequent, the potentially high deposition episodes that will occur under winds from the easterly quadrant of the compass.

3.3 Coastal effects on the windfield

Contrasts in aerodynamic roughness between land, intertidal sediment and open water surfaces as discussed (Section 2.3.2) have an effect on the overlying coastal windfield. Along coasts, air blowing from the sea possesses maritime characteristics and the mean wind profile will be adjusted to the relatively smooth surface below. As it crosses intertidal sediments and then the land the airflow readjusts to the new roughness elements beneath. This adjustment is not instantaneous but occurs gradually with increasing distance from the location at which the changes occurred. As indicated earlier this transition zone may be between 1 and 2 km of the shoreline. This has significance the Severn estuary where there is a decrease in tidal area with distance landwards. Thus, in the inner estuary (Fig. 3.1) it is likely that boundary layer airflow is characterised by the nature of the coastal plain while in the outer channel there will be development of airflow which is more adjusted to the surface of the extensive tidal area (Harrison, 1987). This is also an important consideration in the Severn as it has a very large tidal range, 10m at Avonmouth, and the state of the tide will affect the transition zone with large mud banks exposed at low water. The proportion of exposed intertidal sediment increases upstream in the Severn with particularly extensive areas of muddy subtidal and intertidal sediment being found in the Bridgwater Bay area (Dyer, 1984).

3.4 The Maritime Effect

As discussed in section 2.6 the consideration of metal recycling from within the estuarine system will be important in the analysis of metal deposition to the Severn. Particulate enriched aerosol is rapidly formed where winds are greater than 8ms^{-1} and may be carried inland to be deposited on the shores of the estuary as far inland as 5km or more. The shape of the Severn Estuary is such that resuspension should not be a major problem as the greater part of the coastline experiences winds from relatively short fetches. However, the S. Wales coast between Rhoose and Port Talbot and between Clevedon and Burnham on Sea in Somerset an Avon may be more prone to resuspension, having a greater exposure to the west from which direction winds are generally the strongest. Derbyshire and Draper (1963) produced a chart for estimating the wave height given the wind speed, duration of wind and the length of fetch. For winds from the south-west with a fetch of 600 nautical miles and a wind speed of 15 ms^{-1} which had a duration of 12 hours which might be experienced on the Port Talbot coastline the predicted wave height would be 3.75 metres. Alternatively, southerly winds with a fetch of approximately 20 km blowing towards Rhoose Airport over the same time period with the same wind speed would only produce wave heights of 1.5 m. Maritime resuspension on islands

within the estuary, such as Lundy, Flat Holm and Steep Holm is likely to be enhanced. During storm conditions the islands in the Severn estuary are visibly enveloped in sea spray.

3.5 Atmospheric pollution in the Severn Estuary

3.5.1 Previous Surveys

Anthropogenic sources of pollutants to the atmosphere include non-ferrous metal manufacture, mining, combustion of fossil fuels, use for fuel additives and the incineration of waste (Cutmore and Harrison, 1986). Increased anthropogenic emissions of trace metals have occurred during the twentieth century owing, in large part, to the greater use of high temperature industrial processing (Nriagu,1979).

On the basis of data collected during 1978 and 1979 it has been estimated (Welsh Water, 1980) that atmospheric deposition accounts for 50% of the Pb and Zn inputs and 10% to 20% of Cd, Cu and Ni but it is only a minor source of Cr, Fe and Mn to the surface water of the Severn estuary. The majority of Cd, Cu, and Pb has been identified as entering from the lower atmosphere via the outer estuary region (Fig. 3.1) within which are the heavily industrialised areas of Avonmouth and Cardiff Bay. A major source of Cd within the outer estuary has been identified as the Avonmouth Municipal Incinerator (Scott, 1987) which emits waste on a continuous basis. This is also responsible for the emission of high concentrations of Pb but records of the ambient air quality in the area indicate that other local sources of the metal, such as vehicle emissions, are more important.

Earlier studies of metal pollution have been carried out within the Severn estuary region by using moss bags as pollutant collectors, particularly in the Swansea Bay and Avonmouth areas. A moss bag consists of a packet of moss, in this case *Sphagnum moss*, contained by a nylon mesh which is then deployed in the field. The moss bags Pattenden (1974,1975,1977) measured atmospheric concentrations of metals including Cu, Ni, Zn, Cd and Pb in the Swansea Bay area by collecting air particulate, dry deposited dust and rain (total deposition) between June 1972 and May 1973. Their results were also compared to Goodman et.al. (1975) who collected samples of metals including Cd, Cu, Ni, Pb and Zn between June 1972 and May 1973 that accumulated on moss bags on a monthly basis.

Pattenden (1974, 1975, 1977) found that by correlating weekly metal concentrations with wind speeds and direction, there were local sources of Ni and Co in the Swansea valley which were attributable to wind blown dusts from the waste tips of the nickel works in the lower Swansea Valley. The Baglan area of Swansea Bay was identified as a source of zinc and lead and that sodium, Chloride and copper concentrations correlated with a maritime source. However, it is likely the copper concentrations associated with wind blown sea spray were not real and were probably a result of sodium interference in the copper determination by neutron activation analysis whereby elevated copper concentrations were measured. For this attempt at source identification weeks were characterised by a particular wind direction and wind data taken from Rhoose Airport. The differences caused by local topography between Rhoose and the study area as discussed in section 3.2.2 mean that these source regions could only have been general estimates of the pollutant trajectories and a week was too long to ensure that the wind was from a particular direction. In addition the local topography would have had the effect of funnelling winds up the valley if they were from the south or west or down it if they were northerly or easterly further limiting this broad trajectory analysis.

Goodman et.al. (1975) found that the quantities of airborne metals captured by moss bags (dry deposition) were similar to those collected by Pattenden in the Swansea Bay region and that the possible sources of metals were the same. They found that metal concentration was proportional to exposure time and the method of isoplething results from several sites was used to identify sources. Comparison with Pattenden's data showed that moss bags tend to overestimate dry deposition and in some cases the measured metal concentrations from moss bags were higher than total deposition from both wet and dry sources. This overestimation is a result of the moss surface which is more efficient at catching large particles and retaining them as opposed to the smooth surfaces of funnels and filter paper.

The deployment of moss bags is an important consideration in the resulting data as moss bags that are placed with their longest axis vertical and normal to the emission source tend to catch more material and therefore will be biased to local sources and dependant on wind direction. The authors concluded that moss bags were not likely to be reliable indicators of air concentrations but were probably useful for quantifying deposition to vegetated surfaces. Goodman and Smith (1975) using the same data for the Swansea Bay area from the moss bag study commented that Ni, Cd and Cu concentrations in the area were elevated and came from local emissions.

The lead concentrations were attributed, largely, to emissions from the combustion of leaded petrol and that they were elevated in the winter months. This was thought to be a consequence of the greater frequency of lower atmospheric temperature inversions during the winter months trapping emissions beneath the steep sided valley walls. The emissions from the iron and steel industry and possibly from power stations were thought to contribute to the lead loadings. Zinc concentrations were also high and were thought to emanate from urban and industrial activity with coal burning from power stations and coking plants being important factors. Goodman (1979) indicated that the principal sources of metals collected by moss bags were from wind blown dusts from contaminated soils and waste tips either from then-active industrial processes or the legacy of earlier activity dating back to the Industrial Revolution. It was also noted that wet moss bags were much more efficient than dry bags at intercepting metals with Ni and Co concentrations doubling under wet conditions. Thus, care needs to be taken to ensure that moss bags are deployed under similar conditions so that the results are not biased by different collecting efficiencies.

The Avonmouth area has also been a focus for metal deposition studies using moss bags. Little and Martin (1972) reported a deposition study carried out using Elm and Hawthorn leaves as well as soil samples. The emissions from the Commonwealth Smelting plant in Avonmouth (Fig 3.3), the largest Zn, Pb and Cd smelter in the world were of primary interest and an extensive grid network of samples around the smelter was used. Samples of leaves and soil were collected at 200m intervals within 3km of the plant and at 3km intervals at a distance of 10km. Leaf samples were taken from both exposed (facing the plant) and sheltered sides of trees and it was found that concentrations on Elm leaves were generally higher than on Hawthorn. This was a consequence of the surface of the leaves with Elm having coarse, hairy leaves which were more efficient at intercepting particles.

The study concluded that there was an exponential decline in Zn, Pb and Cd concentrations with increasing distance from the smelter and isopleth maps of the metal deposition distribution around Avonmouth were distended in the direction of the prevailing wind. Thus, under south-westerly winds the majority of the deposition occurred in the area to the north-east of Avonmouth with a 'tail' of deposition in the south-west. This method provided a useful means of mapping the distribution of metals around the smelter but could only provide semi-quantitative results for actual metal loadings as much of the metal will fail to adhere to leaves or be washed off by subsequent precipitation or blown off by wind.

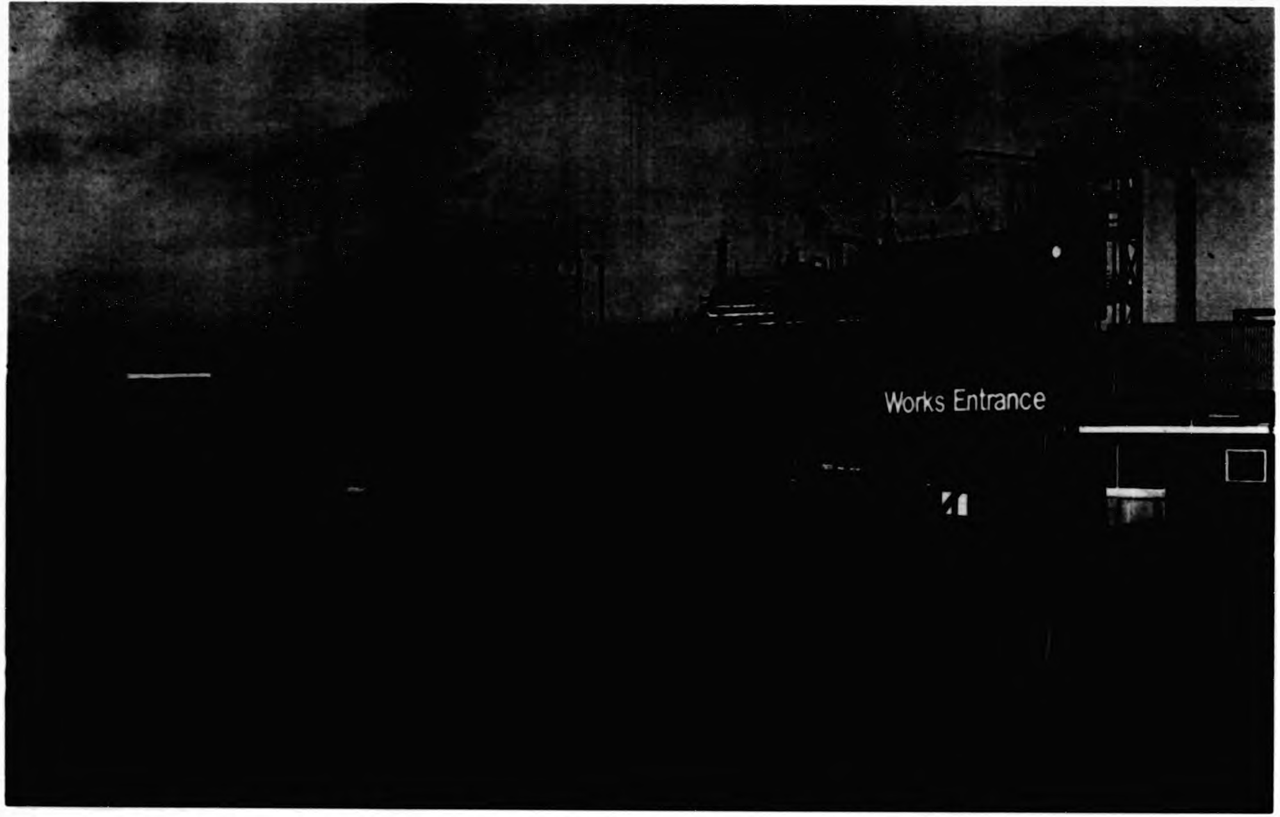


Fig 3.3 Imperial Smelting Company (Commonwealth Smelting), Avonmouth.

In a further study of the Avonmouth area Little and Martin (1974) used moss bags to evaluate Cd, Pb and Zn deposition over a period of ten months. Again, the directional nature of the moss bag was considered and all the bags were placed such that their greatest surface area faced the known source of the smelter. The resulting data was mapped using an isopleth technique and it was shown that the distributions related to wind direction. The sampling interval used was a month, as an optimum before metal saturation occurred, and as a result only broad indications of correlations between wind direction and metal distribution should be made. However, the correlations between the wind-roses and metal distribution patterns were visually and statistically very good with the exception of the Zn distribution in August 1973 when winds were from 60° and it appeared that the majority of Zn had been dispersed out over the waters of the Severn estuary.

A similar moss bag study was carried out in the region of the Avonmouth smelter by Cameron and Nickless (1977). The area studied was much larger than that covered by Little and Martin (1974), 660km^2 as opposed to 250km^2, and the aim was to delineate the boundaries for aerial metal pollution from the smelter. The sample period before analysis was six weeks which may have led to complete saturation of the moss bags and also some moss loss was experienced so this may have led to an underestimation of the metal concentrations. From the results it was estimated that the influence of the smelter in all directions except NE was at about 15km. To the NE concentrations of Pb and Cd exceeded background concentrations by 15 times at a distance of 15 kilometres and it was thought that the influence of the smelter extended far beyond this distance although no figure could be defined from this study.

From the results of these studies around Avonmouth it is clear that the predominantly south west winds are responsible for the majority of dispersal from the smelter but under certain conditions metal pollution to the Severn estuary is likely to be high.

More recently, studies of specific sources of pollution to the Severn have been documented by Davis and Clayton (1985) and (Davis, 1988) in an assessment of particle and heavy metals concentrations around the Commonwealth Smelting Works at Avonmouth and the Port Talbot works of the British Steel Corporation. Scott (1987) reported a study of emissions from the Avonmouth Municipal Incinerator. The findings of these reports indicated that a high proportion of lead, cadmium and zinc and to a lesser extent copper, in the Avonmouth area was emitted from the Smelting works. Similarly, high concentrations of Cd and Pb were being emitted from the refuse incinerator. High concentrations of iron, manganese and Nickel in the Port Talbot area were attributed to the blast furnaces and the Basic Oxygen Steel (BOS) making plant of the steel works. Lead concentrations in the port Talbot area were relatively low and the steel works was not positively identified as the source of this metal although some may have come from the plant. It is more likely that the principal source of lead in this area was from vehicle emissions from the busy M4 motorway which is adjacent to the works.

All these studies used a directional M-Type sampler developed by Warren Spring Laboratory which takes two samples; one is collected continuously and the other is collected only when the wind direction is from a specified arc, which is centred on the source under investigation. Samplers were deployed on a transect basis , generally, in the direction of the south-westerly prevailing wind either side of the smelter, incinerator or the steel works. There were, however, considerable siting differences between samplers especially the height at which they were placed. For example, sites around the Avonmouth smelter ranged from ground level to 4m above the ground and from being amongst heavily industrialised parts of the area to a relatively rural location. The height at which the samplers were placed needed to be consistent because wind speed increase rapidly with height and the samplers placed at different heights would have different collecting efficiencies. This was demonstrated by Rodda (1967) where rainfall was measured at ground level and a height of one foot over a five year period. The gauge at ground level measured rainfall 6.6% higher than at a height of one foot and the differences in wind speed were partly attributable for this difference. Clearly the influence of the height and the proximity of buildings and other pollution sources will have affected the results. An example of a local pollution source whilst measuring the emissions from the Commonwealth Smelting plant would have been the incinerator. The influence of other sources would have been largely overcome by taking a continuous ambient sample and a directional sample. The results, however, clearly indicate that the smelting plant and the municipal incinerator were responsible for a large proportion of the cadmium, zinc and lead emitted into the Avonmouth area with the steel works in Port Talbot responsible for high emissions of nickel.

Another study of the content of particulate discharge from an unidentified U.K. refuse incinerator details the concentrations of lead and cadmium emitted (Wadge and Hutton, 1987). Their results showed that the emissions of cadmium ($6ta^{-1}$) were in agreement with an emissions inventory reported earlier by Hutton and Symon (1986) which identified waste incineration as the single largest source of airborne Cd in the United Kingdom. The high concentrations of Cd reported by Scott (1987) from the Avonmouth incinerator would also suggest that this is an important emission source of the metal.

Seasonal and short-term changes in the quantities of pollutants emitted to the lower atmosphere also occur with increased fuel consumption in the winter months. This was illustrated (Banfield, 1973) in a study of air pollution in south east Wales. Anticyclonic conditions experienced in this area during December 1962 and January 1963 were associated with strong temperature inversions and a very stable lower atmosphere. Colder temperatures resulted in increased domestic smoke emissions in addition to unusually high emissions of SO_2 from the local steel works. The inversion limited the vertical dispersal of pollutants and the valley topography, in combination with low wind speeds, restricted horizontal mixing in the atmosphere. The result was a marked difference in smoke concentrations above and below the inversion layer.

A special edition of Marine Pollution Bulletin (1984) gave an overview of current knowledge of the Severn estuary and this included a summary of atmospheric metal pollution. A survey of bulk deposition in Wales, with particular reference to acidity (Donald and Stoner, 1989) emphasised the importance of easterly airstreams in importing pollutants to the area. Highly episodic incidents of high acidity were correlated with easterly airflows which passed over the east Midlands.

The majority of pollution studies in the region of the Severn Estuary have been centred on the two of the major source areas; Avonmouth and Port Talbot. The Avonmouth area has been identified as a major source of cadmium, lead and zinc and to a lesser extent copper whilst the Swansea Bay area was identified as being a particularly important source of nickel and zinc as well as lead, cadmium and copper. Whilst these studies have highlighted these important source areas and given an indication of pollution on a local scale, the overall quality of the atmosphere and the quantity of atmospheric deposition to the Severn Estuary was not defined. These individual studies have focused, largely, on specific sources such as the Avonmouth

Municipal incinerator and the Port Talbot Steel works and from these results it is difficult to gauge the quantities of metals entering the estuary in total given the complexity of the area meteorologically as well as the number of potential sources.

3.5.2 Severn Estuary Joint Committee Surveys (1977 -1983)

Two major studies of water quality, as a whole, have been carried out for the Severn Estuary Joint Committee (SEJC) and the results reported in the first and second reports of the Severn Estuary Survey and Systems Panel (Welsh Water Authority, 1977,1980). The SEJC was serviced by a Technical Working Party which was charged with evaluating existing chemical, biological and physical data available for the estuary and provided a definitive assessment of the condition of the estuary for future management; amongst other tasks (Owens, 1984). The programme, to establish the quantities of contaminants entering the water mass, was conducted in two phases. Phase I monitored 175 discharges and combined results with river flow data to calculate a mass budget for the estuary (Welsh Water Authority, 1977).

Examination of the resulting data indicated that these inputs could not account for the measured concentrations of metals in the estuarine water, particularly Cd. Phase II of the programme identified the most significant inputs of contaminants from Phase I which were then monitored in 1978/79 together with atmospheric inputs.

The mass inputs calculated were of sufficient magnitude to account for the apparent deficiencies in the inputs budget for various metals. The programme was re-established during 1982/83 using the same methodology but on this occasion the estimated atmospheric input no longer accounted for the deficit in the metals budget for the estuarine waters. On the basis of these studies this project aimed to reassess the atmospheric metal contribution to the Severn estuary. In order to obtain a more accurate appraisal of the inputs a new sampling network and methods of converting the point deposition data to a deposition surface for the estuary needed to be considered. The objective of the study was, therefore, to design a non-source specific survey with improved sampling and data analysis.

4 THE 1989 - 1990 AERIAL INPUTS SURVEY

4.1 Review of SEJC Surveys

The 1978/79 and 1982/83 SEJC Severn estuary atmospheric input surveys involved the collection of Total deposition samples for a range of metals from thirteen sites bordering the estuary (Fig. 4.1). The total atmospheric inputs were estimated by AERE Harwell by bulking the data from appropriate sites according to fixed geographical areas of the estuary (Fig 4.1) and a total determined for each metal in kgday^{-1}. This method, unfortunately, fails to take account of the trajectories of pollutants from emission sources and realistic dispersal and deposition mechanisms as it assumes that the deposition rate will be constant at all sites across the estuary for each zone. The dispersal and deposition mechanisms operating on pollutants operate on a curvilinear decay whereas the method employed by the SEJC assumes that there is no decay with distance away from source areas.

In these programmes the sampling equipment used was an open funnel deployed at 1.5m above the ground with a collecting bottle beneath (Fig 4.2). The bottle and funnel were mounted in a scaffolding frame, which had several shortcomings. The funnels may have not been horizontal, leading to directional bias in rain collection, and airflow around the funnel may have led to undercatch. Splash loss from the open funnel and evaporation loss may also have occurred. Samples from this equipment were

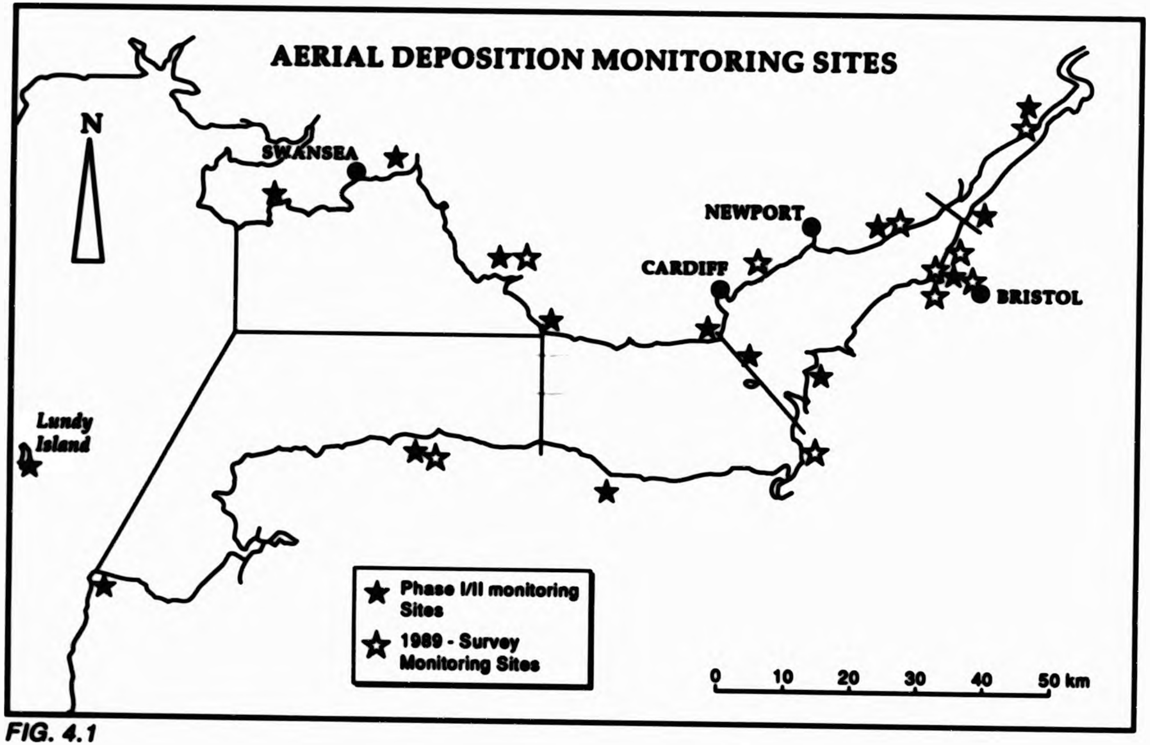

AERIAL DEPOSITION MONITORING SITES
N
SWANSEA
NEWPORT
CARDIFF
BRISTOL
Lundy Island
★ Phase I/II monitoring Sites
☆ 1989 - Survey Monitoring Sites
0
10
20
30
40
50 km

FIG. 4.1

Fig 4.2 Sampling equipment used in phase I/II SEJC sampling programmes.

collected on a monthly basis and analysed by the Water Authority in whose region a sampler was deployed. This may have led to some contamination errors by inconsistent sample handling and systematic laboratory bias may have been introduced into the final results. In 1988, on the basis of these studies it was decided to reassess the atmospheric inputs of metals to the Severn. In order to achieve a more accurate assessment of aerial inputs to the estuary, deficiencies in the sampling design and data interpretation needed to be corrected. This survey aimed to establish a new temporal and spatial sampling framework and alternative methods of converting point pattern data to a deposition surface for the estuary which would incorporate a consideration of pollution trajectories and relevant weather variables.

Initial examination of these historical SEJC data (Playford, 1986) showed some definite patterns that indicated a need for further analysis. A further examination of these data has been made by constructing isopleth maps, based on a visual linear interpolation, for each of the metals Cu, Cd, Ni, Zn and Pb. The conclusions drawn from these maps were as follows:

i) Wind direction showed a marked influence on the distributions of metals over the estuary. The patterns observed were not always as might be expected, especially under easterly airflow conditions. Under westerly wind there was a moderately consistent pattern and the distributions correlated visually with wind direction.

Stability was clearly important under easterly winds and the very heavy concentration of contaminants in the Avonmouth area was considered to be indicative of high atmospheric stability whereby the metals, once released into the atmosphere, were redeposited very near to their emission sources.

ii) The need for more sampling sites along the north Devon coast was apparent since the sampling network was very sparse here (Fig 4.1).

iii) Island sampling sites were vital to compare land based data with that out over the water surface. Concentrations on Flat Holm were very much lower than those on the English mainland possibly indicating that the deposition had fallen out close to the emission sources and that the atmospheric load had decreased rapidly out over that water surface. Wind direction and the volume of rain falling over the water surface may also have had some influence here.

iv) The sampling interval of a month was too long as the variation in wind direction was too great to obtain a representative average.

These data were then re-examined using the statistical technique of analysis of variance (ANOVA) to test whether any significant differences existed between each of the individual sites on a spatial scale and also if there were any differences within each site for the monthly readings on a temporal scale. This was carried out for each of the five metals.

The first examination of the ANOVA results showed that for all metals the concentrations were significantly enhanced at the Avonmouth site. For some metals at the Blackrock site, particularly Zn, the concentrations were also significantly above those found at the remaining sites. The ANOVA was then repeated for each metal but excluding the data for Avonmouth and Blackrock and the results examined for variation on a spatial basis. These indicated that on average there were no significant differences in metal concentrations between the remaining sites of Flat Holm, Magor, St. Mellons, Monknash, Marlas, Trebanos, Penmaen, Hartland Point, and Lee Abbey.

4.2 The Sampling Network

When designing the spatial distribution of the sampling sites in a new survey of the estuary, account was taken of the distribution of the principal sources of pollutants, the complex climatology of the estuary and the problem of resuspension from the water surface. Surface roughness changes at the shoreline suggest that the distance inland of sampling points should be short (within 2km of the shore) such that they be as representative as possible of the tidal area. However, the possible existence of the maritime effect dictates that a location greater than 1 km inland is a preferred option. Cutmore and Harrison (1986) have suggested that sites should be selected between 5-10 km inland to minimise any influence of the maritime effect. However in a later visit to five European Research Institutes, Zabel and Harrison (1986) stated that the existence of a maritime effect was not proven.

Sites were eventually chosen, as far as possible, as suggested by Cambray (1988) that were within 1 km of the shore where there was access to secure sites. For each site certain exposure criteria had to be met in order to ensure that they were as representative of a wider area as possible. They had to be located sufficiently far away from major sources of industry such that specifically local sources of contaminants would not exert a major influence on deposition.

Flat, undisturbed, ground was desirable such that the wind field around the sampling equipment is undisturbed but exposure should not be excessive as there is a risk of undercatch of rainfall (Robinson and Rodda, 1969). Trees and buildings disrupt airflow which have an effect on the collecting efficiency of the sampling apparatus. Permanent vegetation in the vicinity of the apparatus, ideally short grass, is desirable as this reduces the risk of aeolian dust and soil contamination. A standard rainfall observation practice is that no object should be within 2.5h of the sampling device, where h is the height of the object above the ground (Harrison, 1983). A standard Met Office MkII raingauge was used alongside each sampler in order to ascertain the collecting efficiency of the equipment.

The analysis of variance exercise indicated that, owing to the insignificant variations between sites not close to the Avonmouth area, that it was not necessary to increase the spatial sampling resolution along the north Devon/Somerset coastline or in south Wales. The final distribution of the sampling network (Fig 4.3) duly recognised the very steep gradients of change away from the Avonmouth/Severnside industrial complex. Several samplers were concentrated in this region of the shoreline whilst the remaining equipment was deployed as regularly as possible around the upper and lower reaches of the estuary. The area used was smaller owing to the financial constraints on the number of samplers available and the need to concentrate on the Avonmouth area.

4.3 The Sampling Sites

The individual sampling sites were chosen with a regard to security and access as well as being able to meet the above criteria restrictions. As a result most sites were chosen on land owned by the various Water Authorities (before privatisation) and where this was not available other organisations were approached for use of land. The final sites chosen were as follows:

4.3.1 Marlas - SS 813822 (Welsh Water)

The Marlas sewage treatment works was chosen for a Welsh site in

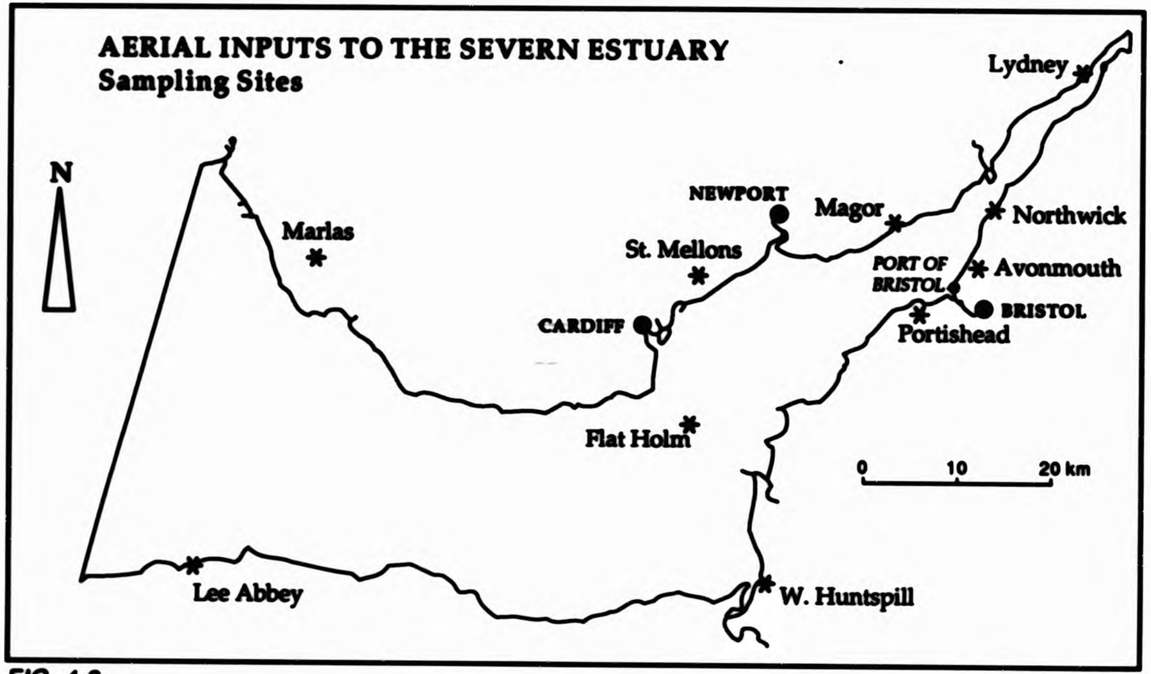

AERIAL INPUTS TO THE SEVERN ESTUARY
Sampling Sites
N
Lydney
Northwick
Magor
NEWPORT
Avonmouth
PORT OF BRISTOL
BRISTOL
Portishead
St. Mellons
CARDIFF
Marlas
Flat Holm
0
10
20 km
Lee Abbey
W. Huntspill

FIG. 4.3

Fig 4.4 St Mellons sampling site

Fig 4.5 Magor sampling site

Fig 4.6 Lydney sampling site

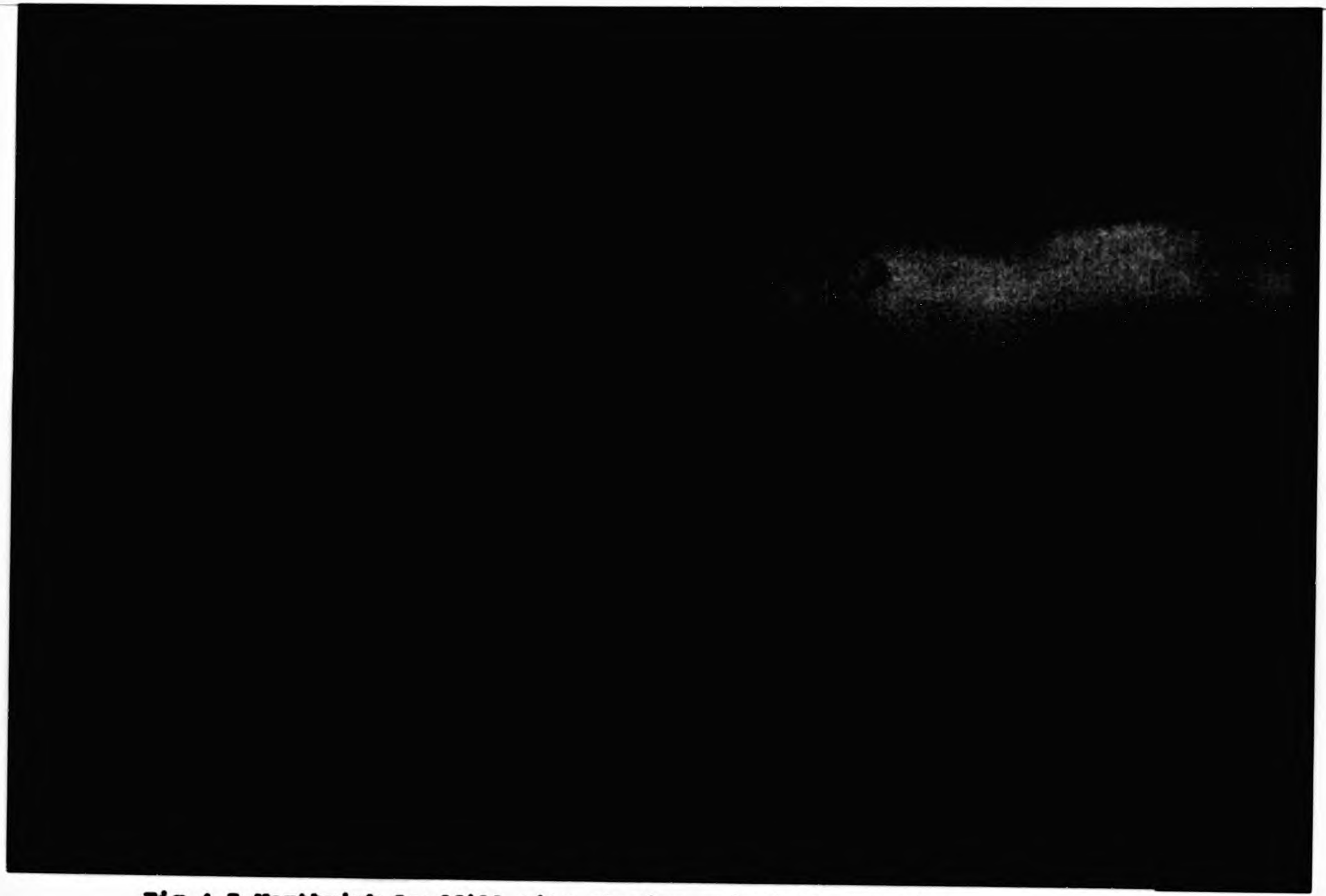


Fig 4.7 Northwick Landfill site showing principal sampling collector and collectors used in variability experiment.

Fig 4.8 Avon Sewage treatment works sampling site.

Fig 4.9 Portishead sampling site

Fig 4.10 West Huntspill sampling site

Fig 4.11 Lee Abbey sampling site

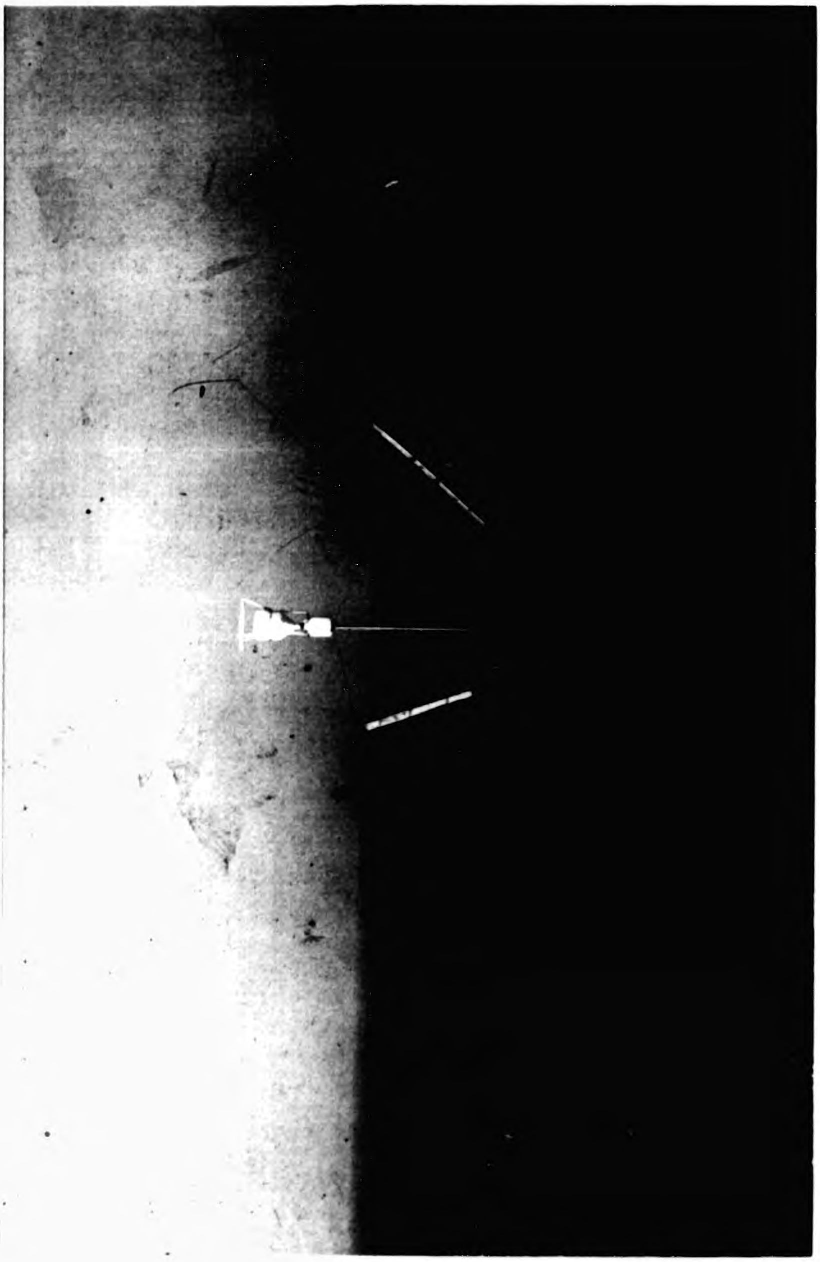


Fig 4.12 Flat Holm sampling site

the outer Bristol Channel area and provided a large area of land for a sampler to be placed without obstruction from buildings. The site was at a distance of 3 km inland which is a little more than the ideal situation but was the only site available. The site was manned during working hours which provided security for the equipment at these times, but was damaged by vandals on one occasion.

4.3.2 St Mellons - ST 253794 (Welsh Water)

The site of the water storage reservoir at St Mellons provided a reasonably unrestricted area of land (Fig. 4.4) for the sampling equipment and a Met Office raingauge was already on site. This gauge was monitored on a monthly basis by Welsh Water and then the NRA (Welsh Region) at St. Mellons and the data was made available.

4.3.3 Magor - ST 436852 (Welsh Water)

The sewage treatment works at Magor are located on a large are of flat, unrestricted land close to the Severn shore (within 1 km) with several possible locations for sampling equipment. The position chosen was on a large field also used for sheep grazing. Initially, it was not thought necessary to protect the sampler from animals but subsequent damage to the equipment led to the placing of a low fence (0.75m) around the device to prevent further sample loss. (Fig 4.5)

4.3.4 Lydney - SO 633015 (Severn-Trent water)

The Lydney sewage works provided an area of flat open land about 1 km from the shoreline (Fig. 4.6) and a standard Met Office raingauge had already been installed by the Water Authority. The site was, again, manned during working hours and access available at most times. The site was unmanned from the end of January 1990 after which time arrangements for access were made.

4.3.5 Northwick Land Refill -ST 557876 (Avon County Council)

The site was a large field owned by ICI Ltd. and leased to Avon County Council for waste disposal (Fig 4.7). The site had been reclaimed and sub-let to a local farmer for sheep grazing. A small fence (0.75m) enclosed the sampler to prevent animal damage. The field lay adjacent to Severn estuary shoreline and the sampler was placed as far away as possible from the shore without being too close (200m) to the main road on its other boundary. This road was the main road from the M4 motorway into Severnside and a potential source of local contamination from the heavy vehicle use.

4.3.6 Avonmouth - ST 536793 (Wessex Water)

The sewage works was used in the 1982/3 survey and again on this project (Fig. 4.8). The site provided a suitably unobstructed position for the sampler location where it did not disrupt vehicle access on the site. This location was within the

Avonmouth industrial area and close to potential sources of heavy contamination particularly from the Avonmouth Municipal Incinerator and Commonwealth Smelting. The site was within 1-2 km from the shoreline. The site was chosen in order to examine more closely the effects of emissions from the Avonmouth area.

4.3.7 Avonmouth - ST 510790

The Port of Bristol Authority agreed to the location of a sampler on their land close to their meteorological station. The position was adjacent to the River Avon where it discharged into the Severn and as such was likely to be strongly influenced by the maritime effect especially under high winds. There was, however, no alternative location where the equipment would not have been subject to obstruction from buildings or vehicle contamination or, indeed, an obstruction to the Port Authority. Similarly, the site was possibly subject to wind blown contamination from the activities of the port itself with constant loading and unloading of shipping. A concrete base was the only substrate upon which to place the equipment and this necessitated some modifications in the deployment of the device which involved setting the base of the support rod into a bucket of concrete. The whole assembly was then tied down to the fence posts surrounding the meteorological station.

4.3.8 Portishead -ST 476759 (Wessex Water)

The Portishead site (Fig. 4.9) was a marginal site for sampler deployment with an area of rough grassland beyond deep treatment tanks. An area of grassland was maintained for the sampling duration in an attempt to meet the site criteria. The site is quite narrow with a line of trees to one side and a high fence the other which may have disrupted the wind flow across the sampler thus sheltering the equipment and leading to overcatch. An alternative site was sought but not found. In the event sampling was discontinued in early 1990 owing to the need for a replacement device on Flat Holm as a result of gale damage. At the same time Wessex Water decided to discontinue the site and the presence of heavy dismantling equipment may have led to serious local contamination.

4.3.9 West Huntspill ST 301467 (Wessex Water)

An area of flat vegetated land (Fig. 4.10) at the West Huntspill sewage treatment works was made available at about 1 km from the shore line. There may have been some sheltering from nearby buildings directly to the north but none were within the specified 2.5h of the sampler. The site was manned during working hours and no access problems were incurred during the routine sampling period.

4.3.10 Lee Abbey SS 698493

This site was used in the previous 1982/3 SEJC survey and manned by South West Water. The Lee Abbey Christian Community Centre agreed to the installation of a sampler on their land (Fig.

4.11). The sampler was placed in a small area of land which was slightly sheltered. It was also close to their domestic waste incinerator (100m) which may have been a local source of contamination. These problems could, however, not be overcome and no alternative position was available which would not have disrupted access to agricultural traffic at the centre. An alternative position in more open land and further from the shore was proposed but the Centre preferred the position they had specified.

4.3.11 Flat Holm - ST 220650

The Flat Holm Project agreed to the installation of equipment on the island close to the permanent Warden's House for security (40m) but not so close as to be sheltered (Fig 4.12, 4.13). The warden agreed to service the sampler should bad weather prevent access to the site. Access was made available to the site by means of the MV Procyon owned by Welsh Water and also by The Flat Holm Project on their service vessel when MV Procyon was unavailable.

A summary of the orientation of the sampling equipment and distance to the shoreline is shown in Table 4.1

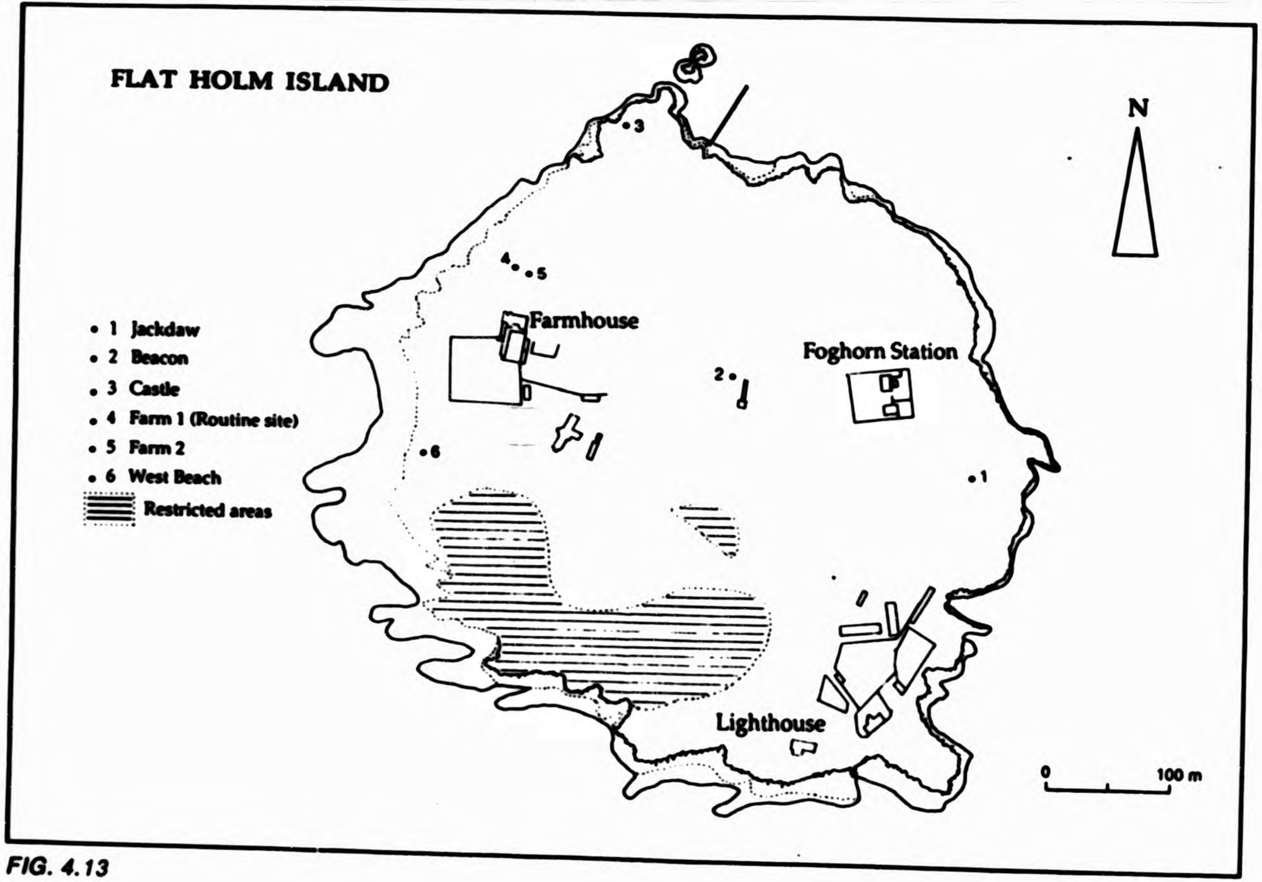

FLAT HOLM ISLAND
N
• 1 Jackdaw
• 2 Beacon
• 3 Castle
• 4 Farm 1 (Routine site)
• 5 Farm 2
• 6 West Beach
▤ Restricted areas
Farmhouse
Foghorn Station
Lighthouse
1
2
3
4
5
6
0
100 m

FIG. 4.13

Table 4.1 Summary of Site positions

SITE	Closest distance to shore km	Bearing of shore from site
MARLAS	3	230
ST MELLONS	3	146
MAGOR	0.75	152
LYDNEY	1	140
NORTHWICK	0.25	310
AVONMOUTH	2	308
P.O.B	0	220
PORTISHEAD	1.5	360
W. HUNTSPILL	0.5	300
LEE ABBEY	0.25	360
FLAT HOLM	0.1	316

4.4 Site comparability

An exposure index for each sampling site was derived using recordings of the angle of the horizon to the sampler along each of eight principal points of the compass (Harrison, 1988). The results of this exercise are summarised in Table 4.2.

The derived aspect gives the direction of greatest exposure experienced at each site and this is shown in degrees and the appropriate direction marked. The shelter index is given and compared with the Climatological Observers' Link (COL) scale of exposure for weather recording stations. The pattern is very much as expected from the site descriptions with the 'Very Exposed' sites being most representative of estuarine conditions. The Port of Bristol, Portishead and Lee Abbey sites give lower degrees of exposure and these are in line with observations made when the sites were selected. These less representative sites were chosen as a result of the time and security restraints operating at the time.

4.5 Sampling Interval and Duration

The large sampling area involved presented a logistical problem. Wind and weather fluctuations demand as short a sampling interval as possible owing to the rapid variations in both direction and meteorological variables. However, the distances and analytical time involved make very short intervals impractical. In previous studies the SEJC employed a sampling

Table 4.2 Site Exposure Characteristics.

SITE	Height m	Derived Aspect deg.	Shelter Index	COL Scale
MAR	20	312.4 NW	12.95	9 V. exposed
MEL	15	129.7 SE	11.92	9 V. exposed
MAG	6	33.96 NE	14.01	9 V. exposed
LYD	10	180.3 S	11.20	9 V. exposed
NOR	7	357.8 N	8.53	9 V. exposed
AVO	6	251.3 W	12.29	9 V. exposed
POB	5	24.21 NE	17.54	7 Mod exposed
POR	10	269.9 W	22.55	6 Sl. exposed
HUN	0	129.2 SE	13.90	9 V. exposed
LEE	120	335.0 NW	21.06	6 Sl. exposed
FLT	15	285.5 W	9.43	9 V. exposed

interval of one month to determine the atmospheric inputs to the estuary. Madsen (1982) evaluated daily, weekly and fortnightly sampling intervals for wet deposition and found that an interval of not greater than two weeks exerted no significant influence on determined precipitation composition.

On this basis, a two weekly sampling programme was instituted for the Severn estuary, to be maintained for a period of one to two years to ensure that as wide a range of weather conditions could be experienced. The routine sampling was maintained over a period of fifteen months from January 1989 to the end of March 1990.

4.6 Instrumentation

The sampling equipment (Fig. 4.2) previously employed by the SEJC consisted of a square scaffolding frame, on which a bottle and funnel was placed in order to trap the rainfall. This design had some drawbacks in that it did not appear to be deployed in a standard manner throughout the network. In some cases the funnel was suspended below the top of the scaffold frame which may have led to serious contamination problems, particularly with Zn. The samplers were often erected such that they were not at a uniform height above the ground and were at an angle to the ground. This would have led to either undercatch or overcatch according to prevailing wind conditions.

It was, therefore, decided to replace the equipment and install

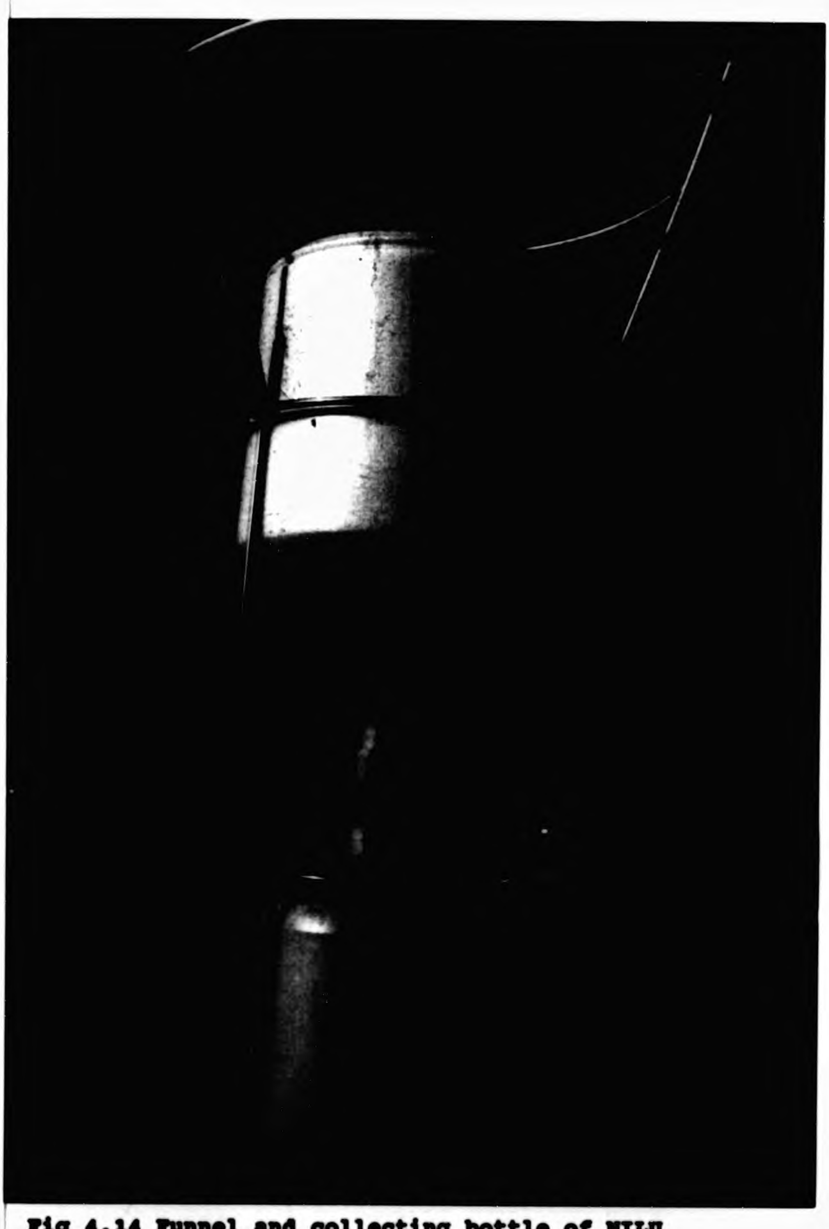
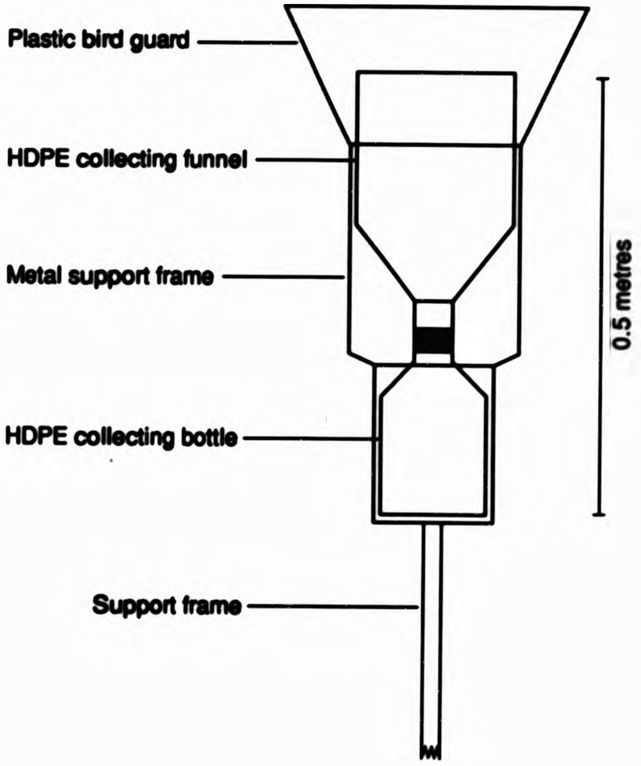


Fig 4.14 Funnel and collecting bottle of NILU precipitation collector.



NILU Precipitation Collector Type RS1

FIG. 4.15

a purpose-built apparatus at each site. The precipitation collector for use in the Secondary National Acid Deposition Network (Hall, 1986) was considered but rejected on the grounds that it was made up of largely metal parts that may have introduced contamination. It would also have been very expensive as each assembly was individually costly. The equipment finally chosen was a bulk sampling device designed and developed by the Norwegian Institute for Air Research (NILU), Type RS1 (Fig 4.14, 4.15).

The design of the NILU collector was based on an evaluation of similar equipment available in various countries and in addition to performance criteria , the transportability, materials of construction and ease of handling influenced the final shape and dimensions of the apparatus. The sampler consisted of a mounting stand which is adjustable in height into which a basket like frame inserts. This frame held a collecting bottle and funnel and supported a bird ring above the funnel. The entire stand slotted onto a ground spike which was, in effect, a short length of angle iron tapered at one end in order to ease insertion into the ground. The ground spike proved to be a weakness in the design as the forces exerted on the plug that connected the stand to the angle iron were strong enough to snap the sampler at ground level. Two modifications were made to the equipment for all sites. The stainless steel bird guard was cut off and replaced with a similar construction made of poly acetal rod. This was done in order to ensure that contamination from the equipment itself was minimised. A circle of 240 μm mesh was placed between the funnel and collecting bottle in order to minimise the ingress of insects, organic matter and other large particulates into the samples.

The design of the funnels with high sided walls minimises splash loss whilst collecting, and their construction from high density polyethylene reduces any risk of metal contamination. The design of the samplers and the height of the funnel at 1.75m above the ground may have led to some undercatch as a result of the sampler itself. This is due to the effects of the wind trajectory being deflected over the top of the funnel as a result of the obstruction. Losses of up to 30% of deposition have been recorded by Warren Spring laboratory, particularly of fine material which has very low settling velocities (Hall, 1990). Ideally samples should be collected at ground level in order to minimise this effect on the wind but deposition samples at ground level would be subject to very high levels of contamination by wind blown dust. The samplers remain open during the entire collecting interval and any dry deposition deposited on the funnel walls was washed down using a solution of nitric acid before sample collection.

In addition to the NILU sampler at each site a Met. Office MkII raingauge was used in order to test the collecting efficiency of the samplers.

4.7 Design and Calibration checks

4.7.1 Sampler Variation

An experiment to test the variability between sampling devices which was intended to give an indication of the reproducibility of results was set up in the grounds of WRc Medmenham. An array of nine samplers was set out in a grid of 3 by 3 devices. These were placed at approximately 5 m intervals in order to minimise disruption of the wind field around each sampler by the adjacent devices. A standard Met Office raingauge was also placed in the field close to the array. A very heavy downpour was experienced within one day of the array being deployed and the samples from each device were collected and stored in 500ml pre-cleaned low density polyethylene (LDPE) Nalgene bottles. The samples were preserved using ARISTAR nitric acid to a solution of 0.5% to meet the requirements of the WRc analysts. A second set of rainwater samples was collected after a two week interval (to coincide with the proposed two weekly routine interval) and treated as for the first set. Both sets of samples were analyzed using graphite furnace atomic absorption spectrophotometry (GFAAS) for Cd, Cu, Cr, Ni and Pb. Zinc was analyzed using flame AA. The results are shown in Tables 4.3.1 and 4.3.2

From this first experiment it can be seen that the variation between the samplers was considerable when collecting for metals at around 50% relative standard deviation although the volumes of rain water were quite similar. Sample handling and variation

variation in dry deposition may have contributed to the differences in concentrations for these determinands although this high level of variation is similar to earlier reports. For example, Neff (1987) found that the error on a single event ranged between 0 and 75% for volume collected. In the experiment at Medmenham the volumes in each sample were not measured but an estimate made. Visually, the sample bottles contained a very similar volume at approximately 250ml and the collecting error would have been very small for wet deposition. This collecting error may well increase under stronger wind conditions, as indicated by Mueller and Kidder (1972) who found by using drop sizes of 1-5 mm in diameter that raingauge collection efficiency varied between 103% of drops collected at a free stream velocity of 10 fts^{-1} to 11% at 50 fts^{-1}.

The second experiment (Table 4.3.2) showed that variation between samplers for Cd, Pb, and Ni was still quite high. The reasons for this variation are not clear but there may have been some contamination during sample handling or very high adsorption losses as the concentrations were lower than those found after a single event. The funnel walls were not washed down with acid before collection as would be the case for routine sampling. These tests show that the variation for collected precipitation was minimal whereas the variations for dry deposition, with local variations in particle size and the wind field were considerable over the small area and contributed significantly to the differences between samplers as well as being lost to adsorption.

Table 4.3.1 Variation of metals within the array of samplers placed in WRc grounds after a single downpour. (23.9.88)

Sample	Cd $\mu g l^{-1}$	Cu $\mu g l^{-1}$	Cr $\mu g l^{-1}$	Ni $\mu g l^{-1}$	Pb $\mu g l^{-1}$	Zn $\mu g l^{-1}$
Blank	0.01	0.16	0.37	<0.50	0.02	2.0
A	0.04	0.79	2.46	0.38	0.16	48
B	0.04	1.39	2.13	0.39	0.62	22
C	0.06	1.05	2.0	0.34	0.44	36
D	0.07	0.68	1.99	0.46	0.43	22
E	0.11	0.93	1.85	0.26	0.21	29
F	0.03	0.82	1.83	0.28	0.42	21
G	0.10	2.77	2.06	0.41	0.39	6
H	0.10	1.37	1.96	0.46	0.17	13
I	0.06	0.89	2.23	0.27	0.07	19
Mean	0.07	1.2	2.06	0.36	0.32	24
s.d	0.029	0.64	0.20	0.078	0.178	12.4
%RSD	43.5	53.5	9.7	21.6	55.6	51.7

Table 4.3.2 Variation of metals at WRc after a two week interval (23.9.88 -6.10.88)

Sample	Cd μgl^{-1}	Cu μgl^{-1}	Pb μgl^{-1}	Ni μgl^{-1}	Cr μgl^{-1}	Zn μgl^{-1}
L.O.D.	0.025	0.6	0.2	0.5	0.6	
Blank	0.00	0.08	0.01	<0.5	0.17	<1.0
A	0.01	0.33	0.08	0.25	20.4	5.06
B	0.00	0.40	0.13	0.56	1.93	4.02
C	0.01	0.37	0.05	0.33	1.63	6.86
D	0.00	0.43	0.05	0.16	1.65	3.89
E	0.01	0.53	0.31	0.75	3.19	5.43
F	0.00	0.25	0.07	0.20	1.59	3.89
G	0.00	0.51	0.07	0.35	1.47	3.82
H	0.03	0.53	0.20	0.58	3.38	6.35
I	0.01	0.57	0.06	0.08	1.86	4.12
Mean	0.01	0.44	0.11	0.36	20.8	9.8
s.d.	0.01	0.11	0.09	0.22	0.71	4.83
%RSD	100	25	82	61	34	1.16

This experiment was repeated at the end of the routine sampling period with a 3 by 3 array in the large field at Northwick landfill site (Fig 4.7). As for the earlier tests the samplers were placed at a distance of 5 m and left for a period of one day followed by a second period of two weeks. The results are shown in Tables 4.4.1 and 4.4.2

From Table. 4.4.1 it can be seen that the relative standard deviations for Cd, Cu, Pb and Zn are relatively low for a period of two weeks whilst those of Cr and Zn are considerably higher at around 80%. Table 4.4.2 shows a very different pattern after one day of deposition collection for the various metals. Cd has a very high value at 83% whilst the remaining determinands are low.

These figures are comparable to those obtained in the earlier experiments and indicate that the variation between samplers is quite high and in this case leaving the collectors out over two weeks gives a smaller variation for Cd, Cu, Pb and Zn whilst a smaller variation is seen for Ni and Cr over a period of one day. The high variations for Ni and Cr seen after the fortnight interval may well be as result of the concentrations measured which were either below the limit of detection or very small which will not give a totally accurate picture of the variation that exists.

Clearly at both the start and end of the routine sampling there was considerable variation according to the determinand being measured and the length of time the samples were collected over. The absolute concentrations also affect the picture seen of variation.

It is not certain whether the variations are genuine or a result of analytical error, variations in dry deposition or the introduction of some contamination to the samples. It is, however, apparent that the variations are not dissimilar to those previously recorded and these provide some measure of the confidence which can be placed on the final results for each metal determined.

Table. 4.4.1 Variation of metals placed at Northwick after two weeks (9.4.90 - 23.4.90)

Sample	Cd μgl^{-1}	Cu μgl^{-1}	Cr μgl^{-1}	Ni μgl^{-1}	Pb μgl^{-1}	Zn μgl^{-1}
A	0.45	3.0	0.7	0.8	27	70
B	0.29	1.8	0.2	0.25	19	53
C	0.52	3.5	0.2	0.25	44	68
D	0.54	2.6	0.1	0.25	18	85
E	0.32	2.2	0.2	0.25	20	52
F	0.34	2.2	0.1	0.25	20	49
G	0.41	2.4	0.1	0.25	21	68
H	0.58	2.7	0.8	1.2	21	126
I	0.32	2.1	0.4	1.1	18	54
Mean	0.418	2.5	0.31	0.51	23.11	69.44
S.D.	0.1086	0.517	0.266	0.405	8.82	24.18
%R.S.D	25.98	20.68	85.8	79.4	38.16	34.8

Table 4.4.2 Variation between samplers left for one day at Northwick (24.4.90)

Sample	Cd μgl^{-1}	Cu μgl^{-1}	Cr μgl^{-1}	Ni μgl^{-1}	Pb μgl^{-1}	Zn μgl^{-1}
A	0.25	7.9	1.0	1.0	25	65
B	0.16	4.4	0.5	0.8	18	37
C	0.27	4.4	0.5	1.1	32	40
D	0.42	8.2	0.6	1.4	25	95
E	0.21	9.6	1.8	1	24	55
F	0.14	2.7	1.0	0.6	20	41
G	0.19	2.8	0.5	0.6	20	39
H	0.98	9.7	0.6	0.8	25	127
I	0.17	3.0	0.4	0.25	19	34
Mean	0.31	5.856	0.76	0.89	23.11	59.2
S.D.	0.26	2.91	0.44	0.4	4.37	31.9
%R.S.D	83.8	49.6	57.8	44.9	18.9	53.8

4.7.2 Contamination from equipment

The release of contaminants from the samplers must be minimised to avoid the possible distortion of results. Two experiments were implemented on the black, pigmented connectors that hold together the bottle and funnel. These were carried out at the start of the routine sampling as well as the end in order to test for any deterioration in the equipment. Five separate connectors were precleaned and placed in precleaned PTFE cups (Nalgene LDPE bottles were employed at the end of routine sampling) and left overnight in a solution of nitric acid (1%) (5% at the end to meet requirements of Wessex Water analysts) in order to establish whether any metals were being leached out of the material. Two blanks containing only deionised water and the nitric acid were also prepared. The results are presented in Tables 4.5.1 and 4.5.2.

The results shown by Table 4.5.1 indicate that for the five connectors tested in this experiment there is unlikely to be a contamination problem from leaching as the majority of the concentrations are below the limit of detection. For Cd, Cu, Cr, Pb and Ni the concentrations in each are negligible when compared to the blanks. For Zn there are some higher values that may be a result of contamination whilst sample handling or a genuine release of metals from the plugs but this should not have been a problem in the field as they were not exposed to acid solutions for any prolonged time. The only exposure to acids occurred when the funnel assemblies were cleaned and

Table 4.5.1 Variation of metals leached from connectors (Before sampler collectors deployed in the field)

Sample	Cd $\mu g l^{-1}$	Cu $\mu g l^{-1}$	Pb $\mu g l^{-1}$	Ni $\mu g l^{-1}$	Cr $\mu g l^{-1}$	Zn $\mu g l^{-1}$
LOD	0.02	0.6	0.2	0.5	0.6	1.0
Blnk 1	0.01	<0.6	<0.2	<0.5	<0.6	<1.0
Blnk 2	0.01	<0.6	<0.2	<0.5	<0.6	<1.0
1	0.02	<0.6	<0.2	<0.5	<0.6	<1.0
2	0.01	<0.6	<0.2	<0.5	<0.6	<1.0
3	0.01	<0.6	<0.2	<0.5	<0.6	1.26
4	0.02	<0.6	<0.2	<0.5	<0.6	<1.0
5	0.02	<0.6	<0.2	<0.5	<0.6	<1.0

Table 4.5.2 Variation of metals leached from connectors (After routine sampling completed)

Sample	Cd $\mu g l^{-1}$	Cu $\mu g l^{-1}$	Pb $\mu g l^{-1}$	Ni $\mu g l^{-1}$	Cr $\mu g l^{-1}$	Zn $\mu g l^{-1}$
LOD	0.02	0.2	0.2	0.5	0.1	1
Blnk 1	0.03	<0.2	<0.2	<0.5	0.4	<1
Blnk 2	0.04	<0.2	<0.2	<0.5	0.1	<1
1	0.32	0.2	<0.2	<0.5	<0.1	11
2	0.07	0.5	0.7	<0.5	0.3	195
3	0.04	0.5	0.4	<0.5	0.2	116
4	0.05	0.6	0.8	<0.5	0.1	111
5	<0.02	1.8	1.3	<0.5	0.4	75

during sample collection. After soaking in acid for cleaning the funnel assemblies were thoroughly rinsed with deionised water such that they were free of contaminants.

Table 4.5.2 indicates that there is no problem from the connectors for all the metals except Zn which exhibited very high readings. It is not apparent whether these readings are genuinely as a result of metal release from the plugs or whether there was serious sample contamination during handling, which is the more likely explanation. There is a possibility that the powder on the surgical gloves may have been introduced into the acid solutions.

4.8 Network Operation

4.8.1 Routine Operation

Rain water samples were collected on a fortnightly basis, wherever possible, and taken to Wessex Water's Saltford Laboratory for analysis. The samples were collected following the same procedure which involved, first, washing down the funnel walls with a known quantity of 1% HNO_3 solution to remove any dry deposition into the sample. The bottle was then replaced with a pre-cleaned (in 5% HNO_3 solution) and left for a further two weeks. The funnels and gauzes were only replaced if they had been fouled by bird droppings, which occurred twice on Flat Holm and once at Northwick landfill site, or were blocked by insects or other particulate waste. A rainfall recording was also taken.

All sample preparation was carried out in two laboratories and will be discussed in chapter 5.

4.8.2 Disruption to routine sampling

Every attempt was made to collect samples on a two weekly basis but there were some occasions when this was disrupted owing to bad weather (especially on Flat Holm), access problems, destruction by grazing animals and once by vandalism. During the winter of 1988/1989 there were problems reaching Flat Holm as well as sheep damage to the equipment at Marlas and Magor. The latter led to the loss of a month's data for both sites and the samplers were reinstated in their original positions with additional sheep fencing to prevent further damage. When Flat Holm was inaccessible the warden on the island collected the sample which was removed from the island at the next opportunity.

Access problems were encountered at Magor and Lydney on two separate occasions. This resulted in the samples being left for a four week interval at Lydney between 9.8.89 and 23.8.89 and at Magor between 3.10.89 and 31.10 89.

Over the Christmas period of 1989/90 a three week interval elapsed between collections owing to the holiday period and logistical problems.

As a result of vandalism a sample was not collected at Marlas on

16.1.90 which necessitated the replacement of sample bottles in both the raingauge and the sampler. The remaining problems arose as a direct result of the violent gales experienced across the South-West during January and February 1990. The equipment on Flat Holm was demolished and that at the Port of Bristol blown over. Since no spare equipment was available, a decision was taken to replace that on Flat Holm with the deposition sampler from Portishead which was the most marginal of sites. Owing to continued foul weather, access to Flat Holm was not possible until the 16th February. Having replaced the equipment on Flat Holm access was further denied as a result of more gales and the warden was unable to collect the samples as he was stranded on the mainland.

The network was dismantled at the end of March 1990 and the equipment then used for further experimentation at Northwick and on Flat Holm.

4.8.3 Northwick Landfill Site - Experimentation

Two separate experiments were carried out at Northwick Landfill site. The first , already described in section 4.7.1, was to examine the variation existing between sampling equipment and position at the site and the second was to identify the influence of the maritime effect. It was intended to see if any significant decreases in Na deposition with distance inland in association with other metals. Samplers were placed at distances of 100, 200, 250, 255, 300, and 350 metres inland and aerial deposition collected after a period of two weeks and also one day. Samples were collected at these intervals to coincide with the routine sampling interval and also to see if any daily differences were definable. Ideally, the distance inland should have been much greater (a distance of several kilometres) but time constraints and the availability of land for setting up the samples was limited.

4.8.4 Flat Holm - Experimentation

An array of six samplers was placed on Flat Holm island such that they covered as much of the island as possible. This sampling exercise was carried out in order to examine spatial differences on the island in deposition and also to see if any variation existed between the routine site and the one very close by; that is between sites 4 and 5, Farm 1 and Farm 2 (Fig 4.13). It was also hoped to see if emission source areas could be identified from the deposition patterns obtained and also to examine daily sampling variations. Samples were collected over a period of four days on a daily basis.

5 LABORATORY METHODS

5.1 Introduction

Two laboratories were used for analysis of the field samples. All sample preparation was carried out at Welsh Water plc's laboratory at Tremains House, Bridgend and all chemical analysis at Wessex Water plc's regional laboratory at Saltford, Avon. Instrumental analysis was performed by the Wessex Water staff at Saltford.

5.2 Sample Preparation

Metals are generally present at very low concentrations in the precipitation samples and are therefore highly susceptible to contamination, particularly during sample collection and storage. In a study of trace metals in precipitation Ross (1986) found that acid washing collectors reduced sample contamination with Cu concentrations being a factor of fifty times larger in samples collected and stored in unwashed bottles. Before deployment in the field collection bottles were, accordingly, cleaned by soaking in 5% HNO_3 solution, on the advice of analysts at the Water Research centre (WRc), for a minimum period of 24 hours. The average time that bottles were soaked was normally one week, the interval between visits to the laboratory. Laxen and Harrison (1986) recommended soaking glassware and collection bottles in 10% HNO_3 solution for a minimum period of 24 hours followed by rinsing in clean, deionised water and then draining the bottles dry. WRc analysts suggested that 5% HNO_3 solution was an adequate strength and is the concentration used routinely for trace metal analysis in their laboratories. Having been soaked the bottles were thoroughly rinsed, three times, in deionised water to remove any trace of the acid or metals from the surfaces of the bottles. Sample storage bottles were treated in the same manner to prevent contamination during storage. The collection bottles were assigned to specific sample sites and used only at those sites in order to prevent any cross contamination. All bottle handling was carried out wearing surgical gloves, to prevent both acid damage and to minimise contamination problems.

The sample collection bottles supplied by NILU were constructed of high density polyethylene (HDPE) and the sample storage bottles, obtained from NALGENE, were made of low density polyethylene (LDPE). In a literature review (Batley and Gardner, 1977) reported by Laxen and Harrison (1981) it was concluded that polythene and Teflon containers were suitable for sample collection and storage with polythene being acceptable for routine sampling. Haraldssen and Magnusson (1983) collected total deposition samples from a roof in HDPE bottles using funnels of both HDPE and LDPE. They found that no significant differences existed between the two types of funnel.

After collection, samples were preserved by addition of ARISTAR nitric acid to a final concentration of 1% to prevent adsorption losses of metals during storage. Two laboratory blanks, consisting only of a 1% nitric acid solution made up in deionised water and two analytical quality control samples containing metals at various concentrations were also prepared. The analytical quality control samples consisted of one sample containing high concentrations and one of low concentrations and the absolute concentrations were varied with each set of samples. The samples from each of the eleven sites, two blanks and two AQC samples were then delivered to Wessex Water plc's laboratory for analysis.

5.3 Sample Analysis

Samples were stored at the Saltford laboratories and then analysed in batches of three sample sets for reasons of economy and time management. All samples were analysed for the following determinands; Cd, Cu, Cr, Ni, Pb, Zn, Al, Na and Chloride. The metals Cd to Al were analysed on account of their toxicity to marine organisms. They were also analysed in order to provide data for atmospheric inputs to tie in with the overall inputs budget of metals to the Severn Estuary which was to be carried out by sponsoring bodies. Na and Cl^{-1} were analysed for evidence of the maritime effect and the inclusion of recycled metals in the samples. Several analytical methods were used on the samples depending on the determinand in question and total concentrations in the samples were determined. The methods were as follows:

1) Inductively coupled plasma mass spectrometry (ICP/MS)

was used to determine Pb, Al and Zn concentrations (where Zn concentrations were suitably low).

2) Graphite Furnace atomic absorption spectrophotometry (GFAAS or Graphite thermal atomisation, GTA) was used for the analysis of Cd, Cu, Cr, and Ni.

3) Flame AAS was used for the analysis of Na and Zn in those samples where the concentration of Zn was sufficiently high. ICP/MS could only be used for these samples after very high dilution.

4) Chloride determination was carried out by discrete colorimetric analysis.

The procedure followed for each sample for each determinand was as follows;

1) All samples were digested to dissolve the particulate fraction. This ensured that the particulate fraction as well as the dissolved fraction were determined in order to obtain the total concentration. The sample bottles were left, unopened, in an oven at 80°C for a period of sixteen hours.

2) Pb, Al and Zn were analysed by ICP/MS. This method relies on total destruction and ionisation of molecular species in a high temperature inductively coupled plasma, and injection of the ionised sample into a quadropole mass spectrometer. The ionic

species are detected and counted by a multi channel analyser and concentrations derived by comparison with standard solutions of the same ions. Matrix (interference) effects were minimal in these samples, but were compensated for by the addition of an internal standard to all samples and calibration solutions. (Poole, 1991).

Metal concentrations were determined against a single point standard with the details shown in Table 5.1. Internal quality control checks were included at values exactly half those shown in Table 5.1 and a zero level baseline check was also employed.

3) Cd, Cu, Cr and Ni were analysed by GFAAS. Samples were injected into a graphite furnace tube with a matrix modifier if necessary and heated according to a repeatable timed temperature. The ash was then rapidly ignited in an argon gas stream to produce a transient absorption signal which was recorder by the spectrophotometer. Two standards were used for calibration and internal AQC check solutions were used at exactly half the calibration range. The calibration details are shown in Table 5.2

4) Na and Zn were analysed by flame AAS. Samples were aspirated directly or after dilution in 1% nitric acid into an air-acetylene flame and the elemental absorbances were measured by a VARIAN AA975 spectrophotometer. Background correction was used for Zn determination. The spectrophotometer was calibrated using three standards with the range used being dependant on the

Table 5.1 Calibration details for ICP/MS

Element	Isotope used amu	Standard Conc. μgl^{-1}
Pb	208	20.0
Al	27	100.0
Zn	66	100.0

Table 5.2 Calibration details for GFAAS

	Wavel. nm	Stand. μgl^{-1}		Modifier	Drying		Ashing		Firing	
					s	°C	s	°C	s	°C
Cd	228.8	1	2	Am. Ox.	35	100	20	300	2	2000
Cu	324.7	10	20	---	35	100	15	800	2	2100
Cr	357.9	10	20	---	35	100	15	1000	2.5	2400
Ni	232.0	10	20	---	35	100	25	800	2	2400

Am. Ox. - Ammonium Oxalate

Table 5.3 Calibration details for Flame AAS.

Elem.	Wavel.	Normal Standards mgl^{-1}			High range Standards mgl^{-1}		
Na	589.0	2.5	5.0	10	25	50	100
Zn	213.9	0.2	0.5	1	5	10	20

actual concentrations found in the samples. For each element two alternative ranges were used as shown in Table 5.3. AQC checks were also run at a value equal to the middle of the three standards.

5) Chloride determination was carried out by discrete colorimetric analysis which involved dispensing samples into reaction tubes and adding accurate additions of a composite reagent. The method relies on the reaction of chloride ions with mercuric thiocyanate. Thiocyanate ions are released to form a reddish brown ferric thiocyanate complex, the optical density of which is measured by a spectrophotometer. This method is a standard method and is documented by HMSO (1981). Calibration was set using three standards at 10, 50 and 100 mgl^{-1} and quality control checks were run at 20 and 80 mgl^{-1}.

5.4 Data Quality Control

All samples were accompanied by analytical quality control (AQC) samples when analyzed by Wessex Water and these proved to be satisfactory for the majority of results received. In the absence of replicate data for each sample it was not possible to produce an estimate of laboratory precision but the AQC results were used to gain a measure of accuracy and calibration error. A paired 't' test to determine the accuracy for each metal, over the whole sampling period was carried out. This test compares the difference between the spiked value and the recovered value over the sampling period and tests if the resulting values are significantly different from zero. The results are shown in Table 5.4.

The results show that the t value for all metals except Zn was not significant at the 99% probability value. Zn, however was significant and it must be inferred that there was some analytical error or that there were errors involved in making up the AQC samples.

The zinc data were then examined in more detail. The nominal values were plotted against the recovered values and a linear regression calculation performed on the data set. The resulting plot and regression equation are presented in figure 5.1. The correlation coefficient for the zinc results was statistically significant with 48 degrees of freedom at the 99.9% probability level but the paired 't' test showed that the differences were also significantly different from zero. The linear regression calculation indicated that there were some high residual values, but removing these did not improve the results for the paired 't' test. The recovered values that were significantly different to the nominal values were largely obtained with the high value AQC samples and generally produced overestimates of the zinc concentrations. As a result of the statistical analysis being carried out after the routine sampling was completed it was not possible to re-assess the Zn analyses so the resulting data were left as they were received from Wessex Water. On the basis of the regression equation shown

Table 5.4 Results of paired 't' test for metal analytical quality control data (Test Mu=0.0 vs Mu≠0.0)

	N	Mean	S.D.	SE mean	t	P value
Cd	50	-0.083	0.832	0.118	-0.71	0.48
Cu	50	-0.225	1.072	0.152	-1.49	0.14
Cr	50	-0.272	1.059	0.150	-1.82	0.075
Ni	50	-0.154	0.532	0.075	-2.04	0.047
Pb	50	-0.186	1.340	0.192	-0.98	0.33
Zn	50	-1.406	2.721	0.385	-3.65	0.0006

in Fig. 5.1 it is possible that the zinc values are overestimated by 8%.

The data from the individual sampling sites was then checked statistically for anomalous values and then used to convert the deposition values for the sites into an overall loading for Severn estuary results. These statistical checks will be described in detail in the following section on the results.

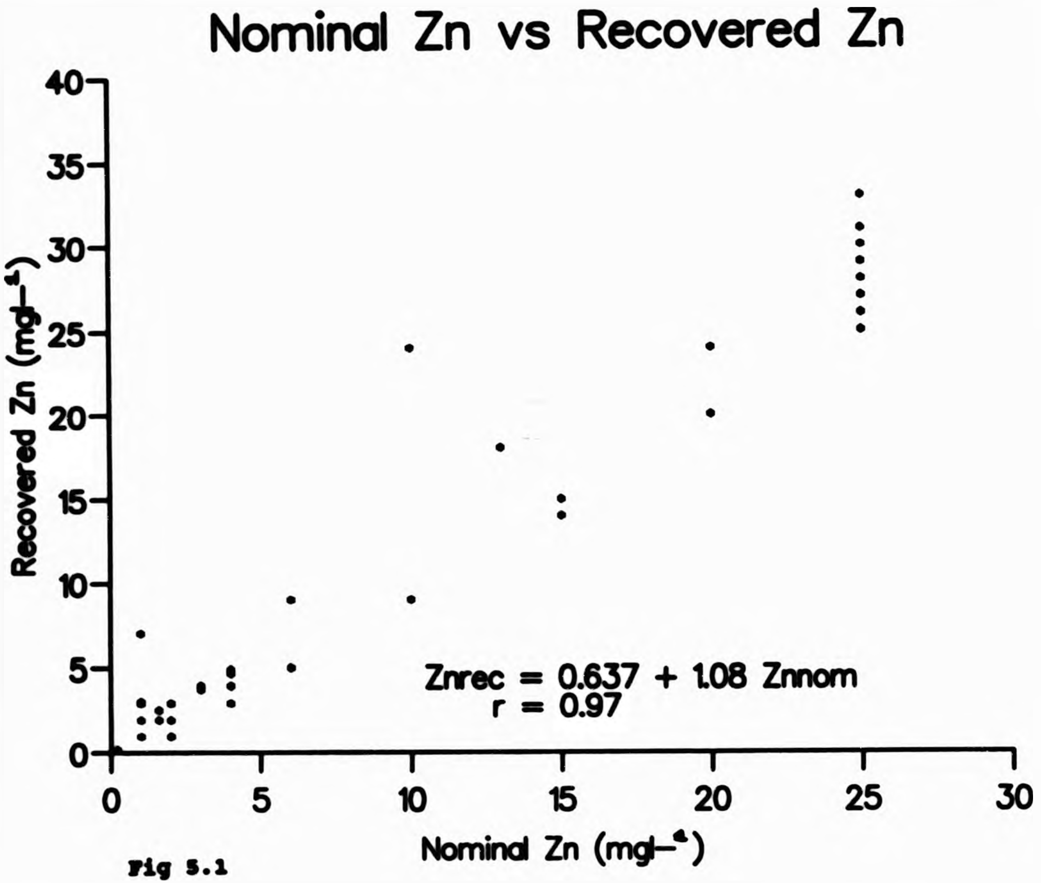

Nominal Zn vs Recovered Zn
Recovered Zn (mgl^{-1})
Nominal Zn (mgl^{-1})
0
5
10
15
20
25
30
35
40
Znrec = 0.637 + 1.08 Znnom
r = 0.97

Fig 5.1

6 RESULTS

6.1 Data Quality

Before proceeding with analysis and interpretation of the data set received from Wessex Water Plc, a checking procedure was carried out to identify any anomalous values. Before checking the data were corrected to allow for the dilution that had occurred. The data were arranged in two ways such that the results for each metal were shown by sampling site for each sampling interval and that the data for each site showed the results for each metal for each interval. The data were then checked by means of linear regression; fitting a straight line to pairs of data by means of the least squares method (Ryan et.al., 1985) using the MINITAB statistical package. MINITAB highlights any unusually high residual (i.e. the difference between observed values and those predicted by the regression equation) values which can then be checked.

The data for individual metals were then subjected to this regression technique by regressing the values at a particular site against the values at four other close sites. For example, Cd results at Magor were regressed against the values observed for Avon sewage treatment works, Northwick landfill site, St Mellons and Marlas. This procedure was carried out for each individual metal at each site and any outlying values noted. The data for each site were then examined to compare the metals at the sites by comparing one element against two others. For example, at Marlas the data for Cd were regressed against the data for Pb and Zn as were Cu, Cr, Ni and Al. The outliers from both these exercises, for each metal, compared and any values that were consistently high were checked and changed to the value predicted by the regression equation or if values were missing they were interpolated from the data set.

Results that were below the limit of detection (LOD) were taken to be half the LOD which may lead to some errors in the final estimations of total deposition but is a reasonable approach to adopt as an arbitrary value. An alternative approach for estimating the mean of a data set with non-detectable values is to use log-probit analysis (Travis et.al., 1990). From probit analysis the mean value of non-detectable values can then be estimated. In this study the proportion of missing values was low for all the determinands except Ni (40%) and it is thought that the mean would not be significantly improved by using this method.

Rainfall data were derived from the measured volumes in the sample collectors and checked in the same manner and corrected. Missing data were obtained from the nearest local raingauge which were supplied by the National Rivers Authority (NRA) region. The data for chloride and sodium and were not corrected as they were not required for the purposes of calculating the metal loadings to the estuary or as in the case of chloride the majority of the data was below the limit of detection.

The resulting data are presented in their corrected form for the metals and their raw state for the remaining determinands in appendix I. (Table I.1- I.9).

Before interpretation the concentration data for each metal and site had to be converted to a loading per unit area. This was achieved by multiplying the concentration by the rainfall amount in mm to give μgm^{2} or $kgkm^{2}$. The results are shown in appendix I, Tables II.1 - II.7. The rainfall values are shown in appendix I, Table II.8.

6.2 Data interpretation

The method used by AERE Harwell to estimate aerial deposition converted the land based concentrations to a loading of μgm^{2} and lumped these together for adjacent areas of the estuary (Fig 4.1). An average value for each-sub area was calculated and this was multiplied by that area. The sub-area totals were then added together for the whole sampling period and a daily input in kilogrammes was derived for each metal. This method did not incorporate any consideration of wind direction and therefore pollution trajectory and it made an assumption that deposition across large areas of the estuary were constant and could be represented by a small number of land based sites with data collected on a monthly basis. It was, therefore, necessary to reappraise the method of extrapolating the land based data to an estimation of deposition over the water surface. There are alternative modelling approaches, as discussed in section 2.4.2, but most require specific knowledge of point sources of contaminants as well as the emission speeds and heights together with source strengths. It would also have been impractical in view of the number and complexity of aerial inputs to the Severn area at both regional and local scales.

Another approach could have been to make use of Thiessen Polygons, a method employed by hydrologists to determine average rainfall to an area which allows for the uneven distribution of rain gauges (Shaw, 1983). It also enables data from adjacent areas to be incorporated in the mean which would have been appropriate for this project as the majority of sampling stations are outside the area under consideration. The method involves the initial weighting of rainfall/deposition data at individual gauges according to the area of the total that they represent followed by a summation of the total areal input. A major limitation of this method is that it fails to take account of wind direction and would also assume constant rates of deposition across large areas which would not be representative of deposition behaviour with increasing distance from emission sources.

An alternative method was suggested by Harrison et.al. (1985). They suggested that a series of reference points be taken along the central axis of the estuary at where estimates of deposition would be made. The airflow at each point would be categorised into directional sectors and the monitoring sites in each sector multiplied by the relative frequency of winds from each sector and an estimate for monthly total deposition in at each representative point made and summed for the entire region. This method assumed that there was a uniform rate of deposition through time and that there was no change in deposition loading between the sampling sites and the reference points along the centre of the channel which, again, would be unrepresentative of plume behaviour.

The final method chosen was an interpolation and mapping approach which would have an inherent wind direction implied within it and would take account, to a certain extent of the behaviour of deposition away from source (i.e. the distance decay), whilst being relatively simple to perform.

6.3 Isopleth Map Technique

The isoplething map technique finally chosen involved interpolating the point data collected at the land-based and island sites to generate a deposition surface across the estuarine areas. Isoplething clearly shows the distribution of metal deposition over the estuary. The study area was defined and then digitised using AUTOCAD and the estuarine outline output as a series of x-y coordinates (programme by Hallet (1990)) and then used within the UNIRAS, UNIMAP 2000, version 6 programme to automatically produce plots for each sampling interval for each metal. The area defined was smaller (2250km^2) than that used in the SEJC surveys (3140km^2) owing to the reduced number of sampling sites and their reduced extension out into the Bristol Channel. The area between isopleth lines on the plots was obtained by digitising, again using AUTOCAD, and each area multiplied by the average deposition for the section of the estuary. These loadings were totalled for each interval and an input budget for the entire sampling period obtained. From this estimates for annual and daily deposition budgets were obtained for each metal.

The method of plotting used by UNIMAP is to interpolate the irregularly spaced data points into a regularly spaced grid (ISG, 1990a). An isopleth map for a continuous surface is generated from these interpolated data values. The interpolation method used to produce plots of metal distribution over the Severn estuary was a 'distance weighted' technique. This technique estimates the values at a series of regularly spaced, arbitrary points from the values at known points. The basis of the interpolation is as follows;

> The value Z_0 is calculated at the point X_0,Y_0 by examining the known values at the four closest points a_i,b_i where $i=1,2,3,4$ in the data set. The distance between a_i,b_i and X_0,Y_0 is calculated and squared to give d_i. The distance weighting w is then calculated such that
>
> $$w = (1/d1) + (1/d2) + (1/d3) + (1/d4) \qquad (6.1)$$
>
> The value at a_i,b_i is then denoted by c_i and used to estimate the value Z_0 at X_0,Y_0 by

$$Z_0 = [(c1/d1) + (c2/d2) + (c3/d3) + (c4/d4) / w] \quad (6.2)$$

(ISG, 1990b)

This method results in regular grid nodes which follow the irregular data points closely and is particularly effective with a small number of data points as is the case in this study.

Preliminary isoplething work on the data by manual plotting using a subjective, linear interpolation method was carried out (Vale et.al. Jan 1990, Jul 1990). The use of natural logarithms and logarithms to the base 10 were also employed to simulate the distance decay curves typical of pollution deposition around a source. It was on this basis that the computerised plotting method was used and plots using linear interpolation and interpolation of $\log_{10}$, $\log_e$ and square root transformed data were also obtained. Plots demonstrating the effectiveness of the linear and different transformation techniques used are shown in Figs. 6.1 - 6.4. These show the values for Cd, over the whole sampling period, obtained by interpolation along the central axis of the Severn estuary with increasing distance from Avonmouth, the principal source area for emissions.

Figure 6.1 shows the linear interpolation relationship between Cd and distance which produces a distinctly curved plot with an r value for correlation of -0.796. This indicates that this method is unlikely to give an accurate estimation of the deposition to the estuary. Figures 6.2 and 6.3 showing the $\log_{10}$

Linear Cd distribution with distance from Avon

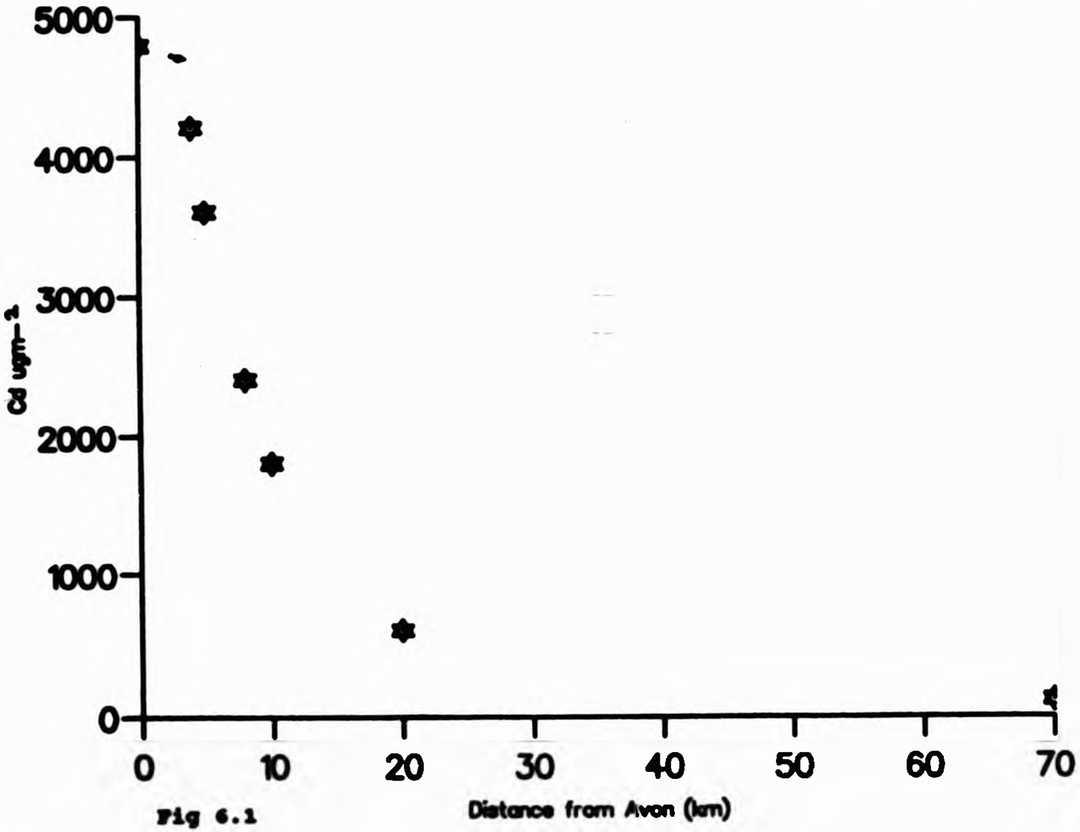
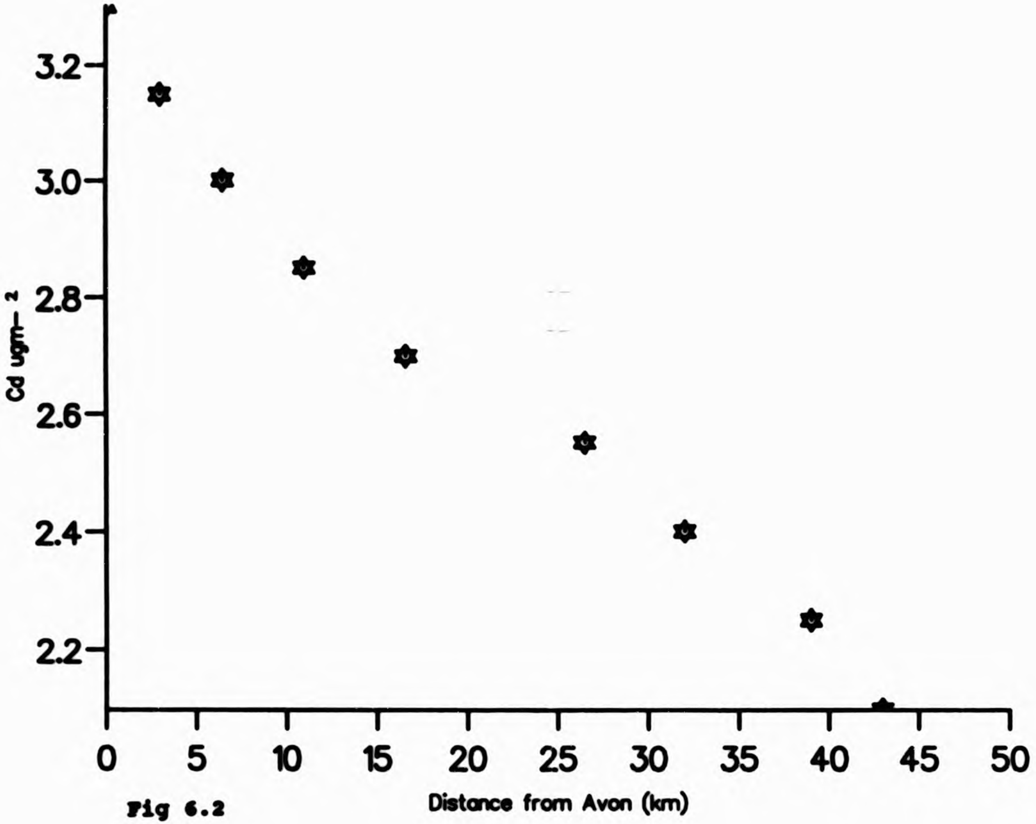


Fig 6.1



Logten Cd distribution with distance from Avon

Fig 6.2

Ln Cd distribution with distance from Avon

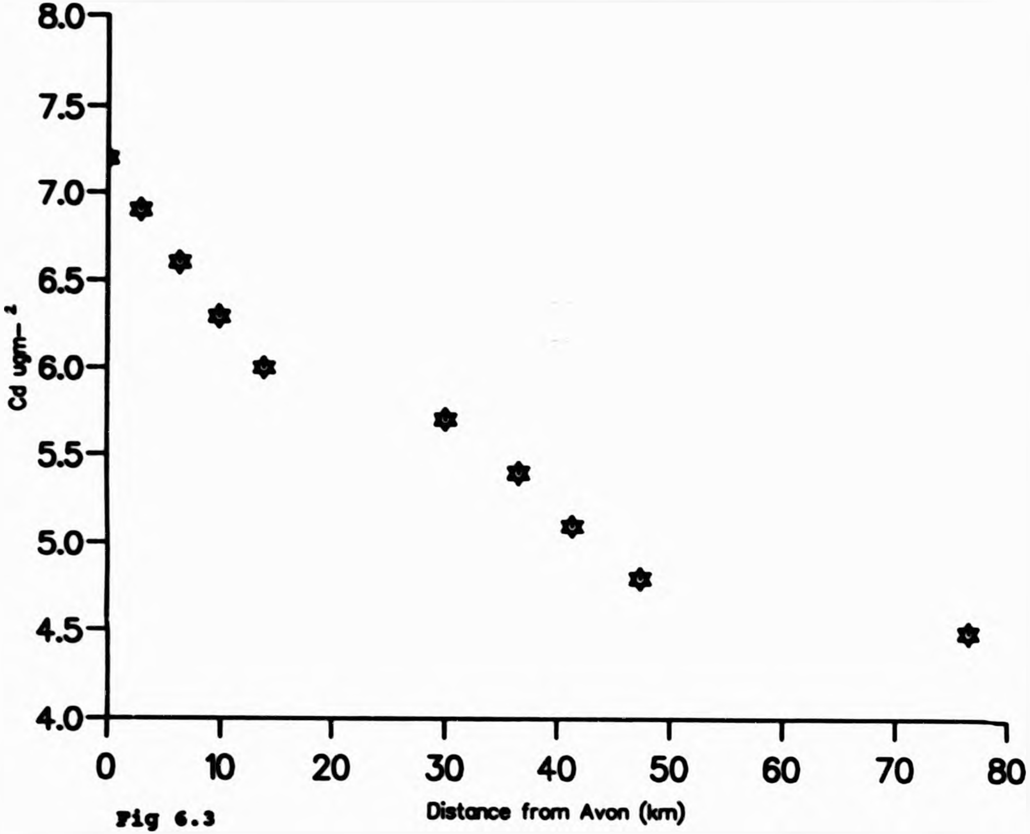


Fig 6.3

Square root Cd distribution with distance from Avon

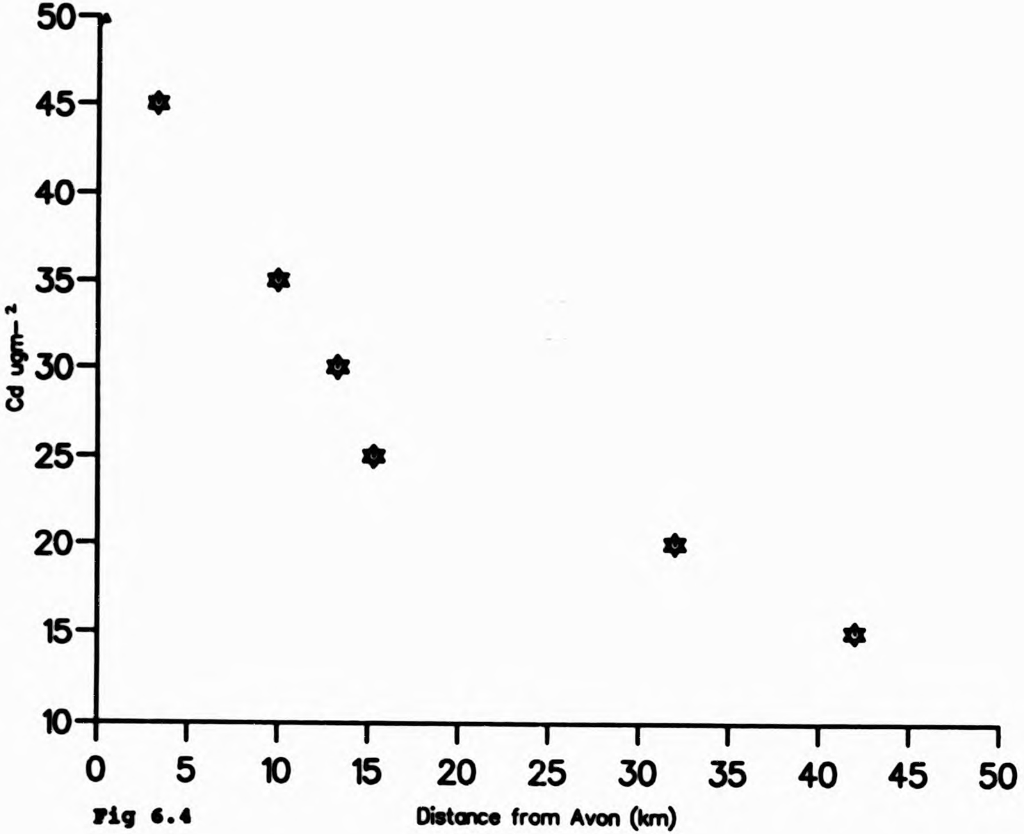
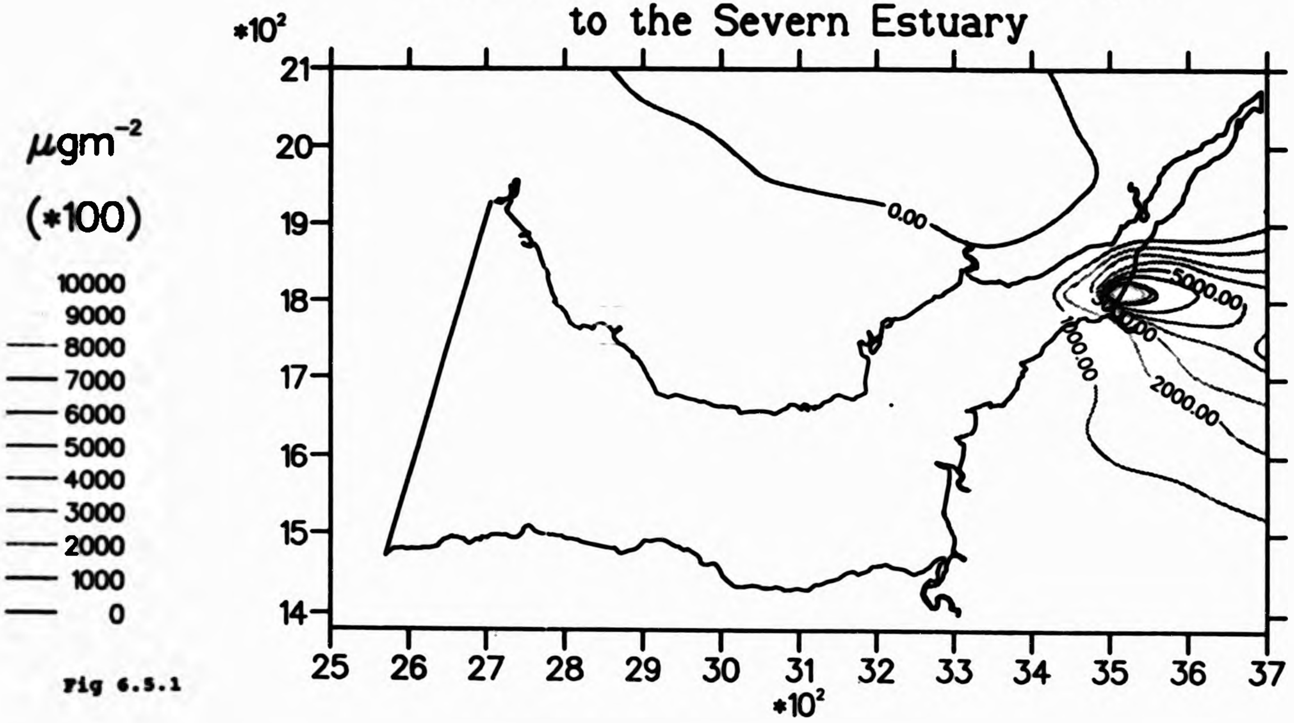


Fig 6.4

and $\log_e$ transformed data with distance give relatively straight line relationships indicating a much better fit for the deposition relationship with distance. The r values are -0.991 and -0.955 respectively which are clearly more acceptable than the linear interpolation method. Fig 6.4 showing the square root relationship with an r value of -0.933 again approximates a straight line but does not give such good correlation as Figs 6.2 and 6.3 but is an improvement on using untransformed data. The improved linear relationships between the transformed data and distance lead to greater confidence in the isoplething method of interpolation which is based on an assumption of uniform rate of change between data points. It is probable that the results from the $\log_{10}$ transformed data will give the most reliable estimates of deposition to the estuary for Cd. On the basis of these relationships all the metals were treated in the same manner and plotted out over the estuarine area.

6.4 Metal distributions across the Severn Estuary

Initially the raw data for Cd, Cu, Ni, Pb and Zn were plotted out on a sample interval basis and the areas between isopleths calculated for each plot and the total inputs for the entire sampling period obtained by adding the individual totals. The plots for the total Cd, Cu, Ni, Pb, Zn and Al deposition for each of the methods are shown in Figs. 6.5.1 - 6.8.7. The multiplication factors that appear on the plots were carried out in order to make sense of the isopleth values as the decimal values were truncated on the original copies of the isopleth



Linear distribution of aerial Cd input to the Severn Estuary

Fig 6.5.1

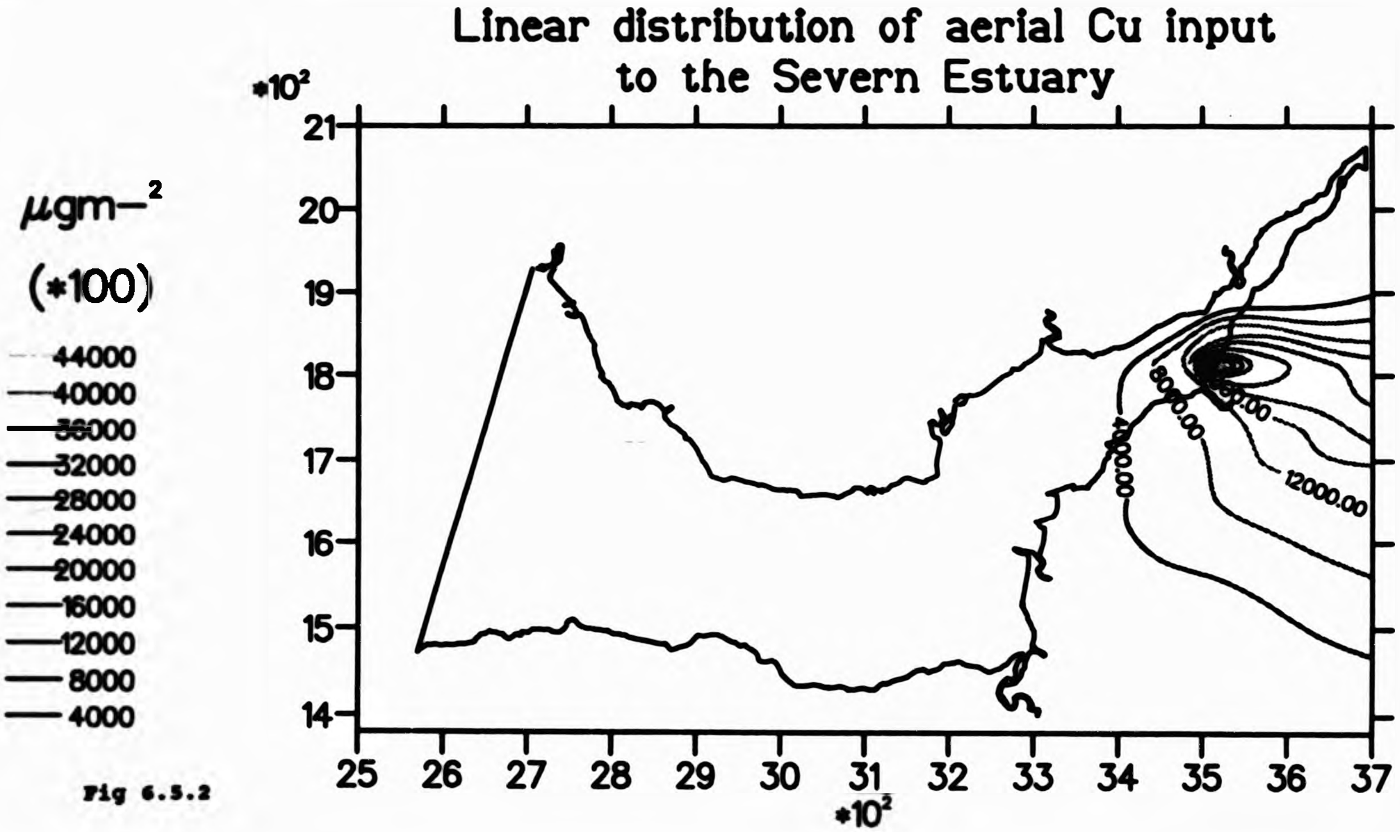

Linear distribution of aerial Cu input
to the Severn Estuary
µgm⁻²
(*100)
44000
40000
36000
32000
28000
24000
20000
16000
12000
8000
4000
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
4000.00
8000.00
12000.00

Fig 6.5.2

Linear distribution of aerial Cr input to the Severn Estuary

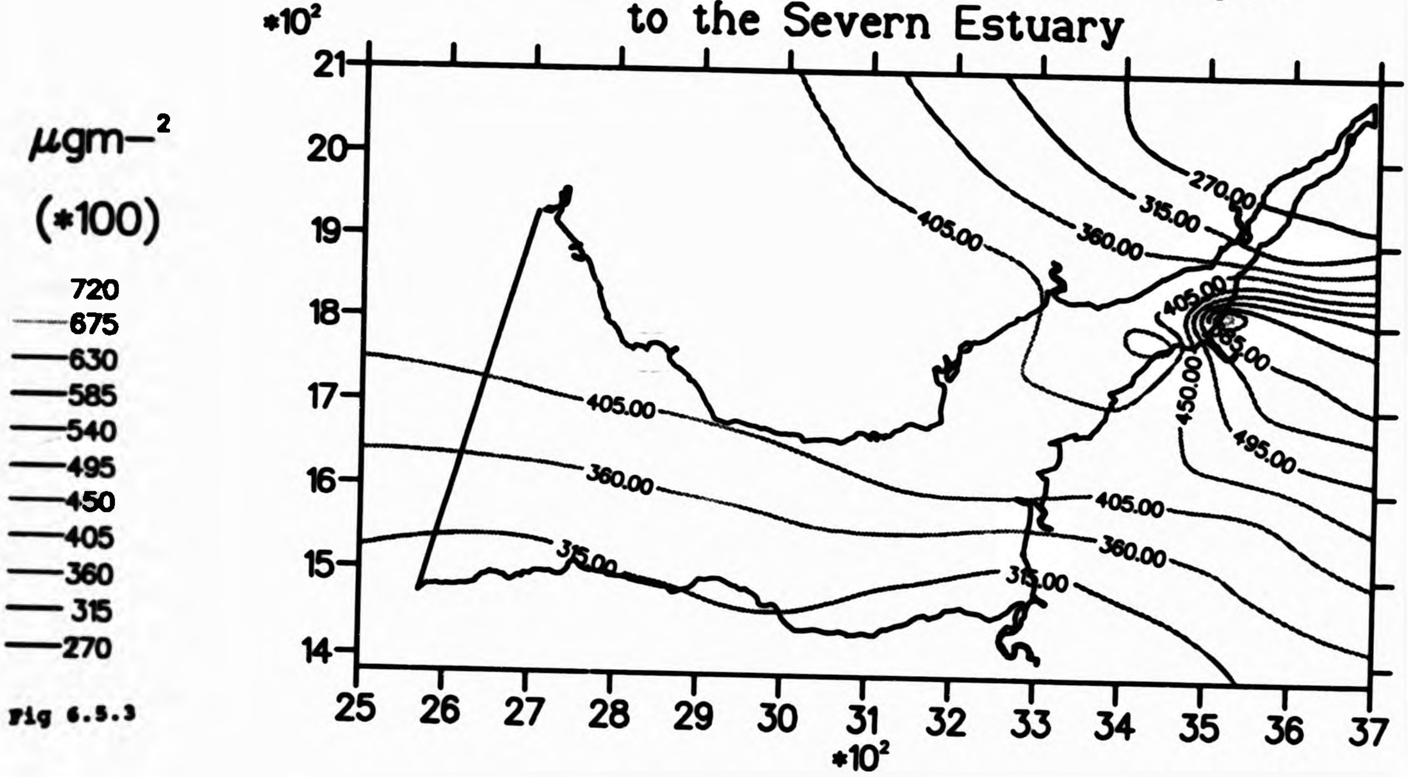


Fig 6.5.3

Linear distribution of aerial Ni input to the Severn Estuary

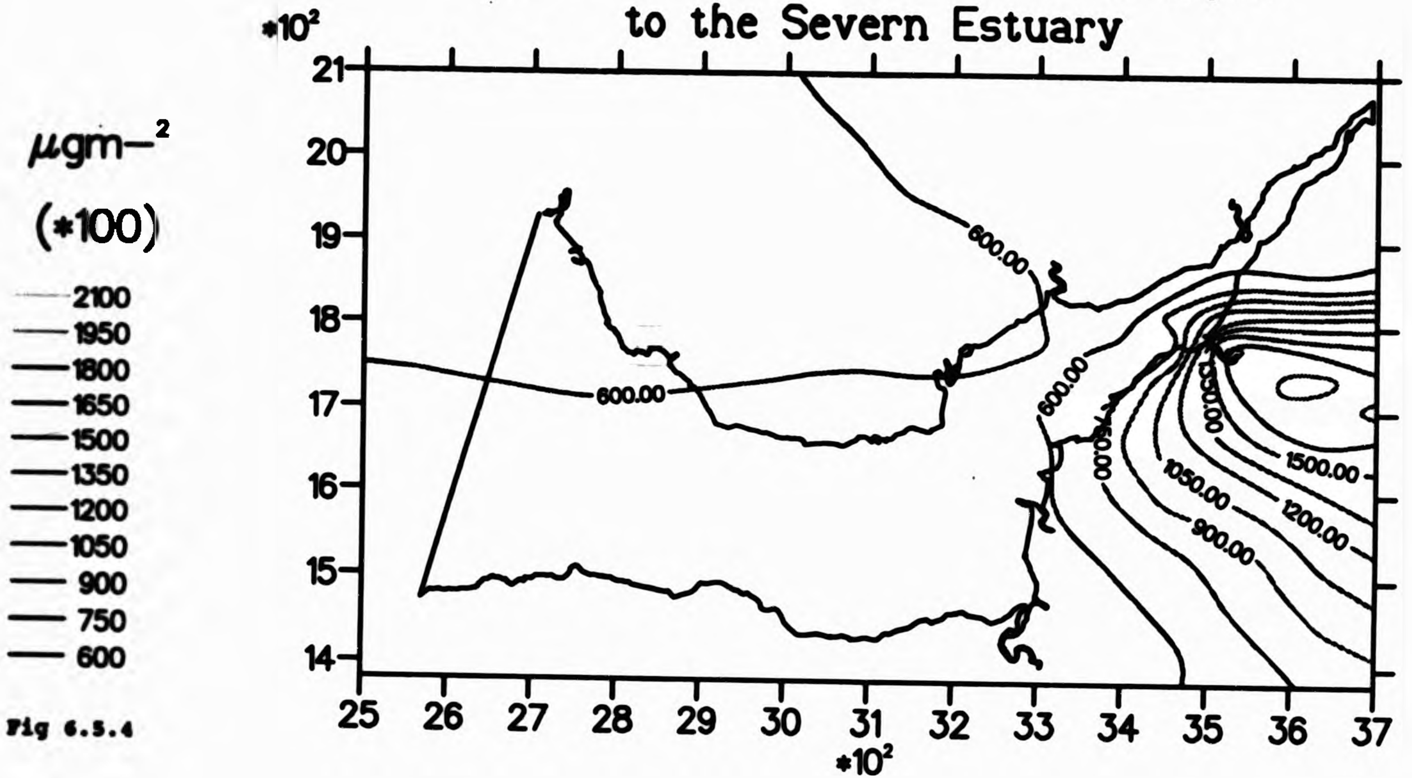


Fig 6.5.4

Linear distribution of aerial Pb input to the Severn Estuary

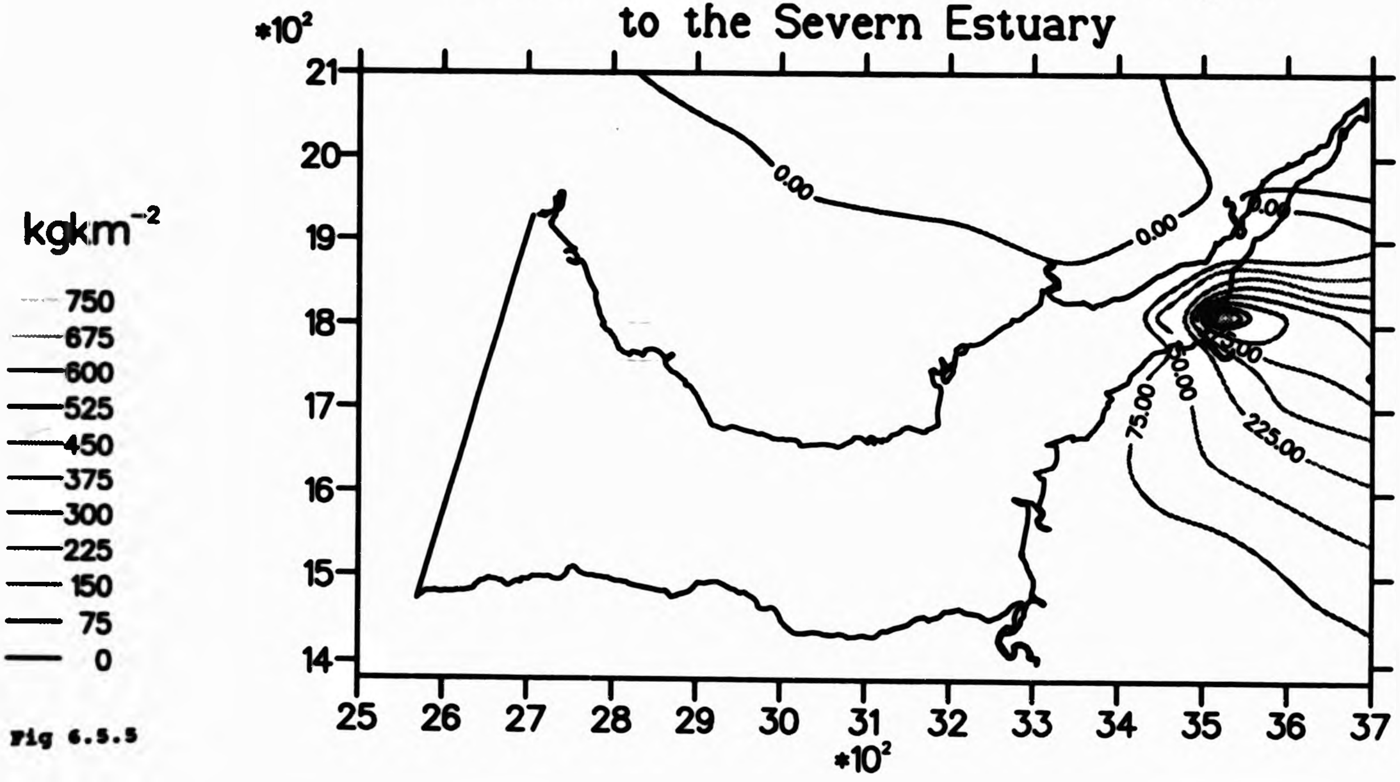


Fig 6.5.5

Linear distribution of aerial Zn input
to the Severn Estuary

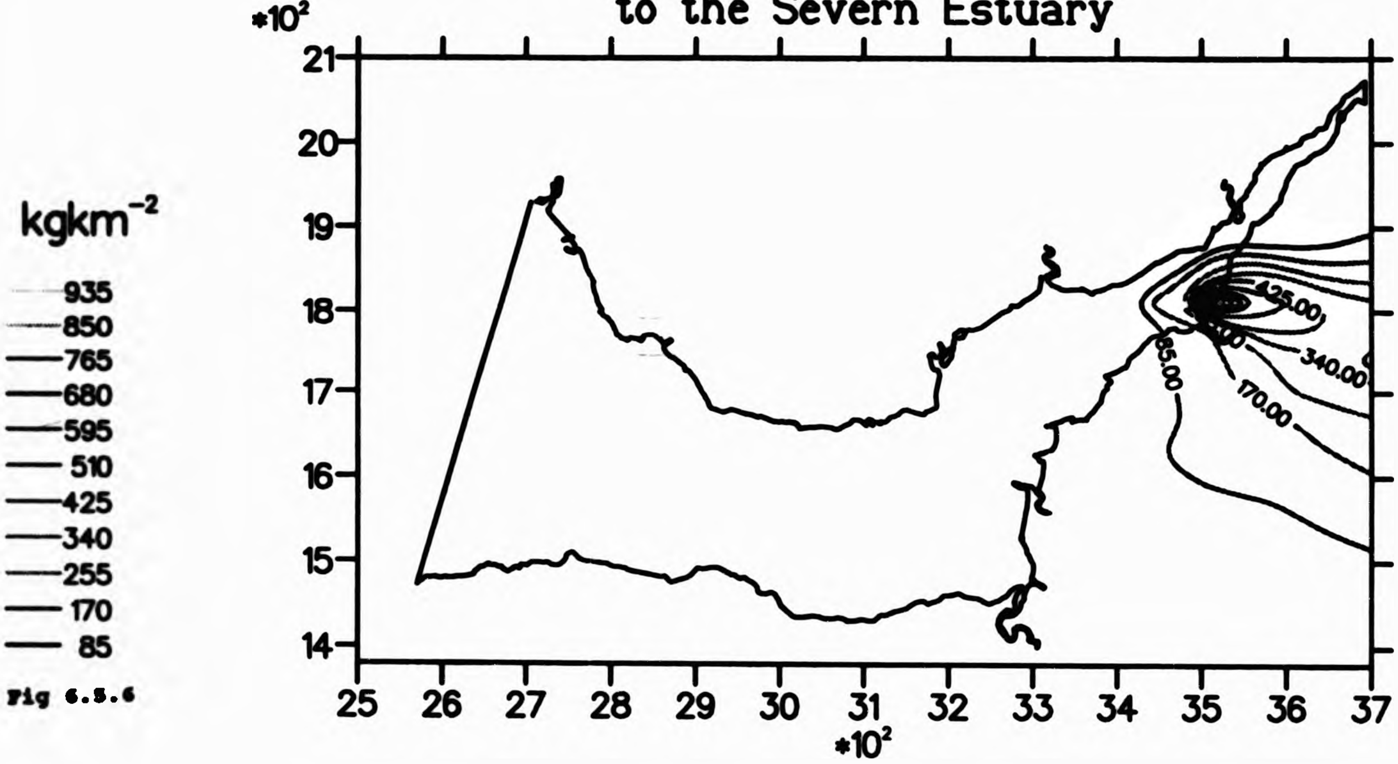


Fig 6.5.6

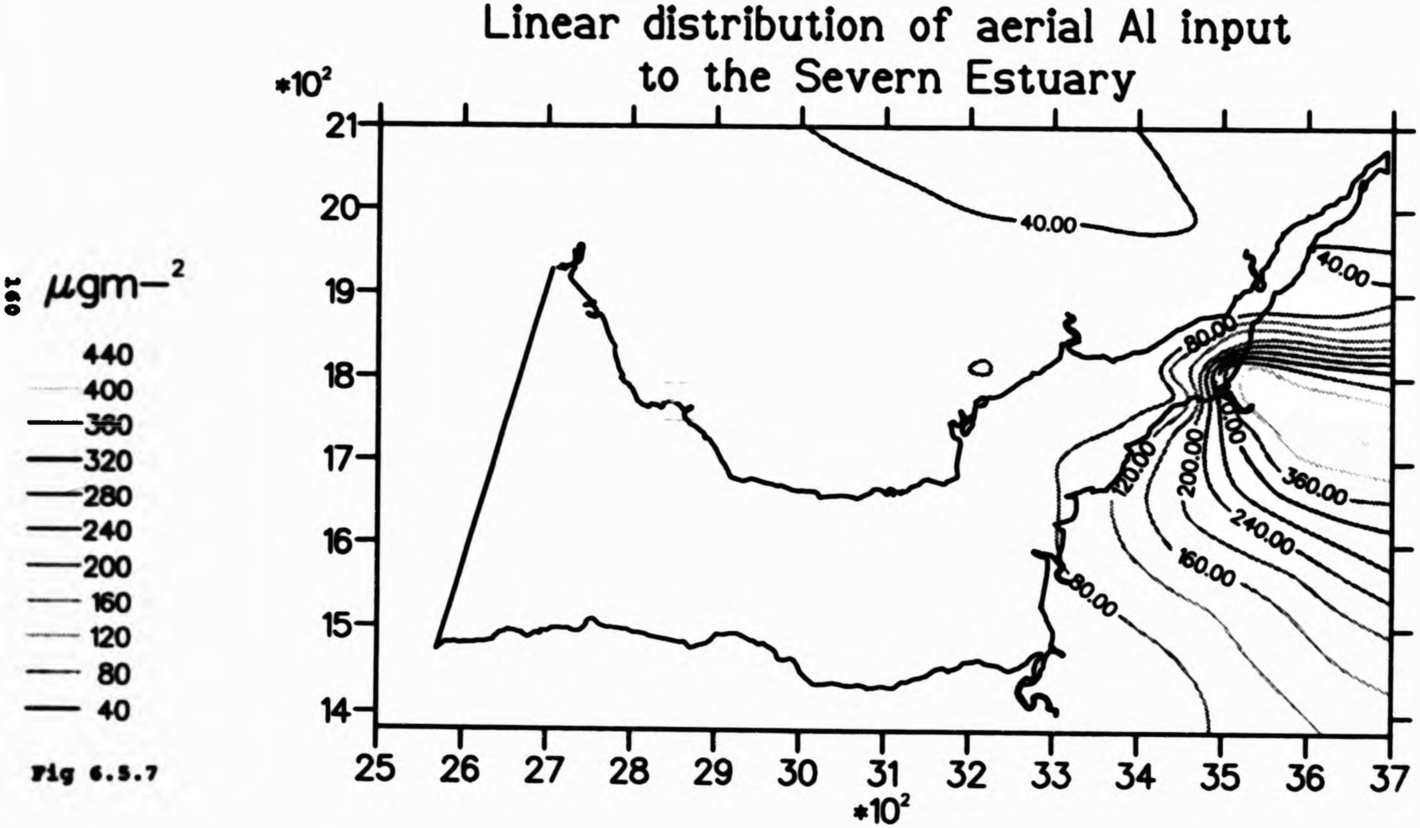

Linear distribution of aerial Al input
to the Severn Estuary
μgm^{-2}
440
400
360
320
280
240
200
160
120
80
40
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
40.00
40.00
80.00
120.00
200.00
360.00
240.00
160.00
80.00

Fig 6.5.7

Logten distribution of aerial Cd input to the Severn Estuary

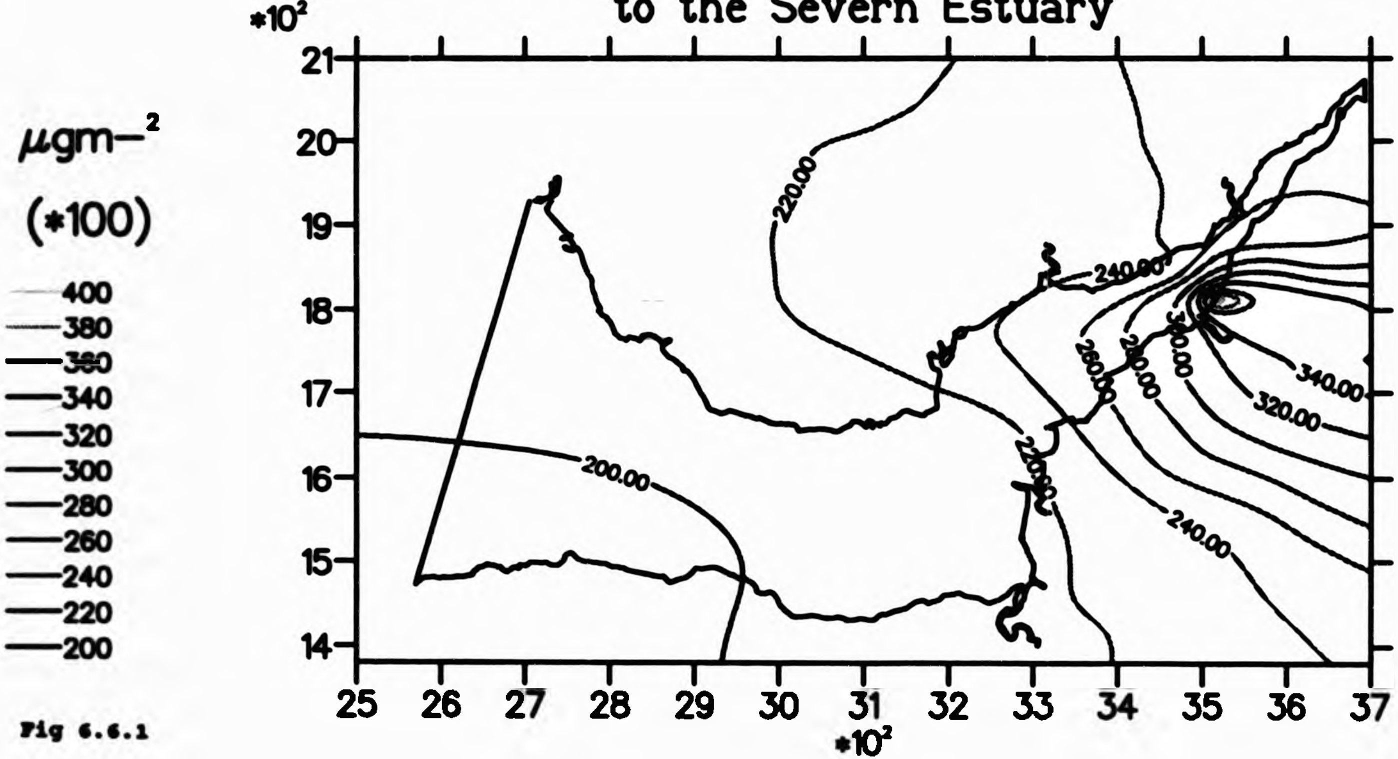


Fig 6.6.1

Logten distribution of aerial Cu input to the Severn Estuary

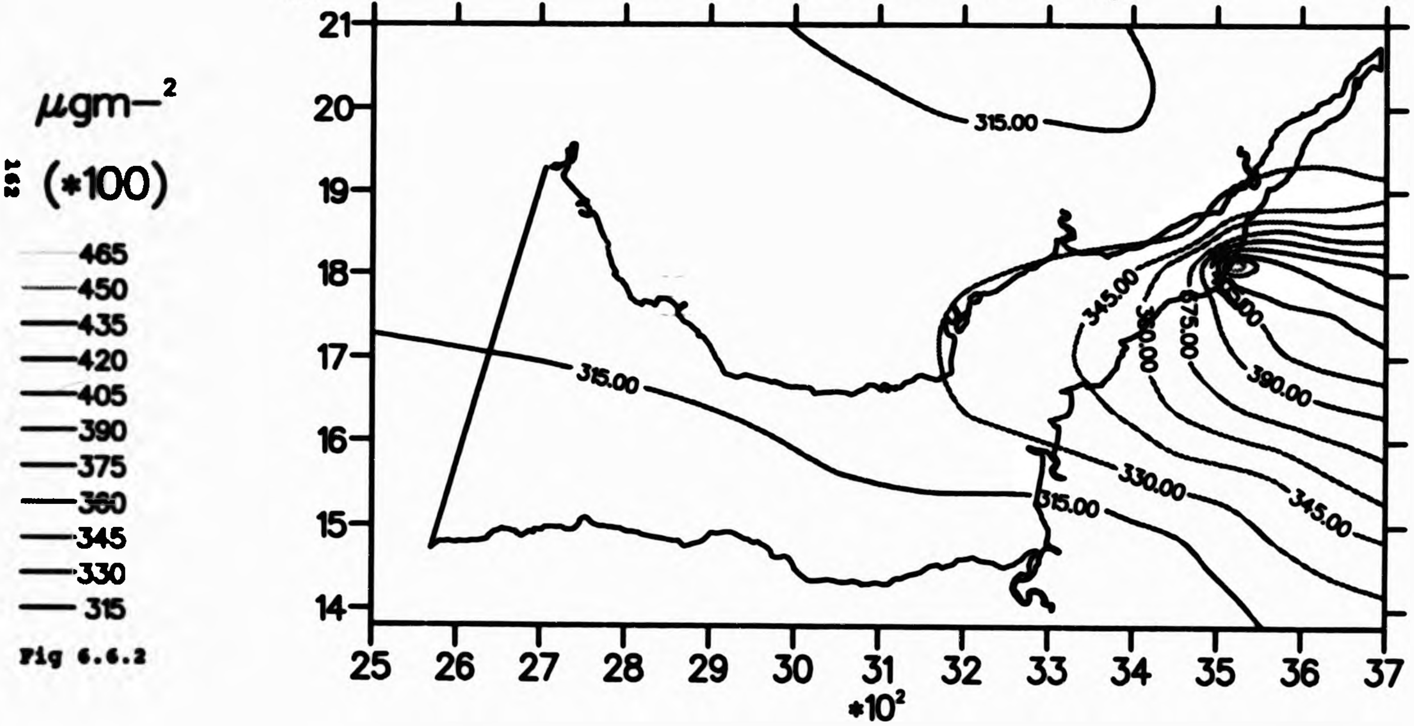
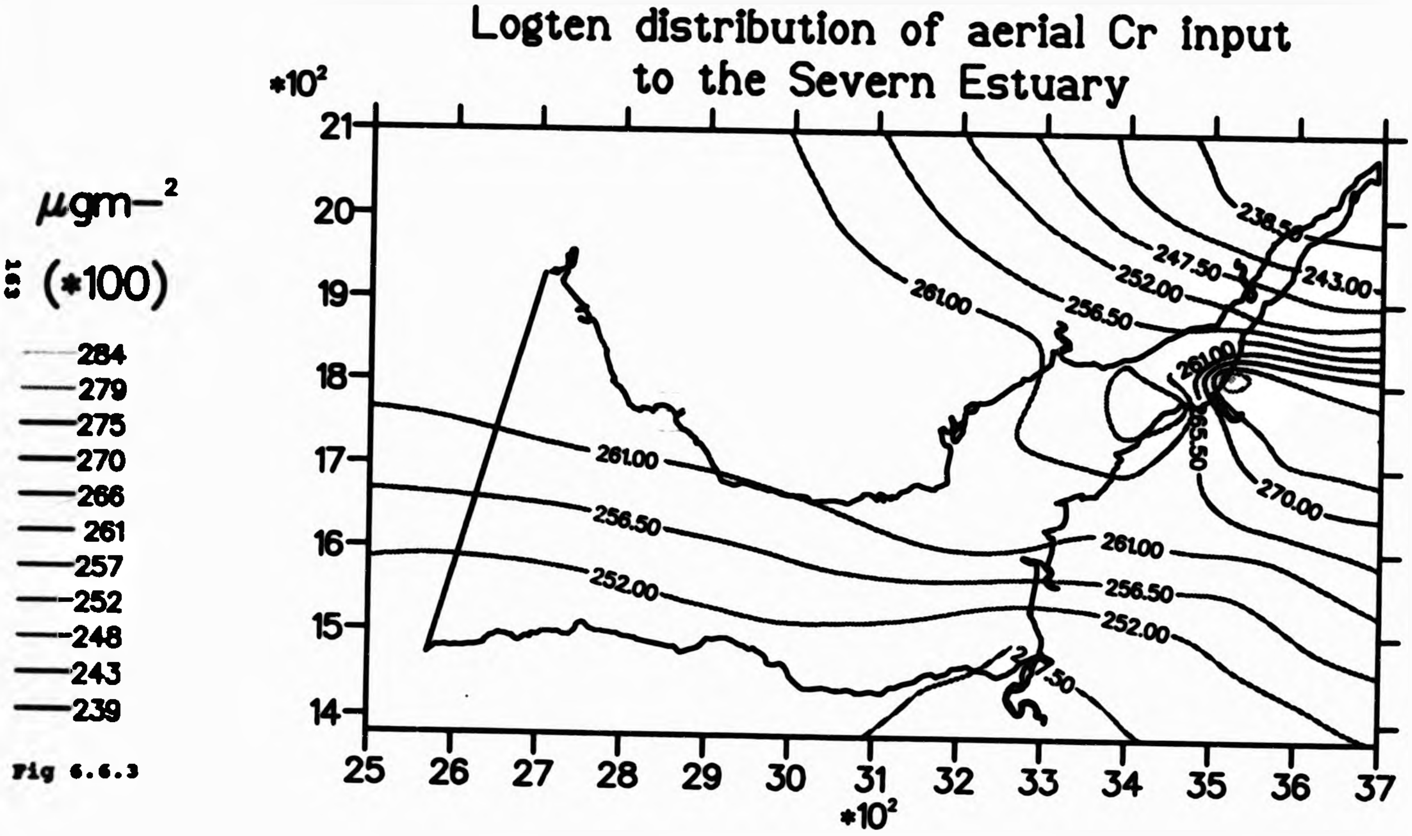


Fig 6.6.2



Logten distribution of aerial Cr input to the Severn Estuary

Fig 6.6.3

Logten distribution of aerial Ni input to the Severn Estuary

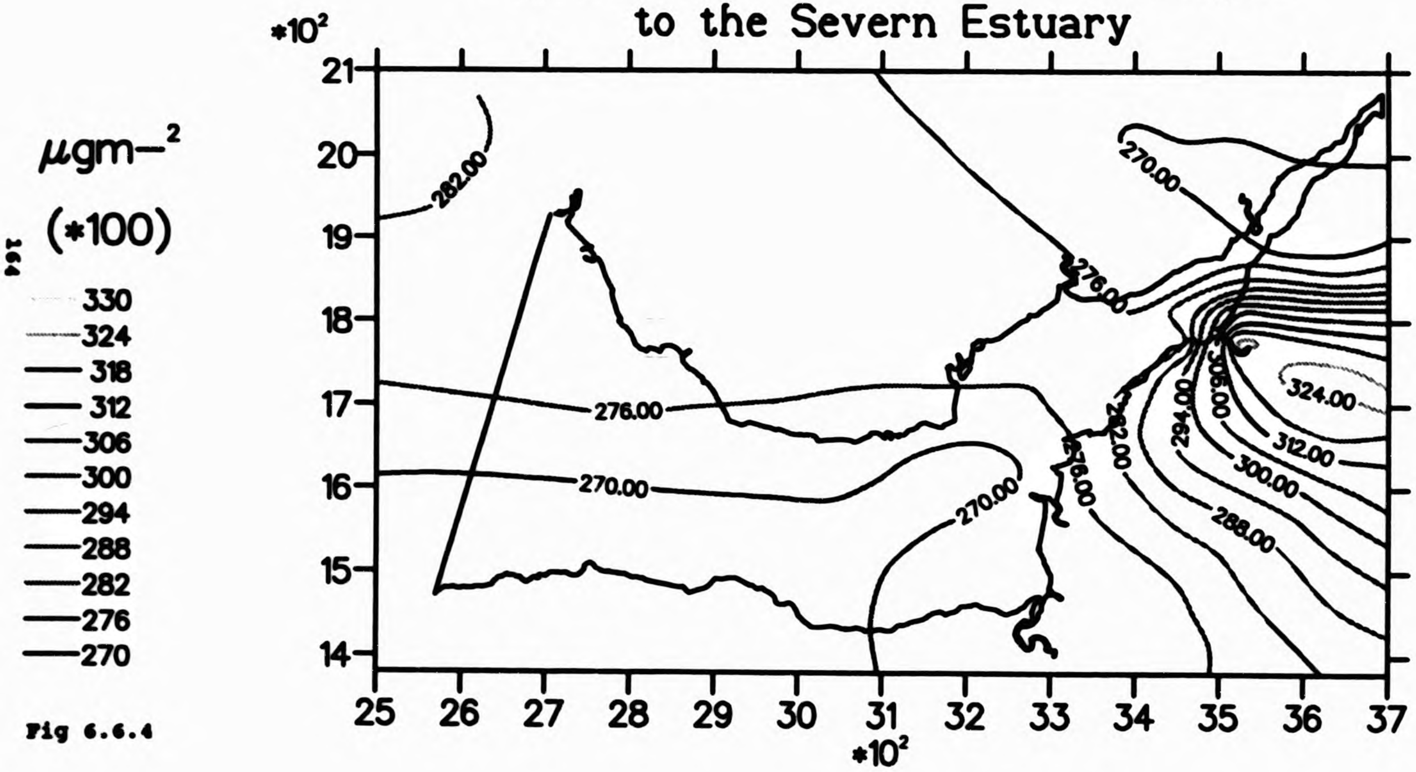


Fig 6.6.4

Logten distribution of aerial Pb input to the Severn Estuary

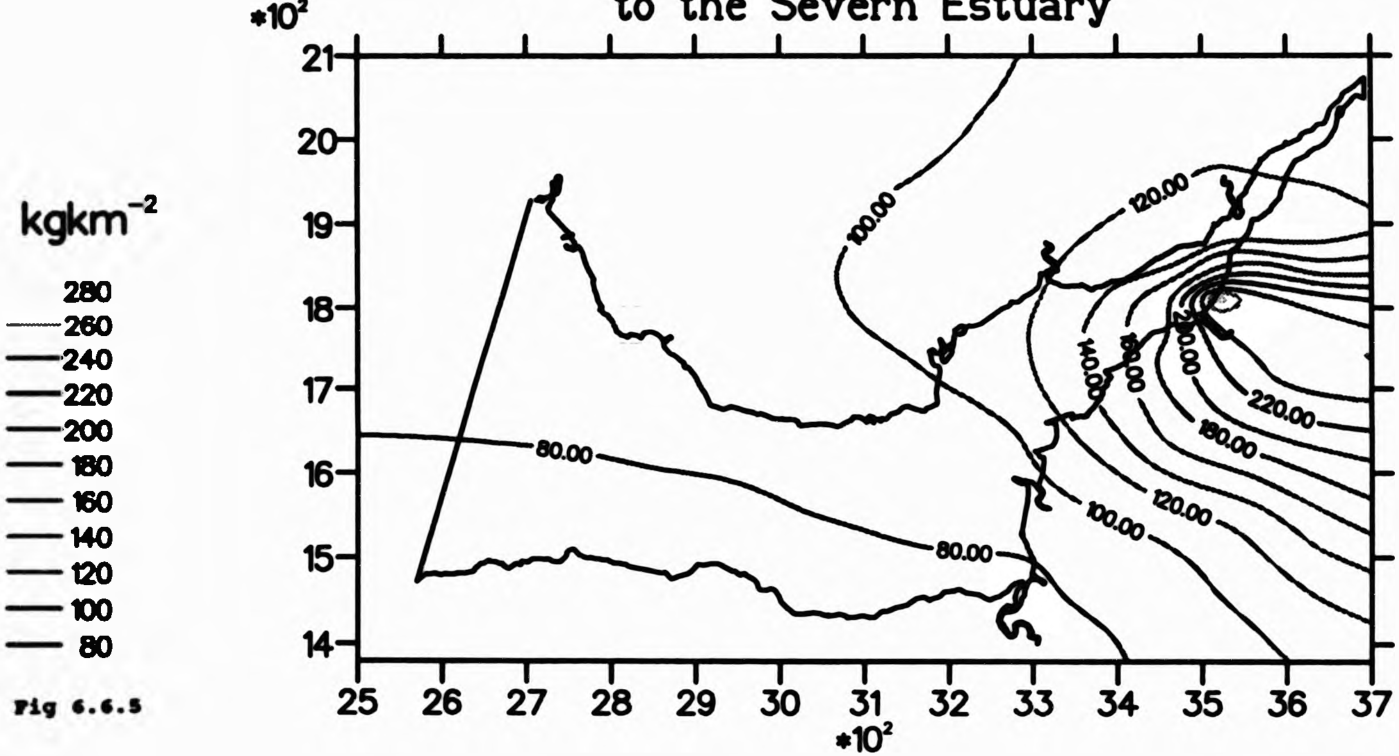


Fig 6.6.5

Logten distribution of aerial Zn input to the Severn Estuary

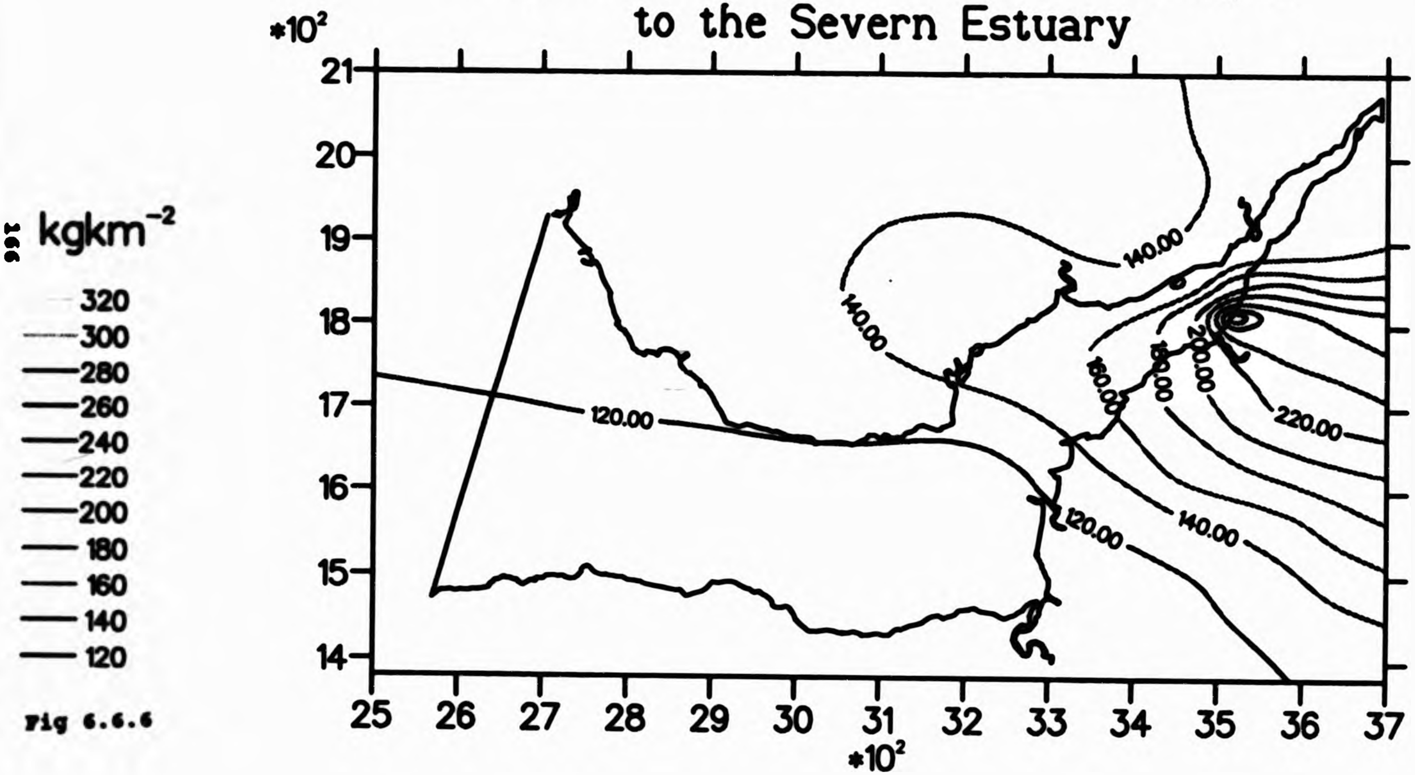
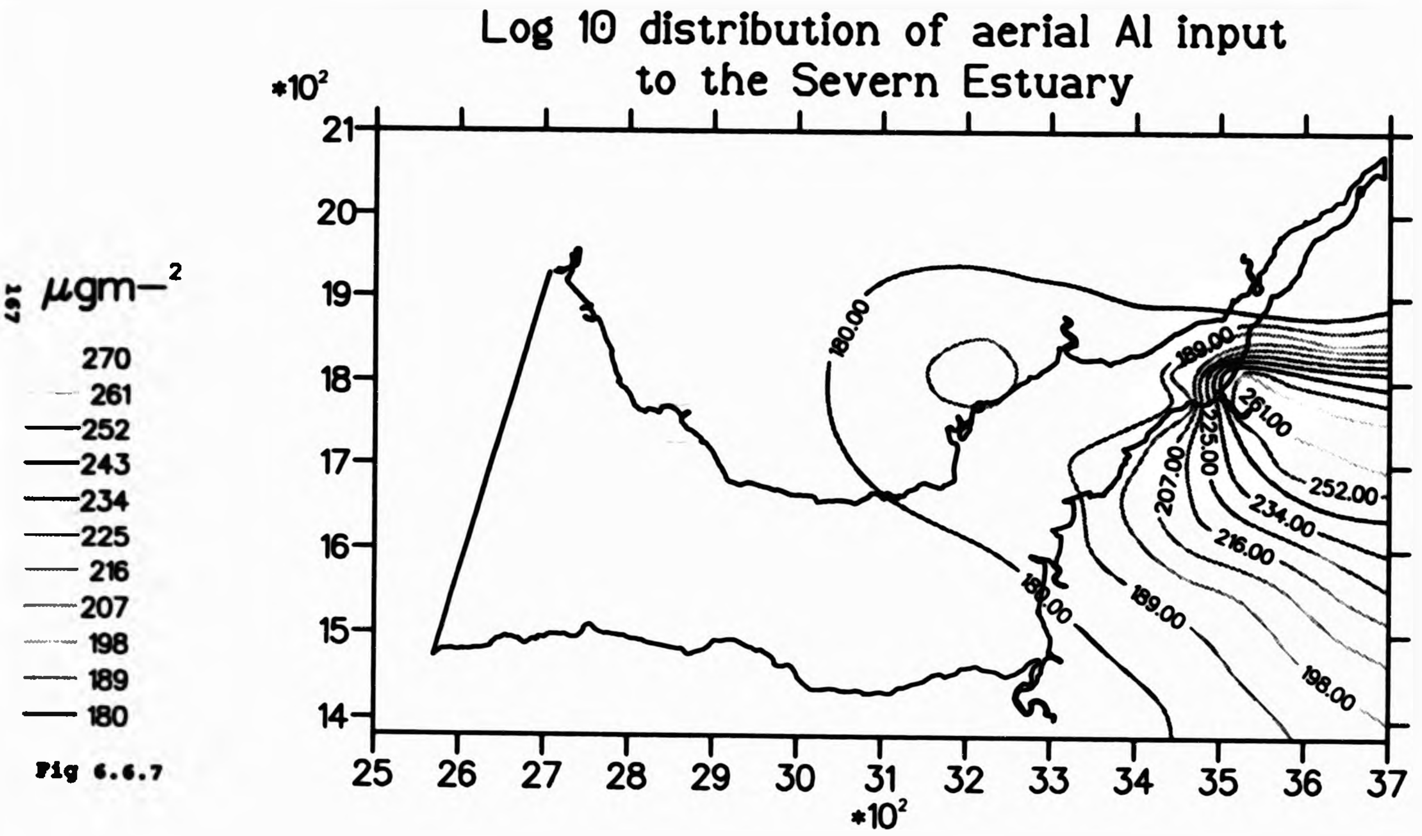


Fig 6.6.6



Log 10 distribution of aerial Al input to the Severn Estuary

Fig 6.6.7

Ln distribution of aerial Cd input to the Severn Estuary

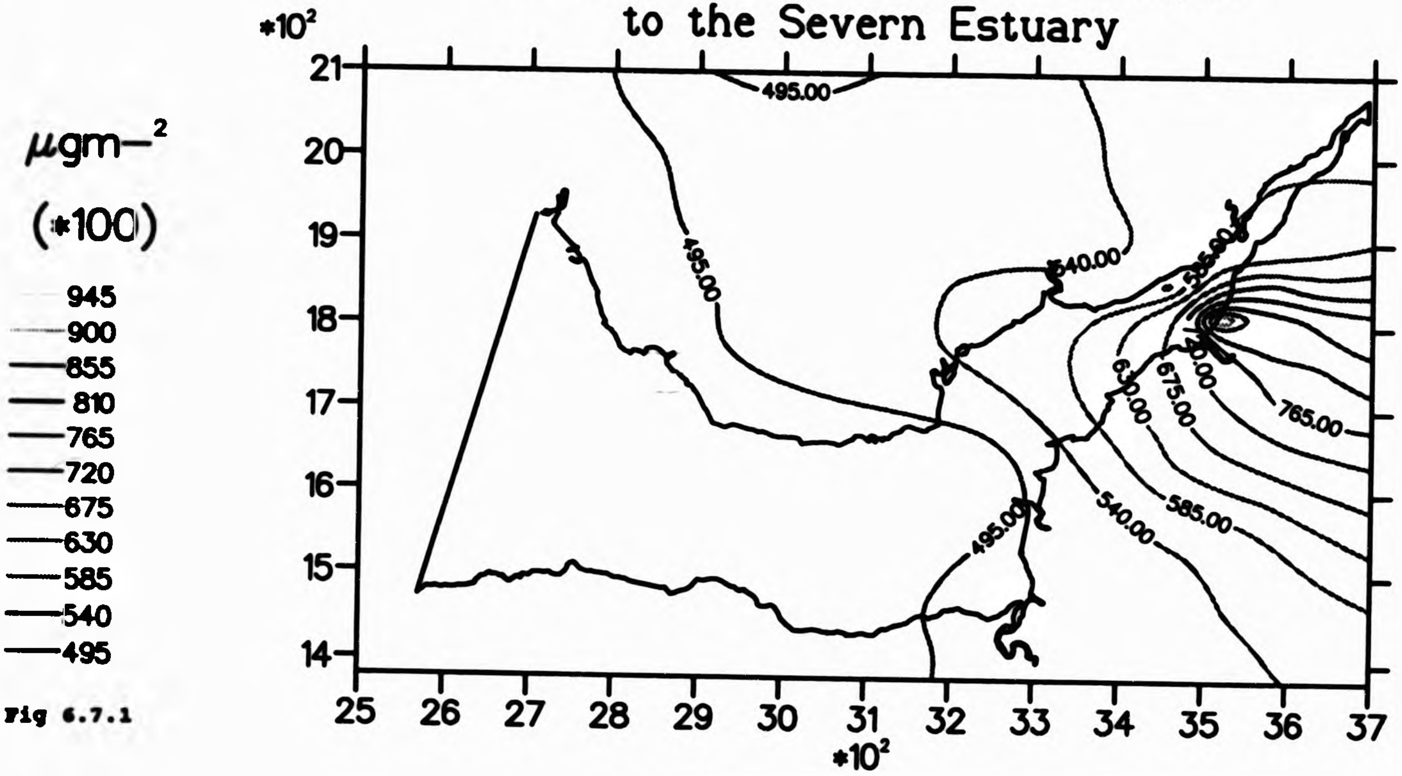
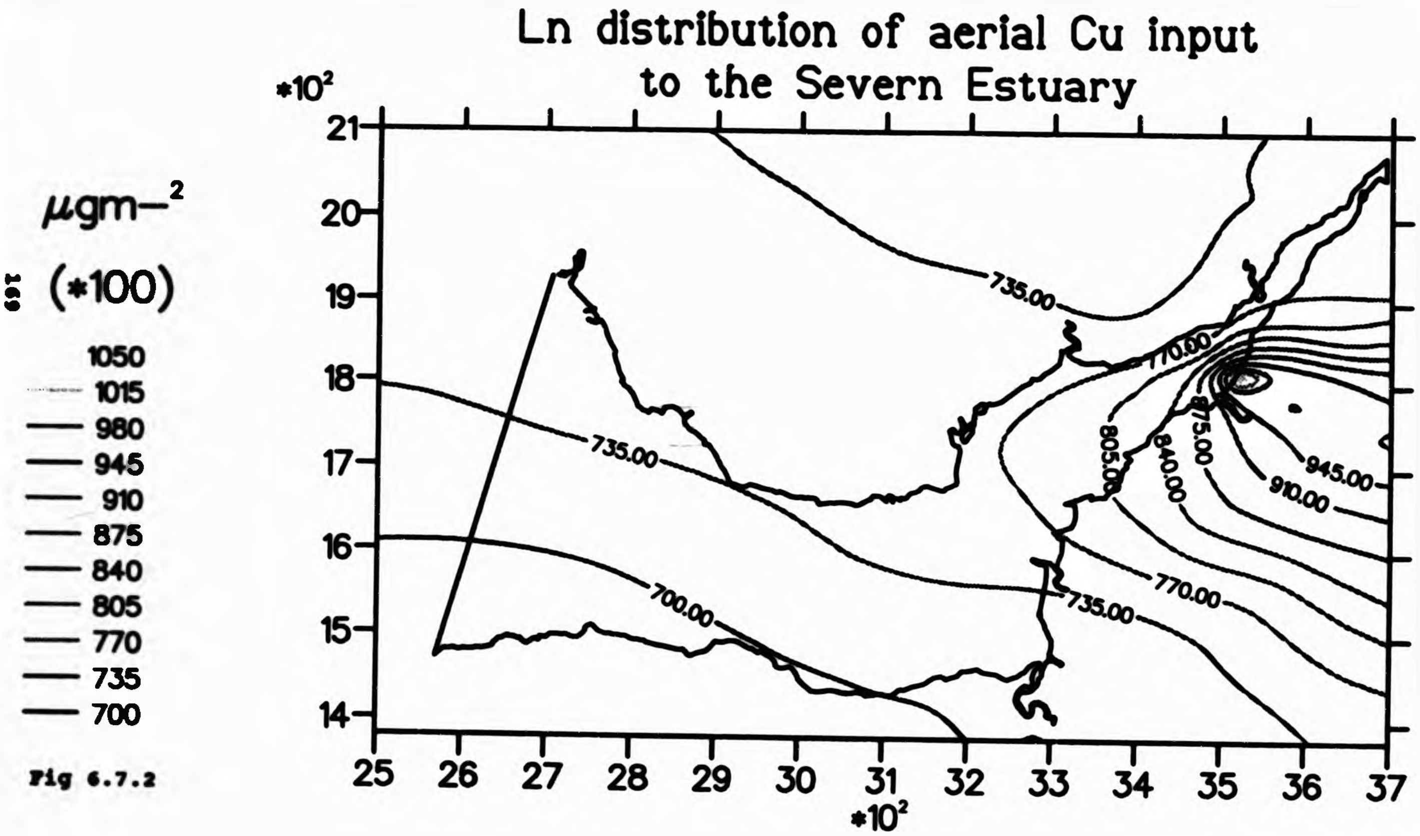
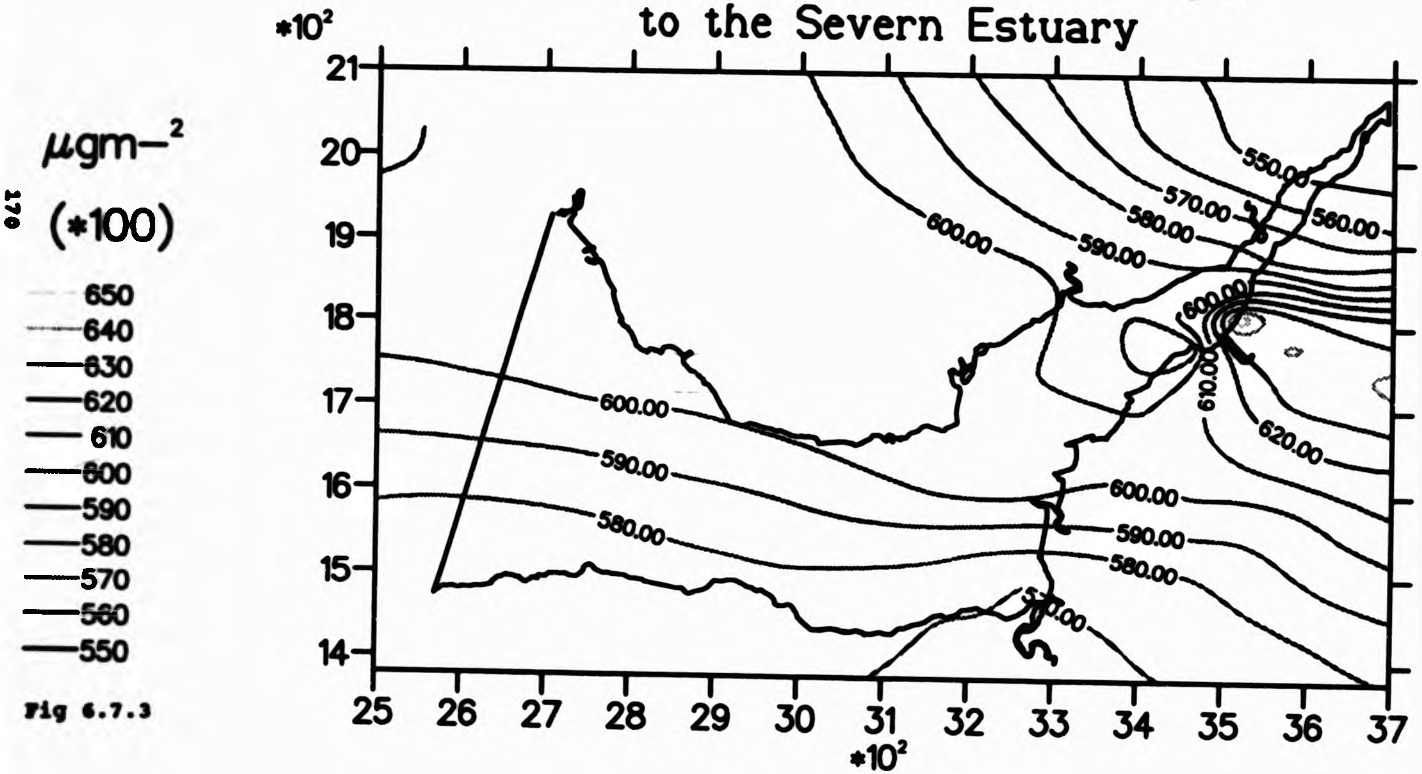


Fig 6.7.1



Ln distribution of aerial Cu input to the Severn Estuary

Fig 6.7.2



Ln distribution of aerial Cr input to the Severn Estuary

Fig 6.7.3

Ln distribution of aerial Ni input
to the Severn Estuary

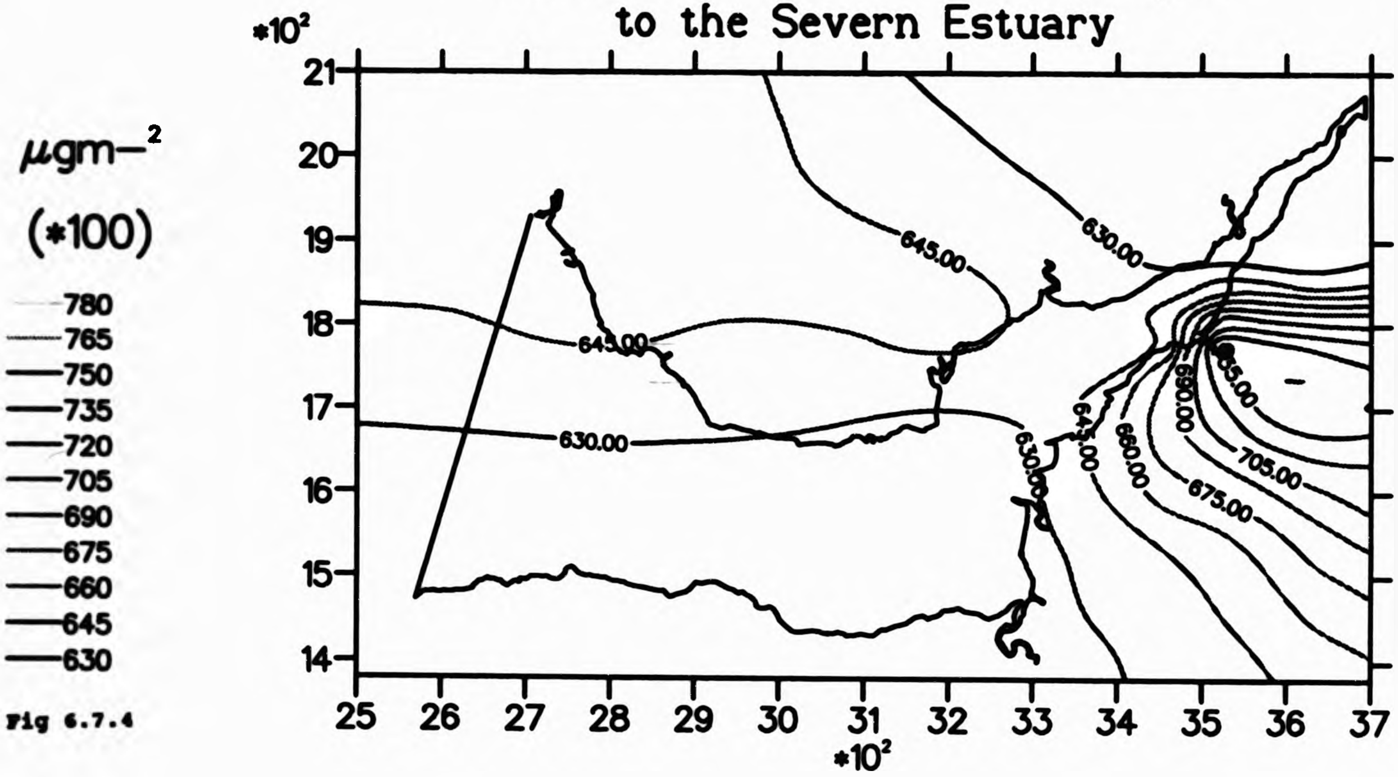


Fig 6.7.4

Ln distribution of aerial Pb input to the Severn Estuary

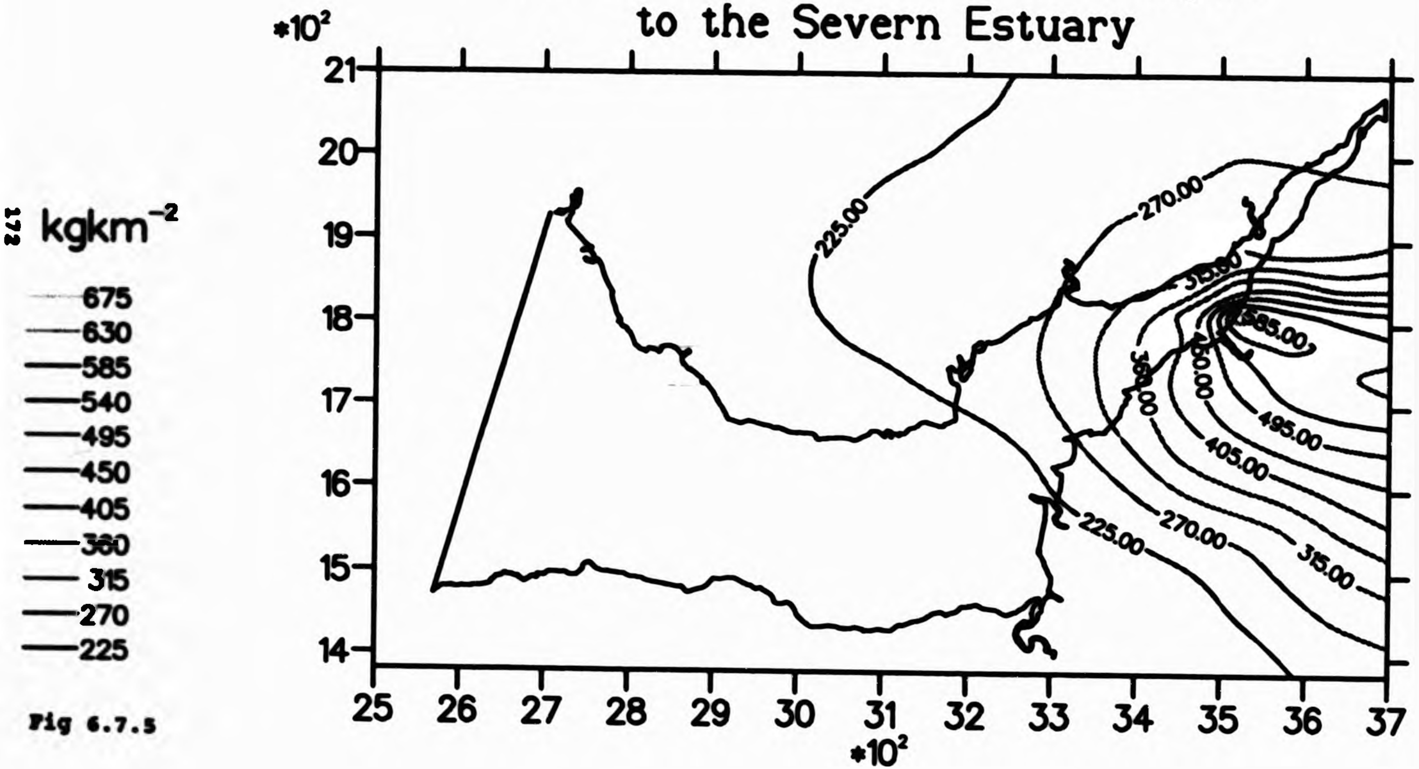
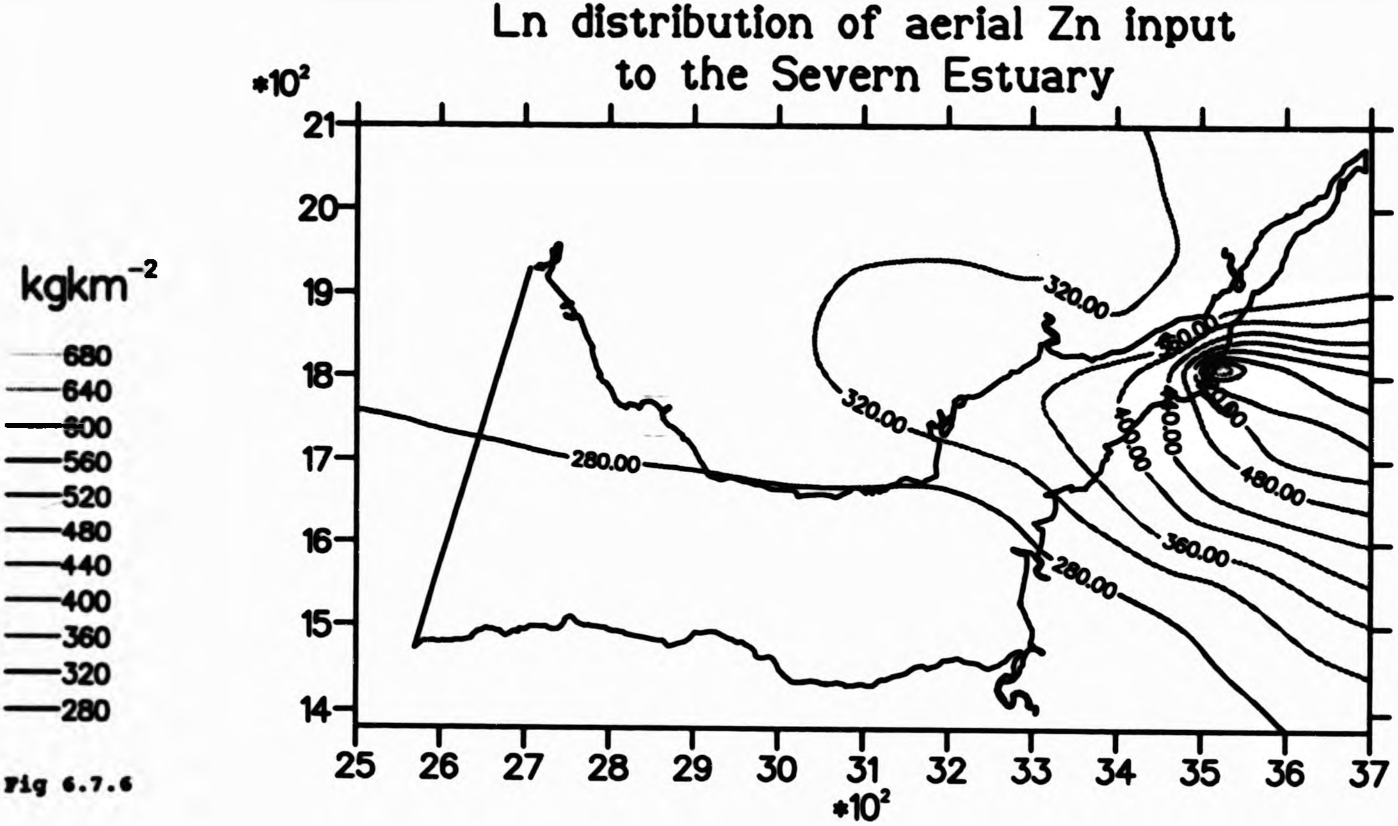


Fig 6.7.5



Ln distribution of aerial Zn input to the Severn Estuary

Fig 6.7.6

Ln distribution of aerial Al input to the Severn Estuary

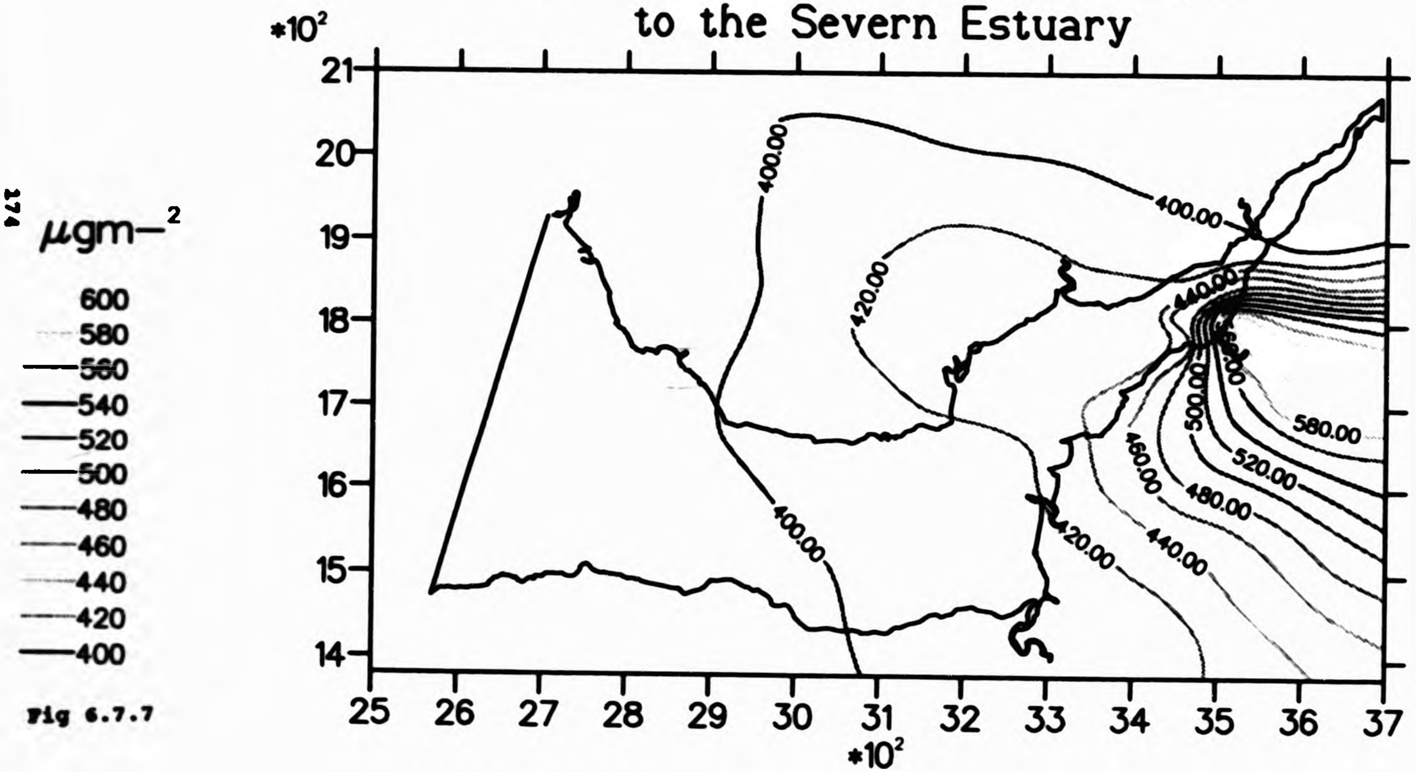


Fig 6.7.7

Square root distribution of aerial Cd input to the Severn Estuary

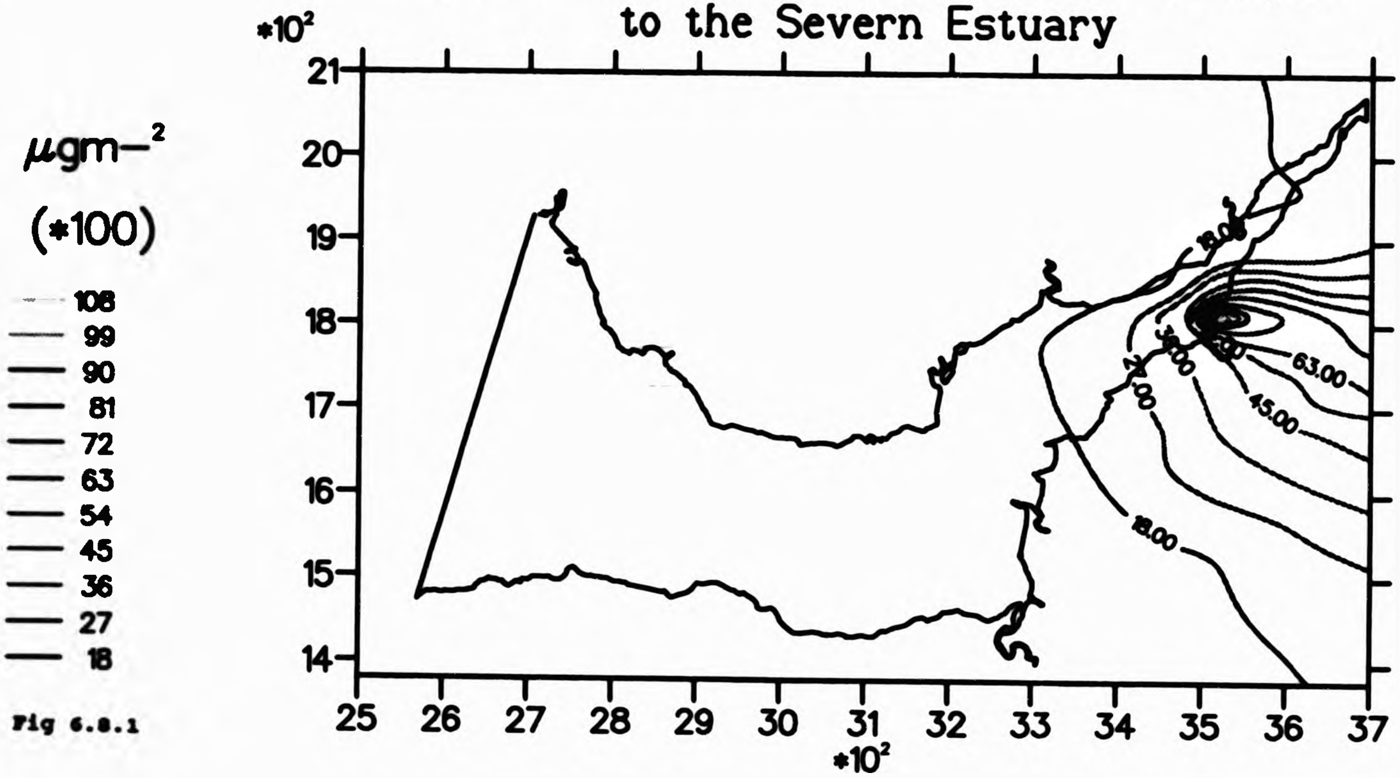


Fig 6.8.1

Square root distribution of aerial Cu input to the Severn Estuary

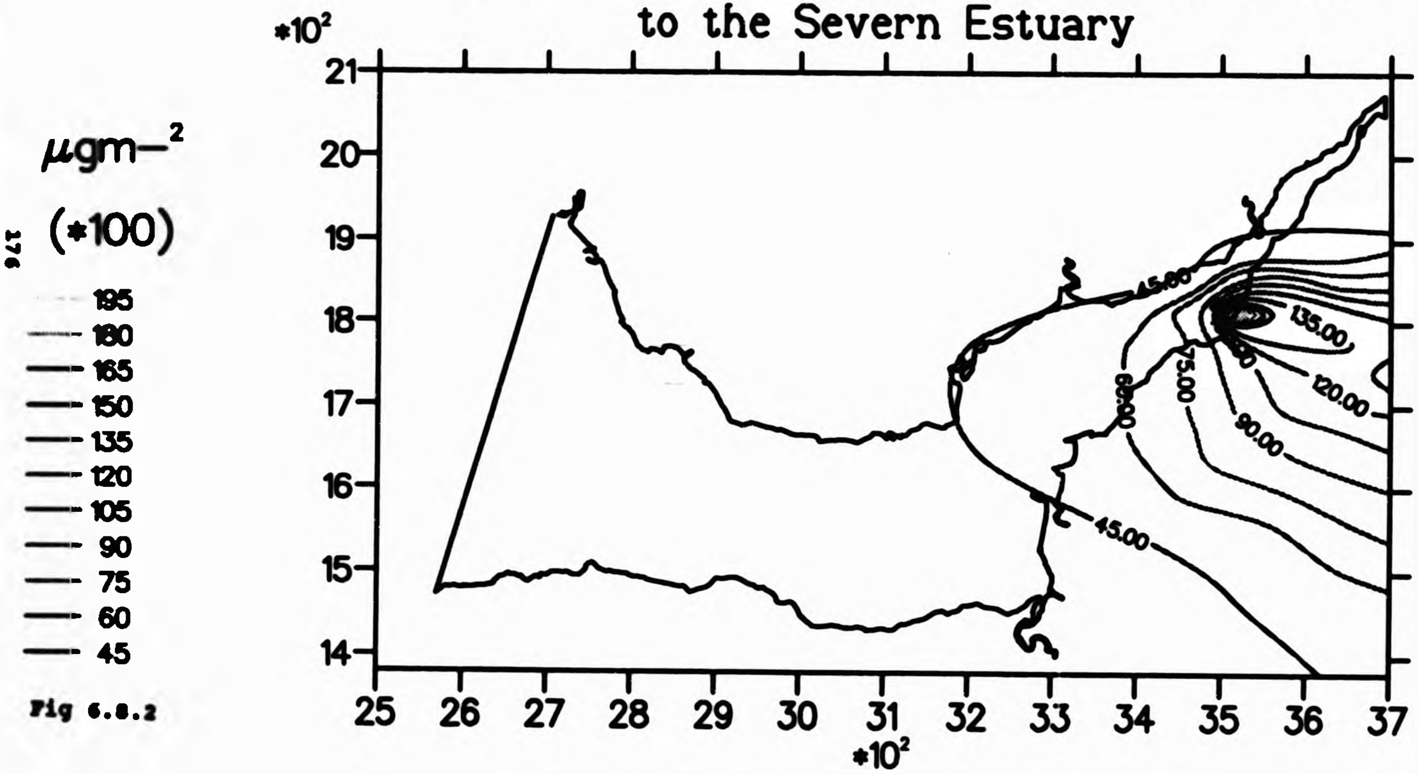


Fig 6.8.2

Square root distribution of aerial Cr input to the Severn Estuary

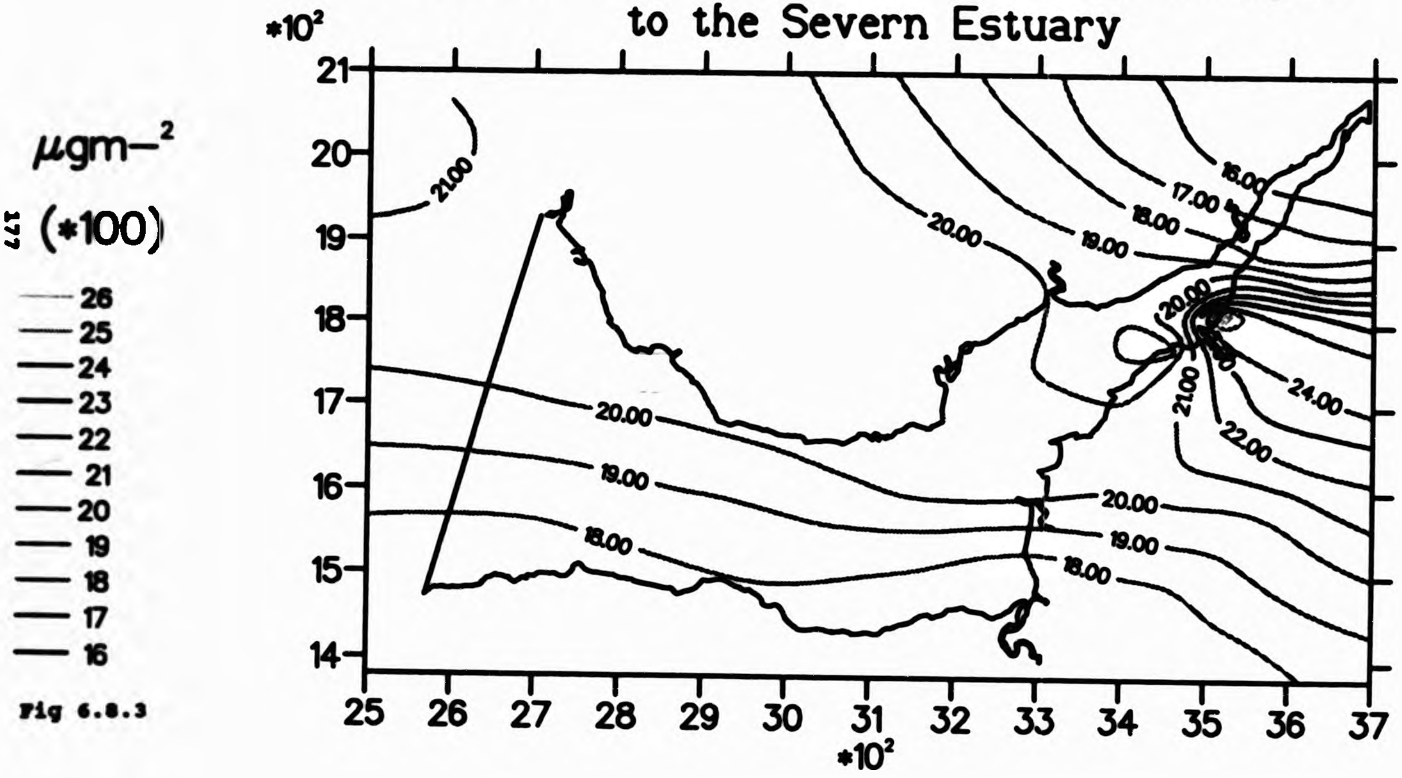


Fig 6.8.3

Square root distribution of aerial Ni input to the Severn Estuary

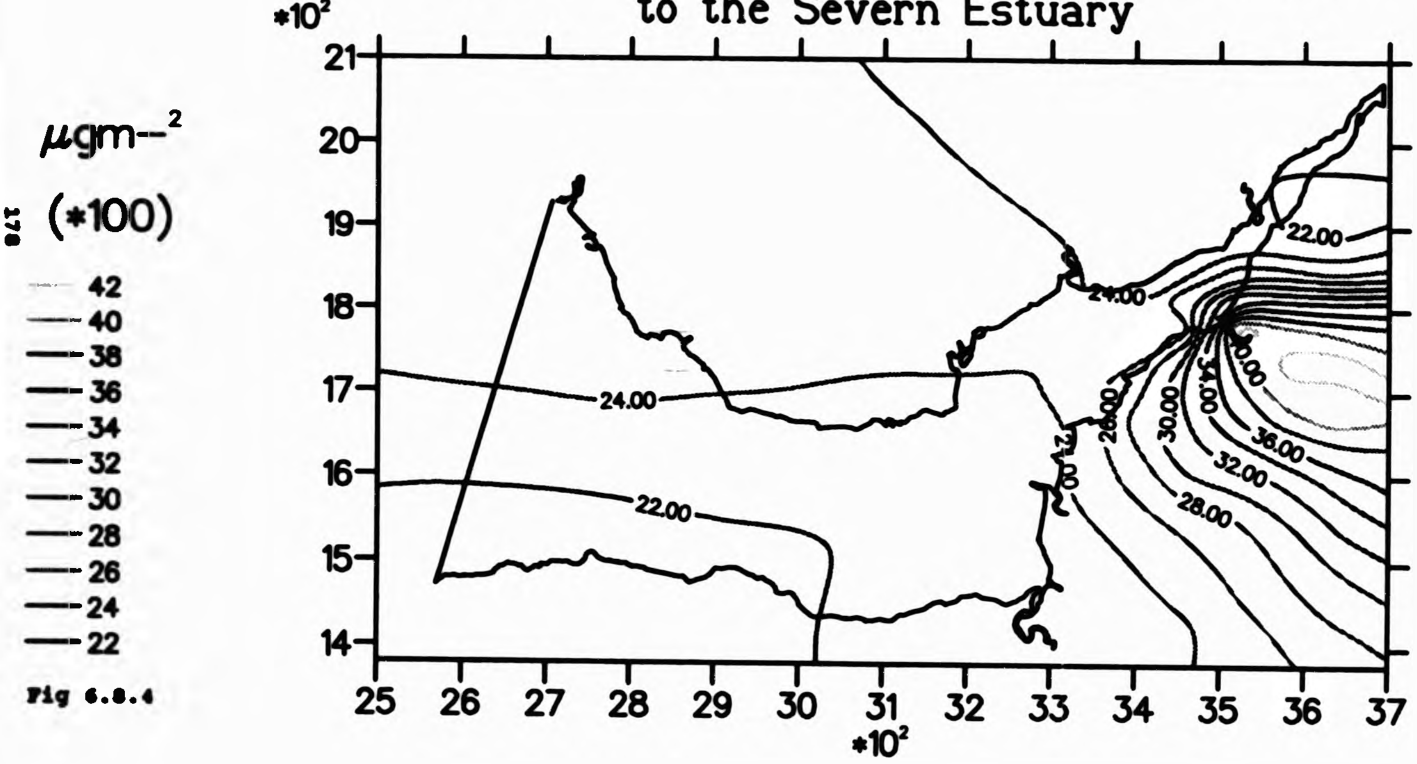


Fig 6.8.4

Square root distribution of aerial Pb input to the Severn Estuary

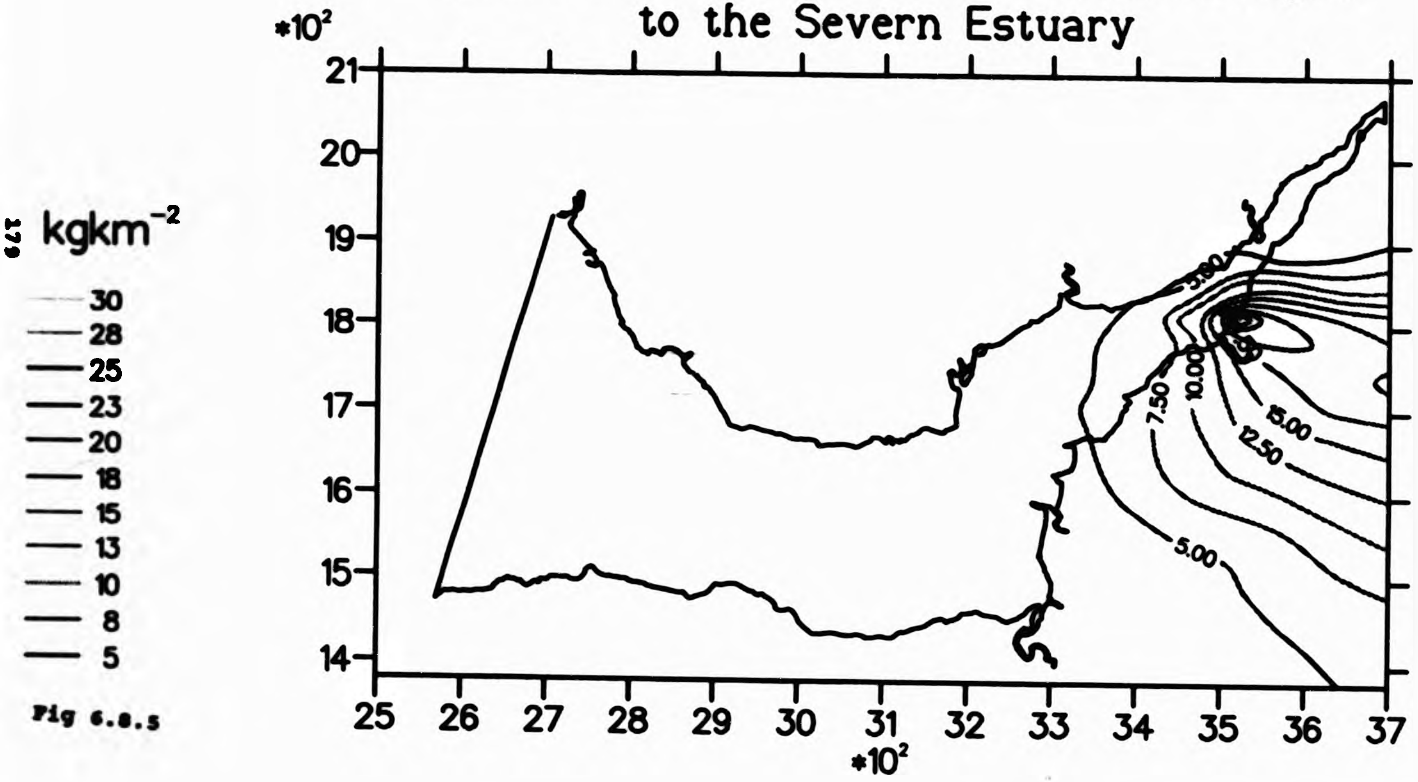


Fig 6.8.5

Square root distribution of aerial Zn input to the Severn Estuary

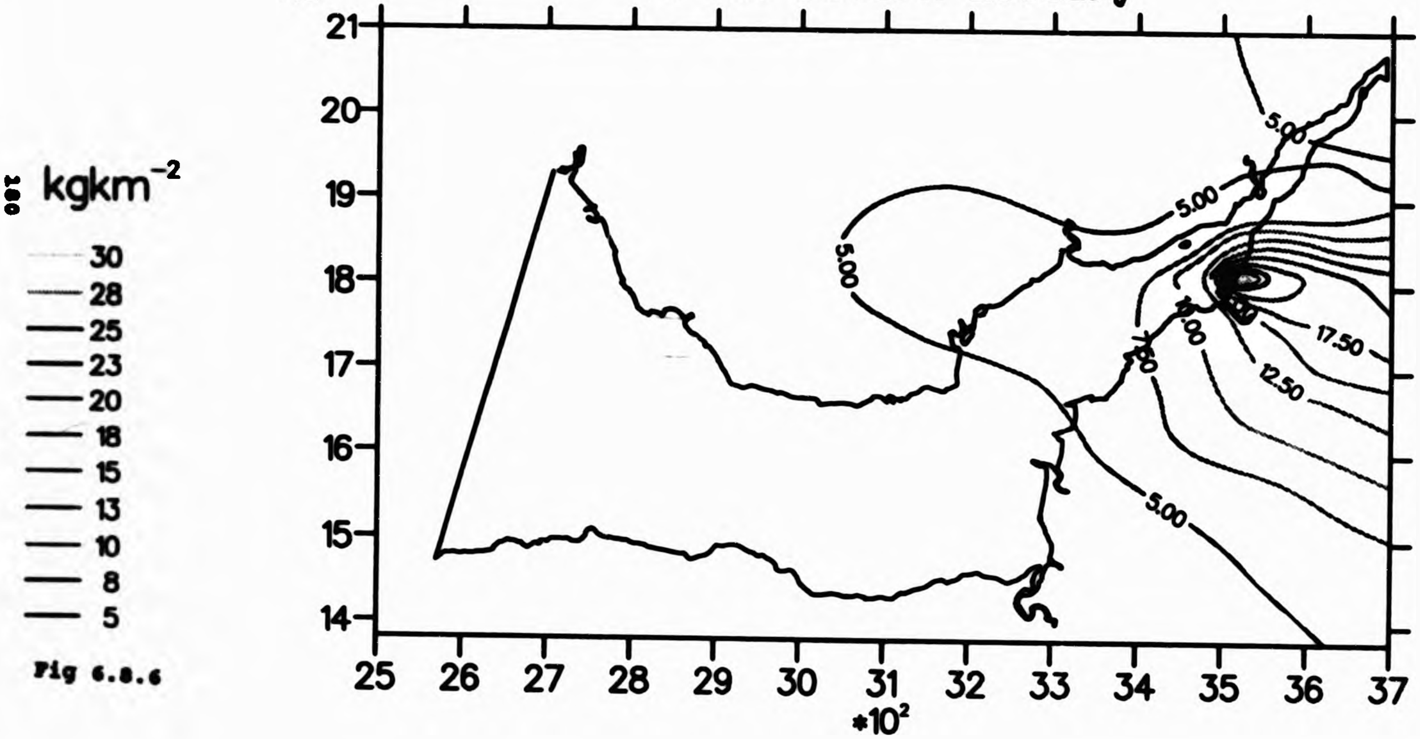


Fig 6.8.6

Square root distribution of aerial Al input to the Severn Estuary

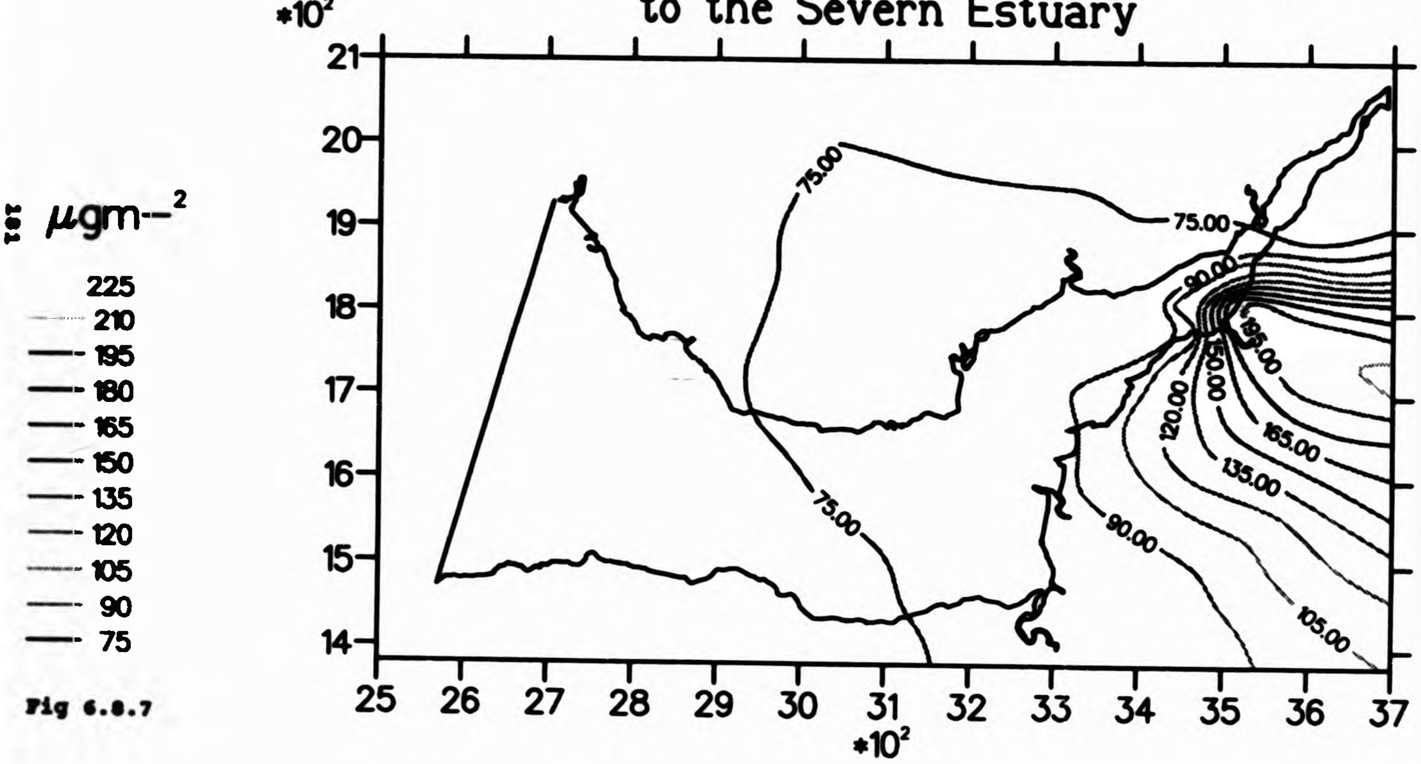


Fig 6.8.7

Table 6.1 Total inputs in kg of metals per sampling interval

Int.	Days	Cum. days	Cd	Cu	Cr	Ni	Pb	Zn
1	15	15	15.75	68.50	13.45	21.90	1653.15	2096.4
2	14	29	10.06	108.81	23.32	42.15	1314.38	2760.7
3	14	43	11.37	76.07	11.22	82.17	1290.40	11115.6
4	14	57	12.37	89.25	6.31	24.04	908.47	923.7
5	7	64	10.45	102.90	23.57	36.15	688.48	1602.7
6	14	78	24.50	181.53	29.20	35.70	2155.49	2566.4
7	14	92	48.35	188.50	32.40	29.20	2342.71	2648.6
8	14	106	9.63	119.94	22.86	47.61	858.92	1523.4
9	14	120	15.89	150.44	11.20	31.64	2066.90	2012.7
10	14	134	13.13	165.55	28.18	35.39	1651.82	2485.9
11	14	148	12.46	163.12	22.35	18.62	1731.13	1496.3
12	14	162	16.47	299.19	22.50	23.79	1303.28	2096.3
13	14	176	55.02	543.57	72.65	46.14	2842.20	5722.6
14	15	191	8.26	42.37	9.83	19.97	276.94	548.3
15	13	204	13.24	144.44	8.51	32.82	1147.75	2680.5
16	14	218	15.80	165.59	56.18	37.32	1609.88	2303.2
17	14	232	14.49	84.64	15.95	11.61	1373.05	1272.4
18	14	246	28.13	167.22	72.82	62.69	2135.47	3150.0
19	14	260	15.53	138.01	23.59	23.84	1276.92	1601.2
20	13	273	13.03	169.48	28.02	19.56	1178.18	1815.9
21	16	289	36.12	168.76	29.91	61.72	6460.42	2358.8
22	13	302	20.82	136.52	12.33	54.50	1269.79	2345.0
23	14	316	22.42	179.46	23.68	37.01	2252.56	2889.0
24	14	330	26.65	189.05	22.32	22.85	2143.73	2856.2
25	22	352	38.49	220.66	73.55	97.18	2079.89	4144.1
26	13	365	29.77	79.71	12.81	38.78	1039.66	1273.1
27	14	379	26.95	117.51	21.69	126.23	995.50	967.6
28	14	393	12.48	139.54	23.76	62.23	881.07	1818.2
29	14	407	14.06	158.24	41.09	33.36	1077.56	2382.9
30	14	421	10.73	83.80	36.22	27.86	1205.63	1774.9
31	13	434	31.75	133.50	27.52	53.56	2659.06	2333.0
Tot.		434	634.17	4775.90	858.99	1297.60	51820.00	77566.0

(Int. - Sampling interval)

Table 6.2 Comparison of estimated daily metal inputs from sampling intervals and total sample period

Metal	Linear Interp. Sampling Int. $kgday^{-1}$	Linear Interp Total Period $kgday^{-1}$
Cd	1.46	1.52
Cu	11.01	9.87
Cr	1.97	1.97
Ni	2.98	2.87
Pb	119.4	104.78
Zn	178.72	149.73
Al	-	0.31

maps. These were corrected for in the deposition estimate calculations.

The resulting values estimated are shown in Table 6.1. This approach was very time consuming so an alternative approach was adopted whereby the total loadings for the entire period were summed and a single plot produced for each metal. The final values were compared and found to be sufficiently alike that the single plot approach was continued for the other transformed interpolation techniques. The raw data for Al were not interpolated on a sample interval basis but only on the total period so no comparison could be made. The values obtained for each method are shown in table 6.2. and it can be seen that they are similar with the total period approach slightly underestimating the value for Cu, Ni, Pb and Zn and resulting in an identical value for Cr and slightly higher for Cd.

In addition to the deposition estimates made by the various interpolation plots an estimation of the inputs was also made using the AERE Harwell blocking technique using the data collected between January 1989 and March 1990. This was made for the purposes of method comparison as well as to examine the possible changes that may have occurred in deposition in the intervening period between deposition surveys. The results for all the techniques are presented in Table 6.3. It must be noted that the estimations using the Harwell technique were made using the original area covered in the 1979 to 1983 surveys. An area correction was then made and the results are presented in Table

TABLE 6.3 Estimated daily metal inputs to the Severn using various interpolation methods and AERE Harwell blocking method

Metal	Linear Interp. Biweekly kgday^{-1}	(A)Linear Interp. Total kgday^{-1}	Ln Interp. kgday^{-1}	Log Interp. kgday^{-1}	Sqrt. Interp. kgday^{-1}	AERE Harwell 1983 kgday^{-1}	AERE Harwell Method 1989/90 kgday^{-1}
Cd	1.46	1.52	0.85	0.84	1.12	21.9	3.91
Cu	11.01	9.87	8.64	8.68	9.48	118.2	21.57
Cr	1.97	1.97	1.94	1.93	1.94	-	2.88
Ni	2.98	2.87	2.75	2.80	2.82	82.2	4.52
Pb	119.40	104.78	57.22	62.28	73.58	443.9	272.1
Zn	178.72	149.73	97.14	96.07	114.86	5595.5	346.74
Al	-	0.31	0.31	0.31	0.33	-	0.57
Area km^2	2250	2250	2250	2250	2250	3140	3140

Table 6.4 Estimated daily inputs to the Severn by AERE Harwell (1983) and by AERE Harwell method (1989/90) using corrected area.

Metal	AERE Harwell (1983) kgday^{-1}	AERE Harwell method (1989/90) kgday^{-1}
Cd	20.3	3.71
Cu	108.4	19.17
Cr	N.D	2.17
Ni	72.0	3.46
Pb	428.5	259.4
Zn	5559.4	320.22
Al	N.D	0.49
Area km^2	2250	2250

N.D. = Not determined in 1983 survey.

6.4. This correction was achieved by reducing the areas in the North Central and South Channel areas such that the total areas measured in the earlier survey and this survey were the same. The loadings for these two channel areas were then recalculated using the new areas and a daily input estimated for each metal.

The implications of these results for atmospheric metal pollution to the Severn estuary will be discussed at a later stage of this report.

6.5 Flat Holm - Daily sampling and Spatial variations.

Daily samples were collected from six sites on Flat Holm island between the 15th and 18th May 1990. The results for Cd, Cu, Cr, Ni, Pb, Zn and Na will be presented with the discussion in the following chapter. Al was not plotted as this is generally used as a reference element for evidence of aeolian, land based input. Na was used instead as an indicator for evidence a of maritime influence on the samples with respect to the island site. There was only one day that rain occurred, the 15th of May. On the remaining days dry deposition was collected by washing down the funnel walls with known volumes of 1% HNO_3. The results were then plotted on outline maps of the island, by hand using a linear interpolation method. These plots will be presented with a further discussion of the results in chapter 7.

6.6 The Maritime Effect

An experiment was carried out at Northwick Landfill site to examine the contribution of sea derived metal concentrations using six samplers placed at various distances from the shoreline. Samples were collected after one day and also two weeks. The resulting concentrations are shown in tables 6.6 and 6.7. Again, Na data were used instead of Al data as it was the contribution of this reference element that was under examination. These values were not converted to a mass per unit area but left as concentrations per litre. The conversion was not necessary for the purposes of the experiment. The data were plotted out on two graphs, one for each sampling interval and the implications of the results will be discussed in chapter 7.

Table 6.5 Variation of metal concentrations with distance inland from Northwick Landfill site after 2 weeks

Dist m	Cd μgl^{-1}	Cu μgl^{-1}	Cr μgl^{-1}	Ni μgl^{-1}	Pb mgl^{-1}	Zn mgl^{-1}	Na μgl^{-1}
100	0.9	14.6	1.4	5.3	71.9	245.9	4.0
200	1.6	24.2	2.7	7.3	137.1	283.4	4.4
250	3.0	207.6	1.2	7.7	124.5	391.4	5.1
255	0.9	12.4	0.7	3.0	67.2	178.1	3.1
300	1.3	16.1	2.5	2.8	74.2	213.2	3.3
350	1.3	21.4	1.7	2.8	121.3	211.5	3.1

Table 6.6 Variation of metal concentrations with distance inland from Northwick Landfill site after one day.

Dist m	Cd μgl^{-1}	Cu μgl^{-1}	Cr μgl^{-1}	Ni μgl^{-1}	Pb mgl^{-1}	Zn mg^{-1}	Na μgl^{-1}
100	1.5	16.0	3.4	4.0	55.9	176.7	0.9
200	0.3	6.6	2.2	1.4	32.8	65.5	0.5
250	1.6	78.1	4.3	3.6	119.3	241.4	2.1
255	1.5	30.8	4.9	4.1	76.2	308.0	1.8
300	1.5	23.6	1.9	6.6	85.9	226.6	1.7
350	0.9	18.1	6.0	2.2	111.8	163.4	0.9

7 DISCUSSION OF RESULTS

7.1 Introduction

The results presented in chapter 6 for the estimation of aerial deposition of metals to the Severn estuary are presented in a slightly modified form in Table 7.1 for daily inputs to take account of the difference in area as used by AERE Harwell and the mapping approach employed in this survey. In order to illustrate the differences between the various methods of interpolation used and the blocking method employed by AERE Harwell the results have been represented as a percentage of the results obtained by linear interpolation. The resulting percentages are shown in Table 7.2. Table 7.3 shows the estimated annual inputs of Cd, Cu, Cr, Ni, Pb, Zn and Al. The daily estimates were obtained by dividing the calculated totals for the entire sampling period by the number of days (434) and the annual inputs derived from these. It must be noted that these derivations for daily and annual aerial inputs assume that deposition takes place at a constant rate which is clearly not the case. The deposition, as discussed earlier in chapters 2 and 3, will be affected a number of factors, the most important of which are the wind direction, wind speed and stability.

TABLE 7.1 Estimated daily metal inputs to the Severn using various interpolation methods and AERE Harwell blocking method

Metal	Linear Interp. Biweekly kgday^{-1}	(A)Linear Interp. Total kgday^{-1}	Ln Interp. kgday^{-1}	Log Interp. kgday^{-1}	Sqrt. Interp. kgday^{-1}	AERE Harwell 1983 kgday^{-1}	AERE Harwell method 1989/90 kgday^{-1}
Cd	1.46	1.52	0.85	0.84	1.12	20.3	3.71
Cu	11.01	9.87	8.64	8.68	9.48	104.8	19.17
Cr	1.97	1.97	1.94	1.93	1.94	N.D.	2.17
Ni	2.98	2.87	2.75	2.80	2.82	72.0	3.46
Pb	119.40	104.78	57.22	62.28	73.58	428.5	259.40
Zn	178.72	149.73	97.14	96.07	114.86	5595.4	320.22
Al	-	0.31	0.31	0.31	0.33	N.D.	0.49
Area km^2	2250	2250	2250	2250	2250	2250	2250

TABLE 7.2 Estimated values expressed as a percentage of linear interpolated results (A)

	A	% of A	% of A	% of A	% of A	% of A
Cd	100	55.9	55.2	73.7	1355.59	244.1
Cu	100	87.8	87.9	96.0	1197.6	194.2
Cr	100	98.5	97.9	98.5	-	110.5
Ni	100	95.8	97.6	98.3	2508.7	120.6
Pb	100	54.61	59.4	70.2	409.0	247.6
Zn	100	64.8	64.2	76.7	3737.0	213.9
Al	100	100	100	106	-	158.1

TABLE 7.3 Estimated annual metal inputs to the Severn using various interpolation methods and AERE Harwell blocking method

Metal	Linear Interp. Biweekly $kgyr^{-1}$	(A) Linear Interp. Total $kgyr^{-1}$	Ln Interp. $kgyr^{-1}$	Log Interp. $kgyr^{-1}$	Sqrt. Interp. $kgyr^{-1}$	AERE Harwell 1983 $kgyr^{-1}$	AERE Harwell method 1989/90 $kgyr^{-1}$
Cd	532.9	554.8	310.25	306.6	408.8	7409.5	1354.15
Cu	4018.7	3602.6	3153.6	3168.2	3460.2	38252.0	6997.1
Cr	719.1	719.1	708.1	704.5	708.1	N.D.	792.04
Ni	1087.7	1047.6	1003.8	1022.0	1029.3	26280.0	1262.9
Pb	43581.0	38244.7	20885.3	22732.2	26856.7	156402.5	94681.0
Zn	65232.8	54651.5	35456.1	35065.6	41923.9	2042321.0	116880.3
Al	-	113.15	113.15	113.15	120.5	N.D.	178.9
Area km^2	2250	2250	2250	2250	2250	2250	2250

7.2 Comparison of interpolation methods

Tables 7.1 - 7.3 show the differences in the interpolation methods used to generate a deposition surface of metals to the Severn estuary. Of the methods used, linear interpolation produces the highest estimates of daily and annual deposition to the estuary for all the metals except Al. The highest Al deposition values were generated by using the square root interpolation. The square root values are generally the next highest when compared to linear interpolation (between 70 and 99% of A, Table 7.2) followed by the $\log_{10}$ and natural log interpolation which produce similar results (55-98% of A).

Distance decay curve simulation as discussed in section 6.3 suggested that Log_{10} interpolation would give the most reliable estimates of deposition for Cd to the Severn estuary. The final estimate for Cd using this method generated the lowest deposition values as it did for Cr and Zn. From table 7.2 it can be seen that the interpolation methods produce similar estimates for Cd, Pb and Zn in proportion to linear interpolation although their absolute values are quite different. This suggests that the metals may behave in a similar manner and that their principal source area is in the Avonmouth area. Cu, Ni and Cr deposition also appear to behave in a similar manner with comparable values being obtained by all methods of interpolation. This suggests that, although a proportion of these metals emanates from the Avonmouth area, the metals have other sources within the Severn Estuary such as the Swansea Bay area and the industrial areas of South Wales.

In order to check the methods of interpolation for Ni, Cr and Cu distance decay simulations showing the estimated deposition with increasing distance from Avonmouth for Ni were produced. These are shown in figures 7.1.1 - 7.1.4 and demonstrate that there is a source of Ni emission into the estuary which has a maximum value between 20-30km from Avonmouth. Nickel deposition rapidly tails off after this potential source area with increasing distance out into the Bristol channel. The best straight line fits, after the peak, are produced by the Log_{10} (r= -0.881) and natural Log methods (r = -0.841) of interpolation although the fit is not as good as that produced by the Cd plot (Fig 6.2). Linear interpolation and interpolation of square root transformed data do not produce any sort of straight line fit (linear r = -0.745 , sqrt r = -0.742). It must therefore be concluded that the Log_{10} and Log_e transformations will produce the most reliable estimates for Ni as well Cr and Cu which produce comparable proportions of deposition when compared to linear interpolation. Thus the most reliable estimates for deposition to the Severn estuary for each of the metals is as follows: Cd 0.84 $kgday^{-1}$, Cu 8.64 - 8.68 $kgday^{-1}$, Cr 1.94 - 1.93 $kgday^{-1}$, Ni 2.75 - 2.8 $kgday^{-1}$, Pb 62.28 $kgday^{-1}$, Zn 96.07 $kgday^{-1}$ and Al 0.31 $kgday^{-1}$.

The behaviour of Al on the basis of these interpolation methods does not correspond to any of the other metals but is unlikely to have a specific source area as it is associated with wind

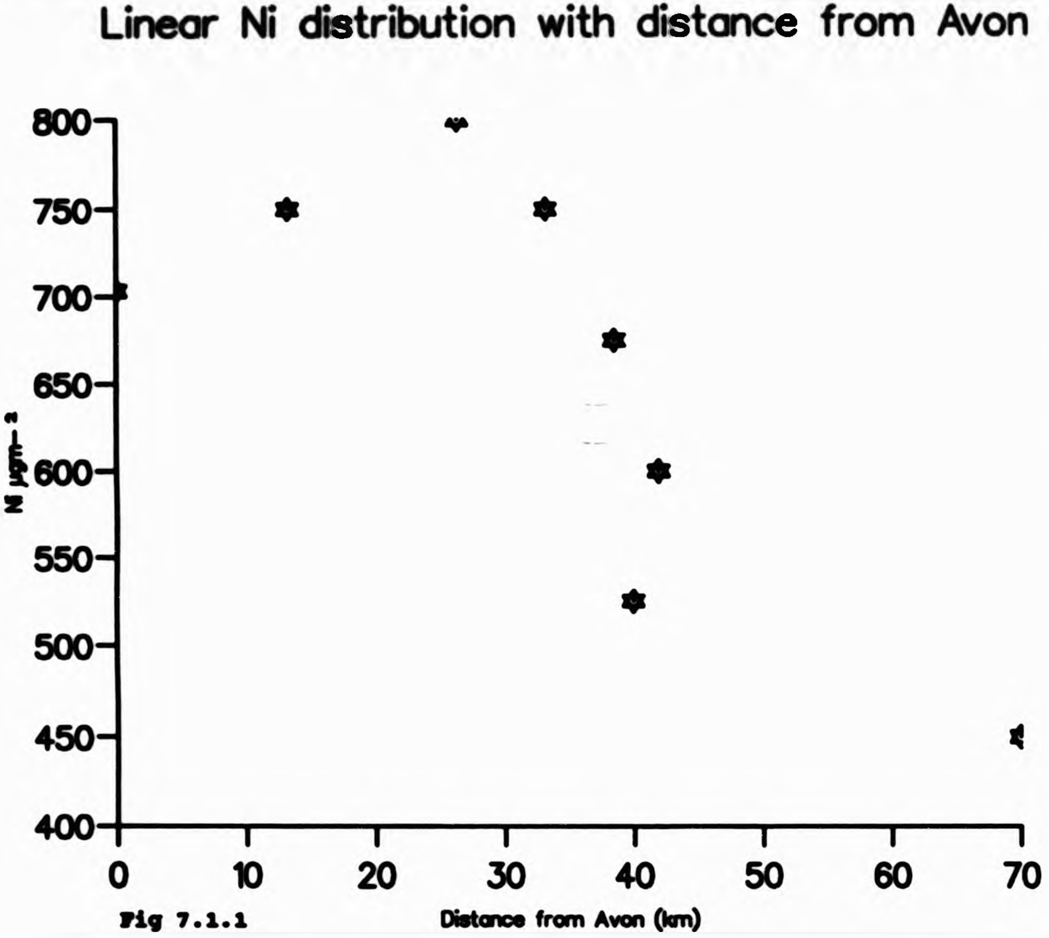

Linear Ni distribution with distance from Avon
Ni µgm-3
800
750
700
650
600
550
500
450
400
0
10
20
30
40
50
60
70
Distance from Avon (km)

Fig 7.1.1

Logten Ni distribution with distance from Avon

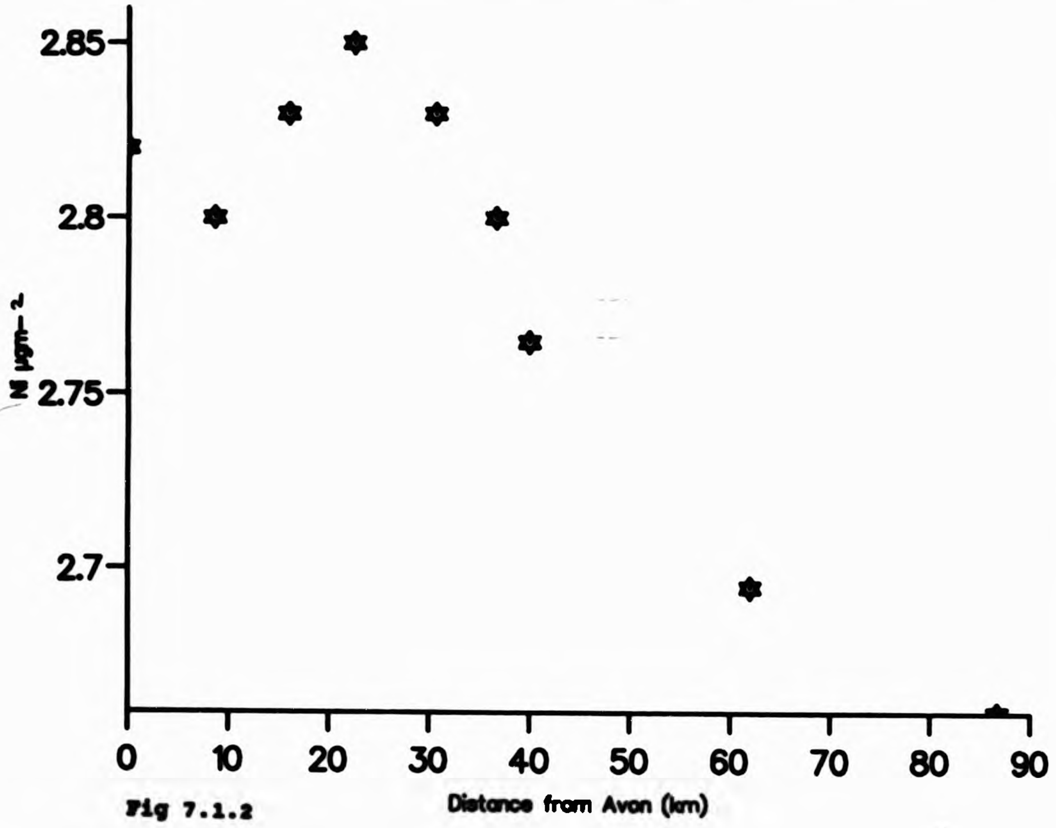


Fig 7.1.2

Ln Ni distribution with distance from Avon

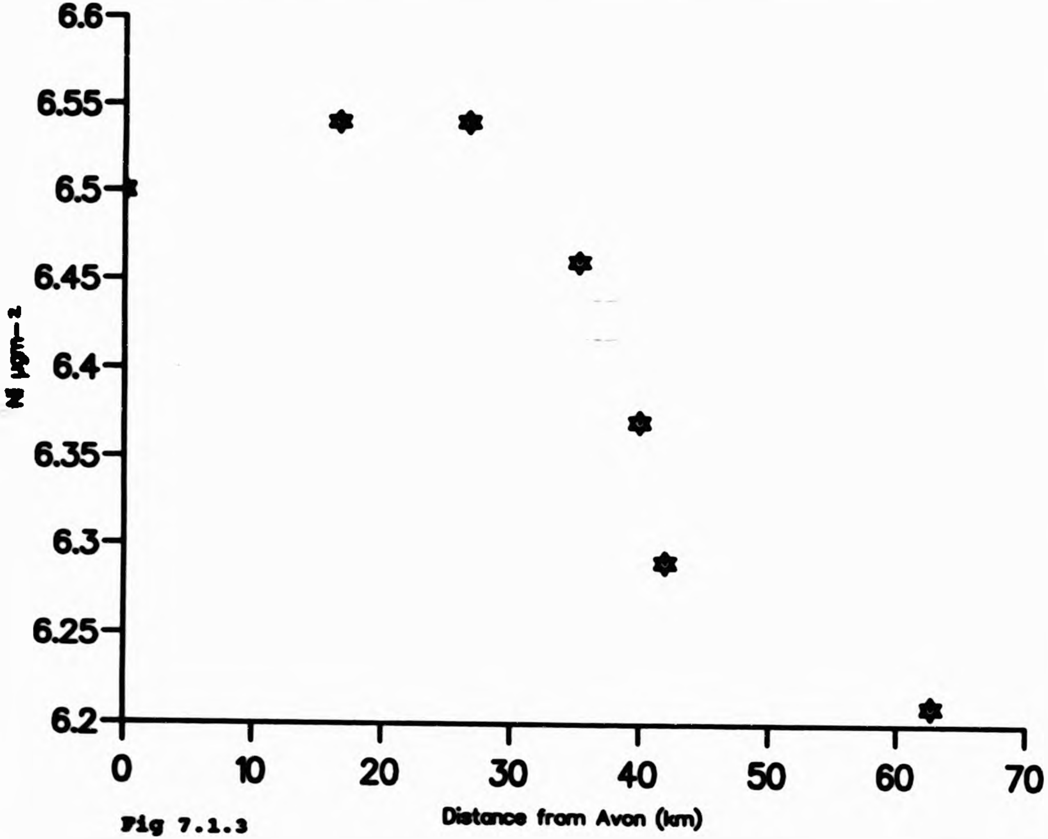


Fig 7.1.3

Square root Ni distribution with distance from Avon

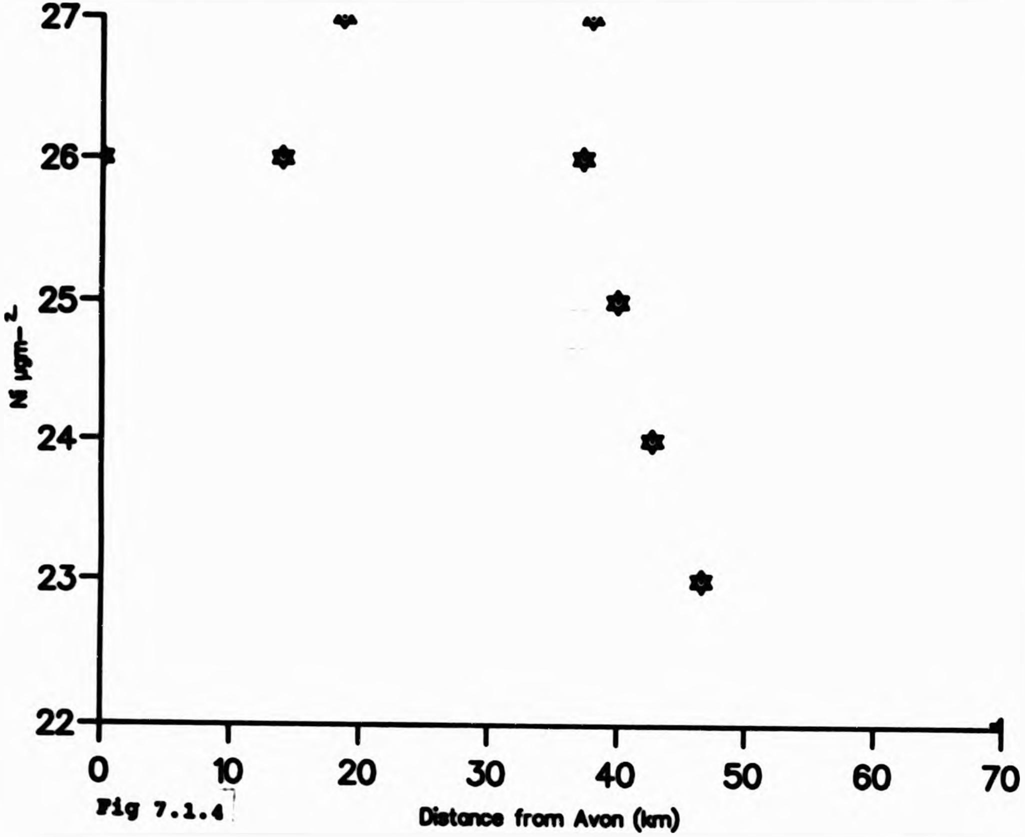


Fig 7.1.4

blown soil and dust. The distribution of Al is therefore more likely to be associated with wind speed and direction, particularly those winds that have crossed land masses. This distribution is reflected to a certain extent by the plots produced for Al by the various interpolation methods in Figs 6.5.7, 6.6.7, 6.7.7 and 6.8.7 although the area of greatest Al deposition appears to be the Avonmouth area.

7.3 Comparison of plots produced with and without Flat Holm data

An exercise to compare the actual values measured in the centre of the Severn Estuary with those predicted by the mapping and interpolation by UNIMAP was carried out by plotting the metal distributions without the Flat Holm data by linear interpolation. The resulting plots are shown in Figures 7.2.1 - 7.2.7.

When compared to the plots shown in Figures 6.5.1 - 6.5.7 these plots show that the distributions for Cd, Cu, Pb and Zn are identical to the plots produced with the Flat Holm data included. The plots for Al are almost identical. These results are probably a result of the Avonmouth area dominating the distribution patterns for these metals.

A clearer comparison can be seen between the plots for Cr and Ni (Figs 6.5.3 and 7.2.3, 6.5.4 and 7.2.4). The interpolation technique estimates that deposition on Flat Holm for Cr would be $360\mu gm^{-2}$ whereas the actual value was $435\ \mu gm^{-2}$. The values

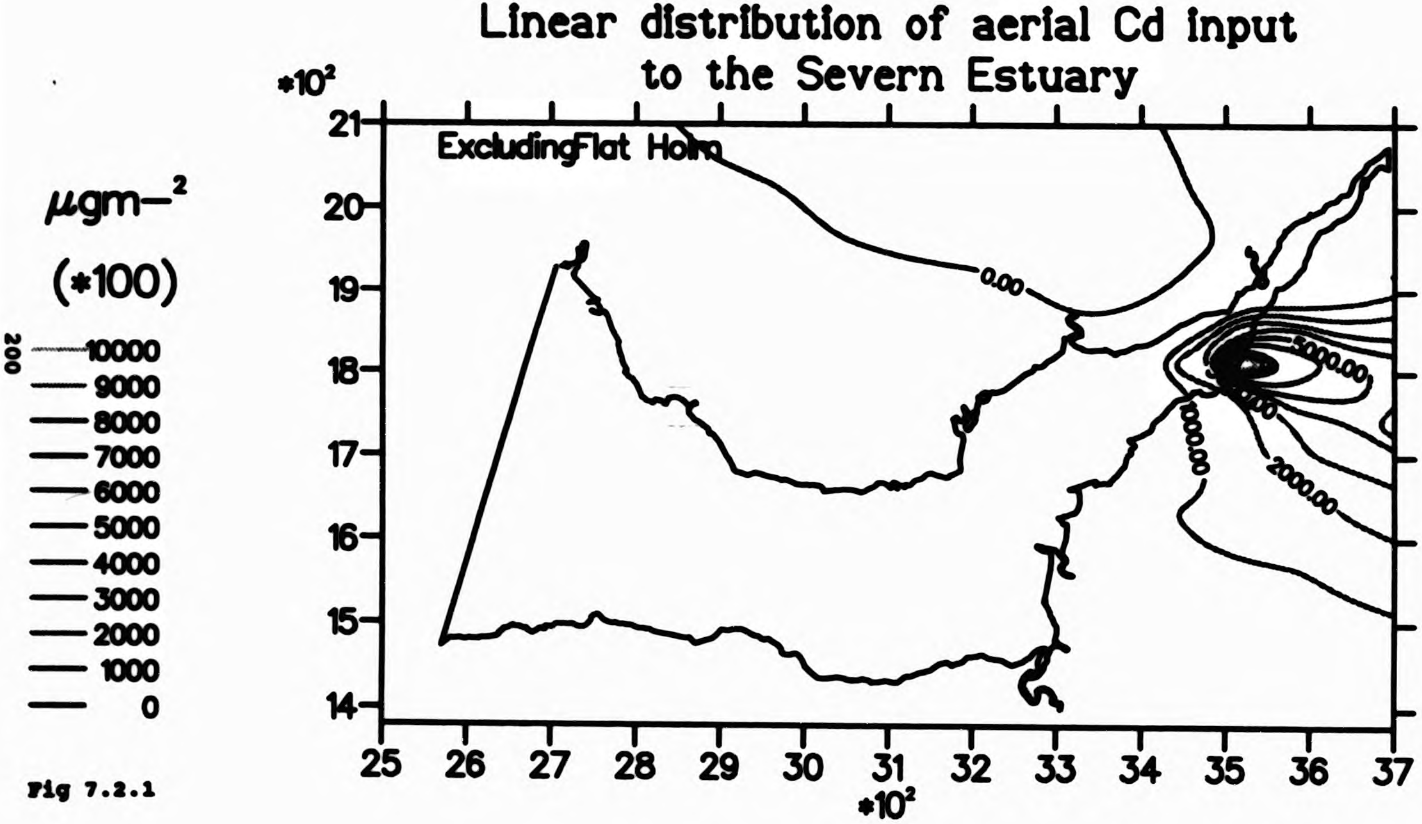

Linear distribution of aerial Cd input
to the Severn Estuary
ExcludingFlat Holm
μgm⁻²
(*100)
200
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
0.00
1000.00
2000.00
5000.00

Fig 7.2.1

Linear distribution of aerial Cu input
to the Severn Estuary

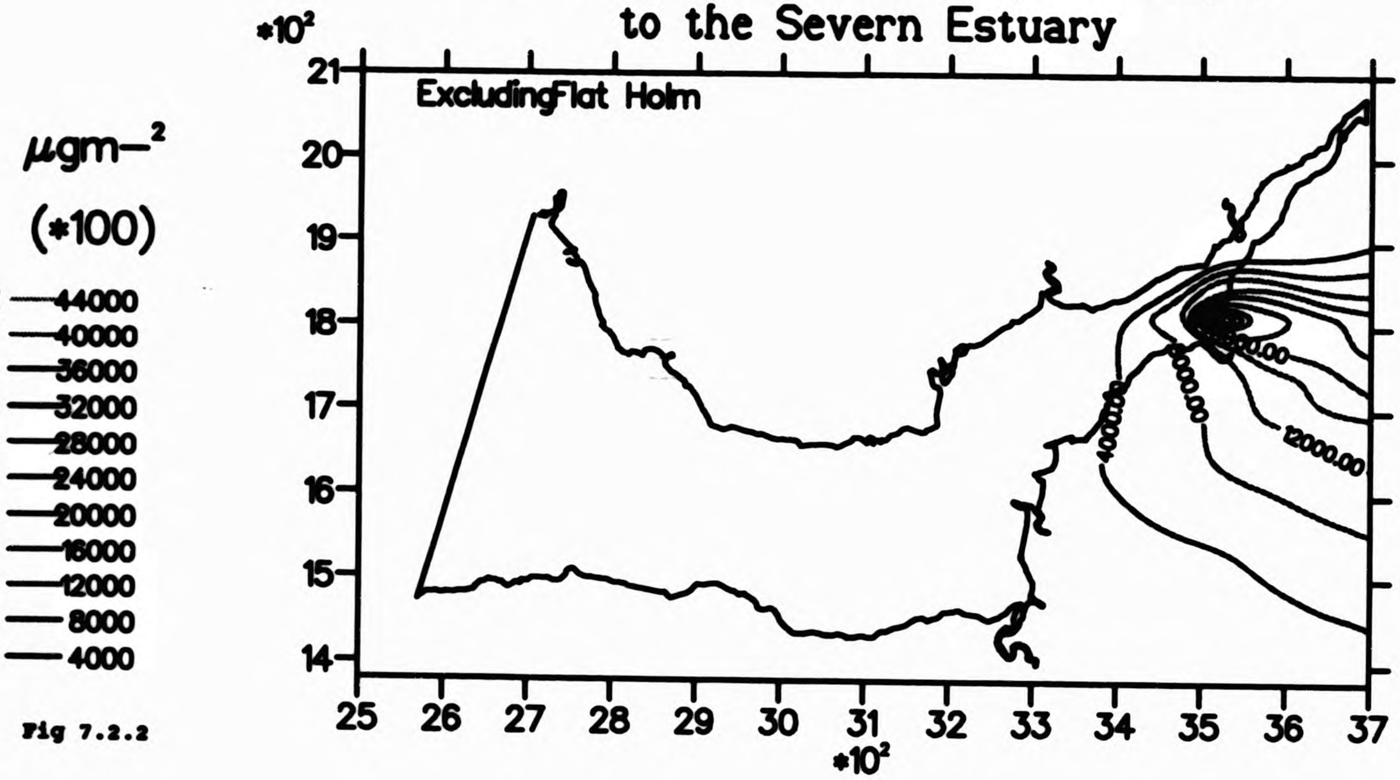


Fig 7.2.2

Linear distribution of aerial Cr input to the Severn Estuary

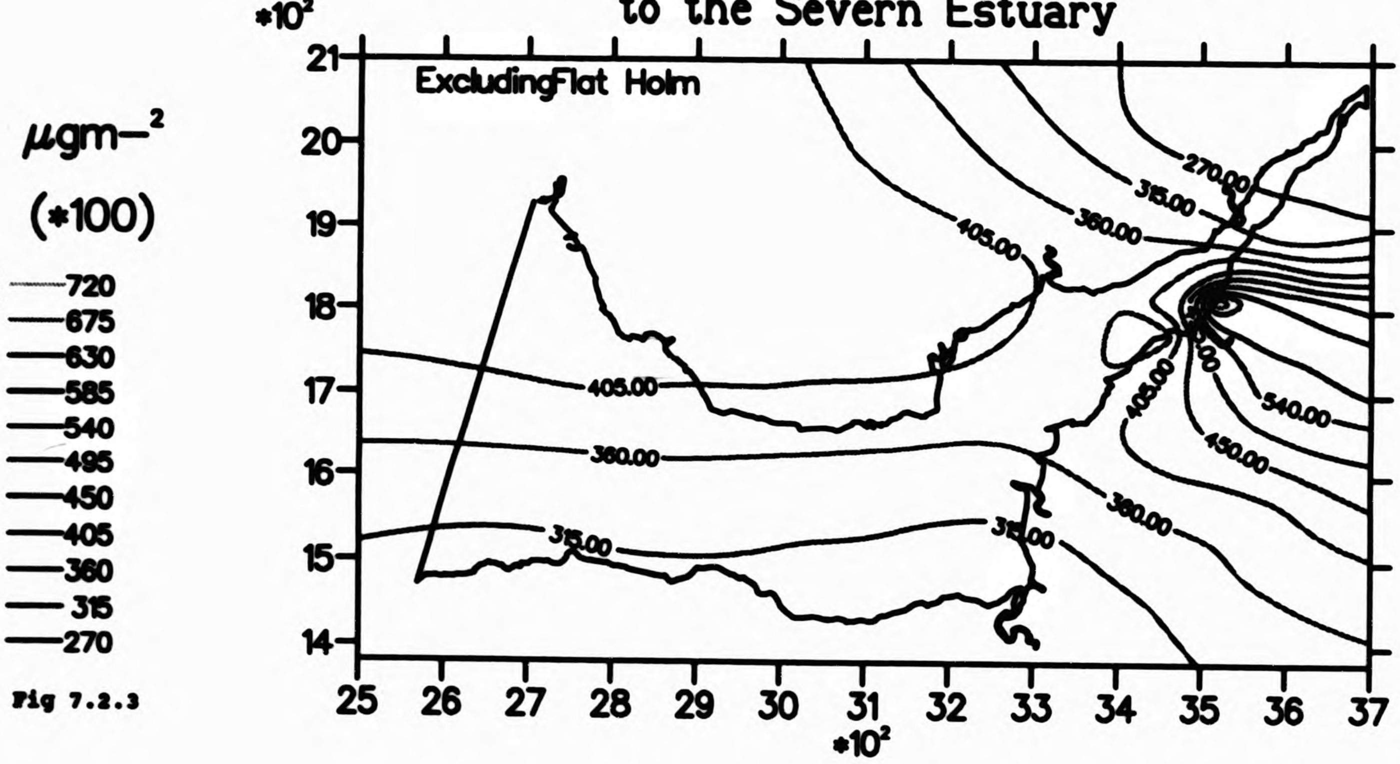


Fig 7.2.3

Linear distribution of aerial Ni input to the Severn Estuary

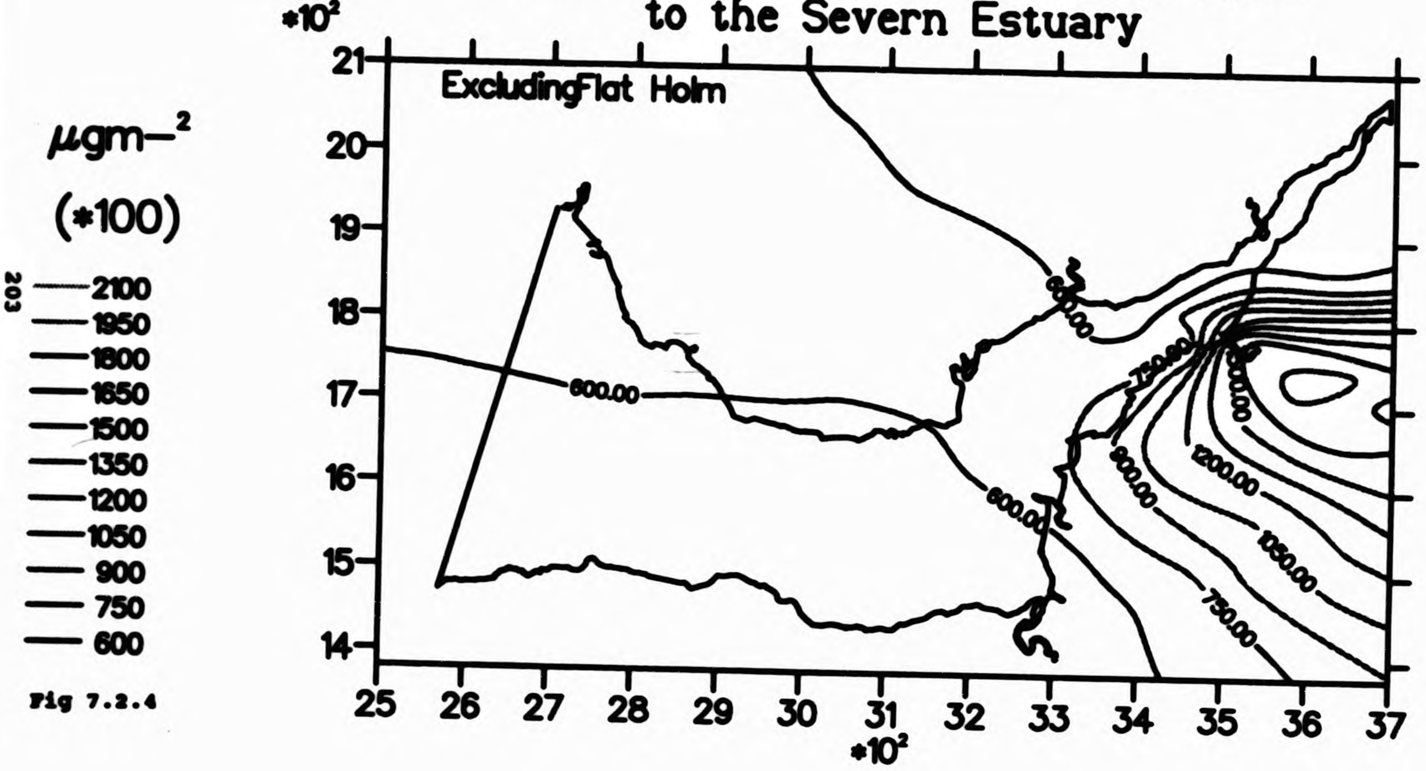
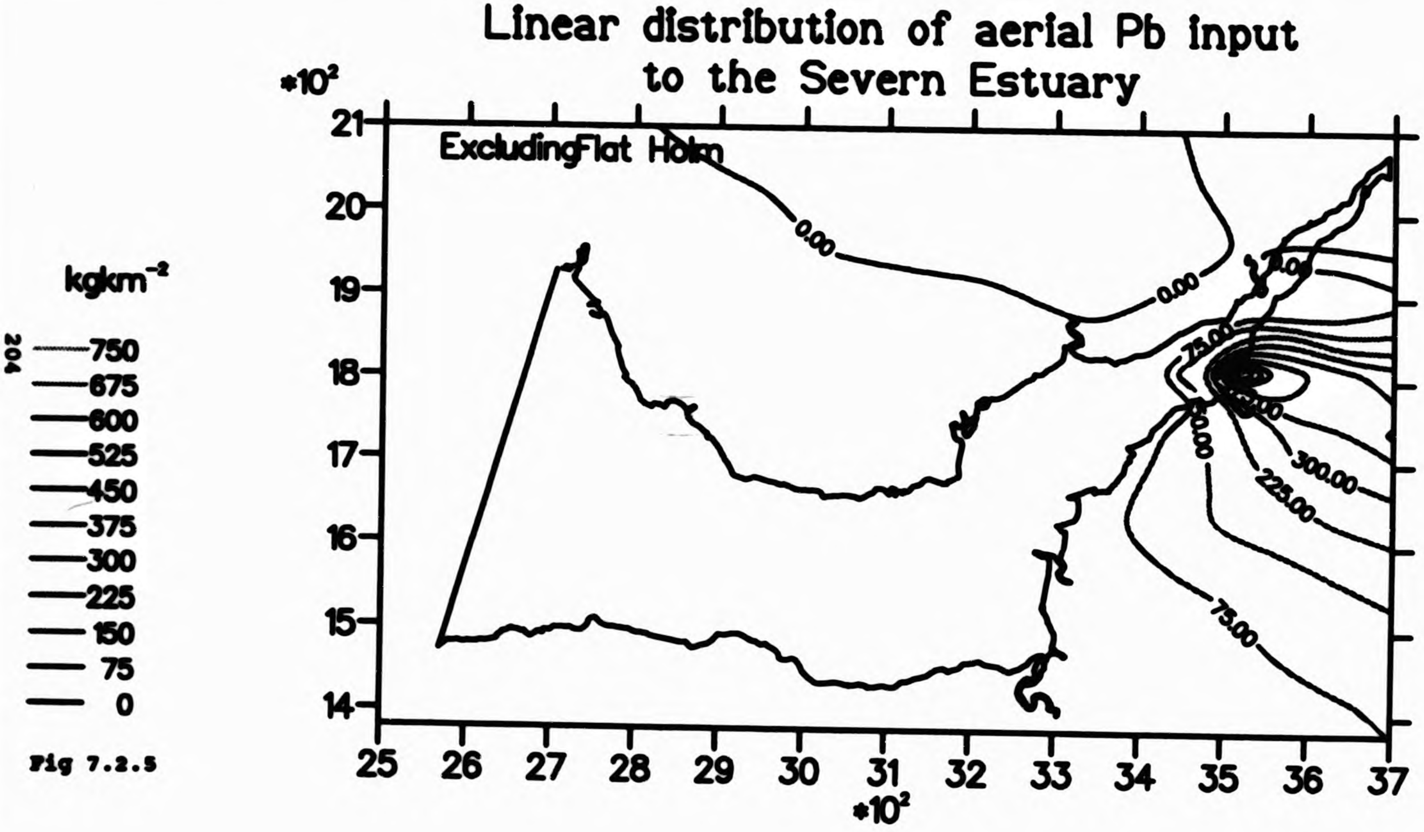


Fig 7.2.4


Linear distribution of aerial Pb input to the Severn Estuary

Excluding Flat Holm

Fig 7.2.5

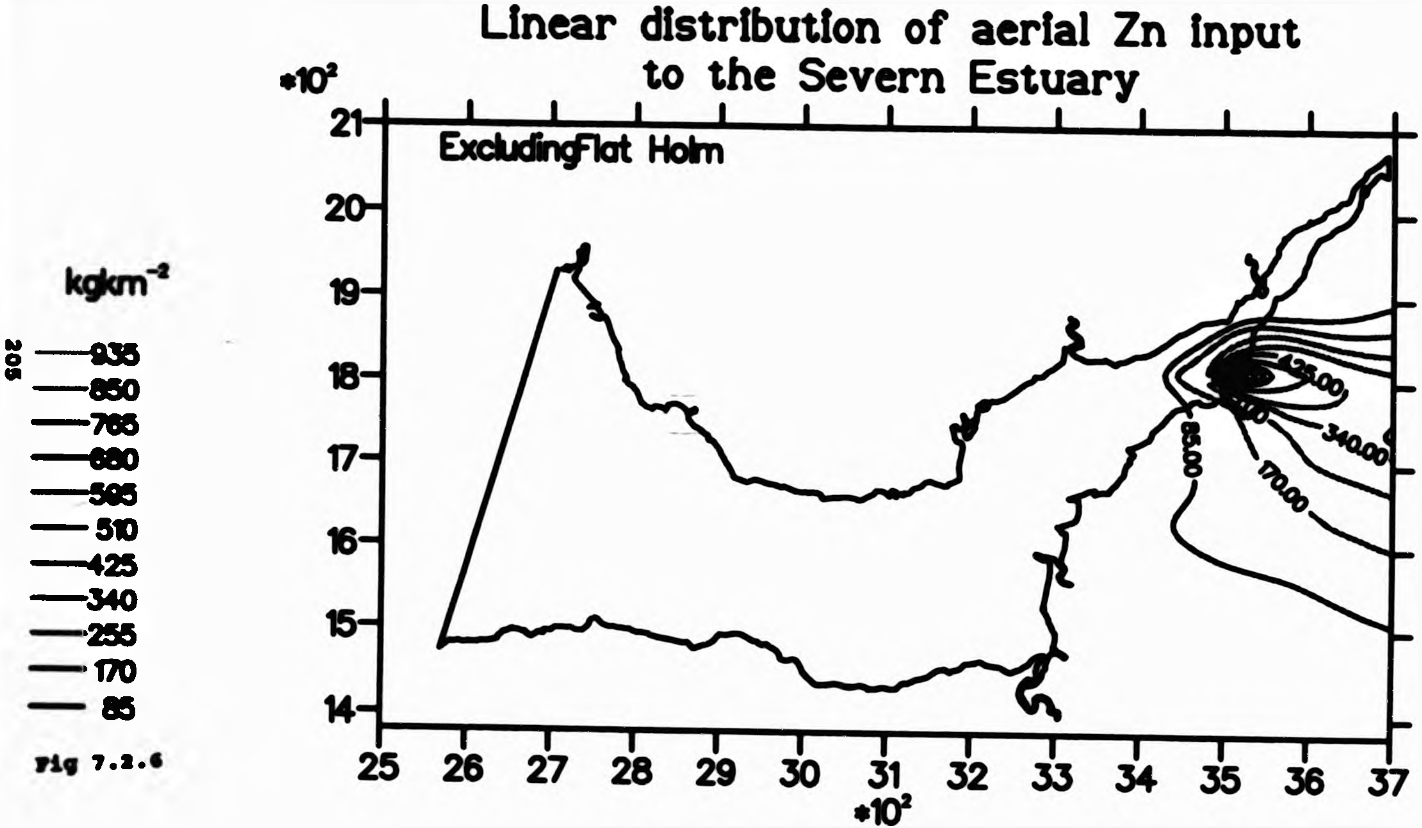

Linear distribution of aerial Zn input to the Severn Estuary

Fig 7.2.6

Linear distribution of aerial Al input to the Severn Estuary

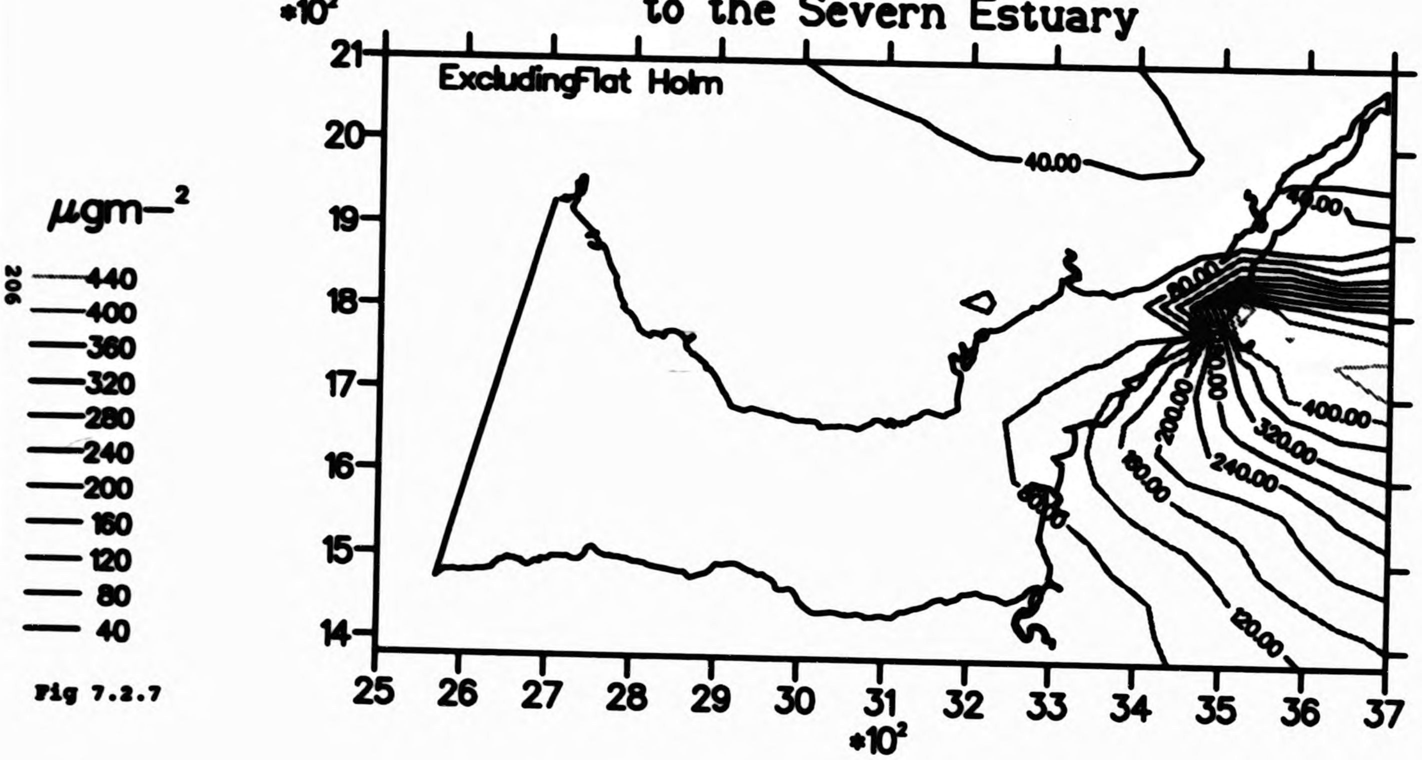


Fig 7.2.7

produced for Ni were 600 μgm^{-2} by interpolation and the actual value was 484.7 μgm^{-2}. Thus, the interpolation method, including all data, underestimates the deposition value for Cr and overestimates the Ni deposition in the centre of the estuary.

As a result of the dominance of the Avonmouth area as an emission source no comparison can be made for Cd, Cu, Pb, Zn and Al but when considering the results it must be noted that the estimated loadings for Cr might be underestimated by up to 17% and overestimated for Ni by up to 24%. These results were, however, produced by the linear interpolation method which is not as reliable as using transformed data to produce the plots. Owing to time constraints it has not been possible to produce comparative plots for the Severn estuary, without Flat Holm data, using the transformed data. If these plots were available the variations between the plots might be quite different.

7.4 Comparison of current to earlier estimates of deposition

The deposition estimates for Cd, Cu, Ni, Pb and Zn derived by using the isoplething technique when compared to the earlier results estimated by AERE Harwell (Tables 7.1-7.3) show a very large decline. This decline ranges from two orders of magnitude in the case of Cd and Zn and one order of magnitude for Cu, Ni and Pb. Al and Cr concentrations were not determined in the 1983 survey of aerial inputs to the estuary so no comparison can be made. These comparisons are made on the basis of the most reliable estimates from the various interpolation methods as outlined in the section above and area corrected estimations for the AERE Harwell technique.

The data obtained in the 1989/90 survey were used to give an estimate of deposition to the Severn estuary using AERE Harwell's blocking technique. These estimations still give up to an order of magnitude decrease in all cases except Ni of the estimated aerial inputs but range from 1.2 times (Ni) to four times (Cd and Pb) as large as the estimates made by using isoplething.

Clearly the use of an improved technique of estimating the atmospheric input from point source data gives a more reliable assessment of the input which takes into account the behaviour of deposition away from a source. The isoplething technique cannot, however, account for the large decreases alone.

The larger area of the Severn estuary used in the previous survey was a possible factor in the reduction of deposition estimates in the current survey. The correction for this (section 6.4) showed that the decreases in deposition estimates using the blocking technique were small (<12%) although possibly significant for Ni (12%) and Cu (11%). The 28% reduction in area was in the outer estuary (Fig 4.1) where inputs to the surface from the local emission sources would be expected to be lower than those to the inner estuary because of greater distances from sources. This explains why the estimates in deposition did not decrease proportionally with the decrease in area and why this cannot explain the decreases observed in deposition to the Severn estuary over the last decade.

The sample collection procedures and equipment used in the 1983 survey were not standardised with each Water authority being responsible for the servicing of equipment as well as sample collection and analysis that fell within their region. It is possible that some contamination was experienced with their samples which may have contributed to the very high values that were derived for the survey. This problem was largely eliminated in the current project by using standard equipment, collecting methods and all analysis.

Therefore it must be concluded that the improvements in both the method of sample collection and analysis combined with new extrapolation techniques as well as significant decreases in contaminant emissions that have all combined to give the lower estimates for aerial inputs to the Severn.

The apparent decline in deposition of metals to the Severn estuary, as opposed to improvements in collection and analytical methodologies, is backed up by two recent reports on water quality in the estuarine waters. Apte et.al., 1989 in a survey of dissolved trace metals in the surface waters of the Severn found that concentrations were lower than those reported by Owens (1984) in a special edition of the Marine Pollution Bulletin. The particular metals analysed were Cd, Cu, Cr, Ni, Pb, Zn and arsenic (As) and all except As and Cr, which were not measured by Owens, showed large decreases in concentration. Pb concentrations in the water, for example, were in the majority below the detection limit of $0.3\mu gl^{-1}$. In Owens' study atmospheric Pb and Zn were claimed to contribute 60% and 40% respectively to the total metal input of the estuary. Apte et.al. suggested that atmospheric deposition of dissolved metals was far less important than previously thought although particulate metal may still have been a significant input.

The second, more recent study of water quality in the Severn was carried out by the NRA Welsh Region (Brown, 1991) and this suggested that dissolved concentrations of Zn, Pb, Cd and Mn had decreased. The decreases recorded were not as substantial as those that had been reported by Apte et.al. and this was tentatively attributed to differences in analytical techniques. Overall copper concentrations had increased slightly since the period 1975-1979 with a peak reached between 1979-82. The estimates of aerial deposition attained in this study suggest, however that the contribution of the atmosphere has decreased considerably since 1982/3 and this is in agreement with both Apte et.al. and Brown who suggest that the majority of Cu in the Severn is discharged via riverine input.

7.5 Relationship between Atmospheric and land based metal inputs to the Severn Estuary.

In the absence of contemporary inputs data to the Severn Estuary via land-based discharges an estimation of the contribution of atmospheric metal inputs collected in this survey has been made with data collected in earlier S.E.J.C sampling programmes. This information was summarised by Owens (1984) and a modified summary to include current aerial inputs information is shown in Table 7.4. The estimation of 1989/90 atmospheric input was calculated by holding the land-based estimates constant and subtracting the 1978/9 estimate for aerial inputs. The current estimates based on the most reliable interpolation methods as discussed in section 7.2 were then added in to the total and a new percentage atmospheric input calculated. The 1978/9 aerial input estimates have been included in Table 7.4 for comparative purposes.

From Table 7.4 it can be seen that the contribution of metals to the Severn Estuary have decreased by an order of magnitude for all metals except Pb. Nonetheless, the contribution of Pb has decreased by 80% . The data reported for all inputs was collected between 1977 and 1979 and recent reports suggest that the overall water quality of the Severn Estuary has improved (Apte et.al.,1990, Brown 1991). It is probable, then that the contributions of rivers and streams, domestic sewage, industrial effluent and sludge dumping have also decreased. Therefore, it is unrealistic to state that the current estimations of the

Table 7.4 Contributions (%) from rivers, discharges, atmospheric deposition and sludge to total input of TOTAL metal contaminants to the Estuary. (After Owens, 1984)

Metal	Rivers and Streams %	Sewage %	Ind. Eff. %	Sludge dumping %	Aerial Input 1978/9 %	Total Input 1978/9 $kgday^{-1}$	Aerial Input 1989/90 %	Total Input 1989/90 $kgday^{-1}$
Cd	32.4	12.5	32.6	1.4	21.1	61.6	1.6	49.4
Cu	54.2	8.6	15.8	2.4	19.0	621.0	1.7	511.7
Cr	-	20.8	55.1	14.9	9.4	224.0*	0.9	201.8
Ni	75.9	7.3	3.3	1.6	11.9	464.0	0.7	411.6
Pb	16.9	4.5	18.5	1.9	57.8	1150.0	11.4	547.6
Zn	30.3	8.8	17.8	0.9	42.4	5160.0	3.1	3078.6

* Excludes input from rivers and streams.

atmospheric input contribution are correct. Thus the results of this survey highlight the need for a new total inputs budget to the Severn estuary to be performed in order to place more accurately the aerial inputs of metals in the wider context of all inputs.

7.6 Sources of metal deposition to the Severn estuary

The sources of metals deposited to the estuarine surface as collected in this survey are difficult to define owing to the lack of emissions knowledge in the local area as well as the sampling interval of two weeks during which considerable changes in meteorological conditions occur. However, some general inferences as to the source area can be made on the basis of the deposition patterns that were described over the whole sampling period. From both the plots for distribution (Figs 6.6.1 - 6.8.7) and the distance decay curves from Avonmouth (Figs 6.1-6.4 and Figs. 7.1.1 -7.1.4) as well as the estimations based on the methods of isoplething some patterns can be seen.

Avonmouth is clearly a very important source area for all the metals studied with elevated deposition values being recorded over the entire sampling period in this area. It is a particularly important source of Cd, Pb, Zn and Cu and to a lesser extent source of the remaining determinands Cr, Ni and Al. Pb values are also high all a round the estuary and these values can be attributed to the emissions from fuel combustion by vehicles using the extensive road network around the estuary. In the Avonmouth area there are two major emission sources of Cd, Pb and Zn as described in section 3.5.1; the Commonwealth Smelting plant and the Avonmouth Municipal Incinerator.

The Commonwealth Smelting plant in Avonmouth is the largest Zn, Pb and Cd smelting plant in the world and the only primary Zn smelter in the United Kingdom. Copper is also produced at the plant and is therefore likely to be a source of contamination of this metal to the Severn estuary (Hutton and Symon, 1986). The high concentrations previously reported of these metals are comparable to the estimates of deposition made in this survey.

Waste incineration has also been identified as the largest single source of atmospheric Cd in the United Kingdom (Hutton and Symon, op.cit) and the combination of both the smelting plant and the incinerator emissions in the Avonmouth area can explain the high concentrations of Zn, Cd, Pb and Cu seen in this survey. A peak in Cd concentrations in the estuarine waters was also observed by Apte et.al. (1990) just off the Avonmouth coast which confirms the importance of this area as a Cd source, via direct discharge as well as atmospheric pathways.

The concentrations of Al were generally elevated in the Avonmouth area compared to the rest of the Severn Estuary although no specific manufacturing process can be found to explain the levels here. Al is usually derived from wind blown dusts and its contribution to the Severn estuary is the smallest of all the metals analysed (Table 7.1) at 0.31 kgday^{-1}. The source of Al is likely to be derived from the soil surrounding the estuary and the distribution will be dependant on the prevailing wind direction. The higher concentrations recorded in the Avonmouth area may be a result of heavy industrial traffic disturbing and suspending soil particulates into the atmosphere.

Peaks in Al concentrations recorded in Bermuda were attributed to the transportation of Saharan dust under easterly conditions and agricultural soil disturbance on the east coast of the United States in the spring (Tramontano et.al., 1987). It is therefore possible that agricultural soil disturbance around the shore of the Severn estuary and the deposition of Saharan dust under southerly wind conditions are responsible for Al deposition to the estuary.

The distributions of Ni and Cr as produced by the isopleth plots showed quite different patterns to Cd, Cu, Pb ,Zn and Al in that the Avonmouth area did not appear to be such an important source area. The concentrations in the Avonmouth area were still elevated over the concentrations observed in the outer estuary but not to the same extent as the other metals. The plots for Ni showing concentration with increasing distance from Avon (Figs 7.1.1 - 7.1.4) showed a distinct peak in deposition at a distance of some 25-30 km downstream of the area.

In order to try and identify the sources for Ni and Cr to the estuary as well as secondary sources of the other metals an attempt was made to fit a model to the deposition patterns observed. This was achieved by taking the deposition values for each site, for each metal and plotting these against distance from Avonmouth. The data were then transformed by using Log_{10}, Log_e and square root calculations to produce the closest relationship possible between distance and deposition (i.e. the best straight line fit). The best fit that could be described was achieved by plotting the $\log_{10}$ ($r = 0.96$ for Cd) of the metal deposition value against the $\log_{10}$ of the distance from Avonmouth. These plots are shown in Figs 7.3.1 - 7.3.7. The regression line describing the best fit was then used to calculate the residual values. This was done in order to minimise the influence of the values recorded at Avonmouth thereby highlighting any other source areas of metals within the estuary. The residual value distributions were then plotted out over the estuarine surface using UNIMAP. These plots are shown in Figs. 7.4.1- 7.4.7.

The residual distributions of Cd shown in Fig 7.4.1 show that the inner and outer estuary are not a source area for the metal but the influence of the Port Talbot/Swansea Bay area show increasingly high residual values. This suggests that this area of the estuary is another source of Cd to the estuary although no specific emission sources are known. The patterns for Cu, Pb Zn and Al are very similar to those described by Cd and again

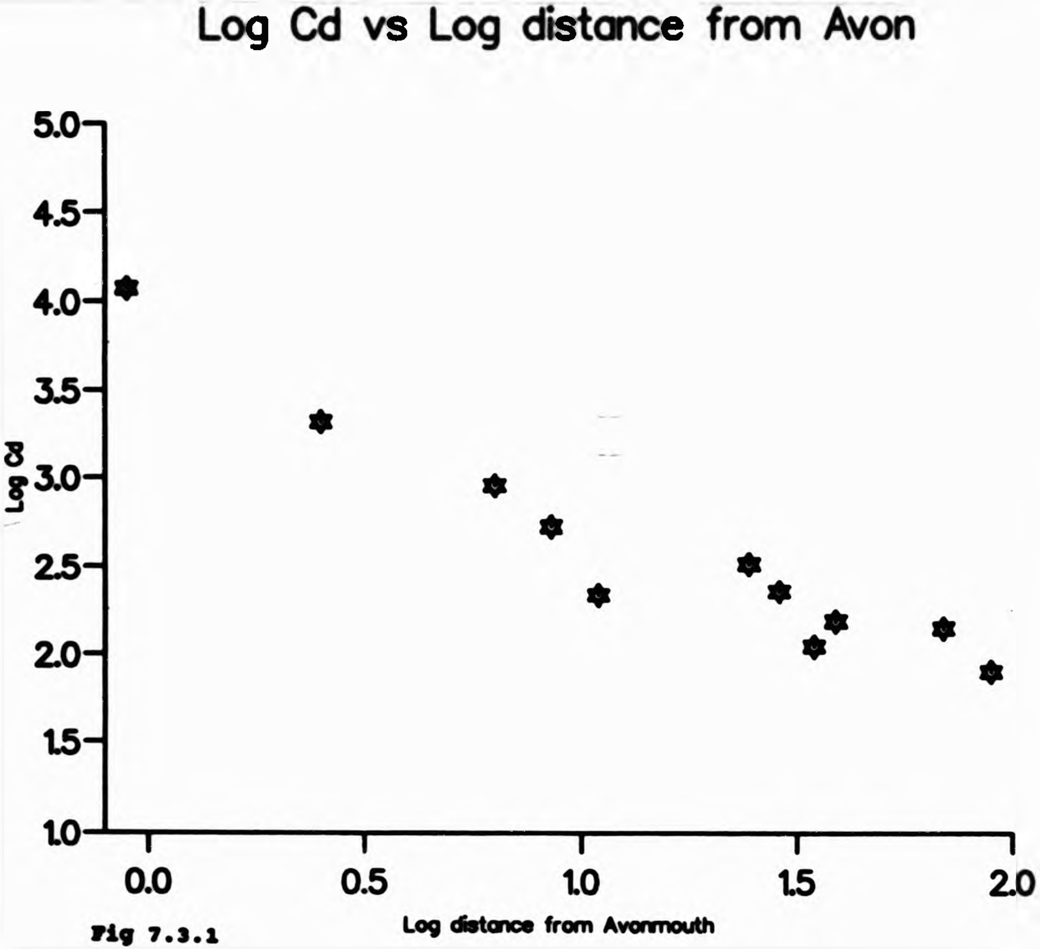

Log Cd vs Log distance from Avon
Log Cd
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.0
0.5
1.0
1.5
2.0
Log distance from Avonmouth

Fig 7.3.1

Log Cu vs Log distance from Avon

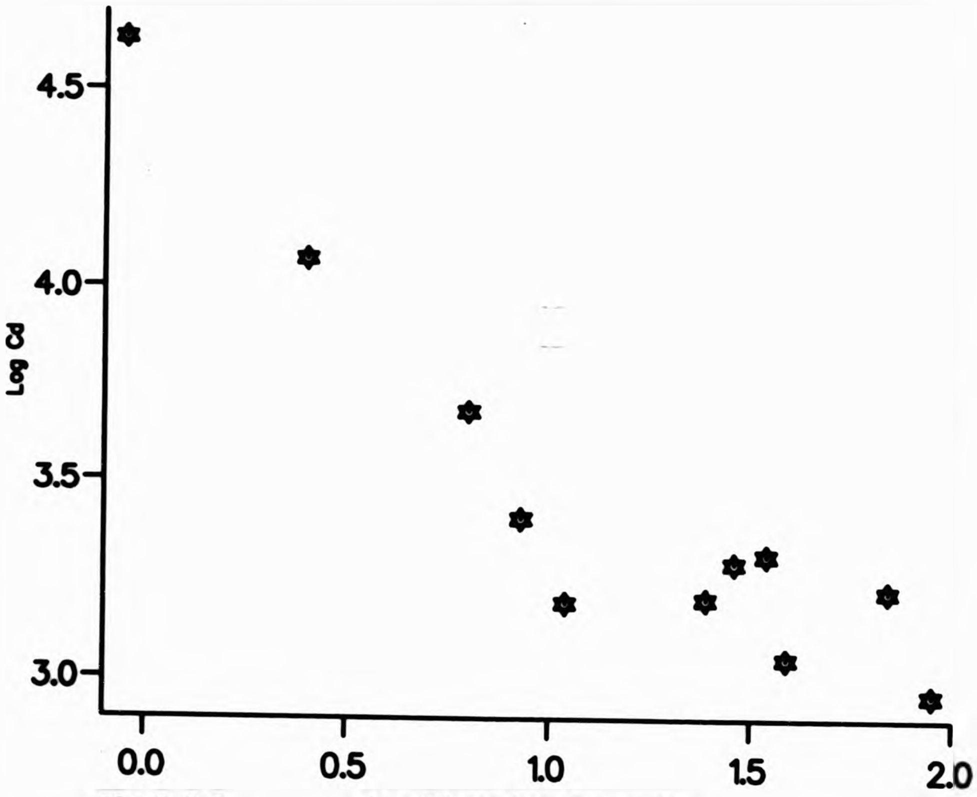


Fig 7.3.2

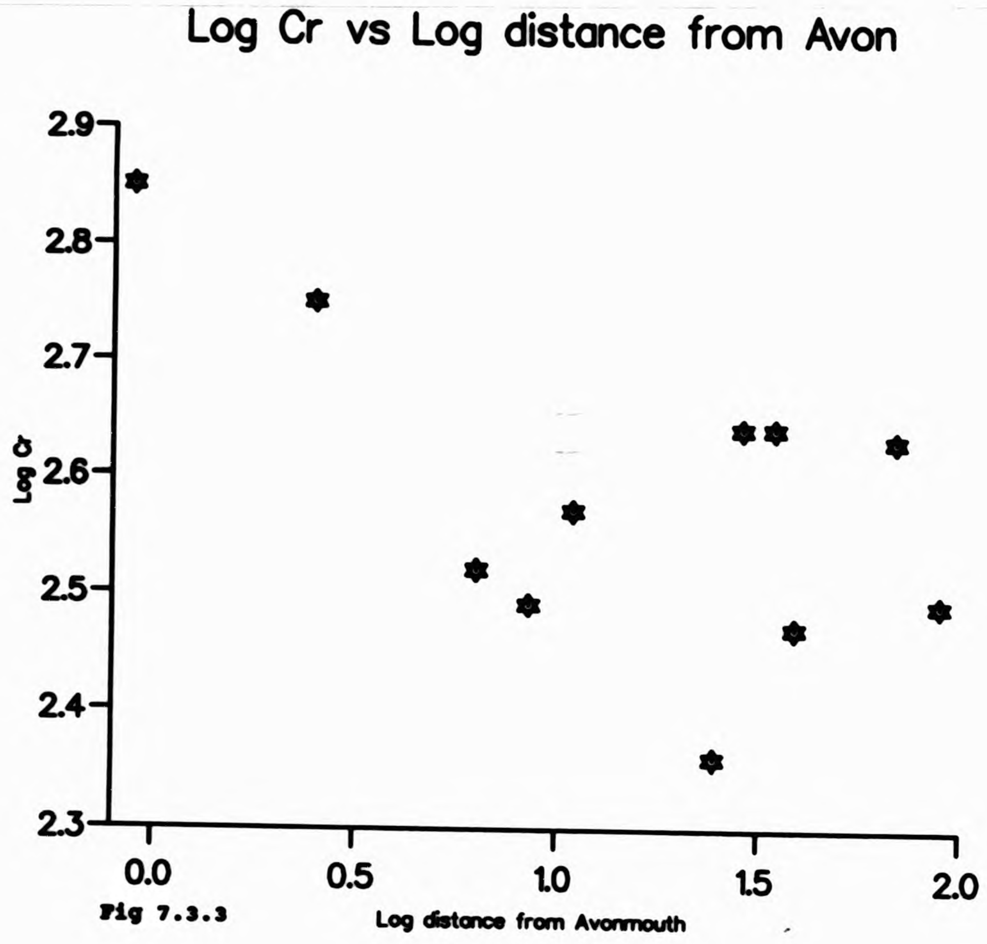

Log Cr vs Log distance from Avon
Log Cr
2.9
2.8
2.7
2.6
2.5
2.4
2.3
0.0
0.5
1.0
1.5
2.0
Log distance from Avonmouth

Fig 7.3.3

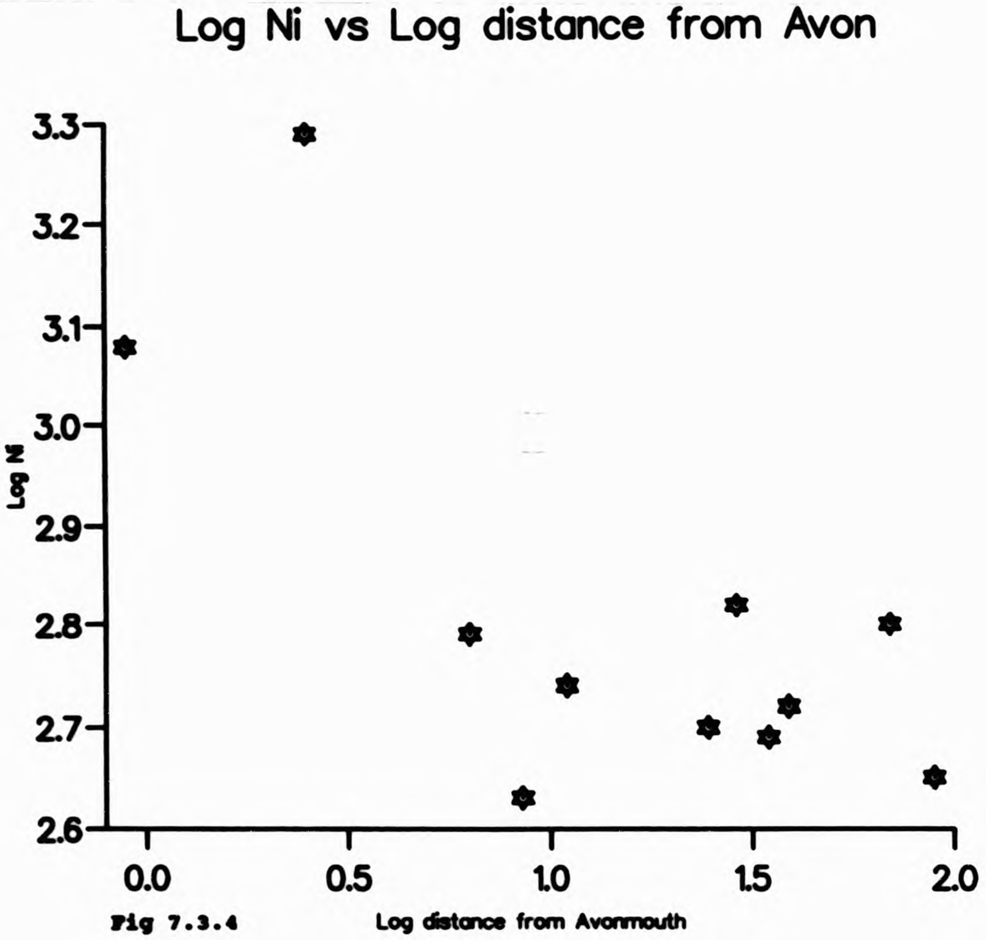

Log Ni vs Log distance from Avon
Log Ni
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
0.0
0.5
1.0
1.5
2.0
Log distance from Avonmouth

Fig 7.3.4

Log Pb vs Log distance from Avon

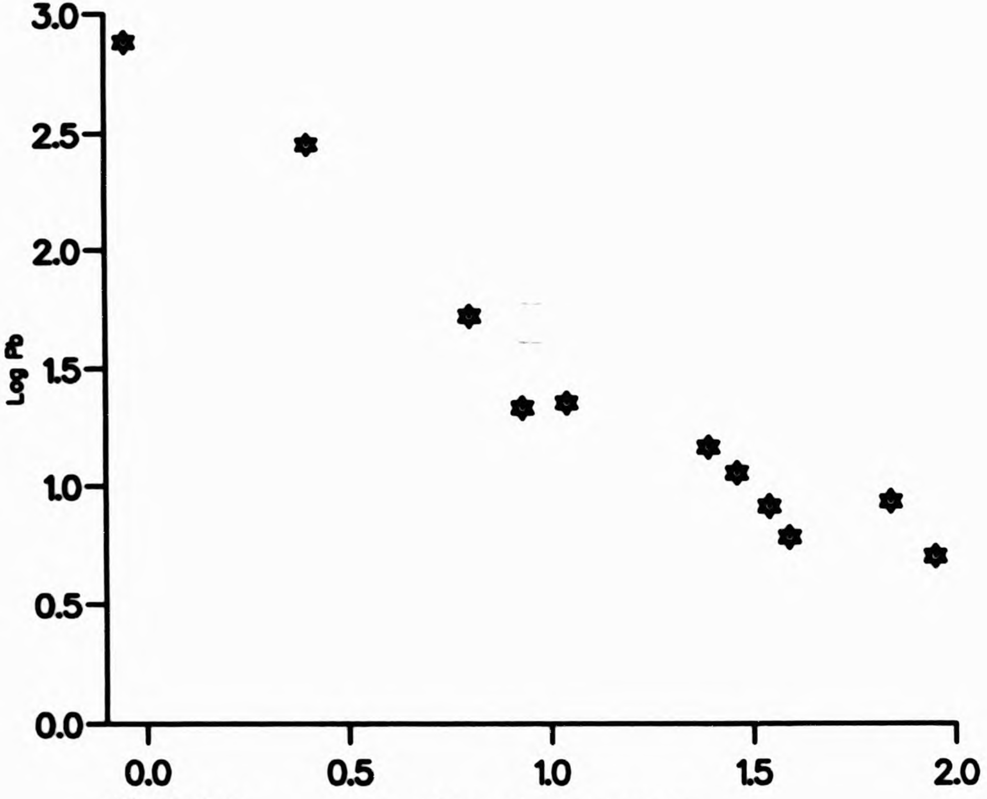


Fig 7.3.5

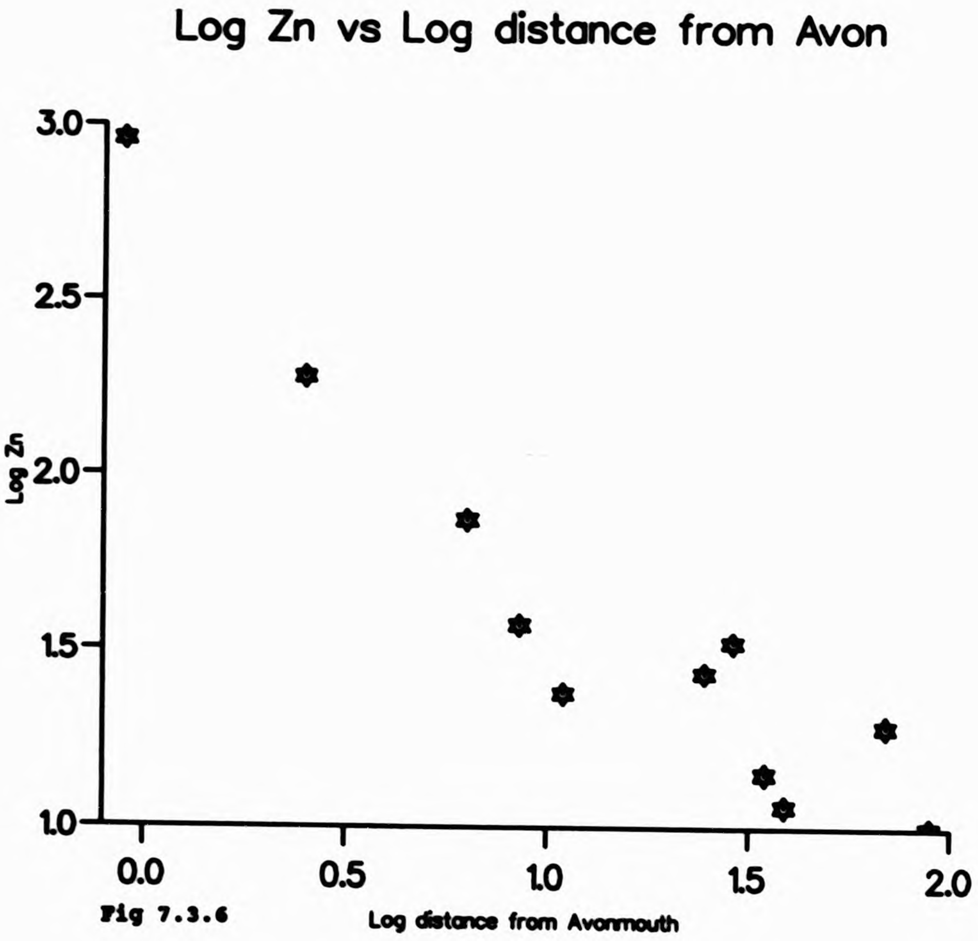

Log Zn vs Log distance from Avon
Log Zn
3.0
2.5
2.0
1.5
1.0
0.0
0.5
1.0
1.5
2.0
Log distance from Avonmouth

Fig 7.3.6

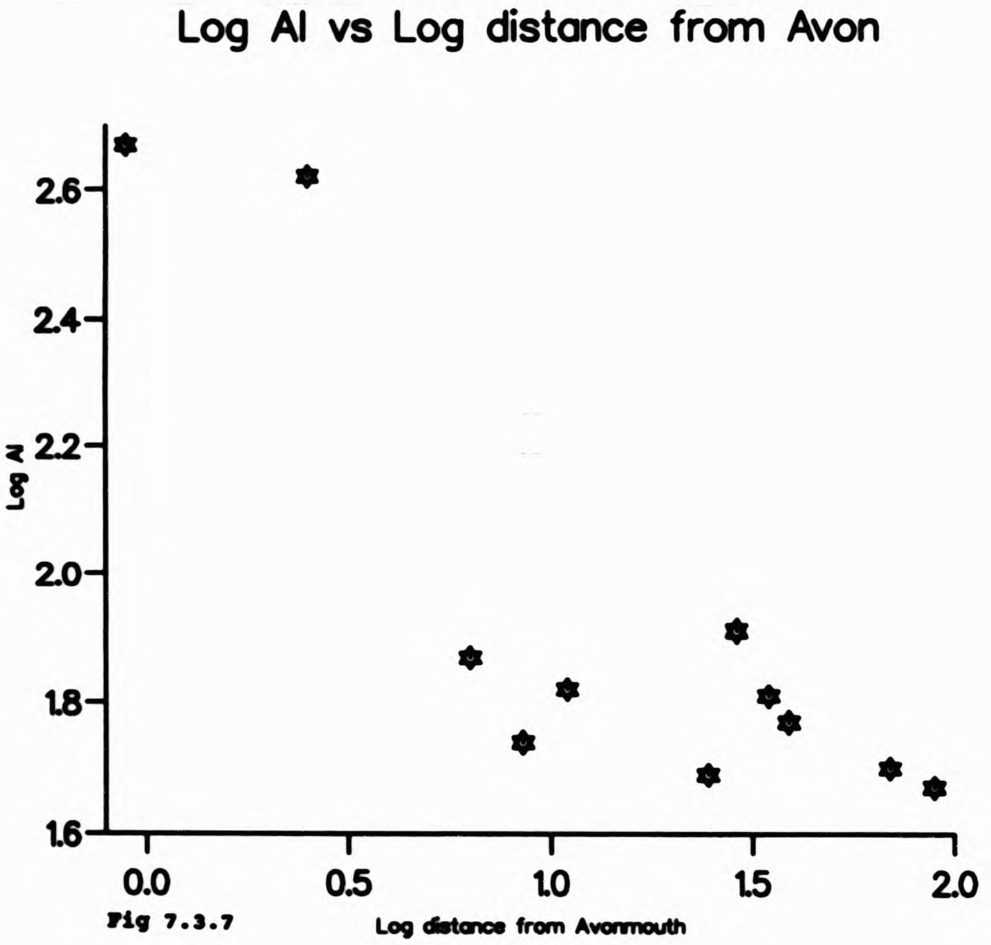

Log Al vs Log distance from Avon

Fig 7.3.7

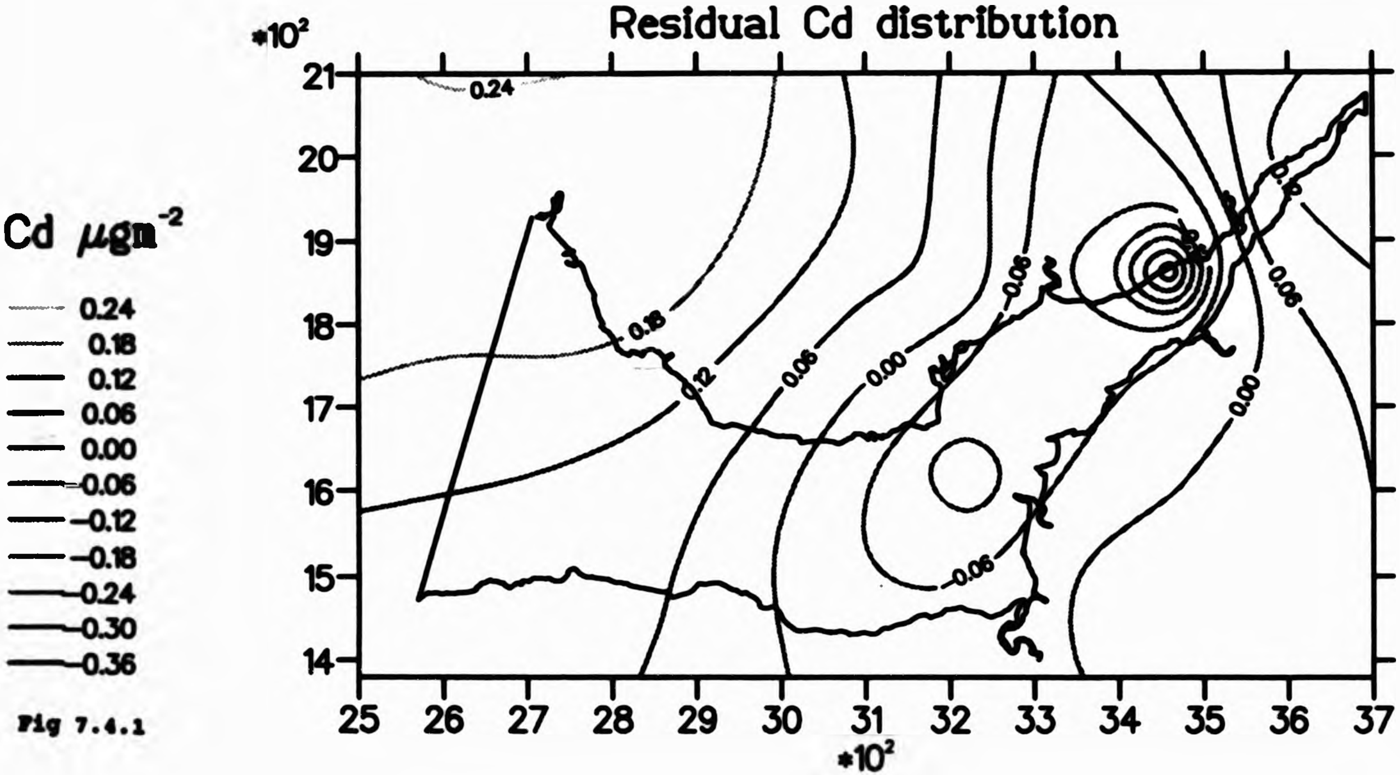

Residual Cd distribution
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
0.24
0.18
0.12
0.06
0.00
-0.06
0.00
0.06
0.00
Cd µgm⁻²
0.24
0.18
0.12
0.06
0.00
-0.06
-0.12
-0.18
-0.24
-0.30
-0.36

Fig 7.4.1

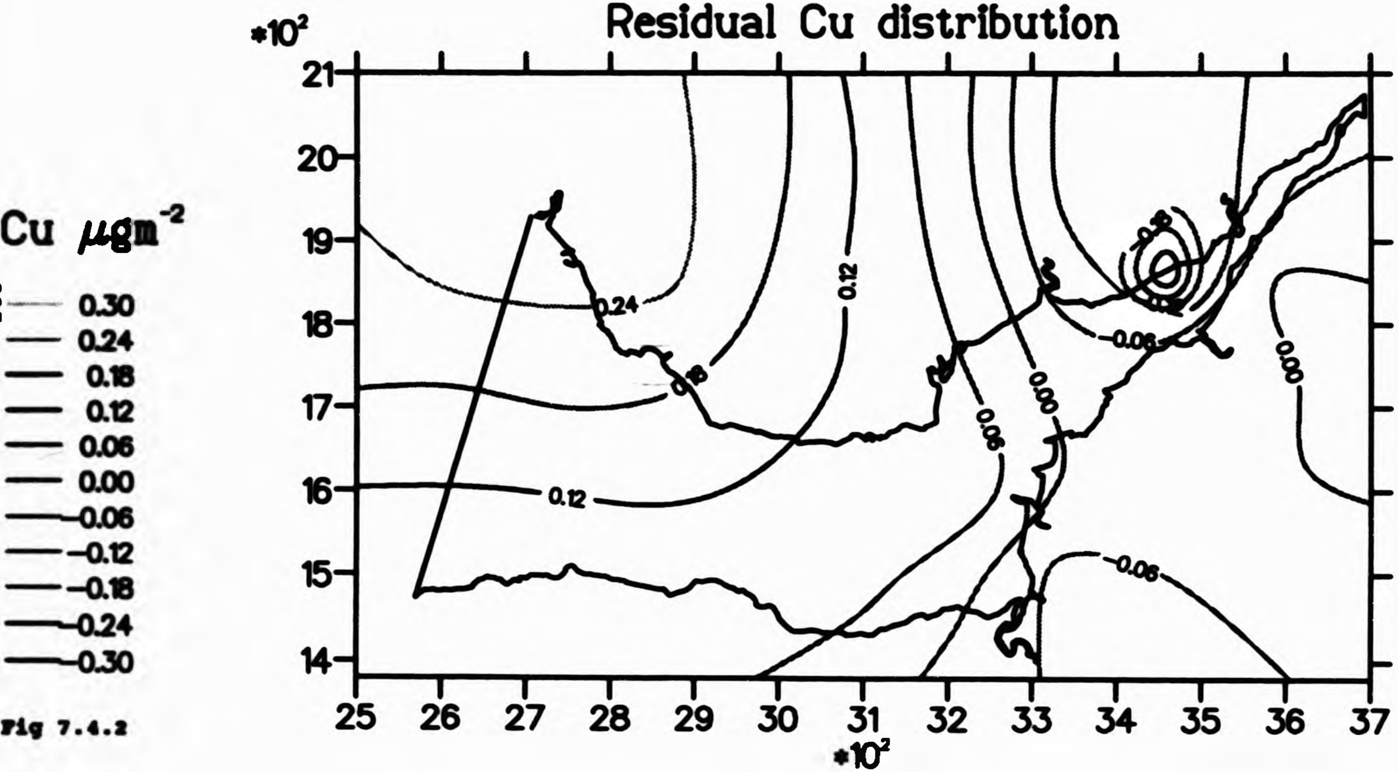

Residual Cu distribution
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
0.24
0.18
0.12
0.12
0.06
0.00
0.06
0.18
0.12
0.00
-0.06
Cu μgm⁻²
0.30
0.24
0.18
0.12
0.06
0.00
-0.06
-0.12
-0.18
-0.24
-0.30

Fig 7.4.2

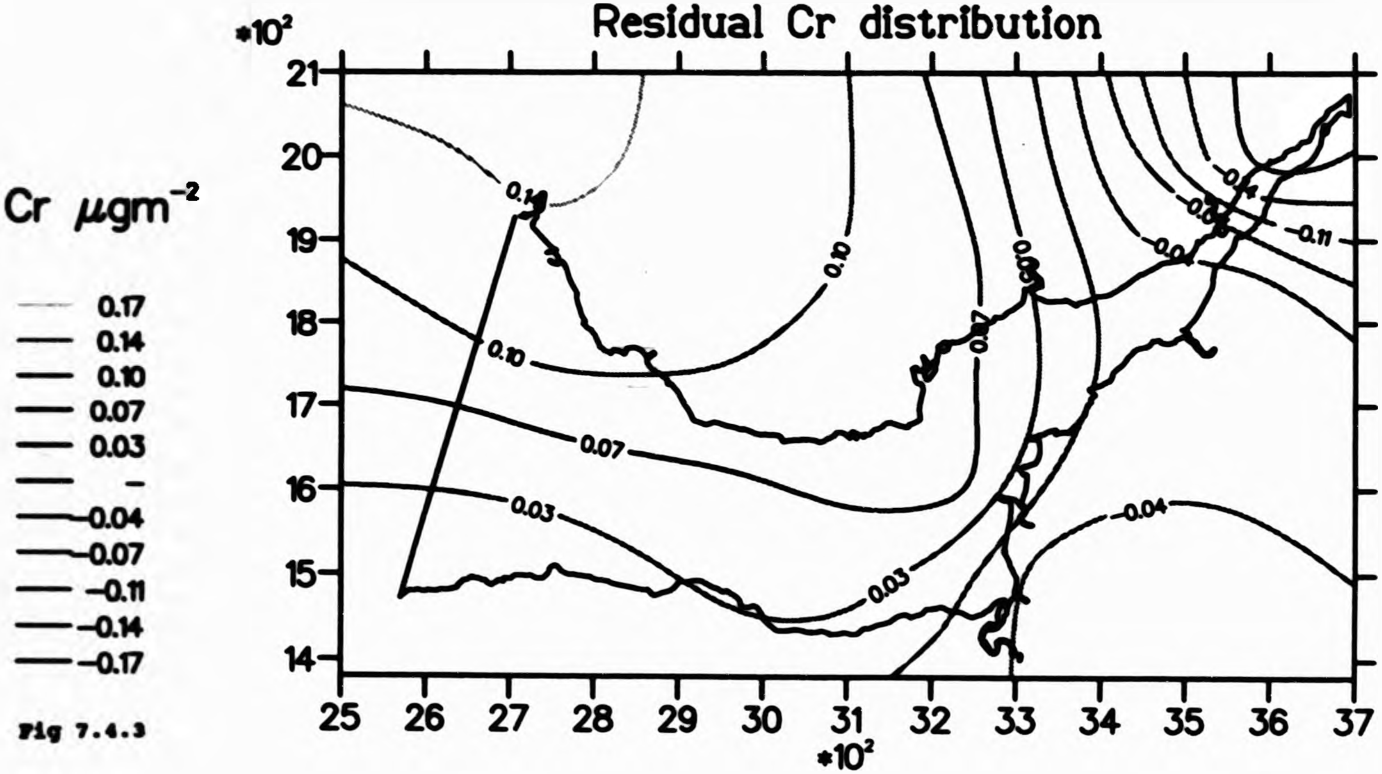
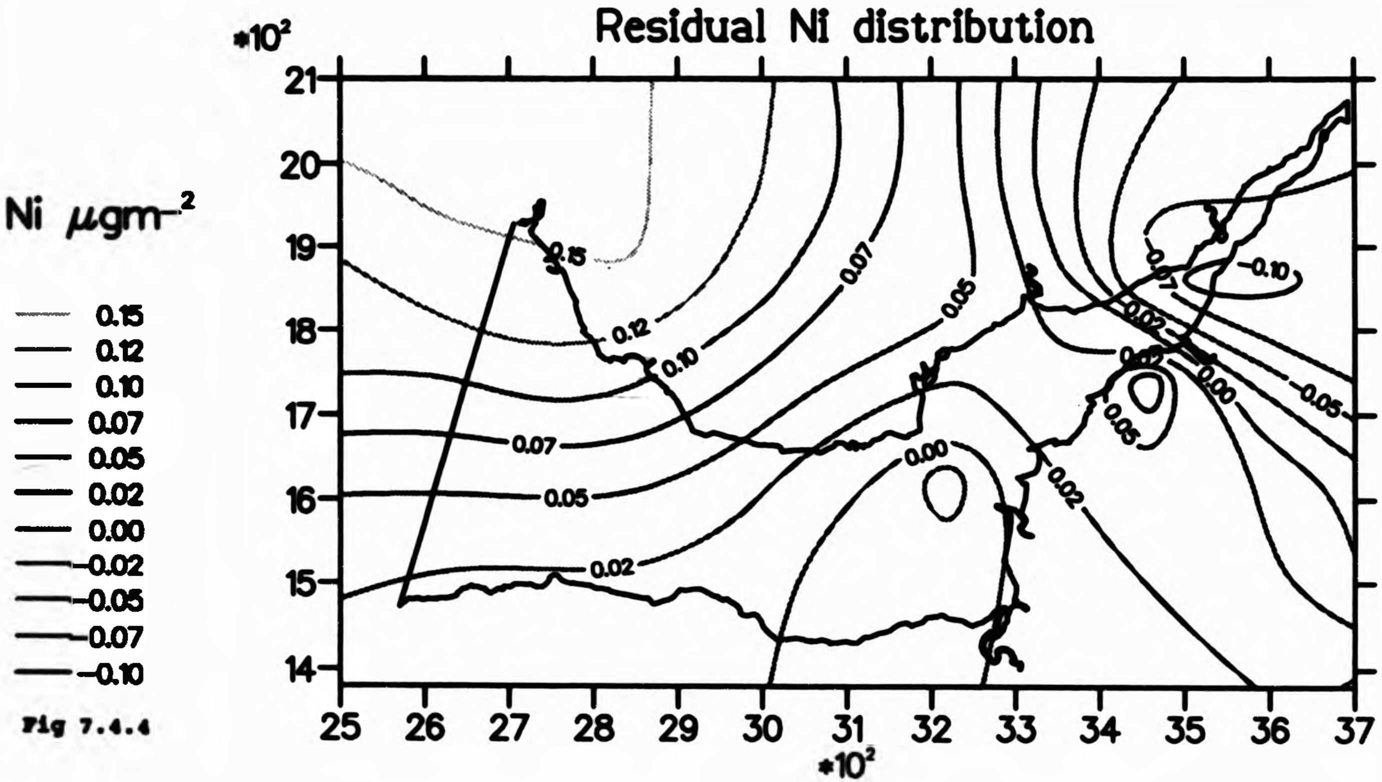

Residual Cr distribution
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
0.14
0.10
0.10
0.07
0.07
0.03
0.03
0.10
-0.04
-0.11
Cr μgm⁻²
0.17
0.14
0.10
0.07
0.03
-
-0.04
-0.07
-0.11
-0.14
-0.17

Fig 7.4.3



Residual Ni distribution

Fig 7.4.4

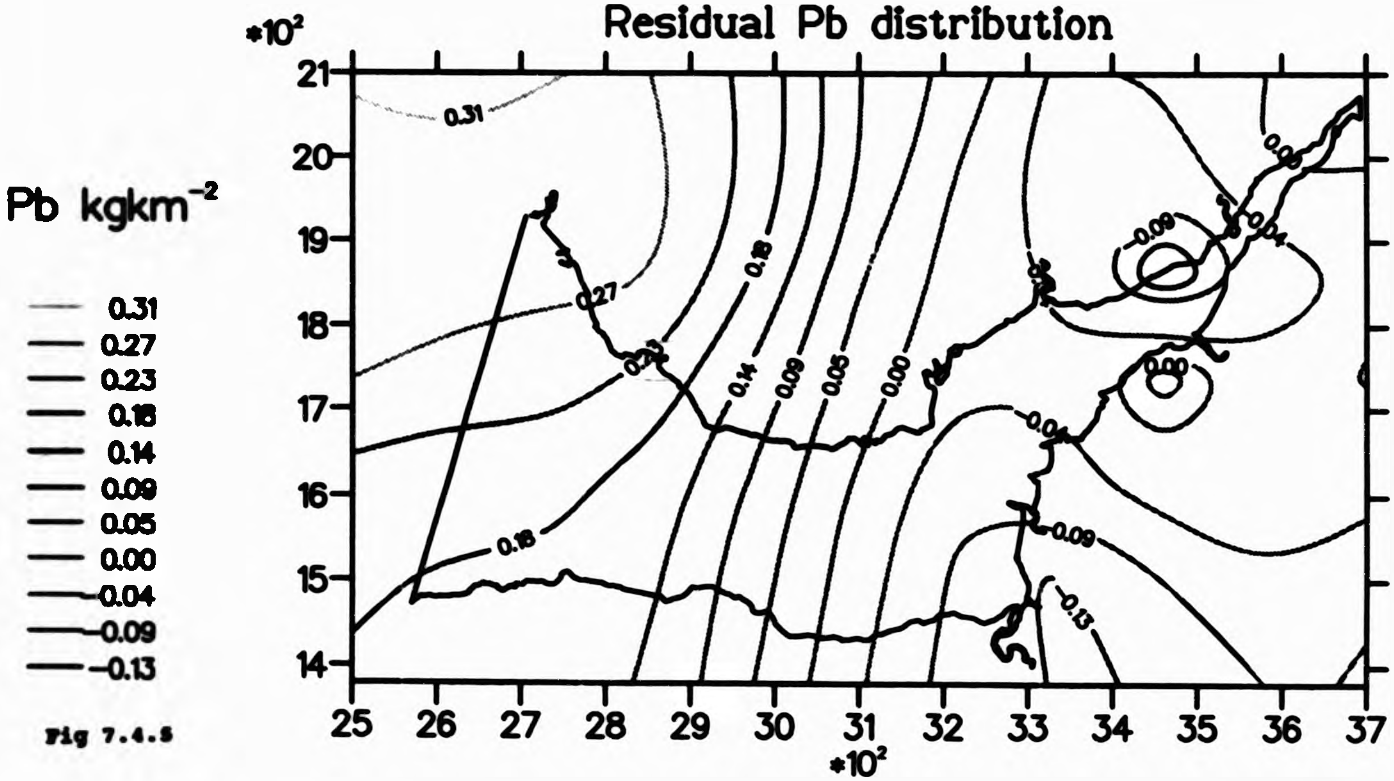

Residual Pb distribution
Pb kgkm⁻²
0.31
0.27
0.23
0.18
0.14
0.09
0.05
0.00
-0.04
-0.09
-0.13
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
0.31
0.27
0.23
0.18
0.14
0.09
0.05
0.00
0.18
-0.04
-0.09
-0.13
-0.09
0.00
0.04

Fig 7.4.5

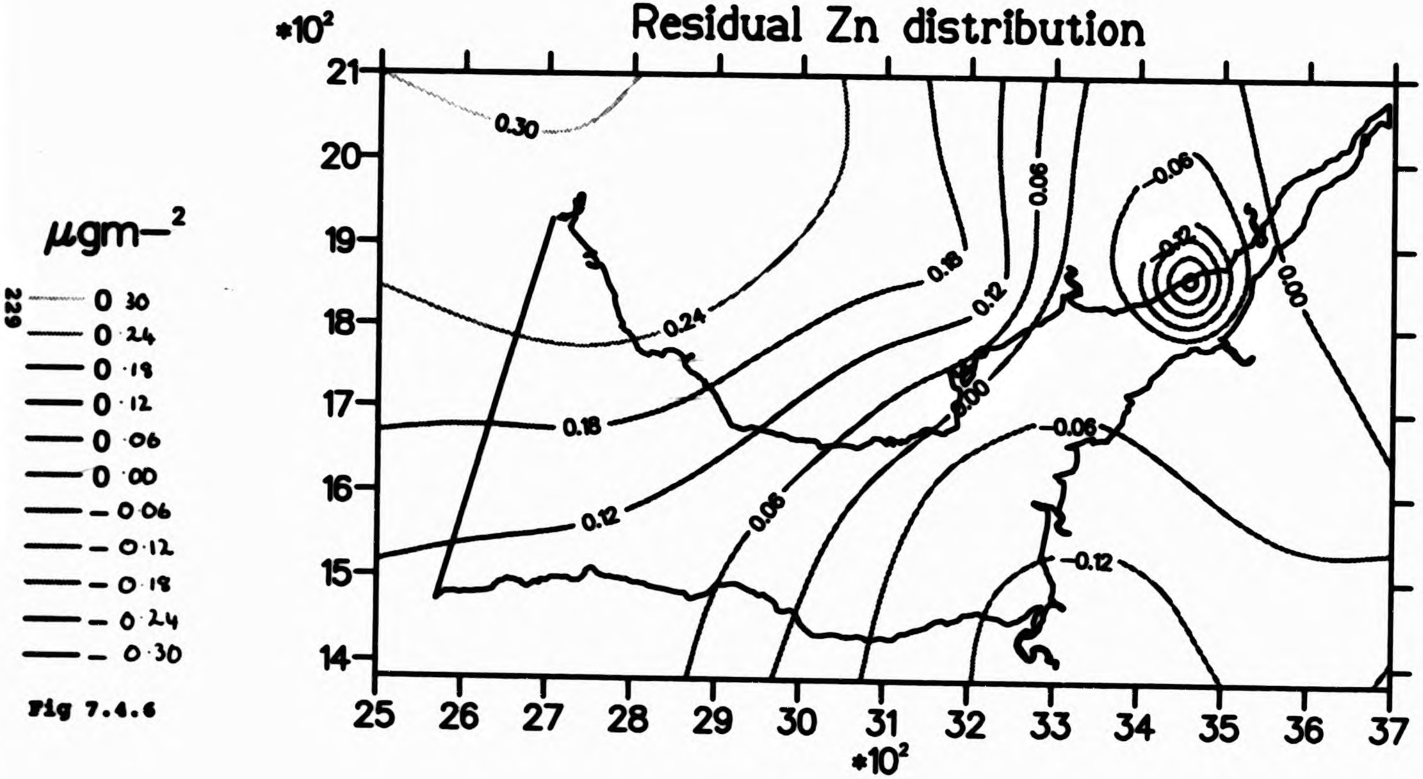
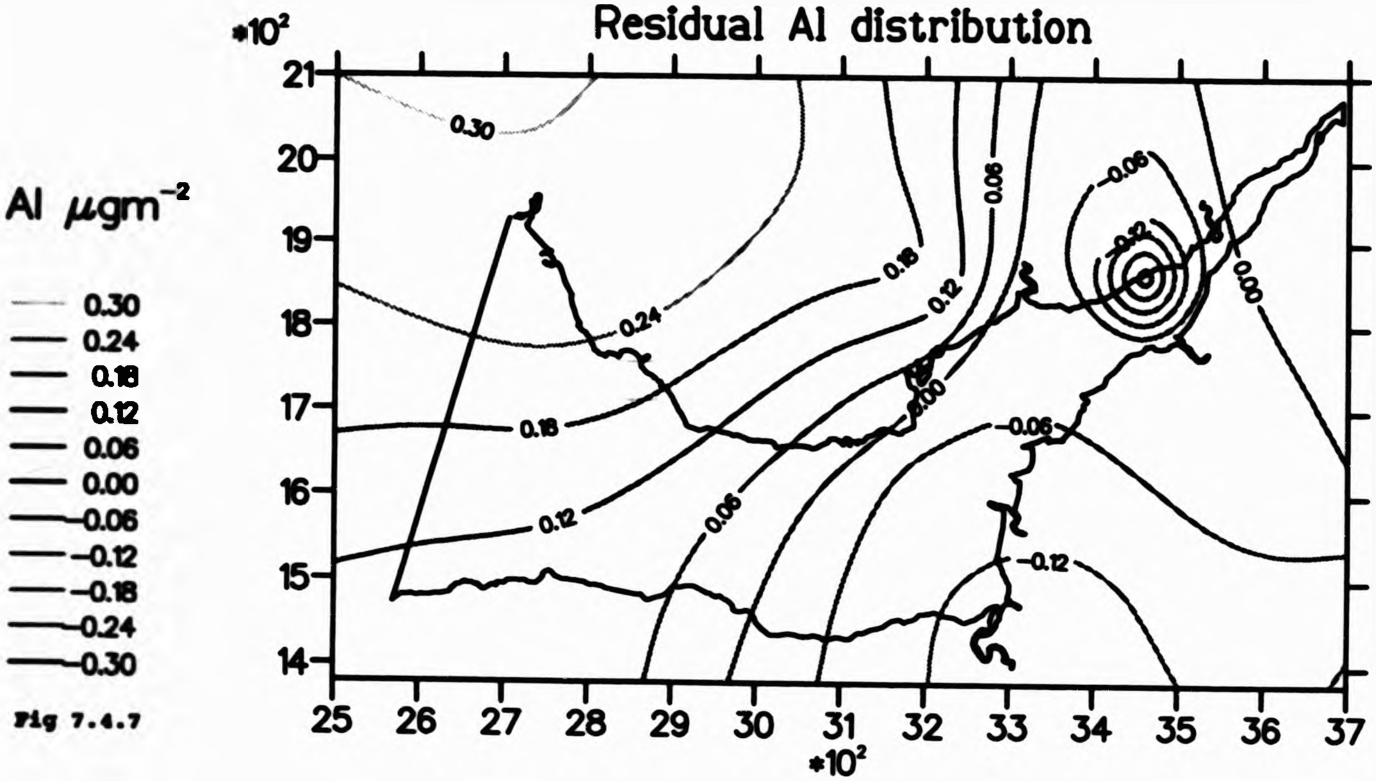

Residual Zn distribution
*10²
21
20
19
18
17
16
15
14
25
26
27
28
29
30
31
32
33
34
35
36
37
*10²
0.30
0.24
0.18
0.12
0.06
0.00
-0.06
-0.12
µgm⁻²
0 30
0 ·24
0 ·18
0 ·12
0 ·06
0 ·00
– 0·06
– 0·12
– 0·18
– 0·24
– 0·30

Fig 7.4.6



Residual Al distribution

Fig 7.4.7

this suggests that the swansea Bay area is an important secondary source of these metals. A potential source for the emissions of Pb, Zn and Cu is the British steel works in Port Talbot. The emissions from this work have been described by Scott (1979) in a study of the atmosphere around the plant and it is quite possible that it is a source to the Severn of these metals.

The patterns described by the residual distributions for Cr and Ni (Figs 7.4.3 -7.4.4) are similar to those described by the other metals but they differ in that the residual values are high much closer to the Avonmouth area. This suggests that there is a possible source of these metals in the South Wales area between Newport and Cardiff. The only major manufacturing plant in this area is the Llanwern Steel works which is a strip mill. This plant is a possible source of Cr and Ni but no information on the emissions from the plant could be found. An approach was made to the steel works concerning their emissions but no details were made available.

The Swansea Bay area, from the residual patterns appears to be an important source of Ni and Cr to the estuary. A potential source of Ni in the area is wind blown material from the waste tips of the nickel works operational and emissions from the plant itself. The Ni works is located at a distance of approximately 10km from the shore up the lower Swansea Valley and is quite close to the site of a closed zinc smelter (4.5km downstream) (Goodman, 1970). The Zn smelter closed in 1971 and the waste tips from this site are a probable source of Zn emissions to the estuary.

These residual plots produced for all metals were based on the deposition values recorded at the collecting sites and the distances from Avonmouth and, therefore, only show potential additional sources within the defined area. It is quite possible that additional sources may emanate from other areas outside the Severn Estuary such as Southern Ireland which are not taken into account by this simple modelling approach. The results from this exercise do appear, however, to indicate that the Swansea Bay area is an important secondary source of Cd, Cu, Cr, Ni, Pb, Zn and Al and that the South Wales coastline between Cardiff and Newport is a potential source of Cr and Ni.

7.7 Associations between metals

In order to ascertain whether any associations between metal inputs to the estuary over time existed a correlation exercise between individual determinands was implemented. The correlation exercise was used to compare the fortnightly total deposition values as calculated by from the UNIMAP plots and the results are presented in Table 7.5

Table 7.5 Correlation coefficients for metals (r)

Metal	Cd	Cu	Cr	Ni	Pb
Cu	0.56				
Cr	0.55	0.61			
Ni	0.32	0.05	0.30		
Pb	0.60	0.36	0.30	0.15	
Zn	0.22	0.28	0.23	0.36	0.17

With 29 degrees of freedom r is significant at;
r = 0.35 (95%)
r = 0.46 (99%)
r = 0.56 (99.9%)

From this exercise it is clear that there are some relationships between the patterns of metal deposition over the period studied.

There exist, for example highly significant (99.9%) correlations between Cu and Cd, Cu and Cr as well as Cd and Pb. Less significant (99%) relationships are seen between Cd and Cr as well as Pb and Cu (95%) and Ni and Zn (95%).

The relationships between Cd and Pb and Cd and Cu are in line with earlier observations of atmospheric sources of Cd (USEPA, 1978a) whereby sources able to cause measurable ambient concentrations of Cd were identified as, amongst others, primary copper and lead smelters. The strong association between Pb and Cd is likely to be a function of the emissions of the metals from the Avonmouth Municipal Refuse incinerator (Scott, 1987) as well as Commonwealth Smelting Ltd in Avonmouth (Davis and Clayton,1985, Davis, 1988). The remaining associations between metals are not so clear but it is likely that their sources within the estuary are similar and a result of industrial high temperature processing.

No significant correlations were observed between Zn and Cd or Zn and Pb which might have been expected from the nature of the emissions from the above sources. On this basis a correlation exercise was then undertaken using the data for each metal at the Avonmouth sewage treatment works to examine more closely the relationship between metal deposition in the area. The results are shown in table 7.6

Table 7.6 Correlation coefficients (r) for metals deposited at Avonmouth Sewage Treatment Works

Metal	Cd	Cu	Cr	Ni	Pb	Zn
Cu	0.58					
Cr	0.02	0.19				
Ni	0.28	0.34	0.38			
Pb	0.63	0.53	0.35	0.26		
Zn	0.64	0.72	0.22	0.33	0.87	
Al	0.37	0.13	0.11	0.19	0.06	0.03

With 29 degrees of freedom r is significant at;

r = 0.35 (95%)
r = 0.46 (99%)
r = 0.56 (99.9%)

From table 7.6 it can be seen that there are strong associations between Cu and Cd, Cu and Pb and Cu and Zn as well as Cd and Pb and Zn. Zn and Pb are also very strongly correlated. These correlations in the Avonmouth area are therefore much clearer than those shown in Table 7.5 for the above metals and are closer to what might be expected in view of the industrial processing operations taking place as already described.

The strong association between Cd and Zn (r = 0.64) is a result of the refining of Zn ore at the smelting plants whereby Zn minerals contain small amounts of Cd (O'Neill, 1985). Cadmium is a by-product of Zn smelting and is used for electroplating, anti-corrosive coating, pigments in paint as well as in Ni/Cd batteries. (Fergusson, 1990). It is the disposal of these products, particularly batteries, by incineration that contributes the high Cd emissions from this source and Cd from incineration is generally emitted in the form of its chloride. The most toxic Cd species are elemental Cd and cadmium oxide (CdO) and they are the predominant form of Cd emissions emitted in Europe by various sources (Pacyna, 1989). Lead emissions from petrol combustion are usually emitted in the form of tetra-alkyl compounds as well as in its elemental form and as $PbCl_2$ from smelter emissions (Pacyna, 1989).

7.8 Seasonal Variation of deposition

Seasonal variations in metal deposition to the Severn estuary might have been expected to correlate to the seasonal changes in meteorological conditions experienced throughout the sampling period. Increased combustion of fuels over the winter months might be expected with corresponding elevation of Pb deposition. A temporal variation in domestic smoke and sulphur dioxide concentrations were observed in the Newport/Cardiff area of south Wales by Banfield (1963) with increased emissions in the winter months. These were associated with a thermal inversion trapping pollutants below the inversion lid and also the topography limiting horizontal dispersal. A study of wet deposition in Sweden of Cd, Pb, Zn, Cu, Fe and Mn also showed strong temporal variations (Ross, 1987). Cd, Pb and Zn concentrations were highest between February and April whilst Cu, Fe and Mn were highest between May and July.

In order to determine if any corresponding seasonal variation of metal deposition to the estuary occurred sample inputs were plotted against the number of days from the start of the sampling and the corresponding months were shown. From this (Fig 7.5) there is no obvious seasonal variation to be seen although a series of fluctuations in the mass deposited throughout the year are observed. This highlights the episodic nature of deposition of the metals throughout the sampling period. There is one clear fall in deposition levels for all metals and this occurred during July and August of 1989. This is representative of the dry deposition that fell out during these months. There was very little rain over the summer period and it would appear that the majority of deposition to the Severn is driven by wet processes.

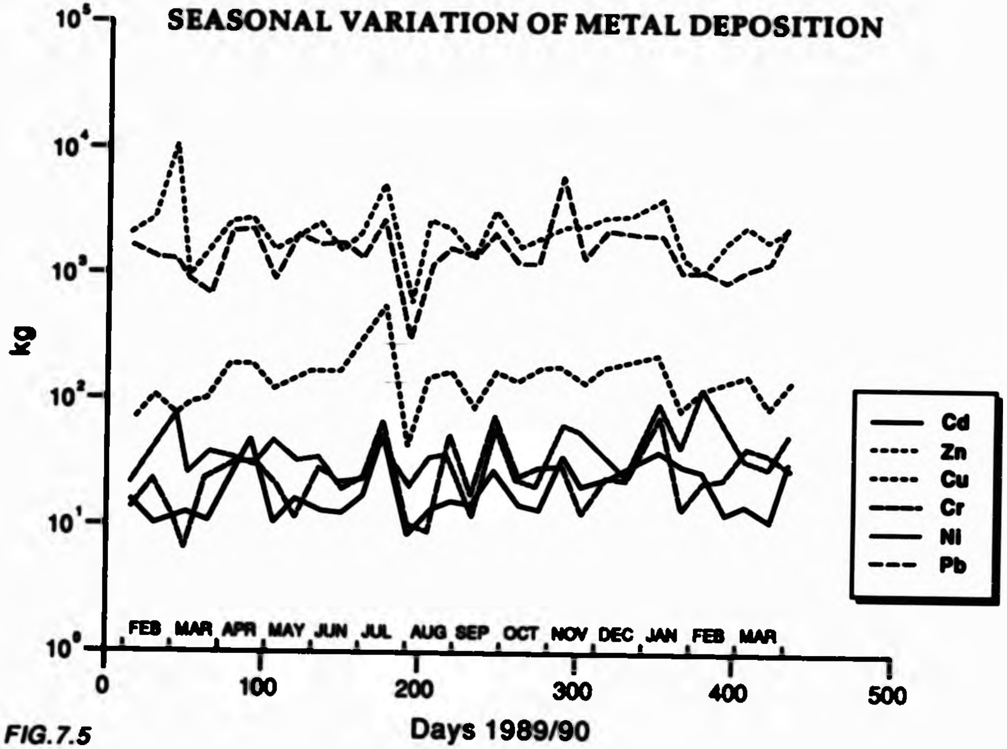

SEASONAL VARIATION OF METAL DEPOSITION
kg
10^5
10^4
10^3
10^2
10^1
10^0
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
JAN
FEB
MAR
0
100
200
300
400
500
Days 1989/90
Cd
Zn
Cu
Cr
Ni
Pb

FIG.7.5

7.9 Resuspension and the Maritime Effect

An experiment was carried out at Northwick Landfill site to see if there were any significant decreases in Na deposition with distance inland in association with other metal determinands. Samplers were placed at distances of 100, 200, 250, 255, 300 and 350 metres inland and aerial deposition collected on two occasions; after a two week interval and also one day. These sampling intervals were chosen to see if any daily changes could be observed and also to coincide with the routine sampling period. The results were plotted against distance and shown in Figs. 7.6 and 7.7.

From these plots there are no clear inferences as to the existence of a resuspension problem, some general observations can be made. After one day there was a decrease in concentration for all determinands up to 200m after which there was a rapid increase followed by a levelling out of concentrations. After two weeks the patterns observed were quite different with a slight increase followed by a sharp rise and fall between 200 and 255m inland. Further inland a general levelling out is again seen.

The experiment was carried out after the routine sampling period in May 1990. During this time the wind speeds were very low ($<4ms^{-1}$) and there was only 1.8mm of rain over the two week period and none after one day's sampling. Very different results

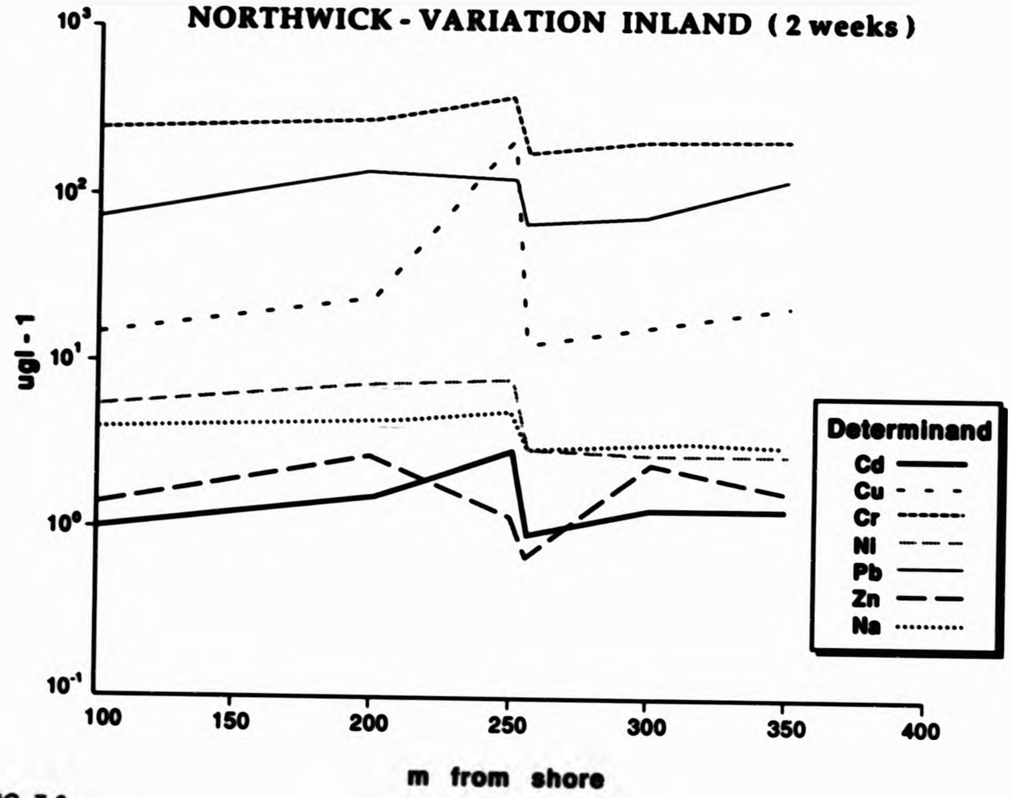
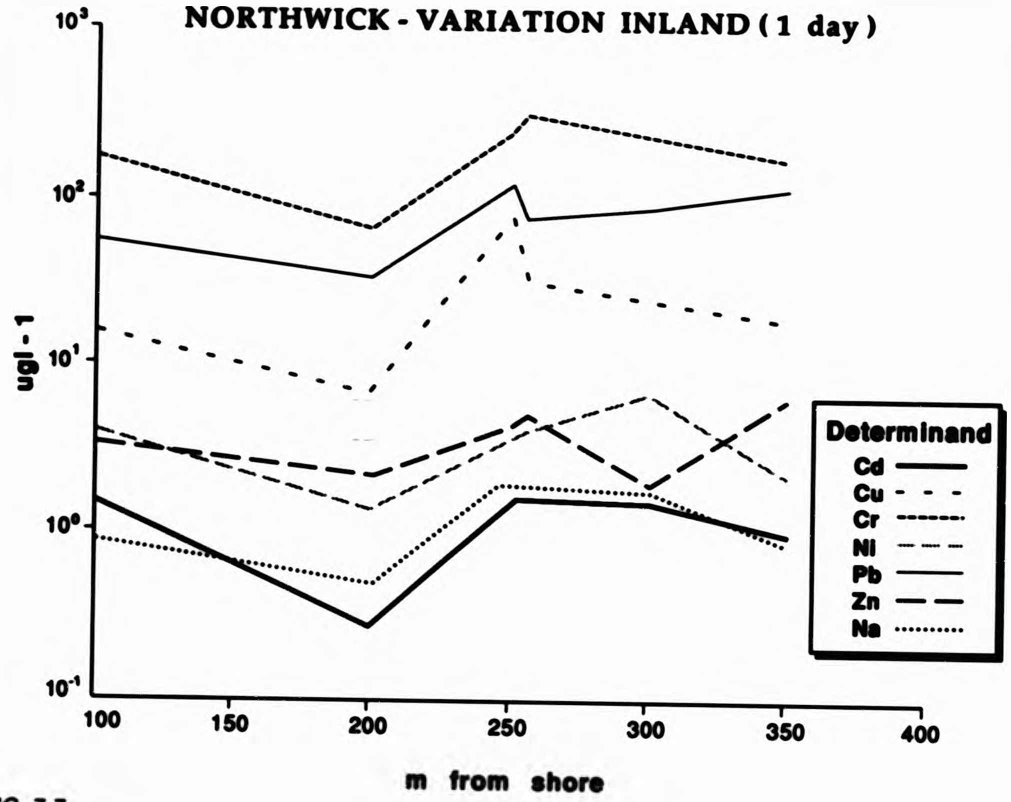

NORTHWICK - VARIATION INLAND (2 weeks)
10^3
10^2
10^1
10^0
10^{-1}
ugl - 1
100
150
200
250
300
350
400
m from shore
Determinand
Cd
Cu
Cr
Ni
Pb
Zn
Na

FIG. 7.6



NORTHWICK - VARIATION INLAND (1 day)

FIG. 7.7

may have been obtained if the exercise had been carried out over the winter months when wind speeds are generally much higher (Fig 3.2). Strong south-westerly winds would have been more likely to produce sea spray and associations, if any, between Na deposition and the other metals would have been more easily discernible.

Ideally, the distance inland needed to be much greater to confirm previous experiments, for example Pierson et.al (1974) examined deposition up to 5km inland. The limitations on the design for this experiment were, unfortunately unavoidable given the time and site constraints operating. This is an area that needs to be given more specific consideration if further atmospheric input determinations are to be carried out.

7.10 Flat Holm - An Intensive Study

7.10.1 Background

At the end of the routine sampling programme a series of samplers was set up on Flat Holm such that they covered as much of the island as possible (Fig 4.13). It was not possible to place equipment on the southern side of the island since this area was in use for research on the nesting bird population. The remaining sites were distributed such that they were subject to as little disruption as possible from the overgrown vegetation and buildings on the island. Samples were collected on a daily basis for four days and the results are summarised in table 7.7 in and in Figs 7.8.1 to 7.8.7.

From Table 7.7 it is clear that there are considerable differences between the deposition values on the 15th May 1990 when compared to the following days. The values for the sample collected on the on the 15th were much higher than those collected after this date and this is a result of wet deposition processes. This sample was the only sample collected containing wet deposition. There is also a possibility of some contamination having been introduced into the sampling equipment before deployment on the island, however, every attempt was made to avoid this. The weather conditions during the rest of the week were dry.

The positioning of samplers at sites Farm 1 and Farm 2 was intended to see if there were any similarities between amounts of metals collected at the two sites and therefore obtain a measure of sampler variation. The results on all days show that there are considerable differences between the two collectors with the collector at Farm 2 collecting considerably higher metal levels for wet and dry deposition on the 15th May. Over the following days the collector at site Farm 1 appeared to collect generally higher levels of dry deposition. The reasons for these variations are not clear but may be attributed in some

Table 7.7 Daily deposition loadings of metals for Flat Holm

Site	Cd	Cu	Cr	Ni	Pb	Zn	Na
15/5/90							
J	236.6	1455.9	91.0	45.5	91903.7	31847.8	445.9
WB	78.0	487.5	487.5	48.75	2437.6	30226.6	263.3
C	124.1	1241.1	362.0	25.9	2689.1	61021.7	170.7
B	54.9	862.4	117.6	19.6	1411.2	17640.0	129.4
F1	88.8	683.3	68.3	17.1	5124.7	7174.6	785.8
F2	314.7	839.0	269.7	179.8	7790.5	6292.3	668.2
16/5/90							
J	1.7	11.3	0.8	4.5	180.0	172.5	19.1
WB	0.4	2.6	4.4	0.4	32.3	95.9	29.3
C	0.6	3.2	5.3	0.5	22.2	137.2	27.9
B	0.5	6.4	4.0	4.0	19.3	88.3	18.5
F1	1.6	12.2	6.1	7.4	92.9	146.8	33.0
F2	0.4	3.9	4.9	6.9	62.9	59.0	22.1
17/5/90							
J	2.5	1.8	0.3	1.5	111.7	229.3	1.1
WB	0.5	2.6	1.6	1.3	5.2	31.4	8.0
C	3.2	6.1	0.6	6.4	6.1	177.0	7.8
B	0.5	2.6	0.5	1.3	5.2	36.6	1.7
F1	0.7	5.3	1.1	1.3	17.6	42.6	6.0
F2	0.4	4.1	0.3	1.5	15.4	23.7	4.7
18/5/91							
J	2.6	2.1	2.1	1.4	155.2	214.0	2.3
WB	0.6	5.3	1.5	1.4	16.0	31.9	2.2
C	1.2	6.0	0.6	3.7	41.5	90.3	2.9
B	0.7	2.6	1.6	1.3	12.8	31.6	0.9
F1	1.4	4.1	1.2	2.9	18.8	41.2	2.0
F2	0.8	2.1	1.1	1.3	16.6	26.8	2.1

J - Jackdaw
WB - West Beach
C - Castle
B - Beacon

F1 - Farm 1
F2 - Farm 2
(Fig 4.13)
All values to 1dp.

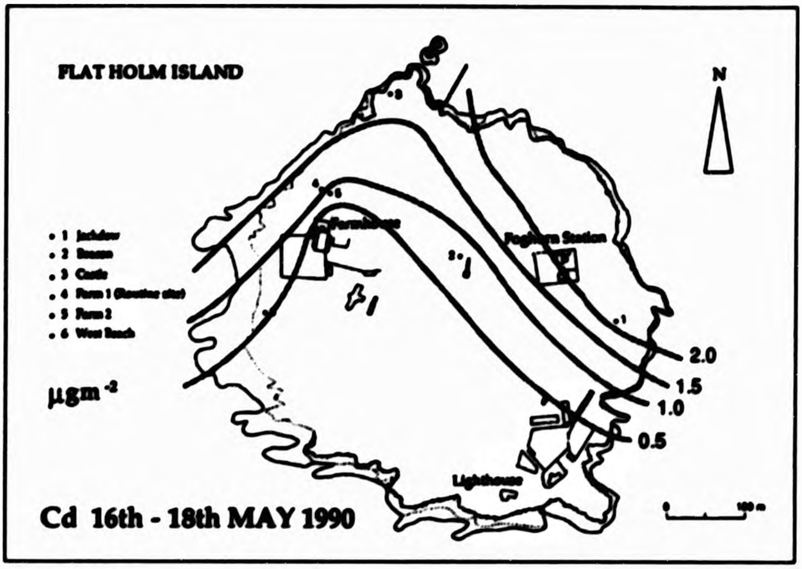


FIG. 7.8.1

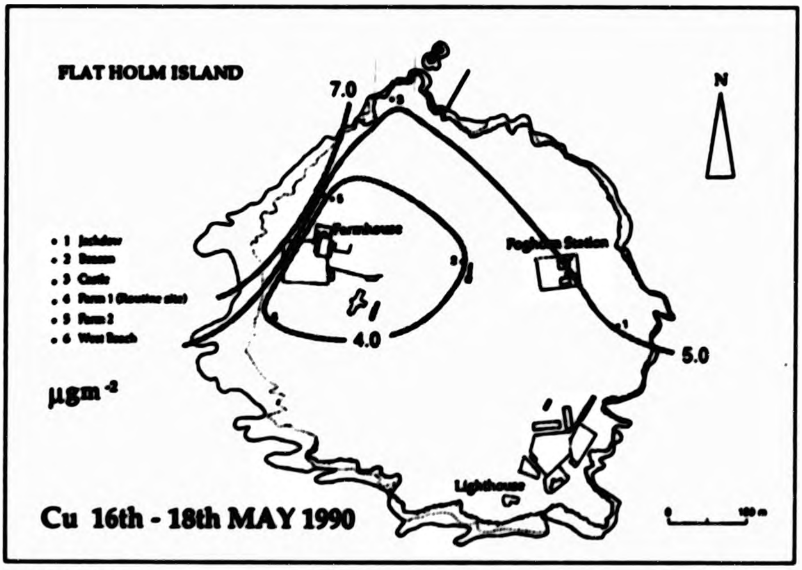


FIG. 7.8.2

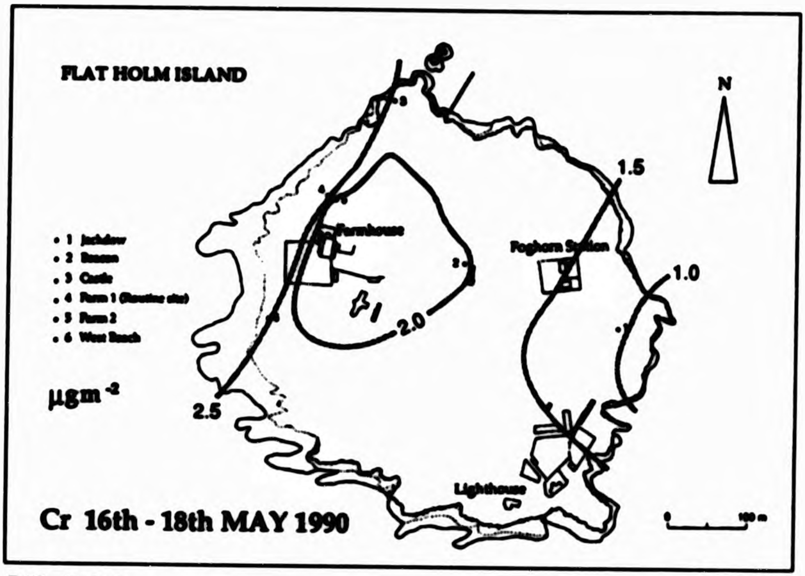


FIG. 7.8.3

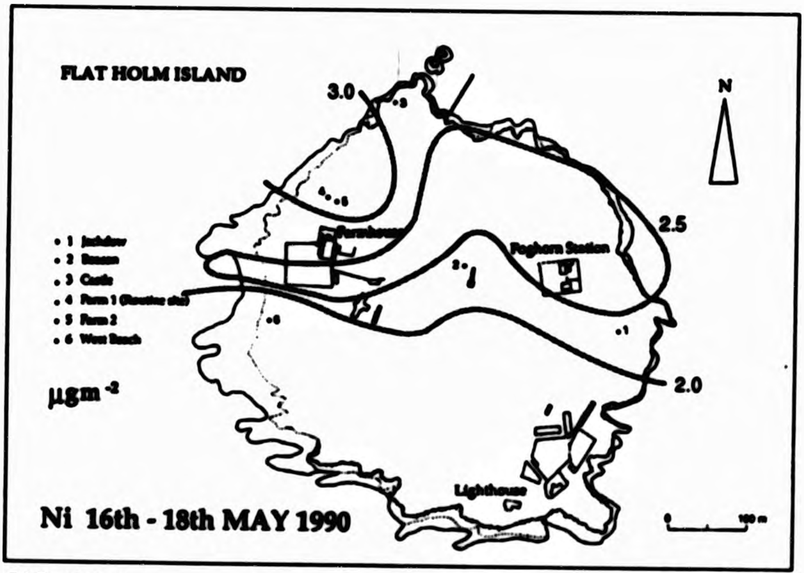


FIG. 7.8.4

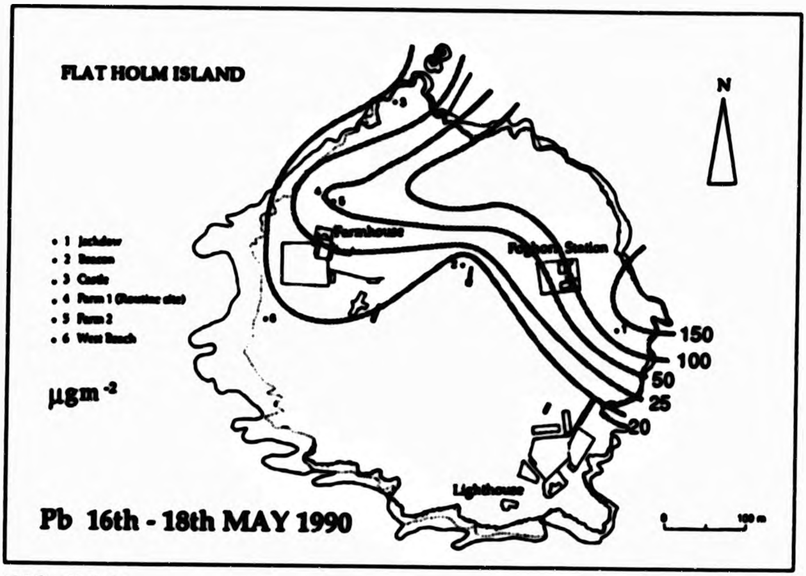


FIG. 7.8.5

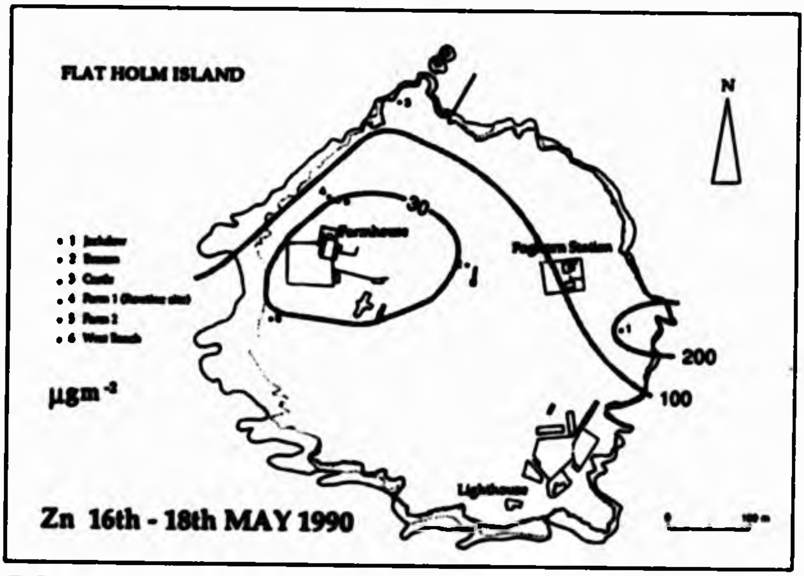


FIG. 7.8.6

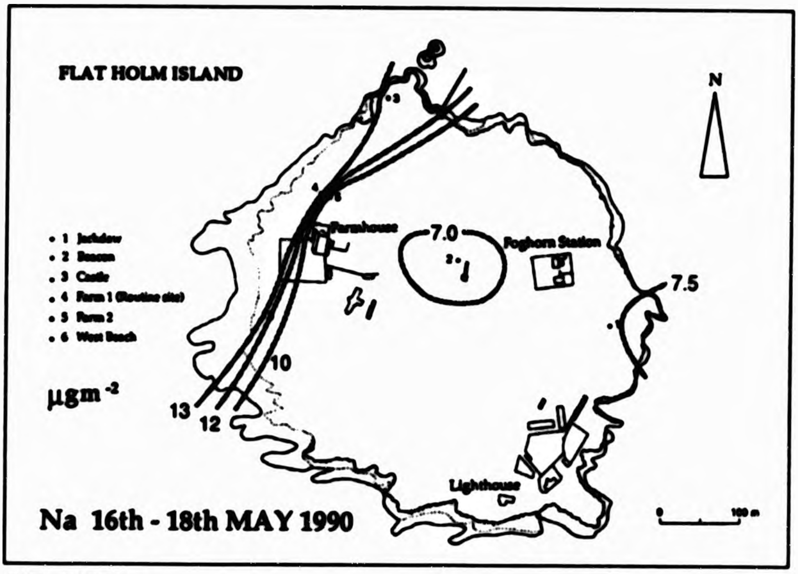

FLAT HOLM ISLAND
N
• 1 Jackdaw
• 2 Beacon
• 3 Castle
• 4 Farm 1 (Routine site)
• 5 Farm 2
• 6 West Beach
$\mu g m^{-2}$
Farmhouse
7.0
Foghorn Station
7.5
10
13
12
Lighthouse
0
100 m
Na 16th - 18th MAY 1990

FIG. 7.8.7

way to differences in dry deposition.

Figures 7.8.1 and 7.8.7 show the distributions of dry deposition collected over the period 16th May to the 18th may and averaged and the plots for each metal show quite marked differences in the patterns of metal distribution across the island. These will be discussed separately as follows:

7.10.2 Cadmium

The distribution of Cd over the sampling period (Fig 7.8.1) shows quite low values that exhibit a gradient from north-east to south-west. This pattern of deposition is indicative of the influence of a source to the north east of the island, almost certainly the Avonmouth area.

7.10.3 Copper

Figure 7.8.2 shows the distribution of copper deposition to the island over the period. There is a gradient from the north-west to the south of Flat Holm with a fairly constant amount of copper deposition experienced across the centre. The source of the metal was most likely from the South Wales mainland, possibly the Swansea Bay region although the influence of the Avonmouth industrial complex cannot be ruled out as a source on this occasion.

7.10.4 Chromium

Similarly to the Cu distribution the pattern exhibited by Cr (Fig 7.8.3) shows a gradient from the north-west of the island, decreasing toward the south-east. The influence of South Wales as a source of Cr is again strongly indicated.

7.10.5 Nickel

As with Cu and Cr, Fig 7.8.4 shows a gradient from the north-west of the island which decreases toward the south. The masses of Ni deposited over the island are quite small as, for the other metals determined and a source from the South Wales mainland is likely to have been responsible for the pattern exhibited.

7.10.6 Lead

In sharp contrast to Cu, Cr and Ni the distribution of lead (Fig. 7.8.5) across Flat Holm shows the influence of Avonmouth and the English mainland as a potential source of the metal. There is a very steep gradient decreasing from north-east with a tongue of higher deposition around the farm house. It is possible that the combustion of fuel for power generation on the island may have contributed some lead to the resulting distribution. Again, the concentrations of Pb recorded are quite low in comparison to results obtained for the mainland and the island during routine sampling (Table II.5) and is likely to be a result of the lower dry deposition that occurs in the Severn estuary area when compared to wet deposition processes.

7.10.7 Zinc

Figure 7.8.6 shows a similar distribution as Pb across the island for the study period although contaminant contribution from Flat Holm itself does not appear to have been a factor. The potential sources of Zn are also the Avonmouth/Severnside complex as well as contributions from south Wales industrial activity.

7.10.8 Sodium

The distribution of Na (Fig 7.8.7) clearly illustrates the effect of salt deposition into the sampling equipment derived from the sea under the westerly winds experienced during the sampling period. A gradient decreasing inland from the west coast of Flat Holm and slightly increasing toward the eastern shoreline was seen. The majority of Na deposited will have come from the sea.

7.11 Confidence in results

The estimated values of deposition to the Severn estuary have been made on the assumptions that the data collected is representative of the region and that the analysis of samples was satisfactory. The analytical quality control (section 5.4) carried out with all the sample analysis showed that the results for all metals except Zn were satisfactory. The Zn analysis showed that there was an overestimation of Zn in the samples, possibly by up to 8% which may be significant to the deposition estimates made on the basis of this data.

The sampler variations at Northwick landfill site (section 4.7.1) were also quite considerable for most metals with percentage relative standard deviations for Cd at 25.98, Cu - 20.68, Cr - 85.8, Ni - 79.4, Pb - 38.16 and Zn - 34.80 over a period of two weeks. As discussed it is not certain whether these values were obtained as a result of variations in dry deposition or the introduction of contamination into the samples but they do provide a measure of the likely variations that occur in the data and therefore the confidence that can be placed on the results. Similarly, variations between the adjacent samplers deployed on Flat Holm were quite high.

However, the results, despite the possible variations that might have occurred if the samplers had been placed at alternative locations, show that there have been considerable reductions in atmospheric deposition of heavy metals to the Severn estuary since 1983 and that improvements in sampling techniques and in data interpretation have been made. The relationship of the results obtained and the weather conditions experienced over the sampling period will be discussed in detail in the following chapter.

8 RELATIONSHIP BETWEEN AERIAL DEPOSITION AND WEATHER VARIABLES

8.1 Background

A two week sampling programme was adopted in this survey of atmospheric metal deposition which limits the assessment of the role of weather variables in determining the spatial distributions of deposition. The small spatial and temporal scales of fluctuation in atmospheric behaviour and atmosphere-surface interaction associated with a variable middle latitude climate as well a diverse physiographical surface make it impossible to employ stochastic pollution dispersion models. The range of temporal variability seen in atmospheric motion has been documented by Eliassen and Pedersen (1977) into micro-scale, medium scale and large scale motions. Micro-scale motion occurs in the form of eddies that range in size from a centimetre to 100 metres across and which may have a duration of 10 - 1000 seconds whilst medium scale motion can be sub-divided into convective motion and gravity waves. Convective motion takes the form of cumulus and cumulonimbus clouds which range from 1-5km across and 10-100km across respectively. Their respective lifetimes are one hour and six hours. Gravity waves are in the form of mountain airflows that may extend up to 50 km horizontally. Large scale atmospheric motions are between 500-1000km across in the case of tropical cyclones which may last for up to a week and may be as long as 10000 km long in the case of the Jet Stream.

As a result of these temporal variations and the length of the sampling interval, the assessment of any relationships between deposition values for each metal and weather variables confidence has therefore been placed in statistical associations between these values. This approach has the advantages of simplicity and reliance upon readily available weather data sources. In order to assess the relationships the data for each metal were bulked into four zones of the estuary and compared with the weather variables. The zoning of the deposition data into four areas was carried out on the basis of the spatial variations demonstrated in the plots of metal distribution (Figs 6.5.1 - 6.8.7) such that each area represented the general levels of deposition observed. The zonation was also in the interests of the NRA whereby it was hoped to develop a means of predicting patterns of deposition based on a reduced number of sampling sites in relation to weather variables.

Three sites representing different areas of the estuary were then examined on an individual basis to further examine any associations between them and the weather variables.

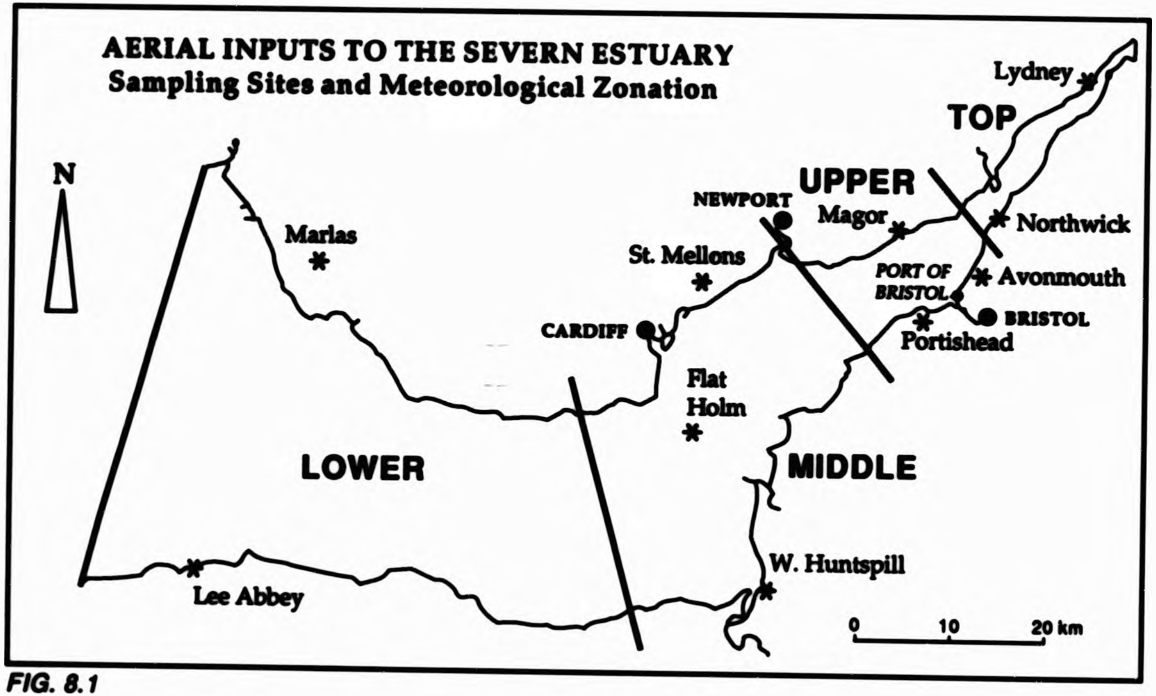

AERIAL INPUTS TO THE SEVERN ESTUARY
Sampling Sites and Meteorological Zonation

FIG. 8.1

Table 8.1 Zoning of Sampling Sites

Zone	Code	Sites
Top	T	Lydney, Northwick
Upper	U	Avonmouth, Port of Bristol, Portishead, Magor
Middle	M	St Mellons, Flat Holm, West Huntspill
Lower	L	Marlas, Lee Abbey

Table 8.2 Mean zonal deposition and interzonal ratios

	Mean Deposition				Mean Ratio		
	T	U	M	L	UM	ML	UT
Cd *	13.84	121.10	5.29	3.56	41.28	2.29	12.98
Cu *	66.85	484.8	53.90	41.88	11.65	1.56	8.57
Cr *	8.84	15.97	12.07	11.61	1.95	1.53	3.08
Ni *	16.11	35.37	17.76	17.61	2.74	1.17	8.16
Pb +	0.58	8.97	0.27	0.23	39.06	1.53	20.00
Zn +	1.04	9.51	0.63	0.47	19.30	2.24	10.94
Al *	1.71	8.50	2.14	1.56	5.16	1.68	8.47

* Deposition values in μgm^{-2}

\+ Deposition values in $kgkm^{-2}$

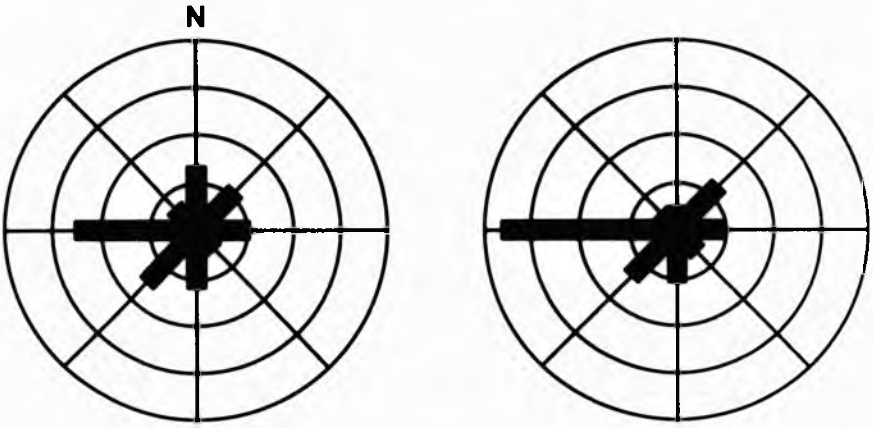
8.2 Selection of variables

The aerial deposition values from each of sampling sites were bulked into FOUR zones which were defined as follows; top (T), upper (U), middle (M) and lower (L). (Table. 8.1, Fig 8.1). Deposition values in mass per unit area were derived for each metal for each area. Three ratios were calculated to indicate the horizontal gradients of change along the estuary. These ratios were defined as follows; upper:middle (UM), middle:lower (ML) and upper:top (UT). The mean zonal deposition and interzonal ratios for each metal are shown in Table 8.2. These ratios were used, rather than simple differences between the zones, because atmospheric diffusion processes generate distribution patterns that are based on decay curves. Generating the ratios allows a direct comparison between all the zones.

The weather variables selected were wind direction and speed, stability, atmospheric pressure, cloud amount and rainfall. Routine surface observations for Rhoose Airport were used for the synoptic observing times of 06.00 and 12.00 GMT. Although data were available for four synoptic times these times were the closest to the times of minimum and maximum surface and air temperature and the associated extremes of lower atmosphere stability. Wind direction and speed were also obtained from the Met Office for Lundy island. There were, thus, 28 values of wind direction, force and cloud amount over a sampling period of fourteen days. Diurnal change in atmospheric pressure is relatively small and was noted for 12.00 only. These data were extracted from daily synoptic weather charts produced by the Met Office and published by the London Weather Centre. Stability data for Rhoose airport, on an hourly basis, were also supplied by the Met Office. Total rainfall for each period was obtained from direct measurements of the volumes collected in the sampling devices.

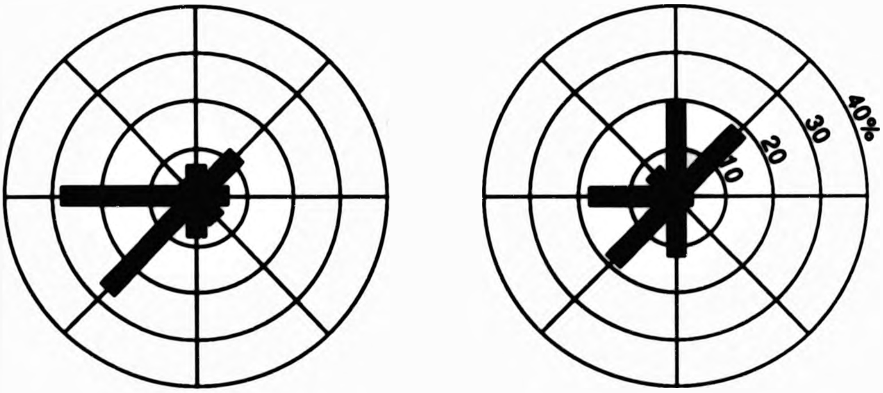
8.2.2 Wind direction

The eight principal points of the compass (NE,E,SE,S,SW,W,NW,N) were used to record wind direction. From these data two variables were generated; percentage frequency of winds from the sector SW to NW (W%), or from the sector NE to SE (E%) and the ratio between these (W/E). These sectors were used on the basis that the dominant wind direction in the Severn Estuary is generally from the west (Fig 8.2) and plumes, particularly from the Avonmouth area, would be expected to be carried inland. Easterly airflows are often associated with lower atmospheric stability (section 3.2.1) and increased deposition of metals might be anticipated under these conditions. Wind direction data for Lundy were treated similarly to obtain percentage frequency of winds that were westerly and easterly. In addition the percentage of winds from the quadrant S to W (%SWL) and the quadrant N to E (%NEL) were generated for the data for Lundy island. The SWL% data were generated to coincide with the more frequent south-westerly wind experienced in the Severn Estuary



Mumbles Head

Rhoose Airport
(near Cardiff)



Bristol Weather Centre

Lundy (South)

FIG. 8.2 SEVERN ESTUARY: WIND ROSES JAN 1989 —MARCH 1990 as well as the orientation of the estuary which is likely to funnel and accentuate winds from this direction. As for the Rhoose data, the variable NELA was produced on account of the stability associated with winds from the north east under Continental polar air masses which are infrequent but may have caused high metal deposition. The ratios between these quadrants were also generated to give W/E(L) and SW/NE(L). The frequency of winds experienced across the Severn estuary over the sampling period are shown in figure 8.2 by wind roses for the weather recording stations of Mumbles head, Rhoose Airport, Bristol Weather centre and Lundy.

8.2.2 Wind speed

The data for wind speed (ubar) were, initially, in coded form for the Rhoose airport data and the mean wind speeds over each sampling period were derived after decoding the data to knots with an error of ± 2 knots. Wind speeds in knots were given directly for the Lundy data (ubarL) and a mean was derived for each sampling period. The wind speed affects plumes in terms of turbulent mixing of the lower troposphere and to distance the distance downwind that is transported from the source. The strongest winds in the Severn are experienced from the west (Fig 3.2) and these will promote both diffusion and transport of pollutants, thus reducing their concentrations and carrying them inland, particularly from the principal source area of

Avonmouth. Thus, it was hoped to demonstrate the relationship between the wind speed and the gradients of deposition of metals in the Estuary.

8.2.3 Mean cloud amount

The mean cloud amount (Nbar) was determined in oktas for each sampling interval. Clouds provide a medium for the entrainment of pollutants especially at low levels where stacks may emit directly into them. This can result in rapid dispersion of pollutants if the clouds are associated with fast moving medium and large scale atmospheric motion such as are experienced under cyclonic conditions. In the Severn Estuary this would result in lower levels of pollutant deposition as pollutants would be carried inland under ,generally, westerly air streams. Conversely, stable conditions are associated with shallow layers of cloud which may be in the form of uniform stratus or fog layers (Harrison et.al., 1985). This would have the effect of producing high deposition in local areas within the Severn as pollutants are rained out from the clouds or washed out from below the inversion layer that is often experienced under these conditions. Pollutant entrainment in cloud and its subsequent wet deposition is related to the height of the cloud base and cloud thickness as well as to the total cloud cover. Despite this limitation, mean cover was used as a weather variable in the absence of data on cloud height and thickness as well as maintaining simplicity which would be in the interests of the

NRA should a predictive model be formulated.

8.2.4 Atmospheric pressure and Stability

Lower atmospheric pressure is usually associated with greater instability and was recorded in the form of deviation from 1000mb (ppp) for ease of handling. Initially this was used as a surrogate for lower atmosphere stability although stability data for Rhoose Airport were obtained later. Rhoose Airport gave a representative analysis of stability in the Severn region and was supplied in as Pasquill stability codes with values for 1 to 10. The Pasquill stability codes range from 1 with very unstable conditions to 10 with very stable conditions. The coding is summarised in Table 8.3. The Pasquill stability categories were defined to describe the stability of the lowest layers of the atmosphere so that they could be used for estimating the dispersion of air pollution released from the ground or from industrial stacks (Met Office, 1991). The ten codes given are then categorised into three major groups; Very unstable, neutral and very stable.

The Met Office stability codes are generated as a function of total cloud amount, wind speed and time of year. During the day an estimate is made of the incident solar radiation and this is combined with wind speed to estimate the stability category. The stability at night is generated simply as a function of cloud cover and wind speed.

Table 8.3 Pasquill Stability Codes

Code	Stability conditions
1	Very unstable
2	
3	Moderately unstable
4	
5	Slightly unstable
6	
7	Neutral
8	Slightly stable
9	Moderately stable
10	Very stable

Very unstable conditions occur typically on warm, sunny summer afternoons with light winds and almost cloudless skies when there is strong solar heating of the ground and the air immediately above the ground. Thermals are formed (packets of warm rising air) and the lapse rate is described as superadiabatic, i.e. the E.L.R is greater than Γ. Under these conditions pollutant dispersal is likely to be very wide. Very unstable conditions also occur under maritime polar airmass conditions where cool showery weather is experienced in all seasons, especially at coastlines (Barry and Chorley, 1987).

Neutral stability occurs under cloudy conditions or whenever there is a strong surface wind to cause vigorous mechanical mixing of the lower atmosphere. Neutral conditions occur by both day and night and the times that are normally considered neutral are the period immediately after sunrise and just before sunset. Under neutral conditions the E.L.R is equal to or less than Γ.

Very Stable atmospheres occur, typically, on cold, clear and calm nights when there is strong cooling of the ground and the lowest layers of the atmosphere by long wave radiative cooling and a strong temperature inversion forms. Very stable conditions (10) and stable conditions (8,9) only occur at night, under conditions of radiative cooling from below, and only a moderate temperature inversion occurs with the latter two codes. The E.L.R is less than the Γ under stable conditions.

For the purposes of comparison with deposition data the stability data (stability data) were categorised into two times of day; 0000 -0600 (am) and 1200-1800 (pm), and a representative code was obtained for each day. This was done in order to identify the extremes of diurnal stability variation. The sampling intervals were then further categorised to give percentage stable (amst) and percentage neutral conditions (amn) in the morning and percentage unstable (pmust) and percentage neutral (pmn) conditions in the afternoon. The frequency of each stability class at all times of day was also generated for the whole sampling period. These are shown in figures 8.3 and 8.4 and they indicate the dominance of neutral stability conditions that occur in the region. Neutral conditions are more frequently observed in the winter months as are stable conditions. A greater frequency of unstable conditions are seen between April and September and whilst these conditions are observed over the rest of the year they are dominated by neutral stability at these times.

8.2.6 Measured Rainfall

Measured rainfall was obtained directly from the volumes recorded in the collecting bottles and checked against recordings made in standard raingauges at the sites. The rainfall values were bulked into the same zones as the metal deposition data. The majority of precipitation, which generates

% Frequency of Stability *January 1989 — March 1990*

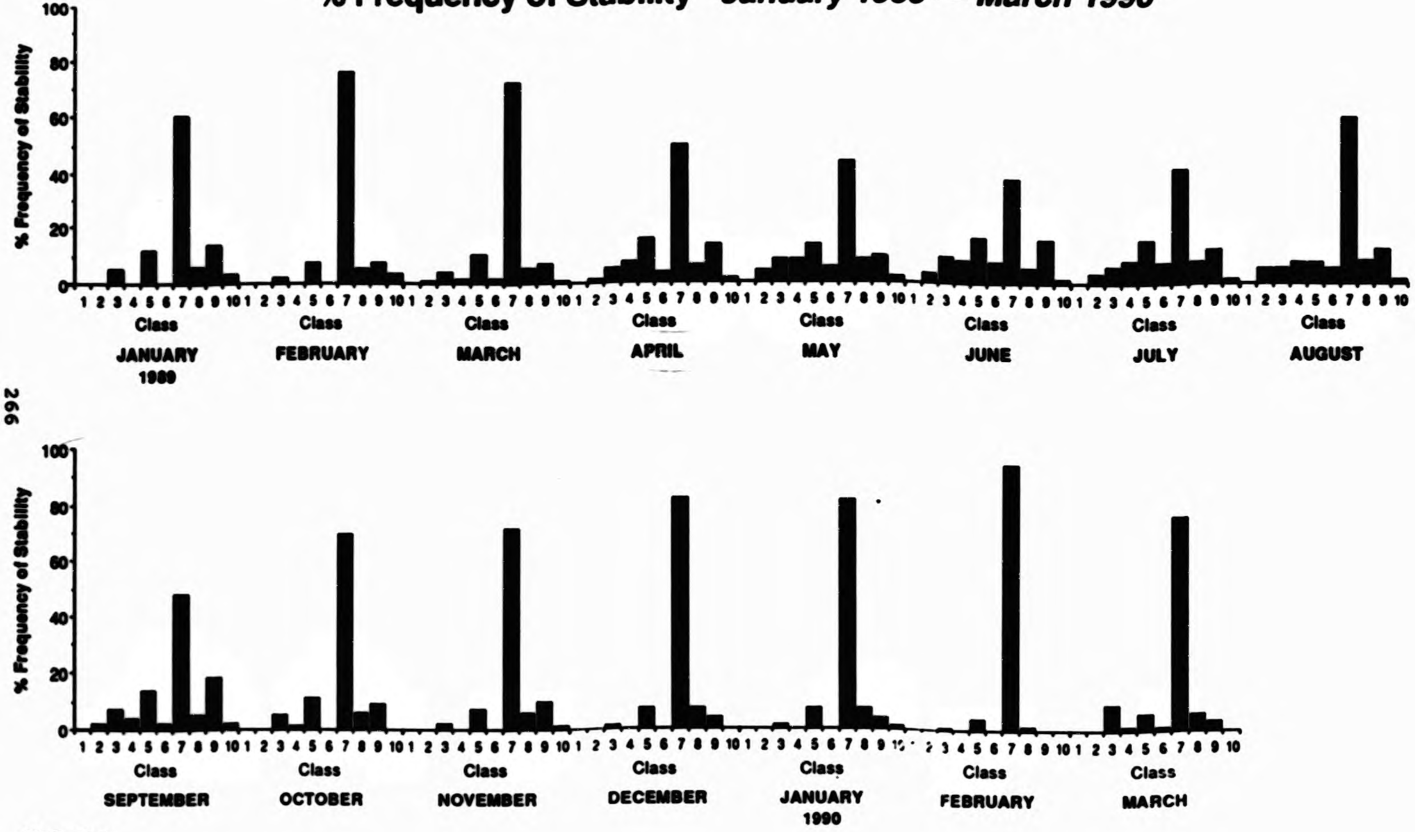


FIG. 8.3

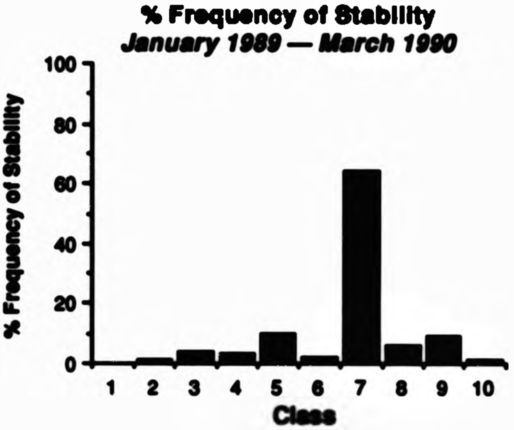

% Frequency of Stability
January 1989 — March 1990
% Frequency of Stability
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
Class

FIG. 8.4

wet deposition, in the Severn Estuary is closely associated with westerly airstreams in cyclonic weather systems (Harrison et.al., 1985). The bulk of this precipitation occurs as frontal rainfall which is likely to be enhanced , to a certain extent, in the coastal areas as a result of orographic uplift.

Having obtained the data for the various weather variables these were then correlated with each other (Table 8.4) and then correlated against the data for the metals on an individual basis (Tables 8.5-8.11). A key to the variables used in the correlation matrices is shown in Table 8.4. A straight line correlation was assumed between the weather variables as well as the deposition data although this may not have been the most appropriate approach. The approach is, however, in line with previous work carried out in the Severn Estuary as reported by Pattenden (1974) whereby the available data on wind direction and speed was used to generate correlations with metal deposition concentrations and extract information on the location of sources.

Table 8.4 Key to variables used in correlation matrices for weather variables and deposition

Variables:

RAIN	Average of zonal rainfall (mm)
rainbar	Average of zonal rainfall (mm)
train	Average rainfall in zone T (mm)
urain	Average rainfall in zone U (mm)
mrain	Average rainfall in zone M (mm)
lrain	Average rainfall in zone L (mm)
%W	Percentage frequency winds NW-SW (Rhoose Airport)
%E	Percentage frequency winds NE-SE (Rhoose Airport)
%WL	Percentage frequency winds NW-SW (Lundy)
%EL	Percentage frequency winds NE-SE (Lundy)
%SW	Percentage frequency winds W-S (Lundy)
%NE	Percentage frequency winds N-E (Lundy)
W/E	Ratio of above
W/E(L)	Ratio of above
SW/NE(L)	Ratio of above
Ubar	Mean wind speed (knots)
UbarL	Mean wind speed (knots) Lundy
PPP	Mean atmospheric pressure (mb -1000)
Nbar	Mean cloud amount (oktas)
amn	Percentage frequency neutral stability (0000-0600 gmt)
amst	Percentage frequency stable (0000-0600 gmt)
pmust	Percentage frequency unstable (1200-1800 gmt)
pmn	Percentage frequency neutral stability (1200-1800 gmt)

Table (8.5) Correlation matrix for weather variables

	%W	%E	%WL	%EL	%SWL	%NEL	W/E	W/E(L)	SW/NE(L)	Ubar	UbarL	PPP	Nbar	amn	amst	pmust	pmn
RAIN	0.182	-0.199	**0.508	-0.047	**0.536	-0.300	0.008	0.157	0.076	***0.591	***0.638	***-0.770	0.357	***0.612	***-0.612	*-0.423	***0.571
%W		***-0.907	***0.663	***0.702	***0.591	***-0.762	***0.692	***0.696	0.334	**0.516	*0.379	-0.264	0.142	0.246	-0.246	*-0.390	*0.373
%E			***-0.690	***0.798	***-0.615	***0.796	***-0.587	***-0.746	-0.313	*-0.389	*-0.396	0.300	-0.186	-0.239	0.239	0.356	-0.297
%WL				**-0.451	***0.892	***-0.760	***0.570	***0.691	**0.517	***0.709	***0.718	*-0.389	**0.506	***0.668	***-0.668	***-0.575	***0.730
%EL					**-0.494	***0.655	-0.285	***-0.577	-0.343	-0.063	-0.158	0.076	-0.085	-0.059	0.059	-0.013	-0.019
%SWL						***-0.850	0.352	***0.626	***0.716	***0.689	***0.749	*-0.398	**0.582	***0.745	***-0.745	***-0.581	***0.705
%NEL							*-0.374	***-0.744	***-0.705	**-0.540	***-0.596	0.310	*-0.436	***-0.598	***0.598	***0.622	***-0.547
W/E								**0.522	0.103	***0.570	0.304	-0.046	0.176	0.201	-0.201	*-0.387	0.357
W/E(L)									***0.636	*0.370	*0.393	-0.315	0.273	0.327	-0.327	-0.294	0.280
SW/NE(L)										0.356	*0.459	0.186	0.270	***0.607	***-0.607	**-0.492	*0.386
Ubar											***0.849	**-0.561	**0.463	***0.765	***-0.765	***-0.679	***0.857
UbarL												***-0.598	**0.550	***0.836	***-0.836	***-0.656	***0.858
PPP													-0.333	**-0.461	**0.461	0.310	**-0.500
Nbar														***0.685	***-0.685	*-0.450	**0.534
amn															***-1.000	***-0.694	***0.781
amst																***0.694	***-0.781
pmust																	***-0.740

Probability		
	*	95%
	**	99%
	***	99.9%

Degrees of freedom = 28

Table (8.6) Correlation matrix: Deposition and Weather Variables - Cadmium

	Deposition				Ratios		
	Zone T	Zone U	Zone M	Zone L	UM	ML	UT
%W	0.078	0.293	-0.185	-0.211	0.542 **	-0.018	0.282
%E	-0.070	-0.137	0.124	0.228	-0.409 *	-0.135	-0.112
%WL	0.302	0.433 *	-0.113	-0.191	0.535 **	0.063	0.168
%EL	-0.118	0.002	0.074	0.039	-0.185	-0.074	0.139
%SWL	0.424	0.432 *	-0.119	-0.194	0.424 *	0.052	-0.057
%NEL	-0.242	-0.210	0.017	0.239	-0.349	-0.188	0.074
W/E	-0.100	0.354	-0.222	-0.185	0.686 ***	0.026	0.708 ***
W/E(L)	-0.019	0.222	-0.246	-0.207	0.550 **	-0.101	0.273
SW/NE(L)	0.103	0.293	-0.129	-0.182	0.404 *	0.070	-0.016
Ubar	0.403 *	0.502 **	-0.097	-0.146	0.551 **	-0.076	0.209
UbarL	0.419 *	0.280	-0.114	-0.174	0.327	-0.011	-0.137
PPP	-0.489 **	-0.119	-0.136	-0.032	-0.058	0.207	0.328
Nbar	0.358	0.384 *	0.031	-0.091	0.182	0.068	0.009
RAIN(Z)	0.714 ***	0.376 *	0.243	0.146	----	----	----
amn	0.501 **	0.453 *	0.038	-0.058	0.355	0.094	-0.082
amst	-0.501 **	-0.453 *	-0.038	0.058	-0.355	-0.094	0.082
pmust	-0.220	-0.255	-0.128	0.249	-0.286	-0.303	-0.055
pmn	0.337	0.335	-0.069	-0.230	0.376 *	-0.043	0.058

Probability		
	*	95%
	**	99%
	***	99.9%

Degrees of freedom = 28

Table (8.7) Correlation matrix: Deposition and Weather Variables - Copper

	Deposition Zone T	Zone U	Zone M	Zone L	Ratios UM	ML	UT
%W	-0.042	0.043	-0.200	-0.355	0.313	0.235	0.271
%E	0.045	0.113	0.215	0.388*	-0.190	-0.261	-0.117
%WL	0.220	0.164	-0.304	-0.254	0.369*	0.021	0.193
%EL	0.015	0.137	-0.051	0.188	0.016	-0.311	-0.003
%SWL	0.320	0.150	-0.273	-0.269	0.279	0.114	0.023
%NEL	-0.139	0.021	0.319	0.425*	-0.219	-0.218	0.004
W/E	-0.168	0.285	-0.238	-0.277	0.624***	0.130	0.688***
W/E(L)	-0.019	0.054	-0.257	-0.368*	0.367*	0.329	0.185
SW/NE(L)	0.210	-0.010	-0.295	-0.279	0.272	-0.087	-0.062
Ubar	0.128	0.296	-0.192	-0.140	0.365*	0.135	0.313
UbarL	0.162	-0.001	-0.174	-0.134	0.066	0.101	-0.037
PPP	-0.201	-0.078	-0.010	-0.096	0.085	0.020	0.165
Nbar	0.235	0.224	-0.051	-0.092	0.094	0.137	0.010
RAIN(Z)	0.518*	0.185	0.135	0.162	----	----	----
amn	0.354	0.288	-0.187	-0.039	0.300	-0.040	0.026
amst	-0.354	-0.288	0.187	0.039	-0.300	0.040	-0.026
pmust	-0.140	-0.054	0.428*	0.302	-0.287	0.057	0.004
pmn	0.167	0.157	-0.300	-0.156	0.218	-0.006	0.120

Probability
* 95%
** 99%
*** 99.9%

Degrees of freedom = 28

Table (8.8) Correlation matrix: Deposition and Weather Variables - Chromium

	Deposition				Ratios		
	Zone T	Zone U	Zone M	Zone L	UM	ML	UT
%W	-0.194	-0.186	-0.091	*-0.398	0.137	*0.407	-0.262
%E	0.223	*0.386	0.174	*0.413	-0.063	-0.318	0.315
%WL	-0.016	*-0.360	0.078	-0.181	-0.197	*0.390	-0.283
%EL	0.188	0.206	0.076	0.178	-0.020	-0.162	0.064
%SWL	-0.014	-0.297	0.074	-0.121	-0.177	0.278	-0.274
%NEL	0.169	0.290	0.118	*0.374	0.056	-0.260	*0.396
W/E	-0.218	-0.206	0.018	*-0.375	0.120	***0.720	0.088
W/E(L)	-0.253	-0.324	*-0.366	-0.257	0.182	-0.272	-0.196
SW/NE(L)	-0.168	-0.112	-0.019	-0.224	-0.152	0.161	-0.107
Ubar	0.027	-0.267	0.169	-0.090	-0.180	**0.478	-0.161
UbarL	0.004	*-0.446	0.125	-0.115	-0.349	0.323	-0.247
PPP	-0.294	0.200	-0.009	-0.148	0.019	0.134	0.231
Nbar	0.239	0.029	0.348	0.077	-0.239	0.217	*-0.369
RAIN(Z)	**0.536	-0.151	0.346	*0.372	----	----	----
amn	0.149	-0.253	0.220	0.027	-0.328	0.275	-0.248
amst	-0.149	0.253	-0.220	-0.027	0.328	-0.275	0.248
pmust	0.010	0.138	-0.011	0.241	-0.073	-0.266	0.203
pmn	0.017	-0.197	0.195	-0.023	-0.216	0.336	-0.096

Probability
* 95%
** 99%
*** 99.9%

Degrees of freedom = 28

Table (8.9) Correlation matrix: Deposition and Weather Variables - Nickel

	Deposition				Ratios		
	Zone T	Zone U	Zone M	Zone L	UM	ML	UT
%W	0.113	-0.077	0.282	0.081	-0.297	0.242	0.037
%E	-0.077	0.200	-0.209	-0.106	0.322	-0.120	0.035
%WL	0.253	0.180	$\overset{**}{0.529}$	0.337	$\overset{*}{-0.430}$	0.356	-0.266
%EL	-0.078	0.265	-0.070	-0.069	0.212	0.011	-0.002
%SWL	0.289	0.205	$\overset{**}{0.538}$	0.339	$\overset{**}{-0.469}$	0.250	-0.257
%NEL	-0.168	0.000	-0.331	-0.094	$\overset{*}{0.375}$	-0.230	0.098
W/E	0.020	-0.092	0.268	0.008	-0.308	$\overset{**}{0.531}$	-0.088
W/E(L)	-0.171	0.034	-0.058	-0.146	-0.034	0.224	-0.195
SW/NE(L)	0.214	-0.071	$\overset{**}{0.464}$	0.105	$\overset{**}{-0.481}$	0.244	-0.206
Ubar	$\overset{*}{0.381}$	0.280	$\overset{***}{0.613}$	$\overset{*}{0.422}$	$\overset{*}{-0.435}$	0.313	-0.270
UbarL	$\overset{*}{0.391}$	0.234	$\overset{**}{0.566}$	$\overset{**}{0.546}$	$\overset{*}{-0.442}$	0.066	$\overset{*}{-0.370}$
PPP	-0.326	-0.258	-0.346	$\overset{**}{-0.518}$	0.230	0.198	0.219
Nbar	0.299	0.124	$\overset{*}{0.402}$	0.277	$\overset{*}{-0.364}$	0.242	$\overset{**}{-0.520}$
RAIN(Z)	$\overset{**}{0.549}$	$\overset{*}{0.430}$	$\overset{**}{0.538}$	$\overset{***}{0.709}$	----	----	----
amn	$\overset{**}{0.463}$	0.259	$\overset{**}{0.551}$	$\overset{**}{-0.466}$	$\overset{**}{0.550}$	-0.192	$\overset{***}{0.567}$
amst	$\overset{**}{-0.463}$	-0.259	$\overset{**}{-0.551}$	$\overset{**}{0.466}$	$\overset{**}{-0.550}$	0.192	$\overset{***}{-0.567}$
pmust	-0.243	-0.105	$\overset{*}{-0.445}$	-0.235	$\overset{*}{0.424}$	-0.265	0.276
pmn	0.244	0.198	$\overset{*}{0.443}$	$\overset{*}{0.392}$	-0.305	0.162	-0.280

Probability		
	$*$	95%
	$**$	99%
	$***$	99.9%

Degrees of freedom = 28

Table (8.10) Correlation matrix: Deposition and Weather Variables - Lead

	Deposition Zone T	Zone U	Zone M	Zone L	Ratios UM	ML	UT
%W	0.125	0.036	-0.327	* -0.403	0.265	0.279	0.076
%E	-0.064	0.082	* 0.393	* 0.427	-0.195	-0.202	0.065
%WL	0.170	0.054	-0.249	0.138	0.188	0.227	-0.060
%EL	-0.120	0.110	0.249	0.138	-0.107	-0.202	0.065
%SWL	* 0.366	0.093	-0.287	-0.315	0.260	0.173	-0.219
%NEL	-0.259	0.053	* 0.374	* 0.432	-0.191	-0.178	0.273
W/E	-0.119	-0.026	-0.209	-0.315	0.108	** 0.561	0.279
W/E(L)	0.027	0.100	* -0.400	* -0.371	* 0.421	0.221	0.147
SW/NE(L)	0.232	0.148	-0.281	-0.279	0.278	0.205	-0.143
Ubar	* 0.454	0.057	-0.133	-0.252	0.104	0.291	-0.128
UbarL	** 0.522	-0.101	-0.288	-0.260	-0.013	0.126	* -0.405
PPP	** -0.488	0.036	-0.090	0.010	0.080	0.064	0.357
Nbar	0.348	-0.063	0.057	-0.144	-0.069	0.217	-0.312
RAIN(Z)	*** 0.607	0.157	0.215	0.073	----	----	----
amn	** 0.554	0.147	-0.081	-0.148	0.163	0.192	-0.278
amst	** -0.554	-0.147	0.081	0.148	-0.163	-0.192	0.278
pmust	-0.260	0.100	0.289	0.358	-0.090	-0.125	0.244
pmn	0.337	-0.060	-0.186	-0.208	-0.022	0.105	-0.249

Probability		
	*	95%
	**	99%
	***	99.9%

Degrees of freedom = 28

Table (8.11) Correlation matrix: Deposition and Weather Variables - Zinc

	Deposition				Ratios		
	Zone T	Zone U	Zone M	Zone L	UM	ML	UT
%W	0.020	-0.048	-0.242	-0.270	0.265	0.079	0.142
%E	-0.010	0.230	0.071	0.261	-0.065	-0.264	0.042
%WL	0.199	-0.071	-0.093	-0.231	0.063	0.160	0.018
%EL	-0.018	0.291	-0.002	0.035	0.045	-0.158	0.134
%SWL	*0.419	-0.039	-0.079	-0.284	0.062	0.229	-0.179
%NEL	-0.243	0.217	0.035	0.323	0.007	-0.316	0.235
W/E	-0.195	0.134	-0.224	-0.204	*0.429	0.085	*0.560
W/E(L)	0.046	-0.031	-0.250	-0.251	0.244	0.317	0.074
SW/NE(L)	0.242	0.016	-0.069	-0.232	0.218	0.123	-0.122
Ubar	*0.364	0.172	-0.197	-0.265	0.153	0.127	0.093
UbarL	*0.389	-0.132	-0.066	-0.234	-0.188	0.213	-0.268
PPP	*-0.455	0.051	0.129	0.016	0.210	0.080	0.356
Nbar	*0.364	0.085	0.069	-0.149	0.002	0.161	-0.121
RAIN(Z)	***0.696	0.028	0.169	0.062	----	----	----
amn	***0.565	0.132	0.098	-0.138	-0.027	0.250	-0.182
amst	***-0.565	-0.132	-0.098	0.138	0.027	-0.250	0.182
pmust	-0.273	-0.030	-0.086	0.340	-0.073	*-0.379	0.111
pmn	0.288	0.010	-0.160	-0.272	-0.063	0.118	-0.054

Probability		
	*	95%
	**	99%
	***	99.9%

Degrees of freedom = 28

Table (8.12) Correlation matrix: Deposition and Weather Variables - Aluminium

	Deposition Zone T	Zone U	Zone M	Zone L	Ratios UM	ML	UT
%W	-0.015	0.102	0.053	-0.127	0.110	0.133	0.123
%E	0.080	-0.083	-0.007	0.203	-0.108	-0.156	-0.106
%WL	0.139	0.206	0.231	0.068	0.175	0.173	0.215
%EL	0.109	-0.001	-0.012	0.189	-0.018	-0.235	-0.028
%SWL	0.252	0.262	0.315	0.155	0.228	0.243	0.254
%NEL	-0.047	-0.132	-0.087	0.107	-0.141	-0.189	-0.136
W/E	-0.068	-0.043	0.011	-0.143	-0.039	0.133	-0.031
W/E(L)	-0.399*	0.198	-0.095	-0.364*	0.215	0.335	0.252
SW/NE(L)	-0.238	0.051	-0.049	-0.141	0.043	0.237	0.079
Ubar	0.412	0.150	0.423*	0.311	0.113	0.096	0.122
UbarL	0.381*	0.169	0.404*	0.237	0.143	0.138	0.161
PPP	-0.491**	-0.186	-0.390*	-0.384*	-0.185	0.041	-0.154
Nbar	0.373*	-0.060	0.470**	0.276	-0.122	0.301	-0.077
RAIN(Z)	0.486*	0.392*	0.437*	0.387*	----	----	----
amn	0.273	0.179	0.310	0.235	0.146	0.163	0.174
amst	-0.273	-0.179	-0.310	-0.235	-0.146	-0.163	-0.174
pmust	-0.193	-0.034	-0.087	-0.059	-0.045	0.003	-0.016
pmn	0.342	0.131	0.243	0.231	0.111	-0.003	0.103

Probability
* 95%
** 99%
*** 99.9%

Degrees of freedom = 28

8.3 Associations within weather variables

The weather variables used to produce the correlation matrices shown in Tables 8.6 - 8.12 do not operate independently but are linked together and considerable association should be expected between the variables. The matrix of linear correlation between variables (Table 8.5) shows that there are strong correlations between them. These are demonstrated by positive associations between Ubar and W/E (0.570), W/E(L) (0.370), %SWL (0.689), %WL (0.709), UbarL (0.849), and Nbar (0.463), and a negative association with atmospheric pressure (-0.561). These, together, are typical of maritime westerly airstreams. The main precipitation mechanism under these conditions is cyclonic frontal rainfall and is shown by significant correlations between rainfall amount and both wind speed (+ve) at Rhoose and Lundy and pressure (-ve) in all zones of the estuary (Table. 8.3).

Strong associations are also seen between neutral stability conditions in both the morning and afternoon between rainfall, and the wind direction observed at Lundy (+ve from westerly and south-westerly directions and -ve in generally easterly directions) as well as the ratio of SW to NE winds at Lundy (-0.607). Neutral stability is also strongly, positively associated with wind speed at both Lundy and Rhoose airport as well as atmospheric pressure which would be expected as stability estimates are a function of these variables. Strong associations are also seen between the stability characteristics which are generated as a result of the way the data were produced. For example, the correlation between amn and amst of -1.0 is seen as all stability in the morning period was either stable or neutral and there is therefore an inverse relationship between the values. Similarly, strong associations are seen between wind variables.

These correlations provide a confirmation that the weather variables are appropriate and that simple linear correlations are a valid means of examining the deposition data in relation to the meteorological conditions operating. The association between the weather variables, however, produces an autocorrelation problem when relating them to aerial deposition. By incorporating, for example, wind speed, cloud amount, and pressure into linear regressions based initially on wind direction alone no further improvement in R^2 values is obtained.

8.4 Associations between weather and deposition values

8.4.1 Cadmium

A dominant source within zone U, the Avonmouth area, is indicated by large UM and UT ratios (Table 8.2). Correlations between wind variables and Cd deposition are dominant in the matrix with correlations between UM and UT with W/E and W/E(L) being highly significant and to a lesser extent between UM and SW/NE(L) (Table 8.6). The wind speed at Rhoose and the ratio UM also show significant correlation. These associations indicate that the distribution of Cd in the estuary is controlled by a dominant source area (Avonmouth) and a westerly airflow as well as the speed of the westerly winds in the estuary. The very high correlation between deposition and rainfall in zone T also confirms these indications and suggests that wet deposition downwind of the zone U source area is an important driving force in Cd deposition to the Severn Estuary. Correlations between amn and amst in zone T also indicate that stable and neutral conditions in the morning control cadmium deposition whereby vertical mixing is dampened which leads to rapid deposition of Cd once emitted into the atmosphere. The slight association between neutral conditions in the afternoon and the ratio UM (0.376) also indicate the dominant Cd source in the upper estuary. These observations are also confirmed by the plots for Cd distribution as shown in Figs 6.5.1 - 6.8.1 whereby the Avonmouth area dominates the distribution of Cd deposition.

8.4.2 Copper

As with Cd a dominant source area in zone U (Table 8.2) is indicated by the strong UM and UT ratios. The highly significant correlations of these ratios with W/E supports this observation. Only one other weather variable appears to have significant association with the deposition of Cu and is pmust in zone M (0.428) which indicates that unstable conditions lead to strong dispersal of Cu away from zone U (Table 8.7). A positive relationship between deposition and rainfall in zone T (0.518) is seen and provides further evidence of wet deposition of Cu derived from zone U and deposited in cyclonic frontal rainfall. It appears that the Avonmouth area is, again, implicated as an important source area for Cu emissions to the Severn Estuary.

8.4.3 Chromium

The deposition of Cr in the Severn Estuary is unlike Cd and Cu and the variation appears to be driven by a less dominant principal and a secondary source area which are acting in together with meteorological controls. Very small differences are seen in the mean deposition values between zones U and M or in the UM and ML ratios (Table 8.2). In seven of the sampling periods Cr values were higher in zone M than in zone U which suggests that there is an important Cr source within or close to this area. This conclusion is supported by strong correlations between ML and W/E which contrasts with the insignificant correlations between both UM and UT and W/E (Table 8.8). A negative association is also seen between zone L and W/E which further supports a source area in zone M. Deposition values in zone L are also positively correlated with E% and rainfall which also indicates that Cr deposition occurred downwind of zone M. A source area in zone U is also indicated by a positive association between rainfall and zone T which suggests that rain is driving Cr deposition in the area and the positive correlation between zone U and E% (0.386) indicates that this zone is also a source area for Cr emissions.

8.4.4 Nickel

The differences between Ni in zones U and M as indicated by the UM ratio (Table 8.2) is smaller than that seen for the other metals as was the case for Cr deposition. This suggests that there are important sources of the metal away from zone U. For 12 out of the 31 sample periods the deposition values in zone L are higher than those in zone M. This indicates that the industrial complexes around Swansea Bay may be acting as secondary sources of Ni. The Ni works in the lower Swansea valley is an obvious source for Ni deposition in the estuary. There is a very strong positive correlation between mean deposition for zone M and wind speed which would support this view given that the strongest winds are generally from a westerly direction (Table 8.9). The correlations between %W, %SWL and the ratio SW/NE(L) and deposition in zone M also back up these observations indicating that zone L is a probable source area for Ni deposition. Strong correlations between deposition and rainfall in all zones, particularly zone L which is immediately downwind of a Swansea Bay source, indicate the more diffuse nature of sources which is also shown in the Ni distribution plots in figures 6.5.4 - 6.8.4.

Stable and neutral conditions in the morning are also significantly correlated with deposition in zone T, M and L as well as the ratios UM and UT indicating the influence of the upper, Avonmouth zone as a source area for Ni deposition. It appears, therefore, that the distribution of Ni deposition to the Severn Estuary is not controlled by the Avonmouth area alone and its deposition appears to be dominated by wet mechanisms.

5.4.5 Lead

The strongest concentration of Pb deposition is seen in zone U which produces large UM and UT ratios (Table 8.2). Lead deposition is correlated positively with E% and NEL% in zone M and L as well as negative correlations with the ratio W/EL which all indicate that there is a source upwind of these zones. Significant correlations are also observed in zone T with wind speed, rainfall and pressure (Table 8.10) as well as between neutral and stable conditions in the morning. Together these demonstrate that most of the Pb emissions to the Severn Estuary originate in the Avonmouth area. A further conclusion that Pb has a limited distribution seawards and landwards of this source area can be drawn. It is probable that Pb deposition landwards of the Avonmouth area is driven by wet deposition (0.607 in zone T) and that seawards deposition is mainly as a result of dry fallout. The distribution of Pb shown in figures 6.5.5 - 6.8.5 supports the conclusions, drawn from the relationship between its deposition and meteorological variables, here with the dominance of the Avonmouth area very apparent.

5.4.6 Zinc

The deposition of Zn is also related with zone U where high UT and UM ratios are observed (Table 8.2). The gradients of deposition away from this zone are most strongly developed under westerly wind conditions with deposition in zone T being positively correlated with %SWL (0.419) as well as the ratio UM and W/E showing a positive association (0.429). Mean Zn deposition in zone T is positively correlated with rainfall (0.696), wind speed (0.364) and cloud amount (0.364) and negatively with pressure (-0.455), which suggests wet deposition is occurring downwind of zone U in frontal rainfall that results from cyclonic medium scale weather systems (Table 9.11). Correlations between zone T and amn and amst also indicate the influence of zone U as a source for Zn deposition in zone T which is upwind and close to its source area and the importance of stable conditions in limiting the dispersal of this metal.

8.4.7 Aluminium

A dominant source of Al is implicated by large UM and UT ratios (Table 8.2) although the correlations between Al deposition and all the weather variables are weak. There are no significant relationships between the inter-zone ratios. There is some association between Al deposition in zones M, L and T with higher wind speeds, cloud amounts and rainfall as well as lower atmospheric pressure (Table 8.12) indicating that the deposition is driven by wet mechanisms within cyclonic systems. The association between Al deposition and higher wind speeds also bears out the theory that Al is largely derived from soil weathering and disturbance by agricultural practices as discussed in section 7.6.

8.5 Associations between weather variables and individual sites

8.5.1 Reasons for site selection

In order to further examine the role of weather variables and metal deposition in the Severn estuary, three sites were chosen to represent various areas. Marlas, Flat Holm and Lydney were chosen to see if the correlations shown between the bulked variables and the sites were still apparent. Marlas was chosen to represent the outer estuary, Flat Holm as an island site and Lydney as a site in the upper estuary and upwind of the Avonmouth area. The relationships between the weather variables and the deposition data for each of these sites are shown in tables 8.13 - 8.15.

8.5.2 Cadmium

The correlations between weather variables and Cd deposition at Marlas show no significant correlations whatsoever (Table 8.13) whereas those at Lydney show highly significant correlations between rainfall in all zones although those in zone L are slightly less significant (0.552) than in the zones to the west

Table 8.13 Correlation Matrix: Deposition and Weather Variables

	Cadmium			Copper		
	MAR	LYD	FLT	MAR	LYD	FLT
LYD	0.789***			0.424*		
FLT	0.555**	0.456**		0.566**	0.314	
W	-0.184	-0.042	-0.331	-0.315	-0.276	-0.131
E	0.204	0.041	0.441**	0.344	0.236	0.116
WL	-0.200	0.156	-0.365*	-0.282	-0.013	-0.310
EL	-0.005	-0.022	0.406**	0.111	0.156	-0.088
SWL	-0.203	0.229	-0.360*	-0.302	0.075	-0.277
NEL	0.218	-0.050	0.349	0.392*	0.059	0.287
W/E	-0.177	-0.139	-0.215	-0.267	-0.326	-0.135
W/E(L)	-0.201	-0.116	-0.318	-0.348	-0.335	-0.185
SW/NE(L)	-0.149	-0.020	-0.284	-0.289	0.074	-0.302
wbar	-0.184	0.190	-0.137	-0.141	-0.067	-0.169
wbarL	-0.212	0.162	-0.269	-0.059	-0.032	-0.176
ppp	0.009	-0.350	-0.088	-0.101	-0.110	0.011
rbar	-0.122	0.217	0.022	-0.150	0.195	-0.115
train	0.127	0.583***	0.054	0.163	0.403*	0.054
urain	0.146	0.600***	0.095	0.175	0.421**	0.055
mrain	0.125	0.609***	0.083	0.087	0.395*	0.074
lrain	0.084	0.552**	-0.060	0.078	0.350	-0.004
rainbar	0.121	0.594***	0.041	0.127	0.397*	0.044
amn	-0.090	0.276	-0.121	-0.033	0.227	-0.241
amnt	0.090	-0.276	0.121	0.033	-0.227	0.241
pmust	0.267	-0.039	0.131	0.276	-0.051*	0.430
pmn	-0.241	0.147	-0.196	-0.127	0.047	-0.350

Probability:

*	95%
**	99%
***	99.9%

Table 8.14 Correlation Matrix: Deposition and Weather Variables

	Chromium			Nickel		
	MAR	LYD	FLT	MAR	LYD	FLT
LYD	0.268			0.351		
FLT	0.062	0.272		0.420*	0.281	
W	-0.355	-0.230	0.146	0.038	0.099	0.251
E	0.376*	0.247	-0.083	-0.078	-0.050	-0.257
WL	-0.258	-0.177	0.342	0.133	0.210	0.584***
EL	0.079	0.119	-0.013	-0.133	-0.071	-0.058
SWL	-0.225	-0.143	0.285	0.107	0.289	0.495**
NEL	0.368*	0.163	-0.017	-0.031	-0.160	-0.278
W/E	-0.385*	-0.224	0.404	-0.020	-0.039	0.356
W/E(L)	-0.220	-0.345	-0.184	-0.110	-0.173	0.091
SW/NE(L)	-0.183	-0.157	-0.131	0.157	0.238	0.227
ubar	-0.214	-0.092	0.465	0.069	0.364*	0.551**
ubarL	-0.167	-0.046	0.286	0.214	0.400*	0.466**
ppp	-0.035	-0.071	-0.268	-0.175	-0.289	-0.361*
rbar	-0.073	0.111	0.438*	0.011	0.204	0.396*
train	0.213	0.279	0.369*	0.193	0.478**	0.403*
urain	0.192	0.284	0.380*	0.212	0.481**	0.423*
mrain	0.205	0.253	0.464**	0.128	0.459*	0.466**
lrain	0.125	0.196	0.413*	0.263	0.461**	0.485**
rainbar	0.185	0.255	0.412*	0.203	0.476**	0.452*
amn	-0.085	0.097	0.262	0.193	0.442*	0.401*
amst	0.085	-0.097	-0.262	-0.193	-0.442*	-0.401*
pmst	0.337	0.072	-0.100	-0.071	-0.174	-0.320
pmn	-0.093	-0.099	0.359	0.067	0.262	0.385*

Probability:

*	95%
**	99%
***	99.9%

Table 8.15 Correlation Matrix: Deposition and Weather Variables

	Lead			Zinc			Aluminium		
	MAR	LYD	FLT	MAR	LYD	FLT	MAR	LYD	FLT
LYD	0.146			0.393*			0.782***		
FLT	0.123	-0.041		0.461**	0 .389*		0.139	0.391*	
W	-0.401*	0.151	-0.132	-0.273	-0.147	-0.235	-0.305	-0.148	0.249
E	0.429*	-0.079	0.207	0.251	0.175	0.263	0.378*	0.228	-0.189
WL	-0.278	0.096	-0.165	-0.237	0.013	-0.304	-0.118	-0.053	0.287
EL	0.102	-0.133	0.220	-0.020	0.168	0.207	0.288	0.181	-0.215
SWL	-0.316	0.275	-0.236	-0.283	0.192	-0.344	-0.034	0.097	0.393
NEL	0.388*	-0.207	0.274	0.307	-0.058	0.331	0.278	0.070	-0.245
W/E	-0.315	-0.088	0.124	-0.225	-0.260	-0.108	-0.303	-0.198	0.139
W/E(L)	-0.368*	-0.092	-0.284	-0.239	-0.160	-0.232	-0.457*	-0.504**	0.202
SW/NE(L	-0.240	0.160	-0.199	-0.220	0.265	-0.264	-0.214	-0.315	-0.015
ubar	-0.257	0.368*	-0.039	-0.296	0.157	-0.221	0.074	0.212	0.503**
ubarL	-0.250	0.451*	-0.185	-0.241	0.162	-0.247	0.000	0.214	0.497**
ppp	0.053	-0.383*	0.052	0.045	-0.172	-0.026	-0.261	-0.380*	-0.391*
rbar	-0.193	0.204	0.070	-0.175	0.241	0.025	0.132	0.258	0.403*
train	-0.054	0.469**	-0.055	0.025	0.436*	0.035	0.322	0.370*	0.414*
urain	-0.031	0.451*	-0.018	0.049	0.442*	0.063	0.345	0.370*	0.375*
mrain	-0.064	0.415*	-0.009	-0.003	0.428*	0.029	0.330	0.347	0.456*
lrain	-0.079	0.378*	-0.138	0.001	0.403*	-0.041	0.255	0.270	0.377*
rainbar	-0.058	0.433*	-0.058	0.018	0.433*	0.020	0.316	0.343	0.411*
amn	-0.149	0.383*	-0.132	-0.158	0.384*	-0.155	0.059	0.119	0.364*
amst	0.149	-0.383*	0.132	0.158	-0.384*	0.155	-0.059	-0.119	-0.364*
pmust	0.328	-0.192	0.213	0.384*	-0.166	0.261	0.089	-0.069	-0.135
pmn	-0.175	0.300	-0.161	-0.279	0.150	-0.301	0.074	0.195	0.305

Probability:

*	95%
**	99%
***	99.9%

of this. Significant correlations at Flat Holm are observed between wind direction at both Rhoose and Lundy. These are particularly significant for easterly winds. Together, these significant correlations for all sites for Cd bear out the importance of zone U, the Avonmouth area as a source are for Cd and also that Cd deposition is driven, largely by wet deposition mechanisms.

8.5.3 Copper

Similar correlation patterns are seen for copper deposition as for Cd deposition with the only significant weather variable correlation at Marlas being north-easterly winds (Table 8.13). This suggests a possible local source of Cu in the Marlas area or that Cu is dispersed from a source further upstream in the Severn region. Significant correlations are again seen for rainfall in zones T, U and M with Cu deposition. No significant associations are observed between weather variables and Cu deposition on Flat Holm. These associations suggest that Avonmouth is a dominant source area for Cu deposition and that the deposition is largely driven by wet mechanisms and that it occurs mainly to the north of zone U.

8.5.4 Chromium

Table 8.14 shows the associations between Cr deposition and weather variables at each of the sites. Associations between Cr deposition and E winds at Rhoose and NE winds at Lundy are observed as well as a negative correlation with the ratio W/E. No significant correlations are seen for Lydney whereas significant associations for rain in all zones of the estuary are seen for Flat Holm, particularly in zone M of the estuary. This bears out earlier observations that Avonmouth is not a dominant source area for this metal and that a strong source in the middle zone of the estuary is indicated and that wet deposition is a dominant deposition mechanism. This source may be the LLanwern steel works although specific sources of Cr in the area are not known.

8.5.5 Nickel

No significant associations are seen between Ni deposition and weather variables at Marlas. Significant correlations are seen at Lydney for wind speed, rainfall and stable and neutral conditions in the morning. At Flat Holm very strong association is seen between Ni deposition and westerly winds at Lundy and to a lesser extent with wind direction, atmospheric pressure, cloud amount, rainfall in all zones as well as stability conditions in the morning. These associations suggest that Ni emissions are found both in the Avonmouth area as well as a source area downwind of Flat Holm, possibly Swansea Bay and that its deposition is controlled, again, by wet deposition processes. If there is a strong source area in the Swansea Bay area some association between weather variables and Marlas, especially westerly winds might have been expected. It is therefore, difficult to ascertain a specific secondary source area for Ni emissions in the Severn Estuary.

8.5.6 Lead

Lead correlations (Table 8.15) for Marlas show that there is a positive association between E winds and NE winds (at Lundy) indicating that the nearby road system may be responsible for Pb deposition as a result of vehicle emissions in the area. No correlations are seen at Flat Holm for the relationships between weather variables and Pb deposition whereas associations between wind speed, atmospheric pressure, rainfall in all zones and stable conditions (-ve amst) the morning are shown. This indicates that Pb deposition is confined to a dominant source area in the upper estuary; the Avonmouth complex, and that the deposition is controlled by wet mechanisms as well as it's dispersal being limited by stable conditions.

8.5.7 Zinc

An almost identical pattern of Zn deposition and weather variables is seen for this metal as is seen for Pb variables (Table 8.15) which, again, indicates the Avonmouth area as a source with the same controlling factors of wet deposition and stability. An exception is seen whereby Zn deposition correlates with pmust at Marlas which indicates that Zn is widely dispersed under these unstable conditions although it is very difficult to ascribe a source for the metal at this site without other weather variable associations at the site to support any suggestions.

8.5.8 Aluminium

The associations for Al deposition and weather variables at the three sites (Table 8.15) show quite different patterns when compared to other metals. At Marlas the only significant correlations are seen between E and W/E(L) and deposition. W/E(L) is again significant at Lydney as well as atmospheric pressure and rain in the top and upper zones of the estuary. On Flat Holm Al deposition is significantly associated with wind speed, atmospheric pressure, cloud amount, rainfall in all zones as well as stability conditions experienced in the morning. The indications are, therefore, that Al deposition is controlled to some extent by a source in the Avonmouth area which is driven by both wind speeds and wet deposition although it is likely that Al deposition may be derived from sources all around the estuary as a result of soil particulate being blown into the atmosphere.

9 CONCLUSIONS

Four methods of interpolation (linear, $\log_{10}$, $\log_e$ and square root) were employed to estimate the deposition of metals to the Severn estuary. Deposition estimation was approached in two ways for linear interpolation; Firstly by calculating the inputs for each sampling interval and secondly by totalling the data over the entire sampling period and then estimating the daily input. The methods produced comparable results and of the other methods $\log_{10}$ transformations generated the most reliable deposition estimates for Cd, Zn and Pb in terms of a straight line fit with distance from the principal source area of Avonmouth. A combination of Log_{10} and Log_e interpolation proved the most reliable for Ni, Cr and Cu whilst all methods produced similar results for Al. The estimated deposition loadings for each of the metals on the basis of these interpolation methods are shown in table 9.1.

Examination of the analytical quality control data showed that the instrumental analyses carried out at Wessex Water were accurate for all metals except zinc. The results for Zn indicated that the concentrations were being overestimated in the precipitation samples, by as much as 8%, particularly in samples containing relatively high concentrations. This indicated that the estimates for Zn deposition may be exaggerated.

Considerable variation of metal concentrations collected in

Table 9.1 Estimated daily metal deposition to the Severn Estuary Jan 1989 -Mar 1990

Metal	Estimated deposition kgday^{-1}
Cd	0.84
Cu	8.64 - 8.68
Cr	1.93 - 1.94
Ni	2.75 - 2.80
Pb	62.8
Zn	96.07
Al	0.31

precipitation in adjacent samplers were experienced, however, in an experiment at Northwick Landfill site which gives a measure of the confidence that can be placed in the results. The relative standard deviations obtained for each metal collected over a two week period were as follows;

Cd - 25.98%
Cu - 20.68%
Cr - 85.80%
Ni - 79.40%
Pb - 38.16%
Zn - 34.80%

The results may have been obtained as a result of contamination or variations in dry deposition and were similar to results obtained for the collection of precipitation by other workers. However, despite the possible inaccuracies suggested for Zn by the analytical quality control samples and the variations seen between samplers the overall results suggest that considerable decreases of metal deposition to the Severn Estuary have occurred.

In comparison with earlier estimates of deposition of metals, where data was available, the results obtained show that there has been a large decline in metal deposition to the Severn estuary. On the basis of the results given in table 9.1 decreases of two orders of magnitude are seen for Cd and Zn deposition and one order of magnitude for Cu, Ni and Pb. Cr and Al deposition were not estimated in earlier surveys so no comparison was made.

The reasons for this decline were shown to be as a result of improved methodology in both the field and the laboratory and in means by which the estimates were made as well as a real decline in deposition levels within the region of the Severn estuary. The decline observed in deposition of heavy metals was consistent with other work on the water quality of the Severn estuary, which has improved.

Interpolation was used as a basis for interpretation of the aerial deposition data and this approach makes some assumptions about the behaviour of pollution dispersal but it takes better account of distribution over the estuary than does the simple blocking method previously employed. It also approaches a realistic representation of aerial deposition around identified point sources, to a certain extent, and takes some account of the operation of meteorological controls.

The alternative sampling methodology employed has some deficiencies which relate to the indeterminate extent to which samples collected at coastal sites can be regarded as adequately representative of the open waters of an estuary where boundary layer conditions are different. The aerodynamic and physical properties of coastal plains produce major changes in momentum, heat and water vapour exchanges over very short distances away from the mean high water mater. This was illustrated by plotting the metal distributions across the estuary without Flat Holm data. The resulting distributions were unaffected for Cd, Cu, Pb, Zn and Al as a consequence of the dominance of the Avonmouth area as source of these metals. The plots for Cr and Ni, however showed that linear interpolation was underestimating the values for Cr by 17% and overestimating Ni deposition by up to 24%. Estimations were not produced using transformed data so no comparison between interpolation methods could be made.

Care was taken to select sites which had an open exposure and were within as short a distance as possible of the tidal area of the estuary such that they were representative of the maritime wind field. However, maritime resuspension, which was more likely to occur under these siting arrangements may have been a problem. Despite all precautions it must be noted that complex coastal boundary layer changes over short distances, variation in local shelter around sampling sites and an unquantified maritime effect mean that samples taken over the fifteen months of the survey are no more than the best that could be achieved in the circumstances.

It has not been possible to establish the relationship between the estimates based on this new survey and the overall heavy metal budget to the waters of the Severn due to an absence of current water quality data. However, estimates based on the inputs budget calculated on the basis of discharges via rivers and streams, sewage outfalls, sludge dumping as well as atmospheric inputs in 1978/9 were recalculated using the estimates made of deposition in this survey. The results of this calculation showed that the contribution of the atmosphere to the overall water quality of the Severn estuary had declined for all metals except Pb by an order of magnitude. The estimates for Pb, nonetheless, showed a decrease of 80%. These estimates of the declining atmospheric contribution must, however, be treated cautiously because it is clear, from other work, that the overall water quality has improved and it is probable that the contributions via land based inputs have also declined.

The distribution of aerial deposition of metals over the Severn Estuary clearly indicates the predominance of the Avonmouth area as a major source of all metals. This is particularly marked with respect to Pb, Zn, Cd and Cu and is clearly related to the manufacturing base of this area and incinerator emissions, as indicated by Scott (1987) and Davis and Clayton (1987). There would appear to be significant secondary sources of Ni and Cr. These may originate in South Wales and could be associated with metalliferous industries on this side of the estuary, particularly the Swansea Bay area. Predominance of emission from the Avonmouth area gives very steep decreases in deposition due to initially high atmospheric fallout rates, particularly under conditions of wet deposition. Where significant secondary emission sources exist there is considerably less differentiation in deposition between the upper and lower estuary.

The distribution of Pb deposition, whilst being predominantly controlled by the Avonmouth area, is also likely to be governed by emissions from vehicles that use the extensive road network around the Severn.

An attempt was made to identify sources of the metals other than Avonmouth by fitting a straight line relationship to $\log_{10}$ transformed deposition values and $\log_{10}$ transformed distances from Avonmouth. The residual values obtained were then plotted and these plots indicated that the Swansea Bay area was an important secondary source for all the metals examined. Another source of Ni an Cr was also indicated in the Severn estuary originating in the Cardiff/Newport area. The Llanwern Steel works was the only major metalliferous industry in the area but it was not confirmed as a source of these metals.

An examination of the association between metals was carried out by correlating the calculated total deposition estimates for each metal to the estuary on the basis the two week sample interval. These showed that there were significant (at the 99.9% probability level) associations between Cu and Cd, Cu and Cr as well as Cd and Pb. Slightly less significant (99%) associations were observed between Cd and Cr, Pb and Cu as well as Zn and Ni. These observed correlations suggested that the sources for the metals were similar and that they behaved similarly in the atmosphere. A closer examination of metal associations was made for deposition at Avonmouth in order to identify possible relationships between Zn, Cd and Pb in view of the emissions from the Commonwealth Smelting plant. These relationships were identified and were particularly significant between Pb and Zn ($r - 0.87$), Cd and Zn ($r = 0.64$) as well as Cd and Pb ($r = 0.63$)

and indicated the predominance of the smelting plant in Avonmouth as a source for these metals.

There is no clear seasonal variation in metal deposition which may indicate that energy-based sources such as power stations are not major contributors to atmospheric loadings of heavy metals. There would be an expectation of a winter peak due to higher fuel combustion and the occurrence of periods of strong stability in the lower atmosphere under cold anticyclonic conditions. However, there was marked fluctuation between sample periods which could be attributed either to emission rates or to prevailing weather conditions. In the absence of specific data on the former, attention has been focused on the role of meteorological variation.

An attempt to quantify the resuspension gradient inland from the high water mark proved unsuccessful. The attempt was carried out, however, over a particularly dry period with low wind speeds and over a very short distance inland. Given the generally short open water fetches near to most of the sampling sites, with the exception of Flat Holm, resuspension could be assumed to be relatively small. The need for further investigation of the existence of a maritime effect in the Severn estuary is therefore highlighted.

An intensive daily sampling study on Flat Holm emphasised the importance of wet mechanisms of deposition to the Severn with considerably higher levels of metals being collected from rainfall than dry deposition. Considerable variation was seen between different sites on the island for both wet and dry deposition. The distribution of deposition on the island suggested that Avonmouth was an important source of Cd, Cu, Pb and Zn whilst the Swansea Bay area appeared to be a more important source of Cr and Ni. Na deposition was almost certainly controlled by resuspension from the sea.

Distribution of aerial deposition of heavy metals was affected by both airflow conditions and precipitation totals. The steepest gradients of change down the estuary occurred under dominant west wind conditions which would have driven most emissions from the upper estuary inland. In specific cases it was clear that easterly winds resulted in increased deposition of metals which appeared to originate in both the upper and middle zones of the estuary. Westerly wind directions were, however, associated with lower atmospheric pressure, greater cloud cover and stronger winds so it was impossible to identify specific cause effect linkages. The strong correlation between deposition and rainfall totals indicates that there is a dominance of wet deposition, which results in heavy deposition near to and immediately downwind from dominant sources.

There is sufficient indication in the correlations between deposition and weather variables that very broad estimates of aerial loadings could be obtained using a very basic network of routine monitoring sites (eg. Avonmouth, Flat Holm and Marlas) and simple, inexpensive weather observations which are readily available from Rhoose. These estimates would be considerably improved if a programme of daily sampling were carried out in view of the rapidly changing atmospheric conditions that are seen over the Severn estuary.

10 RECOMMENDATIONS

In view of the improvements to the overall water quality of the Severn Estuary and the decreased estimate of the contribution of atmospheric metal inputs, it is suggested that a new inputs budget for all sources of metal contamination is drawn up.

Further work on the maritime effect needs to be carried out in a variety of sites which are exposed to different wind and fetch conditions. The experiment carried out in this project needs to be repeated such that samples are collected much further inland and under varying wind speeds, particularly higher wind speeds. This would create a much clearer picture of how recycled metals are affecting atmospheric deposition samples.

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12 APPENDICES

I Corrected and interpolated data. January 1989 - March 1990
- I.1 Cd
- I.2 Cu
- I.3 Cr
- I.4 Ni
- I.5 Pb
- I.6 Zn
- I.7 Al
- I.8 Na
- I.9 Chloride

II Calculated metal loadings and rain data. January 1989 - March 1990.
- II.1 Cd
- II.2 Cu
- II.3 Cr
- II.4 Ni
- II.5 Pb
- II.6 Zn
- II.7 Al
- II.8 Rainfall (mm)

Table 1.1 Cadmium - corrected and interpolated results

Jan 1989 - March 1990

	[illegible]	[illegible]	[illegible]	LYD	[illegible]	AVON	[illegible]	[illegible]	[illegible]	LEE	FLT
1	0.15	2.04	0.32	0.44	0.77	17.47	3.10	0.45	0.05	0.01	0.04
2	0.14	0.35	0.29	0.90	1.91	29.25	0.06	0.17	0.09	0.05	0.16
3	0.01	0.01	0.06	0.09	0.08	3.06	1.94	0.23	0.01	0.01	0.01
4	0.06	0.09	0.07	0.31	0.75	5.12	0.14	0.06	0.06	0.02	0.06
5	0.22	0.15	0.15	0.27	0.48	2.43	0.08	0.19	0.07	0.06	0.01
6	0.22	0.31	0.45	0.60	1.10	17.38	3.59	1.17	0.43	0.12	0.25
7	0.17	0.28	0.36	0.25	0.42	5.30	1.08	0.57	1.30	0.10	0.20
8	0.30	0.39	0.32	0.65	0.79	6.64	1.74	1.19	0.26	0.15	0.44
9	0.27	0.59	0.85	1.67	1.97	32.08	9.39	4.25	0.46	0.08	0.42
10	0.74	0.75	0.01	0.33	0.48	7.27	6.34	2.35	0.05	0.59	0.65
11	0.26	0.40	0.97	0.70	0.60	16.72	1.94	1.40	0.22	0.13	0.36
12	0.42	0.26	0.46	0.71	0.76	23.30	3.01	2.40	0.33	0.20	0.19
13	0.97	0.28	0.34	1.15	0.67	6.84	1.79	1.28	0.34	0.34	0.29
14	1.27	1.46	2.27	1.25	3.38	96.70	14.65	3.47	0.96	0.51	1.38
15	0.17	0.59	0.38	0.38	0.58	42.43	14.23	6.35	0.74	0.30	0.28
16	0.01	0.13	0.07	0.01	0.40	9.86	0.25	0.08	0.01	0.06	0.15
17	0.10	0.34	0.86	0.19	1.19	135.10	7.96	4.15	0.25	0.07	0.99
18	0.05	0.08	0.30	0.18	0.40	16.24	1.09	0.01	0.19	0.06	0.01
19	0.23	3.11	3.08	1.11	4.51	84.24	65.00	28.12	3.90	0.13	1.18
20	0.47	0.07	0.18	0.39	1.61	35.00	17.01	1.10	0.22	0.10	0.59
21	0.04	0.12	0.04	0.27	0.35	11.00	6.18	0.38	0.09	0.04	0.02
22	0.05	0.11	0.23	0.34	0.60	4.10	3.78	0.33	0.05	0.01	0.22
23	3.44	4.78	4.86	2.10	7.21	287.00	107.00	37.90	1.40	1.13	13.82
24	0.06	0.16	0.74	0.25	0.43	2.88	16.20	14.00	0.11	0.20	0.37
25	0.04	0.10	0.10	0.39	0.28	2.60	4.30	0.74	0.04	0.04	0.09
26	0.14	0.17	0.22	0.40	1.05	31.30	2.35	0.41	0.05	0.01	0.04
27	0.05	0.07	0.09	0.30	0.72	19.00	0.55	0.06	0.07	0.04	0.01
28	0.01	0.04	0.04	0.19	0.48	4.70	0.32	0.05	0.02	0.01	0.01
29	0.05	0.09	0.19	0.37	1.15	16.00	1.99	0.40	0.02	0.11	0.02
30	0.01	0.05	0.16	0.40	0.45	180.00	0.89	4.30	0.06	0.06	0.14
31	0.12	0.25	0.72	1.05	1.95	110.30	2.88	5.05	0.06	0.07	0.31

Table I.1 Cadmium - corrected and interpolated results

Jan 1989 - March 1990

[illegible]	[illegible]	[illegible]	LYD	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	FLT	
1.00	1.96	2.56	3.75	4.79	3.00	70.20	13.33	2.10	0.73	0.38	1.00
2.00	2.27	5.70	3.91	7.00	14.63	222.75	9.30	2.38	4.30	0.30	2.40
3.00	0.40	0.30	0.60	0.66	0.33	20.90	2.13	0.95	0.35	0.10	0.10
4.00	0.35	0.82	1.73	1.76	2.75	29.75	1.43	0.85	1.10	0.47	0.62
5.00	4.80	2.45	1.30	1.90	2.45	12.60	1.65	0.61	0.41	0.10	3.29
6.00	1.27	2.21	3.41	3.26	5.00	90.00	80.40	6.57	2.90	1.06	1.63
7.00	1.97	1.96	2.07	1.38	1.97	26.86	12.34	3.90	1.65	0.81	1.51
8.00	2.10	7.65	6.88	2.56	9.45	48.95	26.00	8.16	4.80	1.68	10.02
9.00	7.80	10.42	8.92	20.72	10.60	300.90	81.38	34.65	8.99	4.36	3.70
10.00	14.44	12.36	5.80	3.85	4.14	91.40	69.76	19.36	11.75	8.38	5.00
11.00	2.47	6.42	7.96	3.56	6.73	66.65	16.96	13.53	2.86	2.37	16.00
12.00	6.06	2.54	5.90	4.26	3.96	89.40	30.06	14.08	4.40	3.48	18.00
13.00	4.52	2.88	2.19	2.92	2.46	26.22	11.80	7.74	1.06	3.52	8.90
14.00	21.40	20.15	21.95	12.80	20.86	322.40	34.43	36.36	13.95	7.78	14.00
15.00	2.38	8.10	3.82	3.06	9.43	277.73	90.15	61.40	16.80	3.38	2.90
16.00	1.43	2.95	1.79	0.25	2.40	40.90	1.53	1.74	1.38	0.81	1.61
17.00	4.68	7.71	9.11	0.45	10.10	214.90	41.90	25.20	3.61	2.46	7.38
18.00	0.88	1.13	0.95	1.15	1.12	44.10	6.61	2.85	1.44	0.40	1.86
19.00	6.18	40.23	39.40	9.76	25.34	402.40	510.40	126.85	36.43	1.68	12.40
20.00	3.86	14.26	0.79	6.30	11.22	217.50	121.30	9.45	5.38	1.19	8.67
21.00	0.40	0.70	0.11	1.10	3.40	23.00	21.38	0.90	0.40	0.40	0.20
22.00	1.10	0.30	0.40	1.06	1.77	27.85	7.43	1.19	0.10	0.10	0.74
23.00	81.92	35.76	31.39	36.56	56.70	806.00	539.00	166.40	17.92	18.90	94.20
24.00	1.90	1.80	3.70	3.45	5.40	31.40	72.00	62.40	2.36	2.36	1.80
25.00	0.40	0.30	0.90	1.30	1.00	15.00	14.00	4.40	0.30	0.90	0.30
26.00	0.73	1.70	1.10	1.40	8.40	96.00	30.00	5.00	1.10	0.30	0.30
27.00	0.40	0.90	0.80	0.80	2.30	26.00	2.80	1.00	0.40	0.20	1.50
28.00	1.70	0.30	0.00	0.20	0.40	7.40	1.10	0.10	0.40	0.20	1.29
29.00	0.30	0.40	0.30	0.70	3.40	70.00	30.07	7.16	0.30	0.10	2.17
30.00	0.40	1.10	0.80	1.20	4.30	510.00	11.20	23.30	1.40	1.40	1.80
31.00	1.80	3.40	5.10	7.30	10.40	110.30	19.80	16.07	1.96	1.34	3.00

Table 1.3 Chromium - corrected and interpolated results cont'd

Jan 1989 - March 1990

	[illegible]	[illegible]	[illegible]	LYD	[illegible]	AVON	[illegible]	POR	HART	LEE	PLT
1	0.05	0.71	0.75	0.73	0.30	0.31	0.34	0.75	1.31	0.44	0.36
2	0.57	2.10	2.21	1.00	0.90	0.10	1.30	0.40	2.30	0.12	1.07
3	0.05	0.05	0.05	0.05	0.32	0.22	0.22	0.05	0.05	0.05	0.05
4	0.05	0.05	0.05	0.05	0.05	1.19	0.05	0.05	0.05	0.05	0.05
5	0.02	0.41	0.05	0.27	0.05	0.05	0.05	0.05	0.05	0.05	0.44
6	0.30	0.40	0.57	0.45	0.00	0.90	3.00	0.27	0.57	0.33	0.45
7	0.06	0.46	0.35	0.23	0.25	0.90	0.36	0.25	0.05	0.12	0.25
8	0.75	1.10	1.35	1.40	1.35	1.45	1.00	0.79	0.70	0.20	1.45
9	0.77	2.30	1.00	2.59	1.46	3.04	3.45	1.02	1.41	0.05	0.40
10	4.30	2.41	1.10	0.05	0.05	1.73	3.05	0.45	0.05	3.37	0.30
11	0.02	1.40	1.04	0.34	0.91	1.90	1.23	0.99	0.30	0.95	0.90
12	1.04	0.41	0.02	0.05	0.00	1.40	1.47	0.00	1.05	0.74	0.40
13	0.30	0.30	0.30	0.01	0.47	0.57	0.47	0.61	0.46	0.01	0.70
14	6.74	4.74	5.49	2.33	3.47	7.46	4.00	4.31	2.79	1.95	3.40
15	0.30	1.05	2.70	0.36	0.92	9.00	4.61	4.70	0.05	1.09	0.40
16	0.34	0.34	0.36	0.05	0.25	0.35	0.05	0.44	0.31	0.44	0.00
17	1.95	1.06	3.43	0.05	1.36	5.53	4.14	3.05	0.95	0.35	1.40
18	0.46	0.90	0.30	0.23	0.32	0.05	0.70	0.45	0.33	0.30	0.45
19	1.37	9.87	12.38	1.08	4.10	6.55	35.32	9.92	4.70	0.73	4.16
20	2.43	3.41	0.19	1.05	1.98	9.30	10.26	0.84	1.42	0.34	1.40
21	0.40	0.10	0.01	0.10	0.10	0.10	0.48	0.10	0.20	0.10	0.10
22	0.05	0.12	0.30	0.12	0.35	0.25	0.12	0.72	0.05	0.10	0.12
23	17.92	29.52	4.86	5.76	5.67	17.42	29.26	7.28	1.92	3.75	9.42
24	0.30	0.70	0.76	0.40	0.90	0.72	3.06	1.76	0.16	0.44	0.20
25	0.10	0.10	0.40	0.10	0.30	0.30	0.05	0.05	0.05	0.40	0.70
26	0.44	0.70	0.20	0.30	0.30	1.30	0.40	0.10	0.10	0.05	0.10
27	0.10	0.10	0.20	0.05	0.20	0.30	0.20	0.05	0.20	0.05	0.30
28	0.05	0.05	0.05	0.20	0.05	0.05	0.10	0.05	0.40	0.05	0.42
29	0.40	0.05	0.05	0.05	0.20	0.40	1.07	0.45	0.05	0.40	0.53
30	0.05	0.05	0.05	0.70	0.50	2.10	1.10	1.30	1.30	0.40	2.90
31	0.40	0.56	1.28	0.30	0.75	4.70	2.20	1.50	1.30	0.56	0.70

I.

Table 1.4 Nickel - corrected and uncorrected results (ugl⁻¹)

Jan 1989 - Mar 1990

	MAR	MEL	HAG	LYD	HOR	ANCH	PGB	POR	HUNT	LEE	FLT
1	1.47	0.99	0.75	0.73	1.90	1.72	1.96	0.90	0.87	0.25	1.26
2	1.56	3.00	2.21	2.00	1.57	5.85	3.80	1.19	2.56	0.25	2.14
3	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
4	0.25	0.25	0.25	0.25	0.25	0.99	0.25	0.25	0.25	0.25	0.25
5	1.63	0.25	1.30	0.60	0.25	0.77	0.25	0.25	0.25	0.25	0.25
6	0.25	0.25	0.85	0.25	0.25	2.10	13.17	1.75	1.42	0.25	0.82
7	0.25	0.25	0.25	0.25	0.90	1.02	1.46	0.25	0.25	0.25	0.25
8	1.00	1.73	2.25	2.70	3.30	4.43	5.40	2.36	1.85	0.70	2.79
9	2.77	3.04	2.12	6.29	3.01	5.64	7.20	3.86	2.25	0.95	2.20
10	4.74	0.25	1.30	0.25	0.95	2.77	6.90	1.30	2.94	2.99	1.20
11	0.96	0.25	0.86	0.25	0.25	2.13	2.14	0.25	0.25	0.25	0.70
12	1.56	0.25	0.25	0.25	0.25	3.04	3.51	1.06	1.47	0.92	0.25
13	0.58	1.04	0.69	1.62	0.94	0.57	0.25	1.45	0.25	0.25	0.25
14	11.91	2.37	0.25	0.25	0.25	12.80	86.63	7.82	3.98	2.72	5.70
15	1.82	8.10	2.91	0.25	2.07	9.72	6.61	5.17	8.04	0.25	1.00
16	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.77	0.25	0.25
17	0.25	0.25	0.25	0.25	0.25	14.10	10.90	3.64	0.25	0.25	2.95
18	0.25	0.25	0.81	0.25	0.25	0.81	0.95	0.25	0.56	0.60	0.08
19	2.29	11.39	6.60	0.25	0.25	14.31	119.14	4.96	0.25	0.25	3.84
20	2.42	2.40	0.25	0.25	1.98	8.00	14.04	1.80	0.25	0.25	0.15
21	0.25	0.25	0.25	0.25	0.25	0.60	5.57	0.25	0.25	0.25	0.25
22	0.70	0.25	0.50	0.25	0.25	0.94	2.48	0.25	0.25	0.25	0.62
23	26.80	19.40	7.29	7.04	8.10	29.48	84.70	14.04	12.00	5.40	21.90
24	0.25	0.70	0.70	0.75	1.00	2.14	11.14	3.60	0.25	0.25	0.25
25	0.25	0.25	0.25	0.25	0.25	0.70	1.30	0.25	0.25	0.40	0.70
26	0.50	1.10	0.90	0.90	1.80	2.00	2.30	1.80	1.50	0.25	0.80
27	0.60	0.60	1.00	0.70	0.80	1.00	2.40	0.70	1.00	0.60	1.65
28	0.25	0.90	0.25	0.80	0.25	0.60	0.80	0.25	0.25	0.40	0.25
29	0.25	0.25	0.25	0.25	0.50	1.80	3.79	0.66	0.25	0.25	0.25
30	0.25	0.60	1.20	0.60	0.90	6.40	3.00	1.94	2.30	0.60	1.20
31	1.32	1.00	1.50	3.30	1.90	2.90	3.10	2.13	2.10	0.86	1.70

Table 1.5 Lead - corrected and uncorrected results (μgl^{-1})

Jan 1989 - March 1990

	MAR	HEL	MAG	LYD	WER	AVON	POO	POR	HUNT	LEE	FLT
1.00	17.93	14.77	19.30	20.30	39.00	1406.00	929.10	66.00	6.38	3.40	7.76
2.00	15.76	27.00	28.05	50.00	29.25	2700.00	144.60	22.10	8.70	4.34	10.94
3.00	2.00	4.30	4.10	6.40	6.45	364.30	56.00	5.41	3.02	1.50	3.10
4.00	3.90	4.45	6.35	11.30	3.30	406.60	45.50	3.99	3.17	1.44	4.31
5.00	17.40	10.20	7.00	14.20	26.40	188.20	61.90	8.47	4.49	2.46	0.25
6.00	29.21	13.53	31.24	29.34	50.00	1350.00	1060.20	96.40	20.40	7.90	16.30
7.00	8.36	12.45	26.15	9.20	17.52	519.00	112.00	31.44	7.96	6.33	9.32
8.00	10.50	37.40	31.50	44.00	48.00	1025.20	320.00	67.50	20.97	9.00	42.90
9.00	39.38	62.93	2216.90	96.20	109.40	7161.00	3167.40	567.38	61.02	10.85	17.00
10.00	107.30	72.34	39.26	19.25	27.85	2318.20	1264.60	184.19	48.86	34.51	29.00
11.00	10.41	37.85	41.52	20.40	32.76	243.20	246.20	85.30	10.46	11.45	25.00
12.00	19.85	16.32	18.84	10.14	29.90	2192.00	768.20	208.44	20.90	10.40	16.00
13.00	16.24	21.85	17.25	32.40	28.10	342.00	386.00	78.20	9.20	20.90	18.00
14.00	142.90	118.30	141.12	70.02	238.90	5440.50	1443.00	385.00	67.70	28.00	50.00
15.00	13.90	40.30	35.40	16.20	41.40	6536.70	1502.50	361.90	57.42	11.74	11.00
16.00	4.44	7.30	6.35	1.46	23.40	649.60	82.40	8.35	3.20	1.86	13.40
17.00	19.30	34.40	53.40	7.54	73.40	8596.00	1215.10	315.10	14.40	19.36	40.00
18.00	6.27	6.70	6.15	12.70	15.70	904.00	92.00	35.05	9.77	4.40	0.10
19.00	36.44	235.29	231.00	67.75	150.46	5616.00	6637.00	1240.30	215.46	18.30	70.40
20.00	40.46	65.10	5.40	27.30	70.40	3000.00	1134.00	86.10	15.46	5.27	60.41
21.00	1.70	3.20	0.51	7.00	8.40	330.00	1048.20	70.00	2.00	1.10	3.00
22.00	1.40	2.40	3.00	10.90	27.14	315.90	153.40	18.40	2.00	0.40	0.06
23.00	409.40	434.40	326.00	172.00	342.70	85160.00	11165.00	2840.00	102.00	72.00	911.00
24.00	5.90	13.00	47.40	11.85	34.20	288.00	1306.00	720.00	12.32	13.92	18.00
25.00	2.70	5.40	6.00	3.20	12.00	140.00	130.00	37.00	2.20	2.00	5.00
26.00	2.41	9.00	7.40	10.40	90.00	1470.00	360.00	30.00	5.00	0.30	3.00
27.00	2.40	3.00	4.00	3.40	20.00	410.00	46.00	4.70	3.50	1.40	0.10
28.00	3.10	2.00	2.20	39.00	15.00	140.00	82.00	1.30	1.10	0.00	0.10
29.00	2.40	3.90	6.30	9.40	40.00	920.00	156.50	42.21	1.00	0.90	0.10
30.00	2.70	5.20	5.70	17.00	33.00	4200.00	128.00	217.87	6.40	5.10	32.00
31.00	10.70	21.00	46.30	60.37	100.30	8330.00	271.00	306.02	7.40	7.42	22.00

Table 1.8 Sodium - results (mgl⁻¹)

Jan 1989 - Mar 1990

	[illegible]	MEL	MAG	LYD	MOR	AVON	POR	PUR	MATT	LBE	FLT
1.00	22.00	9.94	10.00	13.10	15.00	21.86	14.67	10.50	10.15	11.40	16.20
2.00	15.62	10.00	13.40	20.00	20.25	47.25	20.10	15.30	14.47	14.12	34.71
3.00	5.00	0.50	0.50	0.50	0.50	8.83	0.50	0.50	10.40	5.00	5.00
4.00	5.00	0.50	0.50	7.02	11.25	0.50	81.90	0.50	0.50	0.50	7.38
5.00	8.16	10.00	5.00	0.50	0.50	6.40	0.50	0.50	6.00	6.46	*
6.00	5.00	9.86	8.52	9.78	12.00	15.00	51.30	0.50	14.20	6.65	0.15
7.00	11.07	9.30	9.30	8.12	5.00	16.94	13.44	12.43	15.21	10.35	11.34
8.00	13.50	17.27	22.50	25.63	31.50	32.42	100.00	18.00	32.42	16.00	25.63
9.00	*	19.53	*	35.30	35.42	45.57	54.34	29.31	30.91	19.00	18.00
10.00	*	0.35	*	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
11.00	15.07	29.44	15.57	19.86	16.30	13.68	13.86	14.85	13.44	12.76	11.00
12.00	5.00	0.50	0.50	0.50	0.50	14.40	0.50	10.36	14.63	9.20	*
13.00	4.12	13.00	8.05	11.34	9.36	11.40	12.90	10.90	9.20	8.12	7.00
14.00	47.64	35.40	39.20	35.01	38.10	64.30	30.16	39.10	47.76	31.10	*
15.00	5.00	24.30	20.00	14.40	80.50	81.00	84.16	61.40	60.30	16.35	13.00
16.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
17.00	5.00	0.50	0.50	0.50	0.50	30.70	0.50	0.50	0.50	0.50	25.00
18.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
19.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
20.00	26.26	34.10	5.00	18.90	24.30	37.50	43.20	14.70	9.00	11.90	*
21.00	12.00	5.00	6.00	0.50	0.50	12.00	0.50	9.00	6.00	11.00	12.00
22.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
23.00	5.00	131.20	0.50	85.20	81.00	100.50	100.10	32.00	76.00	0.50	5.00
24.00	5.00	0.50	0.50	0.50	10.00	0.50	32.40	0.50	9.40	12.00	5.00
25.00	5.00	0.50	0.50	0.50	0.50	0.50	9.00	12.00	12.00	10.00	14.00
26.00	5.00	14.00	0.50	0.50	0.50	22.50	0.50	0.50	0.50	0.50	5.00
27.00	5.00	0.50	0.50	0.50	0.50	6.00	7.00	8.00	7.00	0.50	*
28.00	5.00	5.00	0.50	0.50	12.00	0.50	0.50	0.50	0.50	0.50	*
29.00	5.00	0.50	0.50	0.50	9.00	9.00	0.50	0.50	0.50	0.50	*
30.00	5.00	0.50	8.00	6.00	15.00	68.00	7.00	0.50	17.00	10.00	69.00
31.00	5.00	0.50	0.50	0.50	0.50	52.70	0.50	0.50	0.50	0.50	*

Table 1.7 Aluminium - corrected and [illegible] results (ugl⁻¹)

Jan 1989 - March 1990

	MAR	MEL	MAG	LYD	NOR	AVON	POB	POR	HURT	LDE	FLT
1.00	0.08	0.06	0.06	0.04	0.06	0.20	0.08	0.05	0.05	0.05	0.07
2.00	0.04	0.11	0.07	0.08	0.07	0.16	0.11	0.05	0.05	0.01	0.01
3.00	0.01	0.02	0.02	0.01	0.01	0.05	0.06	0.02	0.02	0.01	0.01
4.00	0.01	0.01	0.01	0.05	0.05	0.04	2.60	0.02	0.06	0.01	0.05
5.00	0.05	0.05	0.05	0.01	0.01	0.01	0.05	0.01	0.01	0.01	0.01
6.00	0.09	0.12	0.17	0.16	0.20	0.17	1.03	0.18	0.20	0.08	0.15
7.00	0.06	0.06	0.07	0.05	0.05	0.43	0.12	0.05	0.02	0.04	0.06
8.00	0.09	0.79	0.25	0.30	0.34	0.40	0.50	0.22	0.21	0.08	0.40
9.00	0.20	0.33	0.33	0.48	0.30	0.83	1.72	0.57	0.42	0.11	0.16
10.00	0.34	0.39	0.21	0.11	0.08	0.42	1.29	0.31	0.21	0.30	0.14
11.00	0.07	0.25	0.21	0.12	0.16	0.30	0.31	0.18	0.12	0.13	0.12
12.00	0.10	0.08	0.15	0.08	0.06	0.44	0.42	0.16	0.13	0.11	0.01
13.00	0.10	0.07	0.06	0.08	0.06	0.07	0.14	0.13	0.02	0.07	0.06
14.00	0.91	0.79	1.10	0.50	0.58	4.03	2.51	1.10	0.04	0.23	0.01
15.00	0.08	0.24	0.42	0.13	0.12	1.35	3.01	0.71	0.94	0.25	0.12
16.00	0.02	0.06	0.10	0.01	0.02	0.04	0.05	0.06	0.08	0.04	0.07
17.00	0.10	0.21	0.51	0.01	0.19	1.26	0.06	0.46	0.29	0.11	0.63
18.00	0.01	0.02	0.04	0.01	0.01	0.04	0.09	0.05	0.05	0.01	0.10
19.00	0.34	2.13	1.02	0.79	0.48	0.98	4.94	2.07	2.26	0.11	0.09
20.00	0.20	0.40	0.06	0.19	0.22	0.45	0.86	0.23	0.14	0.01	0.11
21.00	0.01	0.01	0.01	0.01	0.01	3.60	2.64	0.01	0.01	0.01	0.05
22.00	0.01	0.05	0.05	0.01	0.01	0.53	0.59	0.01	0.01	0.01	0.01
23.00	3.07	2.38	1.38	1.02	0.01	7.37	7.70	1.66	0.51	0.54	1.10
24.00	0.05	0.15	0.11	0.14	0.16	0.47	1.28	0.54	0.14	0.11	0.04
25.00	0.06	0.06	0.05	0.05	0.07	0.02	0.05	0.03	0.05	0.04	0.01
26.00	0.01	0.14	0.07	0.01	0.06	0.38	0.20	0.10	0.05	0.01	0.05
27.00	0.01	0.05	0.03	0.03	0.08	0.06	0.11	0.05	0.14	0.05	0.12
28.00	0.06	0.07	0.09	0.08	0.10	0.01	0.13	0.05	0.05	0.08	0.14
29.00	0.01	0.05	0.02	0.01	0.06	0.15	1.78	0.12	0.01	0.02	0.10
30.00	0.01	0.08	0.06	0.01	0.12	0.48	0.34	0.24	0.29	0.10	0.09
31.00	0.12	0.19	0.29	0.12	0.27	0.77	0.49	0.37	0.25	0.18	0.24

Table I.8 Sodium - results (mgl^{-1})

Jan 1989 - Mar 1990

	MAR	MEL	MAL	LYD	BOR	AVON	POO	POR	HURT	LEE	FLT
1.00	22.00	9.94	18.00	13.10	15.00	21.86	14.67	10.50	10.15	11.60	16.20
2.00	15.62	18.00	13.60	20.00	20.25	47.25	20.10	15.30	16.47	14.12	34.71
3.00	5.00	0.50	0.50	0.50	0.50	8.83	0.50	0.50	10.40	5.00	5.00
4.00	5.00	0.50	0.50	7.02	11.25	0.50	81.90	0.50	0.50	0.50	7.38
5.00	8.16	10.88	5.00	0.50	0.50	6.40	0.50	0.50	6.00	6.66	*
6.00	5.00	9.84	8.52	9.78	12.00	15.00	51.30	0.50	14.20	6.65	0.15
7.00	11.07	9.20	9.20	8.12	5.00	16.94	13.44	12.43	15.21	10.35	11.34
8.00	13.50	17.27	22.50	25.63	31.50	32.62	320.00	14.00	32.62	16.00	25.63
9.00	*	19.53	*	55.50	35.62	45.57	56.34	29.51	30.91	19.00	18.00
10.00	*	0.55	*	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
11.00	15.07	29.64	15.57	19.04	16.38	13.66	13.86	14.85	13.44	12.74	11.00
12.00	5.00	0.50	0.50	0.50	0.50	14.40	0.50	10.56	14.63	9.20	*
13.00	4.12	13.80	8.05	11.34	9.36	11.40	12.98	10.98	9.20	8.12	7.00
14.00	47.64	35.60	39.00	35.01	30.10	64.50	50.16	39.10	47.76	31.10	*
15.00	5.00	24.30	20.00	14.40	80.50	81.00	84.14	61.40	60.30	16.38	13.00
16.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
17.00	5.00	0.50	0.50	0.50	0.50	30.70	0.50	0.50	0.50	0.50	25.00
18.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
19.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
20.00	26.26	34.10	5.00	18.90	24.20	37.50	43.20	14.70	9.00	11.90	*
21.00	12.00	5.00	6.00	0.50	0.50	12.00	0.50	9.00	6.00	11.00	12.00
22.00	5.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	5.00
23.00	5.00	131.20	0.50	83.20	81.00	100.50	100.10	52.00	76.00	0.50	5.00
24.00	5.00	0.50	0.50	0.50	18.00	0.50	32.40	0.50	9.40	12.00	5.00
25.00	5.00	0.50	0.50	0.50	0.50	0.50	9.00	12.00	12.00	10.00	14.00
26.00	5.00	14.00	0.50	0.50	0.50	22.50	0.50	0.50	0.50	0.50	5.00
27.00	5.00	0.50	0.50	0.50	0.50	6.00	7.00	8.00	7.00	0.50	*
28.00	5.00	5.00	0.50	0.50	12.00	0.50	0.50	0.50	0.50	0.50	*
29.00	5.00	0.50	0.50	0.50	9.00	9.00	0.50	0.50	0.50	0.50	*
30.00	5.00	0.50	8.00	6.00	15.00	60.00	7.00	0.50	17.00	10.00	69.00
31.00	5.00	0.50	0.50	0.50	0.50	52.70	0.50	0.50	0.50	0.50	*

Table 1.9 Chloride - results (mgl^{-1})

Jan 1989 - March 1990

	MAR	HEL	MAS	LYD	MOR	AVON	POB	POR	RUN	LEE	FLT
1.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
2.00	0.52	7.50	8.50	<4.0	<4.0	<4.0	9.15	<4.0	<4.0	<4.0	42.72
3.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	6.00	11.00
4.00	7.02	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	6.90	7.02	9.84
5.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	5.44	<4.0	<4.0
6.00	7.62	<4.0	<4.0	<4.0	<4.0	<4.0	145.44	<4.0	<4.0	10.64	14.96
7.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
8.00	*	<4.0	*	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
9.00	*	<4.0	*	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	46.00
10.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	46.00
11.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	6.00
12.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
13.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
14.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
15.00	<4.0	<4.0	<4.0	<4.0	11.30	<4.0	<4.0	<4.0	<4.0	<4.0	8.00
16.00	<4.0	<4.0	<4.0	*	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
17.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	44.30
18.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
19.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	14.68	<4.0
20.00	<4.0	<4.0	*	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	10.20	<4.0
21.00	34.0	15.0	15.00	5.0	18.0	16.0	*	17.0	6.0	13.00	83.00
22.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
23.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
24.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
25.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	13.0	<4.0	<4.0	6.0	6.00
26.00	*	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
27.00	26.0	16.0	10.0	<4.0	8.0	10.0	22.0	23.0	53.0	28.0	<4.0
28.00	22.0	<4.0	<4.0	<4.0	6.0	<4.0	22.0	7.0	4.0	13.0	<4.0
29.00	11.0	11.0	21.0	9.0	16.0	12.0	<4.0	<4.0	28.0	21.0	*
30.00	18.0	14.0	34.0	19.0	30.0	38.0	9.0	*	71.0	44.0	445.00
31.00	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	27.0	*	<4.0	<4.0	<4.0

Table II.1 Cadmium µgm^{-2}

	MAR	HEL	MAG	LYD	NOR	AVON	POB	PORT	HINT	LEE	FLT
1	1.91	54.24	5.09	7.70	12.24	249.82	39.37	7.15	0.52	0.17	0.38
2	2.67	5.25	3.22	7.20	12.22	187.20	8.17	1.89	0.86	1.67	0.77
3	0.83	0.95	5.25	7.31	6.75	294.90	129.59	17.57	0.48	1.07	0.62
4	2.86	6.99	3.79	14.79	23.85	211.97	3.79	2.29	1.24	0.95	2.10
5	4.91	3.35	2.38	6.02	10.70	69.50	2.17	7.26	1.56	4.39	0.14
6	6.29	10.85	12.03	7.62	8.80	279.04	39.85	20.47	8.21	2.87	5.57
7	5.95	15.15	26.71	11.71	25.41	339.56	101.44	25.42	64.92	3.02	10.42
8	2.54	4.33	2.05	3.02	5.06	63.08	13.57	13.21	2.47	2.38	4.88
9	2.40	4.13	4.42	5.01	9.86	359.35	35.68	27.20	2.16	0.74	1.34
10	6.29	3.07	8.02	3.30	4.30	79.24	59.60	29.84	4.07	1.77	2.08
11	5.72	2.70	9.80	15.89	4.85	254.14	28.91	19.68	2.44	1.29	2.88
12	4.62	5.88	6.10	4.18	11.65	313.20	34.62	28.78	2.51	1.92	3.63
13	49.37	14.70	12.98	57.39	33.85	391.25	79.83	48.90	12.98	17.31	12.03
14	1.27	1.44	2.27	1.25	3.28	96.70	14.63	5.47	0.96	0.51	1.38
15	2.62	2.83	4.35	3.91	5.97	505.68	37.33	10.80	1.63	1.44	3.11
16	0.41	5.80	2.89	0.44	23.37	501.87	12.32	4.84	0.70	2.63	6.95
17	1.46	1.15	3.96	1.90	5.71	499.87	19.90	14.53	2.22	0.74	1.89
18	1.72	4.84	10.18	9.74	34.30	826.62	53.74	49.01	13.30	5.44	0.52
19	1.43	3.73	4.27	5.33	9.47	185.33	71.50	30.95	3.51	1.27	3.78
20	3.67	7.05	1.44	4.54	11.11	291.50	78.25	8.85	1.78	0.80	5.25
21	3.48	13.75	4.20	23.19	30.42	922.90	334.96	27.78	4.01	2.90	1.58
22	2.95	7.35	13.18	12.22	28.44	195.57	168.59	17.85	1.99	0.58	8.16
23	2.42	5.24	5.35	3.27	7.95	318.92	118.58	72.01	2.48	2.49	6.91
24	1.90	4.74	15.32	3.96	4.39	29.95	163.62	181.43	1.39	3.86	7.14
25	4.33	11.94	11.78	34.67	26.85	261.20	294.84	65.95	4.20	4.59	7.19
26	4.23	3.37	3.09	7.25	30.71	544.95	38.25	8.20	1.18	0.40	0.77
27	2.48	5.65	7.16	16.16	43.20	879.70	20.02	3.01	3.48	2.81	0.48
28	0.67	3.63	2.80	15.12	35.14	381.64	16.03	3.66	1.21	0.79	0.56
29	2.70	7.16	7.26	12.95	34.73	508.80	51.14	9.28	0.83	6.37	0.81
30	0.17	0.56	1.55	2.65	4.28	888.00	3.12	52.03	0.33	0.57	3.12
31	2.72	4.00	8.95	13.76	15.99	939.25	22.18	80.98	1.09	1.25	4.46

Table 11.2 Copper ppm

	MAR	HEL	MAG	LYD	NOR	AVON	POB	PORT	HUNT	LEE	FLT
1	24.89	48.90	59.63	83.82	47.70	1003.86	171.83	33.39	12.78	10.15	10.26
2	43.36	90.63	43.40	56.00	93.63	1425.60	88.35	26.42	41.70	14.70	11.52
3	33.12	47.75	52.50	53.59	27.85	1602.87	142.28	42.02	14.09	10.66	6.21
4	16.09	60.02	95.59	83.95	87.45	1231.65	38.75	32.47	22.77	22.42	21.70
5	109.85	54.63	23.85	42.37	54.63	366.08	27.91	23.30	9.14	7.32	47.05
6	34.32	77.35	65.13	41.40	46.40	1431.00	892.44	114.98	56.92	25.33	36.35
7	68.95	106.04	98.74	65.15	119.19	1623.36	758.67	154.10	56.80	24.44	78.67
8	28.67	78.26	38.91	12.29	60.48	464.83	282.80	98.58	44.45	26.71	111.22
9	70.22	72.94	44.38	62.16	49.17	2545.41	309.24	217.92	40.45	41.95	11.84
10	139.74	50.59	58.31	40.81	56.72	999.42	655.74	248.41	57.58	25.14	14.00
11	34.34	35.31	80.40	80.36	66.63	1016.58	252.41	166.42	34.32	23.44	128.00
12	66.66	57.40	74.95	37.06	60.28	1209.60	345.60	158.46	34.96	35.33	343.00
13	230.07	151.20	118.48	145.71	121.28	1499.78	526.28	295.67	54.26	179.17	340.35
14	21.4	20.15	21.95	12.8	20.84	322.4	54.43	36.36	13.95	7.78	14.0
15	35.11	30.88	43.65	31.52	97.13	2249.61	287.35	104.72	36.94	15.74	27.75
16	59.06	131.57	73.95	11.10	128.31	2539.91	75.43	165.27	89.60	53.22	74.38
17	37.91	37.01	41.91	4.50	48.48	795.13	104.75	88.20	32.13	25.85	23.62
18	45.84	68.36	47.34	62.21	78.40	2244.60	325.87	171.21	100.00	36.24	96.53
19	38.32	48.28	43.56	46.85	53.63	885.44	361.66	136.44	50.79	16.17	39.94
20	45.71	115.31	6.32	48.51	77.42	1152.75	958.90	70.08	45.20	9.32	77.14
21	34.76	80.22	11.55	94.49	297.50	1929.70	1160.64	65.79	40.00	29.00	15.84
22	64.79	33.40	22.92	52.94	83.90	1004.56	331.38	64.30	3.18	5.76	27.45
23	57.34	61.34	34.75	51.84	62.37	1125.60	592.90	316.14	26.08	41.58	47.10
24	60.04	53.28	78.25	59.34	55.08	224.64	727.28	806.94	32.26	34.85	34.74
25	43.28	59.70	106.82	106.68	95.90	1392.00	982.80	392.04	31.50	105.23	39.95
26	22.65	33.64	19.47	20.72	142.76	1626.20	300.00	100.00	25.85	19.85	5.79
27	33.12	72.43	63.68	44.96	138.00	1111.20	101.92	50.10	31.56	14.04	72.45
28	113.56	45.35	8.80	15.92	43.92	617.12	35.11	7.32	36.30	15.72	72.11
29	14.23	47.76	19.10	24.50	108.72	2480.40	998.94	146.11	20.70	5.79	88.32
30	10.14	20.60	7.76	6.48	42.75	3774.00	39.20	281.95	8.80	13.30	40.14
31	40.84	54.40	63.24	98.25	85.28	939.25	152.44	250.73	35.48	27.57	54.72

Table 11.3 Chromium µgm^{-2}

	MAR	HEL	MAG	LYD	NOR	AVON	POB	PORT	HUNT	LEE	FLT
1	8.63	13.56	11.92	12.78	4.77	4.43	4.32	11.92	22.92	7.70	3.42
2	10.09	33.39	24.53	8.00	5.76	51.84	12.16	7.95	20.90	4.01	5.14
3	4.14	4.78	4.37	4.86	18.57	16.81	14.70	3.82	2.38	5.33	3.11
4	2.38	3.66	2.70	2.38	1.59	49.27	1.36	1.91	1.84	2.38	1.75
5	18.29	9.14	0.00	6.02	1.12	1.43	1.36	1.91	1.12	3.66	9.15
6	10.87	17.15	10.09	8.25	6.40	14.31	34.19	5.07	10.09	12.67	15.16
7	30.10	24.09	14.69	11.71	13.91	38.77	33.88	10.26	2.70	3.62	13.02
8	9.52	12.21	8.64	6.72	8.64	15.48	14.06	8.77	6.65	4.45	18.09
9	6.85	14.73	9.83	7.77	7.54	28.98	21.39	11.65	6.34	0.46	1.92
10	37.23	9.08	10.89	0.53	0.69	18.86	28.67	8.25	0.25	10.11	8.96
11	18.04	8.14	10.50	12.26	9.01	30.10	18.33	12.18	6.08	5.44	7.20
12	11.44	9.27	10.41	0.44	13.46	21.68	19.20	9.42	7.98	7.10	7.64
13	29.52	30.45	31.38	40.42	23.17	32.48	20.96	23.30	24.89	41.23	29.05
14	6.74	4.74	5.49	2.33	3.47	7.66	4.60	4.31	2.79	1.95	3.40
15	4.62	5.18	20.25	3.71	9.48	72.90	15.20	7.99	0.11	5.23	4.44
16	9.91	10.70	14.87	2.22	10.97	17.82	2.46	27.83	35.70	30.22	34.96
17	15.80	5.09	15.78	0.50	6.53	20.46	10.35	10.60	8.45	3.67	4.76
18	38.96	54.45	29.52	12.44	15.40	2.55	34.51	27.22	25.10	27.18	35.29
19	8.49	11.84	13.62	5.18	8.61	14.41	60.85	10.91	3.69	7.15	13.31
20	20.51	27.62	1.52	8.08	13.66	50.35	47.20	6.30	13.12	2.72	13.26
21	34.76	11.46	1.85	8.59	8.75	8.39	26.02	7.31	13.36	7.25	7.92
22	2.95	8.82	11.46	6.11	16.59	10.97	5.35	11.90	1.59	5.76	4.45
23	12.54	32.47	5.35	8.64	6.26	26.39	32.19	13.83	7.88	6.93	4.71
24	9.48	20.72	14.49	10.32	9.18	7.49	30.91	22.70	2.02	8.51	3.86
25	10.82	11.94	47.12	8.89	47.95	18.56	3.51	4.45	5.25	45.88	95.93
26	19.33	13.86	3.54	4.44	8.30	20.76	9.00	2.00	2.35	1.99	1.93
27	8.28	8.87	15.92	2.81	12.00	13.09	7.28	2.50	10.52	3.51	18.35
28	3.34	4.53	3.50	15.92	3.66	4.86	5.01	3.66	24.20	3.93	23.48
29	21.64	3.98	1.91	1.75	6.04	19.08	25.96	10.44	2.07	23.16	21.57
30	0.84	0.94	0.48	3.78	4.75	15.54	3.85	18.15	7.15	3.80	95.75
31	10.90	8.94	14.88	3.95	6.15	39.95	16.94	24.15	23.53	10.02	10.08

Table 11.4 Nickel $\mu g m^{-2}$

	MAR	MEL	MAG	LYD	NOR	AVON	POB	PORT	HUNT	LEE	FLT
1	18.67	18.91	11.92	12.78	23.85	24.60	24.89	14.31	15.23	4.37	11.97
2	29.80	47.70	24.53	22.40	10.05	37.44	36.10	13.21	24.32	8.35	10.27
3	20.70	23.87	21.87	20.30	21.10	19.10	16.70	19.10	11.93	26.65	15.52
4	11.93	18.30	13.52	11.93	7.95	24.43	6.78	9.55	5.18	11.93	8.75
5	36.35	5.57	19.08	15.16	5.57	22.02	6.78	9.55	5.57	18.30	3.58
6	7.15	8.75	16.24	3.17	2.00	33.39	146.19	30.62	27.12	5.97	18.29
7	8.75	13.52	11.93	12.73	35.09	66.61	88.33	11.15	13.52	7.55	13.02
8	22.86	19.20	14.40	13.34	21.63	42.08	42.12	26.20	17.58	11.13	30.97
9	24.65	21.28	11.02	18.87	13.85	38.92	27.36	24.70	10.12	8.74	7.04
10	40.29	1.02	11.88	2.65	13.01	30.19	65.61	16.51	14.41	8.97	3.84
11	21.12	1.38	8.69	5.68	2.47	32.38	32.18	3.08	3.00	2.47	5.60
12	17.16	5.65	3.17	2.17	3.83	41.04	40.37	11.34	12.69	8.83	4.78
13	29.52	54.60	37.33	80.84	46.34	32.60	11.15	55.39	13.52	12.73	10.38
14	11.91	2.37	0.25	0.25	0.25	12.89	86.63	7.82	3.98	2.72	5.70
15	28.03	38.88	21.83	2.58	21.32	78.73	15.20	8.79	17.69	1.20	11.10
16	10.32	11.15	10.32	11.10	11.93	12.73	12.32	15.13	53.90	16.42	11.55
17	2.03	1.20	1.15	2.50	1.20	52.17	27.25	12.74	2.22	2.62	9.44
18	14.32	15.13	41.23	13.52	17.50	41.23	45.85	15.13	39.20	54.36	4.15
19	14.20	13.67	7.26	1.20	0.52	31.92	131.05	5.46	0.22	2.45	12.29
20	18.88	20.09	2.00	1.92	13.66	42.40	64.58	14.18	2.03	2.00	1.34
21	21.73	28.65	26.25	21.48	21.87	50.34	301.89	18.27	16.70	18.13	19.80
22	41.23	16.70	28.65	12.73	11.85	44.84	110.61	13.52	7.95	14.39	23.00
23	18.82	21.65	8.02	10.56	8.91	41.27	93.17	26.68	19.20	11.88	10.99
24	7.90	20.72	14.49	12.90	11.02	22.46	112.72	47.47	3.15	3.33	4.82
25	27.05	29.85	29.45	22.23	23.98	64.96	91.26	22.27	26.25	45.88	55.93
26	17.52	21.78	15.93	13.32	29.88	34.60	34.50	36.00	35.25	9.93	15.44
27	49.68	48.42	79.60	39.34	48.00	46.30	87.36	35.07	52.60	42.12	79.69
28	16.70	81.63	17.50	63.68	18.30	48.72	40.08	18.30	15.13	47.16	13.98
29	13.52	19.90	9.55	8.75	15.10	57.24	97.40	15.31	10.35	14.48	10.18
30	4.22	11.28	11.64	3.24	8.55	47.36	10.50	23.47	12.65	5.70	26.76
31	29.96	16.00	18.60	43.23	12.30	24.65	23.87	34.29	38.01	15.04	24.48

Table 11.5 Lead kg/km^2

	MAR	MEL	MAG	LYD	NOR	AVON	POB	PORT	HUNT	LEE	FLT
1	0.228	0.282	0.310	0.355	0.620	20.077	11.800	1.049	0.112	0.063	0.073
2	0.301	0.429	0.311	0.464	0.187	17.280	1.374	0.245	0.083	0.145	0.052
3	0.166	0.411	0.359	0.526	0.544	27.833	3.761	0.413	0.144	0.160	0.192
4	0.190	0.326	0.343	0.552	0.108	16.730	1.233	0.152	0.066	0.078	0.151
5	0.394	0.227	0.126	0.318	0.546	5.381	1.678	0.324	0.100	0.195	0.004
6	0.835	0.474	0.597	0.373	0.400	21.445	11.768	1.687	0.542	0.191	0.363
7	0.295	0.684	1.152	0.472	1.060	33.943	6.776	1.411	0.431	0.191	0.486
8	0.133	0.418	0.202	0.224	0.465	9.739	2.496	0.749	0.199	0.156	0.698
9	0.352	0.440	11.528	0.289	0.584	49.411	12.036	3.632	0.278	0.100	0.054
10	0.912	0.296	0.389	0.204	0.370	25.268	11.887	2.339	0.235	0.104	0.093
11	0.229	0.204	0.419	0.463	0.324	3.697	3.668	1.052	0.222	0.115	0.200
12	0.209	0.369	0.229	0.158	0.458	29.992	8.034	2.147	0.159	0.177	0.306
13	0.827	1.147	0.953	1.617	1.385	19.542	13.683	2.682	0.498	1.064	0.747
14	0.143	0.119	0.141	0.070	0.234	5.440	1.463	0.305	0.068	0.029	0.058
15	0.215	0.194	0.266	0.167	0.436	52.948	3.454	0.615	0.127	0.056	0.122
16	0.192	0.321	0.271	0.074	1.116	33.065	4.072	0.505	0.224	0.122	0.619
17	0.158	0.166	0.247	0.075	0.352	31.885	3.038	1.103	0.128	0.203	0.154
18	0.359	0.410	0.313	0.687	1.099	46.054	4.375	2.121	0.604	0.417	0.005
19	0.227	0.282	0.254	0.325	0.316	12.355	7.302	1.365	0.194	0.179	0.225
20	0.315	0.527	0.044	0.210	0.486	15.900	5.216	0.666	0.125	0.042	0.538
21	0.148	0.367	0.054	0.670	0.733	27.687	100.00	0.731	0.134	0.080	0.238
22	0.083	0.174	0.218	0.555	1.286	15.068	6.042	0.995	0.064	0.034	0.299
23	0.287	0.478	0.356	0.259	0.997	35.644	12.281	4.444	0.153	0.158	0.456
24	0.186	0.385	0.985	0.204	0.349	2.995	13.999	9.288	0.155	0.185	0.347
25	0.292	0.469	0.707	0.285	1.151	12.992	9.126	3.297	0.231	0.321	0.463
26	0.073	0.178	0.134	0.154	1.494	25.431	5.400	0.616	0.136	0.012	0.073
27	0.215	0.307	0.318	0.202	1.280	18.983	1.676	0.235	0.184	0.098	0.005
28	0.207	0.254	0.154	3.104	1.098	11.368	4.108	0.110	0.067	0.063	0.006
29	0.130	0.310	0.241	0.336	1.480	29.256	4.023	0.979	0.075	0.052	0.004
30	0.046	0.098	0.055	0.092	0.313	31.080	0.448	2.636	0.036	0.049	0.714
31	0.243	0.336	0.577	0.909	0.824	70.805	2.093	4.940	0.134	0.133	0.317

Table 11.6 Zinc kg/km²

	MAR	MEL	MAG	LYD	NOR	AVON	POS	PORT	HUNT	LEE	FLT
1	0.290	7.145	0.572	1.015	1.069	26.095	3.519	0.644	0.254	0.114	0.222
2	0.434	0.930	0.717	0.976	0.274	22.320	1.269	0.359	0.257	0.268	0.095
3	0.190	0.859	0.805	1.250	1.015	27.833	2.469	0.607	0.454	0.224	0.460
4	0.223	1.288	0.563	1.060	1.829	16.258	0.810	0.277	0.171	0.026	0.215
5	1.607	0.607	0.310	0.425	0.849	4.395	0.280	0.370	0.263	0.480	0.175
6	1.198	0.732	0.949	0.559	0.704	28.143	7.213	2.145	0.705	0.445	0.546
7	0.409	1.120	0.933	0.711	1.404	28.778	7.454	1.714	0.905	0.219	0.754
8	0.210	0.784	0.398	0.537	0.648	7.747	2.028	0.809	0.376	0.265	1.454
9	0.998	0.942	0.645	0.677	0.970	44.919	7.969	3.341	0.405	0.265	0.173
1	1.576	0.580	0.843	0.464	0.871	37.714	9.221	2.795	0.680	0.257	0.256
11	1.115	0.408	1.136	1.327	0.703	3.235	3.212	1.339	0.425	0.234	0.472
12	0.799	0.891	0.958	0.437	1.050	42.552	4.995	3.281	0.381	0.371	0.002
13	4.192	1.811	2.489	2.425	2.076	15.488	6.315	3.373	0.747	2.372	1.660
14	0.242	0.179	0.333	0.202	0.317	5.442	1.296	0.438	0.119	0.062	0.190
15	0.328	0.337	1.061	0.538	1.184	71.077	3.456	0.168	0.162	0.459	0.389
16	0.246	0.843	0.690	0.170	1.676	48.416	1.745	0.702	0.538	0.434	0.758
17	0.332	0.243	0.429	0.162	0.535	26.126	1.414	2.227	0.287	0.092	0.260
18	0.392	1.984	0.769	0.812	1.645	72.054	3.890	3.279	0.855	0.453	0.356
19	0.327	0.647	0.517	0.611	0.728	15.444	7.582	1.918	0.296	0.116	0.389
20	0.614	1.306	0.191	0.534	0.956	18.550	9.315	0.992	0.292	0.109	0.848
21	0.688	1.606	0.218	1.546	2.275	36.916	10.811	1.442	0.534	0.145	0.475
22	0.471	0.735	0.688	1.122	1.734	10.883	15.788	1.285	0.199	0.345	0.876
23	0.485	0.821	0.472	1.152	0.695	47.838	11.858	7.015	0.258	0.327	0.762
24	0.316	0.858	1.449	1.109	0.477	3.276	14.362	15.488	0.161	0.447	0.598
25	0.325	1.075	1.414	1.422	1.918	14.848	35.100	5.257	0.315	0.573	0.559
26	0.397	0.455	0.372	0.459	2.067	30.421	2.925	0.504	0.094	0.079	0.097
27	0.414	0.565	0.796	0.731	1.480	22.487	1.276	0.401	0.579	0.211	0.024
28	0.134	0.998	0.490	1.114	2.050	15.428	1.703	0.659	0.182	0.079	0.028
29	0.162	1.433	0.995	0.805	2.265	54.860	7.205	2.003	0.207	0.058	0.029
30	0.084	0.301	0.243	0.232	0.456	53.280	0.424	3.406	0.094	0.105	0.602
31	0.327	0.381	0.986	2.299	1.082	54.910	2.425	5.534	0.405	0.150	0.475

Table 11.7 Aluminium ppm[a]

	MAR	HEL	MAG	LYD	DOR	AVON	POB	PORT	HURT	LEE	FLT
1	1.02	1.15	0.95	0.78	0.95	2.06	1.02	0.80	0.52	0.52	0.67
2	0.76	1.75	0.78	0.44	0.45	1.02	1.04	0.56	0.47	0.33	0.08
3	0.83	1.91	1.75	0.81	0.84	2.29	4.01	1.53	0.95	1.07	0.62
4	0.48	0.73	0.54	2.38	1.59	1.46	70.46	0.76	1.36	0.48	1.05
5	0.67	0.67	0.80	0.28	0.22	0.29	1.16	0.38	0.22	0.73	0.14
6	2.57	4.20	3.25	2.05	1.40	2.70	11.43	3.15	3.02	1.91	3.35
7	2.10	3.25	3.34	2.95	3.05	28.08	7.26	2.23	1.08	1.21	3.13
8	1.14	0.77	1.40	1.44	2.18	3.80	3.90	2.44	1.99	1.27	4.44
9	1.78	2.31	1.72	1.44	1.38	5.73	6.54	3.45	1.89	1.01	0.51
10	2.09	1.40	2.08	1.17	1.10	4.76	12.13	3.94	1.85	0.90	0.46
11	1.54	1.38	2.12	2.72	1.38	4.56	4.42	2.21	1.44	1.29	0.96
12	1.10	1.81	1.91	0.70	0.92	8.44	4.83	1.71	0.99	1.06	0.19
13	5.09	3.67	3.25	3.99	2.96	4.08	6.24	4.97	1.08	3.56	2.49
14	0.91	0.79	1.10	0.38	0.38	4.03	2.51	1.18	0.86	0.23	0.01
15	1.23	1.15	3.15	1.34	1.34	10.94	6.92	1.21	2.07	1.20	1.33
16	0.83	2.48	4.13	0.44	0.95	2.06	2.46	2.42	3.40	2.43	3.23
17	0.81	1.01	2.35	0.10	0.91	4.46	2.10	1.61	2.98	1.15	2.02
18	0.57	1.21	2.04	0.54	0.78	2.04	4.44	1.81	2.10	0.91	5.19
19	2.11	2.56	2.00	3.79	1.43	2.16	5.43	2.28	2.05	1.08	2.36
20	1.56	3.26	0.32	1.46	1.32	2.38	3.96	1.73	1.13	0.08	0.98
21	0.87	1.15	1.05	0.86	0.87	382.06	143.09	0.73	0.47	0.72	3.96
22	0.59	2.00	1.72	0.51	0.47	25.28	26.31	0.54	0.32	0.38	0.37
23	2.15	2.42	1.52	1.53	0.80	10.32	8.47	3.15	0.76	1.19	0.35
24	1.58	4.44	2.28	2.41	1.63	4.80	12.93	6.97	1.76	1.44	0.77
25	6.49	7.16	5.09	4.46	6.71	1.86	3.51	2.47	5.25	4.99	0.80
26	0.30	2.77	1.24	0.15	1.00	5.19	3.03	2.00	0.78	0.40	0.96
27	0.83	2.42	2.39	1.40	4.80	2.78	4.00	2.30	7.36	3.51	5.80
28	4.01	6.35	6.30	6.37	7.32	0.01	4.51	3.46	3.05	6.29	7.83
29	0.54	2.39	0.76	0.35	1.01	4.77	45.75	2.78	0.41	1.16	4.07
30	0.17	0.56	0.58	0.88	1.14	3.95	1.19	2.90	1.59	0.95	2.01
31	2.72	3.04	3.40	1.57	2.21	6.93	3.77	5.94	4.53	3.22	3.44

Table II.8 Rainfall mm

	MAR	MEL	MAG	LYD	NOR	AVON	POB	PORT	HUNT	LEE	FLT
1	12.70	19.10	15.90	17.50	15.90	14.30	12.70	15.90	17.50	17.50	9.50
2	19.10	15.90	11.10	8.00	6.40	6.40	9.50	11.10	9.50	33.40	4.80
3	82.80	95.50	87.50	81.20	84.40	76.40	66.80	76.40	47.70	106.60	62.10
4	47.70	73.20	54.10	47.70	31.80	41.40	27.10	38.20	20.70	47.70	35.00
5	22.30	22.30	15.90	22.30	22.30	28.60	27.10	38.20	22.30	73.20	14.30
6	28.60	35.00	19.10	12.70	8.00	15.90	11.10	17.50	19.10	23.90	22.30
7	35.00	54.10	47.70	50.90	60.50	65.30	60.50	44.60	54.10	30.20	52.10
8	12.70	11.10	6.40	4.80	6.40	9.50	7.80	11.10	9.50	15.90	11.10
9	8.90	7.00	5.20	3.00	4.60	6.90	3.80	6.40	4.50	9.20	3.20
10	8.50	4.10	9.90	10.60	13.70	10.90	9.40	12.70	4.90	3.00	3.20
11	22.00	5.50	10.10	22.70	9.90	15.20	14.90	12.30	12.00	9.90	8.00
12	11.00	22.60	12.70	8.70	15.30	13.50	11.50	10.70	7.60	9.60	19.10
13	50.90	52.50	54.10	49.90	49.30	57.20	44.60	38.20	54.10	50.90	41.50
14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	15.40	4.80	7.50	10.30	10.30	8.10	2.30	1.70	2.20	4.80	11.10
16	41.30	44.60	41.30	44.40	47.70	50.90	49.30	60.50	70.00	65.70	46.20
17	8.10	4.80	4.60	10.00	4.80	3.70	2.50	3.50	8.90	10.50	3.20
18	57.30	60.50	50.90	54.10	70.00	50.90	49.30	60.50	70.00	90.60	51.90
19	6.20	1.20	1.10	4.80	2.10	2.20	1.10	1.10	0.90	9.80	3.20
20	7.80	8.10	8.00	7.70	6.90	5.30	4.60	7.50	8.10	8.00	8.90
21	86.90	114.60	105.00	85.90	87.50	83.90	54.20	73.10	66.80	72.50	79.20
22	58.90	66.80	57.30	50.90	47.40	47.70	44.60	54.10	31.80	57.55	37.10
23	0.70	1.10	1.10	1.50	1.10	1.40	1.10	1.90	1.50	2.20	0.50
24	31.60	29.60	20.70	17.20	10.20	10.40	10.10	12.90	12.60	13.30	19.30
25	108.20	119.40	117.80	88.90	95.90	92.80	70.20	89.10	105.00	114.70	79.90
26	30.20	19.80	17.70	14.80	16.60	17.30	15.00	20.00	23.50	39.70	19.30
27	82.80	80.70	79.60	56.20	60.00	46.30	36.40	50.10	52.60	70.20	48.30
28	66.80	90.70	70.00	79.60	73.20	81.20	50.10	73.20	60.50	78.60	55.90
29	54.10	79.60	38.20	35.00	30.20	31.80	25.70	23.20	41.40	57.90	40.70
30	16.90	18.80	9.70	5.40	9.50	7.40	3.50	12.10	5.50	9.50	22.30
31	22.70	16.00	12.40	13.10	8.20	8.50	7.70	16.10	18.10	17.90	14.40