

COMMONWEALTH DEPARTMENT OF HEALTH



Australian Radiation Laboratory

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of a Titanium Dioxide Plant at Bunbury,
Western Australia**

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ABSTRACT

A study of radioactivity levels in environmental samples collected in 1982-3 from the environs of the Laporte Australia Limited titanium dioxide plant at Bunbury in Western Australia is described. Radioactivity levels were determined in samples of sediment, water, algae and seafood (crabs and mussels) from the Leschenault Inlet, close to the site at which Laporte plant "liquid" effluent is disposed, and from other areas along the south-west coast of Western Australia including Busselton (Geographe Bay), Wonnerup, Mandurah (Peel Inlet) and Perth (Swan River). Samples of town drinking water from Bunbury, Capel and Perth were also analysed.

Radioactivity levels in the ilmenite feed and "liquid" effluent of the Laporte plant are approximately half those observed in an earlier (1980-1) study. There is evidence for an enhancement of radionuclide concentrations in sediment from Leschenault Inlet originating from the Laporte plant effluent. Despite this effect, radioactivity levels in the sediment of the Inlet are no greater than those that occur at certain other locations along the south-west coast of Western Australia. The investigation of radioactivity levels in water, algae and seafood indicates that the only significant transfer of radionuclides from the sediment is the bioaccumulation of radium in algae, a phenomenon which occurs in estuarine waters throughout the region. In terms of the radiation exposure to members of the public who consume crab flesh or mussels from Leschenault Inlet, there is effectively no risk to health.

UNITS

Throughout this report, the SI units for activity (becquerel, Bq) and dose-equivalent (sievert, Sv) are used. In terms of older units, 1 Bq = 27.0 pCi and 1 Sv = 100 rem.

INTRODUCTION

The Laporte Australia Limited plant at Bunbury in Western Australia produces the white pigment titanium dioxide from the mineral ilmenite. Ilmenite is a dark-coloured fine-grained constituent of mineral sand which is mined in the nearby Capel area. Ilmenite itself is not radioactive but the mineral monazite, which occurs with the ilmenite, is radioactive due to the natural presence of thorium and uranium. Monazite is present as an impurity (ca. 0.14% by mass) in the ilmenite feed used at the Laporte plant, and a previous study (Cooper, Statham and Williams, 1981) determined radioactivity levels at various stages throughout the Laporte plant.

In that study, the principal radionuclides detected in the ilmenite feed were ^{226}Ra , ^{228}Ra and ^{228}Th , and it was found that approximately 14 MBq of activity due to ^{226}Ra (a radionuclide in the ^{238}U decay chain) and 67 MBq of activity due to each of ^{228}Ra and ^{228}Th (radionuclides in the ^{232}Th decay chain) enter the plant daily. Essentially all of this naturally-occurring radioactivity leaves the plant in the form of acidic effluent, which is pumped to disposal lagoons close to the Leschenault Inlet (Figure 1), and allowed to neutralise and drain away.

A preliminary study of possible environmental effects of radioactivity in the effluent (Cooper, Statham and Williams, 1981) established that due to the presence of the high sulphate ion concentrations and the low pH of the effluent, thorium remains in solution whereas radium, which forms an insoluble sulphate compound, tends to coprecipitate. Filtered water samples from several shallow bores close to the disposal lagoons showed some ^{228}Th activity (the maximum found being 9 Bq/l) but essentially no activity due to radium. Low levels of ^{228}Ra were found in filtered sea water samples from the Leschenault Inlet adjacent to the effluent disposal site (typically ca. 0.1 Bq/l), and ^{228}Ra and ^{228}Th were found to be in equilibrium in sediment samples from the Inlet (with a maximum observed activity of 0.16 Bq/g).

The only seafood samples from Leschenault Inlet investigated for radioactivity levels were crabs, collected in early December (1980) at the start of the crab season. No radioactivity was found in the crab flesh, whereas the shells of the crabs showed low levels of activity due to ^{228}Ra and ^{228}Th , with a $^{228}\text{Ra}/^{228}\text{Th}$ ratio of five rather than the normal value of unity, indicating that the crabs preferentially concentrate radium in their shells. A further program of study, to determine radionuclide concentrations

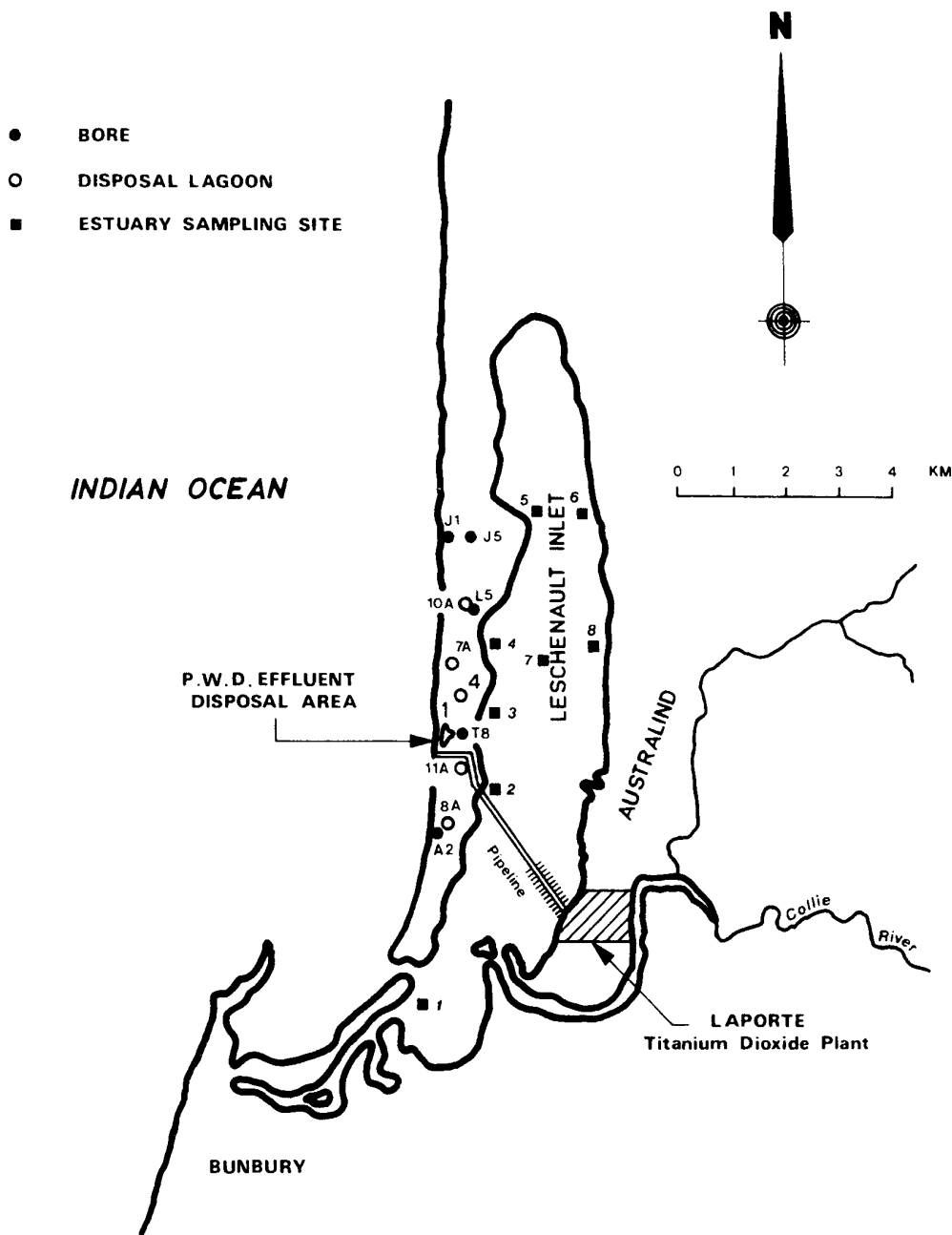


Figure 1. Map of the Bunbury area showing the locations of the Laporte titanium dioxide plant, effluent disposal area, and the sampling sites 1-8 in the Leschenault Inlet.

in seafood from the Bunbury area, was foreshadowed. In such a study there are several important questions to consider. Is there evidence of a significant build-up of radioactivity in sediment from the Leschenault Inlet due to either leakage of effluent from the lagoon area or spillage into the Inlet as a result of the occasional pipeline rupture? If so, is this radioactivity bound to sediments and immobile, or is it available for transfer into the food chain, particularly into species such as crabs and mussels which can remain in the Inlet for significant periods of time? It is also important to consider whether radioactivity levels in samples from the Inlet are a natural phenomenon due to the widespread occurrence of mineral-bearing sands throughout this region.

We present below an investigation of radionuclide concentrations in samples of sediments, water, algae and seafood (crabs and mussels) from the Leschenault Inlet, and from other areas along the coast (Figure 2) including Busselton (Geographe Bay), Wonnerup, Mandurah (Peel Inlet) and Perth (Swan River Estuary). Samples of town drinking water from Bunbury, Capel and Perth were also analysed. All these samples were collected in 1982 as described below.

In February, 1983 a major rupture of the effluent pipeline occurred and several thousand m³ of effluent spilled into Leschenault Inlet. It was, therefore, of interest to obtain samples from the Inlet subsequent to this event to investigate whether radioactivity levels had increased. Samples of sediment, water and mussels from Leschenault Inlet were obtained in August, 1983 for comparison with the data from samples obtained in 1982.

EXPERIMENTAL

Sample Collection

The majority of samples were collected between 30 March and 1 April 1982, with the exceptions of the crabs from Busselton and barnacles from Wonnerup which were obtained in the week 16-20 August 1982, and additional samples from Leschenault Inlet which were collected on 2 August 1983.

Leschenault Inlet. - Sediment samples were obtained from each of the eight sampling sites shown in Figure 1, together with three samples from along the pipeline route (centre of pipeline, south-east of centre and north-west of centre). The activities of the various radionuclides present in the sediment samples are presented in Table 1. Samples of the Inlet water were collected from near the centre of the pipeline, and from sites 4 and 6 (Figure 1).

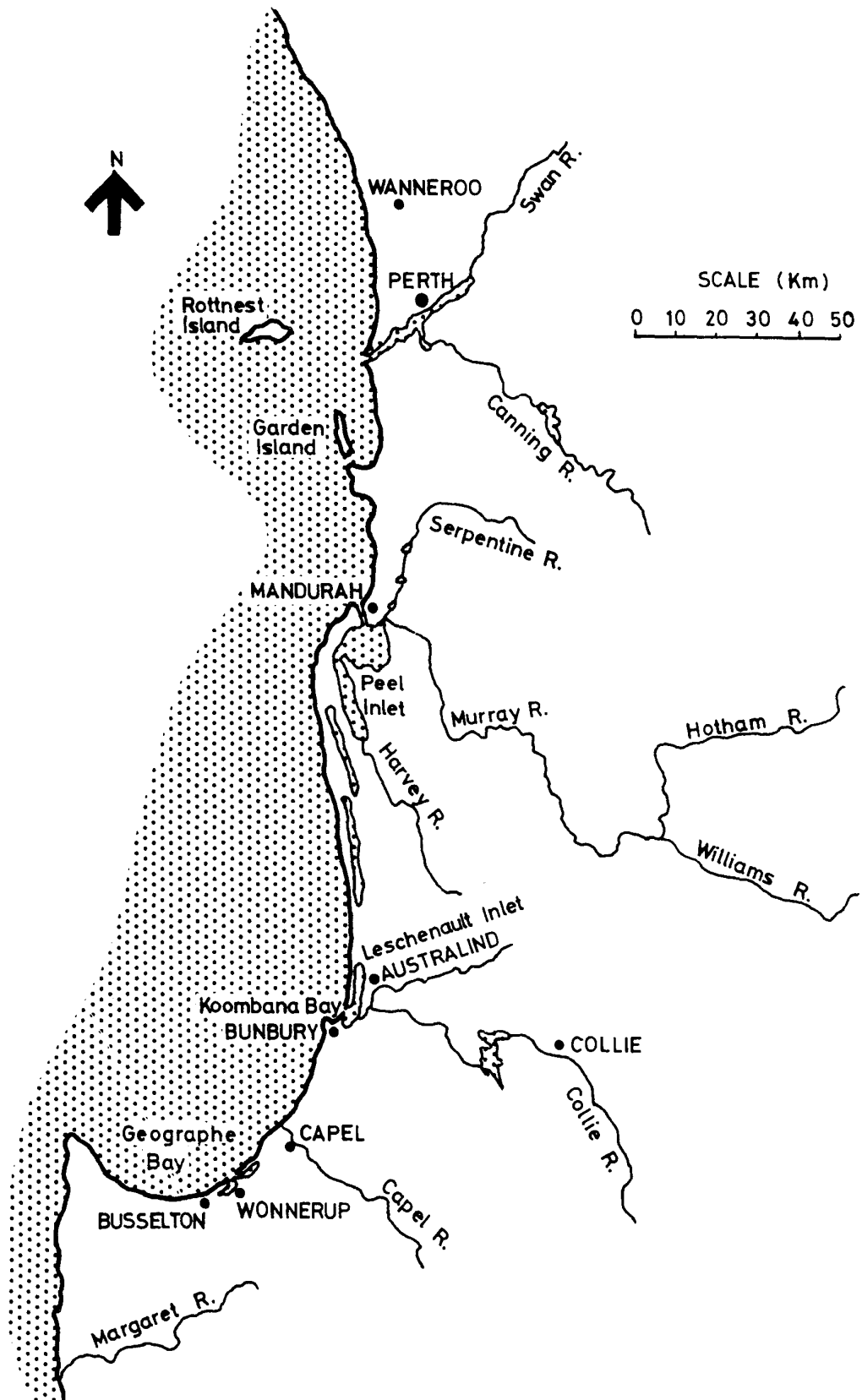


Figure 2. Map of the south-west coastal region of Western Australia.

Algae samples were obtained from near the centre of the pipeline, from a position north-west of the centre, and from sampling sites 3, 4 and 6 (Figure 1).

Ten medium-size crabs were obtained from near the centre of the pipeline, and eight medium-size crabs from near site 4 (Figure 1). Mussels were obtained from off the pylons supporting the pipeline, near the centre of the Inlet. Two batches, each of 100 mussels, were analysed.

Subsequent to the pipeline rupture of February 1983, the following samples were collected. Sediment samples were obtained from each of the sampling sites shown in Figure 1, together with two others from the area in which the effluent spillage occurred. Two 5 l samples of water were obtained, from the centre of the pipeline and from close to where the pipeline rupture occurred. A sample of mussels (150) was obtained from off the pipeline.

Busselton. - Sediment and water samples were obtained from Geographe Bay, from off the short jetty. Eight small sand crabs from a beach inlet (drain) south of Busselton, and eight medium size crabs from the Bay, were analysed. No mussels were available from the area, but seven ocean oysters were obtained. For these, the average fresh weight of flesh was 7.7 g/oyster, and the only radionuclides detected were ^{238}U , ^{210}Pb and ^{40}K with activities of 4(3), 5(5) and 45(6) mBq/g fresh weight respectively.

Wonnerup. - Sediment and water samples were obtained from the inlet beside an old bridge. Close to this site was evidence of an early sand-mining operation. No mussels or crabs were available from this area, but a sample of barnacles was obtained from the piles of the bridge. No radionuclides apart from ^{40}K [24(9) mBq/g fresh weight] were detected in the flesh, whereas the barnacle shells had measurable amounts of ^{226}Ra , ^{228}Ra , ^{228}Th and ^{40}K [1.1(3), 3.4(4), 0.8(2) and 8(2) mBq/g fresh weight respectively].

Mandurah. - Samples of sediment, water, algae and mussels (44) were obtained from Peel Inlet in the vicinity of Station 4 of the Waterways Commission (at Coodanup, straight out from the mouths of the Murray and Serpentine Rivers).

Swan River Estuary. - Samples of sediment, estuary water, algae, crabs (6) and mussels (100) were obtained from the vicinity of Point Walter.

Drinking Water. - Town drinking water samples were obtained from domestic outlets in Bunbury, Capel and Perth.

Laporte Plant. - In order to correlate the results of the present environmental survey with those of the earlier study of radioactivity levels at different stages throughout the Laporte plant (Cooper, Statham and Williams, 1981), current samples of ilmenite feed were obtained from two different suppliers. The first was a combination of samples labelled "AMC 3238 period ending 16/10/81" and "AMC 3289 period ending 15/11/81", and the second was the December 1981 sample from the Cables company.

A 1 l sample of plant effluent for the February/March period, 1982, was obtained. This was filtered through a 0.45 μm filter, and the solid portion and the coprecipitate from the liquid portion were analysed by γ -ray spectrometry.

Sample Processing and Analyses

Sediment samples were dried and ground to provide a uniform matrix before being analysed. Water samples were acidified to prevent plating-out of any radionuclides present on container walls, and were filtered (0.45 μm membrane filter) to remove suspended solids with the exception of all town drinking water samples which were analysed without being filtered. A coprecipitation procedure was used to precipitate all radionuclides which were then analysed as a solid. Algae samples were weighed wet, dried, then ashed at 400 °C for 48 h. The crab samples were separated into edible flesh, gut (including all remaining organs and tissue) and shell portions. All portions were ashed at 400 °C for 48 h before being analysed. Mussel samples were separated into shell and flesh portions, the former being ashed and the latter freeze-dried before analysis. Barnacles from Wonnerup and ocean oysters from Busselton were treated similarly to the mussels

Iron Content of Sediment Samples. - The eleven sediment samples taken from the Leschenault Inlet (Table 1) were analysed for iron content by atomic absorption spectrophotometry. In each case 1 g of sample was digested in 25 cm^3 of conc. HNO_3 and 25 cm^3 of conc. HCl , and solutions were made up to 25 cm^3 before analysis.

Gamma-Ray Spectrometry. - All samples were analysed for radioactivity by high-resolution γ -ray spectrometry. The spectrometry system consists of a lithium-drifted germanium detector (Ortec model VIP10), the output of which is fed via a preamplifier, amplifier, and analog-to-digital converter (Nuclear Data ND 570) to a Nuclear Data model ND 6600 data acquisition, control, and processing computer. The spectrometer was calibrated by use of standard sources consisting of pitchblende and monazite (New Brunswick Laboratory) in silica matrices. The geometries of these standard sources were identical to those of the samples.

Activities were calculated from the areas of full-energy spectral peaks for γ -rays, corrected for background and continuum effects. All spectral peaks of statistical significance were considered. The estimated uncertainties in the activities, given in parentheses, refer to the least significant figure(s). These are expressed as estimated standard deviations of the mean. They were determined from counting statistics, or when statistically valid, from the scatter of individual estimates of the activity.

The two relevant radioactive decay chains for the radionuclides found in ilmenite are those of uranium (^{238}U) and thorium (^{232}Th). The principal long-lived members of these series are listed in Table 1.

Because all samples were sealed and allowed to equilibrate for at least two weeks before being measured by γ -ray spectrometry, all short-lived isotopes in the chains were in equilibrium with the longer-lived parent radionuclides. Hence γ -ray intensities from short-lived daughter isotopes were able to be used to calculate activities of the parent radionuclides.

RESULTS AND DISCUSSION

The Laporte Plant

The results of radioactivity measurements on ilmenite feed and plant effluent in the period October 1981 to March 1982 (Table 2) indicate that radioactivity levels in both the ilmenite feed and total effluent for this period were about half those levels found for the period August 1980 to May 1981 (Cooper, Statham and Williams, 1981). Possible reasons for this decrease in radioactivity levels are improvements in the methods of removal of radioactive monazite from the ilmenite by the relevant mining companies, or the mining of the ilmenite from different areas. If the latter was responsible, clearly a considerable variation in radioactivity levels entering and leaving the Laporte plant may be expected over a period of time.

TABLE 1

Principal long-lived radionuclides of the uranium and thorium series.

Radionuclide	Half life
<u>(a) Uranium Series</u>	
^{238}U	$4.5 \times 10^9 \text{ y}$
^{234}U	$2.5 \times 10^5 \text{ y}$
^{230}Th	$7.7 \times 10^4 \text{ y}$
^{226}Ra	1600 y
^{210}Pb	22.3 y
^{210}Po	138 d
<u>(b) Thorium Series</u>	
^{232}Th	$1.4 \times 10^{10} \text{ y}$
^{228}Ra	5.75 y
^{228}Th	1.91 y

TABLE 2

Activities in ilmenite feed (Bq/g) and liquid effluent
(Bq/l) at the Laporte Australia Limited plant

Sample	^{238}U	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th
Combined AMC ilmenite feed samples for periods ending 16/10/81 and 15/11/81	0.018(11)	0.065(1)	0.013(14)	0.270(3)	0.262(3)
Cables Co. ilmenite feed, December 1981	0.027(2)	0.084(1)	0.023(13)	0.154(3)	0.141(3)
Liquid portion of plant effluent, Feb./March 1982 ^a	0.18(11)	0.21(2)	ND ^b	0.25(5)	3.25(10)
Solid portion of plant effluent, Feb./March 1982 (Bq/l) ^a	0.39(4)	0.72(2)	0.3(3)	2.50(6)	0.66(2)

^a Radionuclide activities in the total effluent are the sums of those in the liquid and solid (2.05 g/l) portions: ^{238}U , 0.57(12); ^{226}Ra , 0.93(3); ^{228}Ra , 2.75(8); ^{228}Th , 3.91(10) Bq/l.

^b ND indicates that the activity was below the limit of detection.

By use of the same flow-rates of ilmenite feed (177.6 tonne/day) and total effluent (8500 m³/day) as used in the 1981 study, we are able to calculate the daily throughput of radioactivity at the Laporte plant. From the results in Table 2, we calculate an average daily intake of 37 MBq due to each of ²²⁸Ra and ²²⁸Th and 13 MBq due to ²²⁶Ra in the ilmenite feed. It is reasonable to assume that equilibrium exists between ²³²Th and its daughter radionuclides, ²²⁸Ra and ²²⁸Th, in the ilmenite feed. From the specific activity of ²³²Th (4 kBq/g), we calculate that there is an average of 0.052 g of ²³²Th present in each kg of ilmenite, which is equivalent to a mass of 9.2 kg of thorium entering the plant each day with the ilmenite feed. This is to be compared with a daily intake of 17.8 kg of thorium found in the 1981 study.

From the activities determined in the total effluent sample for February/March 1982 (Table 2), we calculate that 7.9, 23.4 and 33.2 MBq of activity due to ²²⁶Ra, ²²⁸Ra and ²²⁸Th respectively leaves the plant daily in the effluent. Having regard to expected daily variations, we conclude that essentially all of the thorium which enters the plant in the ilmenite feed passes via the total "liquid" effluent to the disposal ponds whereas some of the radium is left behind in the plant. Similar conclusions can be made from the results of the 1981 study, where it was found that radioactivity tended to accumulate in scale and sediment throughout the plant. At times, it was found that higher amounts of radioactivity were present in the total "liquid" effluent, correlating with increased levels of sediment in the effluent, possibly due to the cleaning of sediment from tanks at the plant. In particular, radium was preferentially deposited in scale at the Moore filter tanks (Cooper, Statham and Williams, 1981), and this may largely account for the lower levels of ²²⁸Ra compared with ²²⁸Th levels generally observed in the total "liquid" effluent in both the 1981 and the present studies.

In the previous study, it was established that in the presence of high sulphate ion concentrations and low pH in both the plant feed liquor and the effluent, thorium remains in solution whereas radium, which forms an insoluble sulphate compound, tends to coprecipitate and is found in solid residues throughout the process. The results presented in Table 2 for the liquid and solid portions of the total effluent, which show thorium preferentially in the liquid and radium preferentially in the solid portion, are in accord with this observation. An analogous situation exists in the milling of uranium ores (Ring, Levins and Gee, 1982).

Sediment Samples

Levels of radioactivity in sediment in Leschenault Inlet correlate fairly well with the proximity of the sampling site to the effluent disposal area (Table 3 and Figure 1). Relatively high levels of the radionuclides present in the Laporte effluent (^{238}U , ^{226}Ra , ^{228}Ra and ^{228}Th) are found in sediment along the pipeline from its centre to the point where it terminates at the shore of the disposal area, at sites 3 and 4 on the western shore of the Inlet adjacent to the disposal lagoons (close to where there is evidence for leakage of effluent from the lagoons into the Inlet), and at site 7 in the middle of the Inlet. At some sites in the Inlet, radioactivity levels are at background values (along the south-east section of the pipeline and along the eastern shore of the Inlet), while other sites show intermediate levels of radioactivity.

Liquid effluent from the Laporte plant contains relatively high concentrations of iron, a waste product in the process for converting raw ilmenite to titanium dioxide pigment. Therefore, it was considered worthwhile to determine the concentration of iron in sediment from the Leschenault Inlet, as any correlation between enhanced levels of both iron and radioactivity would provide additional evidence that the radioactivity originates from the plant effluent. The results given in Table 4 provide clear evidence for such a correlation. Sediments which have the highest radioactivity levels (from the pipeline centre, pipeline north-west, and sites 3, 4 and 7; Figure 1) also have the highest iron concentrations. The $^{228}\text{Ra}/\text{Fe}$ ratio for sediment samples from the Inlet also depicts this correlation, with the ratio being approximately constant throughout the sampling sites in the Inlet (the largest value of $^{228}\text{Ra}/\text{Fe}$ being only a factor of four times the smallest value) by comparison with the concentration of iron (where the largest value is 50 times the lowest concentration).

There is a considerable variation in the total radium (^{226}Ra and ^{228}Ra) content of sediment samples taken from other areas in the south-west region of Western Australia. Values for ^{226}Ra activity range from ca. 5 mBq/g in sediment from Geographe Bay (Busselton) and the Swan River to 40 mBq/g in organic sediment from the Peel Inlet at Mandurah. At these same locations the ^{228}Ra content varies from ca. 10 to 90 mBq/g. Even though there is evidence for the accumulation of radionuclides in the sediment of Leschenault Inlet due to both accidental spillage and leakage of effluent over a period of time, the radium levels of sediment from all of the sampling sites in the Inlet are within the range of concentrations measured at other places.

TABLE 3

Activities (mBq/g) in sediment samples^a (1982)

Sample site	²³⁸ U	²²⁶ Ra	²¹⁰ Pb	²²⁸ Ra	²²⁸ Th	⁴⁰ K
<u>Leschenault Inlet</u>						
pipeline south-east	3(2)	3.0(3)	ND ^b	5.7(7)	5.6(2)	268(5)
pipeline centre	28(6)	24.6(8)	42(8)	54.2(14)	53.7(6)	458(10)
pipeline north-west	57(6)	28.9(6)	40(7)	71.5(13)	67.3(6)	404(8)
site 1	31(6)	16.2(5)	25(7)	43.3(14)	44.4(5)	397(9)
site 2	7(4)	7.9(8)	6(5)	21.3(10)	19.8(4)	340(7)
site 3	59(6)	32.9(5)	42(7)	90.6(18)	91.1(7)	411(8)
site 4	43(5)	29.7(5)	17(7)	73.9(12)	71.5(6)	490(8)
site 5	40(5)	12.5(8)	20(7)	42.9(11)	39.4(5)	421(9)
site 6	ND	1.4(4)	ND	3.7(9)	3.8(3)	373(7)
site 7	71(7)	23.5(9)	38(11)	64.4(26)	63.0(9)	458(13)
site 8	10(5)	3.1(4)	28(8)	4.3(8)	5.8(3)	254(7)
<u>Busselton (Geographe Bay)</u>						
short jetty	13(6)	4.2(5)	19(12)	8.5(13)	10.0(5)	169(8)
<u>Wonnerup</u>						
beside old bridge	34(4)	18.6(5)	22(6)	33.9(15)	34.4(5)	252(7)
<u>Mandurah (Station 4, Peel Inlet)</u>						
organic sediment	61(8)	39.8(10)	31(11)	94.3(20)	96.7(9)	969(16)
sandy sediment	23(4)	13.8(6)	22(7)	31.9(11)	32.8(5)	613(10)
<u>Swan River</u>						
near Point Walter	8(4)	5.4(4)	6(8)	9.5(9)	10.3(4)	266(8)

^a Samples were ground and homogenised before being analysed in a standard 68 mm (diameter) x 12 mm geometry pack.

^b ND indicates that the activity was below the limit of detection.

TABLE 4

Concentration of iron (mg/g) in sediment samples from the
Leschenault Inlet^a (1982)

Sample site	Fe concentration	²²⁸ Ra:Fe ratio (mBq/mg)
pipeline south-east	3.0	1.9
pipeline centre	20.3	2.7
pipeline north-west	32.0	2.2
site 1	6.8	6.4
site 2	2.9	7.3
site 3	30.5	3.0
site 4	17.3	4.3
site 5	14.2	3.0
site 6	1.0	3.7
site 7	35.3	1.8
site 8	0.7	6.1

^a Samples were ground and homogenised before digestion in acid and analysis.

Under the conditions which exist in the Inlet it is quite likely that normal processes such as sedimentation and resuspension provide control over the levels of radionuclides. The radium content is also dependent upon the type of sediment. Highly organic sediment from the Peel Inlet at Mandurah has a radium concentration which is three times larger than sandy sediment from the same site.

Enhanced levels of thorium and uranium (and their daughter products) in the sediments of Leschenault Inlet can occur by two possible pathways, direct spillage of solid and liquid effluent and/or leakage of liquids from the effluent disposal area on the peninsula. The previous study (Cooper, Statham and Williams, 1981) showed that only thorium isotopes are likely to be transported by ground-water movement from the lagoon area into the estuary because of the high solubility of thorium in the liquid phase of the effluent.

There is little quantitative evidence which would support strongly one or other of the two pathways. However, the existence of equilibrium between ^{228}Ra and ^{228}Th in all sediment samples would suggest that either direct spillage of material is the principal source of radium in the sediments or that the transport processes involving thorium are extremely slow and are of the order of several years. Irrespective of the origin of the radioactivity, once soluble thorium from the effluent encounters the neutralizing conditions within the Inlet waters it will precipitate or become readily adsorbed on to sediments and suspended particulates. Thorium will become rapidly immobilized in the sediments of the Inlet with no tendency for further transport or biological uptake. Evidence from this study and other environmental studies of thorium suggest that this is the most likely fate for thorium isotopes.

Any chemical disruption of the equilibrium between the parent ^{232}Th and the first long-lived daughter ^{228}Ra (half-life 5.75 y) will be re-established within several years if there is no significant dissolution of ^{228}Ra . Two observations support the establishment and retention of an equilibrium between ^{232}Th and its daughters. Within experimental error the long-lived daughters of ^{232}Th , ^{228}Ra and ^{228}Th , are found to be in equilibrium in sediment samples and the distribution coefficient for radium between sediment and water is estimated to be very low which indicates low radium solubilities in the waters of the estuary.

In the case of ^{226}Ra and its parent ^{238}U the situation is that uranium, like thorium, will be soluble in the acidic effluent and mobile for some time in ground-water. However, the chemical disruption of the equilibrium situation between ^{238}U and ^{226}Ra which occurs in the plant process and in the liquid effluent will persist as equilibrium will not be re-established for millennia. It is quite likely that the ^{226}Ra which we observe in the sediments of the estuary is either a natural occurrence or has accumulated over a period of time as a result of direct spillage of effluent. Like ^{228}Ra , ^{226}Ra appears to be relatively immobile due to the unfavourable chemical composition of the estuarine water and the high organic content of the sediments in the Leschenault Inlet.

Radioactivity levels in sediment samples from Leschenault Inlet collected in 1983 after the major pipeline rupture of February 1983 (Table 5) are generally consistent with those from samples collected in 1982 (Table 3), allowing for small variations in exact sampling sites. No gross effects due to the pipeline rupture are in evidence; there is no dramatic increase in any activity from any site, although there is a general indication of a small enhancement of activity levels at sites close to where the rupture occurred (pipeline centre, site 2). Also sites very close to the position of the rupture (sites 9 and 10 which were not monitored in the 1982 survey) show relatively high levels of radioactivity.

Water Samples

The measurement of very low levels of radioactivity in water samples by gamma-ray spectrometry is only possible to relatively low precision, even when large (e.g. 8 l) samples are available for analysis. The present analyses of natural water samples from Leschenault Inlet and other sites in the Busselton to Perth area (Table 6) serve to indicate that there is no detectable contamination of the Inlet water with any of the radionuclides present in the Laporte plant effluent. This conclusion is not unexpected, considering the tidal nature of the Inlet, and the large dilution factors involved. From the data in Tables 3 and 6, we estimate the distribution coefficient for radium between sediment and water in the Inlet to be less than 10^{-3} g/cm^3 . This threshold value indicates a very low transfer of radium from sediment into solution in the waters of the Inlet.

TABLE 5

Activities (mBq/g) in sediment samples from Leschenault Inlet^a (1983)

Sample site	²³⁸ U	²²⁶ Ra	²¹⁰ Pb	²²⁸ Ra	²²⁸ Th	⁴⁰ K
pipeline south-east	25(12)	2(2)	22(14)	18(3)	18(1)	328(18)
pipeline centre	21(11)	27(1)	28(14)	73(4)	81(1)	407(17)
site 1	21(13)	24(2)	37(23)	46(3)	39(1)	769(33)
site 2	74(9)	31(2)	65(21)	81(4)	78(1)	418(20)
site 3	39(6)	27(1)	36(17)	75(7)	66(2)	481(21)
site 4	52(11)	21(1)	24(14)	54(2)	62(2)	471(17)
site 5	51(11)	13(1)	35(15)	48(4)	48(1)	405(13)
site 6	8(9)	4(1)	ND ^b	17(3)	17(1)	562(20)
site 7	18(13)	16(2)	46(19)	60(3)	51(2)	461(21)
site 8	17(10)	ND	23(16)	11(3)	6(1)	209(16)
site 9 ^c	43(13)	35(1)	35(16)	92(4)	89(1)	368(16)
site 10 ^c	48(13)	27(2)	43(17)	76(3)	70(2)	364(18)

^a Samples were ground and homogenised before being analysed in a standard 68 mm (diameter) x 12 mm geometry pack.

^b ND indicates that the activity was below the limit of detection.

^c Sites 9 and 10 were close to where effluent spilled into Leschenault Inlet in the pipeline rupture of February, 1983. Site 9 was at the shoreline between sites 2 and 3 (Figure 1), and site 10 was ca. 400 m out from site 9 in the Inlet.

TABLE 6

Activities (mBq/l) in water samples^a (1982)

Source	²²⁶ Ra	²²⁸ Ra	²²⁸ Th	⁴⁰ K
Leschenault Inlet, pipeline centre ^b	20(14)	ND ^c	ND	1407(102)
Leschenault Inlet, site 4 ^d	197(30)	ND	ND	1614(339)
Leschenault Inlet, site 6 ^e	ND	63(52)	ND	298(254)
Busselton jetty	29(7)	ND	ND	1619(98)
Wonnerup inlet, old bridge ^f	62(36)	ND	ND	584(337)
Peel Inlet, Mandurah ^g	ND	ND	ND	826(203)
Swan River	16(8)	38(18)	ND	1616(99)
Bunbury town drinking supply	14(3)	28(6)	6(2)	ND
Capel town drinking supply	22(2)	24(4)	ND	103(28)
Perth city drinking supply ^h	21(2)	29(5)	4(1)	ND

^a All water samples were filtered through a 0.45 µm filter paper before analysis, with the exception of the three drinking water samples which were analysed unfiltered. Activities were determined by γ-ray spectrometry on solid coprecipitates from the water samples. Unless otherwise indicated, 8.00 l of water samples was used for the analysis. ⁴⁰K values may be underestimated as the coprecipitation method will not necessarily remove all K from solution.

^b A sample of plankton plus water (0.68 l) from the pipeline centre vicinity of the Leschenault Estuary was analysed as the solid coprecipitate and gave ²²⁸Ra, 160(54) and ⁴⁰K, 8728(474) mBq/l. Both ²²⁶Ra and ²²⁸Th were undetected.

TABLE 6 CONTINUED

- c ND indicates that the activity was below the limit of detection.
- d 2.13 l sample.
- e 3.26 l sample.
- f 2.68 l sample.
- g Station 4, Peel Inlet; 3.15 l sample.
- h 10.00 l sample.

The analyses of drinking water samples from Perth, Bunbury and Capel will help to establish a baseline for the activities of the naturally-occurring radionuclides ^{226}Ra , ^{228}Ra and ^{228}Th in these domestic supplies. We note that, despite large standard deviations (uncertainties) in the measured activities (Table 6), it is clear that radium levels in all three drinking water supplies are significantly greater than thorium levels, and the natural $^{228}\text{Ra}/^{228}\text{Th}$ equilibrium does not hold.

Although the coprecipitation method used in the analysis of the water samples may not result in a complete ^{40}K determination, the results presented in Table 2 indicate the relatively large radioactivity levels due to naturally-occurring ^{40}K (of half-life 1.28×10^9 y) in natural waters with high salt contents.

Two samples of water from Leschenault Inlet, collected some months after the major pipeline rupture of February 1983, show no enhancement of activity levels due to the radionuclides ^{226}Ra , ^{228}Ra and ^{228}Th (Table 7).

Seafood Samples

Radioactivity measurements were performed on samples of algae, crabs and mussels (Tables 8-10) from Leschenault Inlet and other areas along the coast from Busselton to Perth. Both crabs and mussels, in season, from the Leschenault Inlet and elsewhere form part of the human diet.

The results presented in Table 8 provide evidence that thorium and, in particular, radium levels are enhanced in algae from certain sites in the Inlet, and also in algae from the Peel Inlet, Mandurah. The latter result correlates with the finding, discussed above, of enhanced levels of activity due to ^{226}Ra , ^{228}Ra and ^{228}Th in sediment from the Peel Inlet. We note that algae from some areas of Leschenault Inlet (in the vicinity of the pipeline) had levels of activity comparable with those found in algae from the Swan River, Perth, whereas enhanced levels of radioactivity were found in algae from other sites close to the effluent disposal lagoons (sites 3 and 4), and also at a site further into the Inlet (site 6) where radioactivity levels in sediment were found to be at background values.

Radioactivity levels in the flesh component of crabs from Leschenault Inlet, Busselton and the Swan River were all very low, and for crabs from Leschenault Inlet not significantly above zero, for the radionuclides ^{226}Ra ,

TABLE 7

Activities (mBq/l and mBq/g fresh weight respectively) in water samples^a and mussels^b from Leschenault Inlet (1983)

Sample	²²⁶ Ra	²²⁸ Ra	²²⁸ Th	⁴⁰ K
water, pipeline centre	ND ^c	11(13)	ND	521(69)
water, site 9 ^d	23(6)	17(11)	ND	442(72)
mussel flesh, pipeline	1.5(2)	3.6(5)	1.1(1)	35(2)

^a For both water samples, 5.00 l of water was filtered (0.45 µm filter paper), and activities were determined by γ-ray spectrometry on solid coprecipitates.

^b The flesh from a sample of 150 mussels was freeze-dried before analysis. The average fresh weight of flesh per mussel was 2.26 g.

^c ND indicates that the activity was below the limit of detection.

^d Site 9 was at the shoreline between sites 2 and 3 (Figure 1), close to where effluent spilled into Leschenault Inlet in the pipeline rupture of February, 1983.

TABLE 8

Activities (mBq/g) in dried algae samples^a (1982)

Sample site	²³⁸ U	²²⁶ Ra	²¹⁰ Pb	²²⁸ Ra	²²⁸ Th	⁴⁰ K
Leschenault Inlet, pipeline centre	25(6)	9(1)	5(1)	43(2)	23(1)	1039(21)
Leschenault Inlet, pipeline north-west	8(5)	8(1)	ND ^b	23(3)	15(1)	1251(19)
Leschenault Inlet, site 3	69(7)	29(1)	4(1)	119(3)	46(1)	508(18)
Leschenault Inlet, site 4	7(1)	21(1)	ND	116(3)	32(1)	1728(29)
Leschenault Inlet, site 6	22(4)	17(1)	ND	61(3)	26(1)	1973(25)
Mandurah, Peel Inlet (Station 4)	ND	17(2)	ND	80(6)	39(2)	2579(57)
Swan River	24(6)	14(1)	ND	44(2)	21(1)	981(20)

^a Samples were dried at 110 °C for ca. 24 h. The average ratio of wet to dry weights was 6.6. Samples were then ashed at 400 °C for four days and counted as the ash; activities presented here are given per g dry weight.

^b ND indicates that the activity was below the limit of detection.

TABLE 9

Activities (mBq/g fresh weight) in crab samples^a (1982)

Sample site	Type	Average fresh weight (g/crab)	²²⁶ Ra	²²⁸ Ra	²²⁸ Th	⁴⁰ K
Leschenault Inlet, pipe- line centre	Flesh	42.0	0.3(1)	0.2(1)	0.1(1)	105(1)
	Gut ^b	19.0	0.4(2)	1.2(3)	0.2(1)	89(3)
	Shell	70.3	1.2(2)	9.0(5)	2.2(2)	88(3)
Leschenault Inlet, site 4	Flesh	41.5	ND ^c	0.5(3)	ND	106(3)
	Gut	17.5	0.2(4)	4.0(3)	1.2(1)	72(2)
	Shell	73.6	1.3(3)	17.8(7)	4.0(2)	82(5)
Busselton, ocean	Flesh	35.7	ND	1.1(3)	1.4(1)	102(3)
	Gut	20.8	ND	0.9(5)	1.0(2)	76(4)
	Shell	81.6	0.8(4)	10.6(10)	4.4(4)	83(5)
Busselton, beach inlet	Flesh	8.2	1.9(5)	2.1(5)	1.7(2)	81(4)
	Gut	7.6	ND	ND	ND	109(8)
	Shell	19.7	ND	0.7(3)	ND	84(2)
Swan River	Flesh	107.5	ND	0.6(3)	ND	119(3)
	Gut	45.9	ND	0.7(5)	ND	79(3)
	Shell	179.2	1.3(1)	5.6(3)	1.5(1)	85(2)

^a Samples were ashed at 400 °C for ca. 24 h and activities were determined for the ash. The results are presented here as activities per g fresh weight.

^b Gut includes all organs and tissue other than edible flesh.

^c ND indicates that the activity was below the limit of detection.

TABLE 10

Activities (mBq/g fresh weight) in mussel samples^a (1982)

Sample site	Type	Average fresh weight (g/mussel)	²²⁶ Ra	²²⁸ Ra	²²⁸ Th	⁴⁰ K
Leschenault	Flesh	1.33	ND ^c	3.0(9)	ND	31(4)
Inlet, pipeline ^b	Shell	3.18	0.2(4)	3.3(5)	0.4(2)	4(3)
Leschenault	Flesh	1.74	ND	ND	ND	48(3)
Inlet, pipeline ^b	Shell	2.99	ND	1.9(7)	ND	13(4)
Mandurah,	Flesh	1.83	ND	ND	ND	40(4)
Peel Inlet	Shell	5.40	2.3(5)	4.5(8)	1.8(2)	9(4)
Swan River	Flesh	2.02	ND	ND	ND	64(4)
	Shell	3.16	0.7(3)	2.1(7)	0.6(3)	19(3)

^a Flesh samples were freeze-dried and shell samples were ashed at 400 °C before analysis.

^b Two batches, each of 100 mussels, were obtained from the same area and each was analysed individually.

^c ND indicates that the activity was below the limit of detection.

^{228}Ra and ^{228}Th (Table 9). However, naturally occurring ^{40}K was responsible for an activity level of ca. 100 mBq/g in all samples of crab flesh. Clearly, radium in particular is accumulated in the shells of crabs, and as found in the previous study (Cooper, Statham and Williams, 1981), the $^{228}\text{Ra}/^{228}\text{Th}$ ratio in the shells is ca. four.

Mussels from off the effluent pipeline in Leschenault Inlet, together with samples from Mandurah (Peel Inlet) and Perth (Swan River), were analysed for radioactivity levels in flesh and shell portions (Table 10). Apart from an activity of 3.0(9) mBq/g due to ^{228}Ra in one sample of mussel flesh from Leschenault Inlet, no radioactivity due to ^{226}Ra , ^{228}Ra and ^{228}Th was detected in any of the 1982 samples of mussel flesh. Low levels of activity due to all three radionuclides were detected in the samples of shells from mussels from most of the locations. In this regard, we note that radioactivity levels in the shells of mussels from Leschenault Inlet are not enhanced with respect to those in the shells of mussels from other sites (Table 10).

As with the samples of crab flesh, relatively high levels of radioactivity [average value 41(5) mBq/g] due to the naturally-occurring isotope ^{40}K were detected in mussel flesh.

A sample of mussel flesh collected from off the effluent pipeline in the Leschenault Inlet some months after the major pipeline rupture of February 1983 showed distinct, albeit relatively low, levels of activity due to the three radionuclides ^{226}Ra , ^{228}Ra and ^{228}Th (Table 7). The level of ^{228}Ra [3.6(5) mBq/l] was similar to that observed [3.0(9) mBq/l] in one sample of mussel flesh collected in 1982 (Table 10). It is reasonable to assume that radium is preferentially taken up by the mussels and incorporated in flesh and shell components, and that ^{228}Th is then formed within the mussel by ingrowth from its parent ^{228}Ra (Table 1). The results presented in Tables 7 and 10, where ^{228}Th levels of activity are consistently and significantly lower than ^{228}Ra activities in both flesh and shell components, are in agreement with this assumption. The rate of ingrowth of ^{228}Th activity will be ca. 2% of its equilibrium value per month, and hence significant over the normal lifespan of a mussel.

Whilst distinct, low levels of activity due to each of ^{226}Ra , ^{228}Ra and ^{228}Th are observed in the sample of mussel flesh obtained after the

pipeline rupture, it is not possible from our results to attribute any increase in levels of radioactivity in mussel flesh to that event. The levels observed (Tables 7, 10) are close to the limits of detection by the technique of gamma-ray spectrometry, and it may be that enhanced sensitivity in the measurements given in Table 7, perhaps due to the approximately 100% increase in sample size, is responsible for the observation of activity due to ^{226}Ra and ^{228}Th in the mussel flesh whereas none was detectable in the earlier samples. Other factors that may account for this difference are the age of the mussels (which may differ between samples), and the variation due to small changes in the position of sampling. It is worth noting that the mussels sampled in 1983 (Table 7) were considerably bigger (2.3 g flesh/mussel) than those sampled the previous year (Table 10, average 1.5 g flesh/mussel).

Of the radionuclides detected in the flesh of crabs and mussels, the two isotopes of radium are the most radiotoxic. From the largest concentrations of these two isotopes observed (Table 9), and by use of data published by the International Commission for Radiological Protection (ICRP, 1979), the estimated maximum effective dose-equivalent that would result from the consumption of 1 kg of crab flesh (ca. 25 medium-size crabs) is 1.5 μSv . For the flesh of mussels (Table 7), the estimated maximum effective dose-equivalent that would result from the consumption of 1 kg of flesh (ca. 500 good-size mussels) is 2.2 μSv . By comparison, the estimated annual effective dose-equivalent for these two isotopes of radium found in Perth drinking water (Table 6), based on a consumption rate of 2 l/day, is 14.4 μSv . To place these dose-equivalent values in perspective, we note the ICRP recommendation (ICRP, 1977) that the annual whole-body dose-equivalent to a critical group of the public should not exceed 5000 μSv .

CONCLUSIONS

The present study indicates a similar situation at the Laporte plant to that described previously (Cooper, Statham and Williams, 1981), with the exception that observed levels of radioactivity in the ilmenite feed and "liquid" effluent are approximately halved.

Radionuclides in sediment from Leschenault Inlet show a distribution pattern which indicates that enhanced levels of uranium and thorium and their daughter nuclides originate from the Laporte plant effluent. Despite this environmental perturbation, radioactivity levels in the sediment of the Inlet are no greater than those that occur at some other locations along the south-west coast of Western Australia.

Investigation of radioactivity levels in water, algae and seafood from the region indicates that the only significant transfer of radionuclides from the sediment is the bioaccumulation of radium in algae. However, this phenomenon is not limited to the Leschenault Inlet but occurs in other estuarine waters also.

In terms of the radiation exposure to members of the public who consume crab flesh or mussels from Leschenault Inlet, with levels of radioactivity similar to those determined in the present study, there is effectively no risk to health.

Measurements performed on samples of sediment, water and mussels from Leschenault Inlet collected some six months after a major rupture of the "liquid" effluent pipeline show no clear evidence for any significant enhancement of radioactivity levels as a result of the spillage of effluent directly into the Inlet.

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