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# REPORT ON THE CONTROL OF DISCHARGES OF TITANIUM DIOXIDE WASTE TO THE HUMBER ESTUARY.

## - MAIN REPORT.



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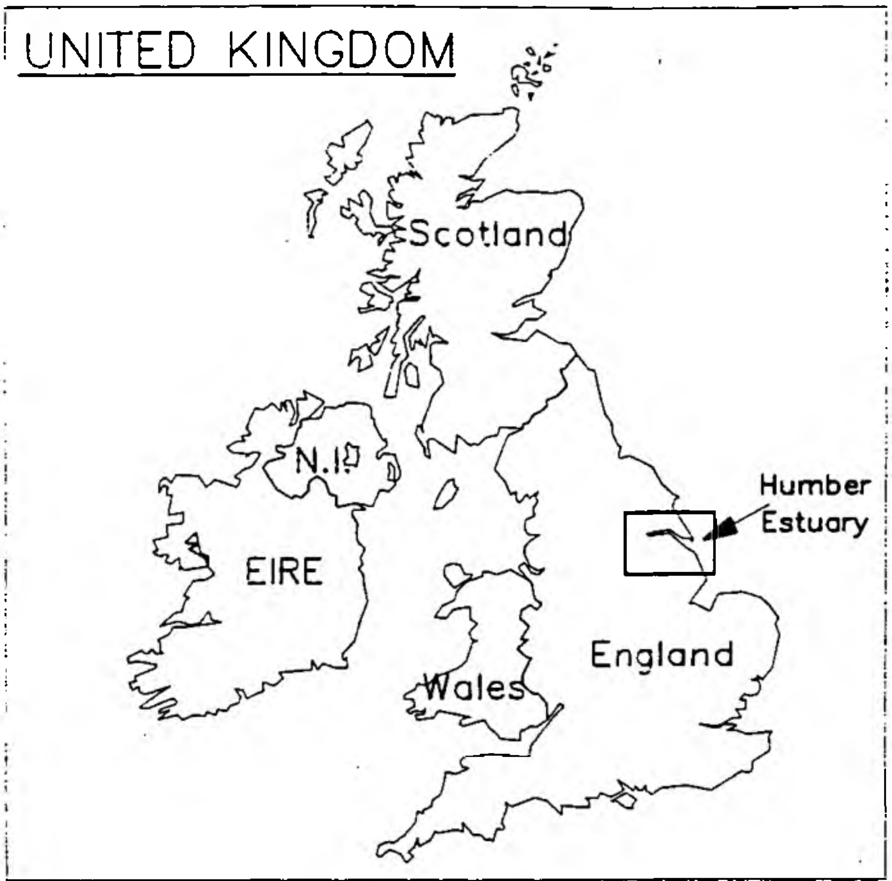
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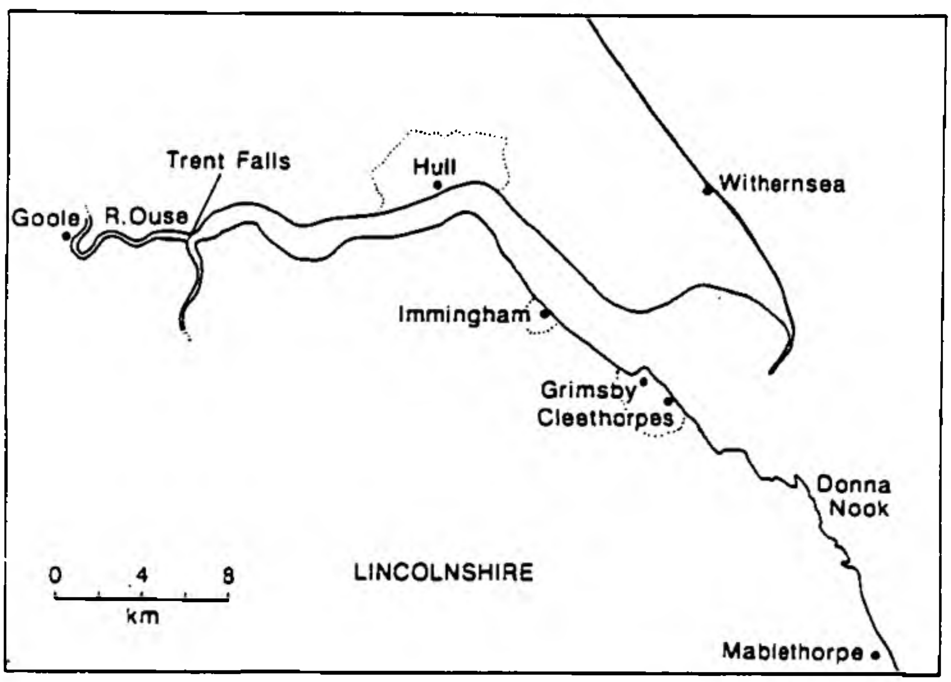
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# EXECUTIVE SUMMARY


In the UK there are three factories which manufacture the white pigment, titanium dioxide. Of these three the two biggest, Tioxide UK Ltd and SCM Chemicals Ltd, are located on the south bank of the Humber estuary. They each discharge effluent from the manufacturing process to the Humber.

The 1978 EEC Directive on Waste from the Titanium Dioxide Industry required the UK to reduce the pollution caused by these two discharges.

Detailed investigations carried out to quantify the impact the two discharges were having on the Humber confirmed that the impact was restricted to the area immediately around the outfalls. It was decided that both outfalls should be relocated to deeper water where dilution and dispersion would be significantly greater. These new outfalls began operating in August/September 1988.

During the summer and early autumn of 1989 a major chemical and biological water quality survey was carried out around both the new and old outfalls. This survey confirmed that the areas of impact around the new outfalls were substantially smaller than those found previously around the old outfalls. This was particularly the case around the new Tioxide outfall which is in very deep water and where it was difficult to find any significant impact. There was also strong evidence of a biological recovery around the old Tioxide outfall. Around the old SCM outfall there was less evidence of recovery but the new outfall is not far away and may be having some impact.

Fish caught in the vicinity of the outfalls showed no evidence of external damage nor were their body burdens of iron and other metals elevated.

A further pollution reduction programme has been agreed for both factories under the terms of the recent 1989 EEC Directive on Titanium Dioxide Waste. The 1989 survey work will form a sound benchmark against which the improvements achieved by that further programme can be evaluated.

The shoreline of the South Bank of the Humber Estuary showing the reduction in Iron Staining between 1984 and 1989.

1984.

1989.

# REPORT ON THE CONTROL OF DISCHARGES OF TITANIUM DIOXIDE WASTE TO THE HUMBER ESTUARY.

## 1. GENERAL

### 1.1 INTRODUCTION

1.1.1 The Anglian Region of the National Rivers Authority (Anglian NRA) is responsible for implementing the EEC Titanium Dioxide Directives in so far as they apply to the discharge of effluents to the Humber estuary from the two titanium dioxide factories located there. Pollution reduction programmes set for these factories under the 1978 Directive have now been implemented. New pollution reduction programmes under the 1989 Directive have been set.

1.1.2 A major water quality survey of the estuary was carried out by the Lincoln Division of Anglian Water (the predecessor of Anglian NRA) in 1984 as the first stage of the initial reduction programmes. A report on this survey was prepared and submitted to the European Commission by Her Majesty's Government (HMG). The report described the survey and recommended that the outfalls from both factories be extended further into the Humber estuary so as to reduce their polluting impact. This was done and the new outfalls started operating in Autumn 1988.

1.1.3 Further major water quality survey work on the estuary has been carried out by the Anglian NRA during 1989. This survey work has determined the extent to which the polluting impact of the discharges has diminished by the first reduction programme and sets a baseline against which the improvement that will be achieved by the second reduction programme can be judged.

1.1.4 This report describes the 1989 survey work. It shows that there has been a substantial reduction in impact since 1984 with the worst of the previously affected areas having largely recovered from pollution. It quantifies the size of the mixing zones around the new outfalls.

### 1.2 THE EEC DIRECTIVES

#### 1.2.1 The 1978 Directive (the main Directive)

This Directive requires that:

i) any discharge of effluent be authorised (ie consented);
ii) the effects of any discharge be monitored;
iii) a pollution reduction programme be drawn up and implemented for each discharge.

The UK pollution reduction programmes had three phases:

- i) research into methods of effecting a better dispersion of the effluents;
- ii) physical alteration of existing discharge arrangements;
- iii) monitoring of the new discharge arrangements to ensure better dispersion had been achieved.

### 1.2.2 The 1982 Directive (the Monitoring Directive)

This Directive expands the monitoring provisions of the main Directive and requires:

- i) the water around each outfall to be analysed three times a year;
- ii) the life around each outfall to be examined once a year;
- iii) the sediment around each outfall to be examined once a year.

### 1.2.3 The 1989 Directive (the Harmonisation Directive)

The main Directive provides for the pollution reduction programmes of individual member states to be 'harmonised'. The 1989 Directive aims to achieve this. It strictly controls the discharge of waste to river from 31 December 1989. Subject to certain conditions, member states may delay implementation.

Subject to such delayed implementation being granted the 1989 Directive, for sulphate route processes, requires that:

- i) the discharge to river of solid waste, strong acid waste (pH <5.5) and some treated metallic wastes be prohibited from 1993;

- ii) the discharge of weak acid waste (equivalent to 0.5% $H_2SO_4$ or less) and neutralised low level metallic waste (pH >5.5) be restricted to 1,200kg (as $SO_4$) per tonne of $TiO_2$ produced from 1993 and to 800kg from 1995.

For chloride route processes the Directive requires that:

- i) the discharge to river of solid waste and strong acid waste be prohibited from 1993;

- ii) the discharge of weak acid waste, treated metallic waste and neutralised low level metallic waste be restricted (depending which ore is used) to 130kg, 228kg or 450kg (as Cl) per tonne of product from 1993.

HMG has taken the necessary steps to delay application of the Directive. Details of new pollution reduction programmes were sent to the Commission before the 31 December 1989 deadline. If the Environmental Quality Objectives (EQO) approach is to be used to implement the 1989 Directive, it must be demonstrated that the effect is equivalent to the limit value approach both in terms of protecting the environment and of avoiding distortion of competition.

## 1.3 DESCRIPTION OF ESTUARY

1.3.1 The Humber estuary is the largest estuary in Great Britain. It drains 20% of England, including the industrial areas of the East Midlands and Yorkshire. From Trent Falls , the confluence of the River Trent and the Yorkshire Ouse, to Spurn Point it is 62km long. At its widest point, near Grimsby, it is 7km wide; the tidal range is up to 7m. The estuary is used by industries ranging from food manufacturers to industrial chemicals for the reception of liquid wastes. The outfalls along the South Bank between Immingham and Grimsby are shown in Figure 1.

1.3.2 There is a migratory salmon run through the Humber estuary; it is limited in extent but numbers are gradually increasing. The zone of oxygen depletion around Trent Falls is the main barrier to migration.

1.3.3 The water quality in the estuary is of a relatively high quality being NWC Class A below Grimsby and Class B upstream. Exceptions to this general rule exist around several industrial discharges where there is evidence of localised pollution.

1.3.4 Immingham is now the major port on the estuary, being the second largest container port in the UK. It is certain that this area will develop even more than it has in the past 40 years; already there is an excellent infrastructure and availability of land, labour, power and water. Inevitably, there will be increased pressure on the Humber estuary to receive more industrial effluent and this will be reflected in the policy adopted by Anglian NRA in setting and reviewing consent conditions.

## 1.4 WATER POLLUTION CONTROL RESPONSIBILITIES

1.4.1 The waters of the Humber form the boundaries between three regions of the National Rivers Authority ie Anglian, Severn Trent and Yorkshire. Water quality in the Humber is managed jointly by the three regions via the Humber Estuary Technical Management Committee. There is collaboration on sampling, analysis, reporting and decision making. Each region however, is responsible for controlling discharges from its own area into the estuary.

1.4.2 On the south bank of the Humber between Winteringham and Donna Nook, Anglian NRA is the controlling authority. The Humber estuary constitutes "coastal waters" within the definition of the Water Act 1989 (successor to the Control of Pollution Act 1974) and all discharges to it are now controlled according to this Act.

1.4.3 UK water pollution control practices have to conform to EEC Directives; the Water Act provides a mechanism to implement these Directives. Within this framework Anglian NRA is responsible for applying the EEC titanium dioxide Directives to two discharges of liquid effluent to the Humber from the south bank of the estuary; one being from SCM Chemicals Ltd., (SCM) and the other from Tioxide UK Ltd., (Tioxide).

1.4.4 Under the 1978 Directive a pollution reduction programme had to be implemented for each discharge of waste from a titanium dioxide producer. For the two Humber discharges these programmes involved extending the outfall pipes further into the estuary in order to increase the rate at which the effluents were diluted and dispersed. This increased dilution and dispersion has dramatically reduced the area of the estuary in which a polluting effect can be detected.

1.4.5 Under the 1989 Directive a further reduction programme has to be implemented. For the two Humber discharges this will involve treating the waste prior to any effluent being discharged to the estuary.

1.4.6 The UK uses the "environmental quality objective" (EQO) approach to control pollution in rivers and estuaries. In the EQO approach, the main uses of the watercourse are identified and then environmental quality standards (EQS's) are defined to protect these uses. These standards are the concentration levels above which an adverse effect will begin to be detected. If the water can be shown to meet the EQS then it will not be classed as unsatisfactory or polluted.

1.4.7 Since it would not be realistic to require that discharges themselves comply with the EQS's, it must be accepted that there will be a mixing zone: ie an area within which the discharge is gradually diluted from its original concentration to the EQS value. It is the responsibility of the pollution control authority to determine whether a given mixing zone is of an acceptable size or not. In an estuary where water flow is bi-directional and the velocity profile is sinusoidal the definition of a mixing zone is not simple and mathematical modelling techniques are necessary to determine mixing zone size.

## 1.5 THE PREVIOUS 1984 MAJOR SURVEY

1.5.1 The 1984 survey measured the size of mixing zone around the short outfalls then being used by SCM and Tioxide to discharge effluent to the Humber estuary. The two principal pollutants in the effluents are ferrous iron and acid. Field survey work was carried out to determine at what concentrations these pollutants could be found in the water around each of the outfalls. EQS's of 1mg/l for soluble iron (expressed as an annual average) and of pH 6.0 for acid (expressed as a 95%ile) were used to characterise the boundary of the mixing zone.

1.5.2 As the main effect of the two pollutants is to damage the life inhabiting the bed of the estuary, biological analysis of the bed was carried out around each outfall. This data was also used to assess the size of the mixing zone. This was defined as the area within which it was possible to see moderate to severe biological damage.

1.5.3 Dispersion of any effluent plume in an estuary is much more variable than in a non-tidal river due to the far more complex water circulation patterns in an estuary. Thus a mixing zone in an estuary is not stable and will extend both upstream and downstream of the outfall due to the ebb and flow of the tide.

1.5.4 The results of the 1984 survey work are given below in Table 1:

TABLE 1

Mixing Zone Sizes in hectares

| Outfall | pH 6 or less* | 1mg/l Fe or more** | Area of moderate to severe biological effect<br>5mg/l Fe or more** | 10mg/l Fe or more** | 20mg/l Fe or more** |
|---|---|---|---|---|---|
| SCM (50m pipe) | 27ha | 130ha | 38ha | 9ha | 2ha |
| Tioxide (800m pipe) | 160ha | 550ha | 240ha | 97ha | 5ha |

* as a 95%ile ** as an annual average

1.5.5 Following the 1984 survey pollution reduction programmes were agreed. The objectives chosen for the programmes were: 80% decreases in the areas within which a moderate to severe environmental impact could be observed; and a reduction in the iron staining of the shoreline.

## 2. THE DISCHARGES

### 2.1 THE OLD OUTFALLS

2.1.1 In 1984 both pipes discharged at the low water mark. This resulted in little or no depth of water being available at low slack water. At high slack the situation was better with at least 4m of water being available on neap tides and up to 7m on springs. Mixing zone sizes were large (Table 1).

2.1.2 Adjacent to the Tioxide factory there is a wide expanse of intertidal mudflats. The low water mark is 800m from the flood bank and the outfall pipe was of a similar length. The impact of the discharge was very evident with impoverished biological life in the area around the end of the pipe, heavy iron staining of the flood bank wall and no growth of brown seaweed on the wall although green seaweed was present.

2.1.3 Adjacent to the SCM factory the bed of the estuary slopes much more steeply. The low water mark is only about 50m from the shore and hence the SCM pipe was only 50m in length. Biological impoverishment of the bed, iron staining on the flood bank wall and lack of brown seaweed were all evident.

### 2.2 THE NEW OUTFALLS

2.2.1 Following the 1984 survey it was agreed to replace both pipes by longer outfalls in order to improve dilution and dispersion. This decision was subjected to critical examination at a Public Local Inquiry called by the Secretary of State for the Environment in October 1987. The outcome of the Inquiry was approval for the longer pipes. They began operating in the summer of 1988.

2.2.2 The Tioxide discharge was relocated to the main deep water channel; a distance of approximately 2.2km from the shore. At the discharge point this channel is at least 5m deep at low water and can be up to 12m deep at high water on spring tides. No diffuser was fitted as modelling work showed little advantage in having one in as turbulent a mixing area as the deep channel.

2.2.3 The SCM discharge was relocated 300m offshore and fitted with a 50m diffuser. Whilst its new location is short of the main deep water channel it is in a subsidiary channel of deeper water. Minimum depth of water above the outfall is about 2.5m rising to over 9m at high water of a spring tide.

2.2.4 During construction of the new outfalls both headworks were fitted with flow measurement and flow proportional sampling devices. This provides an accurate assessment of the load being discharged. When the consents were being reviewed to authorise the new outfalls the opportunity was taken to restrict mercury to a lower level than had previously been the case.

## 3. RECENT MONITORING PROGRAMME

### 3.1 BIOLOGICAL BASELINE SURVEYS

3.1.1 Once the location of the new outfalls had been agreed biological surveys were carried out at those locations to establish a baseline against which any apparent future change could be judged. These surveys were full grid surveys and provide a reference point for the impact of the new discharges as well as for the reduction in impact that will follow from the implementation of the second pollution reduction programme.

3.1.2 A baseline survey was carried out around the location of the new SCM pipe in September 1985 and around the location of the new Tioxide pipe in September 1986.

### 3.2 BIOLOGICAL MINI GRIDS

3.2.1 In July 1988 just before the new outfalls began to operate, partial grid surveys were carried out around the discharge points. These surveys were not as detailed as the baseline grid surveys of 1985 and 1986 with only selected points within the main grid being resampled. Fewer samples were collected to facilitate seasonal repetition of the surveys (in September 1988 and in March and July 1989). Repeat full grid surveys could only have been done once in any year and as they were originally carried out in September repeats should also be in September for maximum comparability.

3.2.2 Full grid surveys in September 1988 would have been too early as the new discharges were only just starting. Full grid surveys in September 1989 would not have been worked up in time for this report. Thus the assessment of the impact of discharging at the new outfall locations has been judged mainly on data from the mini grid surveys. The July 1988 surveys provide a 'before' picture and the March and July 1989 an 'after' with the September 1988 survey giving a check on early damage.

3.2.3 In future years further mini grid survey work will be carried out. At some stage a further full-scale grid survey may also be necessary but one is not planned at the moment.

### 3.3 CHEMICAL BASELINE SURVEYS

3.3.1 Water column surveys do not need to be carried out prior to the start of a discharge where the circulation pattern of the surrounding body of water prevents it having a permanent association with the outfall location. When the tide is running the plume from any outfall pipe streams away from the pipe broadly in the direction of the tide. The water uptide of the outfall and beyond the edges of the plume downtide is the diluting estuary water. This gives an adequate baseline. It is convenient to collect baseline water quality data at the same time as sampling the discharge plume.

### 3.4 CHEMICAL MONITORING

3.4.1 Chemical monitoring around the new and old outfalls, except for the 1984 and 1989 major survey years, has been in accordance with the 1982 Monitoring Directive. This monitoring includes water quality monitoring on three separate days through the year and provides snapshots of water quality around the outfalls in the 1985 - 1988 period.

3.4.2 An additional two day survey was carried out in October 1988 soon after the new outfalls started discharging. The objective of the survey was to see how difficult it was to locate the plume around each outfall and hence enable plans to be made for the 1989 survey work. It proved to be valuable experience. There was little evidence of a plume at the surface but one could be found below the surface; sometimes many metres below.

## 4. THE 1989 SURVEYS

### 4.1 MATHEMATICAL MODELLING

4.1.1 Mathematical models of both outfalls were produced in 1984 by the Water Research Centre (WRc) the main UK water pollution research establishment. These models have been updated and used to evaluate the 1989 chemical survey data.

4.1.2 The models were used in 1984 to predict the size of mixing zone that would be found around each of the proposed new outfalls both for acid and for iron. These predictions are given in Table 1. They were based on the 1984 effluent loads.

4.1.3 By 1989 effluent loads had changed. The models were used to recalculate the mixing zone size for the effluent loads currently being discharged. The calibration of the models was checked against the actual concentration levels of acid and iron found in the estuary during the 1989 water quality surveys. Finally the mixing zone sizes they were predicting were compared with those derived from the biological survey work.

4.1.4 The details of the mathematical modelling work are recorded in Appendix 1.

### 4.2 BIOLOGICAL MONITORING

4.2.1 Mini grid survey data was collected on four occasions during the period July 1988 to July 1989. Full details of the results of this work, the monitoring techniques used and how the data have been interpreted are given in Appendices 2, 3, 4, 7 and 13 with data for the old outfalls discussed in Appendices 5 and 12.

### 4.3 CHEMICAL MONITORING

4.3.1 There has been intensive chemical monitoring around the two outfalls on five separate occasions during the period July to October 1989.

4.3.2 The first two surveys took place in July and measured pH distribution around the outfalls. Surface and depth pH readings were taken continuously up to 1km from the outfall for a full tidal cycle. Neap tides were chosen as being likely to give worst conditions.

4.3.3 The three remaining surveys (at the end of August, mid September and early October) measured soluble iron concentrations.

4.3.4 Full details of the chemical survey results, and the sampling and analytical methods used area given in Appendices 8 to 11 with data for the old outfalls discussed in Appendix 6.

## 5. SUMMARY OF SURVEY RESULTS

### 5.1 IMPACT AT THE NEW OUTFALL SITES

5.1.1 The 1989 survey work has confirmed the predictions made in 1984: ie that if the outfalls were repositioned into deeper water the pollution caused by the discharges would be dramatically reduced.

5.1.2 The chemical water column work established that a plume could be found streaming away from both outfalls when the tide was running. However the maximum concentration levels of iron and acid within that plume were considerably lower than those found in 1984.

5.1.3 The iron and acid data collected around both outfalls not only produced lower maximum values than 1984 but also showed that the distance over which elevated values could be found were significantly shorter than in 1984. In contrast to 1984 the size of zone around the SCM outfall appeared to be bigger than that around Tioxide. This is attributed to the Tioxide outfall being in deeper and more turbulent water.

5.1.4 As in 1984 some discontinuous patches of water with elevated acid and iron values were found outside the main plumes. This is considered to be caused by the pool formed at slack water being broken up as the tide starts to run. These patches are not likely to have a significant effect.

5.1.5 Heavy metals other than iron are found in titanium dioxide waste. The concentrations of these other metals found in the plumes from the new outfalls are such as to produce mixing zones which are insignificant compared to those for iron . Acid and iron are the main problem.

5.1.6 The results from the biological monitoring around the new outfalls showed that the discharges were having a very limited impact compared to that observed in 1984 around the old outfalls. At the Tioxide outfall it was difficult to be certain there was any effect. Whilst there was some paucity of benthic life this is to be expected in an area on the shoulder of a deep channel where there is a high degree of scour.

5.1.7 Around the SCM outfall there was evidence of some impact. A weak effect could be seen over an area of approximately 19 ha.

### 5.2 RECOVERY AT THE OLD OUTFALL SITES

5.2.1 There was strong evidence of a recovery of biological activity at the old Tioxide outfall site. This was apparent both from sub tidal and inter tidal life. At the old SCM site there was only marginal or patchy improvement. Damage here in 1984 was less intense than at the old Tioxide site and hence a more limited change is to be expected. Since the new SCM outfall is much closer to the old one than is the case for Tioxide there is the possibility of some low intensity influence.

5.2.2 The sea wall along a significant length of the south Humber estuary consists of large stones and a typical rocky shore marine life can be found inhabiting it. In 1984 the sea wall in the immediate vicinity of both factories was heavily iron stained and there was no brown seaweed growing there - only green seaweed. By 1989 there had been a dramatic reduction in the iron staining and there was a sparse but widespread growth of brown seaweed. Animal life to the west of the SCM outfall and the east of the Tioxide site has increased substantially since 1984 indicating an almost complete recovery. In the area between the two outfalls whilst there is some improvement it is not as complete. There are a number of other industrial effluents discharged in this area.

5.2.3 As part of the routine monitoring of the Humber estuary, brown seaweed is collected from the flood bank wall in the near vicinity of the two outfalls and analysed for metal content. The 1989 data showed a dramatic reduction in the amount of iron present compared to previous years. Analysis of ragworms collected from around the old outfalls showed they still had elevated levels of iron. But as these organisms absorb metals from the sediments in which they live and feed (unlike seaweed which absorbs metals from the water column) this is not surprising. It will take some time for the sediments around the old outfalls to return to a background level of iron.

5.2.4 A number of flat fish (Dover Sole and Flounder) were collected from the general area of the new and old outfalls but the results of analysis were inconclusive. Given that these animals are mobile and do not remain in one area only gross contamination is likely to show up. There was no evidence of such gross contamination. Nor was there any evidence of morphological abnormalities.

## 5.3 OVERALL EFFECT OF MOVING THE OUTFALL LOCATION

5.3.1 The prime objective in moving the outfall locations was to reduce dramatically the area over which the discharges were having an adverse effect. This has been achieved.

5.3.2 The water column data showed that the distance over which low pH values and high iron values could be found was very much shorter than in 1984. However water column data cannot be interpreted directly because they are derived from a series of spot samples taken in an environment that changes with time. These data need to be interpreted via a mathematical model which is able to present a picture that is averaged over time.

5.3.3 The WRc models were used to interpret the water column data by determining the size of the mixing zone (ie the area within which the EQS was not met) around each outfall for both iron and pH. The boundary of these mixing zones are the EQS values of 1.0mg/l for soluble iron (as an annual average) and pH 6.0 (as a 95%ile) for acid. Table 2 below gives details of mixing zone size for 1989 with the values for 1984 around the old outfalls for comparison.

TABLE 2

Mixing zone sizes in hectares

| | SCM | | Tioxide | |
|---|---|---|---|---|
| | Iron | Acid | Iron | Acid |
| 1984 | 130 | 27 | 550 | 160 |
| 1989 | 92 | 0.6 | 44 | 0 |

5.3.4 The model shows that the mixing zone for acid around the new Tioxide outfall is so small it cannot be measured. Around the SCM outfall an acid mixing zone is found but it is only 2.2% the size of the 1984 zone. For iron the result is not as dramatic but even so the size of mixing zone around the Tioxide outfall is only 8% the size of the 1984 one. For SCM the iron mixing zone size is about 70% of that in 1984. It should be remembered that the surface area of the Humber estuary is in excess of 20,000ha so all the mixing zone sizes are very localised in extent and have no impact on the estuary as a whole.

## 6. IMPLEMENTATION OF SECOND POLLUTION REDUCTION PROGRAMME

6.1 The 1989 Harmonisation Directive requires a further pollution reduction programme to be implemented at each factory. Second pollution reduction programmes for the UK factories have been sent to the Commission by the UK government in accordance with Articles 5 and 7 of the Directive. These programmes involve reducing the polluting loads discharged to the estuary.

6.2 It will be some years before these second reduction programmes are complete. However the 1989 survey data will form a sound benchmark against which the improvements achieved by these programmes can be quantified.

## 7. CONCLUSIONS

7.1 The first pollution reduction programmes set for the two Humberside titanium dioxide factories have been completed successfully.

7.2 The size of mixing zone created around the new outfalls is similar to that predicted in 1984 for the relocated outfalls. Whilst plumes from both outfalls can be found the acid and iron levels in these plumes are rapidly diluted and dispersed.

7.3 The biological impact of the discharges at their new locations is limited. The Tioxide outfall causes a negligible effect.

7.4 The area immediately adjacent to the old Tioxide outfall where the most severe biological damage could previously be found has substantially recovered despite there having been only one season's recruitment so far. Only moderate damage was found in 1984 around the SCM outfall but at present there is only limited evidence of a recovery. Further work in future years will be needed to investigate this.

7.5 Fish in the area show no evidence of external damage nor is their body burden of iron or other heavy metals elevated.

7.6 Sediments in the area of the old outfalls still have levels of iron that are higher than background but they have decreased and are expected to decrease still further.

7.7 Further survey work in the estuary will be needed to monitor the effect of implementing the next pollution reduction programme. The 1989 survey work will form a sound benchmark against which any improvements can be judged.

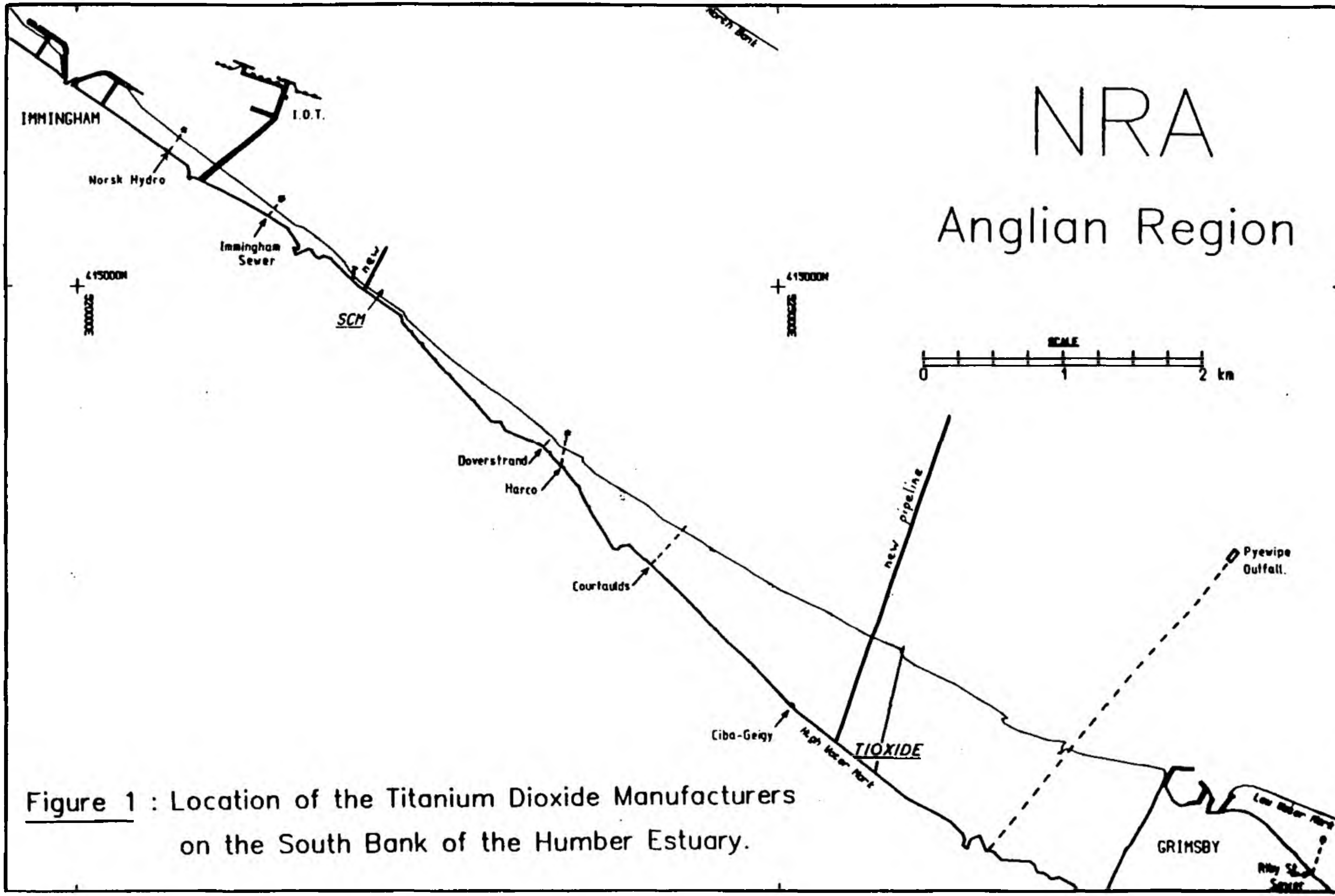


Figure 1 : Location of the Titanium Dioxide Manufacturers on the South Bank of the Humber Estuary.