Environmental Impact Assessment Report
Volume 3, Appendix 7.3: Environmental Intertidal Survey-Contaminants Report

MarramWind Offshore Wind Farm

December 2025

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MarramWind Ltd.

MarramWind Intertidal Contaminants Report

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2.0	10/10/2023	All	All	Client Comments Addressed as per Comments Log	LMB

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Executive Summary

MarramWind is a floating Offshore Wind Farm (OWF) being developed by MarramWind Limited, a company wholly owned by ScottishPower Renewables UK Limited (SPR). MarramWind OWF will be located to the north-east of Scotland about 100km off Fraserburgh. The location of this OWF is ultimately determined by the Option Area Agreement (OAA) which is the spatial boundary of the NE7 Plan Option in which the electricity generating infrastructure will be located.

The planned export cable route extends south-west towards the coast and splits into three cable route landfall zone options: D (Scotstown Beach), E (Lunderton Beach) and F (Sandford Bay). APEM was commissioned to undertake a survey of intertidal habitats and biological communities in the vicinity of each of the three landfall zones.

This report summarises the findings of the sampling for contaminants in each of the three export cable route landfall zone options of the MarramWind development. Results of the associated macrobenthic core and particle size samples are available in a separate report (APEM, 2023).

The area was surveyed between 16th and 19th July 2023. In each landfall zone transects were established at 500 m intervals along the beach (4 transects in Landfall D and E and 3 at Landfall F). Each transect had three sampling stations: one each at upper-, mid- and lower-shore. One contaminant sample was collected from each transect at the corresponding mid-shore station. At two of the Landfall F transects, coarse sediments prevented collection of contaminant samples. An additional sample at a nearby location was taken.

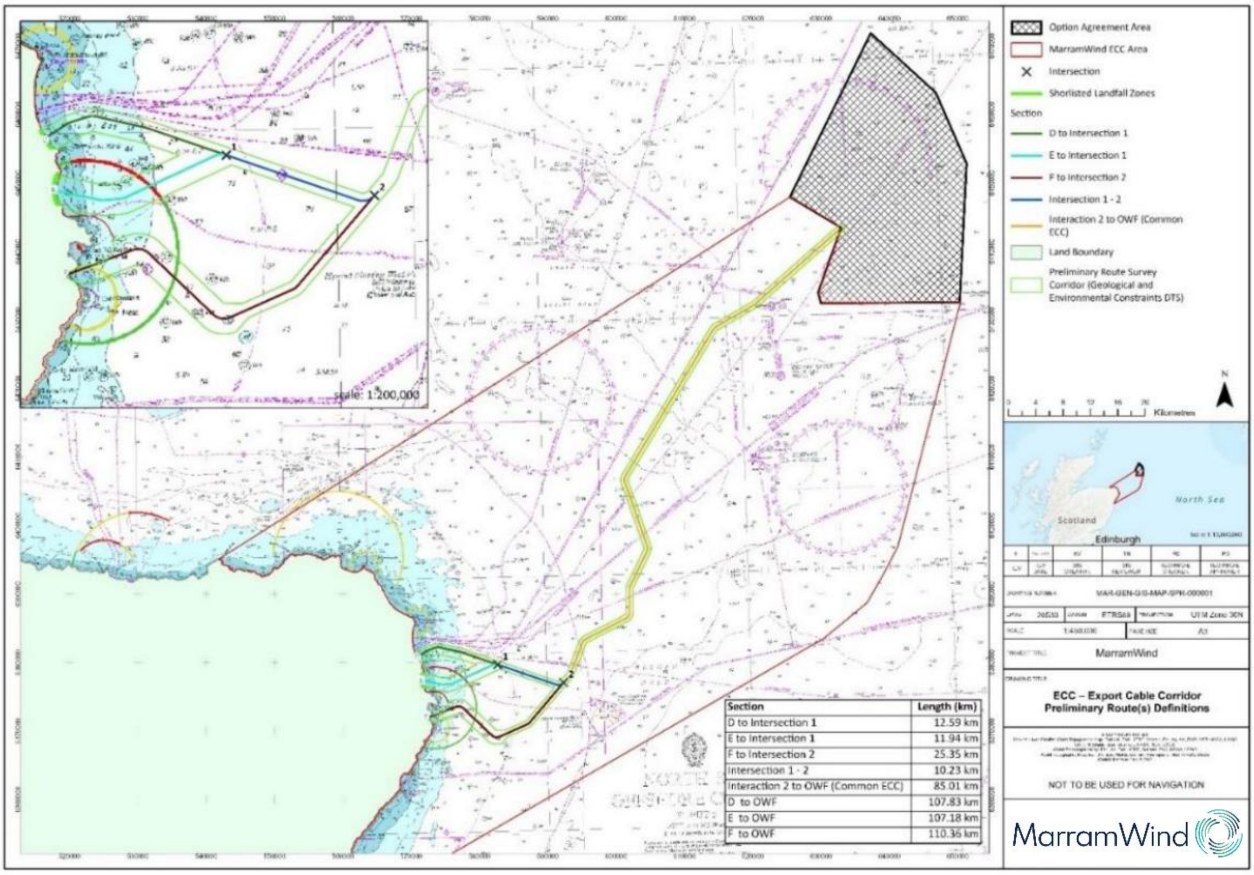
The chemical analyses of the sediment showed that most concentrations were below the Background Concentration (BC), the concentration that it should naturally occur in undisturbed environment. The only exception was observed for Arsenic concentrations. Arsenic was found in concentrations above the Threshold Effects Level (TEL), the maximum concentration at which no effects are observed, but largely below the Probable Effects Level (PEL), the lower limit of the range of concentrations at which adverse effects are always observed. The TEL for Arsenic is lower than the BC, meaning that natural occurring levels are likely to have an effect on organisms.

1. Introduction

APEM was commissioned by MarramWind Limited, a company wholly owned by ScottishPower Renewables UK Limited (SPR), to design and undertake a survey of intertidal habitats and biological communities in the vicinity of three MarramWind Export Cable Corridor landfall locations.

The offshore wind farm area is situated about 100 km off Fraserburgh, north-east Scotland (Figure 1). The offshore area was surveyed in 2022, including geophysical, environment and shallow geotechnical surveys. The planned cable route extends south-west from the wind farm area towards the coast and shallow geotechnical survey works along the route are to be finished before the end of 2023.

The cable route splits into three potential export route options about 30 km before landfall. Intertidal surveys were required at the landfall of each of the three options. The three potential landfall zones currently being considered have been designated as options, D (Scotstown Beach), E (Lunderton Beach) and F (Sandford Bay).



Section	Length (km)
D to Intersection 1	12.59 km
E to Intersection 1	11.94 km
F to Intersection 2	25.35 km
Intersection 1 - 2	10.23 km
Interaction 2 to OWF (Common ECC)	85.01 km
D to OWF	107.83 km
E to OWF	107.18 km
F to OWF	110.36 km

Figure 1. Map showing location of the Marram Wind proposed wind farm area and possible cable routes (image from the scope of work provided with the tender invitation)

1.1 Survey Objectives

The objective of the work commissioned was to design and undertake surveys to obtain baseline ecological conditions for EIA purposes. The following approaches were used:

- Macrobiota surveys (biotope maps, core samples and quadrats);
- Particle size analysis (PSA);
- Contaminant analysis.

This report presents the methodologies adopted by APEM for the survey and analyses data, and the results of the contaminants samples.

2. Methodology

2.1 Survey Permissions

Some consents or notifications were required prior to the survey. These included, but were not limited to:

- Notice of intention to carry out an Exempted Activity
- Crown Estate (General Marine Works License or equivalent)
- Other voluntary or statutory notifications

As per the information in the Scope of Work provided, APEM assumed that any necessary permissions and notifications were made by SPRUK. APEM supported this process by providing timely responses to any requests for information.

2.2 Survey Timings

Landfall D was surveyed on 18th July 2023, Landfall E was surveyed on 17th July 2023 and Landfall F was surveyed on 16th and 19th July 2023.

Table 1 (below) shows tidal information for each survey day and location.

Table 1 Tidal information for the landfall zones on the survey dates

Location	Landfall F	Landfall E	Landfall D	Landfall F
Date	Sun 16th July 2023	Mon 17th July 2023	Tue 18th July 2023	Wed 19th July 2023
Hight tide	12:49	01:12	01:50	02:34
Height	3.4 m	3.47 m	3.53 m	3.74 m
Low tide	06:41	07:25	08:03	08:43
Height	1.00 m	1.1 m	1.03 m	0.89 m
High tide	13:13	13:42	14:21	15:07
Height	3.4 m	3.37 m	3.4 m	3.54 m
Low tide	18:59	19:34	20:08	20:48
Height	1.1 m	1.29 m	1.26 m	1.24 m
Sunrise	04:33	04:35	04:37	04:39
Sunset	21:51	21:49	21:48	21:46
Daylight length	17:18 hours	17:13 hours	17:10 hours	17:07 hours

2.3 Health and Safety

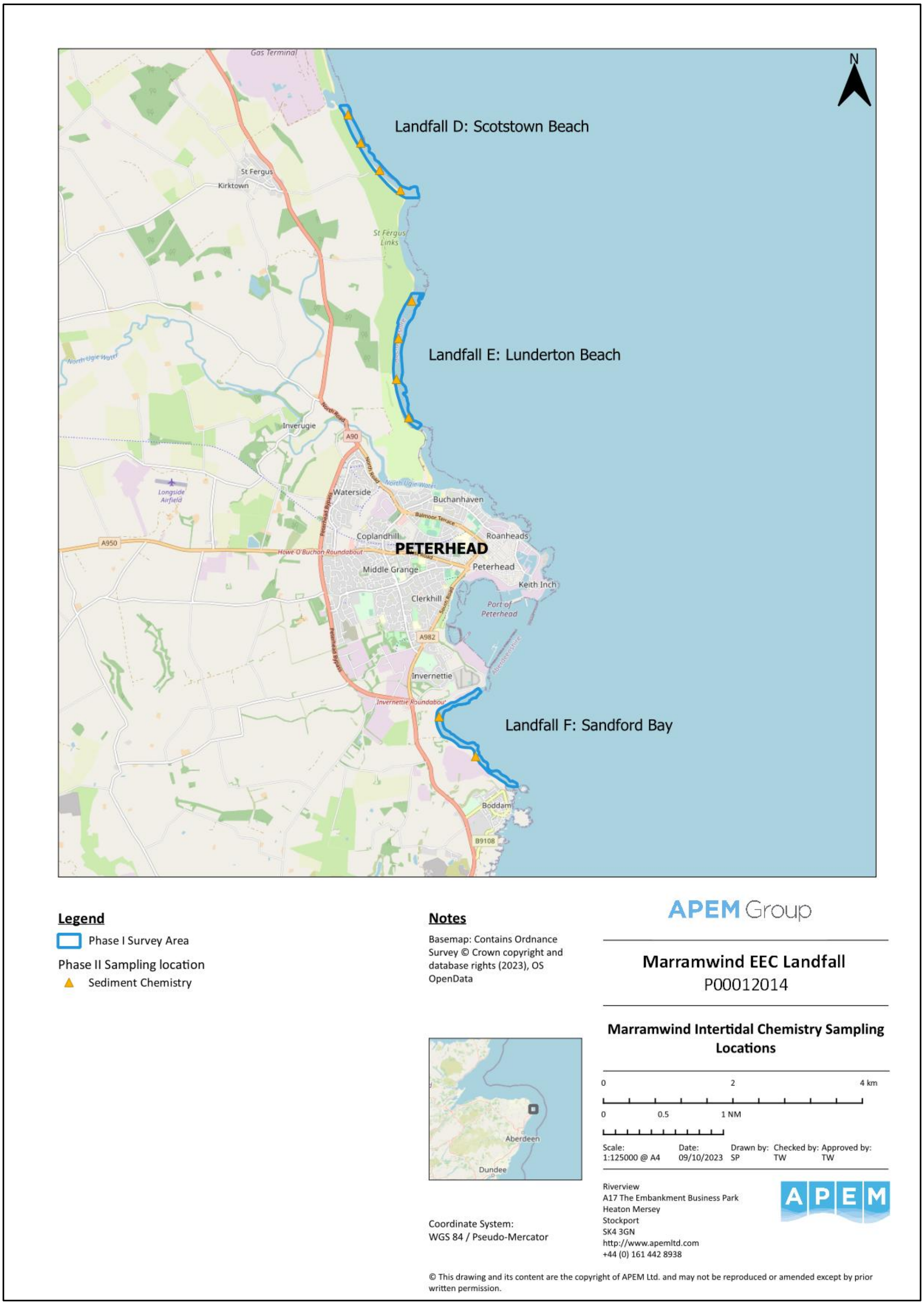
A Risk Assessment was carried out prior to the survey work. In addition, daily dynamic risk assessments were completed by the lead surveyor (Georgina Brackenreed-Johnston) to address any site-specific issues.

Primary health and safety concerns were becoming trapped by incoming tides and exposure risks. All staff wore appropriate Personal Protective Equipment (PPE) for survey work, including life jackets and waterproofs, to minimise exposure risks; the team carried a field first aid kit and throw rope.

All staff were provided with emergency contact numbers, the entry and exit points to the beach, tidal information for the survey areas and the times of sunrise and sunset for each day; these were carried at all times. Check-in and out calls were made to office-based staff at previously agreed times, coinciding with expected times on and off shore.

2.4 Survey Design

Intertidal surveys were completed at each of the three proposed cable landfall zones, to include both hard and soft substrata. Any designated features of nearby Marine Protected Areas (MPAs) or other designated sites were noted. The surveys comprised Phase I habitat mapping, together with quantitative Phase II, core or quadrat sampling, at representative habitats for macrobenthic communities, Particle Size analysis (PSA) and contaminants samples. Transects were surveyed at 500 m intervals across each landfall zone (Figure 2). Landfall zones D and E were each 2 km long, so included four vertical transects. Landfall F was approximately 1.16 km long and included three vertical transects. Macrofaunal and particle size samples were collected at the upper, lower, and mid shore. Contaminant samples were collected at the mid shore location.



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Coordinate System: WGS 84 / Pseudo-Mercator

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Figure 2. Map showing Phase I survey area and Phase II location of sediment chemistry stations.

Details of each of the three Phase I survey areas and the Phase II contaminant samples collected and recorded from each landfall zone are shown in Figures 3, 4 and 5, for Landfall zones D, E and F, respectively. Details of sampling positions and dates that contaminant samples were collected are presented in Table 2, below. Sampling stations were named D, E and F, to represent each landfall zone, followed by 1, 2, 3 or 4, to represent transect numbers. Biological and PSA samples were followed by U, M or L, for upper, mid, or lower shore, all contaminant samples were taken at the corresponding mid shore location.

At Landfall F it was not possible to collect contaminant samples from stations F2 and F3 due to the presence of large boulders; however, an additional sample was collected at a nearby location, named WP35, where unusual sediment was noted. Location details of this site can be found in Table 2 and Figure 5.

Table 2. Details of sampling positions and dates.

Zone	Station Number	Contaminant Sample collected	Date collected	Latitude	Longitude
Landfall D	D1	Y	18/07/2023	57.567722	-1.818901
	D2	Y	18/07/2023	57.563825	-1.815636
	D3	Y	18/07/2023	57.560052	-1.810770
	D4	Y	18/07/2023	57.557278	-1.805426
Landfall E	E1	Y	17/07/2023	57.541991	-1.802523
	E2	Y	17/07/2023	57.536813	-1.805923
	E3	Y	17/07/2023	57.531152	-1.806424
	E4	Y	17/07/2023	57.525854	-1.803312
Landfall F	F1	Y	19/07/2023	57.484435	-1.795471
	F2	N	16/07/2023	57.481272	-1.791290
	F3	N	16/07/2023	57.478491	-1.784724
	WP35	Y	19/07/2023	57.478950	-1.786065

Figure 3. Map showing contaminant sample locations at Landfall D.

Legend

▭ Phase I Survey Area

Phase II Sampling location

▲ Core, PSA & Chemistry

Notes

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APEM Group

Marramwind EEC Landfall
P00012014

Landfall E: Lunderton Beach Intertidal Chemistry Sampling Locations

Scale:	Date:	Drawn by:	Checked by:	Approved by:
1:22500 @ A4	09/10/2023	SP	LMB	LMB

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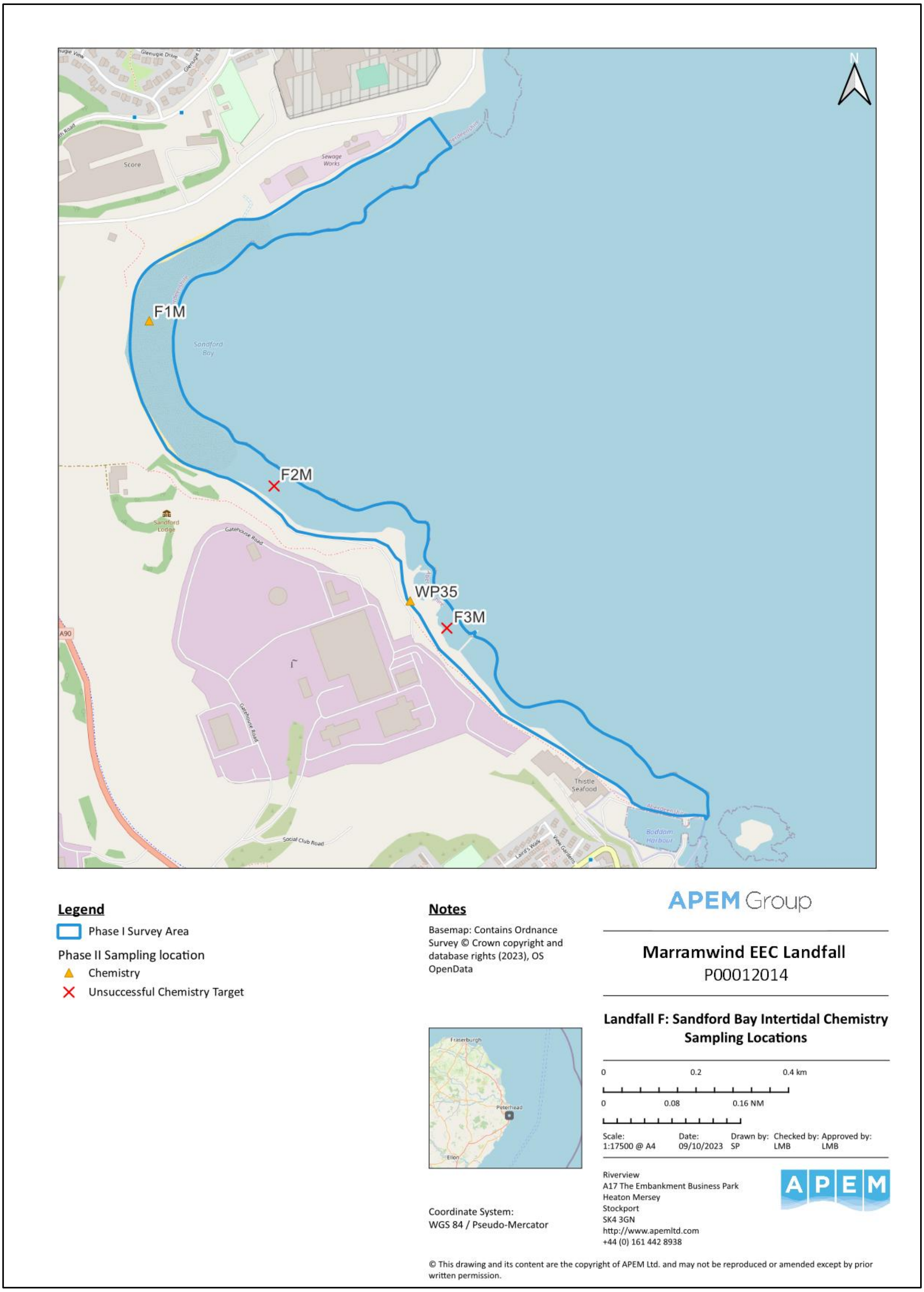
Figure 4. Map showing the location of the contaminant samples at Landfall E.



Legend

▢ Phase I Survey Area

Phase II Sampling location

▲ Chemistry

✕ Unsuccessful Chemistry Target

Notes

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Coordinate System:
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APEM Group

Marramwind EEC Landfall
P00012014

Landfall F: Sandford Bay Intertidal Chemistry Sampling Locations

Scale:	Date:	Drawn by:	Checked by:	Approved by:
1:17500 @ A4	09/10/2023	SP	LMB	LMB

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Figure 5. Map showing the location of the contaminant samples at Landfall F.

2.4.1 Sediment sampling

At the mid shore location on each transect, samples were collected for contaminants analysis of:

- Heavy Metals (Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Zn).
- Polycyclic Aromatic Hydrocarbons (PAHs).
- Polychlorinated Biphenyls (PCBs).
- Total Organic Carbon (TOC).
- Total Petroleum Hydrocarbons (TPH).
- Organotins (Tributyltin (TBT) and Dibutyltin (DBT)).

For chemical analyses samples were obtained from surface sediments, to a depth of approx. 5 cm. For metals analysis, 500 ml of sediment was collected, whilst for organics analysis 200 ml (2x100 ml) was collected. To avoid contamination, metals samples were obtained using a plastic scoop and placed in a plastic pot, whilst samples for organics analysis (e.g. Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs)) were obtained using a metal scoop and placed in amber glass jars. All sample containers were appropriately labelled, sterile containers provided by the processing laboratory. The chemical samples were frozen as soon as practicable following collection and were transported to a third-party laboratory for analysis.

All samples were clearly labelled externally with a minimum of the following information:

- Contract and work order numbers;
- Reference of the sample zone and station;
- Date and time of sampling.

2.5 Sample analysis

All samples collected during the survey were transported to APEM’s Letchworth laboratory, where biological samples were analysed. PSA and contaminant samples were transported to SOCOTEC for analysis.

2.5.1 Sediment Chemistry

Sediment chemistry samples were analysed to determine the current levels of contamination across the survey area in comparison to OSPAR background levels.

A full description of the methods used in the analysis of the sediment chemistry samples is provided in Appendix 1, with summary methods and rationale provided in the following paragraphs. Sediment contaminants were compared against standard reference limits detailed in OSPAR (2014a), CCME (1999), Buchman (2008), Spencer & MacLeod (2002).

Heavy and Trace Metals

Metals are generally not harmful to organisms at concentrations normally found in marine sediments and some are essential for normal metabolism but can become toxic above a critical threshold. In order to quantify potential effects on marine life, Long *et al*. (1995) defined “effect range low” (ERL) values as the lowest concentration of a metal that produced adverse effects in 10% of the data reviewed, whilst “effect range median” (ERM) values designate the level at which half of the studies reported harmful effects. Consequently, metal concentrations recorded below the ERL are not expected to elicit adverse effects, while levels above the ERM are likely to be toxic to some marine life.

Heavy metals were extracted using an aqua regia digestion. The metals were then analysed using either ICP-MS (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) or ICP-OES (Al, Ba, Fe). Normalisation was conducted using the pivot values contained in the current Coordinated Environmental Monitoring Programme (CEMP) normalisation procedure or using a simple ratio approximation as concentrations of some metals were too low across the site to utilise pivot values.

Total Organic Carbon (TOC)

A portion of air-dried and ground sample was mixed with concentrated sulphurous acid. This was then warmed to 40°C for an extended period of time. The resultant mixture was then heated to dryness at 100°C. The dried residue was analysed for carbon content using an Eltra induction furnace fitted with a nondispersive infrared sensor (NDIF) cell. The total quantity of carbon liberated was calculated and reported as a percentage of the original mass of sample.

Total Petroleum Hydrocarbons (TPH)

Total Petroleum Hydrocarbons are found in marine sediments as a result of offshore oil and gas rigs, and exploratory drilling. Contamination can also originate from domestic, industrial, natural and mobile sources (land and sea based), and can be generally attributed to processes involving burning. The seabed can be a basin for the influx of sediments and petroleum related pollutants from rivers and estuaries. These pollutants are known carcinogens and therefore it is important that they are monitored in environmental situations.

TPHs are extracted from as received marine sediment by solvent extraction. 15 ml of methanol and 60 ml of DCM are added to an aliquot of the supplied sediment (15 g) and mixed on a magnetic stirring plate for 1 hour. The solvent extract is then water partitioned and concentrated to 1 ml. A clean up stage utilises silica gel which removes polar organics that may be readily extracted and contribute to the chromatographic are count (for TPH), but are not petroleum hydrocarbons.

Analysis is carried out by GC/FID and quantified by comparison with a solution containing diesel hydrocarbons. This method covers the determination of TPHs $nC_{10} – nC_{37}$ and the individual n-Alkanes of hydrocarbons $nC_{10} – nC_{37}$, pristane and phytane.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are natural components of coal and oil and are also formed during the combustion of fossil fuels and organic material. They are one of the most widespread organic pollutants in the marine environment, entering the sea from offshore activities, operational and accidental oil spills from shipping, drilling activities, river discharges and the air (UKOOA, 2001).

PAHs include potentially carcinogenic, mutagenic and toxic compounds that concentrate in fatty tissues of organisms. They can adversely affect reproduction and may affect immune systems. Since they are bio-accumulative the higher levels of the food web, especially fish-eating birds and marine mammals can be particularly affected. Because of these properties, the OSPAR Commission identified PAHs as chemicals for priority action (OSPAR, 2009), focussing on a set of 6 PAH compounds as priority hazardous substances: anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene; as well as naphthalene as a priority substance.

Polycyclic aromatic hydrocarbons (PAHs) were analysed at each station using Gas Chromatography Mass Spectrometry (GC-MS). Normalised total PAH data was calculated by using a simple ratio approximation to allow comparison to OSPAR background assessment concentrations (BACs; OSPAR, 2014a).

Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls are a group of substances which are very persistent, concentrate in fatty tissues and have varied harmful effects on marine organisms. PCB compounds are potential endocrine disruptors and pose major environmental concern. Because of their properties, the OSPAR Commission has selected the group of PCBs as chemicals for priority action.

OSPAR environmental monitoring has concentrated on a set of 7 PCB congeners, which cover the range of toxicological properties of the group (CB congeners 28, 52, 101, 118, 138, 153, 180). CB153 is generally present in the highest concentration and correlates well with the other analysed PCBs. CB118 is representative of the more toxicologically relevant mono-ortho/planar PCBs.

Although production of PCBs was banned in the mid-1980s some inputs to the marine environment still remain from PCB-containing equipment, waste disposal, remobilisation from marine sediments contaminated with PCBs as a result of historic releases and formation as by-products in thermal and chemical processes.

PCBs were analysed using a solvent extraction followed by Gas Chromatography coupled to a triple quadrupole mass spectrometer (GC-MS-MS).

Organotins

Organotin compounds are highly toxic and considered endocrine disruptors, mutagenic and bioaccumulative. They are highly persistent in the marine environment and have been used as antifouling ingredients in paints (primarily tributyltin (TBT)) to prevent the settlement and growth of aquatic organisms on ship hulls, fishing nets or cages, oil rig supports, and different tools used in seawater. Tributyltin degrades to dibutyltin (DBT) and monobutyltin (MBT) over time.

Organotins were analysed using an acid digest and solvent extraction before being analysed by GC-MS.

3. Results

3.1 General descriptions of Landfall Zones

The three landfall zones, summarised in Figure 2, were predominately sandy beaches near Peterhead, northeast Scotland. Two of the beaches, Landfall D (Scotstown Beach) and Landfall E (Lunderton Beach) are located to the north of Peterhead, with Scotstown beach about 3 km north of Lunderton Beach and 5 km north of Peterhead. Landfall F (Sandford Bay) is about 2 km south of Peterhead.

3.1.1 Landfall D (Figure 3)

Landfall D was an exposed sandy beach, extending about 4 km north to south between Rattray Head and a stony shoal near St Fergus, with the survey area about 2 km long, at the southern end, south of Annachie Burn and the St Fergus Gas Terminal. Annachie Burn itself was outside the survey area but formed a small estuary with some standing water.

3.1.2 Landfall E (Figure 4)

Landfall E was an exposed sandy beach, about 2 km long extending north to south between two ill-defined stony points. Most of the survey area comprised a shallow sandy bay with gently sloping smooth or rippled clean sand on the mid to lower shore, about 300 m wide.

3.1.3 Landfall F (Figure 5)

Landfall F was a moderately exposed sandy beach, about 1.16 km long extending north to south between the southern outskirts of Peterhead (Burnhaven) and the SSE Power Station. It was a horseshoe-shaped bay with hard substrata around most of its shoreline on the northern and southern sides and a shorter stretch of sand in the centre. There were industrial developments to the North (engineering works, sewage works) and South (Power Station), with outfall pipes on the southern shore. It was not possible to collect contaminant samples from the planned stations on transects F2 and F3 due to the presence of large boulders (Figure 6 (a) and (b)). An extra sample, WP 35 was collected from a nearby location (see Table 2 and Figure 5) where unusual sediment was encountered.

Figure 6. Landfall F - view facing (a) South West and (b) South East when positioned between transects F2 and F3.

3.2 Intertidal sediment chemistry analysis

Total Organic Carbon (TOC)

The TOC content (Table 3) ranged from 0.13% at station WP35 to 0.35% at stations D2 and E4, with a relatively low variability of 0.22%.

Table 3. Results of Total Organic Carbon

	Landfall D				Landfall E				Landfall F	
	D1	D2	D3	D4	E1	E2	E3	E4	F1	WP35
Total Organic Carbon % LOD = 0.02	0.27	0.35	0.31	0.30	0.21	0.26	0.27	0.35	0.23	0.13

Heavy and Trace Metals

Normalised heavy and trace metal concentrations recorded at the sites are listed in Table 4 and Figure 7. Most heavy and trace metals were found in concentrations below the BC, the concentration that it should naturally occur in undisturbed environment.

At station WP35 higher concentrations of heavy and trace metals were observed, compared with other stations, these were below the threshold limits for most heavy and trace metals but exceeded the BC for Zinc and exceeded the Threshold Effects Level (TEL) for Nickel.

The low levels recorded for Cadmium and Mercury prohibits graphical representation, but the values are included in Table 4.

The current environmental focus of the Coordinated Environmental Monitoring Programme (CEMP) around heavy metals is on Cadmium, Mercury, and Lead (OSPAR, 2014b). Cadmium and Lead occur within the natural environment but can be toxic whilst mercury is extremely toxic to humans and biota (OSPAR, 2014a).

Cadmium did not exceed the TEL, the maximum level at which no effects are observed, or the Background Assessment Concentration at any stations and only exceeded the BC by 0.03 mg/kg at station WP35.

Excluding station WP35, Lead concentration was consistent between stations ranging between 1.6 mg/kg and 2.8 mg/kg, falling below all comparable threshold levels. In comparison to the other stations the Lead concentration was elevated at station WP35 (16.3 mg/kg); however, it was still below all comparable threshold levels.

Similarly, Mercury was also recorded in low concentrations and consistently below the limit of detection for the analytical method used (0.01 mg/kg). In the majority of stations, with exclusion of stations E1, E2 and F1, Arsenic was recorded above the TEL, the maximum concentration at which no effects are observed. However, it is notable that the TEL is lower than the BC for mercury.

Table 4. Normalised concentration of heavy and trace metals (mg/kg)

Analyte	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc	Aluminium	Barium	Iron	Mercury
Unit	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
LOD	0.5	0.04	0.5	0.5	0.5	0.5	2	10	0.5	36	0.01
D1	11.4	0.04	2.9	1.2	2.3	2.3	7.1	1150	13.0	6360	0.02
D2	11.7	0.07	2.9	1.0	2.4	2.3	7.8	871	11.8	5300	0.01
D3	10.4	0.07	2.8	0.7	2.1	1.8	6.2	838	10.4	4870	0.01
D4	7.6	<0.04	2.5	0.8	1.6	1.7	7.3	737	8.98	3980	<0.01
E1	6.1	0.05	2.8	1.4	1.8	2.1	7.6	780	8.35	3450	<0.01
E2	6.7	<0.04	2.5	1.1	1.7	2.2	6.3	928	9.35	4260	<0.01
E3	7.6	<0.04	2.3	1.1	1.8	1.8	6.8	864	9.38	4320	<0.01
E4	8.3	0.05	2.5	0.8	2.0	1.6	5.6	812	10.1	4440	<0.01
F1	2.0	0.08	2.6	2.1	2.8	2.0	9.5	1490	10.7	3920	<0.01
WP35	10.9	0.23	28.2	12.9	16.3	30.8	114.0	1770	9.6	5000	0.04
Min	2	0.04	2.3	0.7	1.6	1.6	5.6	737	8.35	3450	0.01
Max	11.7	0.23	28.2	12.9	16.3	30.8	114	1770	13	6360	0.04
Mean	8.27	0.084	5.2	2.31	3.48	4.86	17.82	1024	10.17	4590	0.02
Median	7.95	0.07	2.7	1.1	2.05	2.05	7.2	867.5	9.85	4380	0.015
%RSD	36.14	-	155.5	162	129.9	187.6	189.7	33.66	13.66	18.09	-
TEL	7.24	0.7	52.3	18.7	30.2	15.9	124	-	-	-	0.13
PEL	41.6	41.6	160	108	112	42.8	271	-	-	-	0.7
OSPAR ERL	-	1.2	-	-	47	-	-	-	-	-	0.15
NOAA ERL	8.2	1.2	81	34	46.7	20.9	150	-	-	-	-
BC	15	0.2	60	20	25	30	90	-	-	-	-
BAC	25	0.31	81	27	38	36	122	-	-	-	0.07

Colour coding is applied in sequence from greatest to smallest value. Therefore, exceedance of the highest value also implies exceedance of lower thresholds (e.g. ERL>BAC>BC).
TEL = Threshold Effects Level: Maximum concentration at which no effects are observed (Source: CCME, 1999)
PEL = Probable Effects Level: Lower limit of the range of concentrations at which adverse effects are always observed (Source: CCME, 1999)
ERL = Effects Range Low: 10th percentile values in effects (Sources: OSPAR, 2014a; Buchman, 2008) [consistent with Spencer & MacLeod, 2002])
BC = Background Concentration
BAC = Background Assessment Concentration

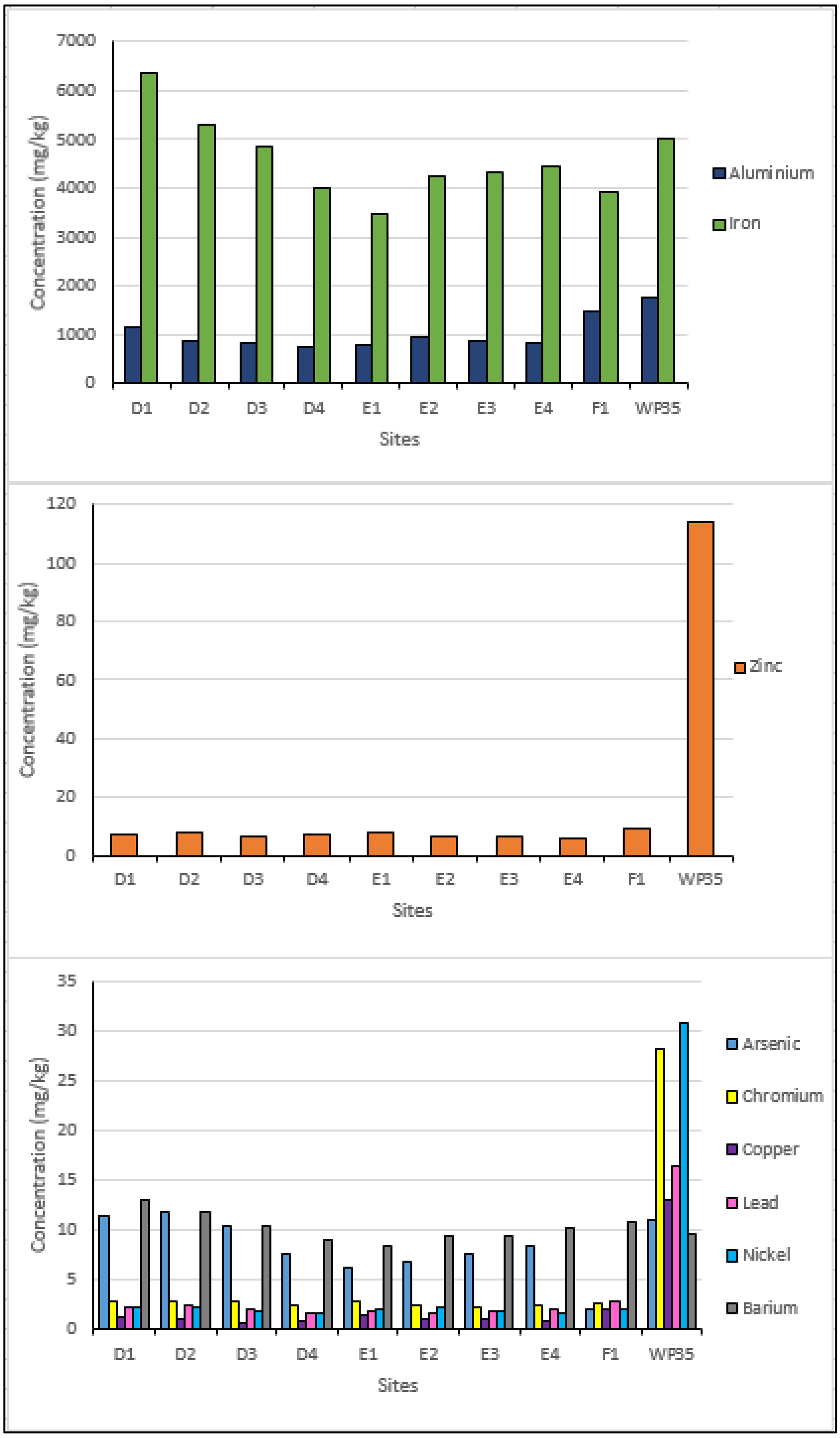

Figure 7. Graphs to show concentration of Aluminium (Al) and Iron (Fe), Zinc (Zn) and Arsenic (As), Chromium (Cr), Copper (Cu), Lead (Pb), Nickel (Ni) and Barium (Ba).

Total Petroleum Hydrocarbons (TPH)

A summary of hydrocarbon concentrations are presented in Table 5.

TPH concentrations ranged from 0.174 mg/kg at site E3 to 0.901 mg/kg at site F1, with a mean of 0.43 mg/kg and an intermediate variability of 51.9% RSD.

Total n-alkane (nC10-37) concentrations ranged from 0.0309 mg/kg at station F1 to 0.0425 mg/kg at station D3 with a mean of 0.036 mg/kg. Stations E1, E2, E3 and WP35 had concentrations lower than the Limit of Detection (LoD)

Table 5. Summary of hydrocarbon data

	TPH (mg/kg)	Total n-alkanes (mg/kg)	Carbon Preference Index	Proportion of Alkanes (%)
Station	**LOD =0.1**	**LOD = 0.028**		
D1	0.214	0.0354	0.65	16.54
D2	0.285	0.0365	0.97	12.81
D3	0.348	0.0425	0.87	12.21
D4	0.502	0.0392	0.84	7.81
E1	0.36	<0.028	1.44	-
E2	0.328	<0.028	1.12	-
E3	0.174	<0.028	2.16	-
E4	0.674	0.0318	1.19	4.72
F1	0.901	0.0309	1.09	3.43
WP35	0.515	<0.028	-	-
Min	0.174	0.0309	0.65	3.430
Max	0.901	0.0425	2.16	16.542
Mean	0.4301	0.03605	1.15	9.586
Median	0.354	0.03595	1.09	10.011
%RSD	51.9	12.2	38.6	53.276

The Carbon Preference Index (CPI) is a useful tool to indicate the likely sources of concentrations of n-alkanes. The lower the CPI the greater the anthropogenic inputs and values greater than 4 tend to imply a greater biogenic n-alkanes (Jaffé et al., 1996). Petrochemical derived n-alkanes exhibit a wide distribution range, no predominance of odd over even n-alkanes and thus CPI values close to 1 (Aboul-Kassim & Simoneit, 1996). The CPI ranged from 0.65 at station D1 to 2.16 at station E3, suggesting that they are skewed towards petrogenically derived *n*-alkanes.

The pristine/phytane ratio is often used as a proxy for redox conditions of the depositional environment, although caution should be exercised when interpreting the values. Both pristine and phytane are common constituents of crude oil and where they are found in similar ratios (i.e. values close to 1) it may be indicative of petroleum contamination. It was not possible to calculate pristine/phytane ratios at any of the stations as the concentrations of pristine and phytane were below the limit of detection (<1 µg/kg) at all sites except 0.00161 mg/kg of Pristane at station F1 and 0.00867 mg/kg.of Phytane at station D3. Full results are presented in Appendix 2.

Polycyclic Aromatic Hydrocarbons (PAHs)

Concentrations of PAH individual aromatics are presented in 6. There are no values that exceed the OSPAR Effect Range Low (ERL) for any of the PAHs. There are no values that exceed the Cefas Action Level (cAL 1) for any of the PAHs.

Table 6. Concentrations of PAHs (mg/kg) considered priority substances or priority hazardous substances.

Analyte	Naphthalene (mg/kg)	Anthracene (mg/kg)	Benzo [b] fluoranthene (mg/kg)	Benzo [k] fluoranthene (mg/kg)	Benzo [a] pyrene (mg/kg)	Indeno [123,cd] pyrene (mg/kg)	Benzo [ghi] perylene (mg/kg)	Total PAHs (mg/kg)
LOD	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.034**
D1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
D2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
D3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
D4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
E1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
E2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
E3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
E4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
F1	<0.001	<0.001	0.0024	0.0029	0.0033	0.0023	0.0019	0.0551
WP35	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
Min	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.034
Max	<0.001	<0.001	0.00242	0.00285	0.00333	0.00225	0.0019	0.0551
Mean	-	-	-	-	-	-	-	-
Median	-	-	-	-	-	-	-	-
%RSD	-	-	-	-	-	-	-	-
OSPAR Effect Range Low (ERL)	160	-	-	-	430	240	85	
Cefas Action Level (cAL 1)	-	-	100	100	100	-	100	
BC	5	3	-	-	15	50	45	
BAC	8	5	-	-	30	103	80	

Polychlorinated biphenyls (PCBs)

All PCB concentrations (Appendix 2) fell below the limit of detection (0.08 µg/kg) except for site E3, detailed in Table 7. However, concentrations at this station fell below the OSPAR EAC limits and the Background Assessment Concentration.

Table 7. PCB concentrations at site E3

E3			
Analyte	**Limit of Detection**	**Units**	**Concentration**
PCB 101	0.08	µg/kg (Dry Weight)	0.13
PCB 105	0.08	µg/kg (Dry Weight)	0.17
PCB 110	0.08	µg/kg (Dry Weight)	0.10
PCB 118	0.08	µg/kg (Dry Weight)	0.10
PCB 128	0.08	µg/kg (Dry Weight)	0.10
PCB 138	0.08	µg/kg (Dry Weight)	0.10
PCB 141	0.08	µg/kg (Dry Weight)	0.09
PCB 149	0.08	µg/kg (Dry Weight)	0.12
PCB 151	0.08	µg/kg (Dry Weight)	0.17
PCB 153	0.08	µg/kg (Dry Weight)	0.11
PCB 156	0.08	µg/kg (Dry Weight)	0.11
PCB 158	0.08	µg/kg (Dry Weight)	0.13
PCB 170	0.08	µg/kg (Dry Weight)	0.19
PCB 18	0.08	µg/kg (Dry Weight)	<0.08
PCB 180	0.08	µg/kg (Dry Weight)	0.18
PCB 183	0.08	µg/kg (Dry Weight)	0.09
PCB 187	0.08	µg/kg (Dry Weight)	0.19
PCB 194	0.08	µg/kg (Dry Weight)	0.16
PCB 28	0.08	µg/kg (Dry Weight)	<0.08
PCB 31	0.08	µg/kg (Dry Weight)	<0.08
PCB 44	0.08	µg/kg (Dry Weight)	0.10
PCB 47	0.08	µg/kg (Dry Weight)	0.13
PCB 49	0.08	µg/kg (Dry Weight)	0.11
PCB 52	0.08	µg/kg (Dry Weight)	0.12
PCB 66	0.08	µg/kg (Dry Weight)	0.12

Organotins

Tributyltin (TBT) values were below the limit of detection (1 µg/kg) at all stations and Dibutyltin (DBT) values were below the limit of detection (1 µg/kg) for all stations except E2 and E4, as shown in Table 8 below.

Table 8. Concentrations of Organotins.

Analyte	Dibutyltin (mg/kg)	Tributyltin (mg/kg)
LOD	**0.001**	**0.001**
D1	<0.001	<0.001
D2	<0.001	<0.001
D3	<0.001	<0.001
D4	<0.001	<0.001
E1	<0.001	<0.001
E2	0.0018	<0.001
E3	<0.001	<0.001
E4	0.0017	<0.001
F1	<0.001	<0.001
WP35	<0.001	<0.001

Sediment Moisture

Sediment moisture (Table 9) was relatively consistent at all stations other than WP35, ranging from 17.3% at station E1 to 28.3% at station E4. Station WP35 had considerably lower moisture content (2.40%) compared to other stations.

Table 9. Percentage moisture content.

Station	Total Moisture @120°C (%)
	LOD = 0.2
D1	25.6
D2	26.2
D3	26.8
D4	22.2
E1	17.3
E2	27.3
E3	20.0
E4	28.3
F1	27.9
WP35	2.40

4. Discussion

Contaminant analysis for Landfall D and Landfall F found that other than Arsenic all tested contaminants were either below the detectable limit or below the threshold limit. Normalised arsenic concentrations were higher than the TEL but still fell below BC, as arsenic can have effects on organisms at lower concentrations than are naturally found in sediments.

Sediment grain size also has a significant impact on the absorption of chemical pollutants, with finer particles tending to have a higher pollution load index than coarse particles. In addition, fine sediments may be more easily transported away from their sources, thus expanding the potential for pollution impacts. However, fine sediments are also usually found in more stable environments where pollutants may be sequestered until remobilised by a disturbance event.

Results from Landfall F showed different results between planned station, F1 and the new station WP35. Station F1 had similar results to stations at Landfall D and E. At planned stations F2 and F3 it was not possible to collect a sample due to large boulders, therefore an extra station (WP35) was added. The location of this station can be seen visually in Figure 5 and details of positioning are shown in Table 2. Field surveyors noted that the sediment was pinkish in colour. This is possibly due to the erosion of granitic rocks where the red/pink colour has long been attributed to the presence of ferric iron oxides, probably hematite in the alkali feldspar minerals which form a major constituent of such rocks, to iron oxides; this has been attempted to capture visually in Figure 8.

At station WP35 higher concentrations of heavy and trace metals were observed, compared with other stations. All concentrations were below the BC, except for Cadmium and Zinc which were above the BC value, but below the TEL. Nickel levels were also recorded above the TEL. This station also had a lower percentage water content compared to other stations (see Table 9).

Figure 8. Images of the sediment at station WP35.

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Appendix 1 Sediment Chemistry Analysis Methods

Total Organic Carbon

Sediment Total Organic Carbon (TOC)

A portion of air-dried and ground sample was mixed with concentrated sulphurous acid. This was then warmed to 40°C for an extended period of time. The resultant mixture was then heated to dryness at 100°C. The dried residue was analysed for carbon content using an Eltra induction furnace fitted with a nondispersive infrared sensor (NDIF) cell. The total quantity of carbon liberated was calculated and reported as a percentage of the original mass of sample.

Hydrocarbon Concentrations

Extraction Procedure for Hydrocarbons

Each analytical sample was spiked with an internal standard solution containing the following components: aliphatics - heptamethylnonane, 1-chlorooctadecane and squalene. The sample was then wet vortex extracted using three successive aliquots of DCM/Methanol. The extracts were combined and water partitioned to remove the methanol and any excess water from the sample.

Solvent extracts were chemically dried and then reduced using a Kuderna Danish evaporator with micro Snyder.

Column Fractionation for Aliphatic and Aromatic Fractions

The concentrated extract was transferred to a pre-conditioned flash chromatography column containing activated Silica gel. The compounds were eluted with Pentane/DCM (2:1). An aliquot of the extract was then taken and analysed for THC content and individual n-alkanes by large volume injection GC-FID.

Quality Control Samples

The following quality control samples were prepared with the batches of sediment samples:

- A method blank comprising of baked anhydrous sodium sulphate (organic free) treated as a sample.
- A matrix matched standard sample consisting of baked sand spiked with Florida mix and treated as sample.

Hydrocarbon Analysis

Analysis of total hydrocarbons and aliphatics was performed by using an Agilent 6890 with a FID. Appropriate column and GC conditions were used to provide sufficient chromatographic separation of all analytes and the required sensitivity.

Carbon Preference Index (CPI)

The carbon preference index is calculated as follows:

$$CPI = \frac{\text{odd homologues } (nC_{11} \text{ to } C_{35}}{\text{even homologues } (nC_{10} \text{ to } nC_{34}}$$

Petrogenic:Biogenic (or P:B) Ratio

The Petrogenic:Biogenic Ratio is calculated as follows:

$$P{:}B \text{ Ratio} = \frac{P = \text{sum of } nC_{10} \text{ to } nC_{20}}{B = \text{sum of } nC_{21} \text{ to } nC_{35}}$$

Calibration and Calculation

GC techniques require the use of internal standards in order to obtain quantitative results. The technique requires addition of non-naturally occurring compounds to the sample, allowing correction for varying recovery.

Target analytes concentrations were calculated by comparison with the nearest eluting internal standards. A relative response factor was applied to correct the data for the differing responses of target analytes and internal standards. Response factors were established prior to running samples, from solutions containing USEPA(16) PAHs + Dibenzothiophene for the GC-MS, Florida mix (even n- Alkanes nC10-nC40) for individual GC-FID targets and a Diesel/Mineral Oil mix for total oil determination.

The mean detection limits used for the sediment total hydrocarbons and n-alkanes were:

1. n-alkane – 1 ng/g (ppb)
2. Total Hydrocarbons – 100 ng/g (ppb)

Normalisation of PAH

Normalised total PAH data was calculated to allow comparison to OSPAR background assessment concentrations (BACs; OSPAR, 2014a). Normalisation was undertaken using a simple ratio approximation. All total PAH concentrations (based on the 11 PAH components outlined in OSPAR, 2014a) have been normalised to the 2.5% total organic carbon content of the sediment at each station.

Heavy and Trace Metal Concentrations

Sediment samples were homogenised and a portion of each sample was air dried at room temperature. Each sample was then ground down to a fine powder (<100 µm) by hand using a metal free mortar and pestle. A clean sand sample was hand ground prior to preparation of the field samples as a blank.

Sample Digestion Procedure

Metals in Sediment by ICP-OES/ICP-MS (Aqua regia)

A portion of air-dried and ground sample is digested with Aqua Regia. Once cooled the extract is filtered and pre-diluted before being analysed. Analysis is performed by ICP-MS or ICP-OES and quantified by comparing the results against a calibration curve for each of the target analytes.

The mean reporting limits are given in Table 10 below.

Table 10. Reporting Limits for Heavy and Trace Metals Analysed

Analyte	Method	Unit	RL
Al	ICP-OES	mg/kg	10
As	ICP-MS	mg/kg	0.5
Ba	ICP-OES	mg/kg	1
Cd	ICP-MS	mg/kg	0.04
Cr	ICP-MS	mg/kg	0.5
Cu	ICP-MS	mg/kg	0.5
Fe	ICP-OES	mg/kg	10
Hg	ICP-MS	mg/kg	0.015
Ni	ICP-MS	mg/kg	0.5
Pb	ICP-MS	mg/kg	0.5
Zn	ICP-MS	mg/kg	3

Analytical Methodology

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The instrument is calibrated using dilutions of the spectroscopic solutions. The final calibration solutions are matrix matched with the relevant acids. The calibration line consists of five standards.

Inductively Coupled Plasma- Mass Spectrometry (ICP-MS)

The instrument is calibrated using dilutions of the spectroscopic solutions. The calibration line consists of seven standards.

The analytes are scaled against internal standards to take account of changes in plasma conditions as a result of matrix differences for standards and samples. The internal standards have a similar mass and ionisation properties to the target metals.

Normalisation

Normalisation is a procedure used here to correct concentrations for the influence of the natural variability in sediment composition (i.e. grain size, organic matter, and mineralogy). Natural and anthropogenic contaminants tend to show a much higher affinity to fine particulate matter compared to coarse (OSPAR, 2009) due to the increased adsorption capacity of organic matter and clay minerals.

In sites where there is variability in grain size between stations, effects of sources of contamination will at least partly be obscured by grain size differences.

Normalisation can be performed through linear regression or by simple contaminant/normaliser ratios linear regression normalisation takes into account the possible presence of contaminants and cofactors.

The binding capacity of the sediments can be related to the content of fines (primary cofactor) in the sediments. The level of fines can be represented by the contents of major elements of the clay fraction such as aluminium (secondary co-factor). Figure 9 represents the general model for normalisation of the contaminants.

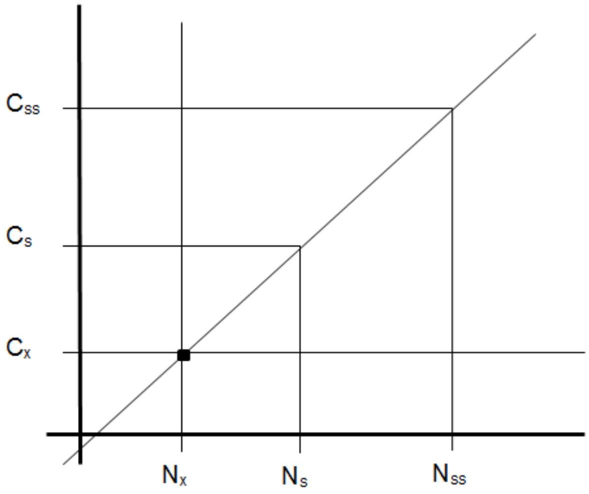

Figure 9. Relation between the contaminant C and the cofactor N

C_x and N_x represent the contaminant and the co-factor contents, respectively, in pure sand. The regression line will always originate from this point and pivot depending on the sampled contaminant concentrations (C_s and N_s). These ‘pivot values’ are derived from the statistical analysis of contaminant concentrations in pure sand.

The linear relationship between the pivot point and the sampled concentrations allows determination of the contaminant content for any preselected co-factor content (Nss) by interpolation and extrapolation. When comparing to the OSPAR BCs and BACs the secondary cofactors for normalisation are 50,000 µgg-1 of Al for metals and 2.5% TOC when normalising organics. The slope of the regression line (PL) can be represented by Equation 1, which can then be re-arranged to give the contaminant content C_{ss} that is normalised to N_{ss} in Equation 2.

$$PL = \frac{dC}{dN} = \frac{C_s - C_x}{N_s - N_x} = \frac{C_{ss} - C_x}{N_{ss} - N_x}$$

Equation 1: Slope of the regression line expressed in terms of Nss

$$C_{ss} = (C_s - C_x)\frac{N_{ss} - N_x}{N_s - N_x} + C_x$$

Equation 2: Rewritten equation giving the contaminant content C_{ss} normalised to N_{ss}

This method is limited by the sampled concentration of the contaminant. If a measured concentration falls below the C_x ‘pivot value’ for that metal or if the concentration of Al falls below the N_x ‘pivot value’, the method will give a skewed result (often a negative concentration). The pivot values for the contaminants are given in Table 11**.**

Table 11. Pivot Values for Metals with OSPAR Background Concentrations (OSPAR, 2008).

Metal	Al	As	Ba	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
Digestion Type	Partial	Partial	n/a	Partial	Partial	Partial	n/a	Partial	Partial	Partial	Partial
N_x or C_x (mg/kg)	4,000	3	n/a	0.03	13	1	n/a	0	2.5	2	8

If a metal is found to be below these values the alternative method of a simple ratio between contaminant/normaliser.

$$C_{ss} = \frac{N_{ss}}{N_s} C_s$$

Equation 3: Ratio method for the normalisation of a contaminant

Normalisation of Heavy and Trace Metals

In order to reduce the granular variability on heavy and trace metal data acquired. Metals were normalised to Aluminium based on the procedure outlined in OSPAR (2008a; 2008b), this method incorporates the pivot values of metals and has been adopted in place of simple ratio derived normalisation methods. Metals which do not have a pivot value (Ba and Fe) or which were too low to utilise it (As and Pb), were normalised using a simple ratio approximation. These data were then compared with BCs and background assessment concentrations (BACs), where applicable.

Polychlorinated Biphenyls (PCBs)

A portion of air-dried and sieved sample was spiked with ^{13}C labelled internal standards, ultrasonically solvent extracted and concentrated under nitrogen. A clean-up stage was employed to remove contaminants that may interfere with the analysis. The sample extract was analysed by Gas Chromatography coupled to a triple quadrupole mass spectrometer (GC-MS-MS). Quantification was performed by comparison with a solution containing each of the targeted compounds, normalised to the ^{13}C labelled internal standards.

Organotins

A portion of the sample was digested with hydrochloric acid and methanol before being extracted into toluene. The extract was then derivatised using sodium tetraethylborate (STEB) before concentration and a copper/silica clean-up was performed. The extract was analysed by GC-MS and quantified by comparing the results against a calibration curve for each of the target analytes.

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Appendix 2 Raw Data

Please see Excel file attached within this document

MarramWind