

FINAL REPORT

RSG Project 98/26

Metal Analyses of Surface Sediment Samples collected for the Rockall Studies Group (RSG) in the Rockall Trough

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"This Project, including data and survey results acquired for the purpose, has been undertaken on behalf of the Rockall Studies Group (RSG) of the Irish Petroleum Infrastructure Programme Group 2 which was established by the Petroleum Affairs Division of the Department of the Marine and Natural Resources on 4 June, 1997 in conjunction with the award of exploration licences under the Rockall Trough Frontier Licensing Round. The RSG comprises: Agip (UK) Ltd, Anadarko Ireland Company, ARCO Ireland Offshore Inc, BG Exploration & Production Ltd, BP Exploration Operating Company Ltd, British-Borneo International Ltd, Elf Petroleum Ireland BV, Enterprise Energy Ireland Ltd, Mobil Oil North Sea Ltd, Murphy Ireland Offshore Ltd, Phillips Petroleum Exploration Ireland, Saga Petroleum Ireland Ltd, Shell EP Ireland B.V., Statoil Exploration (Ireland) Ltd, Total Oil Marine plc, Union Texas Petroleum Ltd and the Petroleum Affairs Division of the Department of the Marine and Natural Resources."

EXECUTIVE SUMMARY

Surface sediment samples were collected at sites within the Rockall Trough at water depth ranges from 700 to 2774 metres. The study area was predefined by the availability of samples. The work was undertaken by the British Geological Survey (BGS), on behalf of the Irish Petroleum Infrastructure Programme (PIP), during their gravity core survey in 1998. A small sample from the top of the uppermost section of the core (the 'sea-bed') was taken, placed in a foil bag, labeled, frozen and sent to the Marine Institute, Dublin.

Methods were developed and validated for lead, cadmium, chromium, copper, nickel, zinc, vanadium, strontium, barium, lithium and aluminium using atomic absorption spectroscopy following total digestion, and for mercury, using cold vapour atomic fluorescence spectroscopy following partial digestion. The measured metal concentrations were normalised to lithium to compensate for the influence of natural variability in the concentrations of contaminants in sediments.

The analytical quality assurance programme included the use of a number of Certified Reference Materials (BCSS-1 and PACS-1, both of which were obtained from the National Research Council of Canada and QTMO49MS obtained from QUASIMEME) to validate the accuracy and precision of the analytical methods developed and to provide ongoing quality control. Participation in QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring) an international proficiency-testing scheme also helped to underpin the analytical quality.

The mean concentrations of trace metals detected in these samples were 0.069 ± 0.071 mg kg⁻¹ Hg, 8.51 ± 2.40 mg kg⁻¹ Pb, 0.251 ± 0.442 mg kg⁻¹ Cd, 28.7 ± 8.18 mg kg⁻¹ Cr, 17.1 ± 8.78 mg kg⁻¹ Cu, 18.3 ± 7.33 mg kg⁻¹ Ni, 41.4 ± 26.6 mg kg⁻¹ Zn, 45.4 ± 25.9 mg kg⁻¹ V, 950 ± 440 mg kg⁻¹ Sr, 324 ± 106 mg kg⁻¹ Ba, 19.7 ± 10.6 mg kg⁻¹ Li and 2.70 ± 1.19 % Al. Natural variation in concentrations of metals in sediments was modeled by linear regression using 95% confidence intervals. The concentration of lithium was used as an independent variable.

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Section 1: INTRODUCTION

1.1 OBJECTIVES

When the RRS Challenger (RSG project 97/50) collected 47 gravity cores in summer 1998, the topmost few centimeters of 32 cores were frozen and sent to the Marine Institute (MI) in Dublin. The principle objectives were:

- To develop and validate methods for the analysis of a range of metals of environmental interest in sediment samples from the Rockall Trough
- To determine the spatial distribution and establish baseline concentration ranges of the metals in 32 surface sediments samples collected from the area around the Rockall Trough.

1.2 SAMPLE COLLECTION & STORAGE

The study area was predefined by the availability of samples. Surface sediment samples were collected at water depth ranges from 700 to 2774 metres, from sites within the Rockall Trough and generally the samples consisted of muds and sands. The work was undertaken by the British Geological Survey (BGS), on behalf of the Irish Petroleum Infrastructure Programme (PIP), during their gravity core survey in 1998.

During this survey, a small sample from the top of the uppermost section of the core (the 'sea-bed') was taken and stored for metal analyses from 32 sites (Appendix 1). The position of each sampling site was determined using Differential Global Positioning Systems (DGPS). Samples were placed in polycarbonate lined foil bags, labeled, frozen and sent to the Marine Institute, Dublin. On arrival in Marine Institute, samples were stored in a freezer at – 30°C. The freezer temperature is monitored on a daily basis to ensure it remains within the limits set.

1.3 GRAVITY CORE DESCRIPTIONS

The following descriptions are taken from BGS Technical report WB/98/29C (British Geological Survey Marine Report Series). The colours are classified according to the soil description colour chart of Munsell.

Core 8/2-sc001

Grey mud (2.5Y6/2) with occasional forams.

Core 8/9-sc001

Brown mud (10YR6/3) with a few forams and quartz grains.

Core 9/7-sc001

Grey mud (10YR6/1) with a few forams.

Core 11/20-sc001

Very muddy sand (2.5Y5/2) containing lithic clasts, forams and shell fragments.

Core 11/20-sc002

Grey foram-rich mud (2.5Y4/2).

Core 11/20-sc003

Medium-grained sand (5Y4/3) of forams, quartz grains, lithic fragments and broken shell debris.

Core 11/20-sc004

Brown mud (10Y5/3) with forams, quartz grains and lithic fragments.

Core 11/20-sc005

Grey/brown mud (10YR4/2) with a few forams and minute lithic fragments.

Core 11/20-sc006

Sandy mud (2.5Y5/2) with forams and lithic clasts. Very soft.

Core 11/20-sc007

Very muddy sand (2.5Y5/2) containing forams and lithic clasts. Very soft.

Core 11/20-sc008

Very muddy sand (2.5Y6/2) containing forams and lithic clasts. Very soft.

Core 11/20-sc009

Muddy sand (2.5Y6/2) containing forams and lithic clasts. Very soft.

Core 11/20-sc010

Muddy sand (2.5Y5/2) containing forams and lithic clasts. Very soft.

Core 16/28-sc001

Fine sand composed mainly of forams and quartz grains in minor clay matrix. Also small rounded lithic clasts of at least two distinct lithologies.

Core 16/28-sc002

Fine-grained sand (10YR6/3) comprising forams, some broken shell debris and lithic clasts.

Core 74/01-sc001

Live and dead coral and very soft mud

Core 74/01-sc002

Medium-grained foram-rich sand (2.5Y5/2) with broken shell debris, spines and at least two types of rounded lithic fragments.

Core 74/01-sc003

Greyish, fine to medium-grained sand (2.5Y5/2) comprising mainly forams but also with small broken shells, echinoid spines and lithic fragments.

Core 74/06-sc001

Fine-grained foram-rich sand (2.5Y5/2) with filaments and very fine comminuted black specks (volcanic fragments?)

Core 75/18-sc001

Grey mud (2.5Y5/2) containing fragments of dead coral. Forams and broken shell debris also present.

Core 77/09-sc001

Mud (2.5Y6/2) with sand-sized forams and lithic clasts. Very soft. Fairly high plasticity.

Core 78/28-sc004

Muddy sand (10YR6/3), mainly forams and lithic clasts. Very soft.

Core 78/28-sc005

Muddy, foraminiferal sand (2.5Y6/2) with lithic clasts. Very soft.

Core 78/28-sc006

Muddy sand (2.5Y6/2) with lithic clasts and forams. Very soft.

Core 78/28-sc007

Slightly muddy, foraminiferal sand (2.5Y6/2) with lithic clasts.

Core 78/28-sc008

Foraminiferal sand (2.5Y7/2) with rare lithic fragments. Very soft.

Core 78/30-sc001

Sandy mud (2.5Y6/4), with forams and lithic clasts. Very soft.

Core 83/03-sc002

Slightly muddy foram-rich sand (10YR7/3) with lithic clasts.

Core 83/05-sc001

Sandy mud (2.5Y7/2) with forams and lithic clasts.

Core 83/05-sc002

Sandy mud (2.5Y7/2) with forams and angular lithic clasts. Very soft.

Core 83/23-sc002

Very fine sand to mud (10YR6/3) with forams, broken shell debris and angular to rounded black lithic fragments.

Core 83/29-sc001

Pale grey gritty clay (10YR7/1) containing forams and other shell debris.

1.4 METALS IN SEDIMENTS

Metals exist in marine sediments naturally as well as from man's activities. Many metals including chromium, copper, iron, manganese, vanadium, strontium and zinc are essential elements for living organisms. However, some trace elements such as mercury, lead and cadmium are not required for metabolic activity and are toxic at quite low concentrations. Heavy metals are one of the serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation potential (Tam & Wong 2000). Anthropogenic inputs from domestic, industrial and shipping activities are ultimately accumulated on the seabed and incorporated into sediments, which are considered to be the ultimate sink for heavy metals released into the environment. As a result, sediments are widely recognised as a suitable medium for assessing environmental quality, since they reflect and integrate contaminant inputs to the marine environment, allowing sources and sinks to be identified.

The natural metal component in sediment is chemically bound to particulates, such that they are generally non-labile. The anthropogenic, or pollution component, however, is more loosely bound in sediments and thus more labile. Differences in natural metal concentrations are largely a function of sediment grain size and natural metal concentrations are generally much higher in fine grain rather than coarse sediments.

The major objective of geochemical exploration in an area is to detect anomalous concentrations of elements. In comparing levels of metals in environmental samples from different locations, it must be recognized that metals are natural constituents of soils and rocks and that concentrations may vary considerably depending on local geochemistry. Thus, higher concentrations, particularly in sediments, do not necessarily reflect man-made contamination but could easily reflect differences in sediment provenance (ICES, 1989).

As the technology for deepwater drilling develops, areas previously considered inaccessible are being explored. With this in mind, the project aimed to establish background levels for a wide range of environmentally important metals from an area around the Rockall Trough (at water depth ranges from 700 to 2774 metres), where exploration is possible in the future. Limited data is currently available for marine sediments for this area and water depth.

A number of metals have been associated with oil exploration. Crude oils represent a complex mix of components. These components are primarily organic, for example, hydrocarbons; however, inorganic components including trace metals are also present. The main metals associated with crude oil are nickel and vanadium (Macias-Zamora et al, 1999). Concentrations of vanadium may be as high as 2000 mg kg⁻¹ (Tissot & Welte 1984). Upon extraction of the crude oil, accidental deposition on surface sediments may occur, resulting in trace metals becoming incorporated in the sediment load, increasing the background levels of the metal content of the local sediment.

Specialist muds used during exploration also contain trace metals. Barytes (the naturally occurring rock form of barium sulphate, BaSO₄) is the standard densification agent used in drilling fluids worldwide. Its high specific gravity (4.5 g cm⁻³ for barium sulphate), low sea water solubility, low abrasive properties, chemical inertness and easy handling are the main characteristics that make it suitable for increasing density of the drilling fluids to control the hydrostatic pressure. Barytes are known to contain many mineral impurities. These may include alkali metals, alkaline-earth metals, heavy metals and rare earth elements, depending on the source of barytes (Ansari et al, 2001). Analysis of barium in marine sediments and earth materials has become an important way to trace drilling mud components in off shore areas (Bowker & Manheim, 1982).

1.5 NORMALISATION

Normalisation is defined as a procedure to compensate for the influence of natural processes on the measured variability in the concentrations of contaminants in sediments. Most natural and anthropogenic substances show a high affinity to fine particulate matter compared to the coarse fraction. In practice, natural and anthropogenic substances entering the marine system are subjected to a variety of biogeochemical processes. As a result, they become associated with fine-grained suspended solids and colloidal organic and inorganic particles (ICES, 1993). The ultimate fate of these substances is determined, to a large extent, by particulate dynamics. They therefore tend to accumulate in areas of low hydrodynamic energy, where fine material is preferentially deposited. In areas of higher energy, this fine particulate matter is mixed with coarser sediment particles that are generally not able to bind contaminants. This dilution effect will cause lower and variable concentrations in the resulting sediment (ICES, 2000).

Two main normalisation approaches are widely used in oceanography. The first is purely physical and consists of characterising the sediment by measuring the content of fine material (granulometric normalisation). The second approach is chemical in nature and is based on the fact that the small size fraction is usually rich in clay minerals, iron and organic matter. These components often exhibit a high affinity for organic and inorganic contaminants due to the high specific surface area of smaller particles, and are responsible for their enrichment in the fine fraction. This enrichment is mainly due to surface adsorption and ionic attraction (Rubio et al, 2000).

Clay and organic carbon contents can be regarded as primary normalisers, which are directly responsible for the sorption capacity of sediments. Aluminium and lithium are secondary normalisers because they are representatives of primary normalisers and do not have uptake capacity for themselves. These parameters may therefore be used to characterise the small size fraction under natural conditions (geochemical normalisation).

1.3.1 Normalisation procedures:

(a) Granulometric Normalisation

The granulometric approach is a procedure that involves the mathematical normalisation of trace metal data to weight percent of various size fractions removed from the sediments. Such granulometric approaches show that linear correlations occur consistently between increasing trace metal concentration and decreasing grain size. The strength of the correlation, however, varies from element to element and from area to area because of the variation in mineralogical composition related to origin rather than to particle size.

(b) Geochemical Normalisation

In this approach, heavy metal concentrations are normalised by relating their total concentrations in non-fractionated (total) samples with the total concentrations of conservative reference elements (ICES, 1992). Aluminium is frequently used to normalise trace metal concentration for natural variability because it is a good tracer for clay minerals. Both clay minerals and feldspars (detrital minerals) contain aluminium. However, use of aluminium has been questioned if sediments originate from glacial erosion of igneous rocks, because in such cases, sandy sediments still contain some feldspars which have low trace metal concentrations (ICES/HELCOM 1993). Lithium is a suitable alternative to aluminium as it is a conservative element and a lattice component of fine-grained major trace metal bearing minerals. It also reflects the granular variability of its host mineral component. In addition, it is present in easily detectable concentrations, and it is usually not present in feldspars or influenced by anthropogenic activity (Loring, 1990).

At present, the simplest normalisation procedure is to express the ratio of the concentration of a given substance to the concentration of the normalising co-factor. (Smedes, Davies et al, 2000). Choice of co-factor may be decided by determining the effectiveness of each co-factor. The effectiveness of each co-factor is assessed based on the correlation between contaminant concentration and normaliser concentration.

1.4 METHOD DEVELOPMENT & VALIDATION

Method development precedes validation although certain aspects of the validation process can be performed during the development stage. Before a method can be developed, a literature search is required in order to find a basis on which to begin the development. The objective of validation of an analytical procedure is to demonstrate that it is suitable for its intended purpose. Systematic laboratory studies need to be considered to ensure that performance characteristics of the method are understood and demonstrate that the method is scientifically sound under the conditions to which it is to be applied (Hutton, 1999).

Typical validation characteristics include:

1. **Accuracy** – the closeness of agreement between the true value (i.e. conventional true value or accepted reference value) and the value found.
2. **Precision** – the closeness of agreement between a series of measurements using the same homogeneous sample under the prescribed conditions of the test.
3. **Specificity** – the ability to assess unequivocally the presence of the analyte in the presence of components which may be expected to be present.
4. **Limit of Detection** – the lowest amount of analyte which can be detected (but not necessarily quantified) in the sample. It is usually defined as the blank response plus three times the standard deviation.
5. **Limit of Quantification** – the lowest amount of analyte which can be quantitatively determined in a sample with suitable accuracy and precision. It is usually the lowest point on the calibration.
6. **Linearity** – the range for which the concentration is directly related to response by a constant factor.

7. **Range** – the interval between the upper and lower concentrations of the analyte in the sample for which it can be demonstrated that the analytical procedure has a suitable level of precision, accuracy and linearity.
8. **Robustness** – this provides a measure of the ability of the analytical procedure to remain unaffected by the deliberate variations in the method parameters. It provides a measure of the reliability of the method when in normal use.
9. **Ruggedness** – the degree of reproducibility of test results obtained by analysis of the same samples under a variety of normal test conditions, such as different laboratories, different analysts, different days etc. It provides a measure of reproducibility of test results under normal expected operational conditions from laboratory to laboratory and from analyst to analyst.
10. **Bias** – the closeness of an obtained analyte value to the certified analyte value.

The first step in the development and validation procedure should be to set minimum requirements for the method.

Section 2: METHOD DEVELOPMENT AND OPTIMISATION

Prior to analysis, samples were freeze-dried and large aggregates broken up. Stones and large shell or coral fragments were discarded and material that passed through a 1mm stainless steel sieve was transferred to glass jars and retained for analysis.

2.1 Sample Decomposition

2.1.1 Microwave Digestion using Hydrofluoric Acid

Historically, in the Marine Institute, freeze-dried sediment (0.2g) was digested using Hydrofluoric Acid (6mls) and aqua regia (3:1; HCl: HNO₃), (1ml). This method was used during the initial optimisation at a temperature of 180°C and a pressure of 350 psi. This resulted in incomplete digestion, with some black particles, possible carbon residuals or organic materials remaining in the solution. A range of acid mixtures was tested during this study and the optimum was found to be reverse aqua regia (1ml) used along with HF (6mls), which resulted in complete digestion.

Reverse aqua regia (3:1; HNO₃: HCl) has been reported (Siaka, 1998) as a preferred digestion method, being vigorous enough to dissolve heavy metals, which are not bound to silicate phases. In addition, sample weight was reduced from 0.2g to 0.1g to further reduce the risk of incomplete digestion and a higher temperature (210°C) and pressure (450 psi) were used, as suggested by the microwave manufacturer. Complete digestion was achieved and these conditions were used in the analyses of all metals, with the exception of mercury, in this study. HF was neutralized after digestion, by the addition of boric acid (3.6g).

2.1.2 Microwave Digestion using Nitric Acid for mercury determination

Historically, in the Marine Institute, the digestion procedure was based upon sample dissolution with Nitric Acid. Suitable marine sediment Certified Reference Materials (BCSS-1 and PACS-1) (0.2g) were digested using Nitric Acid (4mls), using a maximum temperature of 180°C and maximum pressure of 350psi. This resulted in a partial

digestion with fine-grained sand remaining in the vessel after digestion. Analysis of reference materials digested using the method below resulted in recoveries of mercury within the acceptable limits and therefore no changes were made to this method.

2.2 Trace Metal Determination

2.2.1 Cold Vapour Atomic Fluorescence Spectrometry method for the determination of Mercury in marine sediments

An initial method was taken from “SOP for the determination of mercury in marine biota” – Marine Institute internal document. This method required no further optimisation for the determination of mercury in sediments. The reagents and concentration of reagents were as recommended by the manufacturer (PS Analytical). The delay and rise time were set a little longer than recommended but all other parameters were as recommended. The gain and range were dictated by the concentration of the standards and were set on the day of analysis.

2.2.2 Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) Methods

In the development of analytical methods for the analysis of lead, copper, cadmium, chromium, nickel and vanadium, initial methods were taken from “Analytical Methods for Graphite tube Atomisers” – Varian, 1988. These methods required modification for use with the Zeeman instrument. Optimum conditions were chosen based upon peak shape, sensitivity, mean absorbance values and percentage relative standard deviation (%RSD) values obtained in the analysis of standards, a blank solution, and reference materials (RMs) at varying conditions. Optimisation of atomisation temperature, ashing temperature and ramp rate was carried out and optimum conditions are shown in section 2.4.3 Table 2.

2.2.3 Flame Atomic Absorption Spectroscopy (FAAS) Methods

In the development of analytical methods for zinc, aluminium, lithium, strontium and barium, initial methods were taken from “FAAS Analytical Methods” – Varian, 1989.

These methods required very little modification. An air: acetylene flame was used for the determination of zinc and lithium. Aluminium, strontium and barium analysis required a hotter nitrous oxide: acetylene flame. Some elements are partially ionised in the nitrous oxide: acetylene flame and therefore an ionisation suppressant is required, for example, potassium chloride. Optimum conditions are shown in section 2.4.4 Table 3.

2.3 ANALYTICAL INSTRUMENTATION – OPTIMISED CONDITIONS

2.3.1 Sample Decomposition

A CEM Mars5 microwave Accelerated Reaction System incorporating a turntable and 12 high-pressure vessels was used for sample digestion prior to analysis. Optimised conditions are shown below (Table 1).

Table 1. Optimised Microwave Digestion Conditions

	Power Max (w)	Power (%)	Ramp (mins)	Pressure (psi)	Control Temp (°C)	Hold (mins)
HF	1200	100	7.30	450	210	7.30
Mercury	1200	100	7.30	350	180	7.30

2.3.2 Cold Vapour Atomic Fluorescence Spectrometry method for the determination of Mercury in marine sediments

All mercury measurements were performed using a 10.004 Vapour Generator, 10.023 Merlin Fluorescence Detector and a 20.100 auto sampler (P S Analytical Ltd, Kent, UK).

Cold Vapour Atomic Fluorescence Spectroscopy Parameters

Range:	100	Analysis Time (secs):	40
Fine Gain:	1.5	Rinse Time (secs):	60
Delay Time (secs):	10	Zero:	Auto
Rise Time (secs):	30	Filter:	32

2.3.3 Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) Methods

All measurements were performed using a Varian SpectrAA 220 Atomic Absorption Spectrometer with Varian GTA-96 Atomizer and Zeeman Background Correction. GFAAS was used for the analysis of lead, cadmium, chromium, copper, nickel and vanadium. The optimised conditions for each method are tabulated below.

Table 2: Optimised GFAAS conditions for Varian SpectrAA 220 Atomic Absorption Spectrometer

Metal	Wall / Platform Atomisation	Ashing Temperature (°C)	Atomisation Temperature (°C)	Calibration Range (µg l ⁻¹)
Lead	Pyrolytically coated Forked Platform Tube	1000	2500	0 -10
Cadmium	Pyrolytically coated Forked Platform Tube	400	2100	0 – 1.0
Copper	Pyrolytically coated Forked Platform Tube	1200	2600	0 – 40
Chromium	Wall Atomisation	1000	2600	0 - 10
Nickel	Wall Atomisation	800	2800	0 – 20
Vanadium	Wall Atomisation	800	2700	0 - 160

2.3.4 Flame Atomic Absorption Spectroscopy (FAAS) Methods

All measurements were performed using a Varian SpectrAA-20 Plus Atomic Absorption Spectrometer. Some elements are partially ionised in the nitrous oxide-acetylene flame and therefore an ionisation suppressant is required, for example, potassium chloride. FAAS was used for the analysis of zinc, aluminium, lithium, strontium and barium. The optimised conditions for each method are shown in Table 3..

Table 3: Optimised FAAS conditions for Varian SpectrAA-20 Plus Atomic Absorption Spectrometer

Metal	Flame	Ionisation Suppressant	Calibration Range ($\mu\text{g l}^{-1}$)
Zinc	Air : Acetylene	-	0 – 800
Aluminium	Nitrous oxide : Acetylene	0.02% KCl	0 – 80,000
Lithium	Air : Acetylene	-	0 – 125
Strontium	Nitrous oxide : Acetylene	0.02% KCl	0 – 3000
Barium	Nitrous oxide : Acetylene	0.02% KCl	0 – 1000

Section 3: RESULTS

3.1 OVERALL RESULTS

The basic statistical properties of the data obtained are shown in Table 1, along with the provisional (p) 'Ecotoxicological Assessment Criteria' (EAC) values of certain metals as developed in support of the Oslo and Paris Convention Joint Monitoring and Assessment Programme (JAMP). EACs are defined as concentration levels of a substance above which concern is indicated. Criteria for the specific contaminants were derived using all the available ecotoxicological data that passed predefined selection and quality criteria. In a number of cases EACs are provisional due to insufficient information and in these cases higher safety factors are included. These assessment criteria can be used to identify potential areas of concern and to indicate which substances might be a goal for priority action, and should not be used as firm standards or as triggers for remedial action (OSPAR Quality Status Report - QSR2000). EACs need to be refined and updated at periodic intervals (for example, every 5-10 years) in order to take account of changes in the availability of new marine toxicity data.

OSPAR has also developed and adopted 'Background Reference Concentrations' (BRCs) as assessment criteria. In general man-made substances would be expected to have a background concentration of zero. However, due to their persistence and long-range transport many substances are now detected all over the world. Therefore typical concentrations in remote and selected parts of the OSPAR area are used as background/reference concentrations. For naturally occurring substances the BRC is the range of concentrations that would be anticipated to be present in the environment in the absence of any human activity. Ranges of background/reference concentrations of metals for fine-grained sediments are given as metal/aluminium ratios and are shown in Table 1. The range is a range of medians found in world wide low polluted areas. There are few reliable data on the concentrations of trace elements in oceanic Atlantic waters and therefore the OSPAR background reference values cannot be applied to this region (Regional QSR2000 – Region 5 Wider Atlantic). In this study, these values were used only as an indication of baseline values.

Table 1: Summarised results of trace metal concentrations measured in total sediments from 32 surface sediment samples taken from the Rockall Trough (mg kg^{-1} dry weight, unless stated otherwise). Ecotoxicological assessment criteria (EAC) values for trace metals in sediments are taken from the Oslo Paris Conventions for the Prevention of Marine Pollution Joint Meeting (OSPAR) Brussels: 2-5 September 1997. (p= provisional value)

Determinand	Mean	Median	Standard Deviation	Range	Ecotoxicological Assessment Criteria
Mercury	0.069	0.045	0.071	0.025 – 0.353	0.05 – 0.5 (p)
Lead	8.51	8.45	2.40	3.43 – 16.2	5 – 50 (p)
Cadmium	0.251	0.144	0.442	0.027 – 2.57	0.1 – 1 (p)
Chromium	28.7	27.4	8.18	15.1 – 54.2	10 – 100 (p)
Copper	17.1	14.6	8.78	5.89 – 42.7	5 – 50 (p)
Nickel	18.3	15.5	7.33	8.83 – 38.9	5 – 50 (p)
Zinc	41.4	32.9	26.6	18.0 – 149	50 – 500 (p)
Vanadium	45.4	40.3	25.9	16.4 – 139	-
Strontium	950	939	440	214 – 2089	-
Barium	324	316	106	115 – 543	-
Lithium	19.7	17.4	10.6	4.51 – 55.7	-
Aluminium (%)	2.70	2.60	1.19	0.860 – 6.23	-

Table 2: Total metal concentrations (mg kg⁻¹) dry weight in total sediments from 32 surface sediment samples taken from the Rockall Trough

RSG Code	Latitude	Longitude	MI Lab Code	Mercury	Lead	Cadmium	Chromium	Copper	Nickel	Aluminium	Lithium	Zinc	Vanadium	Strontium	Barium	% <63µm	% < 1mm
83/29-sc001	52.0035	-15.2202	SED001	0.231	7.66	0.264	31.5	24.5	19.7	29421	23.5	40.9	50.0	1024	543	93.6	100.0
83/23-sc002	52.317	-15.4465	SED002	0.353	8.46	0.206	19.3	16.8	14.5	15095	12.8	18.0	27.5	996	318	28.8	91.4
74/06-sc001	52.71967	-14.9932	SED003	0.074	6.88	0.347	26.6	10.6	13.0	20262	15.4	22.8	29.7	828	257	49.8	99.4
83/03-sc002	52.9195	-15.4217	SED004	0.050	10.7	0.033	46.3	42.7	29.4	45298	31.4	63.3	101	486	443	65.0	97.1
83/05-sc001	52.9365	-15.1242	SED005	0.043	5.91	0.207	23.6	16.0	17.8	17570	12.2	25.2	25.5	1052	423	59.3	94.6
83/05-sc002	52.93633	-15.0568	SED006	0.055	6.28	0.135	25.7	13.8	14.2	17110	9.97	21.6	26.8	939	299	39.3	97.8
74/01-sc001	52.95667	-14.8312	SED007	0.194	10.4	2.57	26.2	13.6	19.1	13742	11.4	149	24.8	2089	219	0.0	0.0
74/01-sc002	52.94817	-14.811	SED008	0.025	8.80	0.084	26.9	7.14	10.2	20080	13.2	24.8	27.4	915	280	22.8	98.3
74/01-sc003	52.94833	-14.8108	SED009	0.031	9.51	0.157	25.1	7.59	11.2	20775	16.8	33.7	30.0	940	252	21.1	99.1
75/18-sc001	53.4345	-14.4625	SED010	0.174	9.17	0.273	27.9	14.3	25.8	21149	17.9	32.0	30.9	1557	323	57.5	55.0
16/28-sc001-e	54.03117	-13.5197	SED011	0.029	8.44	0.167	26.8	13.0	16.0	24683	9.62	31.6	41.3	740	325	24.1	94.7
16/28-sc002-b	54.0285	-13.5018	SED012	0.077	8.37	0.027	15.1	9.20	12.8	13319	10.5	18.1	23.8	1095	188	10.7	98.5
77/09-sc001	55.83133	-14.3705	SED013	0.046	7.20	0.049	28.3	29.5	23.8	29547	30.6	47.4	51.4	1235	515	95.0	100.0
78/28-sc004-c	56.02033	-14.4348	SED014	0.041	7.68	0.502	21.5	16.8	13.5	13662	15.1	101	26.7	1925	211	45.3	53.3
78/28-sc005-d	56.02117	-14.4593	SED015	0.062	6.17	0.041	28.3	15.0	15.6	19461	8.78	36.1	46.1	1223	259	35.0	100.0
78/28-sc006-e	56.03383	-14.46	SED016	0.030	5.51	0.237	26.7	13.9	13.5	18615	8.89	34.2	38.6	1307	275	43.0	100.0
78/28-sc007-b	56.03433	-14.4378	SED017	0.047	5.64	0.187	29.2	14.0	16.0	18467	9.65	29.3	36.1	1332	221	36.7	99.9
78/28-sc008-a	56.02783	-14.4485	SED018	0.047	3.43	0.521	15.1	9.47	9.01	8606	4.51	19.3	16.4	1153	115	16.3	100.0
78/30-sc001	56.07883	-14.1003	SED019	0.035	9.28	0.152	33.4	26.2	27.3	40813	28.0	56.4	71.8	903	398	74.7	84.6
8/02-sc001	55.89867	-13.7608	SED020	0.062	8.14	0.383	25.2	27.7	25.7	30666	14.7	48.6	44.9	1293	481	94.7	100.0
8/09-sc001	55.83317	-13.25017	SED021	0.063	7.43	0.223	22.6	35.0	32.7	32299	20.8	47.8	39.4	1226	489	93.0	100.0
9/07-sc001	55.77979	-12.7233	SED022	0.061	7.83	0.374	29.3	35.1	26.5	34379	25.1	51.2	44.7	1234	510	97.4	100.0
11/20-sc001-e	55.42533	-10.0315	SED023	0.039	9.04	0.079	23.5	9.56	12.6	27236	20.4	27.3	29.7	618	225	45.5	100.0
11/20-sc002-b	55.4275	-10.0118	SED024	0.027	10.1	0.085	40.8	13.7	20.6	43570	34.1	43.3	59.1	375	265	56.7	99.9
11/20-sc003-a	55.42083	-10.0227	SED025	0.030	8.72	0.116	26.2	5.89	8.83	18485	12.6	22.0	29.7	618	200	6.1	99.8
11/20-sc004-d	55.414	-10.0335	SED026	0.041	16.2	0.078	54.2	19.7	38.9	62309	55.7	74.1	139	214	371	87.0	99.7
11/20-sc005-c	55.41617	-10.014	SED027	0.036	14.5	0.079	45.0	16.1	25.5	47958	38.0	52.7	101	253	324	60.8	87.2
11/20-sc006-d	55.41033	-10.1307	SED028	0.052	9.21	0.084	31.0	15.9	15.5	32194	25.1	32.1	49.7	633	354	83.2	100.0
11/20-sc007-c	55.41383	-10.114	SED029	0.043	9.41	0.082	28.4	12.3	12.9	30188	23.1	24.8	45.6	509	314	68.0	99.8
11/20-sc008-a	55.41683	-10.1203	SED030	0.033	7.96	0.105	28.0	16.2	14.5	33191	24.3	30.2	48.3	578	346	81.5	100.0
11/20-sc009-e	55.41983	-10.126	SED031	0.041	9.76	0.093	30.8	14.9	14.5	31819	24.3	36.8	49.4	581	331	82.9	100.0
11/20-sc010-b	55.42367	-10.1098	SED032	0.036	8.53	0.106	28.0	12.4	13.9	30866	21.7	28.0	46.2	525	302	72.3	100.0

For meaningful temporal and spatial comparisons of the contaminant concentrations in sediment monitoring, it is essential to normalise for the influence of natural variability in sediment composition.

3.2 NORMALISATION

The simplest approach when using geochemical normalisation is to normalise metal concentrations as ratios to another constituent of the sediment. There is no consensus about the most appropriate sediment constituent to be used for normalisation. In this approach, it is assumed that the relationship between a normalising element and another metal is linear i.e. should the concentration of the normalising element vary because of changing mineralogy and particle size, the other metal will adjust proportionally. The normalising element must, therefore, be an important constituent of one or more of the major trace metal carriers and reflect their granular variability in the sediments and its concentration should not be anthropogenically altered. As a result, the regional trace metal/ normaliser ratio remains constant with changes in grain size and sedimentation rates.

3.2.1 Choice of Normaliser

Choice of normaliser is largely dependent on the origin of the sediment. Aluminium is often used because it is an indicator of the amount of aluminosilicates present in the sample. Both clay minerals and feldspars (detrital minerals) contain Al and these Al-containing minerals, especially clay minerals, contain other metals in their crystal structure. Its use has been questioned if sediments originate from glacial erosion of igneous rocks, because in such cases, sandy sediments still contain some feldspars which have low trace metal concentrations (ICES/HELCOM, 1993). In such cases, it has been found that contaminant / aluminium ratios are not suitable for normalising granular variability (Loring, 1990). Lithium is not usually present in feldspars and is therefore a useful alternative to aluminium.

Clay minerals, which are most efficient metal absorbers, also contain Li, whereas feldspars usually don't. For this reason, one could expect an enhanced correlation between Li and trace metals. Another advantage of both lithium and aluminium is that they can be easily measured in sediments. The effectiveness of both Al and Li as co-factors for normalisation was assessed.

3.2.2 Effectiveness of Co-Factors

The effectiveness of each co-factor was assessed based on metal/normaliser correlation. The strength of each correlation was determined by calculating correlation coefficients (r) for each contaminant, which reflects the extent of a linear relationship between two data sets. Table 3 indicates the scale on which the strength of a correlation is assessed (Fowler et al, 1998).

Table 3: Interpretation of correlation coefficients (r)

Value of Coefficient (r)	Meaning
0.00 to 0.19	A very weak correlation
0.20 to 0.39	A weak correlation
0.40 to 0.69	A modest correlation
0.70 to 0.89	A strong correlation
0.90 to 1.00	A very strong correlation

The numerical value of the correlation coefficient (r), falls between two extreme values: +1 (for perfect positive correlation) and -1 (for perfect negative correlation). The closer the value of a coefficient is to -1 or +1, the greater is the strength of the correlation, whilst the closer it is to 0 the weaker it is. Metal/aluminium and metal/lithium relationships are shown in Appendix 3 and 4 and summarised correlation coefficients for both metal/aluminium and metal/lithium are shown in Table 4.

In comparing the strength of metal/lithium and metal/aluminium correlation coefficients, it can be seen that strong or very strong metal/normaliser correlations were obtained for lead, chromium and vanadium using both aluminium and lithium. Modest correlations were obtained for copper, nickel, strontium and barium. Mercury, cadmium and zinc all display weak correlations with both aluminium and lithium. All correlations were positive, with the exception of mercury, cadmium and strontium. From this information, it was concluded that there was no significant difference between Co-Factors.

Table 4: Summarised Metal/Normaliser Correlation Coefficients (r)

Metal	Metal/Lithium	Metal/Aluminium
Mercury	-0.1559	-0.2598
Lead	0.7923	0.7451
Cadmium	-0.2439	-0.3084
Chromium	0.8464	0.8831
Copper	0.4077	0.4888
Nickel	0.6942	0.7340
Zinc	0.2571	0.1836
Vanadium	0.8808	0.9193
Strontium	-0.5758	-0.6495
Barium	0.4472	0.5111
Aluminium	0.9370	-
Lithium	-	0.9370

Lithium however, has the advantage of being a more universal co-factor and has been widely used in place of aluminium in the past few years. It is superior to Al for normalisation of metal data from sediments derived mainly from glacial erosion of crystalline rocks, and equal or superior to Al for those derived from non-crystalline rocks (Loring 1990). For this reason, it has been chosen to normalise metal concentrations.

3.3 ASSESSMENT OF RESULTS

3.3.1 Mercury

Mercury is one of the most toxic elements and is widely distributed at various levels throughout the environment. Sediments serve as a sink for mercury where adsorption of mercury and its toxicity are dependent on its chemical forms. Mercury concentrations in relatively pristine marine sediments are expected to be below 1 mg kg^{-1} (Sadiq, 1992). Elevated concentrations are found in areas where anthropogenic or natural inputs are expected. Results of this study showed that mercury levels ranged from 0.025 mg kg^{-1} to 0.353 mg kg^{-1} , with a median value of 0.045 mg kg^{-1} all of which are below 1 mg kg^{-1} , which would suggest that there is no enrichment in this area. The majority of the concentrations detected are below the provisional EAC values for mercury, suggesting no harm to the marine environment could be expected from levels measured. The remainder of the values fall within the range and therefore the possibility of harmful effects cannot be excluded. The distribution pattern of raw and Li normalised values are shown in Appendix 2, Fig A2.1. Four sample cores (83/29-sc001, 83/23-sc002, 74/01-sc001 and 75/18-sc001) all taken from the flank of the Porcupine bank, showed high concentrations of mercury, but the levels measured were well below the upper EAC value quoted in Table 1.

3.3.2 Lead

Lead as a pollutant, has assumed particular importance due to its relative toxicity to humans. Lead occurs in the environment in a wide range of physical and chemical forms, which greatly influence its behaviour and its effects on the ecosystem. Lead levels ranged from 3.43 mg kg^{-1} (78/28-sc008-a from the eastern flank of the Rockall Bank, which consisted of 16.33% $<63\mu\text{m}$) to 16.2 mg kg^{-1} (11/20-sc004-d, located on the north east Rockall Trough slopes, which consisted of 86.95% $<63\mu\text{m}$), with a median value of 8.45 mg kg^{-1} . With the exception of 78/28-sc008-a, which was below the provisional EAC values for lead, all values were within the range. The distribution pattern of raw and Li normalised values are shown in Appendix 2, Fig A2.2. The lead/lithium ratios, which appear to be higher than the other samples, are due to low lithium values rather

than high lead values, these values appear as outliers in the Pb/Li regression plot in Appendix 3, Fig A3.2.

Samples containing high lead concentrations also contain high levels of lithium, which would suggest that the levels are not a result of enrichment. The maximum value detected was lower than was reported in an ICES baseline study of surface sediments in the North Sea 1990/1991, which detected a mean of 21 mg kg⁻¹ from analysis of 601 samples.

3.3.3 Cadmium

Cadmium is regarded as a priority pollutant because of its toxicity to both marine organisms and humans. It is one of the most important elements to be determined in marine sediments. The natural background concentration of cadmium is relatively low in comparison to other more abundant metals, for example, copper. Cadmium concentrations in pristine marine sediments are generally less than 1 mg kg⁻¹. The levels of cadmium measured in sediments during this study ranged from 0.027 mg kg⁻¹ to 2.57 mg kg⁻¹ with a median value of 0.144 mg kg⁻¹. The maximum value of 2.57 mg kg⁻¹ was found in sample 74/01-sc001, from the flank of the Porcupine Bank, which consisted mainly of coral fragments, which may account for the high concentration of cadmium as compared to the lower concentrations present in the sand and clay samples, where the maximum measured value was 0.521 mg kg⁻¹. All of the concentrations measured in the sand and clay samples were within the provisional EAC values for cadmium in sediments. These values are close to those measured in the ICES baseline study of sediments in the North Sea where a range of 0.010 mg kg⁻¹ to 0.38 mg kg⁻¹ was detected. The distribution pattern of raw and Li normalised values are shown in Appendix 2, Fig A2.3. When normalised, the concentration of cadmium in 74/01-sc001 remains high, this is as a result of low lithium concentration in this sample. This sample appears as an outlier in the Cd/Li correlation (Appendix 3, Fig A3.3). Studies have been carried out in the past on corals, which state that metals may accumulate in coral tissue and skeleton (Esslemont, 2000).

3.3.4 Chromium

Of all metals, chromium has very unique toxicological characteristics, which are dependent on which chemical form is present. Chromium is often a difficult element to determine in geological matrices at trace levels because when present in the mineral form of chromite (FeCr_2O_4) it is highly resistant to acid attack (Liu, 1996). Chromium levels ranged from 15.1 mg kg^{-1} (16/28-sc002-b, from the eastern flank of the Rockall trough, which consisted of $10.71\% < 63\mu\text{m}$) to 54.2 mg kg^{-1} (11/20-sc004-d, from the north east Rockall Trough slopes, which consisted of $86.95\% < 63\mu\text{m}$), with a median value of 27.4 mg kg^{-1} , all of which are within the provisional EAC values for chromium in sediments. The distribution pattern of raw and Li normalised values are shown in Appendix 2, Fig A2.4. As was the case for lead, samples showing high Cr/Li ratios are a result of low lithium values rather than high chromium values. These samples appear as an outlier in the Cr/Li correlation (Appendix 3, Fig A3.4). The values measured are well below those measured in North Sea sediments ICES baseline study ($3\text{-}117 \text{ mg kg}^{-1}$).

3.3.5 Copper

Copper is a biotoxic pollutant and anthropogenic inputs are the major source of environmental contamination. It is widely distributed in nature and once entered in a marine system, copper may remain dissolved or adsorbed on particulates in seawater, be absorbed by organisms or sink to the sediments (Sadiq, 1992). Copper levels in this study ranged from 5.89 mg kg^{-1} (11/20-sc003-a, from the north east Rockall Trough slopes) to 42.7 mg kg^{-1} (83/03-sc002, from the flank of the Porcupine Bank), with a median of 14.6 mg kg^{-1} all of which fall within the provisional EAC values for copper in sediments. The distribution pattern of copper and Li normalised values are shown in Appendix 2, Fig A2.5. Copper shows a modest correlation with lithium as can be seen in Appendix 3, Fig A3.5. Three of the four outliers evident in this correlation (8/02-sc001, 8/09-sc001 and 9/07-sc001) are from the northwest flank of the Rockall Trough. After normalisation, these concentrations remain high due to low lithium values rather than high copper values. Sample 83/03-sc002, containing the highest amount of copper also contains a high lithium concentration, which would suggest that the copper present is at a natural level.

3.3.6 Nickel

Twice as abundant as copper, nickel constitutes about 0.007 percent of the Earth's crust and is a fairly common constituent of igneous rocks. Nickel has also been associated with crude oil. The levels of nickel measured in sediments during this study ranged from 8.83 mg kg⁻¹ (11/20-sc003-a, consisting of 6.11% <63µm) to 38.9 mg kg⁻¹ (11/20-sc004, consisting of 86.95% <63µm), with a median value of 15.5 mg kg⁻¹ all of which fell within the provisional EAC values for nickel in sediments. The distribution pattern of raw and Li normalised values are shown in Appendix 2, Fig A2.6. Samples taken from the northwest flank of the Rockall Trough contain low concentrations of lithium and therefore when normalised, nickel concentrations appear large in comparison to other areas. As a result of this, these samples appear as outliers in the Ni/Li correlation in Appendix 3, Fig A3.6. The values measured are well below those measured in North Sea sediments ICES baseline study 1990/1991 (1.5-113 mg kg⁻¹, mean = 23 mg kg⁻¹).

3.3.7 Zinc

Zinc is never found as the free metal but there are a number of important ores such as sphalerite (zincblende, zinc sulphide, ZnS), smithsonite (zinc carbonate, ZnCO₃) and zincspar (also zinc carbonate, ZnCO₃). Zinc is wide spread around the world. Levels of 107-243 mg kg⁻¹ and 90-240 mg kg⁻¹ have been measured in Gulf of Finland and Bothnian Sea respectively (Leivuori, 1998) and 3-510 mg kg⁻¹ (mean, 39 mg kg⁻¹) measured in North Sea sediments (ICES Baseline Study 1990/1991). The concentration of zinc measured in this study ranged from 18.0 to 149 mg kg⁻¹ with a median value of 32.9 mg kg⁻¹. The majority of which were below the provisional EAC values for zinc in sediments shown in Table 1. Two samples (74/01-sc001, from the flank of the Porcupine Bank and 78/28-sc004-c from the eastern flank of the Rockall Bank), consisted mostly of coral fragments, these correspond to the two highest concentrations of zinc present. The distribution pattern of zinc and Li normalised values are shown in Appendix 2, Fig A2.7. As with cadmium, the highest metal concentration is found in the coral samples. These concentrations remain high after normalisation due to low Li concentrations and appear as outliers in on the plot of Zn/Li correlation (Appendix 3, Fig A3.7), and are the cause of

the poor correlation. Removal of these coral samples would result in a correlation coefficient (r) of 0.7870, which indicates a strong correlation.

3.3.8 Vanadium

Vanadium is not found as the free metal in nature but is present in many minerals. It is also found in phosphate rock and certain iron ores, and is present in some crude oils in the form of organic complexes and in small percentages in meteorites. Vanadium levels ranged from 16.4 mg kg⁻¹ (sample 78/28-sc008-a, from the eastern flank of the Rockall Bank) to 139 mg kg⁻¹ (11/20-sc004-d, from the north east Rockall Trough slopes), with a median value of 32.9 mg kg⁻¹. At present, there are no EAC values for vanadium. The distribution pattern of raw and Li normalised values are shown in Appendix 2, Fig A2.8. The same trends are observed with vanadium as have been observed with lead, chromium and nickel for samples from the northwest flank of the Rockall Trough. Lithium concentrations in these samples are quite low and therefore when normalised vanadium concentrations appear high. The high vanadium concentration present in sample 11/20-sc004-d corresponds to a high lithium concentration and as a result this does not suggest enrichment. Levels of 57-96 mg kg⁻¹ and 49-114 mg kg⁻¹ have been measured in Gulf of Finland and Bothnian Sea respectively (Leivuori, 1998). Higher levels were detected in Baltic Sea sediments during a 1993 ICES/HELCOM Baseline Study (57.6-193 mg kg⁻¹).

3.3.9 Strontium

Strontium metal is rarely found free in nature. The principal strontium ores are celestite and strontianite. From a geochemical point of view strontium is an important trace-to-minor constituent of sediments, in part because of its participation in biological processes and in part because of its varying solubility in low-temperature geochemical processes (Bowker, 1982). The levels of strontium measured in sediments during this study ranged from 214 mg kg⁻¹ to 2089 mg kg⁻¹ with a median value of 939 mg kg⁻¹.

The highest concentrations of strontium were found in samples 74/01-sc001 and 78/28-sc004-c, both of which contain large amounts of coral. At present, there are no EAC values for strontium. The distribution pattern of raw and Li normalised values are shown

in Appendix 2, Fig A2.9. As with cadmium and zinc, the coral samples contain the highest metal concentration and these concentrations remain high after normalisation due to low Li concentrations. These samples appear as outliers in the plot of Sr/Li correlation. The pattern observed with strontium and lithium appears to be the opposite of trends with other metals. As the concentration of lithium increases, strontium concentrations decrease, resulting in a negative correlation, which can be seen in Appendix 3, Fig A3.9. Very little work has been carried on strontium in sediments in the past and as a result no values were available for comparison purposes.

3.3.10 Barium

Elemental barium is never found in nature. It constitutes approximately 0.04 percent of the earth's crust, chiefly as the minerals barite and witherite. Barite occurs in sedimentary rocks such as limestone, in clay deposits formed by the weathering of limestone and in marine deposits, for example, plankton detritus is a source of Biogenic barium. Commercially, barite (BaSO_4) is the standard densification agent used in drilling fluids worldwide. Analysis of barium in marine sediments and earth materials has become an important way to trace drilling mud components in offshore areas however, it is very new research and no values for comparative purposes were available. Barium levels ranged from 115 mg kg^{-1} (78/28-sc008-a from the eastern flank of the Rockall Bank) to 543 mg kg^{-1} (83/29-sc001, from the flank of the Porcupine Bank), with a median value of 316 mg kg^{-1} . At present, there are no EAC values for barium. The distribution pattern of barium and Li normalised values are shown in Appendix 2, Fig A2.10.

3.3.11 Lithium

Lithium does not occur as the free metal in nature because of its high reactivity. It is a lattice component of fine-grained major trace metal bearing minerals. It is structurally combined to clay minerals in micas and may therefore be used as a tracer of clay minerals. Its presence is not usually influenced by anthropogenic activity. Levels of $49\text{--}77 \text{ mg kg}^{-1}$ (mean = 59 mg kg^{-1}) and $26\text{--}147 \text{ mg kg}^{-1}$ (mean = 59 mg kg^{-1}) have been measured in Gulf of Finland and Bothnian Sea respectively (Leivuori, 1998). Higher levels were detected in Baltic Sea sediments during a 1993 ICES/HELCOM Baseline

Study (33.3-140 mg kg⁻¹). The concentration of lithium measured in this study ranged from 4.51 (78/28-sc008-a, consisting of 16.33% <63µm) to 55.7 mg kg⁻¹ (11/20-sc004-d, consisting of 86.95% <63µm), with a median value of 17.4 mg kg⁻¹.

3.3.12 Aluminium

The marine geochemistry of Al has an important bearing on many chemical processes, which may influence the chemical behaviour of trace metals in the marine environment. For example, Al oxide surfaces play an important role in the adsorption of trace metals. Excess Al from seawater is scavenged to settle to the bottom sediment. Aluminium levels ranged from 0.86 % (78/28-sc008-a, consisting of 16.33% <63µm) to 6.2% (11/20-sc004-d, consisting of 86.95% <63µm). Aluminium showed a very strong correlation with lithium, which was to be expected. The distribution pattern of aluminium and lithium normalised values are shown in Appendix 2, Fig A2.11. Values detected in this study are similar to those measured in North Sea sediments (ICES Baseline Study 1990/1991) where aluminium concentrations ranged from 0.1-9.2% with a mean value of $2.2 \pm 1.6\%$ for 532 samples.

3.4 QUALITY ASSURANCE

The analytical quality assurance programme included the use of a number of Certified Reference Materials (CRMs) to validate the accuracy and precision of the analytical methods developed and to provide ongoing quality control. Participation in QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring) an international proficiency-testing scheme, also underpins analytical quality.

3.4.1 Certified Reference Materials

A Certified Reference Material is “a reference material accompanied by a certificate, one or more of whose property values are certified by a procedure, which establishes traceability to an accurate realization of the unit in which the property values are

expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence” (ISO Guide 30, 1992).

During the period of sample analysis, four sediment reference materials were analysed alongside each batch of samples, to ensure the quality of analyses. CRMs used were: BCSS-1, a dried marine sediment, PACS-1, a dried harbour sediment and MESS-1, a dried estuarine sediment, all of which were obtained from the National Research Council of Canada (NRCC). A QUASIMEME reference material, QTMO49MS, a dried marine sediment from a relatively unpolluted site, was also used for validation purposes. QUASIMEME materials are not certified; they are given assigned values derived by the QUASIMEME project office using established reference laboratory data. For a true reflection of accuracy, a CRM is required. The results are shown below in Table 5.

Table 5: Results of the analyses of certified reference materials during this study

Determinand	Reference Material	Assigned Value (mg kg ⁻¹)	Certified (y / n)	Measured Value ± Standard Dev. (mg kg ⁻¹ dry wt.)	No. of Analyses
Mercury	PACS-1	4.57	y	4.56 ± 0.62	9
	QTMO49MS	0.289	n	0.36 ± .01	4
Lead	BCSS-1	22.7	y	19.2 ± 2.7	11
	QTMO49MS	48.07	n	45.2 ± 4.6	12
Cadmium	BCSS-1	0.250	y	0.28 ± 0.04	8
	QTMO49MS	0.383	n	0.48 ± 0.08	6
Chromium	BCSS-1	123	y	81.3 ± 9.2	4
	QTMO49MS	89.38	n	81.5 ± 4.9	6
Copper	BCSS-1	18.5	y	21.0 ± 1.2	4
	QTMO49MS	17.5	n	19.9 ± 2.3	4
Nickel	BCSS-1	55.3	y	49.5 ± 2.6	4
	QTMO49MS	27.81	n	28.3 ± 3.8	4
Aluminium	BCSS-1	6.26	y	6.19 ± 0.15	15
	QTMO49MS	4.69	n	4.91 ± 0.5	15
Lithium	QTMO49MS	41.58	n	46.8 ± 4.6	20
Zinc	BCSS-1	119	y	112 ± 6.9	12
	QTMO49MS	148	n	166 ± 21.5	12
Vanadium	BCSS-1	93.4	y	113 ± 9.2	11
	PACS-1	127	n	138 ± 21.2	10
Strontium	PACS-1	277	y	284 ± 7.0	20
Barium	BCSS-1	-	n	341 ± 31.9	33
	MESS-1	-	n	329 ± 45.2	12

The accuracy of the results from the analysis of reference material was assessed using Z score determination, which involves calculating the error associated with the result. Z scores give an indication of how close the measured value is to the assigned value. A Z-score of zero indicates that the values are the same. A Z-score between -2 and +2 is considered to be a satisfactory performance and the results are suitable for use in international marine monitoring such as the Oslo Paris Convention and the Helsinki Convention. Proportional and constant error values are required in order to calculate a Z score. Total allowable error increases with decreasing concentration. This is in accordance with the observation of Horowitz. The Horowitz Equation states that:

$$CV = 2^{(1-0.5\log C)}$$

where C is the concentration expressed as powers of 10 (e.g. 1ppm = 10^{-6}). The coefficient of variation (CV) doubles for each decrease of concentration of two orders of magnitude (Horowitz, 1982).

Where values for proportional and constant errors were not available, limits of $\pm 25\%$ of the assigned value (which correspond to a Z scores of ± 2) were used. Z scores were used in the assessment of the reference materials used during mercury, lead, cadmium, chromium, copper, nickel, zinc, aluminium and lithium analysis. In the assessment of strontium and vanadium results limits of $\pm 25\%$ of the assigned value were used. All Z scores calculated for reference materials analysed alongside samples were within ± 2 and during the analyses of vanadium and strontium, all values fell within the limits of $\pm 25\%$ and were therefore considered acceptable.

In the case of Barium, no certified value was available for the reference materials used, however, precision was calculated by repeat analysis over a two month period. Following the repeatability studies, statistical analysis was carried out to determine the mean value for each reference material and the limits around this mean based upon ± 2 standard deviations and QUASIMEME limits of $\pm 25\%$. These limits were then used in assessing the accuracy of the results obtained during sample analysis. The mean value obtained was used as the assigned value for barium during the QA of the sample analysis.

Barium results of 341 mg kg⁻¹ and 329 mg kg⁻¹ for BCSS-1 and MESS-1 respectively, indicate results to be in good agreement with those determined by the NRCC and by Krause et al (within $\pm 25\%$), shown in Table 6. This suggests that the accuracy of the method is acceptable for monitoring purposes.

Table 6: Barium reference material results from other laboratories

Reference Material	Concentration (mg kg⁻¹)	Method	Reference
BCSS-1	260	INAA	NRCC
BCSS-1	362	INAA	NRCC
MESS-1	301 \pm 5	XRF	NRCC
MESS-1	290	ICP	Krause et al
MESS-1	340	TXRF	Krause et al

INAA – Instrumental Neutron Activation Analysis

ICP – Inductively Coupled Plasma

XRF – X-Ray Fluorescence

TXRF – Total Reflection X-Ray Fluorescence

3.4.2 Proficiency Testing

Proficiency testing is a method for regularly assessing the accuracy of laboratories in conducting particular measurements. It usually involves the distribution of effectively identical portions of test material to each participant for analysis as an unknown, under routine conditions. Reported results are converted to a score, which enables the participant to assess the accuracy of the result.

The Marine Institute participates in QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring), an international proficiency-testing scheme. This programme provides external QA for national and international monitoring programmes and for individual or collaborative research. Participants may use the assessment of the study data to validate internal QA, support accreditation and support QA of

environmental monitoring data. The Marine Institute participated in two rounds of testing during the course of this work (October 2000 and April 2001).

Two sediment test materials (QTMO51MS – dried marine sediment sampled from Clyde Estuary, Scotland and QTMO52MS – dried marine sediment sampled from the Wadden Sea, The Netherlands) were analysed in October 2000, for mercury, aluminium, zinc and lithium using the methods developed. These results were assessed and their accuracy determined. An assigned value was provided for each determinand and a Z-score (bias) calculated. Results are shown in Table 7.

Table 7: Results of the analyses of QUASIMEME test materials Round 22, October 2000

Test Material	Units	Obtained Value	Assigned Value	Z-score
QTMO51MS				
Aluminium	%	6.85	5.75	1.43
Lithium	mg kg ⁻¹	43.7	45.4	-0.31
Mercury	mg kg ⁻¹	0.727	0.682	0.50
Zinc	mg kg ⁻¹	458.48	653.64	-2.35
QTMO52MS				
Aluminium	%	5.31	4.69	0.98
Lithium	mg kg ⁻¹	43.84	46.54	-0.46
Mercury	mg kg ⁻¹	0.451	0.343	2.26
Zinc	mg kg ⁻¹	172.95	157.62	0.73

In April 2001, two sediment test materials (QTMO53MS – dried marine sediment sampled from the Ayrshire Coast of the Clyde Sea, Scotland and QTMO54MS – dried marine sediment sampled from the North Sea) were analysed for mercury, aluminium, zinc, lithium, lead, cadmium, chromium, copper and nickel. Results are shown in Table 8.

Table 8: Results of the analyses of QUASIMEME test materials Round 24, April 2001

Test Material	Units	Obtained Value	Assigned Value	Z-score
QTMO53MS				
Aluminium	%	7.69	7.06	0.67
Cadmium	mg kg ⁻¹	0.151	0.176	-0.092
Chromium	mg kg ⁻¹	188.86	159.59	1.40
Copper	mg kg ⁻¹	52.69	46.90	0.91
Lead	mg kg ⁻¹	84.77	143.52	-3.10
Lithium	mg kg ⁻¹	69.93	63.40	0.82
Mercury	mg kg ⁻¹	0.433	0.733	-3.11
Nickel	mg kg ⁻¹	57.51	56.94	0.07
Zinc	mg kg ⁻¹	278.86	249.76	0.90
QTMO54MS				
Aluminium	%	6.52	5.92	0.77
Cadmium	mg kg ⁻¹	0.107	0.109	-0.19
Chromium	mg kg ⁻¹	74.88	71.93	0.30
Copper	mg kg ⁻¹	21.88	18.90	1.04
Lead	mg kg ⁻¹	27.03	42.29	-2.43
Lithium	mg kg ⁻¹	54.93	45.66	1.61
Mercury	mg kg ⁻¹	0.106	0.083	1.55
Nickel	mg kg ⁻¹	41.22	31.37	2.23
Zinc	mg kg ⁻¹	142.58	121.85	1.26

Section 4: CONCLUSION

This present study shows that the majority of heavy metal concentrations detected in the samples collected were at background levels. Deeper water regions are rarely exposed to the same levels of anthropogenic inputs as coastal regions and as a result lower concentrations are to be expected.

Mercury levels ranged from 0.025 mg kg^{-1} to 0.353 mg kg^{-1} , with a median value of 0.045 mg kg^{-1} . The mean value of 0.069 mg kg^{-1} is close to that reported in ICES baseline study of surface sediments in the North Sea 1990/1991 ($0.057 \pm 0.08 \text{ mg kg}^{-1}$), which they suggested was below what may be considered as an “upper background level” and implied that the sediments may be considered uncontaminated with respect to Hg. Copper levels ranged from 5.89 mg kg^{-1} to 42.7 mg kg^{-1} with a median of 14.6 mg kg^{-1} which all fall within the provisional EAC values for copper.

Lead levels ranged from 3.43 mg kg^{-1} to 16.2 mg kg^{-1} , with a median value of 8.45 mg kg^{-1} . Chromium and nickel and vanadium levels ranged from 15.1 mg kg^{-1} to 54.2 mg kg^{-1} , 8.83 mg kg^{-1} to 38.9 mg kg^{-1} and 16.4 mg kg^{-1} to 139 mg kg^{-1} respectively.

The highest values of lead, chromium, nickel, and vanadium were measured in sample 11/20-scoo4-d, taken from the North East Rockall Trough slopes. These high values may be accounted for by the fact that this sample also contained high lithium concentration and as a result suggests that the levels are not a result of enrichment. Although high in comparison to other samples, they are below levels detected in an ICES baseline study of surface sediments in the North Sea 1990/1991. In the case of the above metals, samples appearing as outliers showing high metal/Li ratios are a result of low lithium values rather than high metal values.

The levels of cadmium measured in sediments during this study ranged from 0.027 mg kg^{-1} to 2.57 mg kg^{-1} with a median value of 0.144 mg kg^{-1} . The maximum value of 2.57 mg kg^{-1} was found in sample 74/01-sc001, taken from the flank of the Porcupine Bank. This sample consisted mainly of coral fragments, which may account for the high

concentration of cadmium as compared to the lower concentrations present in the sand and clay samples, where the maximum measured value was 0.521 mg kg^{-1} . All of the concentrations measured in the sand and clay samples were within the provisional EAC values for cadmium in sediments.

Sample 74/01-sc001 also contained high concentration of Cr, Zn and Sr as compared to the lower concentrations present in the sand and clay samples. When normalised, these concentrations remain high as a result of low lithium concentration in this sample. This sample appears as outlier in the metal/Li correlations in Appendix 3. Studies have been carried out in the past on corals (Esslemont, 2000), which state that metals may bioaccumulate in coral tissue and skeleton and therefore these materials may contain higher levels compared with surrounding sediment.

In the case of barium and strontium, levels detected ranged from 115 mg kg^{-1} to 543 mg kg^{-1} and 214 mg kg^{-1} to 2089 mg kg^{-1} respectively. There was no published data available for comparison purposes on levels detected in marine sediments from other regions.

Natural variation in concentrations of metals in sediments was modeled by linear regression, using the concentration of lithium as an independent variable. Samples that exceed the upper 95% confidence interval of regression models are usually classified as enhanced. However, samples that exceed the upper limit do not necessarily suggest contamination, they may be a result of other natural sources of enhanced metal (Doherty et al, 2000).

This baseline study has shown that the levels of metals detected in surface sediments from the Rockall Trough are present at background concentrations and within the provisional EAC values for metals in sediments, where available.

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TECHNICAL ANNEX - Trace Metal Analysis

In order to determine the major, minor and trace metal concentrations in marine sediments by wet chemical methods, it is necessary to dissolve all or part of the sample. Sample digestion methods commonly used are: “total” decomposition, strong acid digestion or specific procedures (e.g. Hg). “Total” decomposition methods use hydrofluoric acid (HF) in combination with concentrated oxidizing acids or mixtures, such as aqua regia. HF is the only acid that completely dissolves the silicate lattice and releases all associated metals, such as Al and Li, used for grain size normalisation of the data, and is therefore a prerequisite of a complete digestion of aquatic sediment samples. It is however a highly dangerous acid and needs to be neutralised after the digestion process using boric acid (Wen et al, 1997).

For determination of mercury in sediments most laboratories use separate digestion procedures. It has been shown that for the quantitative release of Hg from sediments, an oxidation step with strong acids is sufficient and the silicate lattice must not be dissolved by use of HF (ICES, 1992). The reliable determination of heavy metals in sediments is dependent on the methodology used, including digestion methods, sieving etc. and is the key to comparison of data. Reagent selection is one of the key steps for a successful dissolution. Choice of reagents is dependent on many factors including matrix, analytes of interest and detection methods.

ANALYTICAL METHODS

Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is the instrumental measurement of the amount of radiation absorbed by unexcited atoms in the gaseous state. It is used for trace level analysis of many metals and some non-metals. It is particularly useful for the analysis of the first row transition metals and the heavier rare earth metals. It is also possible to analyse the alkali metals and the alkaline earth metals.

The principle techniques in AAS are Flame Atomic Absorption Spectroscopy (FAAS) and Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).

(a) Flame Atomic Absorption Spectroscopy (FAAS)

FAAS involves the introduction of an aerosol of a sample into an appropriate flame where a fraction or all of the metallic ions are converted into free atoms. As free atoms they can be detected using a photocell or photo multiplier tube and determined quantitatively. The temperature required for atomisation dictates the fuel and oxidant used. Commonly used fuels and oxidants are air, nitrous oxide and acetylene. Almost all available instruments use pneumatic nebulisation of a liquid sample to deliver a steady flow of aerosol to the flame. Flame atomic absorption spectroscopy is limited to the use of solutions. Its sensitivity is also limited due to the fact that approximately only 10% of the sample reaches the flame and the residence time of the metal atoms in the light path in a normal flame is very short.

(b) Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

GFAAS is a useful alternative to FAAS. In GFAAS the burner head and nebulisation system is replaced with a temperature controlled furnace. A discrete sample volume is introduced into the furnace via a programmable auto-sampler and after thermal pre-treatment is rapidly atomised. This results in a transient signal whose height or area is proportional to the quantity of element under study. Each heating step is independently programmable with temperature ramp and hold times in each step. The use of flameless cells has several advantages, which include, the capability of handling very small sample volumes (5-100 μ l) and of analysing solid samples directly (sometimes without pre-treatment), high sensitivity ($10^{-8} - 10^{-11}$ g) and low noise.

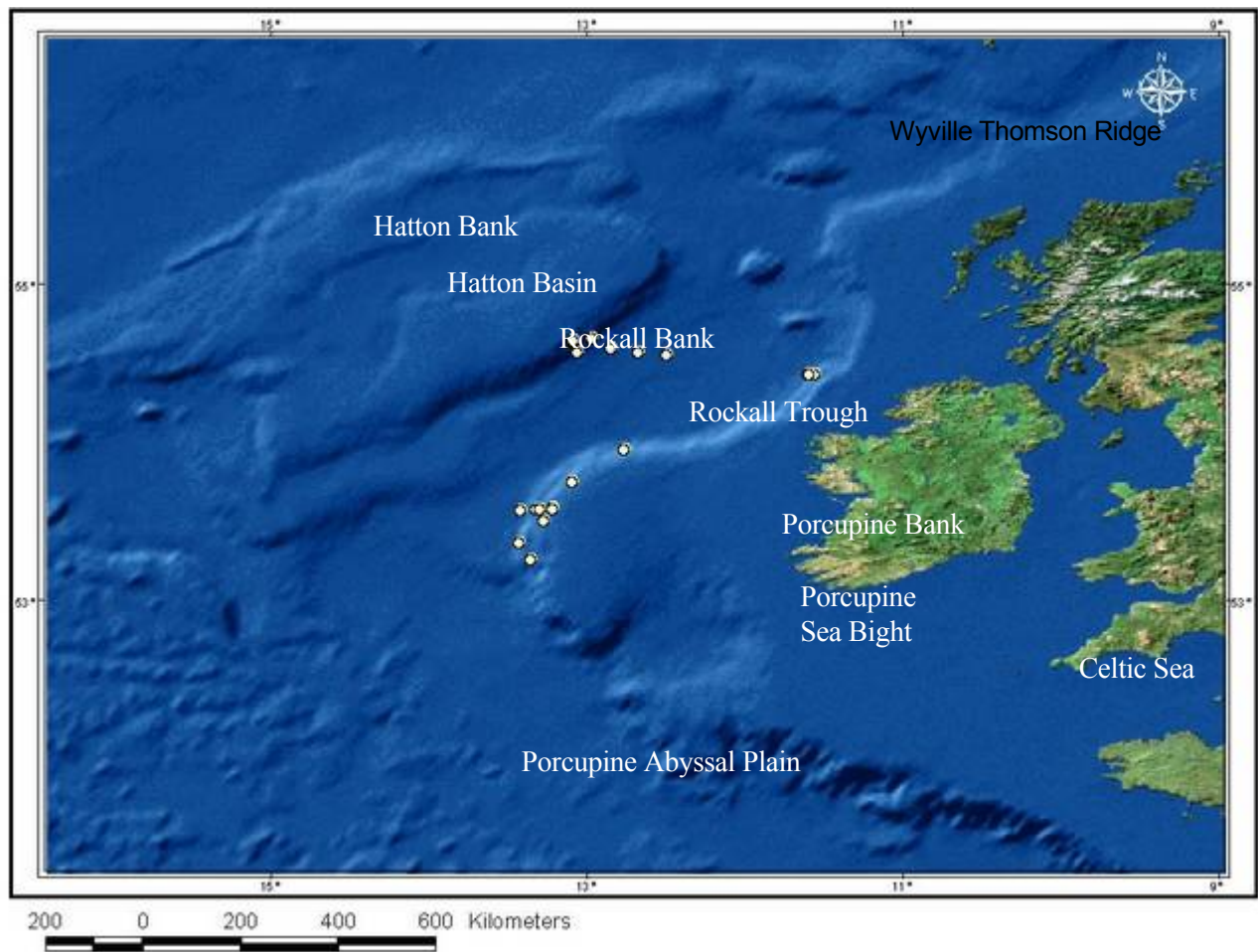
Cold Vapour Atomic Fluorescence Spectrometry (CV AFS)

Cold-Vapour Atomic Fluorescence Spectrometry for Mercury Determination involves the generation of elemental mercury vapour from a digested sample by reduction with tin (II) chloride, which is then purged from solution by an argon carrier stream.

The mercury vapour generated, is detected by atomic fluorescence spectrometry. The sample enters the detector as a gas, which is channeled through a chimney, past a light source and a photomultiplier tube, which are set at right angles to each other. The mercury vapour absorbs the light and fluoresces at its characteristic wavelength (254 nm).

Atomic fluorescence is a radiational de-activation process, which occurs after excitation of free atoms by absorption of radiation of a characteristic wavelength from an appropriate excitation source. AFS has many advantages; sensitivity attainable is controlled by the intensity of the light source, high sensitivity is attainable into the far UV where AAS is insensitive and equipment can be less complex than that required for AAS. Other advantages include; good linearity, low spectral interference and high selectivity.

Appendix 1: Locations of samples collected for the Rockall Studies Group in 1998



Appendix 2: SPATIAL DISTRIBUTIONS

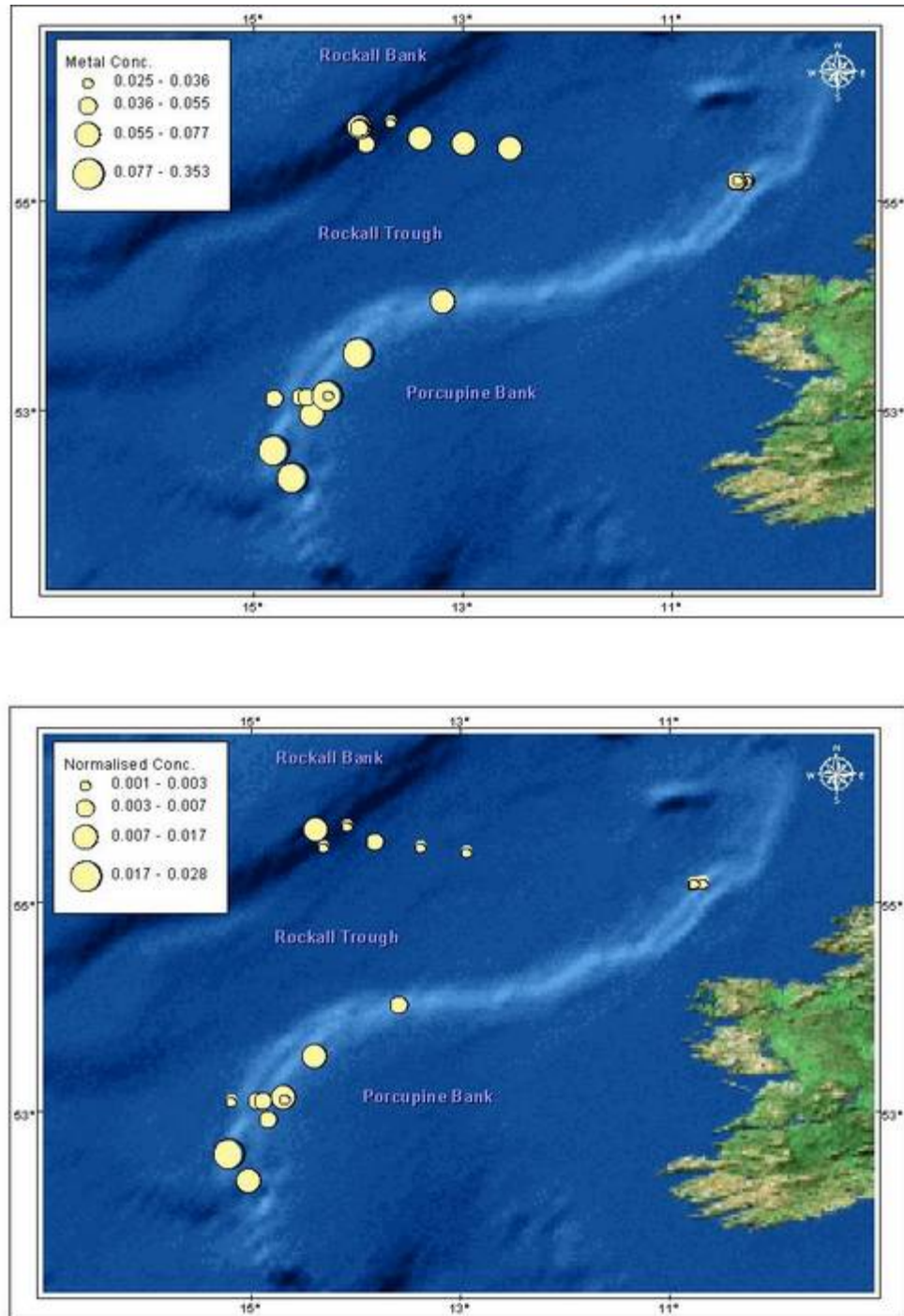


Fig A2.1 Distribution of mercury and mercury/lithium ratio in total sediments. Circle sizes are proportional to the concentration (mg kg⁻¹) and ratio measured. Absolute values are given in Section 3, Table 2.

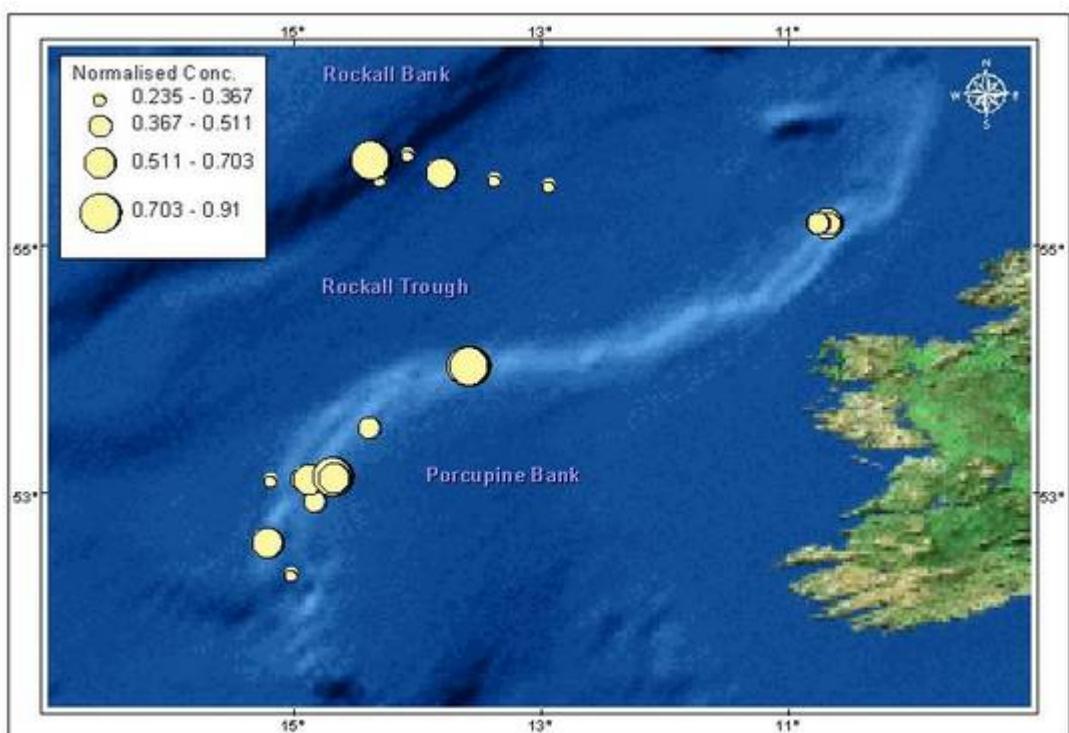
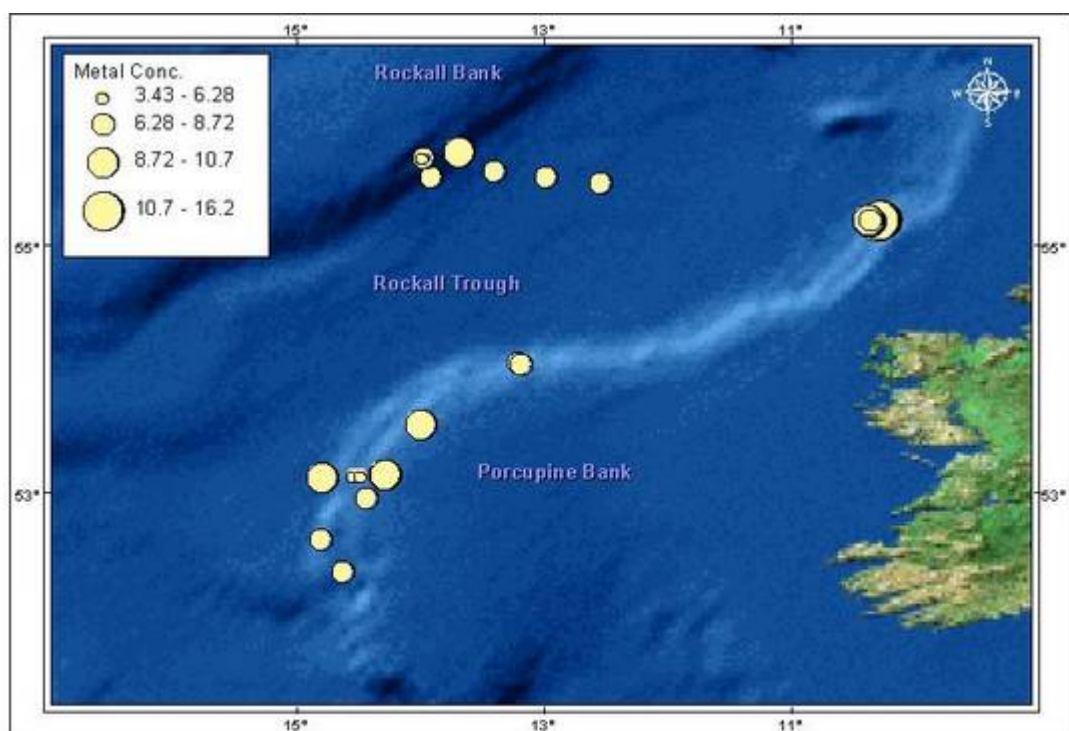


Fig A2.2 Distribution of lead (mg kg^{-1}) and lead/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

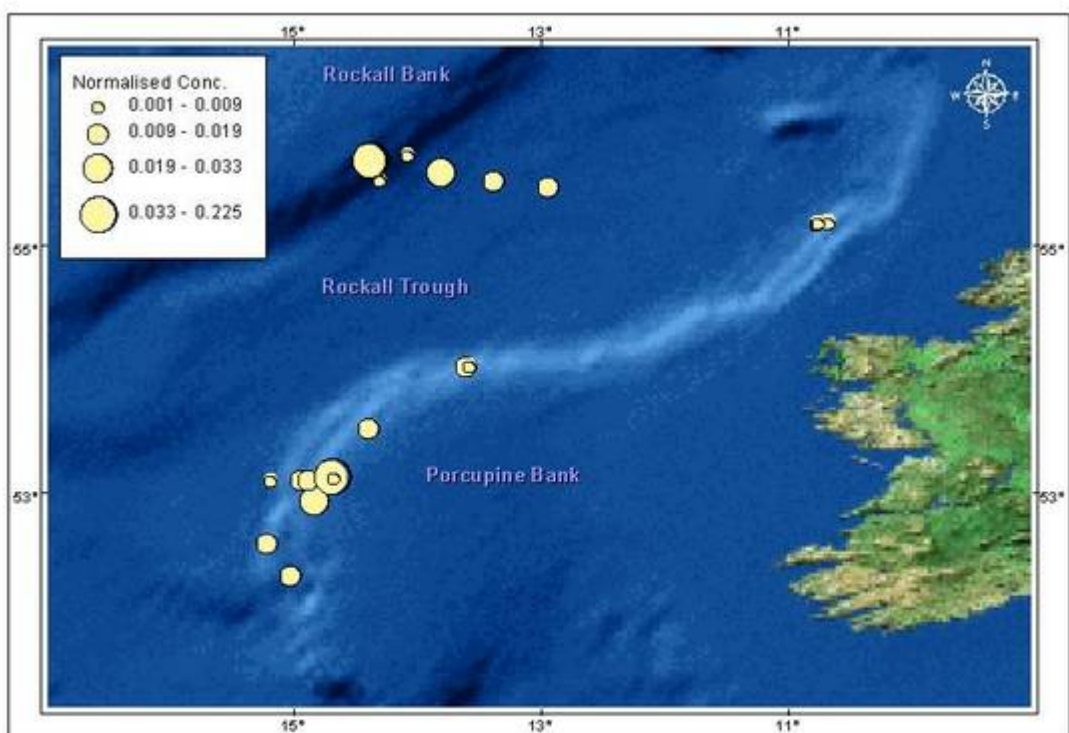
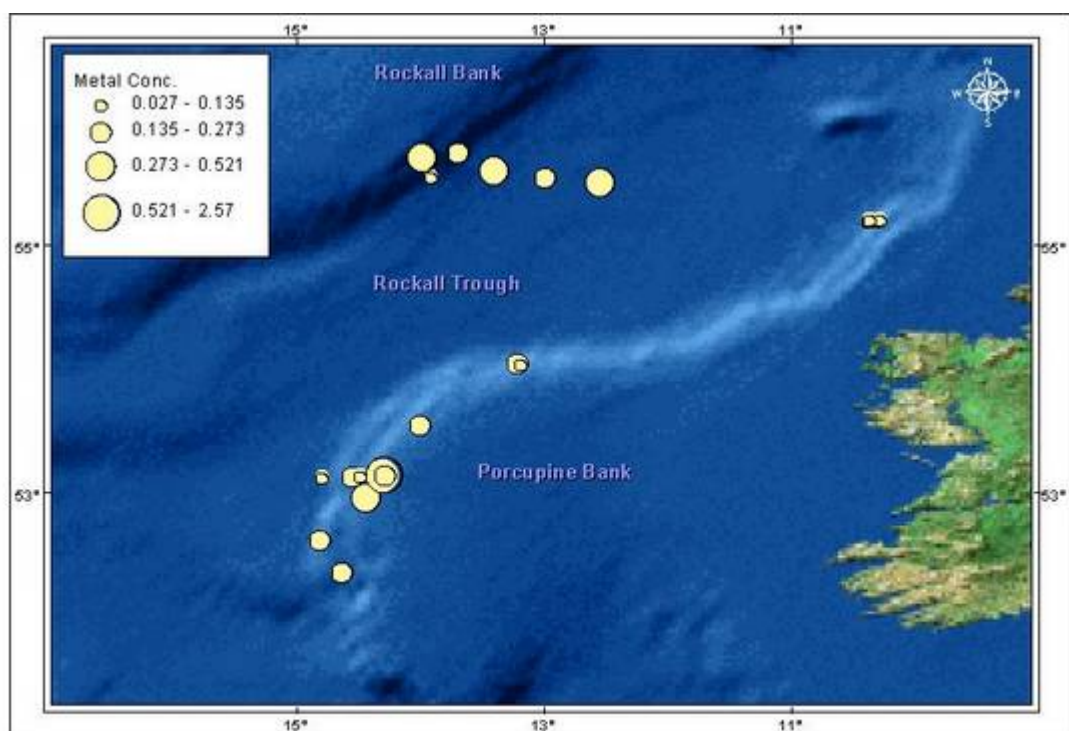


Fig A2.3 Distribution of cadmium (mg kg^{-1}) and cadmium/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

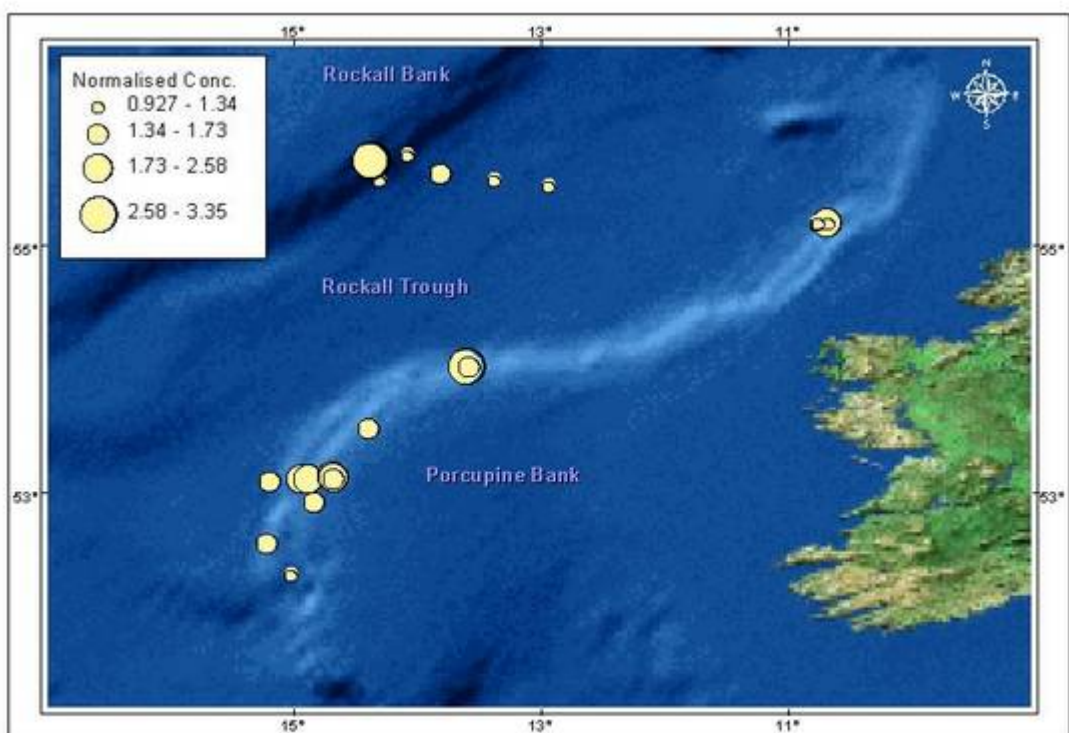
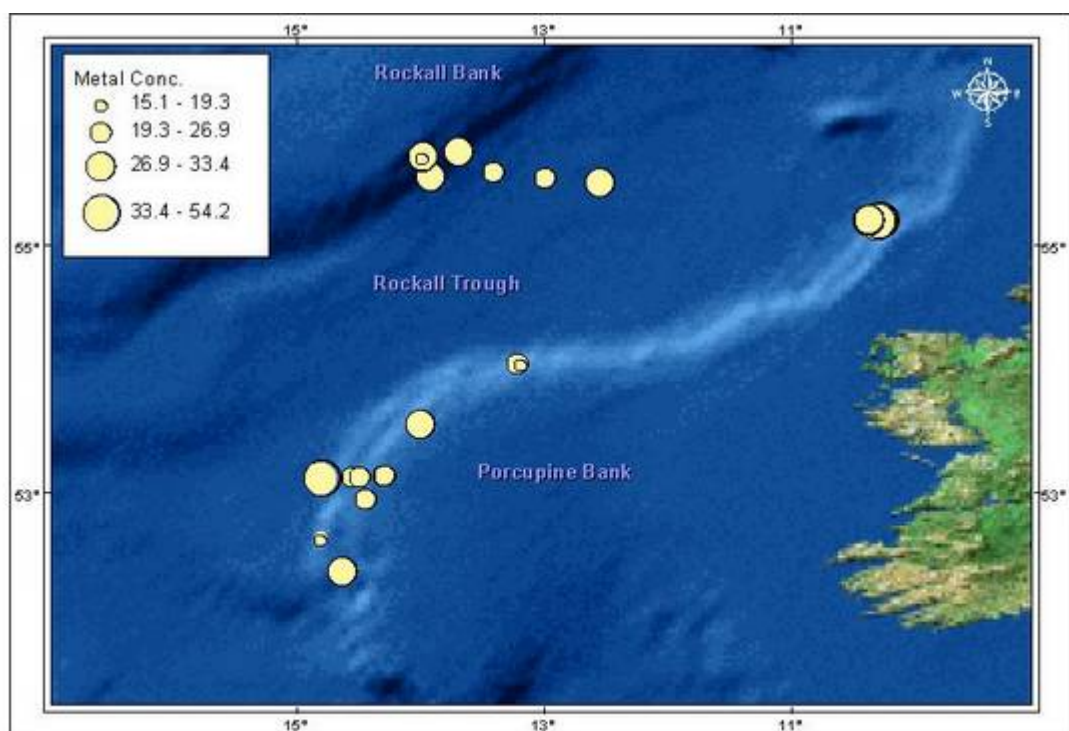


Fig A2.4 Distribution of chromium (mg kg^{-1}) and chromium/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

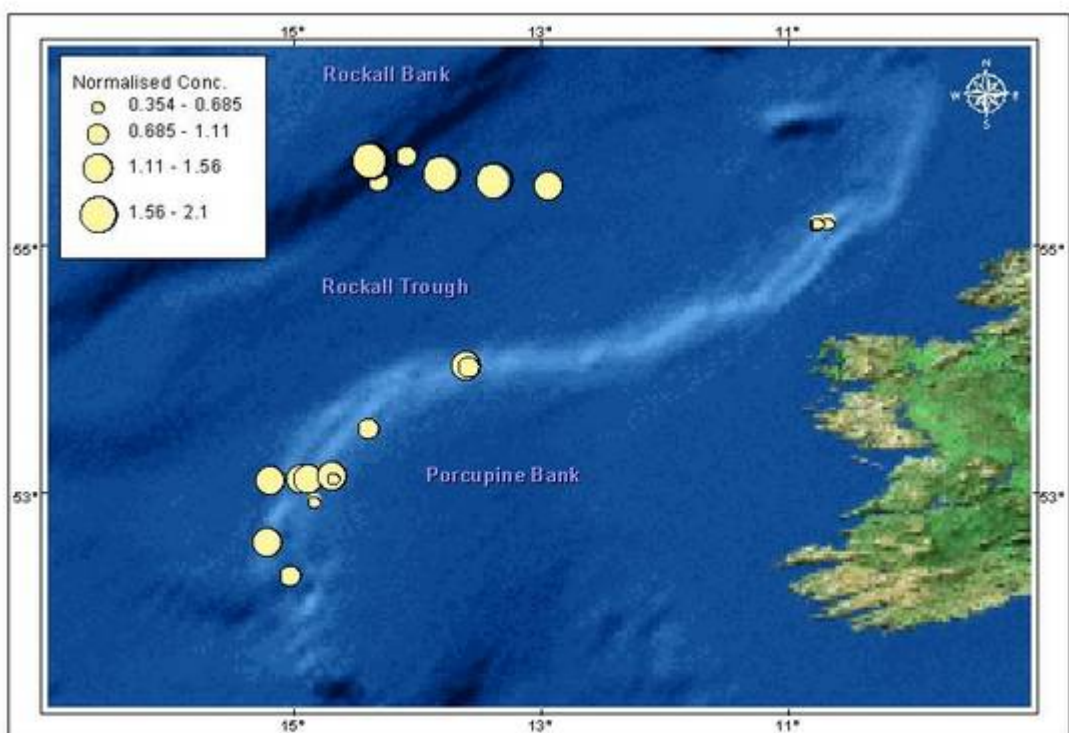
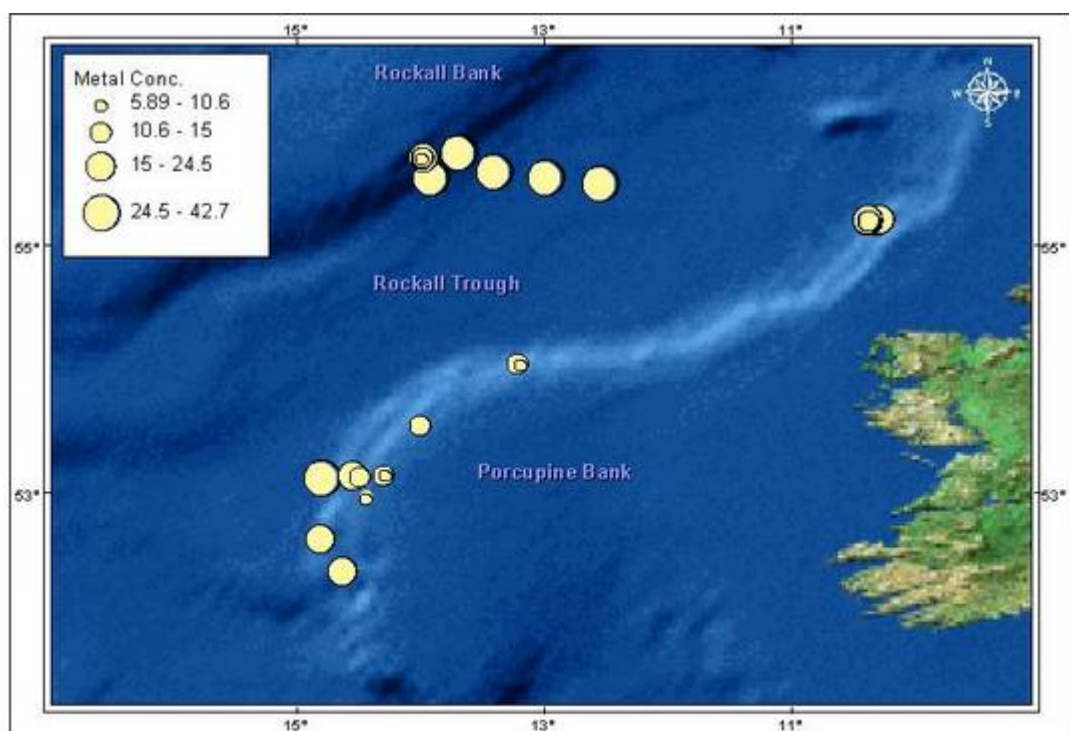


Fig A2.5 Distribution of copper (mg kg^{-1}) and copper/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

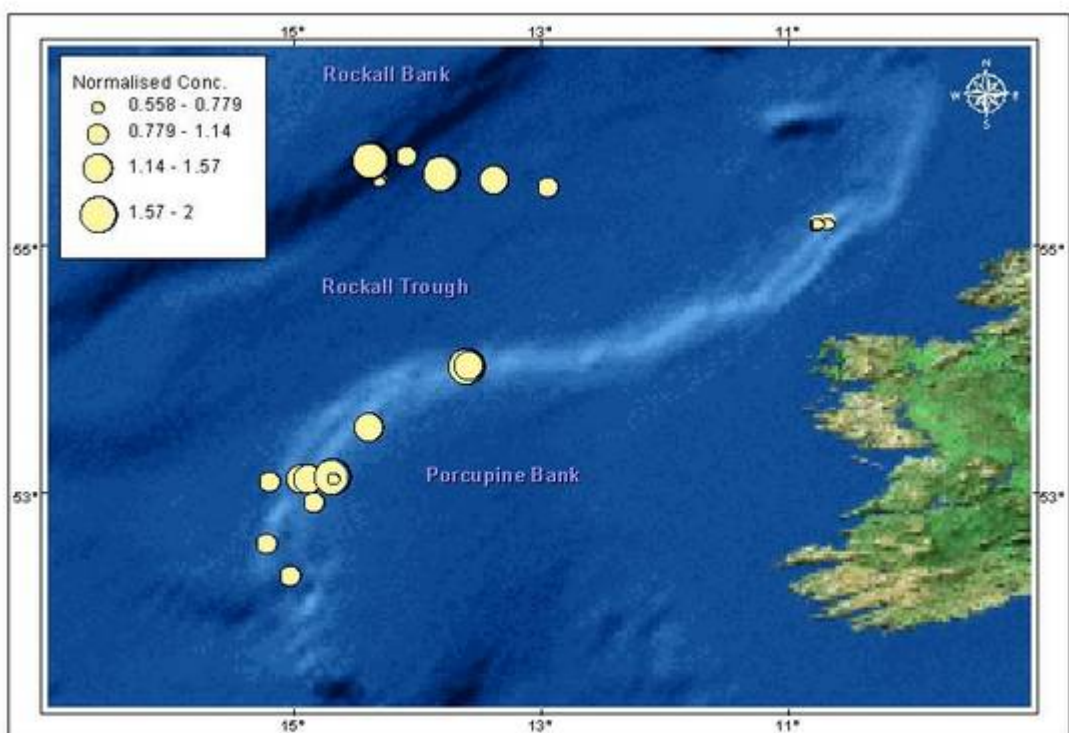
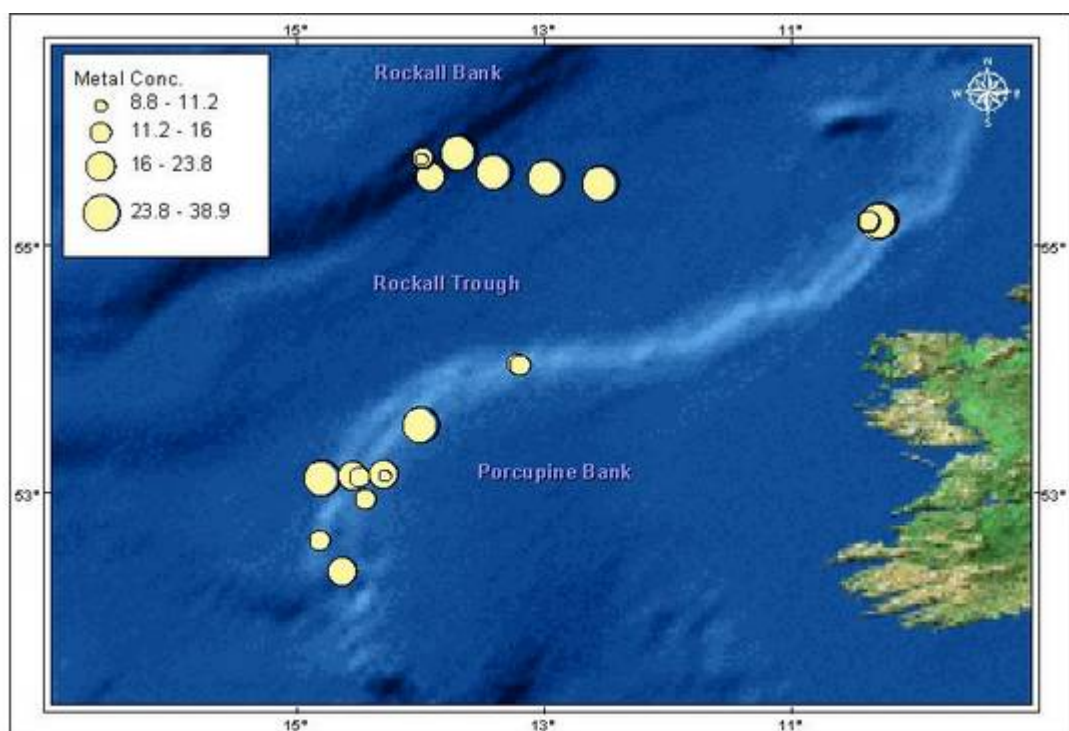


Fig A2.6 Distribution of nickel (mg kg^{-1}) and nickel/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

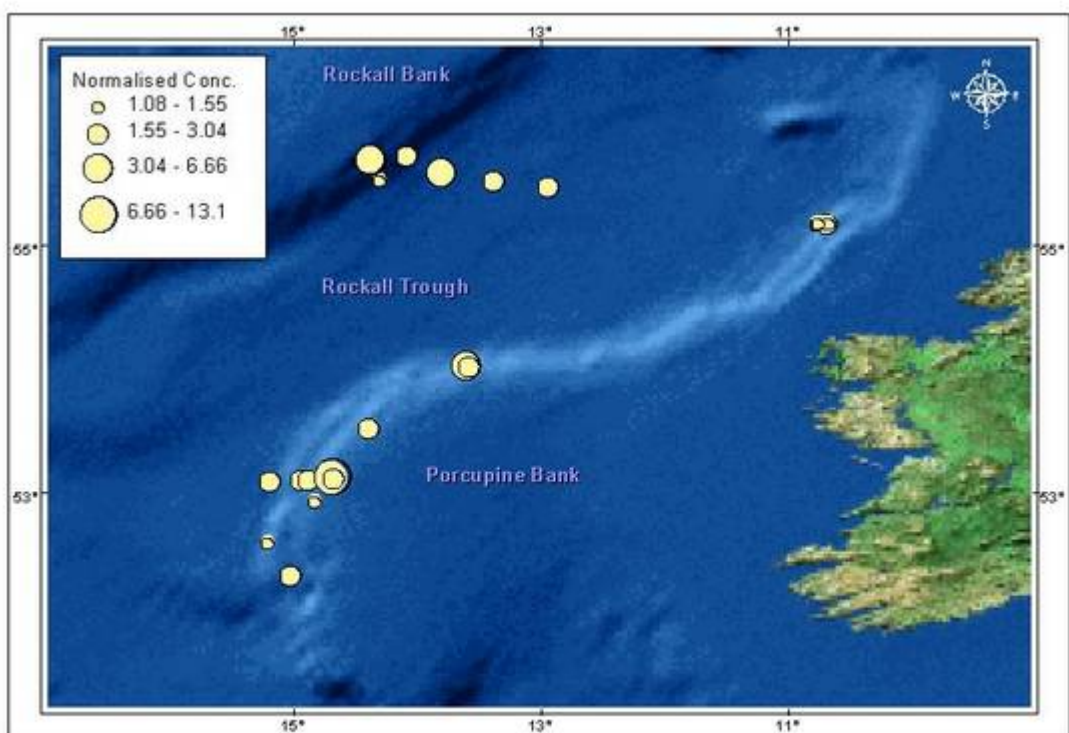
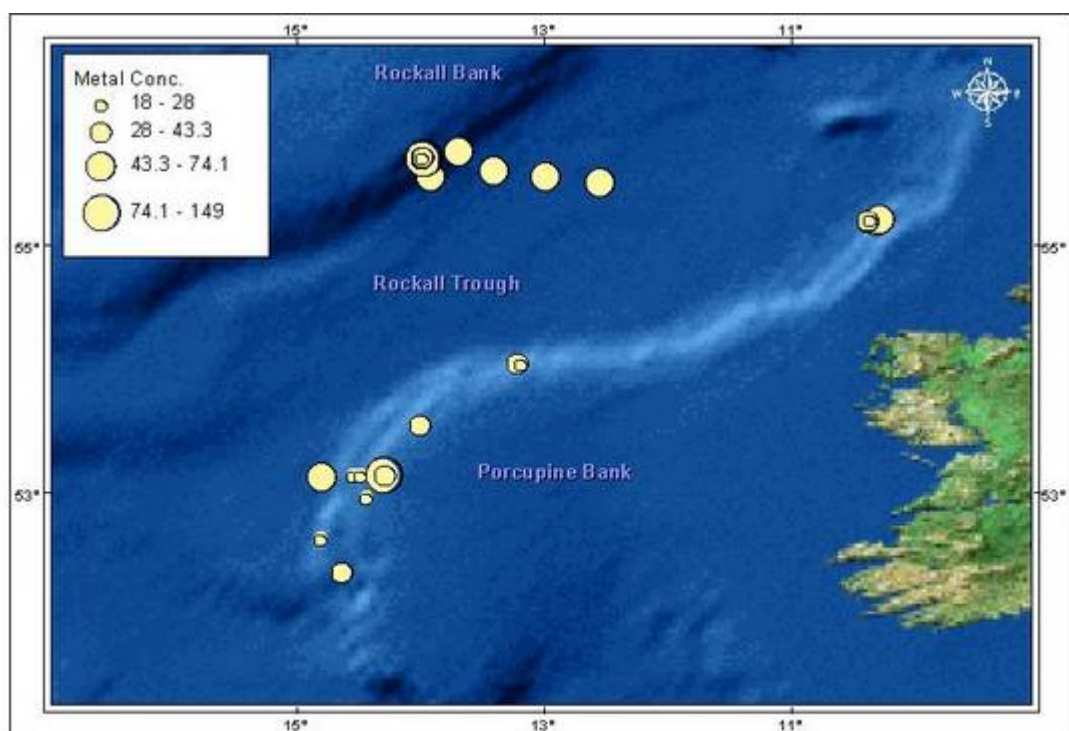


Fig A2.7 Distribution of zinc (mg kg^{-1}) and zinc/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

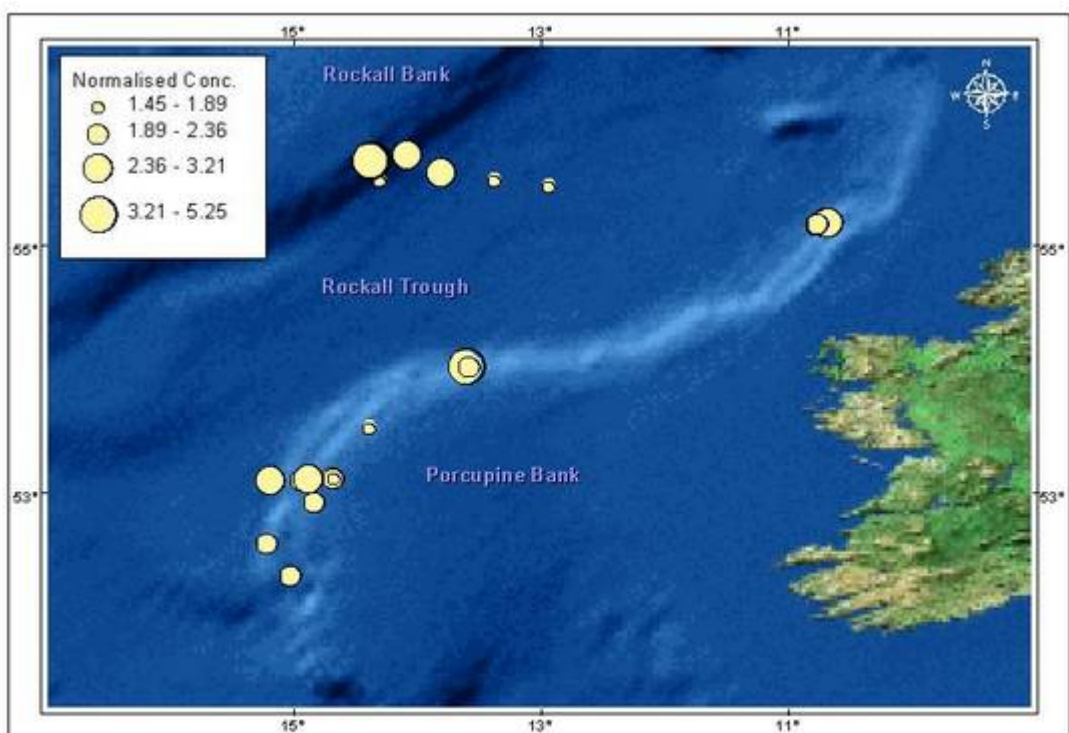
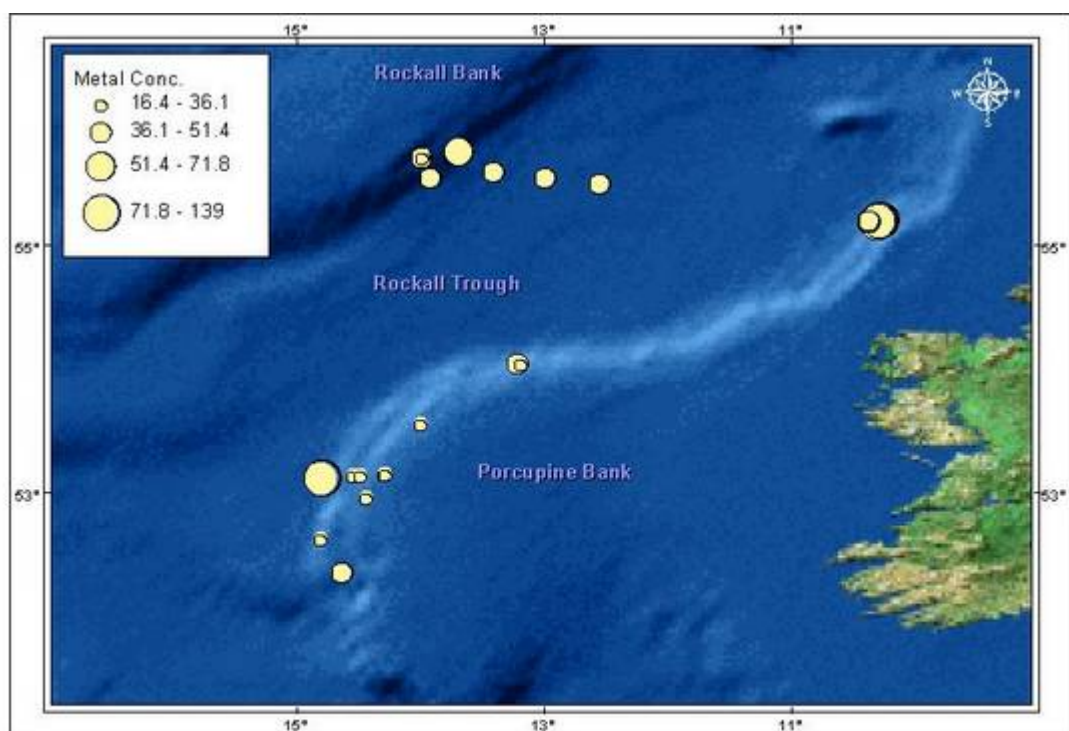


Fig A2.8 Distribution of vanadium (mg kg^{-1}) and vanadium/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

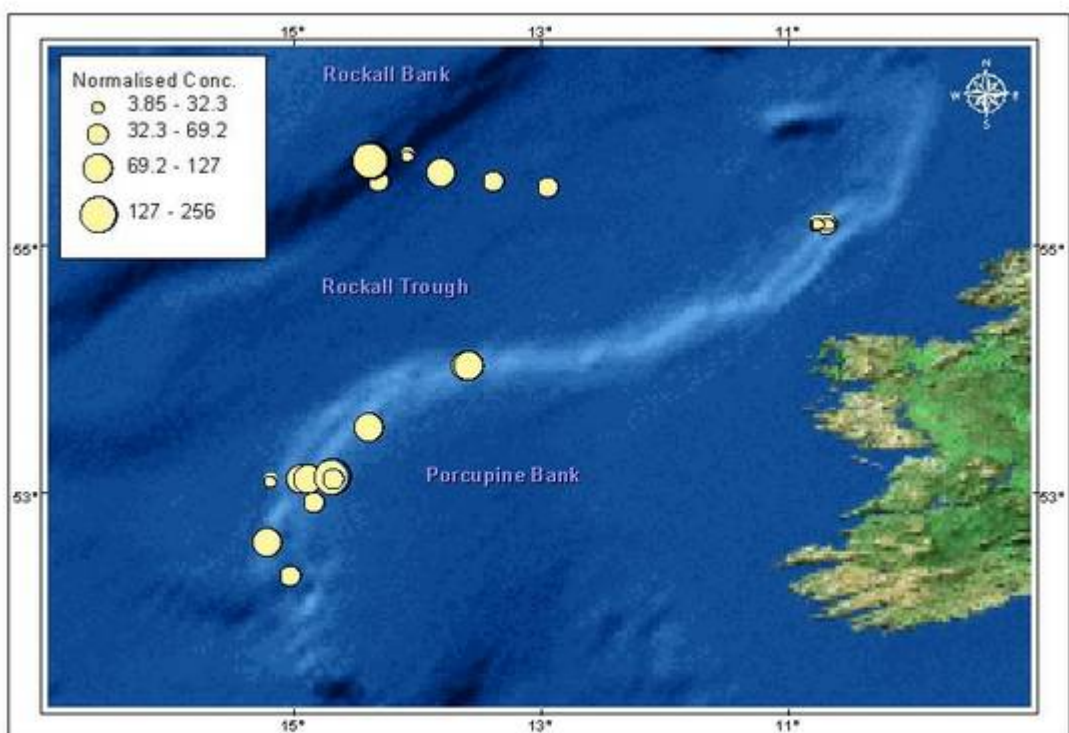
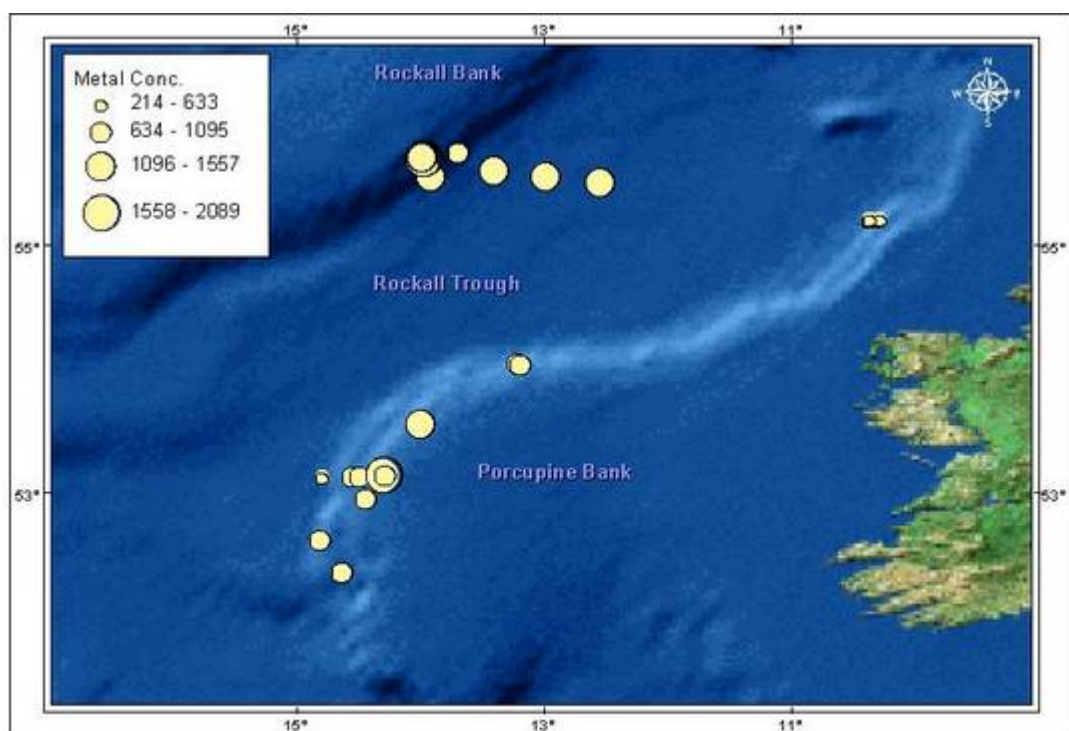


Fig A2.9 Distribution of strontium (mg kg^{-1}) and strontium/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

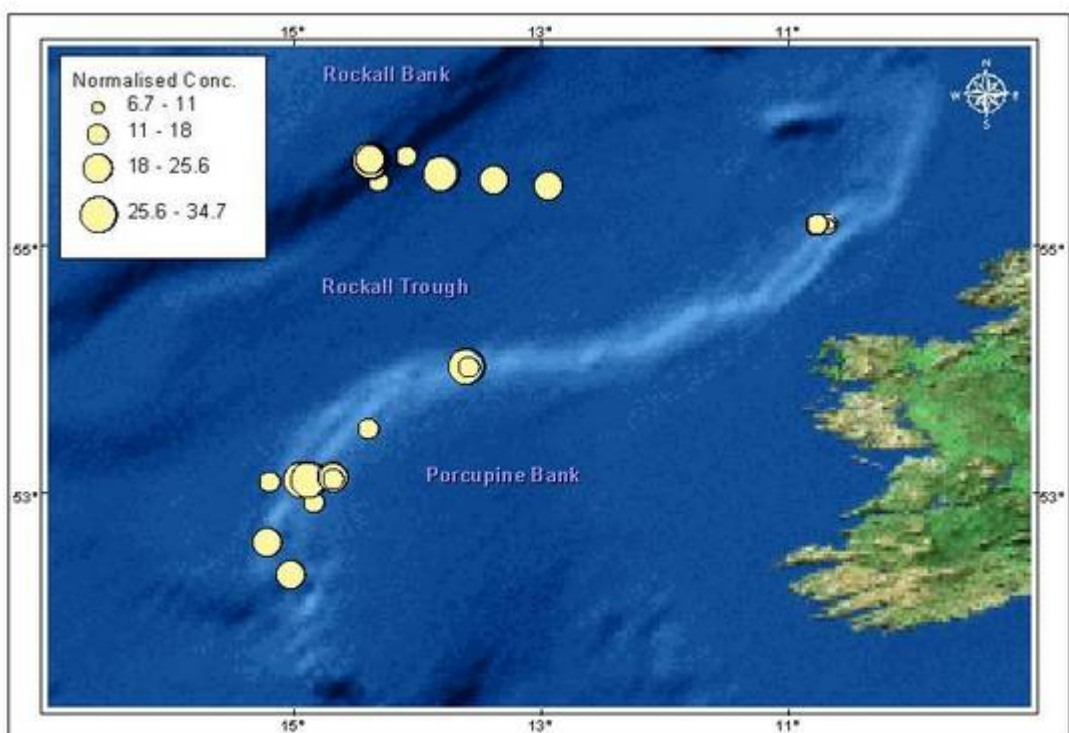
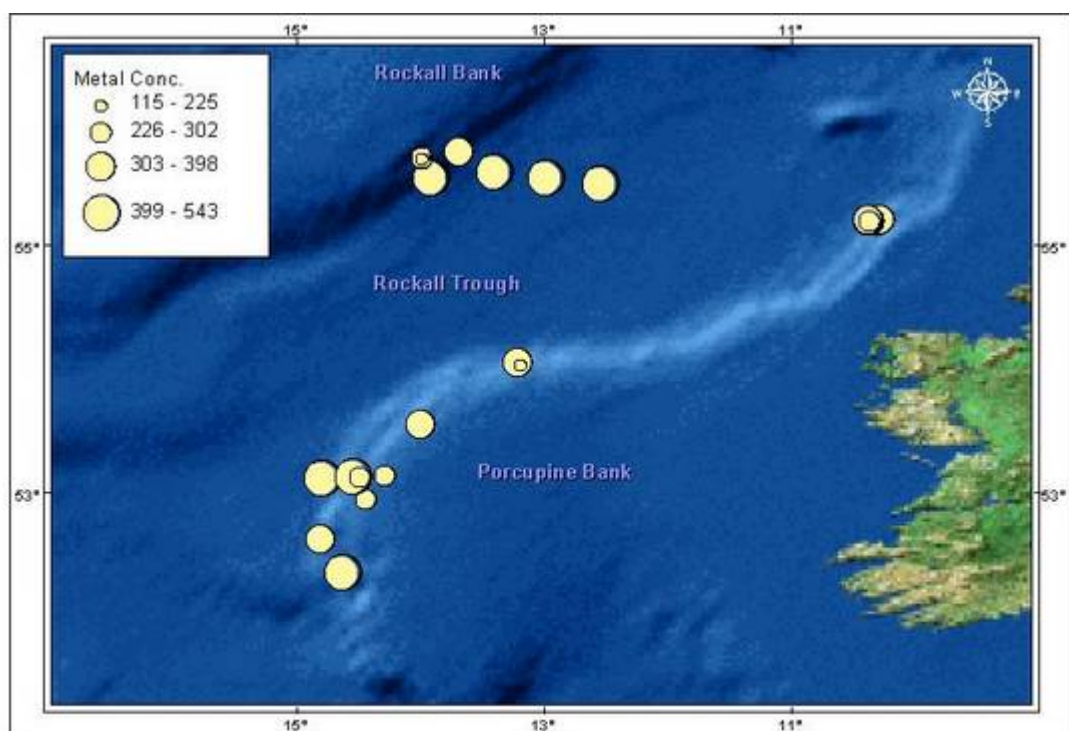


Fig A2.10 Distribution of barium (mg kg^{-1}) and barium/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

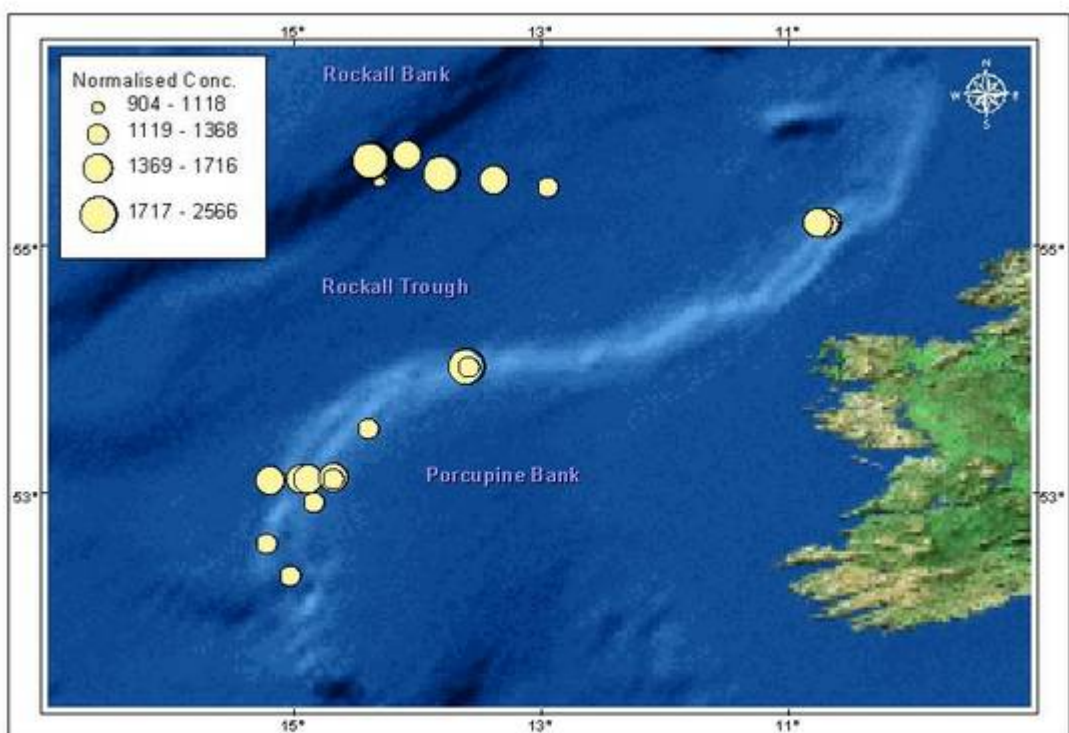
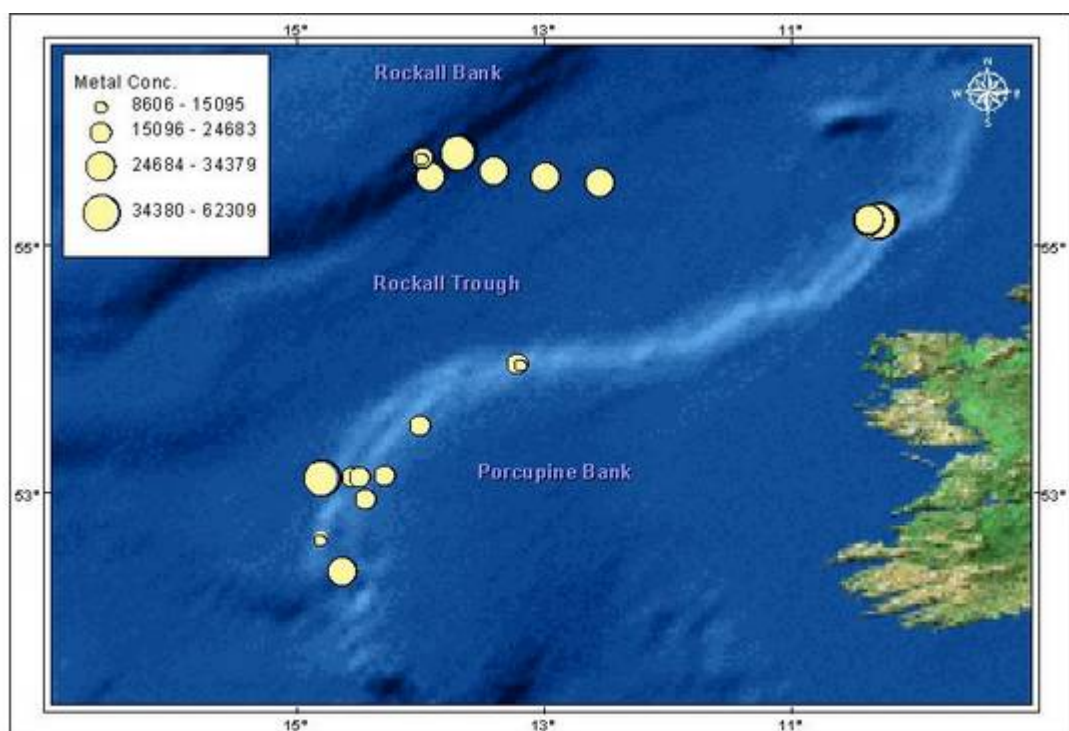


Fig A2.11 Distribution of aluminium (mg kg^{-1}) and aluminium/lithium ratio (mg kg^{-1}) in total sediments. Absolute values are given in Section 3, Table 2

Appendix 3: METAL/LITHIUM RELATIONSHIPS

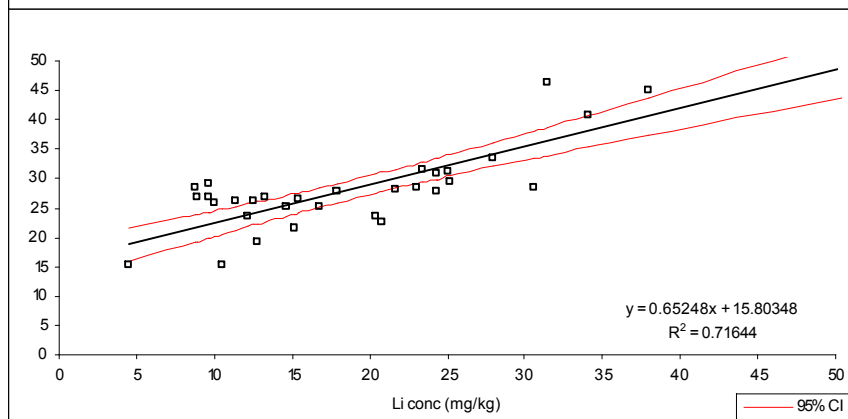
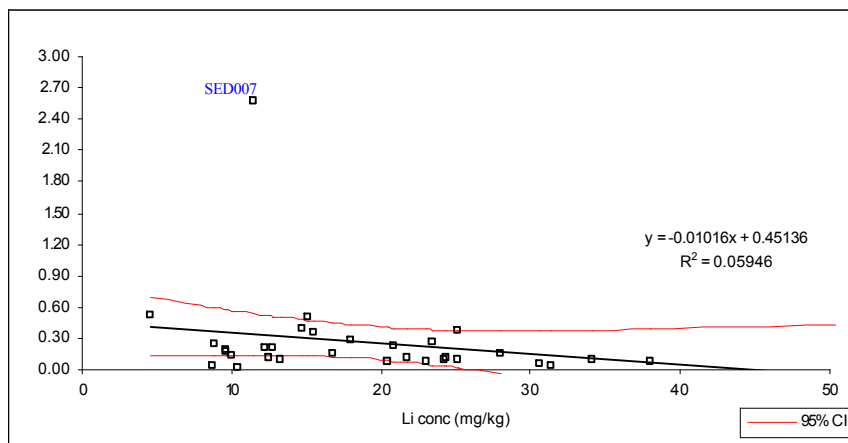
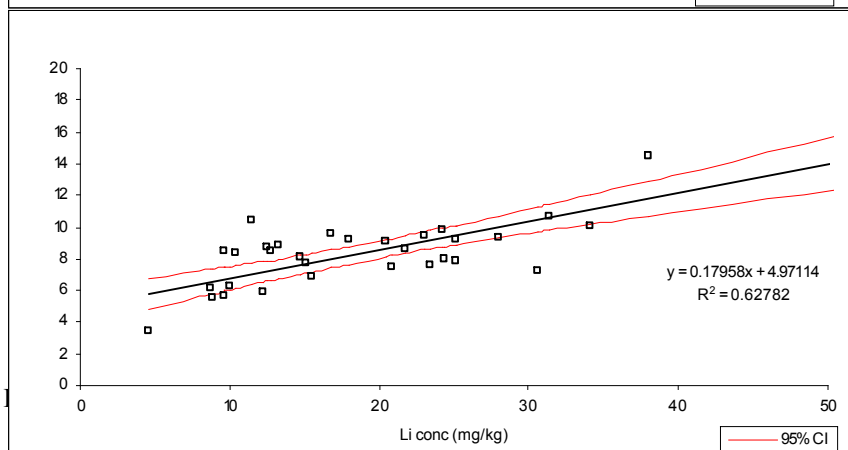
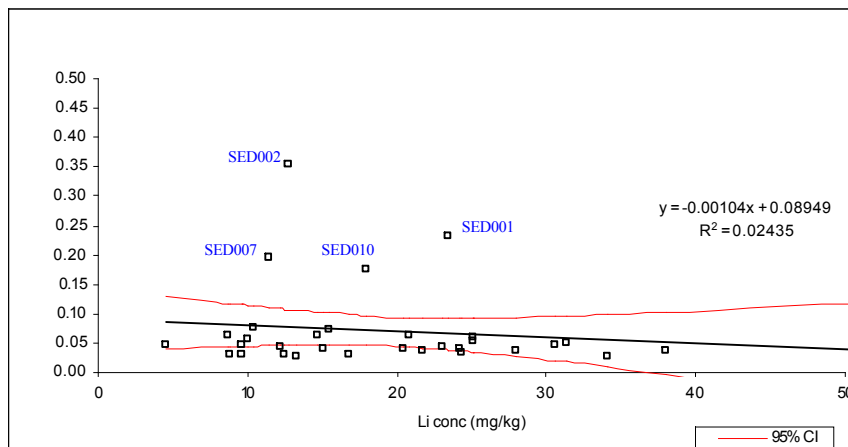
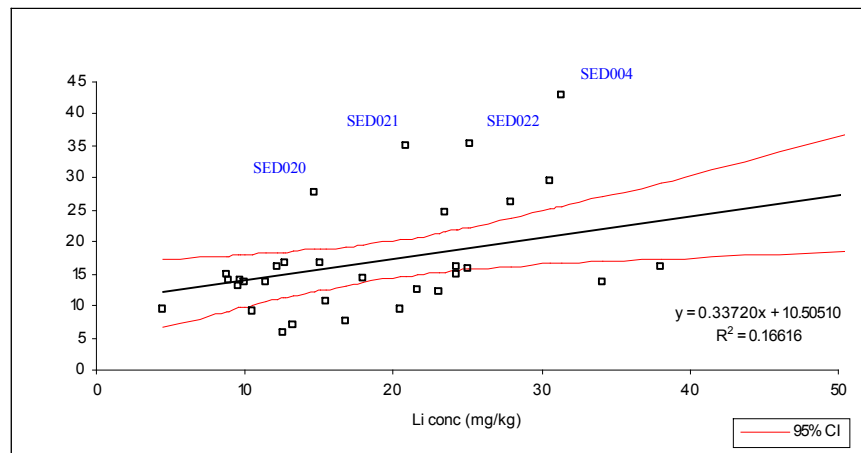
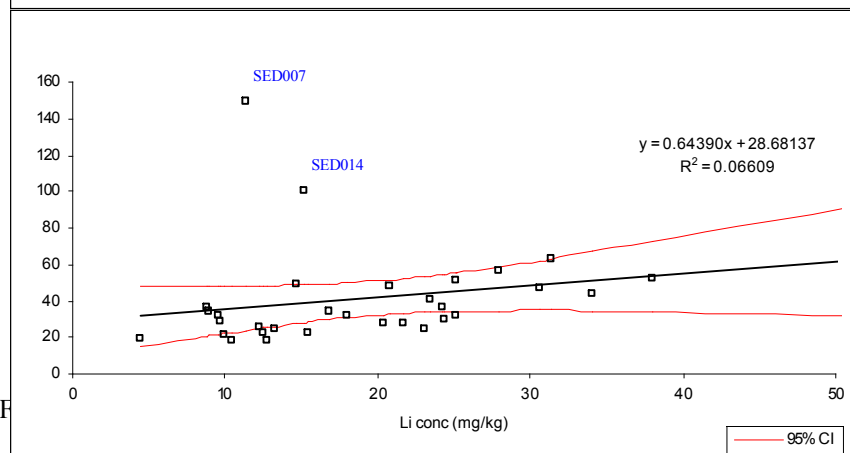
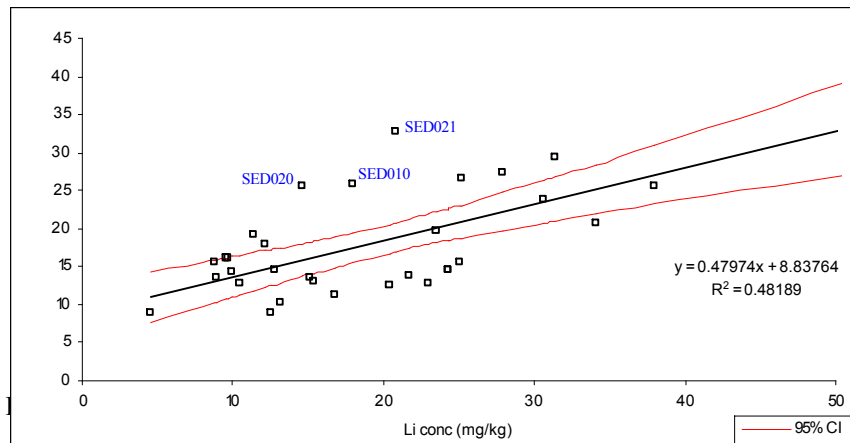


Fig A3.4 Relationship between chromium and lithium, with 95% confidence intervals



vals



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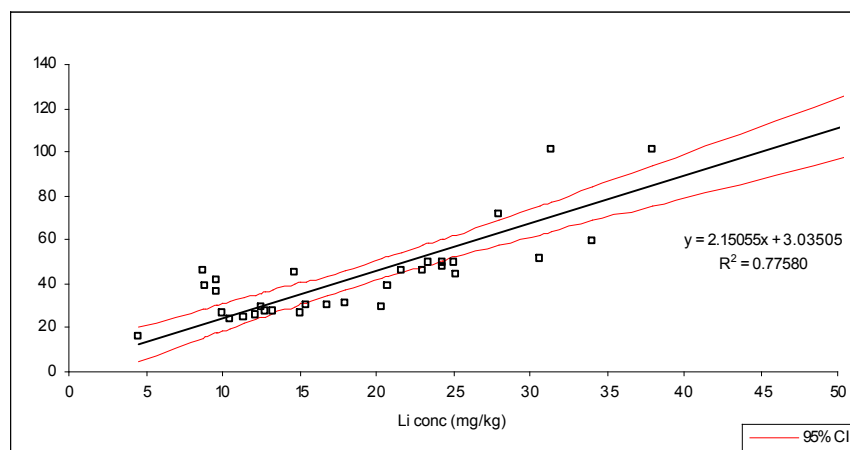
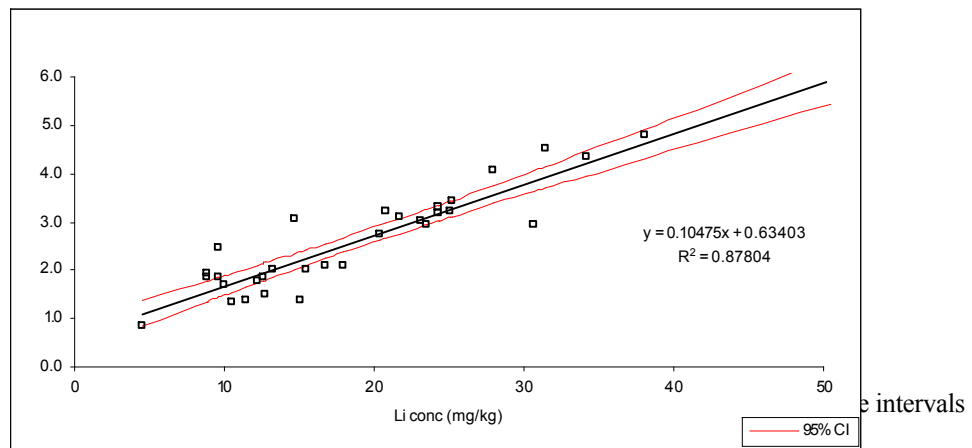
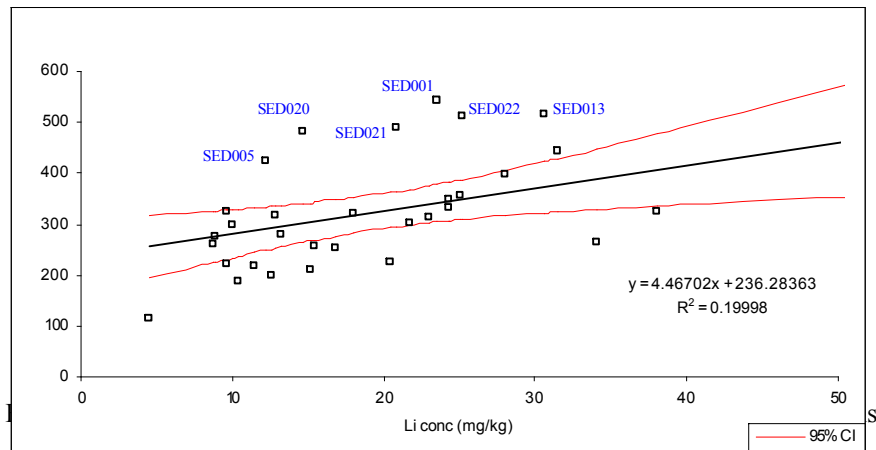
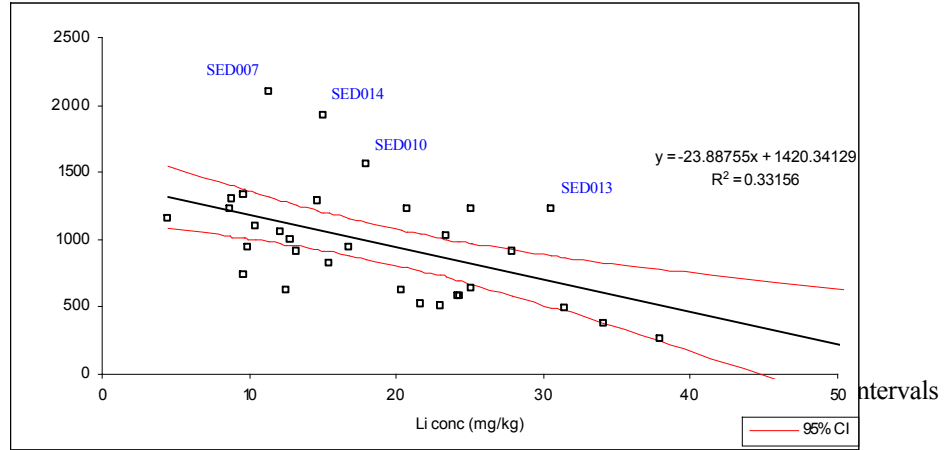


Fig A3.8 Relationship between vanadium and lithium, with 95% confidence intervals



Appendix 4: METAL/ALUMINIUM RELATIONSHIPS

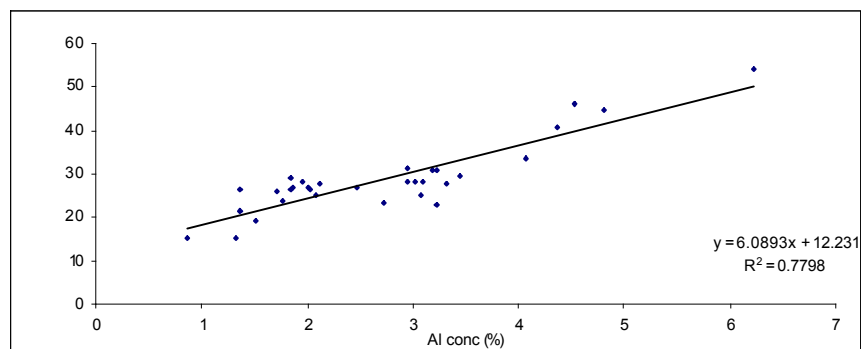
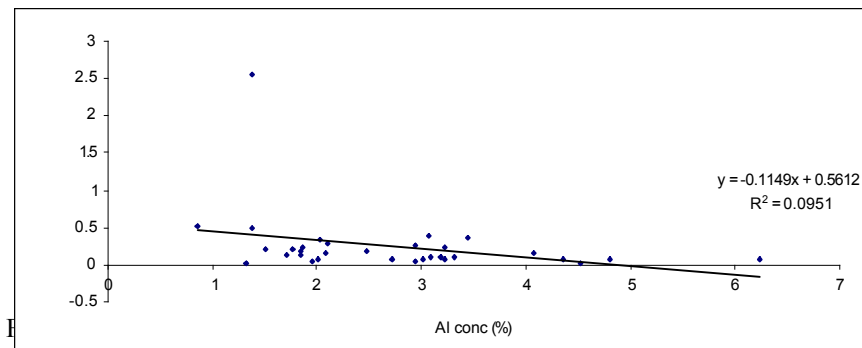
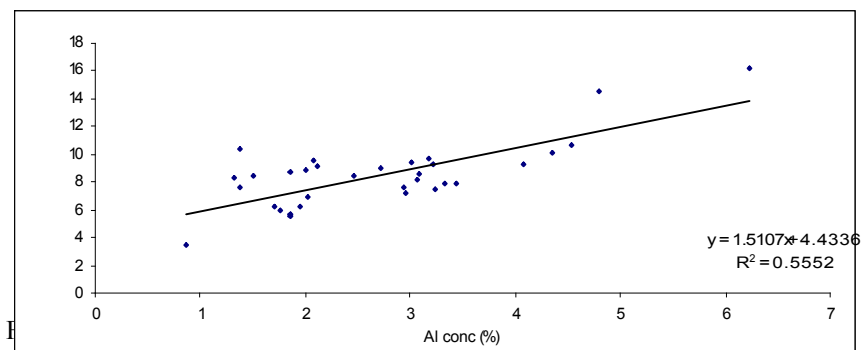
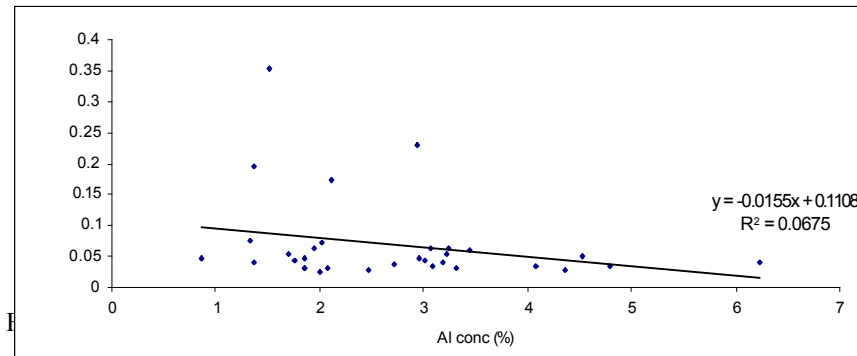


Fig A4.4 Relationship between chromium and aluminium

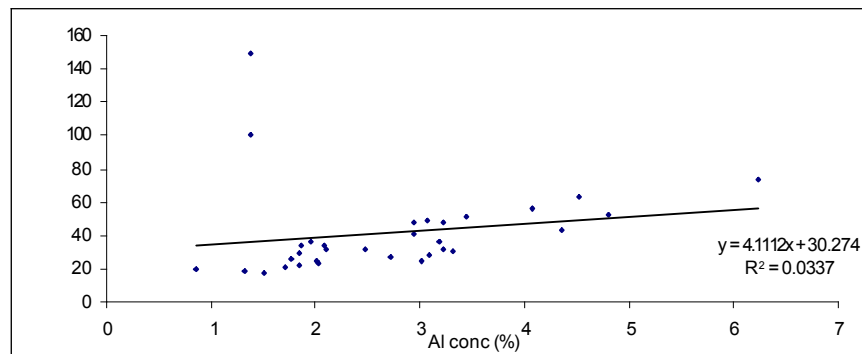
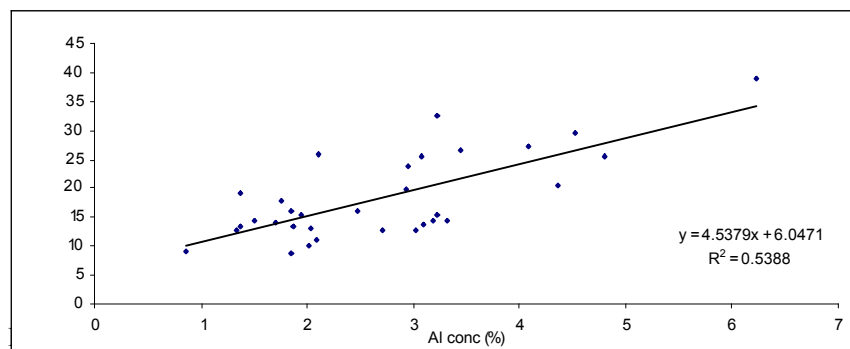
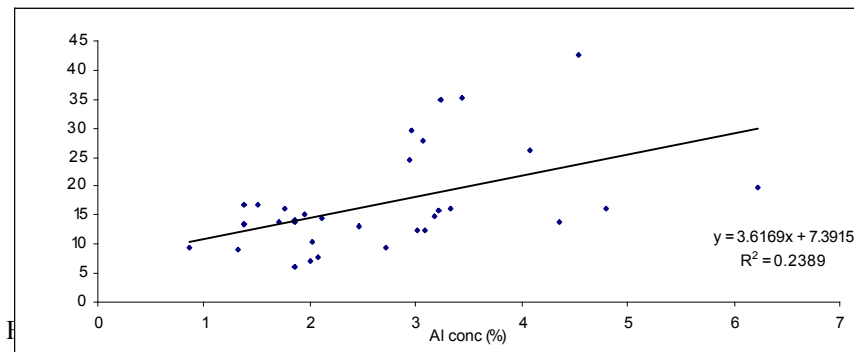


Fig A4.7 Relationship between zinc and aluminium

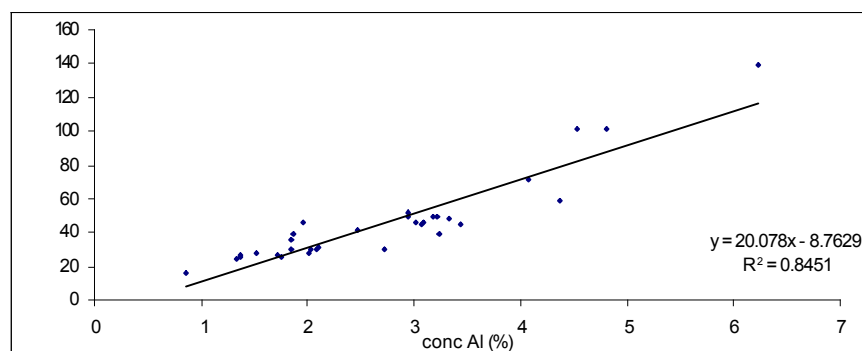


Fig A4.8 Relationship between vanadium and aluminium

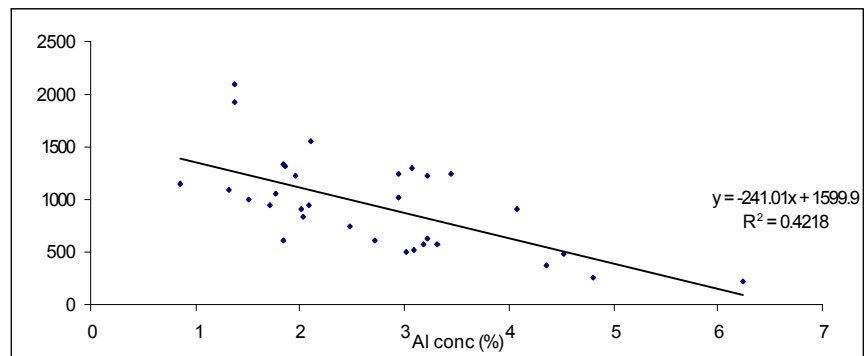


Fig A4.9 Relationship between strontium and aluminium

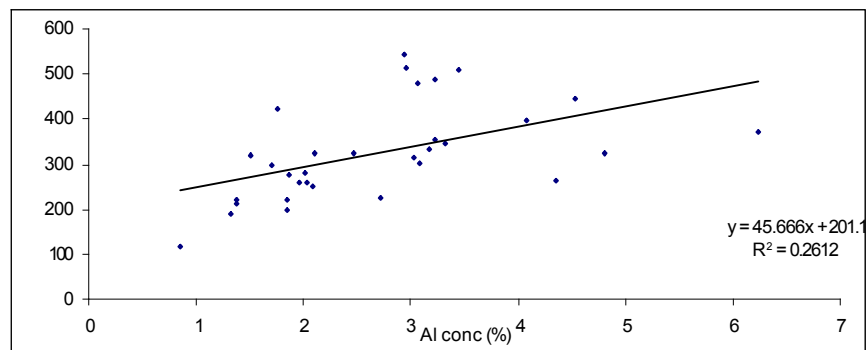


Fig A4.10 Relationship between barium and aluminium