The Use of Energy-Dispersive X-Ray Microanalysis as a Rapid Method for Demarcating Areas Around Marine Outfalls that may be Influenced by Effluent: A Case Study

Michael Alfred Gregory[a]; Christopher John Brouckaert[b]; Timothy Paul McClurg[c]

[a] Govan Mbeki Research Centre, University of Durban-Westville, Durban, South Africa [b] Department of Chemical Engineering, University of Natal, Durban, South Africa [c] CSIR, Division of Water, Environment and Forestry Technology, Durban, South Africa

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Michael Alfred Gregory

Govan Mbeki Research Centre, University of Durban-Westville,
Durban, South Africa

Christopher John Brouckaert

Department of Chemical Engineering, University of Natal,
Durban, South Africa

Timothy Paul McClurg

CSIR, Division of Water, Environment and Forestry Technology,
Durban, South Africa

Abstract: Surveys that monitor pollution in a marine environment often include the measurement of heavy metals and other trace elements in sediments obtained from multiple stations near marine outfalls. This study investigates the use of energy-dispersive x-ray (EDX) microanalysis as a rapid screening method, where characteristic or "signature" elements (SE) in effluent can be located and mapped on the seabed. Thereafter, sediments from stations/areas with high SE can be examined using more sensitive spectroscopic methods, and, if present, trace metals quantified.

Address correspondence to Professor M. A. Gregory, Govan Mbeki Research Centre, University of Durban-Westville, Private Bag X54001, Durban 4000, South Africa. Fax: 031 204 4360; E-mail: gregorym@pixie.udw.ac.za

To serve as controls, 21 samples of sediment were obtained from two "pristine" areas off the Kwazulu Natal coast. A further 99 samples were obtained from stations within 2 km of the Huntsman Tioxide pipeline. Each sample was sonicated to separate the coarse from fine fractions. The fines were collected on a paper filter and mounted next to its corresponding, washed, coarse fraction on a graphite stub. Each sample was coated with C and examined by EDX. Huntsman Tioxide effluent was rich in Ti and Fe. The fine and coarse fractions of all sediments were screened for these elements. A contamination index (I) was constructed from the combined fines, Ti and Fe data. Surfer 16 software was employed to create contour plots showing the distribution of Ti, Fe, and I in fine and Ti in coarse fractions of sediments near the Huntsman Tioxide pipeline. The results showed that EDX was an effective method for locating fallout "hot spots" and delimiting an area affected by effluent.

INTRODUCTION

South African legislation permits the controlled discharge of specific effluents via deep-sea, marine outfalls provided that a wide range of strict conditions are met. Of primary concern are matters pertaining to the protection of human health and ecological integrity. Stringent monitoring programs are applied to ensure compliance. For example, on the east coast of South Africa, the CSIR performs regular, detailed surveys around the Richards Bay, Durban, and Umkomaas outfalls,[1-3] and Physalia Consultant and Forensic Ecologists perform the same function for the Huntsman Tioxide outfall off Amanzimtoti.[4]

One of the approaches used in these surveys is to examine the sediment chemistry on a wide grid of stations encompassing the discharge area[1-6] and to relate this to benthic community structure.[7,8] Current chemical methods usually entail spectroscopy (typically atomic absorption spectrometry, or AA). Co-occurrences of chemical contamination and aberrant benthic communities are then used to demarcate zones of impact.

In a recent pilot study, this group investigated the possibility that energy-dispersive x-ray (EDX) microanalysis might provide a rapid and relatively cheap means of mapping the distribution of elemental contaminants within sediments, and, by inference, allow the recognition of areas where there had been effluent deposition.[9] The rationale was to identify characteristic elements in the effluent and trace them to the seabed. The results, although tentative, suggested that our EDX methodology could both delimit the area influenced by pipeline effluent and identify the most affected sites on the seabed where the fallout from effluent had been concentrated.

This more comprehensive investigation significantly extends the pilot study by analyzing 99 samples of sediment taken within 2 km of the Huntsman Tioxide effluent pipeline off Amamzimtoti. This effluent is rich in several specific tracer metals and therefore lends itself well to

characterization using EDX. The same rationale was followed as in the pilot study.[9] This entailed characterizing the effluent in terms of its trace element *signature* and then seeking this signature on the seabed in the vicinity of the pipeline.

EDX, unlike conventional AA, does not generate a result that may be expressed in terms of absolute chemical concentration. Neither can it provide information on the bioavailability of toxic elements. It is, therefore, of limited use on its own in predicting or rationalizing toxic impact. It does, however, provide a potentially powerful means for tracking effluent dispersal and deposition on the seabed. Corroborative evidence of impact may then be sought by examining the health of benthic communities in the demarcated areas of deposition.

It is anticipated that the EDX methodology, which is described and tested in this paper, could play a useful supplementary role in monitoring marine pollution.

MATERIALS AND METHODS

Samples of sediment were obtained by courtesy of Physalia Consultant and Forensic Ecologist during their routine monitoring survey of the Huntsman Tioxide outfall in 1998. The samples were taken by means of a grab at 99 grid positions within approximately 2 km of the Huntsman Tioxide pipeline off the east coast of South Africa (30°54.5′E/30°3′ES). To serve as controls, 21 samples were selected from two widely separated pristine areas. Eighteen samples (A-series) were obtained 7.5 km off the coast near Umkomaas (30°52′E/30°13.5′S) and 3 (B-series) were obtained in shallow water, 1.5–2.5 km from the Lovu River Mouth (30°52′E/30°7.5′S). Samples of effluent were obtained prior to discharge into the Huntsman Tioxide pipeline.

Identification of Characteristic Elements in Effluent

Particulate material had settled to the bottom of each sample of effluent. This, together with 50 mL of the supernatent, was removed by pipette and centrifuged at 2000 rpm for 2 min. After centrifugation, most of the supernatent was removed and the residue dried onto a graphite disk.

Preparation of Fine and Coarse Sediment Fractions for EDX Analysis

Each sediment sample, half-filled a flip-top, 60-mL polythene container. The container was filled with distilled water and the substrate stirred. The container was placed in an ultrasonic bath for 10 min, and the supernatant

was filtered through a stainless steel, plain weave, 300-μm $\times$ 500-μm mesh and then through Whatman no. 6 filter paper. This was repeated until an adequate amount of fines had deposited onto the filter paper (3–5 washings depending on the amount of particulate material in the sample). The filter paper was removed from the funnel and dried in a partially enclosed Petri dish at 70°C.

Approximately 10 g of the coarse fraction was placed in a clean 50-mL plastic vial. To remove all trace of fines, the sands were ultrasonicated in distilled water for 30 min (3 $\times$ 10 min). The clear supernatant was removed and the coarse fraction dried in an oven at 70°C.

Double-sided carbon tape was fixed to a 2.5-cm-diameter brass stub, and 50% of the surface was pressed into a sample of dried, clean sand. A segment, approximately 1 cm $\times$ 2 cm, of filter paper containing fines from the same sample was affixed next to the sand. To make the samples conductive for scanning electron microscopy, they were each coated with approximately 20 nm of carbon using a Polaron carbon evaporator.

Collection of Data

Both the fine and coarse fractions were examined using a Jeol 6100 scanning electron microscope at 25 kV at a magnification of $\times$22 with a working distance of 15 mm and subjected to "standardless" quantitative analyses using a Noran Voyager 2100 EDX system. Standardless quantitative analysis requires that elemental peak intensities from the sample be recorded and compared with references that represent intensity information for pure elements. These pure elements references are collected at Noran Instruments and provided as part of the software. K-ratios are determined (the intensity of the unknown divided by the intensity of the known) and a ZAF matrix correction applied to the data. This matrix correction is a mathematical model of the interactions occurring in the sample matrix when the beam electrons interact with the atoms of the sample. It then corrects for variations caused by atomic number characteristics, absorption of x-rays, and fluorescent effects. The program then reports all the information used to determine the atomic percent and weight percent. All standardless quantitative analyses are normalized to 100%.

Five areas of coarse and fine fractions were examined for 60 s from each sample with dead time readings being kept between 25–30% (beam current ranged from 0.412 nA to 490 nA for fines; 0.326 nA to 0.520 nA for sands; measured using a Faraday cage). Each analysis was "forced" to include Mg, Al, Si, K, Ca, Fe, and Ti, elements previously found to be the primary components of sediments off the Kwazulu Natal coast.[9] The inclusion of these elements always gave a $\chi^2 < 2$, indicating good conformity. Carbon and oxygen were taken out of the matrix. Each of the five, 60-s analyses covered an area of approximately 13.25 mm^2. The data from the five

analyses were averaged and the amount of a particular element in each sample expressed as a weight percentage (wt%).

Background Measurements

The primary reason for separating the coarse and fine fractions of the sediment was that particulate material issuing from the pipeline is expected to be predominantly fine due to the nature of the industrial process. Any coarse material will in any case settle rapidly and therefore tend to be confined to a small area in the immediate vicinity of the pipeline diffusers. Thus, evidence for industrial contamination was expected to be more marked in the fine fraction. Significant concentrations of Fe and Ti are naturally present in marine sediments, so it was decided to regard as background any concentrations that were below the maximum levels found in the fine fractions of the control groups of samples from uncontaminated areas. These limiting values were 15% for Fe and 1.5% for Ti (Tables 1 and 2)

Presentation of Data

During the course of the study, two sets of data were obtained for each station: those representing fines (particles $<0.3\,\mu m$) and coarse fractions (sands and

Table 1. The mean, standard deviation (SD), and highest and lowest weight percent (wt%) of elements in the coarse fraction of sediments from control A and B stations

	Mg-K	Al-K	Si-K	K-K	Ca-K	Ti-K	Fe-K
Control A							
Mean	0.89	1.15	50.11	0.79	42.21	**0.22**	**1.01**
SD	0.28	0.45	7.6	0.51	7.84	**0.18**	**0.32**
High	1.35	1.96	58.9	1.7	52.2	**0.61**	**1.47**
Low	0.37	0.65	39.3	0.39	33.2	**0.04**	**0.56**
Control B							
Mean	1	1.64	53.28	0.67	39.74	**0.24**	**1.2**
SD	0.18	0.51	4.23	0.24	4.09	**0.08**	**0.3**
High	1.29	2.32	62.66	0.99	45.61	**0.35**	**1.68**
Low	0.69	0.98	47.45	0.4	31.92	**0.07**	**0.85**
Control all							
G. mean	0.95	1.39	51.7	0.73	40.98	**0.23**	**1.1**
SD	0.23	0.53	6.19	0.39	6.2	**0.13**	**0.32**
High	1.35	2.32	62.66	1.7	52.2	**0.61**	**1.68**
Low	0.37	0.65	39.3	0.39	31.92	**0.04**	**0.56**

In "Control all" is shown the grand (G) mean, SD, and highest and lowest wt% of elements in the pristine areas.

Table 2. The mean, standard deviation (SD), and highest and lowest weight percent (wt%) of elements in the fine fraction of sediments from control A and B stations

	Mg-K	Al-K	Si-K	K-K	Ca-K	Ti-K	Fe-K
Control A							
Mean	1.77	12.06	37.1	3	30.74	**1.13**	**11.36**
SD	0.35	3.81	9.35	1	16.2	**0.3**	**2.54**
High	2.37	19.8	54.2	4.88	52.1	**1.5**	**14.7**
Low	1.13	7.12	25	1.69	1.57	**0.69**	**7.33**
Control B							
Mean	3.19	13.07	32.62	2.01	37.25	**0.88**	**7.76**
SD	0.37	2.58	6.25	0.49	9.81	**0.19**	**1.12**
High	3.98	16.29	42.87	2.75	51.4	**1.16**	**9.59**
Low	2.55	9.11	24.6	1.35	23.01	**0.51**	**5.78**
Control all							
G. mean	2.48	12.57	34.86	2.51	34	**1.01**	**9.56**
SD	0.81	3.2	8.05	0.92	13.42	**0.28**	**2.66**
High	3.98	19.8	54.2	4.88	52.1	**1.5**	**14.7**
Low	1.13	7.12	24.6	1.35	1.57	**0.51**	**5.78**

In "Control all" is shown the grand (G) mean, SD, and highest and lowest wt% of elements in the pristine areas.

fragments $>0.3\,\mu m$). In addition, in order to pinpoint regions most affected and to describe the overall distribution of signature elements, a *contamination index* (*I*) was calculated from the combined Ti and Fe wt%. The data are listed in Tables 1 to 3 and portrayed as contour maps in Figs. 1, 2, 3, and 6.

Table 3. The mean, standard deviation (SD), and highest and lowest weight percent (wt%) of elements in the coarse and fine fractions of sediments from 99 stations within 2 km of the Huntsman Tioxide outfall

	Mg-K	Al-K	Si-K	K-K	Ca-K	Ti-K	Fe-K
Coarse							
Mean	0.57	3.73	68.08	2.54	20.01	**0.67**	**2.5**
SD	1.26	1.44	10.3	1.69	11.6	**0.91**	**1.61**
High	12.65	8.71	87	8.57	50.32	**6.26**	**11.79**
Low	0.01	1.31	35.6	0.5	0.56	**0**	**0.63**
Fines							
Mean	2.14	15.85	41.07	3.07	13.44	**3.1**	**17.5**
SD	0.65	2.03	7.58	0.68	7.14	**3.17**	**6.51**
High	3.68	20.45	56.16	4.66	31.16	**16.84**	**43.46**
Low	0.61	9.43	23.34	1.52	2.72	**1.13**	**10.3**

Note both the mean and the highest wt% of signature elements Fe and Ti in both coarse and fine fractions are higher than those at control stations.
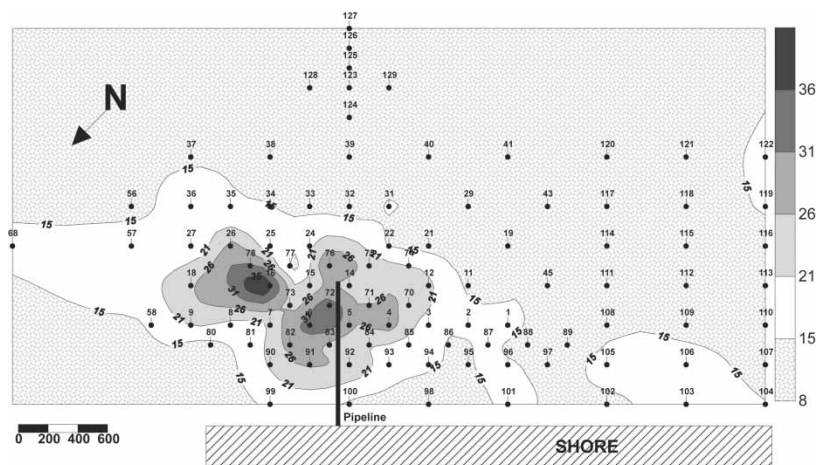
Figure 1. Contour map showing the distribution of Ti in fines in the vicinity of the Huntsman Tioxide pipeline. The larger *italicized* font marks contour values. The bullet and smaller font shows the position of the 99 stations from which samples of sediments were obtained. The scale represents both horizontal and vertical distances.

RESULTS

Effluent

The samples of effluent from the Huntsman Tioxide pipeline contained a white, particulate material within a pale yellow fluid. Scanning electron microscopy revealed the particulate material to be composed of amorphous particles with a diameter of approximately 1 μm. Spot, EDX analyses
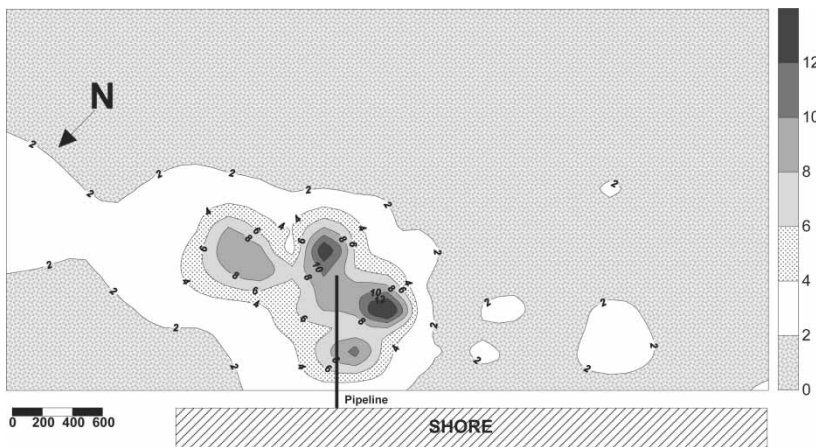

Figure 2. Contour map showing the distribution of Fe in fines in the vicinity of the Huntsman Tioxide pipeline. The sampling grid is omitted for clarity.
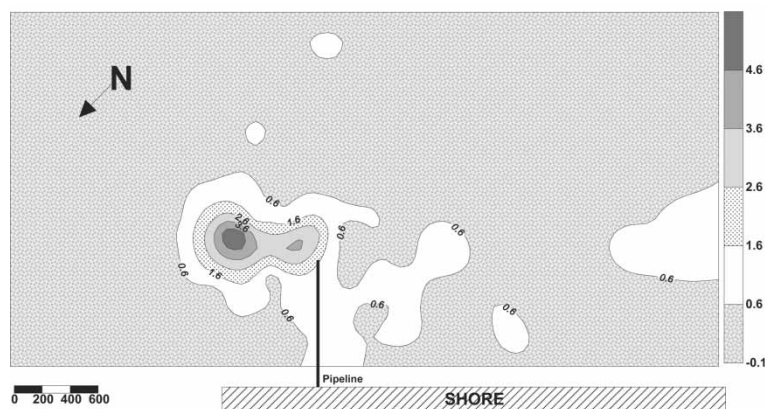
Figure 3. Contour map showing the distribution of Fe in the coarse fraction of sediments in the vicinity of the Huntsman Tioxide pipeline.

revealed these particles to be primarily composed of Ti. The dried supernatent was especially rich in Fe. These elements were used as the "signature elements" for Huntsman Tioxide effluent.

Sediments

Samples from Pristine Areas

Fine Fraction

There were no obvious morphological differences in the appearance of filtered fines from samples taken at the "pristine" control sites (series A and B). The fines ranged in color from gray to pale orange. A summary of the composite means, standard deviations of the means (SD), and range of wt% for Mg, Al, Si, K, Ca, Ti, and Fe is presented in Table 1. The results for the A and B series of samples are first listed separately and then in combination.

Coarse Fraction

The particles in the coarse fractions of the A- and B-series of samples varied between approximately 0.2 mm and 2 mm in diameter, the larger particles generally being shell fragments. The EDX results for the seven target elements are listed in Table 2 in the same format as that adopted for the fine fraction.

Samples from Near Huntsman Tioxide Pipeline

Fine Fraction

The samples appeared as a layer of fine, particulate material adhering to the surface of the filter. There were considerable differences in the appearance of filtered fines between stations. Stations 4, 6, 16, 71, 72, 76, and 78

had a rust-red tinge and were particularly rich in both Fe and Ti, whereas fines from other stations were generally gray/pale-orange in color. The composite means, SD, and range of wt% of Mg, Al, Si, K, Ca, Ti, and Fe are shown in Table 3. The distribution of signature elements Fe and Ti in sediments within the sampling area are presented as contour maps in Figs. 1 and 2.

Coarse Fraction

The size and elemental composition of the coarse fraction of each sample were generally within the normal range.[9] However, particularly high wt% of marker elements Ti and Fe were noted at stations 16 (Ti 3.7:Fe 8.3), 76 (Ti 4.0: Fe 5.9), and 78 (Ti 6.3: Fe 11.8). The composite means, SD, and range of wt% of Mg, Al, Si, K, Ca, Ti, and Fe are shown in Table 3. The distribution of Ti in the coarse fraction of sediments within the sampling area is shown in Fig. 3. Individual sand grains were examined in the sample from station 78 where the highest wt% of Ti and Fe was noted. X-ray maps showed an encrustation of Ti and Fe on the surface of some grains (Fig. 4).

Contamination Index

Fe and Ti are strongly associated with each other, both in the natural sediments of the region and in the material discharged from the pipeline. It was therefore possible to construct a contamination index (I) using a linear combination of the two elements:

$$I = a \times \text{Fe} + a \times s \times \text{Ti} - b$$

Here, a, s, and b are constant coefficients. The numerical values of the coefficients were determined as follows: A linear regression was performed on the set of measured Fe and Ti values, taking Fe as the independent variable and Ti as the dependent variable. The correlation coefficient between the variables
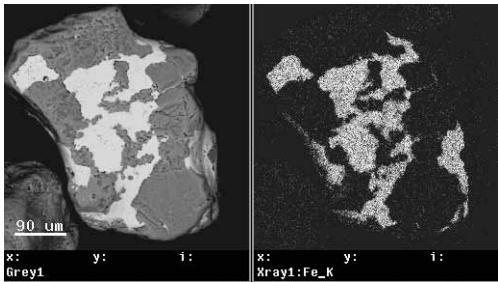

Figure 4. (a) Backscatter-electron, SEM image of a sand grain showing the pale Fe- and Ti-rich amalgam on the surface and (b) an x-ray map demarcating areas rich in Fe. The grain is from position 76 near the Huntsman Tioxide outfall.

was 0.73. The parameter *s* was set to the slope of the resulting line (i.e., 1.29). The values of *a* and *b* were then adjusted to scale *I* to span a desired range. It was decided to set an index value of 0 to correspond to the average levels of Fe and Ti found in the control group and a value of 10 to correspond to the maximum levels found in the control group, so that index values above 10 would strongly suggest contamination. This choice yielded the following formula:

$$I = 2.0413 \times \text{Fe} + 2.6326 \times \text{Ti} - 25.0688$$

The resulting relationship between *I* and the Fe and Ti measurements are shown in Fig. 5. The distribution of *I* for each station was calculated and plotted as a contour map (Fig. 6).

DISCUSSION

Discharge from marine pipelines often contain solids and flocculants that eventually settle on the seabed and merge with the fines of existing sediments where they may serve as tracers to denote "hot spots" and delimit an area influenced by an outfall.[10] Active tracers are readily identifiable substances that are added to an effluent in order to follow the movement and distribution of the material in the marine environment. Active tracers include radioactive isotopes,[11] magnetic and rare-earth markers such as Ta and Co,[12] and bacterial tracers.[13] Passive tracers are substances already present in the effluent as they leave the factory or treatment works. In the case of "sludges" from sewage works, various vegetable residues such as
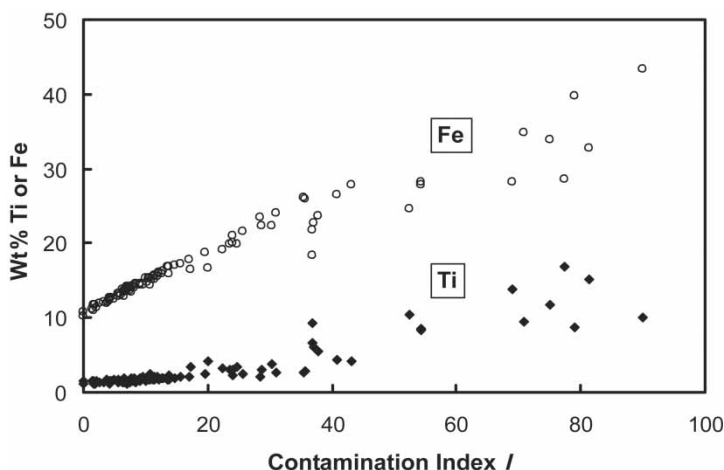
Figure 5. The relationships between the measured wt% of Fe and Ti and the contamination index.
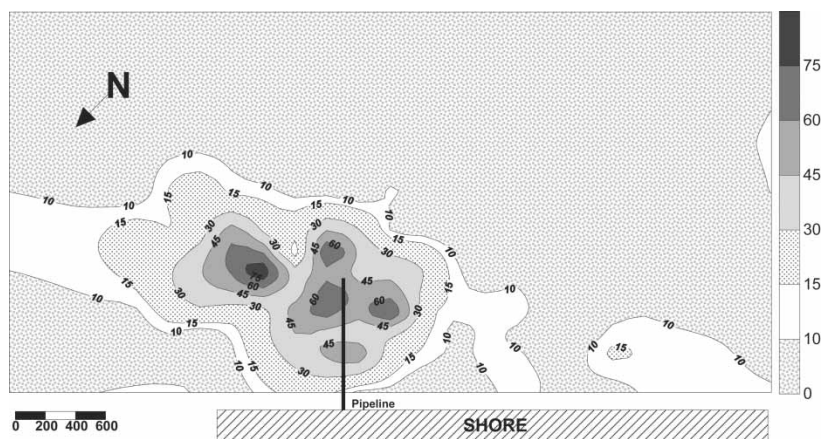
Figure 6. Contour map showing the distribution of *I* (Fe and Ti) in the vicinity of the Huntsman Tioxide pipeline.

tomato[14] and melon seeds[15] have been used as tracers. In addition, synthetic organic compounds such as PCBs and pesticides[16] and a variety of naturally occurring microbial agents[17] have been used to map effluent fallout. In the case of industrial waste, trace metals have been widely used to determine the distribution of potentially toxic effluent.[5,6] Energy dispersive x-ray microanalysis has been used to determine the speciation of marine suspended particles,[18] monitor the translocation and mixing of fill sands,[19] and describe the source and intermixing of seafloor sediments.[20] However, other than our earlier report,[9] EDX does not appear to have been used previously to monitor the dispersal of either active or passive tracer elements in fallout from effluent on the seabed.

The high concentration of Ti in particulate material in the Huntsman Tioxide effluent rendered it a particularly useful "tracer" or "signature" element for EDX analysis. The situation for Fe is more complex. The process separates Fe and Ti originating from the ore by maintaining Fe in the II oxidation state, in which it is water soluble. Thus, most of the Fe in the effluent before it leaves the pipeline is soluble. However, as soon as it comes into contact with oxygenated seawater, it is oxidized to Fe III, which forms an insoluble hydroxide. The hydroxide forms a fine precipitate that tends to aggregate as flocs. These flocs will also tend to capture and incorporate any other fine particles that may be present, in particular the Ti-containing particles. The precipitation and flocculation processes will be affected by the seawater conditions and the rate of mixing of effluent and seawater, so that the distance fine material is carried before settling on the seafloor will be variable. On the other hand, any relatively coarse particles that issue from the pipeline will tend to settle rapidly, and so, in the short term, be found mainly in the immediate vicinity of the outlet.

The EDX analysis revealed seven stations with elevated concentrations of signature elements in the sediments (stations 4, 6, 16, 71, 72, 76, and 78). Four of these stations (4, 6, 71, and 72) showed elevations only in the fine fraction, whereas the remainder (stations 16, 76, and 78) also showed elevations in the coarse fraction. These stations were all in close proximity to the outfalls discharge (<1 km), and their location to the northeast of discharge was consistent with the predominant direction of sediment drift on the Kwa-Zulu Natal coast. The parallel Physalia ecological survey[4] revealed six stations (4, 14, 25, 70, 85, and 86) where there were modified (stressed) benthic communities that appeared to relate to the effluent discharge. These were also in close proximity to the outfall. Although all stations identified by Physalia fell within the high fallout plateau, only one (station 4) corresponded with the hot spots identified by EDX.

The poor correlation between the two sets of data might at first appear anomalous. However, when the nature and behavior of the effluent subsequent to discharge is considered, the disparity is not unexpected. As mentioned above, the effluent is composed of two fractions: a sedimentable fraction of solids and a liquid fraction containing dissolved materials. This latter fraction, with its associated physicochemical properties—such as reduced pH—would be most responsible for toxic effects pending its dilution and dispersal in the water column. The coarse fraction would, on the other hand, be subject to a separate and asynchronous settlement onto the seabed. The two processes of toxic impact and settlement of the solid phase could therefore be separated in space and time.

It is possible that particulate fallout, *per se*, could also exert a toxic impact on the seabed communities. However, in the case of Huntsman Tioxide this is unlikely, as the suite of metals associated with the effluent are not generally considered to be of particular environmental concern. However, the peculiar impact of iron on the sea must be considered. Toxicity tests with iron flocculant in seawater have demonstrated a powerful influence on the fertilization process in those species that release gametes into the water during external fertilization.[21] The breeding potential of a wide variety of marine organisms is thus likely to be reduced in the presence of iron flocculation.

Of particular interest were the large amounts of Ti and Fe in the washed, coarse fraction of some sediments. As sediments in the region of the outfall were not expected to be particularly rich in either element, we investigated this anomaly further. Spot EDX analyses revealed individual sand grains rich in these two elements. X-ray mapping showed that Fe and Ti were present as an "amalgam" on the surface of each particle (Fig. 4). Further investigation suggested that these grains were probably formed in the initial extraction process and were residues from the acid dissolution of the Ti- and Fe-rich slag, which is the first step of the refining process. These grains, therefore, were not a natural constituent of the local sediments but had been discharged with the effluent from the plant.

The use of a passive tracer requires particular care in compensating for background levels in the natural marine sediments. This is especially the case if the coarse fraction significantly influences the elemental composition of the fines. Although no correlation was found between signature elements in the coarse and fine fractions of sediments from either of the uncontaminated control areas, background levels of both Ti and Fe varied substantially from one location to another. The contamination index (*I*) helped to overcome the problem of background variations. It was constructed by combining the two sets of measurements of Ti and Fe data into a convenient single indicator for graphical presentation. The simple linear form of the index was made possible by the strong association between the two elements, not only in the Huntsman Tioxide process and the marine dispersal mechanisms but also in the sediments in the study location. For a different effluent, it might be necessary to adapt the index to suit the specific situation. Furthermore, the particular methodology used to construct the index may not be appropriate in every case, for it was based on the assumption that the foreign material originating from the pipeline would only meaningfully contribute to the elemental composition of the fine fraction of sediments. The Fe- and Ti-rich coarse particles found near the Huntsman Tioxide pipeline showed that this will not always be true, as these were almost certainly contaminated particles originating from the factory. Fortunately, it can be expected that such coarse contamination would settle very rapidly and so, in the short term, be primarily found in the vicinity of the pipeline outlet.

The usual approach in marine pollution monitoring surveys is to measure element concentrations in sediments using AA.[1–5] This methodology can be time consuming and expensive. Although EDX methodology lacks the sensitivity of AA to detect heavy metals in trace amounts (ppm), our results show that it can detect and determine the relative amounts of particulate and flocculant signature elements in effluent fallout on the seabed. The methods described here are relatively quick and simple to perform. Such analyses could be used as a preliminary means of identifying areas of high deposition (hot spots) and delimiting an area influenced by fallout from an outfall. Thereafter, more sensitive techniques (AA) could be focused on areas demarcated by EDX.

In conclusion, this study describes methods for the preparation of fine and coarse fractions of sediments for EDX. In this instance, the relationship between Ti and Fe enabled a contamination index to be created, which helped to overcome the problem of background variations. Adjusting data to accommodate for this relationship reduced positional disparity and established a baseline against which to identify and quantify the amount of signature elements from fallout deposited on the seabed. The results suggest that by demarcating areas influenced by outfalls and identifying hot-spots rich in signature elements, EDX could be employed as a first line of investigation in pollution-impact studies. Such areas could then be subjected to a more focused analysis using more sensitive methods such as AA, which allow more accurate quantification. Finally, this study highlighted a limitation

in the combined use of EDX and ecological surveys to assess impact, but it also has demonstrated the great potential that EDX holds as a tracer for revealing dispersal patterns.

ACKNOWLEDGMENTS

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