

UPL Warehouse Fire - 2nd September 2021 Estuary and Marine Zone

ESTUARY AND BEACH: WATER AND SEDIMENT SAMPLING FOR PESTICIDES, METALS AND ECOLOGICAL TOXICITY

1. Background

A fire which occurred at the UPL Warehouse, 30 Umganu Road Cornubia on the 12th July 2021 resulted in a large amount of contaminated runoff. These pollutants/contaminants are understood to comprise a wide range of herbicides, fungicides, non-specific insecticides, as well as a range of specific target products including, but not limited to, miticides, nematicides, acaricides, rodenticides, and surfactants, fertilisers and a range of other fumigants and attractants. The detailed inventory of substances stored in the warehouse was provided to the environmental specialists on the 18th July 2021. This was critical in informing the more detailed analysis and investigations that were needed to clarify the impact of this unprecedented occurrence.

2. The Issue

As indicated above there was no precedent in the province or even the country for the fire and particularly the consequences thereof in terms of the mixture, fate of the variety of substances stored in the warehouse when exposed to fire and the associated high temperatures. Clearly some substances might be destroyed while others might be broken down or recombined into new compounds. In whatever form the stored materials existed before or after the fire it was rapidly realised that these biocidal substances, which were now being dispersed by air currents generated by the fire and particularly by the water used to extinguish the blaze constituted a major environmental threat to the natural biota as well as human health. The immediate and obvious effects were the blue discolouration of the estuary water as well as, although to a lesser degree, the immediate marine environment. The toxicity of compounds in

the estuary and inshore marine waters was also highly obvious in terms of the deaths of fish in the estuary and crayfish and mole crabs in the sea north of the estuary mouth.

In the absence at the time of information and understanding of the nature and broad potential of the toxins obviously present in the water, and the extent of their dispersal north and south of the estuary mouth, the possibility of human impacts over and above the obvious effect on aquatic animals had to be considered. Invoking of the precautionary principle was therefore behind the decision by the Department of Environment, Development and Tourism, eThekweni and the KwaDukuza Municipalities to close the beaches adjacent to the estuary. The original plume of contaminated water travelled north towards uMdloti but on the basis that north or south winds could disperse outflows from the river via the estuary in either direction the beaches north and south were closed.

Re-opening of the northern eThekweni and KwaDukuza beaches consequently became a major issue because of their social and economic significance. Such a decision would clearly require consideration of the nature of human beach use in terms of recreation and/or marine resource utilisation. The basis by which such a decision could be reached is described under the Terms of Reference (TOR) below. It should be noted that several activities referred to in the Terms of Reference have already been initiated, as described in the balance of this report. The bulleted points below therefore represent a summary of present and proposed future actions.

3. Terms of Reference (TOR)

Marine and Estuarine Research (MER) are ecological specialists with over 40 years' experience of KZN inshore marine environments and particularly estuaries and used this experience in compiling the following bullet points. The TOR for MER can be listed as follows:

- Assess the magnitude and extent of the effect of the chemical spill on the estuarine and inshore marine environments, from both an environmental and a biotic point of view, *i.e* including both plants and animals.

- Develop a suitable chemical and biological sampling programme which would, over time, allow an assessment of the long term effects of the toxins on the functioning and ecological health of the affected environments.
- Maintain a suitably adaptive monitoring system which could allow results to be used by toxicologists and specialist human health experts to inform decisions and policies regarding *inter alia*, human use of beaches, full recreational contact with seawater and use of marine resources such as fish, oysters, mussels and crayfish.
- It is anticipated that while short term effects on the fauna of the estuary and the local marine environment were essentially immediate, the effects on the vegetation are likely to be longer term and would require direct monitoring as well as an assessment of any cascading effects on higher trophic levels.
- It is not anticipated that any physical or biological attempts at remediation of the estuary and inshore marine environment will be undertaken. An initial survey of the benthic macro-invertebrates suggests a virtual annihilation of this component of the aquatic fauna of the estuary. This argues for a monitoring programme to assess the ability of the estuarine system to re-establish itself.

4. When was sampling conducted and other events of significance in relation to estuary and beach health and safety?

It is important to characterise what has already been done to date as this has informed the sampling strategy and investigation. A summarised timeline is included (Figure 1) to provide a snapshot of key events and MER's sampling and recommendations timeline. The steps are described in more detail in the bullet points 1 - 4 below.

Event & Sampling Timeline



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Figure 1: Key events and MER sampling timeline

Summary sampling programme to date

1. Site visit conducted on the 16th July 2021. Samples of water and sediment from the river above the estuary and from the estuary mouth area were sent to Talbot Laboratories on the 17th July 2021 for organic fingerprinting analysis. Fish and crayfish provided to MER by SAAMBR which had been collected on the 15th July were submitted to the same laboratory for tissue analysis.
2. This sampling was followed by a round of meetings of the team which at that time comprised Metamorphosis, Verdant, GroundTruth and the Geomeasure Group. Simultaneous planning and exploratory meetings with the authorities were convened under the Joint Operational Committee to clarify the contents of the warehouse and discuss the way forward with onward risk assessment and analysis.
3. Closure of the beaches by the authorities escalated the need for samples to assess the risk on the beaches of both water and sediments to the public. In response to this concern MER sampled at selected points on beaches between Salt Rock and the uMngeni estuary on the 28th and 29th July 2021, and again on the 17-18 August and 31st August 2021 after appropriate tests had been selected on the basis of the specific contents of the warehouse and identification of an appropriate laboratory had been identified that could quantify the substances of concern. MER was advised by Geomeasure Group that a combination of UIS (JHB) and Element (UK) were the best options and the full suite of river, groundwater, estuary and beach samples taken at the end of July 2021 were sent by Geomeasure to these two laboratories. Results for the beach and estuary samples were received on the 16 and 20 August 2021 from Element via the Geomeasure Group.
4. Subsequent to the above the need to sample bivalve (oysters and mussels) tissues for contamination resulted in MER contracting V&M analytical laboratories in George to conduct all the Marine and Estuary sample analyses, including the sediment and water samples taken on the 17-18 August (results received) and 31 August 2021 (in process).

uMhlanga Estuary:

Five sites were identified (Table 1; Figure2) and occupied during the initial survey and are anticipated to be utilised during any future surveys. Timing of access to these sites is dependent on mouth condition as boat access is not possible during shallow water open mouth periods. All sites will be sampled across the available cross-sectional area at the time (see map below). Water quality testing incorporated both standard *in-situ* physico-chemical measurements and estuary health (bacterial, nutrients) and specialised analytical testing for metals and pesticides/herbicides including techniques such as GC-MS, LC-MS and ICP-MS testing as well as a full suite of oils, and Volatile Organic Compounds.

uMhlanga Estuary Sampling Sites

Site Code	Site Name/area	Latitude	Longitude
UE1	mouth	29°42'19.51"S	31° 5'53.52"E
UE2	southern arm	29°42'29.77"S	31° 5'46.06"E
UE3	middle	29°42'1.36"S	31° 5'40.89"E
UE4	mid-upper	29°41'39.08"S	31° 5'31.23"E
UE5	upper	29°41'43.79"S	31° 4'41.37"E



Figure 2: Estuary sampling sites

Marine environments (beach, rocky-shore)

Sixteen beach sites were sampled on the 28-29 July and 17-18 August 2021. On the basis of the results received the number of sites (Table 2; Figure 3) and parameters assessed was reduced for the sampling undertaken on the 31 August 2021. Bivalve samples from intertidal and shallow subtidal reef sites have been taken at five sites; four north and one south of the uMhlanga estuary.

Beaches:

- Water and sediment quality testing followed the same protocol and procedures as for the estuary analyses. The above procedures are all chemical analyses and the results do not necessarily indicate biotic toxicity or tolerance levels. It could well be argued that the procedures do not give a complete picture of all substances present and also that the possibility of synergistic effects exist whereby combinations of the different compounds or their metabolites and break down products could in combination be more toxic than the individual compounds. This situation then argues for a biologically based test where the response to the overall aquatic environment is assessed. A response based on sea urchin fertilisation and embryo development is a standard technique used in marine assessments, providing a rapid indication of toxicity. The procedure is available at the CSIR laboratory in Durban, so turn around time is dependent on the actual testing (96 hours) and is not extended by transport delays.

Resource Use

- Tests on species used by recreational and commercial harvesters will be carried out by the same V&M laboratory conducting the beach water and sediment analyses. These tests assess metals of concern and pesticide/herbicide contamination. Results will be assessed ecologically by MER in collaboration with Dr Gerhard Verdoon (toxicologist) and for human health /safety by Prof Mary Gulumian (APEX Team),

Table 2: Marine sampling sites - beaches (water and sediment at each)

Marine

Site Code	Site Name/area	Latitude	Longitude
Beaches north of uMhlanga estuary to Shaka's Rock			
B1N	500 m north of mouth - Peace Cottage	29°42'4.27"S	31° 6'7.85"E
B2N	1km north of mouth - Peace Cottage	29°41'50.67"S	31° 6'17.76"E
B3N	2 km north of mouth	29°41'20.06"S	31° 6'32.27"E
B4N	4 km north of mouth - 1st Ave parking lot	29°40'20.74"S	31° 7'2.10"E
B5N	6 km north of mouth - end north beach road uMdloti	29°39'16.26"S	31° 7'36.80"E
B6N	10 km north of mouth - La Mercy access opposite Valley road	29°37'25.57"S	31° 8'56.23"E
B7N	15 km north of mouth - Westbrook	29°35'33.25"S	31°10'15.79"E
B8N	20 km north of mouth - Zimbali main beach	29°33'12.02"S	31°12'18.70"E
B9N	25 km north of mouth - Shad Ln access point	29°31'18.36"S	31°13'40.45"E
Beaches south of uMhlanga estuary to uMgeni estuary			
B1S	500 m south of mouth - boardwalk/UNR	29°42'33.30"S	31° 5'50.11"E
B2S	1 km south of mouth - Breakers Boundary	29°42'48.89"S	31° 5'41.64"E
B3S	2 km south of mouth - Bronze Beach	29°43'4.56"S	31° 5'33.44"E
B4S	3 km south of mouth - Umhlanga Pier/lighthouse	29°43'34.57"S	31° 5'20.87"E
B5S	4 km south of mouth - Eastmoor access point	29°44'36.10"S	31° 4'48.49"E
B6S	8 km south of mouth - Southern end Virginia airport	29°46'26.13"S	31° 3'29.38"E
B7S	12 km south of mouth - Beachwood Mangrove NR	29°48'24.02"S	31° 2'34.00"E
Rocky Shore habitats			
RS1N	Peace Cottage		
RS2N	South uMdloti		
RS3N	Tidal pool complex uMdloti		
RS4N	last rocks before estuary		
RS1S	Umhlanga Lighthouse		

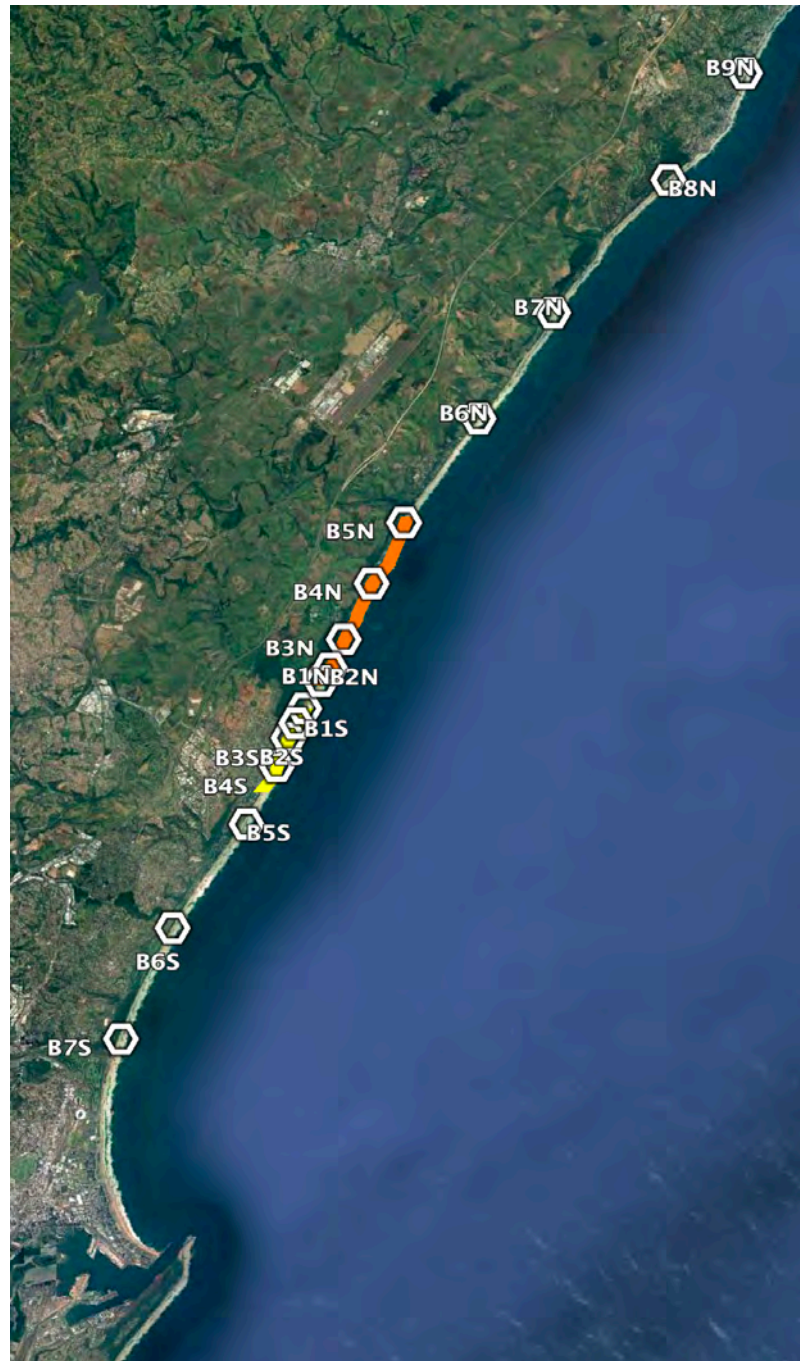


Figure 3: Beach sampling sites stretching from Salt Rock in the north to the uMngeni Estuary in the south.

RESULTS OF BEACH AND ESTUARY WATER AND SEDIMENT SAMPLING ONLY

This short report is focussed on the sampling which informs beach and estuary ecological health and underpins human health decisions.

Organic fingerprinting by GC-MS - preliminary sample to identify compounds present.

Samples were taken in the lower estuary (water and sediment), the contaminated tributary before the confluence with the Ohlanga River, and animal material (crayfish and fish) from the beach mortalities. These were sent to the Talbot Laboratory in Pietermaritzburg for an organic fingerprinting scan using GC-MS. GC-MS is a sensitive, reliable, and recommended technique for identifying unknown organic compounds. Samples are scanned down to levels of 0.1 ppb ($\mu\text{g}/\ell$) against the National Institute of Standards and Technology (NIST) spectral library of reference compounds, including pesticides, volatile organic compounds, petroleum hydrocarbons and micropollutants. It was possible for Talbot to only screen for a total of 70-80 compounds out of the total list of products in the warehouse. Only compounds that returned percentage match returns of greater than 80% are reported in the attached certificates (see Appendix A). The samples were analysed using a GC-MS coupled to an RTC PAL sampler System together with laboratory blanks for comparison purposes. A Solid Phase Micro Extraction, Liquid-Liquid Extraction and purge and trap technique was used.

Summary of certified results (Appendix A):

Tributary/Stream and Estuary Water:

- A variety of substances, 22 in the tributary and 14 in the estuary water, were identified by the scan, including herbicides, insecticides and fungicides.
- Metabolites of adjuvants, solvents and pesticides were identified but given the likelihood of compound breakdown it is impossible to link every metabolite to a specific compound that was in the UPL-Ltd warehouse;

- All the samples registered dimethylsulfide, phosphorodithioate insecticides such as Terbufos and Dimethoate which produce dimethylsulfide during combustion.
- Arsenic was detected as a silylated substance due to the large volume of silicon-based adjuvants in the warehouse (Verdoorn 2021a). This would have reacted with the MSMA or methylarsonic acid (MAA) which is the free acid of MAA.
- The data presented are not quantified at all hence it is impossible to express any statements about risk although Eptam and Trifluralin are indicated as large spikes.
- All of these substances originated from the Cornubia warehouse (Verdoorn 2021a)

Animal samples - crayfish and fish

- Unsurprisingly a lower incidence of substances from the warehouse was present in the crayfish and fish tissues, although herbicides, insecticides and fungicides were all detected by the analysis.
- All of the substances which were detected are deemed to have originated from the Cornubia warehouse (Verdoorn 2021a)

Quantitative pesticide results using LC-MS for both estuary and beach water and sediment.

Two sets of quantitative pesticide results, namely 28-29 July and 17-18 August 2021 are reported and interpreted in this report. The certificates for these results are contained in Appendix B (Element) and Appendix C (V&M).

The beach water and sediment samples taken on the 28-29 July indicated that the only pesticides at any concentration of interest were Atrazine, Diuron and Chlorpyrifos. These pesticides along with others which may be below the detectable limits, would have reached the beaches via the estuary and would have undergone significant dilution. These levels may still have an effect on plants and aquatic animals, particularly Diuron and Chlorpyrifos, but in terms of human health, according to

Verdoorn (2021b), are not considered to have posed a risk as concentrations are well below the Acceptable Daily Intake (ADI) for each of these substances. It was predicted that the concentrations of the pesticides already noted would be declining by the next sampling event following normal degradation and dissipation.

Beach sediments, sea water, estuarine sediments and estuarine water were collected on 17 and 18 August 2021 and were received by V&M Analytical Toxicological Laboratories (Pty) Ltd (V&M ATLS) on 20 August 2021 for broad spectrum pesticide trace analysis. The beach sediments and sea water samples were collected from the same sites as the 28-29 July 2021. A previous assessment by Verdoorn (2021b) assessed the risk for people using the beaches for recreation and surfing as negligible from the perspective of pesticide toxicity. The results from this later sampling exercise confirm this assessment with only four pesticides detected at trace or quantifiable levels. These were two systemic herbicides, Tebuthiuron and Picloram, a selective chloroacetamide herbicide, Metalochlor and a systemic neonicotinoid insecticide, Acetamiprid. The Tebuthiuron was present at levels that will affect ecological functioning acting at a base trophic plant level but with a lower risk to crustaceans and a slightly lower risk to birds within the estuary. Picloram and Metalochlor were also present at levels which will be having a toxic effect on aquatic organisms but very low concentrations in terms of risk to humans (Verdoorn 2021c)

Quantitative water and sediment results for metals

The focus of this report is to provide the results and assessment of compounds of concern in terms of toxicity and human safety. As such the metal of concern included here is arsenic which is one of a suite being sample. Other compounds such as manganese, zinc, will be discussed . Verdoorn (2021c) provided a comprehensive review of the Monosodium Methanearsonate (MSMA), which is an organic arsenical broad spectrum herbicide. This is reflected as arsenic in analytical data but reverse calculated to MSMA quantities for the beaches and sea water. The 28-29 July results and analysis indicated in Verdoorn's (2021c) opinion that the MSMA at this date of sampling posed no acute risk to people and most probably no chronic risk to people either (my personal opinion). If the MSMA is reduced to elemental arsenic, chronic exposure to a daily intake of between 0.05 and 0.5 mg/kg body mass may result in

serious health effects such as liver cancer. The conditions during the fire and in the environment into which MSMA was deposited are not conducive to total reduction of MSMA to elemental arsenic. The significant difference in sediment and sea water concentration of the MSMA indicates very strongly that MSMA is still intact and has not reduced to elemental arsenic. It is noted that upstream of the estuary and beaches the levels of MSMA in the water courses close to the site are in concentrations ranging from 2.45 mg/kg to 443 mg/kg that are of significant and environmental and human health concern.

The recent results received showed a significant decrease in the concentrations of elemental arsenic reported by V&M (Appendix C) when contrasted with the previous survey. Both beach water and sediments have been assessed by Verdoorn 2021d to be at levels which pose "no acute or chronic human health concern".

Toxicity results

Toxicity tests were run for the beaches immediately north and south of the estuary by CSIR for MER. These are valuable indicators of the remaining mix of chemicals which may still be affecting ecological health but are not at detectable levels. The samples were tested using the sea urchin fertilization and embryo-larval test, which are acute and chronic toxicity testing procedures respectively. Water samples were tested as received apart from salinity adjustment on samples that had a salinity <34. Sediment was tested as an elutriate after mixing one part sediment and two parts water. The results of this indicated that the estuary remains a highly toxic environment and the one beach to the south of the estuary is considered to be marginally toxic (Table 3).

Table 3: Results of toxicity testing using sea-urchin embryo-larval test

SUBSTRATE	TREATMENT	SAMPLE ID	TOXICITY	Toxicity Category/Comments
Water	Raw	UE1	HIGHLY TOXIC	Malformed blastula
Water	Raw	UE5	HIGHLY TOXIC	Fertilised eggs died
Water	Raw	B1S	Marginally toxic	Development arrested at prism
Water	Raw	B2S	Marginally toxic	Development arrested at prism
Water	Raw	B2N	Not toxic	
Sediment	Elutriate (1:2)	UE1	HIGHLY TOXIC	Dev arrested at 16 cell
Sediment	Elutriate (1:3)	UE5	HIGHLY TOXIC	Development arrested at 4 cell
Sediment	Elutriate (1:2)	B1S	HIGHLY TOXIC	Eggs died
Sediment	Elutriate (1:2)	B2S	Marginally toxic	Development arrested at prism
Sediment	Elutriate (1:2)	B2N	Not toxic	

Discussion and Recommendations

The general observations of fish and invertebrate mortalities in the estuary and the inshore marine environment as well as the deaths of riparian and wetland vegetation are all testimony to the toxic nature of the estuary environment which have now been unequivocally attributed to the UPL warehouse contents. The results detailed in the previous section indicate that the levels of pesticides and arsenic have declined between the July and August sampling events. At this point the beaches appear to be largely risk free as regards human contact with the beach sand or the sea based on the toxicological assessment by Dr Gerhard Verdoorn. The caveat however is that proximity to the uMhlanga estuary increases any remaining risk and a suitable exclusion zone has been recommended to take account of estuary breaching and flooding events. While contaminated sediments downstream of the discharge points from the factory are being removed, the potential for mobilisation of contaminated water and sediments during heavy rain between the site and the mouth is very real and such pulses from the river and estuary into the inshore marine environment should be anticipated. Both the exclusion zone and sampling regime need to incorporate an adaptive management approach to take account of these factors.

Beach exclusion zone

The clear toxicity of the estuary and the upstream potential for contamination with rains and flooding requires that an exclusion zone is set up for at least the next six months (September - January 2022) which includes the estuary and the beaches for 1km north and south of the mouth. This is mapped in Figure 4.



Figure 4: Beach barriers (red) to prevent access to the exclusion zone placed at 1km north and 1km south of the mouth.

Marine Resources and harvesting for commercial or recreational use and human consumption

Samples have been collected to assess the bivalves on the rocky shores for accumulated toxins. These reached the laboratory today (3 September 2020). Until these test results are received (anticipated 17 September), it is recommended that the embargo on harvesting of marine resources including seawater, sediment, fish, oysters and mussels should remain in place.

N.T. Forbes
Nicolette Forbes
3/9/2021

Anthony Forbes
Prof Anthony Forbes
3/9/2021

References used to support the findings of this report.

Verdoorn G.H. 2021a Interpretation and Comments of Talbot Analytical Results. 18 August 2021.

Verdoorn G.H. 2021b Report: Review of Analytical Results From Elements Laboratories Of Analyses Conducted on Sediments and Water (Marine and Fresh Water) Collected on 28 July 2021 - Griffon Poison Information Centre Report dated 24 August 2021

Verdoorn G.H. 2021c Interpretation of Acute and Chronic Toxicity of Pesticides for Beaches and Sea Water: Focus on MSMA. Excel analysis and report compiled 24 August 2021.

Verdoorn G.H. 2021d Recommendation on Opening of Beaches around the uMhlanga Estuary: Review of Analytical Results From V&M Analytical Toxicological Laboratory Services (Pty) Ltd as Reflected in Report No. 210902 Vm24719 Dated 2 September 2021

APPENDIX A - ORGANIC FINGERPRINTING RESULTS (TALBOT).

Certified file from Talbot attached as 004944_21.pdf

TALBOT ▾

A Level 2 B-BBEE company

[004944/21], [2021/07/30]

Certificate of Analysis

Project details

Customer Details

Customer reference:	POLLUTION INCIDENT TESTING, UMHLANGA CONTAMINATION
Quotation number:	Q2107-100 A
Company name:	MARINE AND ESTUARINE RESEARCH (MER)
Contact address:	P O BOX 417, HYPER BY THE SEA, DURBAN
Contact person:	NICOLETTE FORBES

Sampling Details

Sampled by:	CUSTOMER
Sampled date:	2021/07/16

Sample Details

Sample type(s):	SEDIMENTS SAMPLES, SOLID SAMPLES, WASTE WATER SAMPLES
Date received:	2021/07/20
Delivered by:	CUSTOMER - GILLITTS DEPOT
Sample condition:	COMPOSITE SAMPLE MADE, INCORRECT BOTTLE TYPE
Additional customer information:	HAZARDOUS
Temperature at sample receipt (°C):	13.9
Deviations:	W01061/21 - W01067/21 - Inappropriate bottle type submitted for organics/Oil & Grease

Report Details

Testing commenced:	2021/07/20
Testing completed:	2021/07/30
Report date:	2021/07/30
Our reference:	004944/21

APPENDIX B - PESTICIDE AND METAL RESULTS (ELEMENT).

Certified certificates from Element pertaining to 28-29 July sampling is attached as Element Certificates.pdf

APPENDIX C - PESTICIDE AND METAL RESULTS (V&M)).

Results from V&M Analytical Laboratories from the 17-18 September 2021 sampling event attached as [210902 VM24719 m.pdf](#) and [210902 VM24719.pdf](#)