SEDIMENT GEOCHEMISTRY –
A CASE STUDY APPROACH

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Abstract

The geochemistry of sediments is a very wide field and several important aspects must be taken into account, including, but not limited to, various methodological questions, the analysis of distribution patterns, determination of origins and the assessment of risks. Therefore, this research project adapted a case study approach and analysed several important aspects of contamination in sediments at a time.

In case study 1, the distribution of metals in the sediments was analysed in Bigge and Olpe, two small and fast running watercourses in Germany. The metal/metalloid concentrations showed very different distribution patterns. Mobile elements like zinc showed a very homogenous and predictable pattern, while elements with low mobility stick to the sediment and do not migrate much, leading to areas with different concentrations. In addition, it was found that the local monitoring tools in force, which are largely based on analyses of the water, are not sufficient for a reliable assessment of the environmental quality.

Case study 2 aimed both to investigate the contamination profile caused by a closed landfill within the Christchurch Harbour nature reserve and the strengths/weaknesses of a partial extraction scheme based on the industrial standardised process DIN 19730. It was found that this procedure can predict the actual migration in the homogenous marshland structure rather well. In the vicinity of a linear channel, however, no correlation between the mobility and dispersion could be detected; the channel acts as an effective drainage system for both the landfill itself and the intertidal marshland in its sphere of influence. Partial extractions are limited in their ability to predict the migration of contaminants in the ground directly affected by the channel.

The main objective of case study 3 was the determination of metal distribution within the Poole Harbour estuary, both in regard to total and mobile metal concentrations. In addition, it was tested if the chosen methodology is an efficient protocol (fast, yet scientifically defendable) for the assessment of the environmental quality of an area of that size. The concentrations and mobilities of all analysed contaminants in Poole Harbour were greatest in the heavily industrialised secondary embayment Holes Bay. Although Wareham Channel typically showed higher concentrations in the total content analyses compared to Southern Bights, the potential risk associated with metals, calculated based on both total concentrations and mobile fractions, was comparable in both areas.

In case study 4 a simplified grain-size based normalisation scheme was tested. The efficiency of this approach, together with several other normalisation schemes was evaluated in Wareham Channel, located in the west of Poole Harbour. In such fine-grained environments, neither geochemical analyses based on aluminium, nor granulometric normalisation schemes yielded a substantial improvement. Normalisations based on the much simpler iron-ratio reduced the variance considerably. This approach was then applied to the sediments close to a former weapons facility.

Case study 5 investigated the interactions between the die-back of the cord grass *Spartina anglica* in Poole Harbour and the metal contamination in the sediments. Despite having several evolutionary advantages over other plants in this environment, *S. anglica* is dying back in the estuary since 1925 and the reasons for this process are insufficiently understood. No obvious impact of the metal contamination on *S. anglica* growth/die-back could be detected, although the die-back has influenced, in turn, the metal concentrations in the estuary. The overall cadmium concentrations and potential risk of adverse effects have risen since 1925, but in the zones affected by die-back, cadmium stored in the sediment by *S. anglica* appears to have been washed out rapidly. Existing patches still retain elevated concentrations and are potentially at risk of further cadmium release, especially if sea level rise, caused by climate change, would accelerate the die-back.

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AGARD	NATO Advisory Group for Aeronautical Research and Development (today known as NATO Research and Technology Organisation)
AML	Admiralty Materials Laboratory, Holton Heath
Anon.	anonymous
ANOVA	Analysis of Variance
ANZECC	Australian and New Zealand Environmental and Conservation Council
AR	*aqua regia*
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
avg.	average
AVS	acid volatile sulfide extractions
AWWR	*Arbeitsgemeinschaft der Wasserwerke an der Ruhr* (Ruhr waterworks working group)
BBodSchV	*Bundes-Bodenschutz- und -Altlastenverordnung* (Federal Soil Protection and Contaminated Sites Ordinance)
BCR	*Bureau Communautaire de Référence* (Community Bureau of Reference; today known as → SM&T)
BDH	British Drug House Limited
BNG	British national grid, based on → OSGB36
BP	before present also: British Petroleum (until 1998)
CASI	Compact Airborne Spectrographic Imager
CCME	Canadian Council of Ministers of the Environment

MUNLV	*Ministerium für Umwelt und Naturschutz, Landwirtschaft und Verbraucherschutz* (Ministry of the Environment and Conservation, Agriculture and Consumer Protection of the German State of North Rhine-Westphalia)
MWe	electrical megawatt
NATO	North Atlantic Treaty Organization
n.d.	no date
NERC	Natural Environment Research Council
NMR	National Monuments Record (UK)
NOAA	National Oceanic and Atmospheric Administration
NOEL	no observed effect level
NRC	National Research Council, USA also: National Research Council, Canada (→ CNRC)
NRCan	Natural Resources Canada
NWRI	National Water Research Institute, Canada
OES	optical emission spectrometry
OS	Ordnance Survey
OSGB36	Ordnance Survey Great Britain, 1936 revision
p	significance
p.	page(s)
PDE	Posford Duvivier Environmental
PEL	Probable Effect Level
pers. comm.	personal communication
PES	partial extraction scheme
PHC	Poole Harbour Commissioners
PPPS	Poole power plant station

PSTW	Poole sewage treatment works
psu	practical salinity units
PW_M	*Prüfwert für Mobilanteile* (monitoring value for mobile fractions)
r	coefficient of correlation / Pearson index
r^2	coefficient of determination
RAF	Royal Air Force
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical substances
RNCF	Royal Navy Cordite Factory, Holton Heath
RPI	risk potential index
s	second(s)
SCOPAC	Standing Conference on Problems Associated with the Coastline
SedNet	European Sediment Network
SEI	secondary electron imaging
SEM	scanning electron microscopy
SES	sequential extraction scheme
SFT	*Statens forurensningstilsyn* (Norwegian Pollution Control Authority)
SM&T	Standards, Measurements and Testing Programme (formerly known as → BCR)
SPA	special protected area
spp.	species
SPSS	Statistical Package for the Social Sciences
SQG	Sediment Quality Guideline
SQuiRTs	Screening Quick Reference Tables
SSSI	site of special scientific interest

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t	ton(nes)
TBT	tributyltin
TCA	total content analysis
TEL	Threshold Effect Level
UK	United Kingdom
USA	United States of America
US EPA	United States Environment Protection Agency
USGS	United States Geological Survey
UTM	Universal Transverse Mercator coordinate system
VROM	*Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer* (Ministry of Housing, Spatial Planning and the Environment, Netherlands)
WAC	Washington Administrative Code
WDX	wavelength dispersive X-ray
WFD	European Water Framework Directive (Directive 2000/60/EC)
WGS84	World Geodetic System, 1984 revision
WSDE	Washington State Department of Ecology
WSNWCB	Washington State Noxious Weed Control Board
WW1	First World War
WW2	Second World War
$\bar{x}$	mean value
$\tilde{x}$	median value
XAS	X-ray Absorption Spectroscopy
yr	year(s)
°C	degree Celsius

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1 Introduction

Chemical measurements and standards are of the highest importance for our daily lives. The quality of products, competitiveness of industries and the quality of the environment depend upon accurate and reliable measurements (Quevauviller, 1999). The process of evaluating potential ecological effects is often referred to as “ecological risk assessment” (ERA). This process includes hazard identification, effects and exposure assessment and risk characterisation (Chapman and Wang, 2000).

More than 50 % the world's population already lives within 60 km of the shoreline, which by the year 2020 could rise to over 66 % (United Nations, 1992). In the industrialised world the problem is even more acute, as half the population is estimated to live within only 1 km from the coast (Viles and Spencer, 1995). According to Humphreys and May (2005a) over half the world’s coastlines are suffering from severe development pressure. This research project is focused on the contamination in estuarine sediments, which have recently received increased attention from the scientific community (Caeiro *et al.*, 2005). Particular concerns include the accumulation of trace metals by aquatic organisms (Padinha *et al.*, 2000). Numerous studies worldwide (*e.g.* Abernathy *et al.*, 1984; Sakai *et al.*, 1986; Biksham *et al.*, 1991; Arakel and Hongjun, 1992; Chakrapani and Subramanian, 1993; De Gregori *et al.*, 1996) have described the risk of metal accumulation in sediments in rivers, lakes and coastal areas throughout the world. Owing to these accumulation effects, sediments represent potentially significant hazards to aquatic life as well as the overall health of aquatic ecosystems (CCME, 1995). Furthermore, given that estuaries are major sinks for fine sediments, it is essential to understand the dynamics of sediments in order to protect and manage these environments (Cundy *et al.*, 2007).

1.1 Environment

An estuary is described by Cameron and Pritchard (1963) as:

> *"a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage."*

In contrast to estuaries there are numerous definition for wetlands (Tiner, 1999) and according to Haslam (2003) the only generally agreed definition is, that a wetland is *"whatever a competent expert says it is"*. In this work the definition provided by the US National Research Council (NRC, 1995) will be used:

> *"The minimum essential characteristics of a wetland are recurrent, sustained inundation or saturation at or near the surface and the presence of physical, chemical, and biological features reflective of recurrent, sustained inundation or saturation."*

Natural wetlands are endangered environmental systems. According to Humphreys and May (2005b) no accurate figures are available, but it is possible that half of the world's natural coastal wetlands have been lost. In addition, the remaining wetlands are threatened by pollution. Estuaries and intertidal marshlands belong to the most productive ecosystems in the world (Chapman and Wang, 2001; Wilby and Perry, 2006), while at the same time they often belong to the most densely populated areas (Humphreys and May, 2005a; Wilby and Perry, 2006). Estuaries receive sediments through decreased flow velocities and increased flocculation of fine particles arising from raised salt concentrations in draining canals linked to the estuary (Gibbs, 1987).

1.1.1 Effects of anthropogenic activities on sediments

The world's estuaries and oceans are considered "the ultimate repository" of many substances discharged by human activities deliberately or accidentally, and the coastal zone is at greatest risk from various anthropogenic impacts (Kennish, 1997). A wide range of chemicals entering an aquatic system is stored in its sediments, including metals, radionuclides and persistent organic compounds (Fox et al., 1999). For wetlands that are located within industrial urban areas, sediments represent the major reservoir for metal sequestration and/or metal remobilisation (Gaillard, 2004).

Typical sources associated with the decreasing environmental health are industrial installations, maintenance of harbours and other waterways, domestic development of the coastline and demands of tourism (Kennish, 1997). Dredging, for example, is an important tool to maintain waterways and can in an estuary like Poole Harbour, sum up to an annual displacement of 70,000 m³ (Langston *et al.*, 2003). An example for domestic development pressure are landfills, which have been the primary method of waste disposal within the UK for many years (Williams, 1998). Even a properly designed and maintained landfill will generate leachate to some degree (LaGrega *et al.*, 1994) and the potential for poorly engineered landfills to contaminate coastal waters and sediments is considered high, particularly as some landfills are associated with the direct tipping of waste materials onto an unprepared marsh surface that was in direct hydraulic connectivity with coastal waters (Hübner *et al.*, *in press*).

It has been stressed by numerous authors (*e.g.* Arjonilla *et al.*, 1994; Williams *et al.*, 1994; Alloway and Ayres, 1997; French, 1997; Chapman *et al.*, 1999; EA, 2003; Pirrie *et al.*, 2003; Salomons and Brils, 2004; Cundy *et al.*, 2007) that sediments, especially estuarine sediments, act as sinks for contaminants and are therefore especially sensitive to pollution. Estuarine sediments are commonly contaminated with phosphorus and metals (Gerritse *et al.*, 1998; He *et al.*, 2006). An aggravating factor is that estuaries, particularly those with narrow entrances, are especially susceptible to pollution owing to their poor flushing characteristics (*e.g.* Gray, 1985; Langston *et al.*, 1987; Langston *et al.*, 2003; Wardlaw, 2005).

1.1.2 Use of sediments for environmental impact studies

Metals, owing to their low solubility and typically high adsorption rates, are deposited in the water bed sediment (Sigg, 1985), where they, when undisturbed, can remain nearly indefinitely (Förstner *et al.*, 1999). This effect, called geoaccumulation (*cf.* Chapter 1.3.1), makes them ideally suited for environmental studies.

Sediments record the environmental status of aquatic systems, which gives them a major advantage over other, more dynamic media. They are therefore increasingly used for the environmental assessment of aquatic systems (Birch *et al.*, 2008). Concentrations in waters, for example, may be subject to strong variations, sometimes even between hourly samples (Langston *et al.*, 2003); while undisturbed sediments function as scientific ‘history books’ (Gottgens, 2005): vertical profiles have a considerable documentary effect (Züllig, 1956; Kersten and Kröncke, 1990; Rosenbaum-Mertens, 2003).

In addition to this practical implication, sediments also constitute a habitat for many organisms and are an important component of aquatic ecosystems; aquatic organisms are therefore at risk of being exposed to chemical substances through their interactions with sediments (CCME, 1995).

1.2 Contamination

There are 100,204 entries listed in the EU EINECS database for existing commercial chemical substances alone (ECB, 2007). Humankind has so far created altogether approximately 6 million chemical compounds, the majority in the last century (Alloway and Ayres, 1997). Many measures have been implemented to reduce contamination and there have been major developments around chemicals management. For example, lead concentrations rapidly declined after the phasing out of leaded gasoline, which was accelerated by differential tax rates in many nations, like the United Kingdom and Germany. Additionally, the legislation was gradually tightened (*e.g.* by the Control of Pollution Act 1974 or the Water Resources Act 1991), and new control mechanisms are introduced, like the EU directive REACH ("Registration, Evaluation, Authorisation and Restriction of Chemical substances"; European Commission, 2006b), which aims to provide better identification of the intrinsic properties of chemical substances and to better protect both human health and the environment. This is expected to have far reaching impacts on every aspect of chemical manufacture, use and evaluation both in Europe and globally (Jones *et al.*, 2007).

1.2.1 Contaminants targeted

Metals and their compounds are indispensable to modern society, and nearly every metal has some use in industry, commercial or personal applications (Luoma and Rainbow, 2008). Metals are the “most common environmental pollutants” (Klavins *et al.*, 1998). They are of particular concern since they tend to be trapped in estuaries (Riba *et al.*, 2002). According to Kennish (1997), the largest proportion of the metals is trapped in embayments, inner shelf areas and estuaries. In British waters metallic contamination is most obvious in estuaries (Bryan *et al.*, 1985). In estuaries the increased toxicity of metals such as Cd, Cr, Pb, Hg, Ni and Zn, caused by the reduced salinity, is of great significance (Langston, 1990). For decades, industrial and urban activities have contributed to the increase of metals contamination into marine environment and have directly influenced the coastal ecosystems (Buccolieri *et al.*, 2004). Another large-area source for metal contamination is agriculture (Alloway and Ayres, 1997; Peris *et al.*, 2008). Metal contamination can therefore be primarily attributed to intensive agriculture and urban-industrial expansion (Nicholson *et al.*, 2003). The elements Ag, As, Cd, Cr, Cu, Hg, Pb, Se, Sn and Zn are perceived to be the most environmentally and toxicologically significant (Bryan and Langston, 1992). It has also been argued that Cu may be the most significant contaminant in the marine environment (Langston, 1990).

Sediments are commonly polluted with phosphorus and metals (Kennish, 1997; Gerritse *et al.*, 1998; He *et al.*, 2006). Concentrations by these elements are highly dependent on site-specific contamination inputs (*e.g.* Menon *et al.*, 1998; Chen *et al.*, 2001). Furthermore, the accumulation and distribution of metals and phosphorus in sediments have a substantial impact on the water quality (He *et al.*, 2006; Maguire *et al.*, 2009) and owing to the substantial discharges in the past (Nriagu, 1988) and the persistency of many metals (Mulchi *et al.*, 1991; Alloway and Ayres, 1996; Alquezar *et al.*, 2006), they constitute a considerable and lasting environmental problem.

In view of their importance, *i.e.* in regard to their toxicity (*cf.* Chapter 1.2.3), accumulation in sediments (*cf.* Chapter 1.3.1), persistency and widespread distribution (*cf.* Chapter 1.2.2); the following twelve elements have been in the focus of this study: arsenic, cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, phosphorus, tin and zinc.

1.2.2 Persistency of metals

Metals are conservative pollutants, which are defined as chemicals which are not, or only on a very large time-scale, subject to bacterial attack (Clark *et al.*, 1997). While most metal concentrations decline rapidly in surface waters, with half-life times of less than a month (Di Toro and Paquin, 2000; *cf.* Chapter 1.3.1), in soils and sediments persistence of metals is very high, residence times can be thousands of years. For example, depending on ground parameters the half-life of cadmium is up to 1100 years; those of lead between 740 and 5900 years (Alloway and Ayres, 1996). Metals cannot be degraded by biological or chemical processes and are therefore, unlike organic contaminants, not subject to self-purification processes of waters (Bliefert, 1994). Pollution produced by metals is considered virtually permanent in coastal soils (Mulchi *et al.*, 1991) and contamination caused by them can directly impact upon estuaries for decades (Alquezar *et al.*, 2006).

1.2.3 Distribution and toxicity of metals

Metals pose potentially hazardous conditions owing to their widespread release, high toxicity above certain thresholds and persistent nature (Kennish, 1997; US EPA, 2005). Thirty years ago the number of persons suffering from subclinical metal poisoning alone was believed to be several million (Nriagu, 1988). At that time, the potential toxicity of all metals released annually by human activities exceeded the combined potential toxicity of all the radioactive and organic wastes, as measured by the quantity of water needed to dilute such wastes to drinking water standards (Nriagu, 1988). However, when assessing the environmental impact of metals there are five aspects which need to be considered.

(i) Classification: There are essential and non-essential metal species; which will, together with susceptibility, vary between species. Indeed, for some areas with particularly high metal concentrations, unique plant assemblages have been reported, often including high abundances of otherwise rare species (Schubert, 1996). In addition, some of the traditional classifications have recently been questioned, as research indicated adverse long-term effects on animals, caused by a diet poor in elements believed to be non-essential, such arsenic, cadmium or lead (Fiedler and Rösler, 1993). While both essential and non-essential metals are toxic above certain thresholds, deficits of essential metals may also result in adverse effects. Both tolerance ranges can be extended by induced tolerances (George, 1990; Ivorra *et al.*, 2002), *i.e.* gradually decreasing susceptibility. It was found, for example, that Cu pollution increased tolerance to Cu, Zn, Cd and Ni in bacteria (Diazravina *et al.*, 1994), that plants developed high tolerances for Cu, Co, Se, U or Zn (Fiedler and Rösler, 1993) and that human cells acquired a stable arsenic tolerance following chronic arsenic exposure (Brambila *et al.*, 2002). For mercury, toxicity thresholds cannot be reliably evaluated at all, as each animal/human has an individual threshold dose, owing to genetic and lifestyle-dependent susceptibility differences (Lutz, 2000).

(ii) Bioavailability: Not all metals are available for uptake by aquatic life and there are different factors which control the fraction readily available for uptake; for example, the chemical speciation of the metals, competition between metals or sediment characteristics (Bryan and Langston, 1992). Within the sediments, the bioavailability of some metals change, for example, it may increase substantially by transformation into organo-metallic compounds (Bryan and Langston, 1992). Owing to such temporal changes, the complex composition of sediments (*e.g.* regarding different grain size compositions, chemical interactions like competition or element speciation), the strong effects of fluctuating environmental factors (see below), and the inconsistencies in related methodology (Hübner *et al.*, *in press*), it is a difficult factor to assess.

(iii) Bioaccumulation: Metals/metalloids can accumulate both within individuals and through the food-chain; hence, sublethal concentrations may reach hazardous concentrations over prolonged periods. While early studies were biased towards short term lethality investigations, metals do not usually pose an instantaneous threat (Langston, 1990). However, the risks of chronic effects of contamination are often underestimated (Soldán, 2003) and the bioaccumulation of contaminants represents one of the most significant sources of uncertainty in risk assessment (Linkov *et al.*, 2000).

(iv) Convergent effects: There can be a complex interplay between metals. For example, an iron deficiency increases absorption of cadmium, lead, and aluminium (Goyer, 1997), while a copper excess will replace elements like zinc and iron (George, 1990). Synergistic toxicity effect has been reported for various metals in binary mixtures (Sun *et al.*, 2005; Chen *et al.*, 2006). Likewise, several studies have suggested antagonistic effects, indicating that toxic effects are less probable when metals are occurring in mixtures (Sunda and Huntsman, 1983; Kreppel *et al.*, 1994; Ince *et al.*, 1999; Montvydienė and Marčiulionienė, 2007).

(v) In addition, environmental factors which vary greatly in time and place, such as grain size, pH-value or population stress, can affect bioavailability, toxicity and susceptibility to metals (Hübner *et al.*, 2009). As a general rule, high temperatures and low salinity will, for example, increase the mortality rates caused by metals to aquatic life (Theede *et al.*, 1979; Bryant *et al.*, 1985; McLusky *et al.*, 1986; Langston, 1990; Ozoh, 1992).

1.2.4 The term "heavy metals"

In this context, the term "heavy metal" is commonly used. This is an imprecise term for the metals and metalloids (semi-metals) that are often associated with toxic effects. However, there is no scientific basis to support such a generalisation (Duffus, 2002). The term is also often used synonymously with "trace metals", but without any distinction between essential and non-essential species (Rainbow, 1995).

Furthermore, there is still no authoritative or even uniform definition available. For instance, Beier (1994) defines a 'heavy' metal as a metal with a density of $>4.5\ \text{kg}\cdot\text{dm}^{-3}$; Alloway and Ayres (1996) with $>6\ \text{g}\cdot\text{cm}^{-3}$. Duffus (2002) lists 40 different definitions, the majority based on various chemical and physical properties, particularly different densities and atomic weights. As a result, the number of elements considered to be a "heavy metal" varies between studies. In addition, arsenic is also typically classified as a heavy metal, regardless of the fact that it is not a metal in the first place, but a metalloid (semi-metal).

Hence, the term is often considered meaningless and misleading; its use is strongly discouraged (Nieboer and Richardson, 1980; Duffus, 2002; Duffus, 2003; Hodson, 2004; Chapman, 2007). Nevertheless, it is still more often used than not, and even in recent, peer-reviewed papers it is still used regularly (*e.g.* Tokalioglu *et al.*, 2003; Gryschko *et al.*, 2005; Roussiez *et al.*, 2005; Quinton and Catt, 2007; Singh *et al.*, 2008; Wei *et al.*, 2008; Pan *et al.*, 2009; Pedron *et al.*, 2009; Uba *et al.*, 2009).

Owing to its unclear and potentially misleading nature, the term heavy metal is avoided in this study.

1.3 Geoaccumulation and remobilisation

Contamination in aquatic environments, regardless of type, is usually assessed in three parameters, namely the concentrations in water, sediments and biota (Lacerda *et al.*, 1991; Rainbow, 1995; European Commission, 2000), sometimes suspended particles are considered separately (*e.g.* Pfeiffer *et al.*, 1982; Mwamburi, 2003; Nguyen *et al.*, 2005b).

Concentrations in water and suspended particles are highly variable over time and place (affected by tides, currents, inputs, run-offs, seasons, *etc.*), accordingly analyses only reflect the water quality status at the time of sampling (Matagi, 1996). In addition, concentrations in water are typically very low (Bryan *et al.*, 1985; Rainbow, 1995). Sediments on the other hand accumulate contaminants, particularly metals (CCME, 1995; Rainbow, 1995).

1.3.1 Geoaccumulation

Both total and soluble factions of most metal ions decline fairly rapidly in most surface waters, normal half-life times for metals like arsenic, chromium, copper, lead, nickel and zinc are less than 22 days (Di Toro and Paquin, 2000). Consequently, dissolved metal concentrations in waters are typically very low, often at the analytical detection limits (Rainbow, 1995) and also vary greatly over time, sometimes even between hourly samples (Langston *et al.*, 2003).

However, numerous studies throughout the world warn that sediments in rivers, lakes and coastal areas accumulate metals (*e.g.* Abernathy *et al.*, 1984; Sakai *et al.*, 1986; Kersten and Kröncke, 1990; Biksham *et al.*, 1991; Arakel and Hongjun, 1992; Chakrapani and Subramanian, 1993; CCME, 1995; De

Gregori *et al.*, 1996; Di Toro and Paquin, 2000; Buccolieri *et al.*, 2004; Alquezar *et al.*, 2006). As metals have a low solubility and a typically high adsorption rate, the majority are deposited in the water bed sediment (Sigg, 1985). Owing to this effect, called geoaccumulation, contaminants are not longer present in the water column, but are stored nearly indefinitely in the sediment, where they may constitute a secondary contamination source (Förstner *et al.*, 1999; Salomons and Brils, 2004). Persistence of metals in undisturbed sediments can be very high; pollution produced by them is virtually permanent in coastal soils (Mulchi *et al.*, 1991; Alloway and Ayres, 1996) and can impact upon estuaries for decades (Alquezar *et al.*, 2006).

Mixing of sediments has two effects: it will destroy any clear horizon in the sediment, hence diminishing chances of determining timelines and causations, additionally it is likely to bring metals and metalloids into solution.

1.3.2 Local causes for the redistribution of contaminants

A large quantity of the anthropogenic metals and metalloids ends in the topmost layers of soils and sediments. Most metals are stored in the form of comparatively stable and not readily soluble compounds in the anaerobic sediment. In sediments metals are normally bound to complexes and in greater depths are commonly very stable owing to the anoxic conditions (Löser *et al.*, 2004). However, changes in environmental conditions caused both by natural and anthropogenic impacts, can result in a partial or total release of the contamination.

Dredging often leads to the re-suspension of potentially contaminated sediments, but it is an important tool for maintaining the depth of harbours and channels as well as for the remediation of polluted marine areas (Joksič *et al.*, 2005). Contamination stored in sediments can reappear after mixing, which results in higher concentrations of chemicals in the water column and topmost sediment layers. In the North Sea it was shown that compared to direct discharge, dredging may cause nearly 7-fold increase in zinc-input, and triple the amount of copper and mercury input (Clark *et al.*, 1997). Bothner (1998) found a doubling of the silver concentrations in the upper sediment layer following an unusually strong storm. Likewise, Kersten *et al.* (2005) found that wave-driven re-suspension during gale events produced large pulses of contaminated sediments in the shallow Mecklenburg Bay. The resulting progressive transport model explained 50 % to 80 % of deposited contamination in the deep parts of the Baltic Sea (Luoma and Rainbow, 2008). The dredged material disposal has potential effects on water quality as well, owing to the large quantity of sediments dredged annually and the high concentration of chemical constituents associated with some of these sediments (Brannon *et al.*, 1979).

Physical disturbances of the seabed (dredging, ship anchoring, propeller scour, storm surges, *etc.*) can remove this material and bring it into contact with air (*e.g.* NRCan, 2007), resulting in an oxidisation, for example, of insoluble sulphur compounds to highly soluble sulphates. Oxygenation during dredging can cause a change of the chemical equilibrium; metals may become oxidised and solubilised, before becoming re-sequestered with oxyhydoroxides (Langston *et al.*, 2003). The pH-value also has significant impact on the suspension of metals. For example, a change of just 1.0-1.5 on the pH-scale may bring the complete metal content of mineral substrates into solution (Förstner, 1983). Especially large scale reductions of the pH-values, caused by effects like the acid rain in regions with low buffer-capacity, can lead to considerable metal redistribution. Laboratory tests by Löser *et al.* (2004) have confirmed an increase of the solubility of some elements, including zinc, following increased acidification.

In addition to physical/chemical causes, the die-back of sediment accumulating plants also has the potential to release a considerable amount of possibly contaminated sediment. In Poole Harbour, for example, at least 4 million cubic metres of sediment have already been released due to the decline of the perennial *Spartina anglica* C. E. Hubbard (*cf.* Chapter 7); while the remaining 3 million cubic metres of sediment accumulated by *Spartina*-growth are potentially at risk of being released as well (Swales *et al.*, 2005;

Diaz and May, n.d.). A similar effect is observed in several other areas; for example, the die-back of the common mangrove *Avicennia marina* in Australia (Duke *et al.*, 2003).

1.3.3 Climate change and sea-level rise

Another major factor that can lead to redistribution of chemicals in sediments is climate change. Although research on climate change is not a new topic and can be dated back to at least 1895 (Adams, 1989), it gained increasing interest in the last 20 years. According to the IPCC report (IPCC, 2007) climate change is defined as:

> *“a change in the state of the climate that can be identified (…) by changes in the mean and/or the variability of its properties, and that persists for an extended period, typically decades or longer.”*

Earth's climate is remarkably sensitive to global forcings with predominantly positive feedback loops; and recent emissions of greenhouse gases place the Earth perilously close to a dramatic climate change (Hansen *et al.*, 2007). The 2007 IPCC report states a 90 % likelihood that climate change can be attributed to human activities, in the 2001 IPCC report it was considered to be 66 %. The largest human-made impacts are considered to be carbon dioxide and methane, but other factors influence it as well (Hansen *et al.*, 2007). According to Barnett *et al.* (2005) all currently available climate models predict a near-surface warming trend. This climate change is associated with various consequences, including higher temperatures (IPCC, 2007; Karl *et al.*, 2009), larger water deficits and high light stress (Chaves and Pereira, 1992), considerable financial strains (Dlugolecki and Lafeld, 2005; Stern, 2006; Karl *et al.*, 2009), further decline of boreal fish species (Hübner, 2005; Stenevik and Sundby, 2007; Karl *et al.*, 2009) and an increase in sea level which, on a geological time-scale, is connected with the climate change (Warrick, 1993).

Although the causes as well as the necessary political actions are subject of heated debates and disagreements (*e.g.* Pilkey and Wheeler, 1996; Zillman, 1997; Douglas and Peltier, 2002; Lempert *et al.*, 2004; Pilkey and Pilkey-Jarvis, 2007; Reitz, 2007) it is an established fact that the global mean sea level is rising and will most likely raise furthermore in the following decades. Sea level rise is primarily triggered by a melting of the ice sheets (which may, in turn, contribute to further global warming by reducing the earth's albedo) and an expansion of the sea water caused by increasing temperatures (IPCC, 2007). A hypothetical complete melting of glaciers and ice sheets would raise the sea level by around 70 m, with 88 % attributed to the Antarctic ice sheet (IPCC, 2001; Siegert, 2005). While sea-level rise has been extremely limited (0.1 to 0.2 $mm \cdot yr^{-1}$) for the last two millennia, it has accelerated substantially since the 19th century (IPCC, 2001). According to Gornitz (1993) over the last 100 yr the mean temperature has risen by about 0.5 ˚C and the sea level by 10-20 cm. According to the latest IPCC Assessment Report (IPCC, 2007) the average rate of sea level rise from 1961 to 2003 was 1.8 ±0.5 $mm \cdot yr^{-1}$; the average for the 20th century is reported to be 1.7 ±0.5 $mm \cdot yr^{-1}$. Church and White (2006) confirmed this IPCC result with a slightly lower error of ±0.3 $mm \cdot yr^{-1}$, additionally they report a significant acceleration of sea-level rise of 0.013 ±0.006 $mm \cdot yr^{-2}$. By the 2080s the sea-level in south-east England is expected to rise 26-86 cm and extreme sea levels will be experienced more frequently (Hulme *et al.*, 2002). This, together with the general rise in sea level, could prove critical for estuaries like Poole Harbour (Durell *et al.*, 2006). Wilby and Perry (2006) name several effects of the rising sea level on intertidal habitats, including inundation, accelerated coastal erosion and consequent changes in the sedimentation regimes. Salt marshes are the first areas flooded by sea level rise and many areas already show eroding shorelines and drowning wetlands (Karl *et al.*, 2009). It has been established by several authors (*cf.* Chapter 1.3.1) that these areas act as highly efficient sinks for pollutants; in all likelihood a redistribution of the residual contamination caused by erosion processes will take place as the high flows have the potential to mobilise floodplain sediments and metals (Martin, 2000).

It is worth noting, that apart from its adverse effects, climate change is also predicted to cause some beneficial outcomes, including an increase in vegetation diversity (Rochefort and Woodward, 1992) or a greater habitability at northern latitudes (IPCC, 2007).

1.4 Aims and objectives

Environmental managers and scientists often divide studies into manageable pieces, especially because many subjects are so large that they cannot be studied without being subdivided (Elliott and McLusky, 2002). The geochemistry of sediments is a very wide field and many important aspects must be taken into account, ranging from methodological questions (*e.g.* extraction procedures or grain size normalisations) to the analysis of distribution patterns, determination of origins or the assessment of risks. That is the reason why this study follows a case study approach and analyses important aspects of the sediment geochemistry at a time.

1.4.1 List of objectives

Objectives of case study 1 (*cf.* Chapter 3) were to:

- assess (pseudo-)total concentrations of metals in fast running watercourses in Germany as well as potential differences in distribution patterns;
- determine whether the local monitoring tools in force, which are largely based on analyses of the water, are sufficient for a reliable assessment of the environmental quality.

Objectives of case study 2 (*cf.* Chapter 4) were to:

- investigate the contamination profile caused by a closed landfill, which is located within the Christchurch Harbour nature reserve;

- analyse strengths and weaknesses of a partial extraction scheme based on ammonium nitrate extraction;
- evaluate to what degree a straight artificial channel affects the metal distribution.

Objectives of case study 3 (*cf.* Chapter 5) were to:

- collect high resolution data on the metal distribution within the Poole Harbour estuary, both in regard to (pseudo-)total and mobile metal concentrations;
- test if the chosen methodology (*cf.* Chapter 2) is an efficient protocol (fast, yet scientifically defendable) for the assessment of the environmental quality of an area of this size;
- update an equation for the evaluation of the risk associated with metal contamination for the present environment.

Objectives of case study 4 (*cf.* Chapter 6) were to:

- test a simplified grain-size based normalisation scheme;
- compare the efficiency of different normalisation schemes in a fine grained environment like Wareham Channel by using cobalt as an indicator;
- evaluate the contamination from a known point source in light of the application of the most suitable normalisation scheme.

Objectives of case study 5 (*cf.* Chapter 7) were to:

- investigate if the die-back of the cord grass *S. anglica* in Poole Harbour can be attributed to metal contamination;
- investigate if the die-back of the cord grass *S. anglica* has or had an influence on the metal contamination in the estuary;
- evaluate the degree of potential metal release following the die-back; using three different scenarios.

1.4.2 Explanations of the core objectives:

a) Analysis of methods to derive meaningful data: In the study of risks from metal contamination of sediments, there is a considerable lack of agreement concerning methodologies (*cf.* Chapter 2). In this study, methods, from chemical extraction schemes to sediment quality guidelines, have been carefully analysed and evaluated. Approaches have been selected, highlighting standardised methods in order to produce results offering the highest currently possible comparability.

b) Absolute concentrations and distributions: The primary aim of this study was to provide insights into contamination levels in different aquatic systems, including two estuaries. The largest sampling area, Poole Harbour, was sub-divided into areas defined by their primary usages. The degree to which usage affects the chemical composition was tested, to determine if adverse effects on aquatic life were possible in any of the zones studied (*cf.* Chapters 3, 4 and 5). Distribution pathways of contaminants were assessed in different environments (watercourses, intertidal areas, estuaries with a flat bottom and a channel within an estuary). Mobility is defined as the percentage of the total concentration that can migrate and is crucial in estimating risks from contamination. The suitability of a widely used analytical procedure has been evaluated in different zones and subsequently applied to assess the mobility in areas appropriate for this method, *i.e.* Christchurch Harbour (*cf.* Chapter 4) and Poole Harbour (*cf.* Chapter 5).

c) Normalisation: Metal distributions are affected by the grain size of the associated sediment: fine grained sediments have a high sorptive capacity for contaminants, while environments containing primarily non-cohesive, coarse grained sediments have a low sorptive capability. Various methods have been proposed to counteract this effect and to highlight possible anthropogenic sources, for example expressing concentrations as ratios of an element to a natural abundant metal like aluminium or by using solely the <63 µm fraction. Such methods are not without problems; hence, in this study different approaches have been considered (*cf.* Chapter 6).

d) *Spartina anglica* die-back: *Spartina anglica* is of great importance for coastal management, but has died back in Poole Harbour; so far the reasons for the die-back remain only partially explained. Furthermore, large amounts of contaminants could be released following any die-back, since: (a) metals and metalloids, especially cadmium, are accumulated within the plants, and (b) potentially contaminated sediment currently sequestered by the plants could be remobilised. Therefore, differences in contaminant loads in areas where *S. anglica* has died back and where it still flourishes have been assessed (*cf.* Chapter 7).

2 Methodology

A key property of good results, and consequently for reliable decisions, is comparability (Ellison *et al.*, 2003), defined as the ability to compare results meaningfully wherever they originate. At present, it is extremely difficult to compare the results of different studies. This is partly caused by differences in sediment type and related chemical parameters that make it difficult to compare contaminant levels from different regions, or, in some instances, within the same salt marsh (Williams *et al.*, 1994). Inter-comparability is made even more complicated by the differences in analytical methodology: This is caused by the lack of uniformity in field sampling techniques and chemical analytical methodology (*e.g.* de Groot *et al.*, 1982; Kennedy *et al.*, 1997; Filgueiras *et al.*, 2002). Marine data and information are collected by a variety of UK government, non-government, academic, private sector and other research organisations for many different reasons, resulting in a legacy of differing ways of storing and sharing data and information (Rickards, 2005).

In no field is incoherence more evident than in the study of risks from trace metal contamination of sediments (Luoma and Rainbow, 2008). The SedNet (EU Sediment Network) report by Salomons and Brils (2004) stated that even countries assessing the same river basins “typically” apply different methods, resulting in a severe impairment of inter-comparability. For example, many sediment quality guidelines have been proposed to estimate risks associated with metal concentrations, which in some cases show substantial discrepancies. In addition, methodological questions are a major concern. There have been numerous methods proposed for sequential extraction schemes (Filgueiras *et al.*, 2002). Also regarding the simpler partial extraction schemes there are different protocols, and owing to the different leaching strengths of the numerous suggested extractants it is nearly impossible to compare different environmental studies (Hübner *et al.*, *in press*). Standardisation of sieving techniques is another critical aspect in the overall sediment monitoring strategy (Herut and Sandler, 2006) and more research is required. Despite their importance, normalisation schemes are also poorly harmonised; there are no clear rules regarding the procedure and the choice is subjective (Roussiez *et al.*, 2005). All these aspects are discussed in the following chapters in greater details.

As a result of this lack of harmonisation, laboratories in different countries, and even within the same country, produce metal data which are often incompatible (Loring and Rantala, 1992). In the present study, an emphasis has been put on standardised methods in order to produce results offering the highest currently possible comparability.

2.1 Collection and pre-processing

2.1.1 Site selection

In line with the objectives of the present project (*cf.* Chapter 1.4.1), three different sites were chosen. All three areas are particularly suitable for the specific research questions of the different case studies, but all have in common that limited data are available for them.

a) Bigge and Olpe, Germany
   Most rivers flow through different regions and are subject to numerous anthropogenic impacts (*i.e.* different urban, agricultural and industrial uses). This usually leads to a variety of different contaminants in water and sediment. The two rivers in Germany have only two major, distinctive contamination sources: one natural (copper) in the Olpe and one anthropogenic (primarily zinc and nickel) in the Bigge. This site is therefore ideally suited to analyse the distribution patterns of contaminants in small and fast running watercourses. In addition, environmental monitoring in the present form is largely based on analyses of the water column, while data on the sediment are very limited.

b) Christchurch Harbour, United Kingdom

Landfills, particularly unconfined sites, are a major environmental concern. In Christchurch Harbour a closed landfill is located within a saltmarsh, which is in direct hydraulic connectivity with coastal waters. It consequently has a considerable impact on the surrounding marshland, which is classified as Nature Reserve and Site of Special Scientific Interest (SSSI). In addition, the site provides a range of different features, most notably a linear channel leading from the landfill directly to the estuary – allowing the assessment of a partial extraction scheme based on ammonium nitrate extractions (DIN 19730) under different conditions.

c) Poole Harbour, United Kingdom

Poole Harbour is a large natural harbour and one of the major estuaries of the British south coast. Large parts of the estuary have been classified as Site of Special Scientific Interest and Special Protected Area. The area is considered to be very vulnerable to pollution; nevertheless, the harbour has been, and still is, subject to considerable urban, agricultural and industrial use, but also has parts which are hardly or only moderately affected by human activities. The harbour is also very diverse in regard to its ground composition, which includes very fine grained mudflats in the southern and western regions, a rocky shore in the north-eastern corner and sandy beaches in the eastern part. Most studies describe the marine ecology of the estuary, while sediment research is very limited. Consequently, Poole Harbour has been in the focus of this study and subject of three of its five case studies.

2.1.2 Fieldwork

Ahlf *et al.* (2002) suggest a general sampling depth for sediments of 50-100 cm. The revised instruction manual of the Norwegian pollution control authority (*Norge statens forurensningstilsyn;* SFT) recommends cores that reach to a depth of pre-industrial age (Breedveld *et al.*, 2007). Owing to the long industrial use of Poole Harbour, going back to the Iron Age (*cf.* Chapter 5.1.2), this would not be feasible for such regions in the present study. Considering the equipment used (Table 1) and the sedimentation rates in Poole Harbour (Cundy and Croudace, 1996; Warneke, 2002), an analysis of the past 90 years was possible throughout the harbour (120 years under optimal conditions); which is considered more than adequate for the target of this study (Chapters 5 and 6) and also lies well within the range suggest by Ahlf *et al.* (2002). In the other analysed environments such considerations were dispensable, as the maximal sampling depth was usually limited by ground features.

A wide range of coring devices have been developed, tested and recommended by various authors (University of Arizona, n.d.). Most corers are variations of a limited number of designs: most commonly the gravity-, piston- and vibro-corer (Smol, 2002). In this study three different corer designs have been utilised, each carefully selected to deliver the best result for the particular environment (*cf.* Table 1 and Chapter 10.2 for more details).

Smol (2002) points out the importance of slicing the cores as soon as possible (*i.e.* preferably on the boat, at the latest on shore) to minimise post-depositional mobility. Langston and Spence (1998) describe the necessity to clean all equipment in contact with sample material between the sample locations and recommend that samples are processed as quickly as possible after collection. When analysing trace metal concentrations the sample should be stored in polyethylene bags to minimise sample contamination (Ure, 1995). These recommendations have been implemented in the present study.

Table 1: Overview over the three corer types used in this study

	Beeker	Russian	Bigge
disturbance of the top layer	negligible	low in dry environments, considerable under wet conditions	low in wet, medium in dry environments
core compression	<5 %	<5 % (estimated)	<5 % in sandy sediments, between 5 and 15 % in clayey samples
sample loss	none	none in dry, very high in wet environments	low, only deepest part affected
complexity/efforts	very high	low	very low
weight of complete kit	45 kg	18 kg	1 kg
max. core length	100 cm	50 cm (a)	70 cm
max. overlaying water column	5 m (b)	0 m	0.5 m (b)
not suited for	sand/gravel, dry materials	very wet, especially submerged materials	deep submerged and very coarse materials
best suited for	submerged (0.5-3 m) clayey sediments with only small sand fractions	dry sediments and soils of all fractions, although sand can impair the hinge	lightly submerged (0-0.4 m), wet clay-sand mixtures; remote areas
primary usage in this study	Poole Harbour estuary (UK)	Christchurch Harbour estuary (UK)	tributaries of the lake Biggesee (Germany)
more details	*cf.* Chapter 10.2.1	*cf.* Chapter 10.2.2	*cf.* Chapter 10.2.3

[a]) design allows consecutive sampling in progressive depth steps, but this increases risk of bias substantially

[b]) greater depths are possible, but not recommended

2.1.3 Preparation of the samples

Before the chemical analyses (*cf.* Chapter 2.2) can commence, the material must be processed. Immediately after extraction, the fresh sediment samples were dried at a temperature not exceeding 40 °C, typically at 36 °C, to avoid the loss of mercury (Salminen *et al.*, 1998). Samples which could not be processed within 12 hour (*i.e.* samples from Germany, *cf.* Chapter 3) were stored frozen. Samples destined for DIN 19730 analyses (*cf.* Chapter 2.2.4) were dried at lower temperatures in accordance with the recommendation of Traub and Scharf (2001).

The determination of grain size is critical in sediment analyses (Ranasinghe *et al.*, 2002). Small sediment grains have, in relation to their mass, a higher surface area compared to larger grains, and with the digestion methods used these fractions, in general, show a higher recovery rate (defined as the percentage of the total concentration which is extractable with a given method). Mesh-sizes that are too small require much more effort to mill the sediment, which can constitute a substantial problem with large sample sizes (*i.e.* exceeding 3,000 sub-samples, as in the present study) under time constraints, especially if the grinding process is unduly shortened or omitted completely. Larger mesh-sizes on the other hand allow a varying quantity of larger and smaller particles in the *aqua regia* (AR) extraction, randomly changing the surface:mass relationship and hence affecting the efficiency of the digestion process. With smaller mesh-sizes more grinding effort is required and a certain amount of material may be lost. In that case very small mesh-sizes hold the danger of introducing a strong pre-selection of the sediment by only including the small particles in the analyses, which could distort the outcome, *i.e.* it would no longer qualify as a *total* analysis. However, since the particles are both smaller and much more homogenous, the results become much more precise. Therefore, an acceptable balance must be found. In the literature, samples are sieved with a wide range of mesh-widths commonly ranging between 0.063 and 2 mm. In the overall sediment monitoring strategy the standardisation of sieving techniques is one of the critical aspects (Herut and Sandler, 2006). Sometimes different mesh-sizes are used within the same study (*e.g.* Haslam and Tibbett, 2001; Lakhan *et al.*, 2002; Ranasinghe *et al.*, 2002). This is useful if the distribution of elements in different grain size fractions is to be analysed (*cf.* Chapter 6), but excessive if only the total concentrations of elements are required.

Hübner and Haslam (*submitted*) investigated the effects of different mesh-sizes (*cf.* Chapter 10.3.3) on the subsequent total content analysis (TCA) by gauging the effects on: accuracy (defined as the conformity of the result with the actual values, *i.e.* the correctness of the analyses), precision (defined as the conformity between the sub-samples, *i.e.* reproducibility of the results) and material loss (defined by the quantity of material which could not be included into the extraction procedure owing to the sieve selected). These analyses showed that the unassisted *aqua regia* extraction can produce precise and accurate outcomes if the mesh-size is carefully selected. Figure 1 shows the impact of four different mesh sizes on the precision. For the analysed metals, the average coefficient of variation between the replicates was determined for four different mesh-sizes: 0.1 mm, 0.3 mm, 0.5 mm and 1.0 mm. It is clear that the two smallest analysed sieves have the highest precisions in all sediment types; particularly the 1.0 mm sieve produces unacceptably high variations between the replicates – compared to the 0.3 mm sieve, the coefficient of variation is on average more than three times as high. In fine and coarse grained sediments the 0.1 mm sieve delivers slightly better precisions than the 0.3 mm sieve, but the latter is clearly better suited for mixed sediments. In addition, it requires a lot of time to grind the sediment down to 0.1 mm, and in the coarse group a considerable amount of material may still be lost (Hübner and Haslam, *submitted*). It was therefore concluded that for conditions as encountered in Christchurch Harbour, Poole Harbour and the Biggesee tributaries, a 0.3 mm sieve delivers a reasonable effort/result relationship for total/pseudo-total content analyses. This mesh-size has consequently been used in this study.

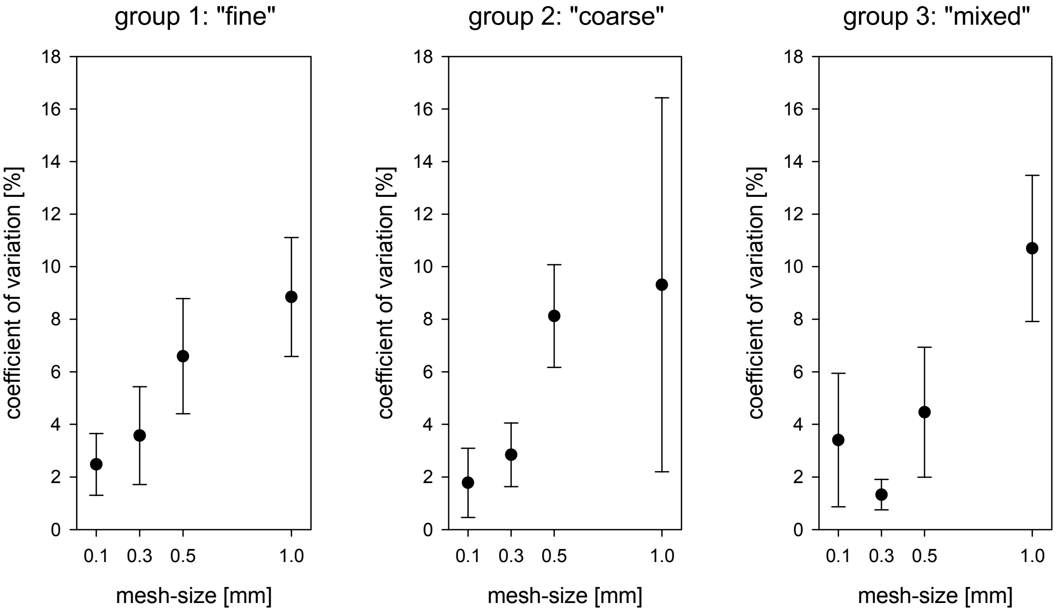

Figure 1: **Effect of the grinding on the precision of hotplate *aqua regia* extractions: the average coefficient of variation between the replicates in the metal analyses**

2.2 Chemical analyses

Analyses require pre-treatment of dissolution of metals from the sample matrix (Nguyen *et al.*, 2005a). In this study, the suitability of total content analyses (TCA), sequential extraction schemes (SES) and partial extraction schemes (PES) has been evaluated. TCA and PES – two crucial elements of the assessment of the risk potential of elements (Bauer *et al.*, 1996) – have subsequently been applied.

All analyses are based on atomic emission spectroscopy. Atomic adsorption/emission spectroscopic means were developed around 1970 and allow precise elemental analyses. With a few exceptions, all earlier published metal data, based on various determination methods, must generally be assumed to be highly inaccurate (Schmidt and Dicke, 1990).

Methodology and rationale related to normalisation techniques have been discussed in detail in case study 4, which exclusively deals with this aspect (*cf.* Chapter 6).

2.2.1 Material

Thorough cleaning of all the laboratory equipment that comes into contact with samples is necessary to avoid contamination of sample material (Raposo *et al.*, 2004). All glassware, plastic funnels and similar materials used in these analyses were washed with Decon90 laboratory cleaning agent, rinsed in deionised water, soaked in nitric acid (>10 %) for at least 8 hours and thoroughly rinsed with deionised water prior to use.

For heating Grant QBD4 and QBT4 digestion blocks were used. All used reagents were trace analysis grade provided by Fisher Scientific. Spectroscopic methods are frequently used for multi-element determinations due to the sensitivity and selectivity of signals produced by atomic optical emission (Pavlíčková *et al.*, 2003). The analyses in this study were performed with a Varian Vista-PRO ICP-OES (Inductive Coupled Plasma, Optical Emission Spectrometry) instrument. The ICP was calibrated using Fisher Scientific ME/1001/08 multi-element standards.

2.2.2 Total content analysis (TCA)

The total content analysis (TCA; also total concentration analysis) is a central tool in the ecological risk assessment process (Väisänen *et al.*, 2002; Hübner and Haslam, *submitted*) and is a crucial element in the estimation of the risk potential of a contaminant (Bauer *et al.*, 1996). In addition, the interpretation and comparison with numerical effect-range guidelines requires the use of strong acid digests, as most of these guidelines themselves are derived from such data (*cf.* Chapter 2.2.6).

In practice, most digestions are a pseudo-total rather than a total content analyses. However, the pseudo-total content is normally sufficiently close to accepted values. Ščančar *et al.* (2000b) compared total and pseudo-total metal concentrations in order to evaluate the efficiency of *aqua regia* extractions and found that over 90 % of the analysed concentrations agree within a 5 % range; while the remaining 10 % showed no statistically significant differences between the means. They concluded that *aqua regia* quantitatively leached all analysed metals. Agemian and Chau (1976) noted that such methods offer a high degree of metal extraction, but may be limited by high silica contents. The quality standards of most European countries are based on pseudo-total metal analyses (Gupta *et al.*, 1996).

Owing to its simplicity, speed and effectiveness, the *aqua regia* (AR) extraction is a widely used TCA method; it is commonly classified as pseudo-total. It has been extensively described by, for example, McGrath and Cunliffe (1985) and became standardised in 1995 under ISO 11466 standard (ISO, 1995). The advantages of this method include the fact that the apparatus is inexpensive, yet free from common contamination-sources, easy to operate and suitable for routine operations (Berrow and Stein, 1983). It is the recommended monitoring-tool for samples with an organic matter content below 70 % (Sastre *et al.*, 2002). AR-extractions are also often performed as bomb digestions (Berrow and Stein, 1983), ultra-sonic- (*e.g.* Väisänen *et al.*, 2002; dos Santos *et al.*, 2005; Ilander and Väisänen, 2009) or microwave- (*e.g.* Feng and Barratt, 1994; Adami *et al.*, 2007) assisted, or supplemented with hydrofluoric acid (HF; *e.g.* Rao and Reddi, 1990; Terashima *et al.*, 1992) in order to increase the effectiveness. Melaku *et al.* (2005) analysed different combinations and volumes of hydrofluoric, nitric and hydrochloric acids and found a good agreement between the procedures and certified values. Ščančar *et al.* (2000a) generally found a good comparability as well, but they reported significantly lower results for the extraction of chromium, nickel and cadmium. Bacon *et al.* (2000) found that results from HF- and AR-extraction were in close agreement. Chen and Ma (2001) compared three different AR-procedures (hotplate, microwave, microwave+HF) and found generally a high precision for all three methods as well as only a slightly lower accuracy (6 % difference) for the hotplate digestion method in comparison with the microwave assisted extraction. The best accuracy was reported for the microwave+HF procedure. The most notable property of HF is its ability to dissolve silica (Berrow and Stein, 1983; Dulski, 1999). It is, however, not only a very dangerous material which requires careful handling (Santos *et al.*, 2009), but is also highly corrosive and can cause considerable damage to expensive analytical instruments, particularly ICP-MS/OES (Nguyen *et al.*, 2005a). Currently, the use of HF is in decline, and this has led to the problem that in some countries, such as Denmark, the necessary expertise has become rare (pers. comm. Odgaard[1], 2009).

The hotplate variant is, owing to its simplicity and efficiency, still one of the most common procedures. Since the AR-method will, given an appropriate pre-treatment of the samples, produce fast and accurate results, this method was the primary tool for the analyses, with careful consideration of the chromium, nickel and cadmium concentrations. The methodology initially described by McGrath and Cunliffe (1985), with the modifications described in the Bournemouth University instruction manual (Anon., 2005) and by Hübner and Haslam (*submitted*), has been applied (*cf.* Chapter 10.3.1). In particular, the relationship between sample material and acid was increased, a relationship 0.250 g sample material to 12 ml AR led to the best outcomes for the contamination levels in the test samples. Furthermore, instead of a volumetric approach, a weight measurement was used. After extraction and drying the metals have been re-dissolved in 25 % HNO_3 for 1 hour.

To maintain a high standard the results were validated as a routine quality control with certified reference materials (CRM), as suggested in literature (*e.g.* Ure, 1995; Dulski, 1999; *cf.* Chapter 2.2.5).

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2.2.3 Sequential extraction schemes (SES)

Chemicals may be permanently locked in sediments, or they can eventually be released; the ability to predict their subsequent fate is a key factor in assessing the effects of environmental pollution (Guo *et al.*, 2007). The mobility of an element is an important parameter, and is, next to the total content analyses, crucial for the estimation of the potential risk associated with an element (Bauer *et al.*, 1996). A wide variety of different extraction techniques have been adopted to selectively extract metals from major chemical phases in order to assess the potential bioavailability (Salomons and Förstner, 1980; Förstner, 1982; Kennedy *et al.*, 1997; Filgueiras *et al.*, 2002). If these methods are applied consecutively, sorted by their increasing dissolving ability, it is called a sequential extraction scheme (SES; Kabala and Singh, 2001; NCR, 2003). SES-methods have considerable use for assessing bioavailability (Langston and Spence, 1998).

The original 5-step SES was proposed by Tessier *et al.* (1979), and two decades later it was still a very common variant (NCR, 1999), but numerous variants have been introduced and disseminated. As a result of these variations and resulting disarray, the SM&T (Standards, Measurements and Testing Programme, formerly known as *Bureau Communautaire de Référence*; BCR) tried to unify the methodology and proposed a new 3-step method (Quevauviller *et al.*, 1993; Ure *et al.*, 1993), but since then various new amendments have been developed, including new 3-step schemes (*e.g.* Barona *et al.*, 1999; Leleyter and Probst, 1999) and a “revised BCR-method” (Rauret *et al.*, 1999; Mossop and Davidson, 2002). Schemes with up to 8-steps (*e.g.* Rosenbaum-Mertens, 2003) have been proposed. Numerous papers deal with comparisons of the different versions and list advantages and disadvantages (*e.g.* Mester *et al.*, 1998; Usero *et al.*, 1998; Tokalioglu *et al.*, 2003; Tlustos *et al.*, 2005; van Hullebusch *et al.*, 2005; Zakir and Shikazono, 2006). A comprehensive review by Filgueiras *et al.* (2002) provides a 21 page-long list of different methods, supplemented with 434 references.

The inter-comparability of the SES is not only extremely limited, but it is also a time-intensive and difficult method to use (Hübner *et al.*, *in press*). To complicate matters further, the effectiveness of sequential extractions is highly disputed. For example, Martin *et al.* (1987) described the disadvantages of SES and pointed out that this methodology gave gradients at best, and that the approach generally fails to estimate the bioavailability of trace elements. When comparing three schemes, Zakir and Shikazono (2006) reported inconsistencies in the soluble/exchangeable fractions and those bound to carbonates. Another study (Joksič *et al.*, 2005) found significant differences between the original and the modified BCR-version. Experiments by Gaillard (2004) for SES-outcomes showed significantly different trace metal speciations compared to both acid volatile sulfide (AVS) extractions and x-ray absorption spectroscopy (XAS). Analyses by Kheboian and Bauer (1987) indicated that metals were not recovered in the appropriate fractions. Rendell *et al.* (1980) warn of the danger of serious misinterpretations owing to the inability of the reagents to prevent losses of soluble metal, leading to re-adsorption. Förstner (1983) pointed out that the majority of these methods are neither selective nor phase-specific and described various difficulties and problems. Many other authors have also criticised the problems associated with SES (*e.g.* Tipping *et al.*, 1985; Rapin *et al.*, 1986; Shannon and White, 1991; Sheppard and Stephenson, 1995; Hall and Pelchat, 1997).

After careful consideration and initial laboratory tests sequential extraction schemes have been discontinued in this study and partial extraction schemes have been employed in preference.

2.2.4 Partial extraction schemes (PES)

Partial (or single step) extraction schemes are a widely used alternative (NCR, 1999). These faster and simpler methods have recently become more common (Meers *et al.*, 2007). Partial extractions use a weak or diluted acid or a chelating agent to remove metals from a particular fraction (Haslam and Tibett, 2004). These extraction methods are faster, less complicated and less error-prone. Originally, this approach was developed to provide agriculturalists with a relatively simple empirical method for judging fertilisation requirements and was later adapted and widely used for the assessment of the bioavailability of metals (Kennedy *et al.*, 1997). Guo *et al.* (2007) stated that compared to SES, PES is a desirable alternative for the assessment of the potentially mobile fraction; and Cid *et al.* (2002) found a good agreement between the metal contents released in the first three fractions of the Tessier method and the results of two PES (EDTA and acetic acid) for most of the elements studied.

The extraction with magnesium chloride ($MgCl_2$) is, for example, one of the methods in use (Kennedy *et al.*, 1997), it is a part of the original 5-step SES (Tessier *et al.*, 1979) and extracts elements from the exchangeable (first) fraction only. Another part of the 5-step method (fourth fraction: bound to organic matter) has originally been proposed as a single extraction procedure by Gupta and Chen (1975), namely the extraction with HCl and H_2O_2.

A very commonly used protocol is the German industrial standardised process DIN 19730 (DIN, 1997), formerly known as interim standard DIN V19730 (DIN, 1993). It uses ammonium nitrate (NH_4NO_3) solution as an extractant and was developed for inorganic pollutants (BBodSchV, 1999) This PES was used to develop trigger values for the assessment of the transfer of metals and metalloids from soils to plants (Gryschko *et al.*, 2005), regulated by the German Federal Soil Protection and Contaminated Sites Ordinance (Hildenbrand and Turian, 1996), the first such regulation in Germany (Prüeß, 1998). Gryschko *et al.* (2005) compared KNO_3 and NH_4NO_3 and consider the latter (DIN 19730) to be a suitable method for the determination of readily soluble and plant available trace elements. While other PES extractants like, for example, EDTA and acetic acid are regarded as primarily suited for the plant-available fractions, NH_4NO_3 only releases electrostatically weakly bound metals and is therefore ideally suited for the determination of the mobile fraction (Schramel *et al.*, 2000). NH_4NO_3 extractions can be used as a sensitive tool to detect the amounts of potentially leachable elements (Prüeß, 1998). Traub and Scharf (2001) tested this method and stated that the it provides comparability, but suggested avoiding temperatures above +20 °C, because that could lead to thermal degradation of the organic matter, which, in turn, changes the extractability of the metals (especially chromium and copper). Owing to its advantages, including the high level of standardisation/ comparability and its specific suitability for the analysis of the mobility, the NH_4NO_3 extraction method has been applied to quantify the mobile fraction in sediments in this study.

Although the ammonium nitrate creates a slightly acidic environment and therefore standardised conditions, different element speciations, which have a strong effect on mobility, cannot be completely ruled out and it should always be kept in mind that elements in different speciations might show variations in extractability with a given partial extraction scheme.

2.2.5 Quality control

Analysis methods like TCA and PES rely on transferring the analyte from the complex matrix into a simpler solution, which is then used to present the analyte for instrumental determination; however, commonly a substantial proportion of the analyte remains in the matrix after extraction (Thompson *et al.*, 1995). The accuracy and precision of extractions might vary with element, sample origin (anthropogenic/natural deposits) and sample properties (Chen and Ma, 2001). Without reasonable verification, metal data may be meaningless (Langston and Spence, 1998). Therefore, different measures have been implemented to reduce uncertainty of the outcomes.

Firstly, materials and methods have been applied which have shown the best accuracy and precision in previous analyses (*cf.* Chapters 2.1.3-2.2.4).

Typically, per sample (defined as the sediment extracted from a given depth at a given location) three replicates (defined as identical sub-samples of a sample, undergoing identical analytical processes) were analysed. The mean ($\overline{x}$), standard deviation (s^2) and coefficient of variation (CV) were calculated. If the average CV of a sample exceeded 0.4, indicating problems such as cross contamination, ICP-calibration errors or typos in the laboratory notes, the according data-set was flagged and further replicates of the sample were analysed.

To verify the methodology, numerous blank samples (often referred to as blank controls or blank determinators) have been introduced to detect possible contamination during the chemical analyses. Filter- and or laboratory wiping paper, which were in contact with sample material or equipment, were randomly analysed as well. Additionally, two sets of certified reference materials (CRMs) have been used: NWRI TH-2 and NCS DC73325. Both were taken through the entire procedure, as recommended by Langston and Spence (1998). The blank samples showed metal concentrations around or below the analytical detection limits. The random paper analyses showed a high sodium and calcium content a well as negligible concentrations of iron and aluminium, while other metals/metalloids were not detectable. The outcomes of the CRM-analyses generally showed a high accuracy (defined as recovery rates close to 100 %; *cf.* Table 2) and good precision (defined by the coefficient of variation between the replicates). Typical metal recovery rates in these analyses were between 85 % and 115 %, which is the restriction required for laboratories by the 1990 US EPA quality assurance plan (US EPA, 1990; Valente *et al.*, 1990). Only aluminium, lead and tin did not meet these criteria. However, all three elements showed consistent results, *i.e.* outcomes had a high accuracy. Consequently, these outcomes may underestimate the true concentrations in the sediments. Contrary to the results of Berrow and Stein (1983) and Ščančar *et al.* (2000a) the applied AR-method also produced results with a high conformity for nickel, regarding both accuracy and precision, and were reproduced in numerous tests. Recoveries between 96.2-109.8 % are considered to be excellent (Fox *et al.*, 2007) and such rates were observed for arsenic, cobalt, copper, nickel and zinc. For mercury no CRM-values were available.

Table 2: CRM recoveries with the applied hotplate *aqua regia* methodology

	recovery rate [%]	coefficient of variation [%]	classification[(a)]
Aluminium	76.09	24.1	problematic
Arsenic	96.01	19.1	excellent
Cadmium	93.05	20.6	acceptable
Cobalt	98.35	8.8	excellent
Chromium	86.27	18.9	acceptable
Copper	104.67	17.4	excellent
Iron	90.48	12.6	acceptable
Mercury[(b)]			
Nickel	103.22	11.4	excellent
Lead	79.27	17.9	problematic
Tin	65.87	12.6	problematic
Strontium	92.77	21.6	acceptable
Phosphorus	86.04	19.2	acceptable
Zinc	99.93	21.1	excellent

(a) based on Valente *et al.* (1990) and Fox *et al.* (2007)

(b) no CRM-values were available for mercury

2.2.6 Interpretation

Caeiro *et al.* (2005) describe three methods for assessing metal contamination: contamination indices (comparison of different clean/polluted sites); background enrichment indices (comparison with different baseline or known background levels); and ecological risk indices (comparison with sediment quality guidelines). Traditionally sediment contamination was assessed by comparison of bulk chemical concentrations with values from others areas; which has limited value in predicting adverse effects on living organisms (Long *et al.*, 1995; Annicchiarico *et al.*, 2007). In order to assess chemical contamination, statutory, harmonised sediment quality guidelines (SQGs) are necessary to put the results into context. Such values are defined as "*numerical limits or narrative statements recommended to support and maintain designated uses of the aquatic environment*" (CCME, 1995).

a) An overview over sediment quality guidelines (SQGs)

In North America researchers and environmental regulators have been working on sediment monitoring and controlling methods for some time (Crane, 2003; Engler *et al.*, 2005), but the research undertaken outside America is less systematic. Australia only began to implement SQGs a few years ago, while in Japan such a step is currently not planned at all (pers. comm. Shibuya[2], 2008). Between EU member states there is a substantial lack of agreement regarding the development and implementation of SQGs (Crane, 2003; den Besten *et al.*, 2003) and currently no uniform guideline values are available to assess the degree of contamination in sediments (Salomons and Brils, 2004; Hübner *et al.*, 2009). The absence of uniform European guideline values makes it especially difficult to put the results of a particular study into context, since the sediment chemistry data alone is not sufficient for the estimation of potential adverse effects (Long *et al.*, 1995). In several studies the need for SQGs has been stressed (*e.g.* Köthe, 2003; Salomons and Brils, 2004) and several authors have called for the incorporation of guidelines into the European Water Framework Directive (WFD; European Commission, 2000), which currently leaves this option open (Annex V: "standards may be set for water, sediment or biota"). Furthermore, the WFD declares in article 16 that the European Parliament and the Council ‘‘shall adopt specific measures against pollution of water’’ and instructs the Commission to submit proposals for quality standards of ‘‘priority substances’’ in surface water, sediments or biota. There are attempts to implement much more concrete measures, including Environmental Quality Standards (EQS; sometimes referred to as European Quality Standards), on that basis (*e.g.* Lepper, 2002; Lepper, 2005; De Coen *et al.*, 2007). However, such attempts are controversial and several theoretical and practical questions are emerging from according proposals (Crane, 2003). Even the Soil Framework Directive (European Commission, 2006a), a fairly anodyne proposal for tackling soil contamination that does not even propose any threshold values, has met a strong resistance from some

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EU member states and is therefore currently on hold (pers. comm. Marmo[3], 2008). The Dutch position is, for example, that related measures should be taken at regional or even local level with limited involvement of the EU (VROM, 2005). The implementation of uniform and mandatory European SQGs in the near future is considered extremely unlikely (Hübner *et al.*, 2009).

At a national level several guidelines have been developed, although mostly for specific regions, most notably for the USA and regions within it (*e.g.* Long and Morgan, 1990; MacDonald, 1994; Long *et al.*, 1995; WSDE, 1995; MacDonald *et al.*, 1996; Buchman, 1999; MacDonald *et al.*, 2003b; Buchman, 2008), Canada (CCME, 1995; CCME, 2002; MacDonald *et al.*, 2003a; CCME, 2007; EC and MDDEP, 2007), the Netherlands (VROM, 1997; Crommentuijn *et al.*, 2000; Crommentuijn *et al.*, 2001) and Norway (Bakke and Breedveld, 2005; Breedveld *et al.*, 2007; Källqvist *et al.*, 2007). Furthermore, US values have been adapted (either unaltered or modified) for the use in, for example, Hong Kong (Chapman *et al.*, 1999a), Australia/New Zealand (ANZECC and ARMCANZ, 2000; McCready *et al.*, 2006a; McCready *et al.*, 2006b), Sweden (Notter, 1993) and various US states (WDNR, 1995; NYSDEC, 1999; Cormack, 2001).

b) Evaluating limitations and suitability of SQGs

In order to assess these as well as the suitability of a particular set of SQGs, seven factors should be considered (Hübner *et al.*, 2009):

1) Geography: Many SQGs values are developed and/or (re-)calibrated for a specific region, e.g. the SQGs for New Zealand/Australia or Canada, and have not been validated for other areas with possible differences in sediment geochemistry or biological diversity. If a research project is to be conducted in Florida, the values by MacDonald *et al.* (1996) can clearly be considered to be much better calibrated than for example the Australian

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[3] Luca Marmo, European Commission Environment Directorate-General, Agriculture, Forests and Soil Unit

(ANZECC and ARMCANZ, 2000) or Norwegian (Breedveld *et al.*, 2007) SQGs. According to Chapman *et al.* (1999b) the appropriate use of SQGs includes the provision that they are used solely in the region where they were developed. However, this is not always feasible, since the majority of the SQGs are developed in and for Northern America; nor is it always advisable, since geography is not the only aspect which should be taken into account.

2) Environment and exposure: SQGs cannot directly include fluctuating environmental factors such as grain size, pH-value, population stress or exposure time, which can affect, for example, bioavailability, toxicity and susceptibility. Several attempts have been made to compensate for some of these weaknesses. Although many of these procedures are site-specific and therefore not, or only to a very limited degree, applicable for direct implementation into general SQGs, they are a very important tools for the optimisation of a single research project under specific conditions. For example, normalisation procedures have been proposed to neutralise the impact of different grain-sizes (*cf.* Chapter 6). Furthermore, the risks of chronic effects of contamination are often underestimated (Soldán, 2003) and SQGs can only consider the implications of long term exposure and bioaccumulation to a very limited degree; SQGs are normally designed for total metal extractions. The Dutch values (Crommentuijn *et al.*, 2000) for example, define the bioavailability invariably as 100 %. The development of SQGs consisting of two separate tables – one for the total and one for the bioavailable content – would be a sound and effective solution. However, analysing the extractable contents separately is highly methodology-specific and can lead to significantly different outcomes. Owing to the considerable lack of agreement in relevant methodologies (*cf.* Chapter 2.2), the development of SQGs designed to be used with a specific single/partial or sequential extraction scheme must be considered extremely unlikely in the foreseeable future.

3) Chemicals: SQGs can obviously only cover well known and thoroughly tested chemicals and not newly developed substances; even for some

typical contaminants like tin, nickel, silver and cobalt only limited data are currently available. Different SQGs often cover different chemicals. In addition, such guidelines can only be used to assess a single chemical at a time and not mixtures of various substances which might react antagonistically/synergistically. Indeed, for some biological species, both synergistic and antagonistic effects have been reported for various metals in binary mixtures (*cf.* Chapter 1.2.3). SQGs can therefore be misread since values exceeding the guidelines do not necessarily mean that adverse effects are inevitable. For example, in a study conducted in the river Clark Fork all measured copper and zinc concentrations indicated the presence of adverse effects according to NOAA's sediment quality guidelines for benthic invertebrates; however, no toxic effects could be detected (NRC, 2002). This problem is inherent to all SQGs and cannot be avoided.

4) Derivation/ecological aspects: SQGs based on the observation of effects are based on different biological species. SQGs based on the BEDS-database rely on a total of 89 different reports, while the WAC 173's SQS/SIZML values (WSDE, 1995) are based on clearly named species, including for example sea urchins or bacteria. The latter has been strongly recommended because compared to animals, anaerobic microorganisms are more tolerant of natural sediment conditions, but more sensitive to a number of pollutants (van Beelen, 2003). If the focus of a research project is a specific species, it could be a considerable advantage if a SQG is used in which the same species has been used for the development in the first place. Also, some SQGs are more conservative in their approach and therefore tend to produce more false-positive results, others are less conservative and tend to result in more false-negatives (Chapman and Mann, 1999)

5) Resilience: An important question is whether a SQG has been thoroughly tried and tested or not. The Norwegian as well as the Canadian EC & MDDEP-values are very recent developments and no application in research projects could be detected so far, therefore experience with them

and reviews about them are very limited. Both the American ER-L/ER-M- and TEL/PEL-based approaches on the other hand have been used in multiple studies worldwide and have been thoroughly tested. For example, a high predictive ability for guideline values, especially ER-Ls and TELs, has been reported using data from estuaries along the Atlantic and Pacific coasts, and the Gulf of Mexico (Long *et al.*, 1998). Chapman *et al.* (1999a) recommended the use of American ER-L/ER-M-values in Hong Kong with only minor modifications. Predictive abilities of multiple SQGs (originally intended for North-America) were observed in the vicinity of Sydney (McCready *et al.*, 2006c) and it was concluded that analysed PEL- and ER-M-values provide an accurate basis for predicting the presence or absence of adverse biological effects in the Tampa Bay estuary, Florida (MacDonald *et al.*, 2004). Further clarifications regarding the isolated, but considerable variations of some SQGs can be considered to be very advantageous.

6) Comparability: Uniform guideline values allow to compare the outcomes of different studies and to put them into context; however, current usage of SQGs suffers from the lack of standardised methods and consistency between regulatory agencies (Adams *et al.*, 2005). The TEL/PEL-based SQGs however, show a very high degree of comparability, regardless of the fact that they have been developed for different operational areas (Canada, USA and regions within the USA). This is partly because of the high interdependency between the guidelines, but these values also show a remarkably close correspondence to sediment quality assessment guidelines, based on completely different data of porewater effect concentrations (Carr, 1997), which have the potential to help verify SQGs (Scroggins *et al.*, 2003). For compatibility of results the TEL/PEL-based SQGs are clearly best fitted, as they are very uniform and widely used. Studies utilising appropriate methodology and either one of them are to a high degree comparable.

7) Strategy: It is generally strongly advised not to use SQGs alone, but as one part of a more comprehensive, "holistic" approach (Chapman *et al.*,

1999b; Burton, 2002; DelValls *et al.*, 2004; Wenning *et al.*, 2005) *i.e.* additional information about the environment like hydrodynamics, toxicities, bioavailability, contamination history, etc. must be carefully considered as well. A summary of various assessment methods has been summarized by Adams *et al.* (2005). As mentioned previously, such SQGs are, predominantly, not intended as pass/fail-criteria or for definitive decision-making. According to Chapman *et al.* (1999b) they are generally not appropriate tools for definitive, regulatory criteria. However, several SQGs are increasingly adopted by various regulatory agencies in several countries (Ross and Munawar, 1994; Cormack, 2001; Burton, 2002) primarily for identification of polluted sites and the setting of cleanup goals (Burton, 2002). Although such guidelines are not definitive indicators of toxicity, they are an effective tool for identifying areas with the potential for adverse biological effects (Long *et al.*, 1995; O'Connor *et al.*, 1998; MacDonald *et al.*, 2003b).

c) Guideline chosen for this study

Owing to the low variations between the SQGs in the TEL/PEL-group, studies utilising appropriate methodology and either one of them are to a high degree comparable. Owing to their advantages, including the consistency within the guidelines, their ease of use, their scientifically defensible basis and the broad coverage worldwide, the application of TEL/PEL-based SQGs is considered to be the most appropriate approach at present (Hübner *et al.*, 2009).

Threshold Effect Levels (TELs) and Probable Effect Levels (PELs) from the Screening Quick Reference Tables (SQuiRTs; Buchman, 2008) have been used in the present study. These SQuiRTs-values were initially developed for internal use by the Coastal Protection & Restoration Division of the National Oceanic and Atmospheric Administration (NOAA) and are now made available through the NOAA's webpage[4]. Contrary to the earlier versions, the latest

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[4] http://response.restoration.noaa.gov/cpr/sediment/squirt/squirt.html

and substantially expanded 2008 edition distinguishes between sediments and soils. They are the most comprehensive set, covering more metals than the other guidelines, although no values for cobalt are included. Cobalt concentrations in river and sea water are, however, extremely small (Hem, 1985), and very little has been published regarding its toxicity (Marr *et al.*, 1998). This set is based on a scientifically defensible basis (weight-of-evidence approach), has a high predictive ability and offer a high degree of comparability, owing to a broad application in numerous studies worldwide and the consistency within the TEL/PEL-subgroup.

3 Case study 1: Distribution patterns in small rivers – Bigge (Germany)

3.1 Introduction

Areas of reduced current velocities (like estuaries and lakes) act as traps for sediment transported by rivers. The lake Biggesee with its tributaries Bigge and Olpe in North Rhine-Westphalia (Germany; *cf.* Figure 2) are ideally suited for an examination of contaminant transport by small and fast running watercourses (*cf.* Chapter 2.1.1).

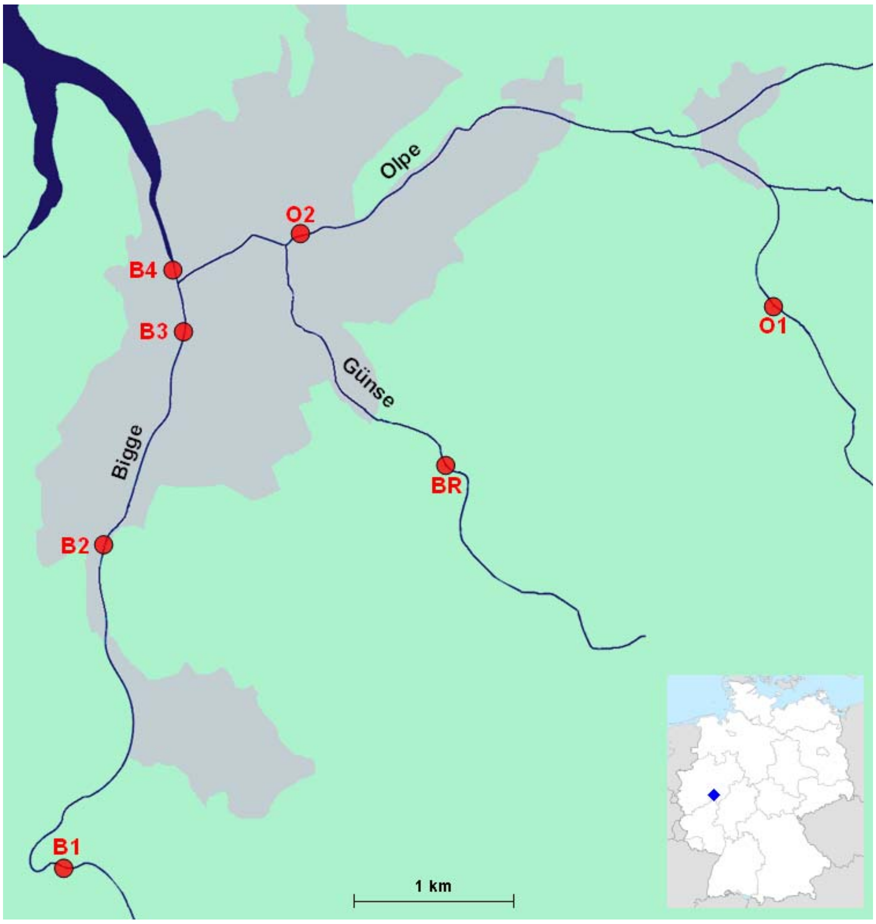


Figure 2: The analysed watercourses Bigge and Olpe (the location within Germany in the lower right corner), the sample locations are marked red

3.1.1 Area description

The site shows several similarities with Poole Harbour; for example, the degree of urbanisation is comparable and the watercourses are similar in size and discharge into an area of reduced current velocities. Unlike Poole Harbour, however, there are only two major, distinctive contamination sources: one natural (copper) in the Olpe and one anthropogenic (primarily zinc and nickel) in the Bigge.

a) Bigge

The Bigge, which was canalised for flood prevention, runs through the busiest industrial region of the area, with more than 80 % of the firms being metal working companies (Kemper, 2000); galvanisation processes and work with galvanised steel are predominant. Effluents of galvanisation processes commonly contain high metal concentrations and in the past these effluents were often released untreated, leading to a substantial contamination of surface waters (Beier, 1994).

The Bigge is a high energy environment, resulting in coarse grained sediment with little sorptive capacity and low depositional rates (Kersten and Smedes, 2002); however, contaminants are mainly present in the silt and clay fractions (Langston and Spence, 1998). The closer to the lake Biggesee, the straighter its course becomes. At the first sampling site, shortly before the city boundary (B1; Figure 3a), it is morphologically moderately compromised and in a comparably natural riverbed: it still includes several bends and ridges, resulting in sections with varying current speeds. Within the city delimiter the Bigge has been artificially straightened for flood prevention reasons (Kemper, 2000; *cf.* Figure 3b), with border reinforcements along wide parts of the shores (Figure 4).

Figure 3: **The Bigge at the city borders (a: sampling site B1) and shortly before the entrance to the lake Biggesee (b: sampling site B4)**

Figure 4: **Border reinforcements along the shores of the river Bigge at sample site B3**

b) Olpe

Several copper mines were operated in the vicinity of the Olpe (Straßburger, 1996), the last mine closed in 1989 (Wermert, 2002). The largest mines, in particular the mine “Rhonard”, were situated approximately 2.5 km east of the city Olpe (Figure 2: close to O1). In earlier times the mined copper was processed in the city centre of Olpe (Kemper, 2000). Unlike the artificially straightened Bigge, the Olpe was restored to a natural state in 1995, and the district government recently granted additional funds for the ongoing reduction of artificial structures of the Olpe (Anon., 2009).

3.1.2 Environmental monitoring in this region

These watercourses are scientifically interesting as relatively little is published about their intrinsic environmental properties. The environmental quality of this region is, however, constantly monitored, and results are published in the series “Ruhrgütebericht”. Bigge and Olpe, too, have been subject to these analyses and are largely considered to be moderately contaminated (“*mäßig belasted*”; Ruhrverband and AWWR, 2007). The 2007 report noted that all watercourses in that planning unit, with only a few exceptions, had a ‘good’ to ‘very good’ condition for most tests, only in regard to zinc and copper did elevated values lead to a lower classification (Ruhrverband and AWWR, 2008). However, the analyses are based on tests of water and suspended particles, which are the typical method of analysing the water quality status of streams (Matagi, 1996). Such analyses will not take account of geoaccumulation (*cf.* Chapter 1.3.1), and the more complex and expensive analyses of sediments are not mentioned in the annual reports, nor in the current management planning draft of the Ministry of the Environment and Conservation, Agriculture and Consumer Protection of North Rhine-Westphalia (MUNLV, 2008).

The mechanisms of metal transport in rivers are complex and only a fraction of the total concentration is typically carried in solution and organic complexes (Gibbs, 1973). Chemical analyses of the water only reflect the water quality status at the time of sampling (Matagi, 1996). Dissolved metal concentrations in waters vary greatly over time and are, in addition, typically very low, often at the analytical detection limits (Rainbow, 1995), which can easily result in false negatives, *i.e.* the underestimation of the potential for adverse effects on aquatic life. Hence, assessments which do not take sediment parameters sufficiently into account are inadequate for a reliable assessment of the environmental quality.

Sediments constitute a habitat for many organisms, which are at risk of being exposed to chemical substances through interactions with sediments (CCME, 1995) and an increase of metal concentrations, particularly these of non-essential elements like cadmium and mercury, can substantially reduce the biological quality of sediments (Kersten and Kröncke, 1990).

This study aimed, therefore, to analyse the metal concentrations contained in the sediments, which are not currently covered in the annual monitoring reports.

3.2 Material and methods

Compared to estuaries, fewer cores are necessary when analysing narrow watercourses, as not a wide area, influenced by tides and currents is analysed, but rather a line with a one-directional water flow. In the present study, three cores have been extracted in the southern tributary, the Bigge (B1-3; *cf.* Figure 2), two cores in the eastern tributary, the Olpe (O1-2); and one further core after the confluence of both watercourses shortly before the river flows into the reservoir (B4). One reference core (BR) was extracted at a small watercourse with limited neighbouring mining, industrial or agricultural activities. These cores demonstrated the environmental quality of the sediments and also showed the different distribution patterns of elements within the Bigge.

The methodology described previously has been applied. Samples were extracted with a Bigge corer (*cf.* Chapters 2.1.2 and 10.2.3) in autumn 2007. Owing to riverbed features, most of the cores were limited to a depth of *ca.* 30 cm; since below that depth the sediment was replaced by a stone layer. Samples were sliced immediately after extraction to avoid post-depositional mobility, but could, owing to the location, not be processed further within 12 hours and were stored frozen. Consequently, no analyses for mobility using the DIN 19730 procedure have been included in this study (*cf.* Chapter 2.2.4). The samples have been dried with a temperature not exceeding 40 °C and prepared with a 0.3 mm sieve (*cf.* Chapter 2.1.3). The (pseudo-)total metal content was determined using *aqua regia* digests (*cf.* Chapter 2.2.2). Typically, for each sample 3 replicates were analysed, but high variations between the replicates triggered the inclusion of further replicates.

3.3 Results and discussion

The background concentrations, measured in the remote reference core (BR), typically showed very low metal concentration and for most metals the lower sediment quality guideline for freshwaters was not, or not substantially exceeded (Table 3).

As expected, the reference core (BR) showed very low concentrations for all targeted elements and only for lead the TEL was with a concentration of 71.5 mg·kg^{-1} clearly exceeded.

The concentrations of chromium and cadmium were very low in all cores, in the majority of cases even below the TEL-values (Figure 5a/b). Both elements were distributed equally in the sediment.

Table 3: Metal concentrations (depth averaged) in the reference core BR

	observed background concentration [mg·kg^{-1}]	TEL [mg·kg^{-1}]	PEL [mg·kg^{-1}]
Aluminium	16318.57	--	--
Arsenic	9.94	5.90	17.00
Cadmium	0.69	0.60	3.53
Chromium	24.28	37.30	90.00
Cobalt	13.83	--	--
Copper	32.91	35.70	197.00
Iron	22891.66	--	--
Lead	40.97	35.00	91.30
Mercury	0.53	0.17	0.49
Nickel	33.28	18.00	36.00
Phosphorus	531.70	--	--
Tin	0.67	--	--
Titanium	82.46	--	--
Zinc	126.85	123.10	315.00

Arsenic and lead were mostly above the TEL, but with few exceptions (all in the Olpe) below the PEL-values (Figure 5c/d). Unlike cadmium and chromium, however, arsenic and lead are very unequally distributed in the sediment. The arsenic concentrations were also highest in the upper parts, indicating a comparably recent anthropogenic source; while lead was more present concentrations in the lower parts of the cores, indicating that concentrations are declining (*cf.* Chapter 10.4.1). One of the main sources of lead is of diffuse nature, primarily the burning of fossil fuels. Cars were a major global source of lead emissions, responsible for as much as 90 % of the atmospheric lead (Bliefert, 1994). Concentrations rapidly declined since phasing out of leaded gasoline; in many nations, like the United Kingdom and Germany, accelerated by differential tax rates. Between 1981 and 1989 lead concentrations in North Atlantic surface waters dropped by 50 % owing to a decrease in atmospheric lead input (Kennish, 1997).

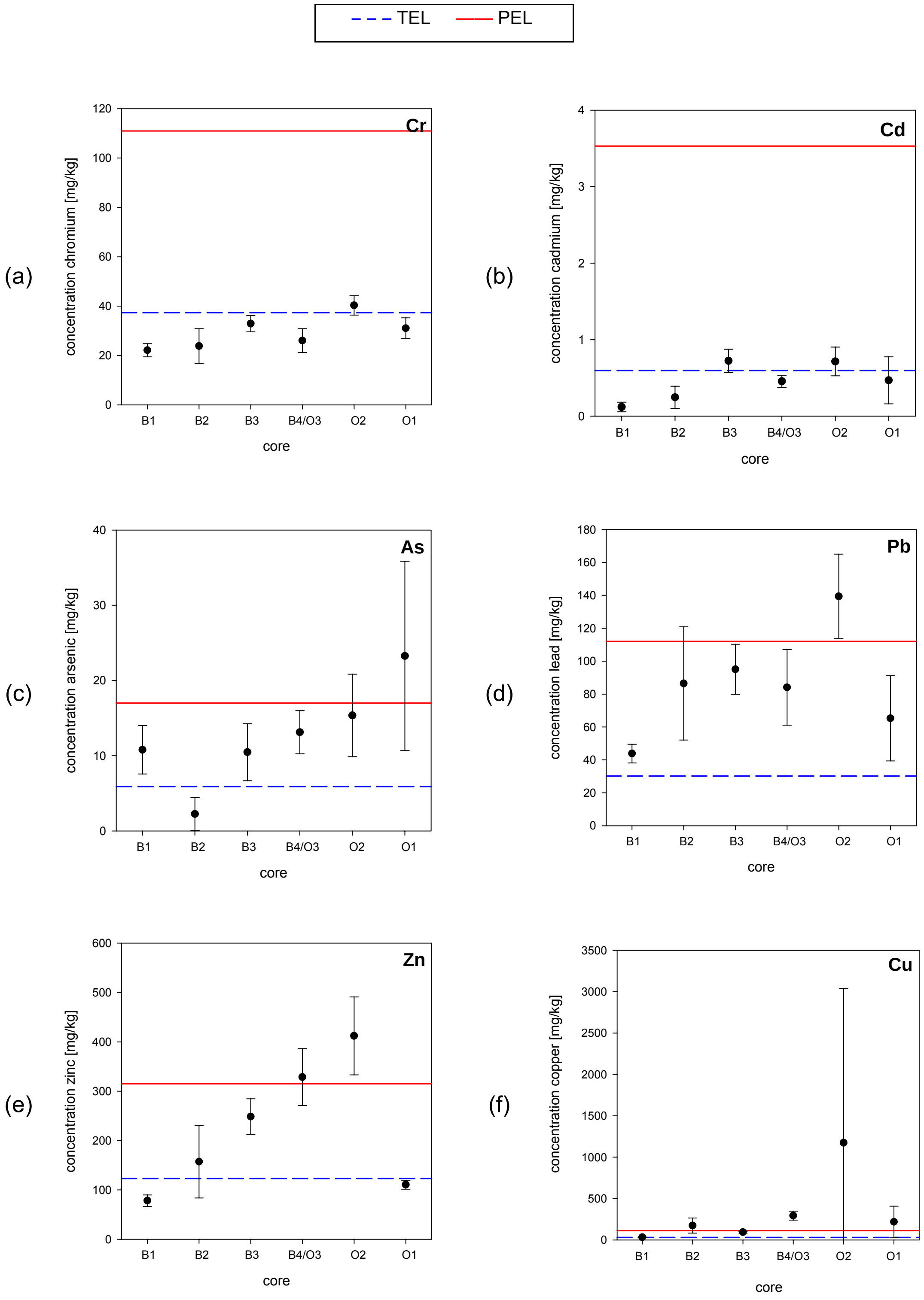


Figure 5: **Mean concentrations (depth averaged) of chromium (a), cadmium (b), arsenic (c), lead (d), copper (e) and zinc (f) in the sediments of the Bigge and Olpe (error bars are standard deviations and indicate the variance in the cores)**

All copper values in the Olpe, except in O1, were clearly above the PEL, and adverse effects on aquatic life are considered probable here. Rather than in the mining area ($\bar{x}_{O1}$: 218.7 mg·kg^{-1}; ~2x PEL), the highest values were recorded in the early processing centre ($\bar{x}_{O2}$: 1184.7 mg·kg^{-1}; ~10.6x PEL). However, in this core a large standard deviation was observed (Figure 5f). Closer investigation showed that this standard deviation was exclusively linked to the deepest layer ($\bar{x}$ =3716.7 mg·kg^{-1}; *cf.* Figure 6), where the observed concentrations were significantly (p<0.001) higher compared to the remaining layers.

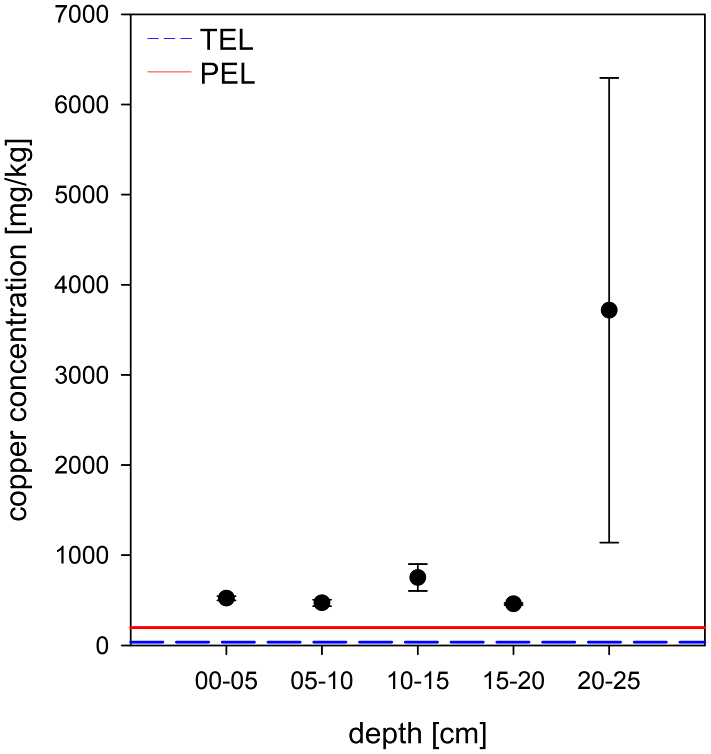


Figure 6: **Copper concentrations per depth layer in the city centre of Olpe (core O2; error bars indicate the standard deviation between the replicates, *N*=3)**

To test for methodological flaws, the complete core was analysed a second time with three times as many replicates for the relevant depth layer (N=9). Since the outcome was virtually identical to the first run, such an error can be ruled out. The anomalous effect is caused by a few isolated clumps with very high copper concentrations in the depth exceeding 20 cm. These presumably originate from the earlier copper mining upstream and have likely been deposited there before the restoration in 1995 (*cf.* Chapter 3.1.1a), with which this depth approximately coincides. The overlying layers showed much lower concentrations ($\bar{x}$=551.8 mg·kg^{-1}) and negligible standard deviations, but even these comparably low concentrations still were clearly well above the PEL-value for freshwater sediments of 197 mg·kg^{-1} (Figure 6). However, unlike zinc, the background concentrations of nickel are already elevated (Table 3), therefore the concentrations in the Bigge are likely not to be attributed solely to anthropogenic sources.

High concentrations were also observed for nickel and zinc. In natural waters, both elements are normally only present in traces (Hütter, 1979), but were detected in high concentrations in most analysed samples, especially nickel exceeded the SQGs considerably (Figure 7).

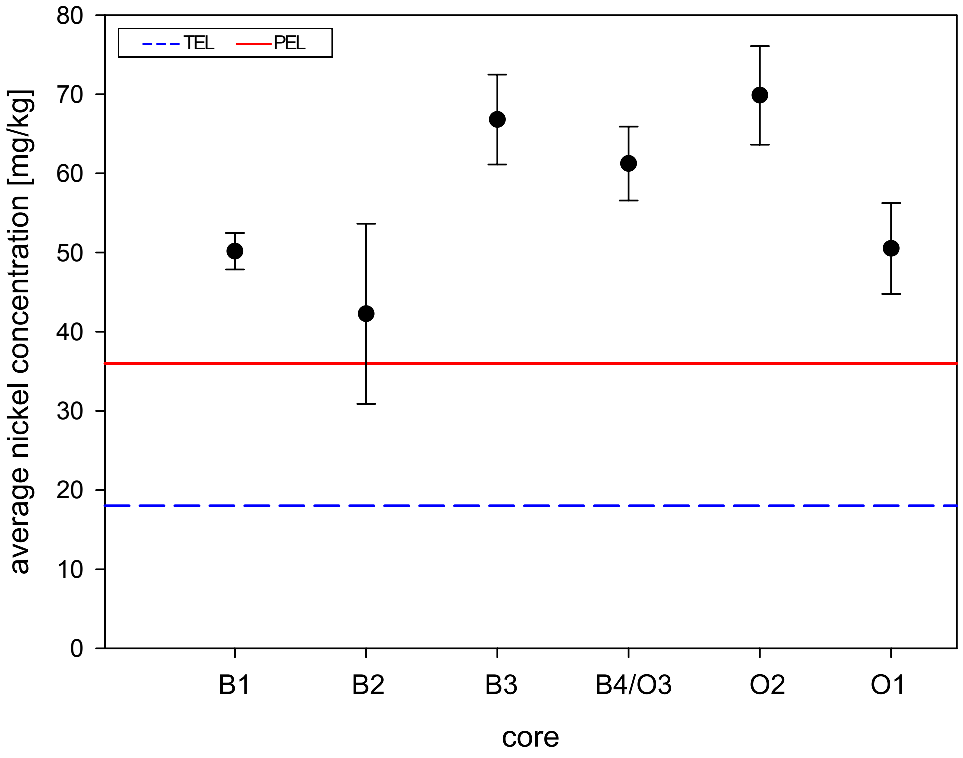


Figure 7: **Depth averaged concentrations of nickel (error bars indicate the standard deviation)**

Both zinc and nickel are common outputs of galvanisation processes (Hüffmeyer *et al.*, 2009), an activity which forms a large part of the local industry. There are no statistics detailing the quantities of zinc used for electro-galvanising, and the relevant trade associations claim not having such data, either. This lack of usable data makes an estimation of zinc emissions caused by such industries impossible (Hillenbrand *et al.*, 2005). In addition, zinc is also commonly associated with raw iron production and tire abrasion, the latter is increasing since the 1980s (Rosenbaum-Mertens, 2003). There is no limit for zinc concentrations in German drinking water (Hüffmeyer *et al.*, 2009).

When these two elements are analysed, the concentrations of both increase downstream towards the lake Biggesee, which has an important function in the regional drinking water system. The mean zinc concentrations showed a nearly perfectly correlated, logarithmic increase ($r^2=0.9783$; *cf.* Figure 8a), while nickel showed overall high concentrations with an increase, but without a clear correlation ($r^2=0.4587$, *cf.* Figure 8b). In the Bigge, nearly all of the measured nickel concentrations were well above PEL, while the zinc concentrations exceeded the PEL-value only immediately before the lake entrance.

For zinc, a high mobility has been reported (*e.g.* Burton *et al.*, 2005; Lions *et al.*, 2007), except for organo- and chloro-zinc complexes (Zarcinas and Rogers, 2002). Nickel had a low mobility, but relatively few studies have been published on this element and several of the common SQG-sets do not cover it (Hübner *et al.*, 2009).

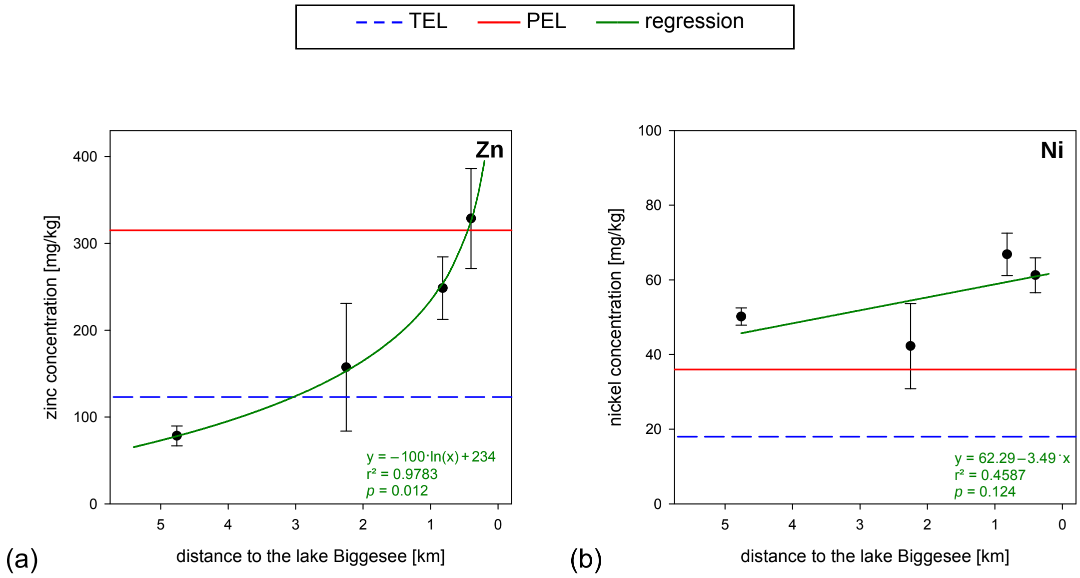


Figure 8: **The concentration of zinc (a) and nickel (b) in the sediments (mean and standard deviation per core; depth averaged) in relationship with the distance covered by the river Bigge before flowing into the lake Biggesee**

3.4 Conclusion

As expected, nickel, zinc and copper were detected in high concentrations, while other elements were only present in very low concentrations (below PEL and commonly below TEL). Elements with low mobility stick to the sediment and do not migrate much, leading to areas with different concentrations. No clear relationship between distance and concentration can be expected. Elements with a high mobility will, by contrast, distribute from the source and move downstream. Given a constant, equal input over the course of the river, there is an accumulation of contamination downstream. Many elements will presumably lie in between these two extremes, but the very high coefficient of determination (r^2) for zinc indicates that this element follows the assumed distribution pattern of elements with very high mobility (Figure 9).

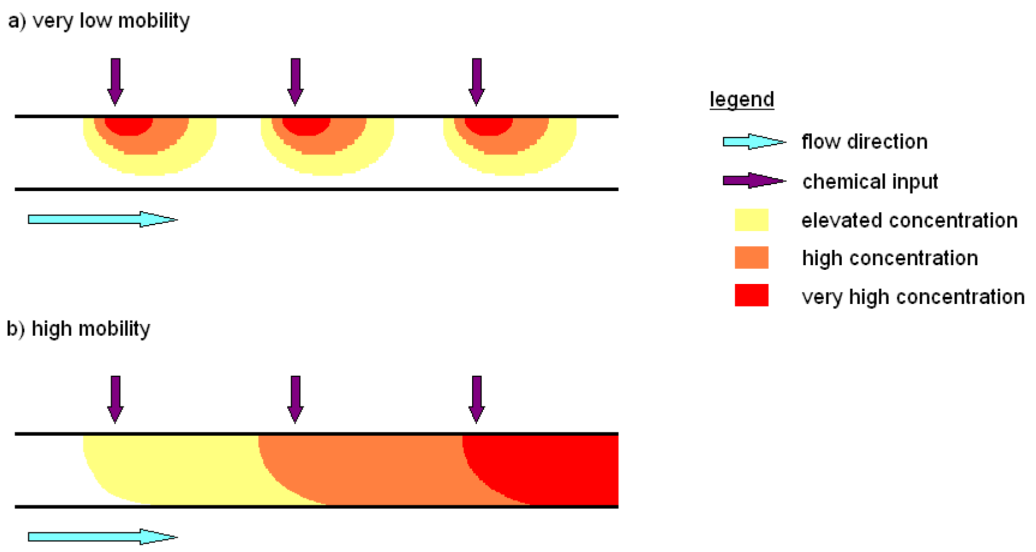


Figure 9: **Assumed distribution patterns of elements in river sediments given a very low (a) and a high mobility (b); view from above**

Furthermore, although most metal concentrations (with the exception of copper) do not reach worryingly high levels (based on the SQuiRTs), these analyses indicate that the results of the water analyses in the annual reports (Ruhrverband and AWWR, 2006; Ruhrverband and AWWR, 2007; Ruhrverband and AWWR, 2008) underestimate the risks caused by concentrations in the sediments (particularly in regard to nickel and copper, but also for zinc and lead within the city perimeter). Considering the low depths, elements could easily be remobilised given a possible acidification of the watercourses and add to the already dissolved metal content. Levels in the sediments should therefore be monitored in light of this risk, especially considering that zinc and copper already show elevated concentrations in the water (MUNLV, 2008; Ruhrverband and AWWR, 2008).

4 Case Study 2: Contamination caused by a landfill in Christchurch Harbour (UK)

4.1 Introduction

4.1.1 Landfills

Landfills have been the primary method of waste disposal within the UK for many years (Williams, 1998). There are over 4,000 licensed landfill sites, varying in design and engineering (Westlake, 1995), which can be classified into three major designs:

(1) 'dilute and attenuate', these are unconfined sites, with little or no engineering of the site;
(2) 'containment landfill', which includes a barrier or collection unit: liquids generated within these landfill should not be able to migrate out in an uncontrolled manner;
(3) 'entombment landfill', where the waste is stored dry.

Until the legalisation was made stricter in the 1970's, by, for example, the Deposit of Poisonous Waste Acts 1972 or the Control of Pollution Act 1974, the majority of landfill sites had little or no engineering and the design of landfills evolved slowly (Lisk, 1991). Although most sources of leachate can be controlled with proper siting and engineering, some infiltration inevitably occurs and even a properly designed and maintained landfill will generate leachate to some degree (LaGrega *et al.*, 1994). Unconfined sites will, of course, pose an even greater risk to the environment. The potential for landfills to contaminate coastal waters and sediments is therefore considered high with an associated risk to the health of local populations, particularly as many urban conurbations are located close to estuaries. Fortunately, a number of important changes have taken place since 1983 to reduce the inputs of metals into soils (Nicholson *et al.*, 2003), but these have little to no effect on closed landfills.

Along the coast of southern England there are a number of closed landfills associated with the direct tipping of waste materials onto salt marsh and reclaimed coastal lands. Waste was often tipped directly onto an unprepared marsh surface that was in direct hydraulic connectivity with coastal waters. These sites received substantial amounts of domestic waste during the 1950/60s and are commonly associated with a range of contaminated land issues such as soil and ground gas contamination (Lisk, 1991). This study explores one example and evaluates the degree to which contamination in coastal sediments can be attributed to an adjacent landfill in Christchurch Harbour.

4.1.2 Area description

Christchurch Harbour has a mean tidal basin area of 1.9 km² and a mean water depth of 2.0 m, occupied by sandy gravels, sands, muddy sands and towards its inner margins, silty muds (SCOPAC, 2004a). The estuary's narrow entrance minimises the amount of flushing. Both private and public fisheries operate in the estuary, and potential contamination of the water is a serious concern (Wheeldon, 2003). The central part of the estuary includes extensive marshes and reedbeds, while on both sides of the estuary former landfill sites are located in some of the low areas of the floodplain (ABPmer, 2009). The area of Stanpit Marsh was designated as a Local Nature Reserve in 1964 and as a SSSI in 1986; however, it has also been a very active landfill of the dilute and attenuate design, where little engineering had been used to contain the waste. Erosion of the landfill caused by, for example, sea level rise, is considered to pose a considerable environmental risk, particularly if a landfill is classified as "semi-toxic" like Stanpit Marsh (Halcrow Maritime, 1999). Leachate has been drained from the landfill site by a linear ditch in the adjacent saltmarsh, leading from the landfill directly to the harbour (Figure 10).

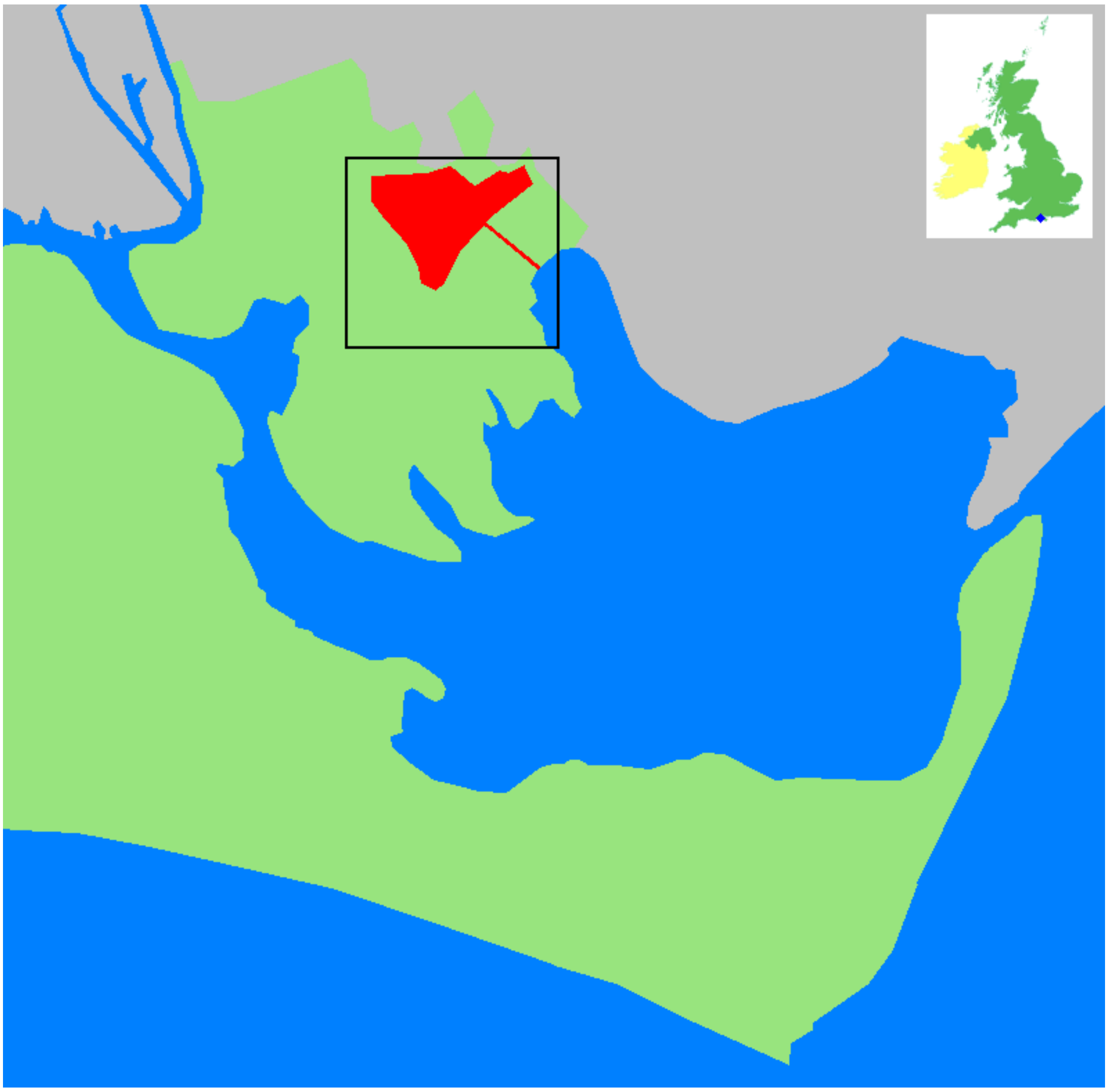
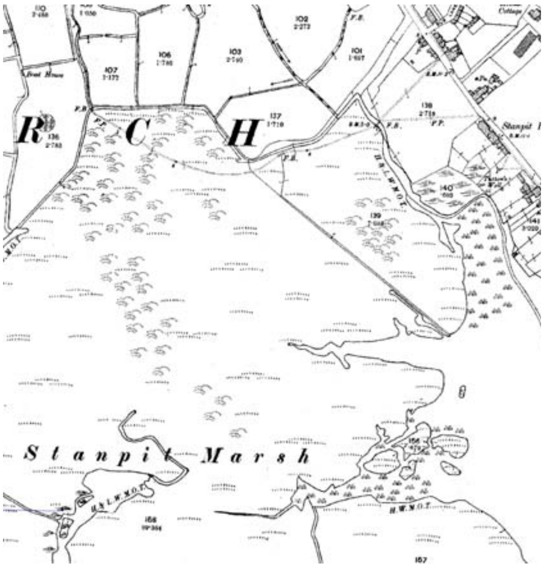


Figure 10: **Christchurch Harbour (location within the United Kingdom shown in the top right corner); the investigated landfill and the channel are highlighted and the box demonstrates the extend of the subsequent figure**

All maps of Figure 11 show the same extend (as highlighted in Figure 10), but in 50 year intervals. The first part is a map from around 1900 (*i.e.* before the landfill was created). The second part, an aerial photo taken in 1950, shows an early stage of the landfill, while the last part illustrates the landfill in today's form.

a) around 1900



(reproduced from Ordinance Survey map:
County Series 1st Revision 1893-1915;
with the permission of the Controller of Her
Majesty's Stationery Office, ©Crown Copyright)

b) in 1950

(English Heritage (NMR) RAF photography)

c) in 2000

(part of the Millennium Map,
copyright Getmapping Plc)

Figure 11: The Stanpit Marsh landfill (*cf.* Figure 10) around 1900 (a), in 1950 (b) and in 2000 (c)

Both landfill and channel are clearly visible on aerial photos – for example taken in the years 1950 and 2000 (Figure 11b/c). Historic maps (analysed time frame: 1849-1981, for example around 1900 in Figure 11a) show that the channel predates the landfill and originally had at least double today's length, *i.e.* it formerly ran through the entire area which is occupied by the landfill today. On most major present-day aerial photos the path of the channel can still be made out in form of a depression halfway through the landfill, indicating that the ground had not been prepared for the foundation of this landfill. Apart from the channel the intertidal marshland is flat and shows little topographic variation. Today the landfill itself is used as a recreational ground.

4.2 Material and methods

4.2.1 Fieldwork

Studies of contaminated areas require that the whole soil profile, including subsurface horizons, are investigated (Kabala and Singh, 2001). Accordingly, eight cores have been extracted in the wetland between the closed landfill and the estuary during low tide events (Figure 12), using a Russian peat corer (*cf.* Chapters 2.1.2 and 10.2.2).

Sample sites were chosen to be in close proximity of each other, so that contaminant levels could be traced along a transect. Three cores each have been extracted in a straight line in the artificial channel (C1, C2, C3) as well as parallel to it in the intertidal marshland (M1, M2, M3), plus two further cores (R1, R2) in between for a more comprehensive picture. Finally, two samples (R3) were extracted outside the sphere of influence of the landfill (from the southern edge of the landfill approximately 400 m in SSW and 600 m in SW respectively) in separate bays; but at otherwise comparable places in the estuary for reference purposes.

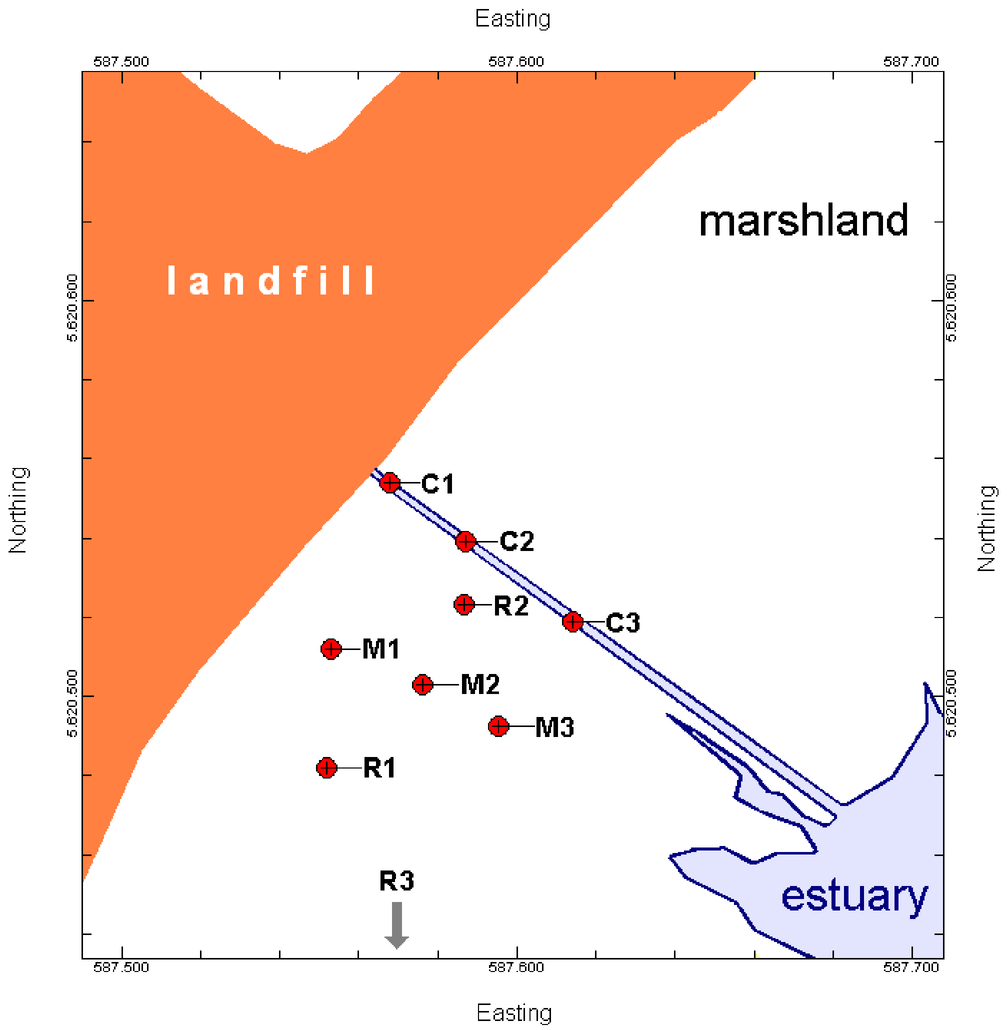


Figure 12: **The locations of the sampling sites at Stanpit Marsh/Christchurch Harbour (used grid is UTM Zone 30U)**

4.2.2 Chemical analyses

The samples have been dried with a temperature not exceeding 40 °C and prepared with a 0.3 mm sieve (*cf.* Chapter 2.1.3). Typically, for each sample 3 replicates were analysed. However, higher variations between the replicates lead to the inclusion of further replicates (*cf.* Chapter 2.2.5). The (pseudo-) total metal content was analysed using *aqua regia* digests (*cf.* Chapter 2.2.2);

in addition, the partial extraction DIN 19730 (*cf.* Chapter 2.2.4) has been applied.

The potentially mobile fraction is commonly assessed using the solubility from different fractions as an indicator, for example using a sequential extraction scheme (SES) for determination of a Mobility Factor (MF; Salbu *et al.*, 1998; Narwal *et al.*, 1999; Kabala and Singh, 2001). However, this approach has four major flaws (Hübner *et al.*, *in press*): (i) analyses based on the attachment of an element to a specific chemical entity will, in effect, only assess the theoretical readiness of a metal to migrate; it cannot determine the actual migration in the ground and has therefore only predictive abilities at best; (ii) SES analyses, usually consisting of between 3 and 8 subsequently applied treatments, are very time-consuming; (iii) this approach works best under the assumption of equal hydrographical conditions at all times, because temporal changes and active impacts are very difficult to be taken into account, especially since (iv) the reliability of sequential extraction procedures is controversial and there is considerable evidence to suggest that these methods are generally unsuitable to accurately and lastingly (*i.e.* without re-adsorption) dissolve metals from specific chemical phases (*cf.* Chapter 2.2.3). Partial extraction schemes (PES) are a commonly used alternative (NCR, 1999); these extraction methods are faster, more economical, less complicated and less error-prone (*cf.* Chapter 2.2.4). As the extraction with ammonium nitrate is recommended for the assessment of the potential mobile fraction (Schramel *et al.*, 2000), this method, based on the industrial standardised procedure DIN 19730 (DIN, 1997), has been used to assess the theoretical mobility of contaminants in the sediments of Christchurch Harbour and to determine the general ability of this procedure to predict metal distribution in intertidal sediments.

Grain size measurements have been performed with a Fritsch Analysette 22, courtesy of ICBM-Terramare (Germany).

4.2.3 Mathematical calculations

Using the gathered data, a Dispersion Index (DI) has been calculated in order to assess the actual migration of various contaminants in Christchurch Harbour. The idea is to calculate what percentage of a given contaminant is migrating over a given distance. By comparing the median concentrations in the corresponding depth layers of neighbouring cores it can be assessed how readily an element is dispersing through the sediment. However, dispersion can be both a horizontal and vertical process. In order to compensate for sedimentation/leakage the surrounding depth layers were also taken into account. For this reason clearly identifiable peaks were compared and traced through the transects (Figure 13). By analysing these peaks, the difference in depth (q1 and q2) in consecutive cores was used to quantify the vertical dispersal between the cores. The concentrations in a depth layer could then be compared with the concentrations in the corresponding depth layer of the subsequent core (same depth -q1 and +q2 to compensate for depth changes; *cf.* Figure 13).

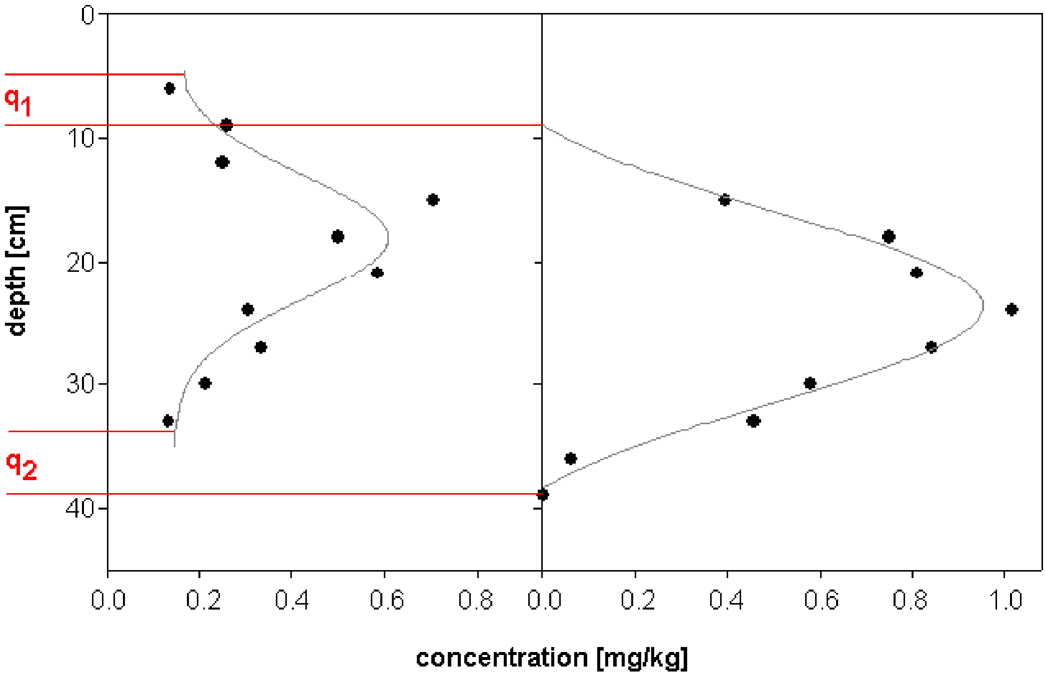


Figure 13: Determination of the average vertical dispersion by comparing clear peaks; here for cadmium in cores M1 (right) and M2 (left)

These calculations have been performed consecutively for all depth layers. The dispersion index is then simply calculated as the arithmetic mean between the cores in a transect (*i.e.* C1→C2→C3 and M1→M2→M3 respectively, *cf.* Equation 1).

Equation 1:

$$DI = \left(\sum_{z=0}^{z_{max}} \frac{\tilde{x}_{Az}}{\tilde{x}_{Bz\rho}} \right) \times d^{-1} \times z_{max}^{-1}$$

with:

DI:	Dispersion Index
$\tilde{x}$:	median concentration
Az:	depth layer z in the core closer to the landfill (core A)
Bzρ:	depth layer between ($z-q_1$) and ($z+q_2$) in the core closer to the estuary (core B)
	q_1: average decrease in depth (upper vertical dispersion) between cores A and B
	q_2: average increase in depth (lower vertical dispersion) between cores A and B
d:	distance between the cores
z_{max}:	deepest depth layer; therefore total number of depth layers in a core

In order to compare the theoretical readiness of a metal to migrate (measured with ammonium nitrate extraction) with the actual migration (as quantified with the DI) both were compared and the coefficients of correlation (also known as Pearson's product moment correlation coefficient; *cf.* Equation 2) were calculated for each element. This coefficient is a measure for the tightness of a linear correlation between the two variables x and y (Baumann, 1971) and is defined as:

Equation 2:

$$r_{xy} = \frac{\sum (x_i - \overline{x}) \cdot (y_i - \overline{y})}{\sqrt{\sum (x_i - \overline{x})^2 \cdot \sum (y_i - \overline{y})^2}}$$

with: $-1 \leq r \leq +1$

4.3 Results

4.3.1 Contamination profile

A very compact layer of sand and gravel between approximately 0.4 and 0.5 m depth was observed running throughout the area. Concentrations of most elements in this layer (especially cadmium, mercury and zinc) were low, which was expected owing to the reduced mass:surface relationship of larger grain particles. Apart from this layer, the sediment showed no substantial variations in grain size distribution, the remaining layers showed a fairly homogenous composition typically ranging from 0.5 to 550 µm, with the largest fraction between 100 and 350 µm (Figure 14). Additionally, there were grains exceeding 550 µm size. As these fractions were outside the effective range of the Analysette 22, they could not reliably be quantified. However, sieving showed that these fractions were negligible.

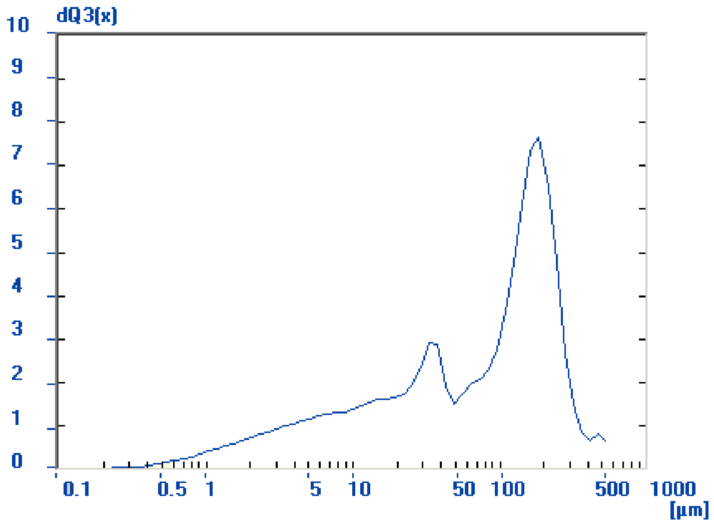


Figure 14: Average grain size distribution in the 0.1-550 µm range for core M2

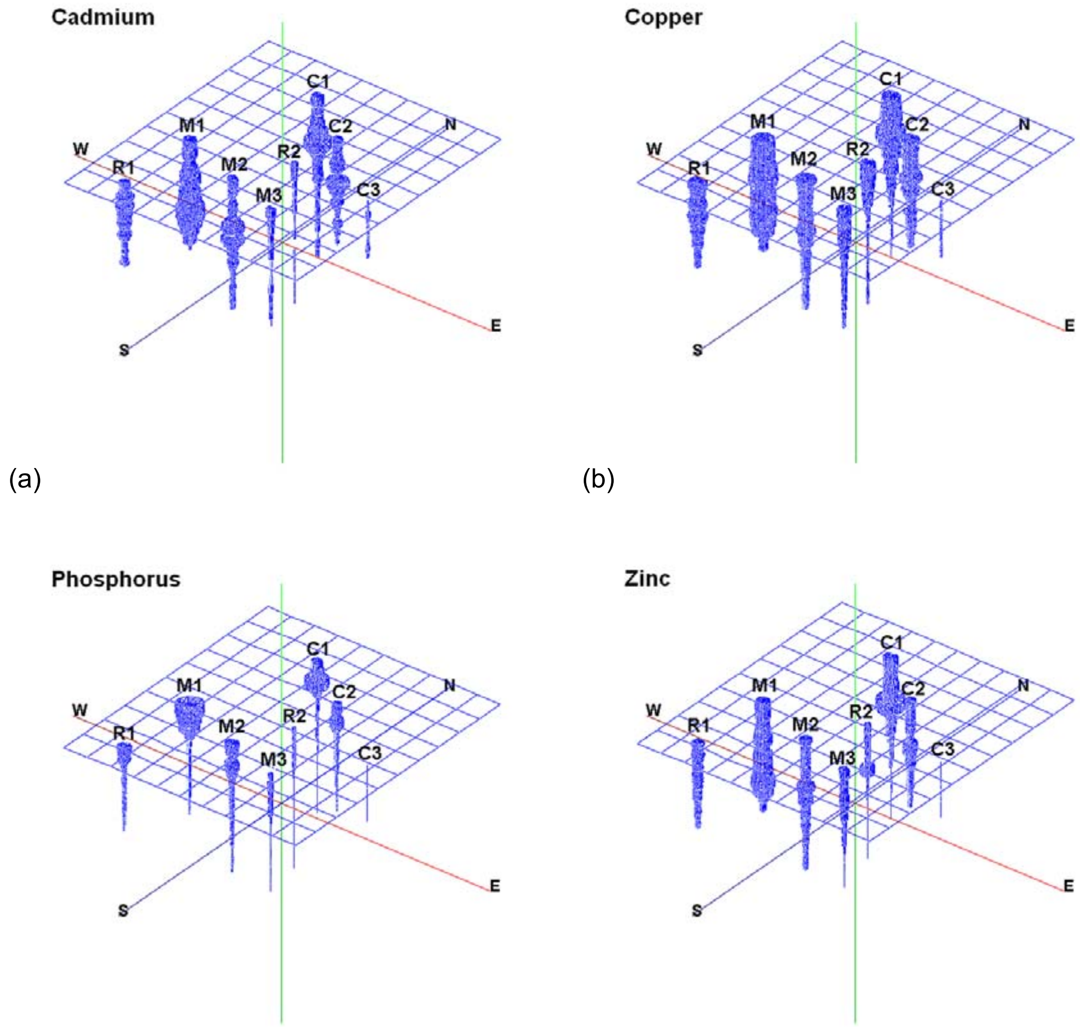
As expected, the concentrations decreased along the transects (Table 4). No clear baselines could be observed in the cores, but based on the NOAA

SQuiRTs values, nearly all metal concentrations in core M1, the beginning of the marshland transect, were between the TEL- and PEL-values ("adverse effects occasional"), but typically at the lower range. This range is often termed possible effects range (PER; *e.g.* in EC and MDDEP, 2007). At the beginning of the channel transect the concentrations have already been lower compared to the marshland transect; and at the end of the transect they were, with the exception of tin and mercury, well below the guideline values (on average 11.3 % TEL).

Table 4: Concentrations (average over 0-40 cm depth) in the reference sample outside the landfill's sphere of influence (R3) as well as the first (M1/C1) and last (M3/C3) core of each transect as well as TEL/PEL-reference values [all values in mg·kg^{-1}]

	R3	M1	M3	C1	C3	TEL	PEL
Arsenic	0.65	12.67	1.35	7.14	0.34	7.24	41.60
Cadmium	0.08	0.56	0.11	0.33	0.05	0.68	4.20
Chromium	4.14	54.43	26.93	21.40	3.32	52.30	160.00
Cobalt	0.84	8.39	3.37	5.29	0.53	--	--
Copper	11.52	33.71	15.86	20.79	4.42	18.70	108.00
Lead	2.48	61.10	18.49	37.97	4.72	30.24	112.00
Mercury	0.44	0.64	0.89	0.64	1.09	0.13	0.70
Nickel	9.17	31.17	16.45	20.70	2.11	15.90	42.80
Phosphorus	198.63	1906.34	462.31	1054.87	164.11	--	--
Tin	0.08	2.27	1.26	1.45	0.10	0.048	--
Zinc	30.47	170.46	51.15	106.96	10.06	124.00	271.00

If the concentrations are plotted three-dimensionally (Figure 15), the figures demonstrate that in both transects concentrations of all analysed elements decrease towards the estuary, but the decrease is substantially greater in the channel transect, where in the remotest core (C3) the concentration were the lowest observed in the sample zone (including the reference samples outside the landfill's sphere of influence).



(a) (b)

(c) (d)

Figure 15: Total extractable metal profiles for cadmium (a), copper (b), phosphorus (c) and zinc (d); the diameter of the column indicates the relative concentration [M=marshland transect; C=channel transect; R=reference cores]

4.3.2 Dispersion of contaminants

The results of the dispersion indices (Figure 16) reflected the visually observed patterns (Figure 15) very well. The distribution rate of all metals, other than that of mercury, is substantially increased in the artificial channel and in the area adjacent to it. Although the mobile fractions in cores C2 and M2 are comparable for most elements, the subsequent cores (C3 and M3 respectively) showed very different results: M3 (the last core of the intertidal marshland transect) showed a constant/continuous decrease of concentrations, while in C3 (the last core of the channel transect) the concentrations were surprisingly low (Figure 15; Table 4).

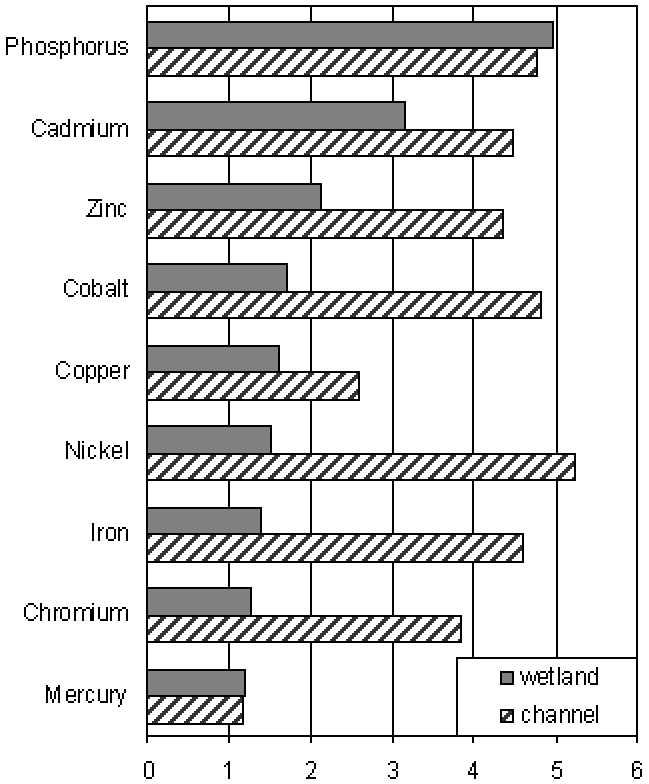


Figure 16: Dispersion Indices (*cf.* Equation 1) for the targeted elements in the intertidal marshland (solid grey bars) and the artificial channel (striped bars)

Lead concentrations showed a couple of localised peaks. A quite dramatic example was observed in core R1 (Figure 17), where at a depth of 23±3 cm the levels for lead were found to be over 2 g·kg^{-1} (2,000 ppm) – more than 30 times the average concentrations observed for this element and 18 times the probable effect thresholds of the NOAA SQuiRTs. These peaks were highly isolated and could not be traced throughout the transects.

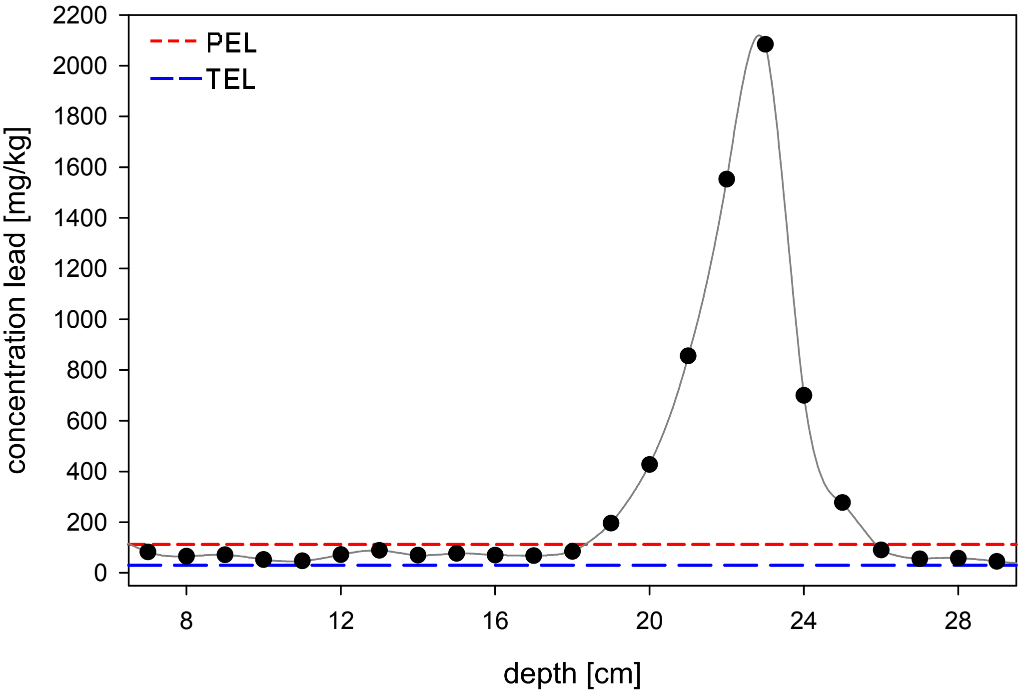
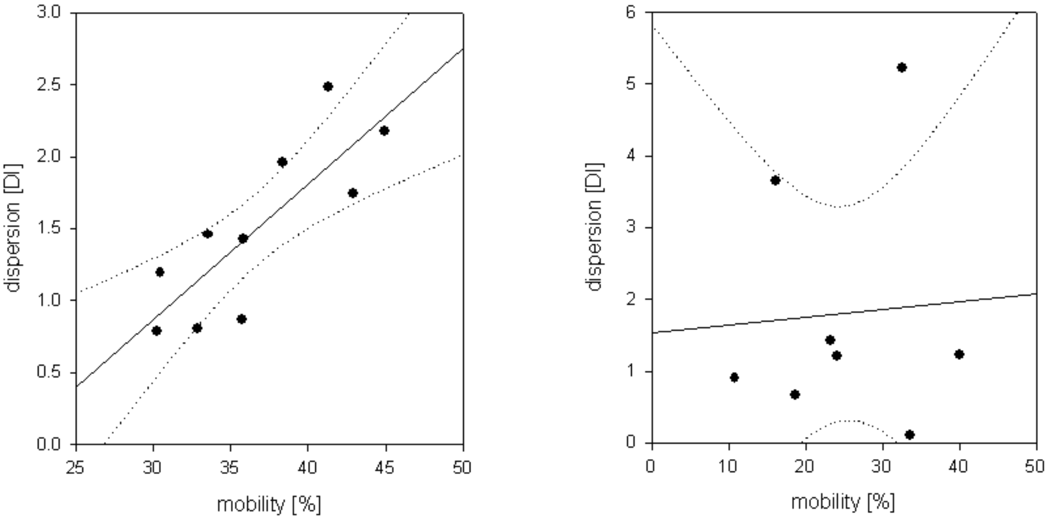


Figure 17: A peak of AR-extractable lead concentration in core R1

4.3.3 Comparison of the theoretical mobility with the actual movement

Only the mobile fraction can migrate in the ground, in theory a higher mobility percentage therefore indicates higher dispersion rates of contaminants. While the results of the ammonium nitrate extractions indicate to what degree a contaminant is available to migrate in soils and sediments, the DI provides a measure of the actual, analytically determined migration patterns in the sediments of Christchurch Harbour. In order to test the reliability of DIN 19730 for the assessment of mobility in the targeted environment, both the mobility (as ratio of the total content) and the observed distribution (measured with the DI calculated only for the according depth layer, not the average of the core) have been compared (Figure 18 shows the results of copper as an example).



(a) (b)

Figure 18: The theoretical mobility measured with ammonium nitrate extraction versus the actual distribution (summarised with the Dispersion Index) for copper in the intertidal marshland (a) and the channel transect (b); line shows the correlation and dashed lines indicate the 95 % confidence interval

Pearson's correlation was calculated (Table 5) for all elements to determine the dependency between both variables; these analyses show how well the mobility of a contaminant corresponds with the actual migration pattern in the sediment. The results show that the mobility gives a reasonable estimation for the dispersion in the marshland transect (average $r^2=0.52$, all variables except mercury are significantly correlated); while no noteworthy correlation could be detected between mobility and dispersion in the artificial channel (average $r^2=0.18$, only phosphorus shows a significant correlation). The reason for the poor correlation between observed dispersion and mobile fractions for mercury is probably the low concentrations of mercury which could be recovered with the ammonium nitrate extractions (*cf.* Table 5).

Table 5: Correlation between the mobility [%; measured with DIN 19730] and the actual dispersion [calculated with the Dispersion Index]

	marshland transect (M1→M2→M3), with *N*=10			channel transect (C1→C2→C3), with *N*=8		
	avg. mobile fraction [%]	Pearson's correlation	significance (2-tailed)	avg. mobile fraction [%]	Pearson's correlation	significance (2-tailed)
Aluminium	30.20%	0.750	0.012 *		(1)	
Arsenic	43.25%	0.725	0.017 *	40.60%	0.171	0.746
Cadmium	45.99%	0.716	0.020 *	21.85%	0.148	0.813
Chromium	47.11%	0.660	0.038 *	30.03%	0.503	0.309
Cobalt	39.29%	0.752	0.012 *	26.29%	0.517	0.294
Copper	36.67%	0.832	0.003 **	24.95%	0.436	0.387
Iron	36.29%	0.803	0.005 **	31.53%	0.751	0.085
Lead		(1)			(1)	
Mercury	17.04%	0.613	0.059	9.71%	0.071	0.894
Nickel	39.99%	0.880	0.001 **	33.39%	0.217	0.679
Phosphorus	35.60%	0.745	0.013 *	48.85%	0.825	0.043 *
Zinc	40.38%	0.749	0.013 *	33.77%	0.233	0.657

* $p < 0.05$ ** $p < 0.01$ (1) insufficient data

4.4 Discussion

The ammonium nitrate extractable fraction for most metals was, in comparison with other studies (*e.g.* Bauer *et al.*, 1996; Bacon *et al.*, 2000; Dieckmann *et al.*, 2003), high except in the artificial channel. This was likely caused by acidic conditions in the ground, as low pH-values are well known to increase the solubility of metals considerably (Förstner, 1983; Löser *et al.*, 2004). However, it also points towards a considerable impact from recent landfill leachate. Acidity is typically close to that of seawater in the lower intertidals (seawater is an effective pH-buffer), but lower in the higher areas. In a similar study area, pH-patterns consistent with the outcomes of this study were found (Munson *et al.*, 1997). The pH-values in a creek were varying with depth (pH 6.0-7.5), while the marshland was more homogenous (pH 6.1-6.7).

The distribution rate of all metals, other than that of mercury, is substantially increased by the artificial channel. This can also be seen in the contamination profiles (Figure 15): core C2 already shows lower concentrations than C1, but core C3 hardly shows any concentration at all. Concentrations are even slightly lower than in the reference cores which are outside the landfill's sphere of influence; which is probably caused by the constant washing out effect – the channel is at this location regularly flooded at high tide. The only elements analysed which appear to be widely unaffected by the impact of the artificial channel are mercury and phosphorous; the first at the lower end of the scale indicating a very low mobility in both the intertidal marshland and the channel. Phosphorus is on the other extreme and showed a very rapid dispersion in both environments. Owing to its mobilities (both estimated with PES and quantified with DI) is can be assumed to be present in the sediment primarily in form of soluble orthophosphate. At greater depths no noteworthy concentrations of phosphorus could be detected (Figure 15c), indicating that the elevated levels are solely of recent origin, which also concurs with the PES and DI-outcomes.

As the study in Germany had already indicated (*cf.* Chapter 3), the DI-values for Christchurch Harbour show that zinc also has a high mobility, which is, moreover, in line with outcomes in literature (*e.g.* Burton *et al.*, 2005; Lions *et al.*, 2007). The difference between nickel and zinc, however, is not quite as high as in the Bigge, which suggests that in Christchurch Harbour a larger quantity of zinc is likely to be present in less mobile organo- and chloro-zinc complexes (Zarcinas and Rogers, 2002).

Of the metals cadmium showed the highest dispersion speed, which was expected as cadmium generally has a lower sorption than, for example, zinc (Förstner, 1983). In addition, the adsorption rate of this element is inhibited by increasing chloride concentrations (Salomons, 1980; Förstner, 1983), and unlike other metals (*e.g.* zinc, copper, nickel and lead) cadmium is lastingly remobilised by high salinity levels (Salomons *et al.*, 1982), *i.e.* the adsorption of this element does not increase rapidly after a reversal of the conditions. In general, the observed dispersion indices coincided largely with the general solubility order Cd≥Zn≥Ni>Cu>Cr=As≥Pb≥Hg (Scheffer and Schachtschabel, 1992; Fuchs *et al.*, 2002). However, the selectivity of metals is influenced by several factors, most notably ground composition. For example, zinc shows in pure montmorillonite the lowest affinity, in labradorite the highest (Alloway and Reimer, 1999).

While a PES procedure indicates what concentrations are available for leaching, the DI indicates what amount actually has leached. In the channel transect the mobility tends to underestimate the actual dispersion, *i.e.* although compared to the marshland transect the ammonium nitrate extractions showed a much lower mobile percentage, the actual dispersion rate (as observed visually and confirmed by the DI-calculations) is substantially higher; which indicates that the mobile fractions are immediately carried away by the channel. It is furthermore reasonable to conclude that the PES procedure DIN 19730, which is easier, faster and more economical than any sequential excitation scheme, is suitable for the assessment of the potentially mobile fraction in such sediments. However, in environments that are subjected to adjacent high water flows and varying pH values, the procedure is only limitedly able to predict the migration of contaminants in the ground, as mobile fractions are washed out immediately, leaving only the low mobile fractions behind.

While for most elements elevated levels could be measured in follow-up cores (*e.g.* Figure 15c), no indication of elevated lead concentrations have been observed in the surrounding cores that could be compared to the peaks like the one observed in core R1 (*ca.* 20-25 cm depth; Figure 17). It is therefore reasonable to assume that the high, yet isolated, lead peaks can be attributed to single and highly localised contamination sources like, for example, discarded lead-acid batteries. Lead binds easily to sediments and is not easily remobilised by increasing pH-values (Förstner, 1983), soluble lead reacts with clays, phosphates, sulphates, carbonates, hydroxides and organic matter such that the solubility is greatly reduced (McLean and Bledsoe, 1996). Although these peaks make it impossible to quantify the dispersion rate (resulting in DI-values of virtually zero), the fact that the occurrences were isolated and that no comparable level of lead was detected in neighbouring cores, it is safe to assume that lead has a very low dispersion rate and is strongly bound to the sediment. This was partially reflected by the mobility tests; although they did not yield such low rates to fully explain the low distribution, the ammonium nitrate extractions did indicate a substantially reduced mobility.

It is also noteworthy that compared to the cores M1, M2 and R1, core R2 shows substantially lower concentrations throughout all analysed elements, although the distance to the landfill is comparable, or even higher (Figure 12). Moreover, R2 is located closer to the artificial channel, which suggests that the channel drains not only the landfill, but also extends its effect into the surrounding area of the intertidal marshland.

Rising sea levels (*cf.* Chapter 1.3.3) lead to an increase in coastal erosion. One management method is called managed realignment (formerly known as managed retreat). This process is defined as "*a form of soft engineering in which land is allowed to flood at each high tide to generate new salt marsh*" (French, 1997) and aims to protect land from the rising sea by sacrificing less valuable land as a buffer-zone; and by migrating existing/planned developments out of harm's way (Neal *et al.*, 2005). In Europe, often low-value zones (like low-grade agricultural land) are assigned for managed realignment schemes by the European Commission policy (French, 1997). Such areas are hard to find and often need to be bought. It is clear, however, that the marshland area adjacent to the Stanpit Marsh landfill is, owing to its metal concentrations, not well suited for this purpose.

4.5 Conclusions

The landfill continues to release leachate containing metals, as the high total concentrations compared to the reference samples as well as the high ammonium nitrate extractable percentages show. Elevated levels of phosphorus were found, which however, owing to its high mobility, is washed out rapidly and hardly present at greater depths in the cores. Other metals appear to leak out at much lower rates, but, owing to their lower mobilities, these elements are not easily washed out and large quantities remain in the sediment.

Sequential (SES) and partial extraction schemes (PES) only indicate the theoretical mobility at a specific time, not the actual long-term migration in the sediment. It was found that the PES procedure with ammonium nitrate extraction (DIN 19730) can predict the actual migration in the homogenous structure of the marshland rather well; particularly in the topmost sediment layers. In the vicinity of the channel, however, no correlation between the mobility and dispersion could be detected and the actual movement is much higher than the PES outcomes generally indicated. The channel therefore acts as a highly effective drainage system for both the landfill itself and the intertidal marshland in its sphere of influence. As mobile fractions are washed out immediately, leaving only the low mobile fractions behind, the PES procedure has only limitedly capability to predict the migration of contaminants in the ground affected by the channel.

5 Case study 3: Distribution patterns in Poole Harbour (UK) – Part 1: Absolute concentrations, mobility and risk potential

5.1 Introduction

Numerous studies have described the marine ecology of the estuary (Thomas *et al.*, 2004), but sediment research in this region is, in comparison, limited. For many estuaries, harbours and embayments comprehensive monitoring schemes have been undertaken, producing large databases. Boston Harbor, for example, has been monitored systematically since 1977 by the US Geological Survey (USGS) and has involved the collection of about 3,000 samples (Bothner, 1998). No such database exists for Poole Harbour; no comprehensive study covering the whole estuary has been carried out despite its ecological and economic importance (Langston *et al.*, 2003). There have been a number of surveys undertaken, however, these are:

- limited in number: *e.g.* Langston *et al.* (2003) point out that the absence of recent data made direct comparisons of metal concentrations in Holes Bay difficult, and Wardlaw (2005) stated that the routine quality monitoring to fulfil the statutory EU Directives included only “some limited sediment analysis”;
- partly inappropriate in their approach: *e.g.* Bowles and English (2005) sampled Holes Bay for various metals, but as a consequence of their research question they sampled selectively and analysed only the uppermost 1 cm of sediment. This approach is not uncommon; for example, one of the largest compatible estuarine databases in Australia contains thousands of samples, which have carefully been collected to exclusively include the upper 2 cm of sediment from all areas (Birch and Taylor, 1999);

- sometimes controversial in their outcomes (discussed below, *cf.* Chapter 5.1.2): for example, GPL (2004) versus Underhill-Day (2008) and Langston *et al.* (2003); or PDE (1992) versus Langston *et al.* (2003);
- focused on single sites without analysing the bigger picture (*e.g.* GPL, 2004; PHC, 2004a) and/or are based on too few cores (*e.g.* Cundy and Croudace, 1995);
- of limited public availability; for example, a "*thorough site investigation including bore holes and harbour silt analysis*" was undertaken in Holes Bay for a proposed second lifting bridge, but the according results are "*not public information*" (pers. comm. Rice[5], 2007).

Our knowledge of residual pollution in Poole Harbour is therefore limited. Poole Harbour with its prime basin, secondary embayments and several islands is a very complex system. Detailed knowledge of: (i) the precise spatial distribution of contaminants; (ii) the historic development, and (iii) the degree these elements/compounds are stable within the sediment-layer can answer a wide array of questions (*cf.* Chapter 1.4.1).

5.1.1 Area description

Poole Harbour is a large natural harbour, about 36 km² in size at high water spring tide (PHC, 2004a; Thomas *et al.*, 2004; Humphreys and May, 2005a). It is a major estuary of the Solent system (Cundy and Croudace, 1996) and has a very narrow entrance. According to the definition of the US National Research Council (NRC, 1995; *cf.* Chapter 1.1), the majority of Poole Harbour can be considered as a wetland (Figure 19).

Four rivers and a variety of small creeks drain into the harbour from the west: Frome, Piddle (also known as Trent), Corfe and Sherford (SCOPAC, 2004b). Close to eastern entrance of the harbour the salinity is similar to that of the

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[5] John Rice, engineering manager for the Full Sail Ahead Project

nearby seawater (median 29.8 psu), but becomes brackish towards the west (median 15.7 psu; Humphreys, 2005).

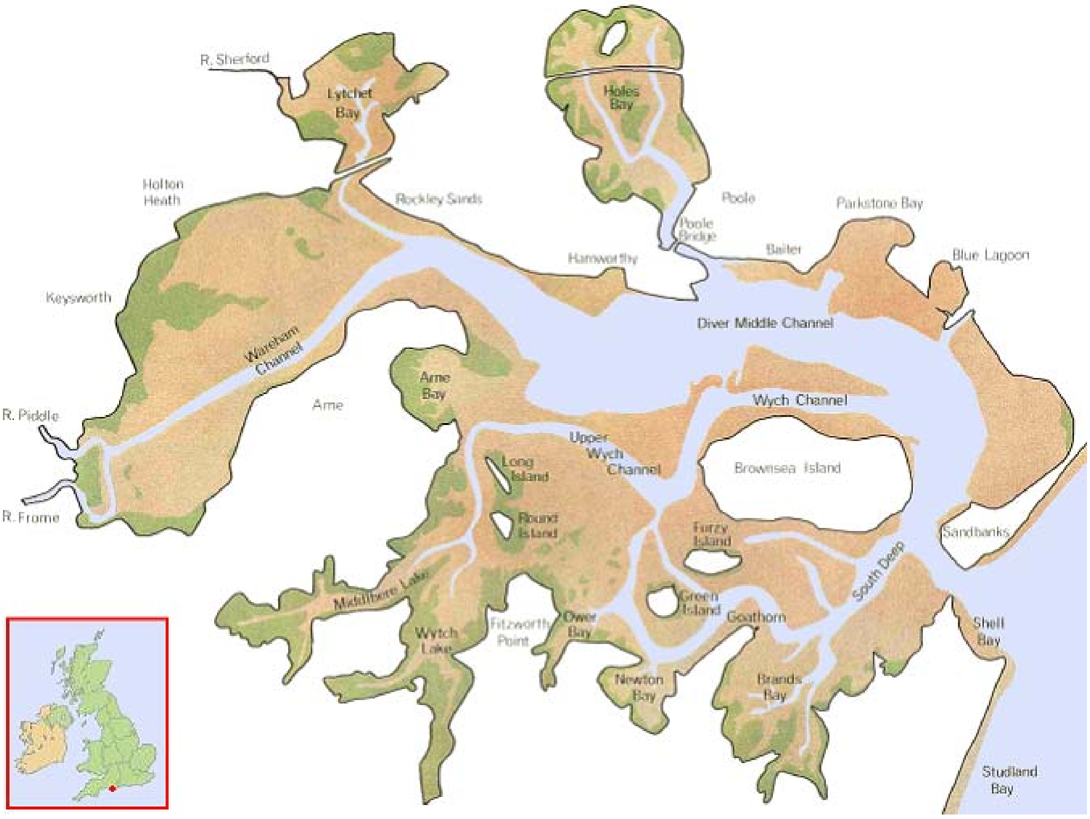

Figure 19: Map of Poole Harbour (adapted from Gray, 1985: copyright NERC, reproduced with permission of the CEH); location within the United Kingdom in the lower left corner

It is a very diverse environment, partly due to its many secondary embayments and islands (Figure 19), and partly due to its various uses: agricultural use in the west, industrial use in the east, and a nature reserve in the south. Essentially, it is a drowned river valley which was formed at the end of the last Ice Age, around 7,000 years BP by the former Solent river (SCOPAC, 2004b; Le Pard, n.d.; PHC, n.d.). The estuary and its adjacent shores contain most of Britain's coastal habitat types within an area that is relatively small in relation to its diversity (Gray, 1985). Alluvial soil has been washed down over thousands of years into the Harbour, which has caused substantial civil engineering problems, since the mud, in places 12 metres deep, cannot support heavy structures (BEA, 1949).

The harbour is dominated by intertidal sedimentary flats and shallow subtidal shoals (PHC, 2004a). The ground consists primarily of sand, gravel and clay, while hard bedrock is scarce (Dyrynda, 2005). The tidal range is extremely low being 1.8 m at spring tides and 0.6 m at neap tides (Humphreys and May, 2005a). Owing to the narrow opening (less than 370 m), the harbour has a limited water exchange: between 22 % (neap tides) and 45 % (spring tides) of the water mass is released into Poole Bay (Wardlaw, 2005). In the wave-sheltered south-western quadrant of the main basin, the secondary embayments and the upper levels of muddy shores are commonly colonised by saltmarsh (PHC, 2004a). Due to the low fetch the wave-activity is comparably mild (Brocklehurst *et al.*, 1991). The computer-model published in the environmental statement report for the channel deepening (PHC, 2004a) demonstrates how the current speed decreases substantially towards the south and west. Only within the harbour entrance do the currents reach velocities of $2.6\ m \cdot s^{-1}$ during spring periods, in the main part of the harbour the velocity is below $0.5\ m \cdot s^{-1}$.

As a consequence of its diversity, Poole Harbour was declared a Site of Special Scientific Interest (SSSI) under the Wildlife & Countryside Act 1981 in 1990 and is now protected by the provisions of Part II as substituted by Schedule 9 to the Countryside & Rights of Way Act 2000 (Powell, 2004; Powell, 2005). The mudflats and salt marshes are of great ecological value as a feeding ground for birds. Birds are partially protected by the EU Directive on the conservation of wild birds (CEU, 1979) under the Special Protection Area (SPA) scheme. Poole Harbour qualified for designation as a SPA in 1999 (Langston *et al.*, 2003; Humphreys and May, 2005a; PHC, n.d.).

As one of the major estuaries in the region, Poole Harbour is extremely important both as industrial/recreational area and as a habitat for wildlife (Cundy and Croudace, 1996). In Dorset’s coastal zone, fishing has always been of major commercial importance. The port of Poole handles

500,000 metric tons of cargo per year (Drake, 2006). A fleet of approximately 300 vessels is currently based in its ports, supplemented by a large number of charter boats for recreational fishing (Welton, n.d.). Poole Harbour is, with its shallow, sheltered waters, one of the main ports of the region. Fishing and aquaculture activities are worth approximately £2 million·yr^{-1} to the local economy (Jensen *et al.*, 2005). Apart from the industrial aspect, Welton (n.d.) points out that tourism is *"Dorset's predominant industry; and the coast is arguably Dorset's most important single tourism asset"*. According to the Poole Harbour Commissioners, the harbour is a destination for around 5,000 recreational crafts/year (PHC, n.d.). However, it is worth noting that intensive tourism activities can produce pollution and damage to the environment that can ultimately deter future tourists (Kocasoy, 1989).

Owing to the imminent 'Twin-Sails Ahead' project (*cf.* Chapter 5.1.3), the sampling in Poole Harbour was started in January 2008 in Holes Bay, the heavily industrialised north-western embayment of the estuary. Holes Bay is mostly surrounded by a narrow belt of low lying land (Figure 20).

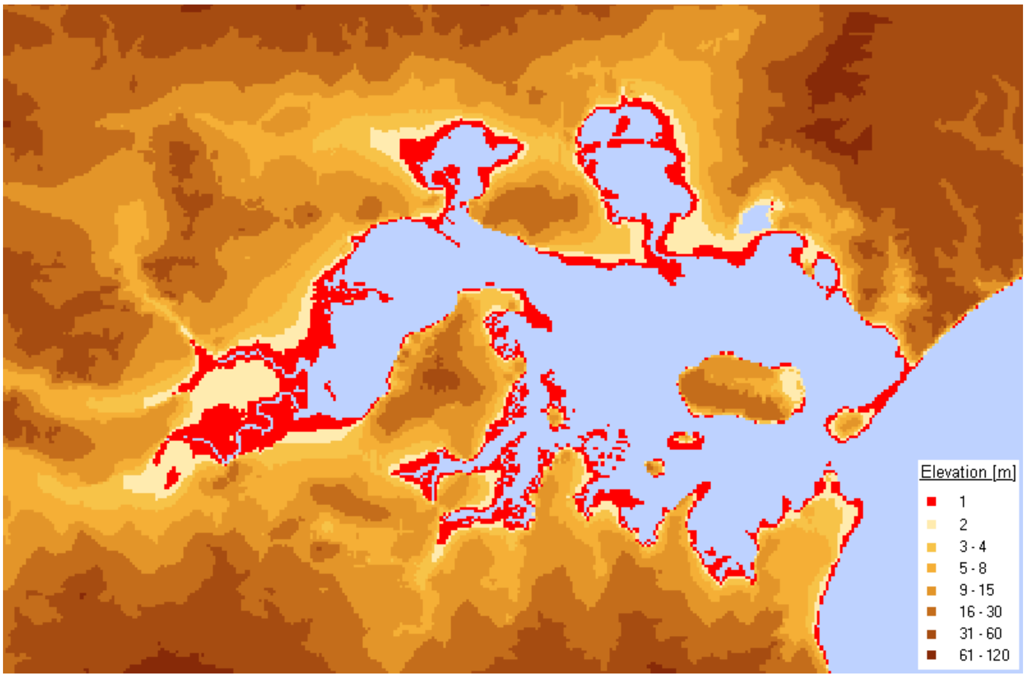

Figure 20: The topography of Poole Harbour (used data: Crown Copyright/database right 2007. An Ordnance Survey/EDINA supplied service)

5.1.2 Sources of contamination in Poole Harbour

In the 1970s, dissolved metal concentrations in Holes Bay could exceed values considered typical for the English Channel by 30-40 fold for copper, nickel and zinc, and more than 100-fold for cadmium and lead (Langston *et al.*, 2003). According to Gibbs (1987) the majority of the toxic metals and organic compounds that are discharged into estuaries and the oceans are transported by the particles delivered by rivers. Considering the extensive industrial, urban and agricultural use of Poole Harbour, this generalisation must be doubted at least for this specific environment, although the riverine input was subjected to close investigation as well.

According to a study by Drake, the environmental quality of the Poole Harbour estuary is generally thought to be good, but it is also considered to be very vulnerable to pollution (Drake, 2006). The estuary has a long record of industrial use, beginning in the Iron Age with trading, fisheries, pottery, mining, iron-smelting, shale- and salt-working (Humphreys and May, 2005a). The first intensive industrial use was reported around 1564, when the first large-scale copperas [6] production plant in England was constructed in Parkstone (Sheldrick, 2006). Between 1852 and 1887 a large pottery production was conducted on Brownsea Island (West, 2006). Today the complete northwest area of Poole Harbour is urbanised.

Background research indicated that in this area the industrial impact is the dominating factor. In the south-western part of Holes Bay a power plant station (PPPS) was constructed in 1946 on approximately 30 acres of reclaimed mudlands. Owing to the insufficient structural strength of the mud, it has been build in on concrete blocks, the largest being 150,000 t in weight (BEA, 1949). It was originally coal fired, but had been oil-fired since 1960 and decommissioned 1980. Ash was originally dumped by ships out to sea (BEA, 1949). The quantity of mussels and barnacles removed from PPPS inlet culverts amounted to up to 300 t/yr. The demand for liquid chlorine for a

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[6] iron(II)sulphate; $FeSO_4$

2,000 MWe power station is 6-10 t/day, and therefore continuous low-level chlorination inputs were introduced. Furthermore, antifouling paint has been used in the area (Coughlan and Whitehouse, 1977), these paints were commonly based on copper or tin. A remediation process of the area reduced hydrocarbon contamination by excavation and bioremediation (GPL, 2004), and today the entire area is owned by JJ Gallagher Land Improvement Holdings and subject to remediation works (pers. comm. Ralph[7], 2008).

In a study of Poole Harbour, Cundy and Croudace (1995) mentioned waste discharge from the Atomic Energy Establishment of Winfrith, Dorset, with activation products of iron, cobalt, chromium, manganese, nickel, zinc produced in the cooling circuitry of a prototype heavy water plant, which was closed in 1990. According to this paper, contaminated material was transported east to Poole Harbour and could be found in samples extracted in Poole Harbour (Wytch Farm and Lytchett Bay).

A factory owned by the chemical company British Drug House Ltd. (BDH; active since 1946 and acquired by Merck KGaA in 1973, although the company name was not changed until 1990), discharged directly into Holes Bay (GPL, 2004). The amount and nature of the discharge is unknown, but anecdotal evidence derived from personal communications with local fishermen and boat owners indicated that the discharge had been a very serious concern. During a catastrophic fire in 1988 (Anon., 1988a; Anon., 1988b) noxious fumes were produced – involving several, non-specified solvents and chemicals stored there (Murthagh, 1988). This event led to an investigation, but the corresponding report (HSE, 1988) as discussed by the Secretary of State at that time (Hansard, 1989) is currently unobtainable (pers. comm. Dales and Coles[8], 2007). The LexisNexis database shows no relevant entries and to date communications with the British Library, the Department of

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[7] David Ralph, Head of Strategic Planning, Borough of Poole

[8] Penny Dale and Janet Coles, Bournemouth University Library

Health and the Government News Network have not led to any tangible outcomes, either.

The Poole sewage treatment works (PSTW, today operated by Wessex Water) discharges on the northern side of the same embayment through two streams. While the Poole Harbour Aquatic Management Plan (Drake, 2006) states that sewage is treated to a high standard before discharge, it is implicated as the major offender in Poole Harbour (Langston *et al.*, 2003) and according to Wardlaw (2005) it is the main source for nitrate and phosphate input in the area. Sewage waters are furthermore associated with metal inputs (LaGrega *et al.*, 1994; Chen *et al.*, 2001; Astin, n.d.). LaGrega *et al.* (1994) noted the importance of cadmium, nickel, copper, lead and zinc in waste water.

In the north of Poole Harbour, a railway track runs right through Holes Bay. Studies dealing with emissions from railway tracks reported substantial amounts of metals, especially iron (Burkhardt *et al.*, 2007) and copper (Hillenbrand *et al.*, 2005), which are released from overhead wires, wheels, rails and brakes. In addition, historical maps indicate a changing variety of chemical industry works, mainly on the eastern shore of Holes Bay and on the Lower Hamworthy peninsula, the later consisting primarily of reclaimed lands, as indicated by an analysis of the available aerial photographs and map-material (*e.g.* Makenzie and Hurd, 1829; Ordnance Survey, 1888; Oldmaps, 1889; Stamp, 1931-4; British Admiralty, 2000; n.d.). This peninsula has been a focus for human settlement and activity since the late Iron Age/Early Roman period (GPL, 2004).

Europe's largest onshore oilfield lies under the harbour (Brocklehurst *et al.*, 1991; Humphreys and May, 2005a). BP operates several wells in the southern part of the harbour, but elevated contaminant levels are considered very unlikely in that region (BP, 1995), primarily owing to use of well-established techniques and pollution control/contingency plans (Planning and Highways Committee, 1985). Wardlaw (2005) describes the operations as a "shining example" of environmentally sound industrial development.

A study undertaken by Boyden (1975) in Holes Bay found high levels of metals and metalloids. Langston *et al.* (2003) noted that it is likely that concentrations have decreased in Holes Bay since this study, but that direct comparisons are difficult owing to the lack of recent data for this area. Bowles and English (2005) also sampled the same area, but their research question focused on the present endangerment of sea birds and not the geochronology, and they therefore only sampled the topmost part of the sediment. The report by PDE (1992) described sediments from the south east of Holes Bay as chemically clean sandy silt. By contrast, Langston *et al.* (2003) suggested that these sediments may not be typical and that much of the silt in Holes Bay could not be accurately classed as chemically clean.

The western part of Poole Harbour is urbanised to a far lesser degree; the two main sources for contamination in this area are the agricultural use of the south-eastern area, introducing high levels of pesticides and nutrients (pers. comm. Sheldrick[9], 2006) and a weapons facility, the Royal Navy Cordite Factory (RNCF), operating through both world wars at Holton Heath. Construction of the factory began during WW1. Between 1915 and 1957 the RNCF manufactured naval gun propellant and explosives such as cordite, picrite and tetryl and associated ammunition (Taylor, 2006). The majority of the facilities were closed in 1959. However, until the end of 1997 a division of the Defence Evaluation & Research Agency was operating there (Bowditch and Hayward, 1996). Extensive research by the Admiralty Materials Laboratory (AML), Holton Heath, on corrosion prevention was conducted in the facility for for at least 14 years after the RNCF's closure, which involved a substantial output of cadmium and various anti-corrosives (pers. comm. Kneller[10], 2009). The AML is listed in a NATO issued directory of high temperature corrosion research (AGARD, 1971), stating that AML's activities focussed on "high temperature sulfidation corrosion in marine gas turbines; studies of alloys and coatings using a low pressure combustion rig; kinetic and other basic

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[9] William Sheldrick, University of Newcastle

[10] Paul Kneller, Bournemouth University

investigations". Today the site encompasses an industrial estate and a large nature reserve.

The natural harbour has been a major contact point for ships. During WWII many ships of the 'Assault Force O' gathered here for D-Day (Blackwell, 1944), today it is a destination for both commercial traffic and between 5,000 (PHC, n.d.) and 7,000 (Langston *et al.*, 1987) recreational crafts/yr as well as a few larger commercial vessels, primarily ferries. Ship traffic has caused effects throughout the entire harbour: for example, through antifouling-paints, litter, cleaning detergents and oil. Houghton (1975) stated that "*copper-containing antifouling paints do not appear to constitute an environmental pollution problem*." – but he also mentioned the problem of accumulation in an area with practically no exchange of water and calculated that a treated surface of 100,000 m² would accumulate 1 ton of copper within 100 days. Another antifouling paint, tributyltin (TBT), has been banned by the UK government for small boats in 1987, and since then the levels of tin have steadily declined (Matthiessen *et al.*, 1995). According to the report from Langston *et al.* (2003) large quantities of TBT were present in the late 1980s, and they noted that it was unlikely that the concentrations would have returned to NOEL-levels (no observable effect level) at certain locations, but also that there was still uncertainty as to the actual levels. Bergmann and Grünwald (2006) noted that for dredging operations TBT still posed a major problem, because in some areas close to harbours and docks TBT concentrations can be found that are 1,000 times higher than the NOEL-level of sediment organisms. TBT is eventually degraded to elemental tin:

$$(C_4H_9)_3Sn \rightarrow (C_4H_9)_2Sn \rightarrow (C_4H_9)Sn \rightarrow Sn$$

TBT analyses are still difficult and expensive, whereas elemental tin can be analysed by the ICP.

In an enclosed and poorly flushed bay like Poole Harbour with its intense ship traffic, an accumulation of copper, tin and other metals is highly likely. The harbour also has a history of problems associated with contamination and hypernutrification (Humphreys and May, 2005a), which have adversely affected species abundance and diversity and led to a low biodiversity in comparison with other UK estuaries and coastal sites (Langston *et al.*, 2003). The overall contamination is expected to increase with depth of the sediment, since the contamination released into the environment is constantly decreasing due to increased regulations and monitoring. In Boston Bay in the United States, an embayment with an industrial profile comparable to Poole Harbour, monitoring conducted over a period of 16 years showed that the concentrations of chromium, lead, mercury, silver, and zinc in surface sediments have decreased by about 50 %, but with some metals still at toxic concentrations (Bothner, 1998).

5.1.3 Sediment accumulation and redistribution

SES analyses suggested that a significant fraction of the metal loading in Poole sediments may not be stable and thus has potential for remobilisation (Langston, 1982; Cundy and Croudace, 1995), and only remains stable because of the sheltered, low-energy conditions in Poole Harbour (Langston *et al.*, 2003).

Dredging, to keep navigational channels open, amounts to an average displacement of 70,000 m^3 sediment per year (Langston *et al.*, 2003). In 2005, a large dredging operation commenced to deepen the main channel in Poole Harbour (Figure 21).

In addition to the main dredging operation in the main channel, another dredging operation in Holes Bay will be undertaken for the construction of a new bridge: the “Twin Sails Ahead” project. The engineering consultants Gifford and Partners Ltd (GPL) have extracted core samples in Holes Bay and concluded that dredging (in this case for the construction of a new bridge) would not pose an imminent danger to the environment (GPL, 2004). By contrast, other studies (Langston *et al.*, 2003; Wardlaw, 2005; Underhill-Day, 2008) suggest that metals and metalloids could be remobilised when the sediment is disturbed. Since these reports, no further data has been published to support either viewpoint.

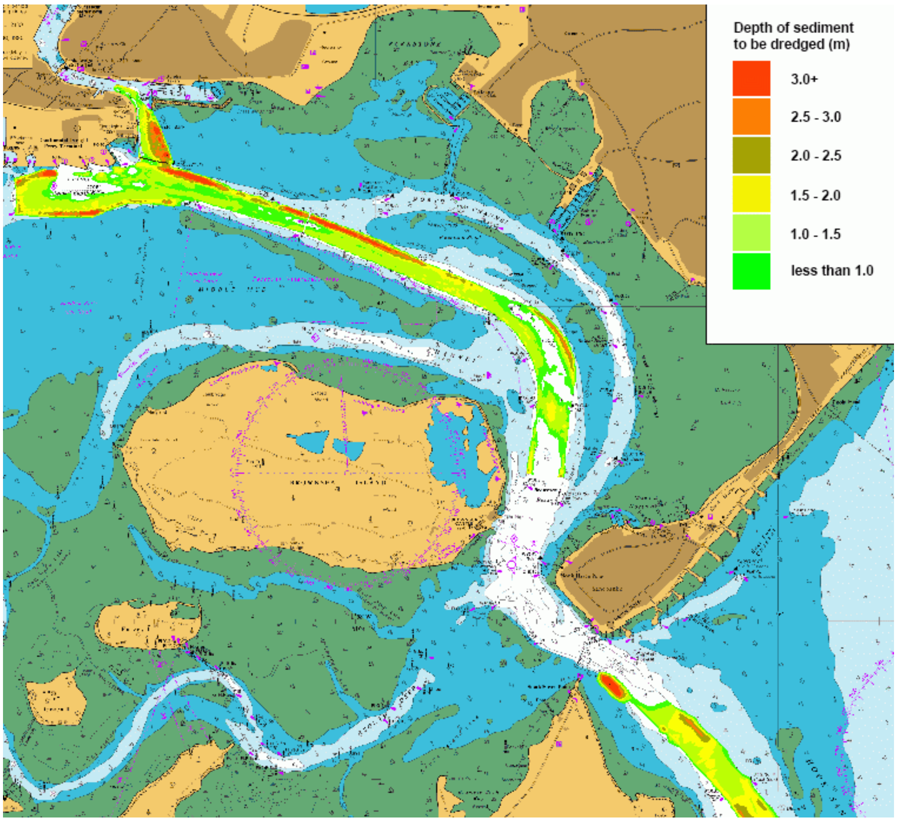

Figure 21: The dredging operation in Poole Harbour (adapted from PHC, 2004b)

This large-scale dredging in a small embayment with very poor flushing characteristics will, however, presumably cause a strong impact; therefore scientific sampling must be concluded before this operation commences. Originally, the start was scheduled for 2007, but, fortunately for this project, postponed (pers. comm. Rice[11], 2007). Early September 2009 PHC announced the start of the operations (Murphy, 2009). Monitoring of the site confirmed that works have commenced immediately thereafter by the "C. H. Horn" (140 gross tons), equipped with a grab system. Compared to a suction based dredging system, grab dredging may lead to a substantially higher remobilisation as the sediment is constantly washed out (Figure 22).

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[11] John Rice, engineering manager for the Full Sail Ahead Project

Figure 22: The "C. H. Horn" during dredging operations in Holes Bay, 05.09.2009

Analyses in the approaches to Poole Harbour, the Swash Channel, showed hardly any contamination at all in the top-layers, only tin and mercury showed elevated levels (Hübner, 2009). All other analysed metal concentrations in the upper part of the sediment (interaction layer) were on average only 10.4 % of their respective TEL-values (*cf.* Chapter 10.4.6). It is therefore reasonable to conclude that the majority of contamination remains within the harbour, primarily owing to its minimal flushing characteristics.

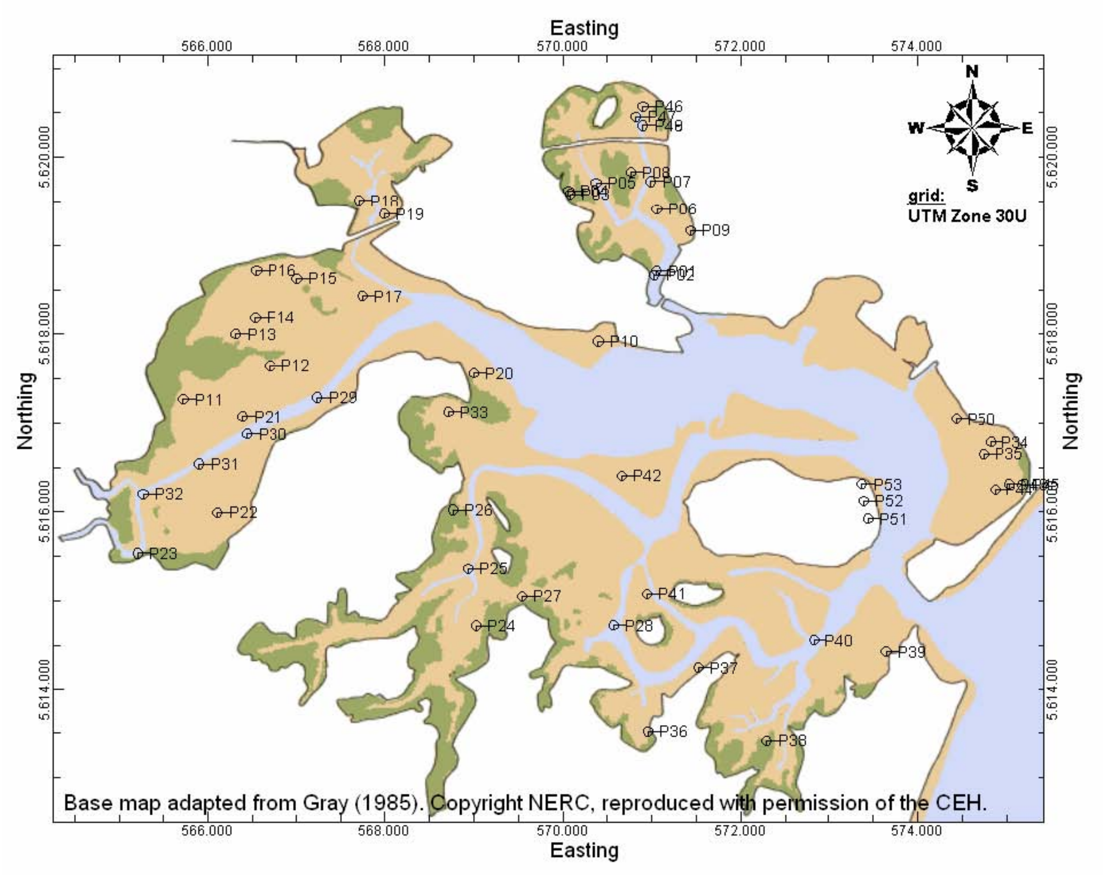
In the contaminant study in Poole Harbour, the null hypotheses are that

a) the metal/metalloid concentrations are below the threshold effect levels, which would indicate that adverse effects are to be expected only rarely (*cf.* Chapter 2.2.6);

b) there are no significant differences between the concentrations in the different sampling zones, which would indicate that the different impacts (for example the considerable industrial use in Holes Bay, *cf.* Chapter 5.1.2) did not cause noteworthy differences in the distribution of different contaminants.

5.2 Material and methods

Detailed cm-by-cm analyses can provide much information on trends over long time frames (Smol, 2002); however, owing to the large size of the estuary, a high number of cores would need to be extracted to avoid the common problem associated with other studies (*cf.* Chapter 5.1), and a cm-by-cm analysis would produce a prohibitively large number of samples. In order to obtain a reasonable balance between spatial coverage and temporal resolution 53 cores have been extracted in the present study. This allowed a reasonable coverage and it is very unlikely that additional cores would have provided significantly more information (*cf.* Figure 23-Figure 30). Samples have been extracted with a Beeker corer type 04.29.SA (*cf.* Chapters 2.1.2 and 10.2.1) between 2007 and 2009.



Base map adapted from Gray (1985). Copyright NERC, reproduced with permission of the CEH.

Figure 23: The sampling locations in Poole Harbour

The literature recommends using sites with low turbation to get reference samples with a clear profile (Smol, 2002). Unfortunately, using only such sites would exclude the majority of Poole Harbour from analyses; however, there is a site which offers such conditions: a sea wall was constructed on the eastern side of Brownsea Island in order to drain St Andrew's Bay and create a meadow as cattle pasture (pers. comm. Thain[12], 2006). According to Mr Thain and the Dorset Wildlife Trust Webpage the wall was constructed in the 1850's; the map-material shows that at least a provisional construction was already existing in 1811 (Makenzie and Hurd, 1829). The area sheltered by this wall resulted in undisturbed reference samples, while the Southern Bights (*i.e.* Brand's Bay, Newton Bay and Ower Bay) provided nearly contamination-free samples for the estimation of the natural background values.

Cores were processed with a resolution of 5 cm (for core lengths, see Chapter 5.3 and Table 7 respectively) and the previously described methodology has been applied. Samples have been dried with a temperature not exceeding 40 °C and prepared with a 0.3 mm sieve (*cf.* Chapter 2.1.3). Typically, for each sample 3 replicates were analysed, but higher variations between the replicates triggered the inclusion of further replicates (*cf.* Chapter 2.2.5). The (pseudo-)total metal content was analysed using *aqua regia* digests (*cf.* Chapter 2.2.2); the mobile fraction using the standardised procedure DIN 19730 (*cf.* Chapters 2.2.4 and 4.4).

To link the contamination with the source, and determine its development with time the age of the sediment layers must be known. Radiometric dating is an effective means, and ^{14}C is commonly used as evidence of recent climate change and environmental effects of human activities (Chernicoff and Whitney, 2007). ^{241}Am also has considerable potential as dating tool, its main advantage is its lower mobility (Appleby *et al.*, 1991; ATSDR, 2006). If the sedimentation rate is known, the depth can be related to the age. Studies by Warneke (2002) and Cundy and Croudace (1996) considered this issue and

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[12] Chris Thain, Reserve Manager Dorset Wildlife Trust

provided sedimentation rates for Poole Harbour with the assistance of radiometric dating. For this approach, a corer with a very low compression is essential (*cf.* Chapters 4.2.1 and 10.2). In addition, contamination horizons can be used to calibrate local differences. Events like the catastrophic BDH fire in 1988 (*cf.* Chapter 5.1.2) usually cause horizons in the sediment, furthermore large-scale catastrophes resulting in worldwide fallouts (*e.g.* atmospheric nuclear bomb testing and volcanic eruptions) can provide evidence for establishing a chronology (Smol, 2002).

Bryan and Langston (1992) provided a comprehensive list of average concentrations for 19 different sites, primarily UK estuaries, including Poole Harbour. These values have been used a reference values in this study.

Bauer *et al.* (1996) described an equation to estimate the potential risk of adverse effects of contamination ("*Gefährdungspotential*"), here translated as risk potential index (RPI). The original formula (RPI_0; Equation 3) is based on the German sewage sludge ordinance (AbfKlärV; BMU, 1992) and takes account of both mobile and (pseudo-)total concentration together with one guideline values for each: the sewage sludge threshold value ("*Grenzwert der Klärschlammverordnung*"; KSV_G) and the threshold value for mobile fractions ("*Prüfwert für Mobilanteile*"; PW_M). Although this approach was originally not intended for sediments, the basic concept is sound and has been adapted for the use in the present study. For this purpose, effect levels for marine and estuarine sediments (*cf.* Table 6), as discussed in Chapter 2.2.6, have been implemented in the calculations. For the first formula (RPI_1; Equation 4) only one essential modification was implemented: the sewage sludge threshold level was replaced by the SQuiRTs threshold effect level for marine sediments. In the second formula (RPI_2; Equation 5) the same basic concept was used, but this time the equation was reorganised: the absolute concentrations were set in relation to the probable effect levels and the mobile fractions to the threshold effect levels, thus basing the equation solely on up-to-date values. If the total available concentration equals the PEL and the mobile fraction equals the TEL, the RPI_2 would take the value of 1.

Equation 3: $$RPI_0 = \sqrt{\frac{TCA}{KSV_G} \times \frac{PES}{PW_M}}$$

Equation 4: $$RPI_1 = \sqrt{\frac{TCA}{TEL} \times \frac{PES}{PW_M}}$$

Equation 5: $$RPI_2 = \sqrt{\frac{TCA}{PEL} \times \frac{PES}{TEL}}$$

with:

RPI_0 = risk potential index [non-dimensional ratio value], original sewage sludge formula
RPI_1 = risk potential index [non-dimensional ratio value], threshold level exchanged
RPI_2 = risk potential index [non-dimensional ratio value], new calculation method
TCA = *aqua regia* extractable content [$mg \cdot kg^{-1}$]
PES = ammonium nitrate extractable content [$mg \cdot kg^{-1}$]
KSV_G = sewage sludge threshold value (“*Grenzwert der Klärschlammverordnung*”) [$mg \cdot kg^{-1}$]
PW_M = monitoring value for mobile fraction ("*Prüfwert für Mobilanteile*") [$mg \cdot kg^{-1}$]
TEL = threshold effect level [$mg \cdot kg^{-1}$]
PEL = probable effect level [$mg \cdot kg^{-1}$]

Table 6: Threshold effect levels (TEL); probable effect levels (TEL) and monitoring values for mobile trace metal contents (PW), all values in $mg \cdot kg^{-1}$

	TEL(1)	PEL(1)	PW(2)
As	7.240	41.600	0.100
Cd	0.680	4.200	0.020
Cr	52.300	160.000	0.050
Cu	18.700	108.000	0.800
Hg	0.130	0.700	0.005
Ni	15.900	42.800	1.000
Pb	30.240	112.000	0.300
Zn	124.000	271.000	5.000

(1) Buchman, 2008 (2) Prüeß, 1992

5.3 Results

Depending on locations and sediment parameters (most notably grain size) cores were between 30 and 100 cm in length (Table 7), with 100 cm constituting the maximal length possible with the equipment used (Table 1); which is, considering the temporal range this length allows, adequate for the objectives of this study (*cf.* Chapter 1.4.1) and also lies well within the range suggested by Ahlf *et al.* (2002). Shorter cores were obtained in Holes Bay at the PPPS, where the solid chalk layer prohibited deeper sampling, in the middle of the main basin and at the Eastern Sandbanks, where the sandy bottom with only small clay fractions made penetration of the ground difficult. In all other areas, cores typically were between 70 and 90 cm in length.

Table 7: Core lengths in Poole Harbour

sampling zone	min [cm]	max [cm]	mean [cm]
Holes Bay	30	100	76.4
Lytchett Bay	100	100	100.0
Wareham Channel	65	100	84.0
Eastern Sandbanks	40	50	46.6
Southern Bights	45	100	88.2
Brownsea Island	50	85	63.3
Σ			76.0

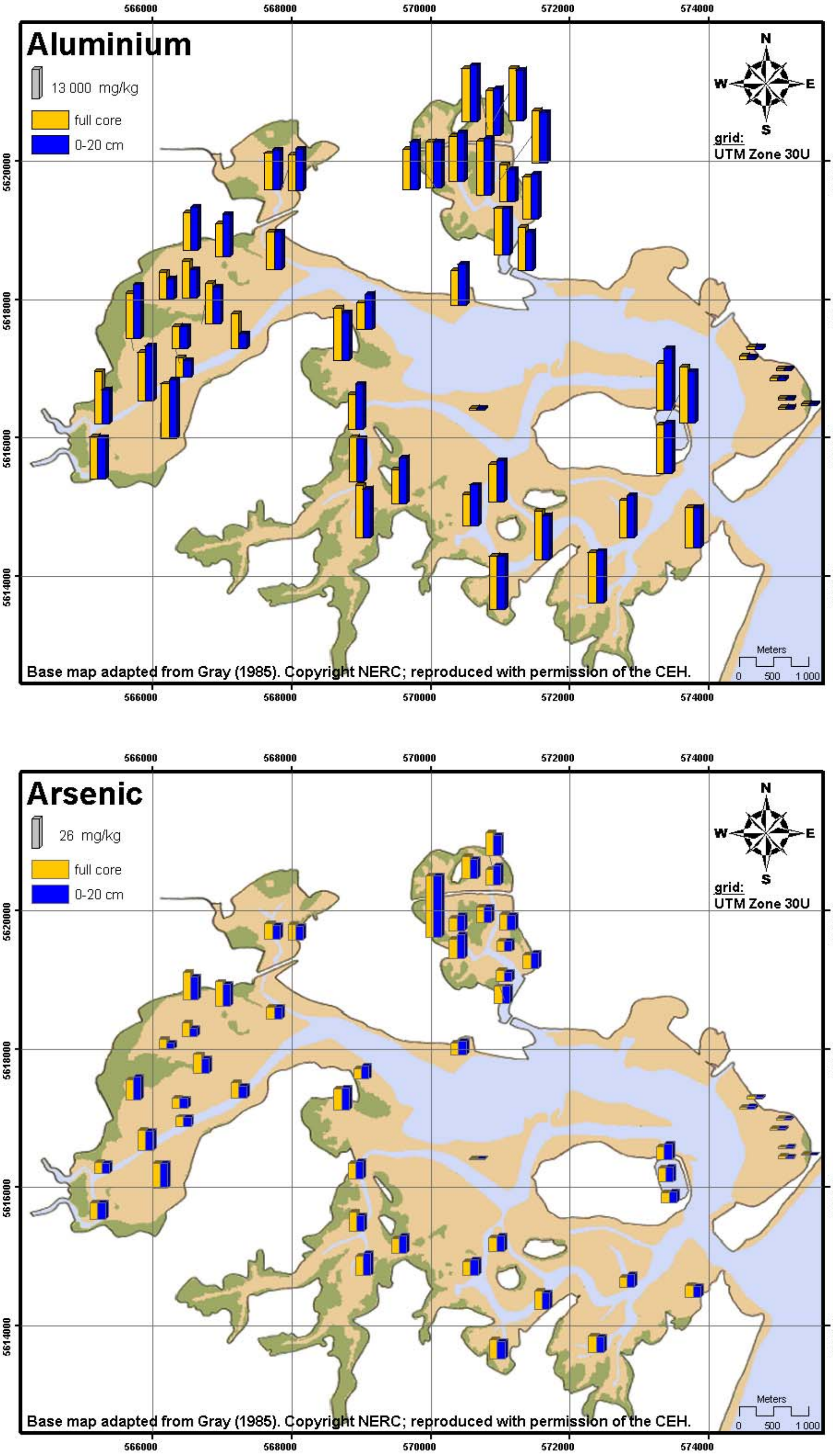
Given that the sampling area was much larger in size and the contamination levels differed substantially, it has been difficult to display the whole sampling area with 3D-plots as was done for the Christchurch Harbour case study (Figure 15). Therefore, first the major elements have been compared for the whole estuary (Figure 24-Figure 30), and then different zones (Holes Bay, Wareham Channel, Southern Bights, Brownsea Island lagoon, Eastern Sandbanks and Lytchett Bay) were assessed in more detail. In addition, three known major point sources (PSTW, PPPS and RNCF; *cf.* Chapter 5.1.2) were analysed in detail.

5.3.1 Overview

The elements cadmium, copper, lead phosphorus, tin and zinc are found in their highest concentrations in Holes Bay (Figure 24-Figure 30; see also Chapter 10.4.1 for plots taking depth changes into account), while arsenic, chromium, cobalt and nickel are much more evenly distributed.

The concentrations of most elements in the southern basins are very low, normally well below TEL and often at the analytical detection limit. In Wareham Channel the concentrations were typically in the TEL-PEL-range, while in Holes Bay by far the highest concentrations have been observed, usually above PEL. This is, for example, clearly visible for tin: while the other areas of Poole Harbour are fairly low, the concentrations (*cf.* Figure 30a) are considerable in Holes Bay: on average 1.78 mg·kg^{-1} for all depths and 2.86 mg·kg^{-1} for the depth between 0 and 20 cm. Given the low recovery rate of this element (56.87 %; Table 2), the real concentration can be assumed to be higher, namely 3.13 and 5.02 mg·kg^{-1} respectively.

Figure 24 through Figure 30 show the concentrations in Poole Harbour as averages of the full core (yellow bars) and averages of the most recent 20 cm (blue bars). The grey bars are references and show the concentration scale of the particular plot.



Base map adapted from Gray (1985). Copyright NERC; reproduced with permission of the CEH.

Base map adapted from Gray (1985). Copyright NERC; reproduced with permission of the CEH.

Figure 24: Average concentrations (means calculated over the complete cores and over the topmost 20 cm) of aluminium and arsenic in Poole Harbour

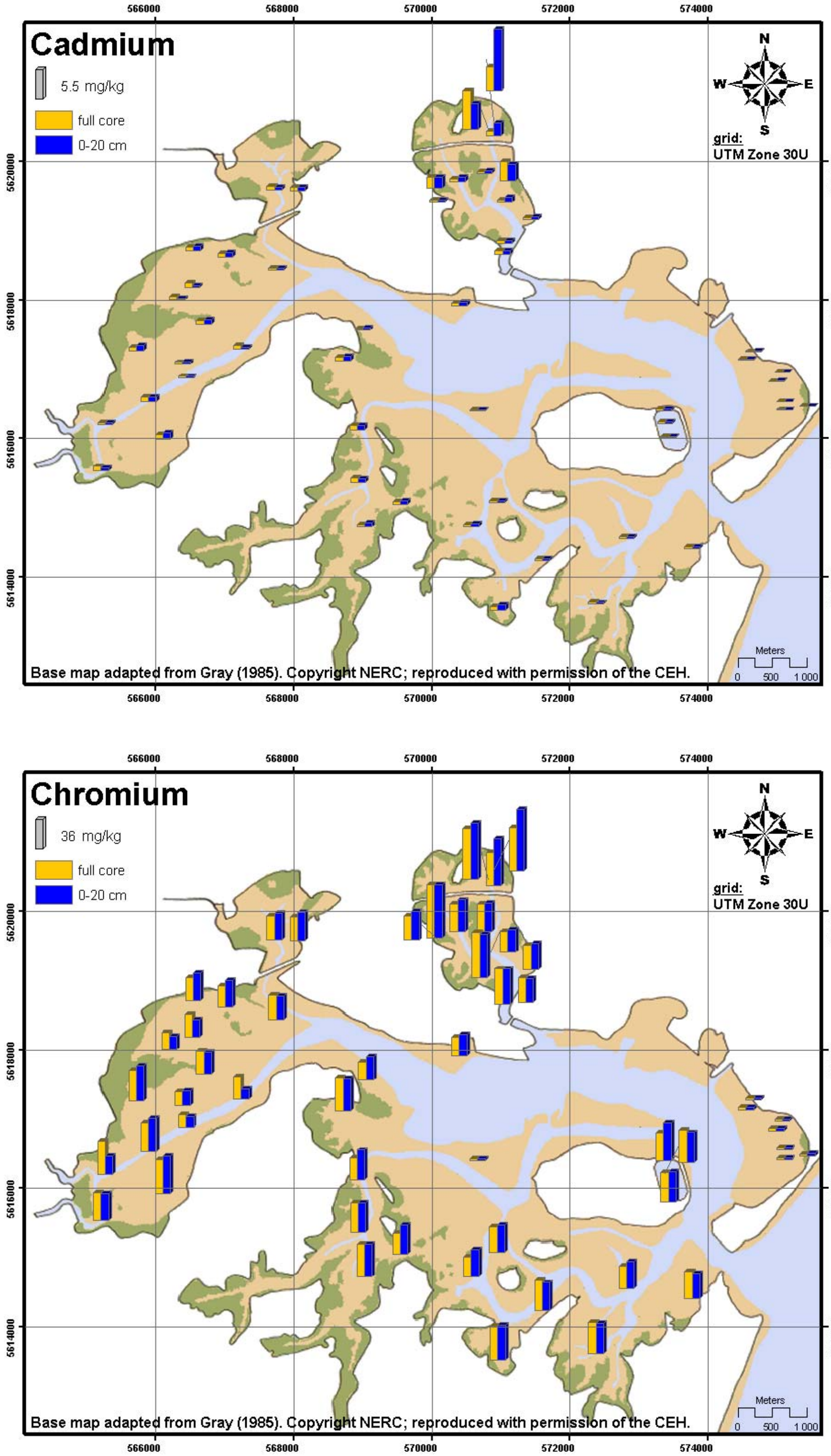


Figure 25: **Average concentrations (means calculated over the complete cores and over the topmost 20 cm) of cadmium and chromium in Poole Harbour**

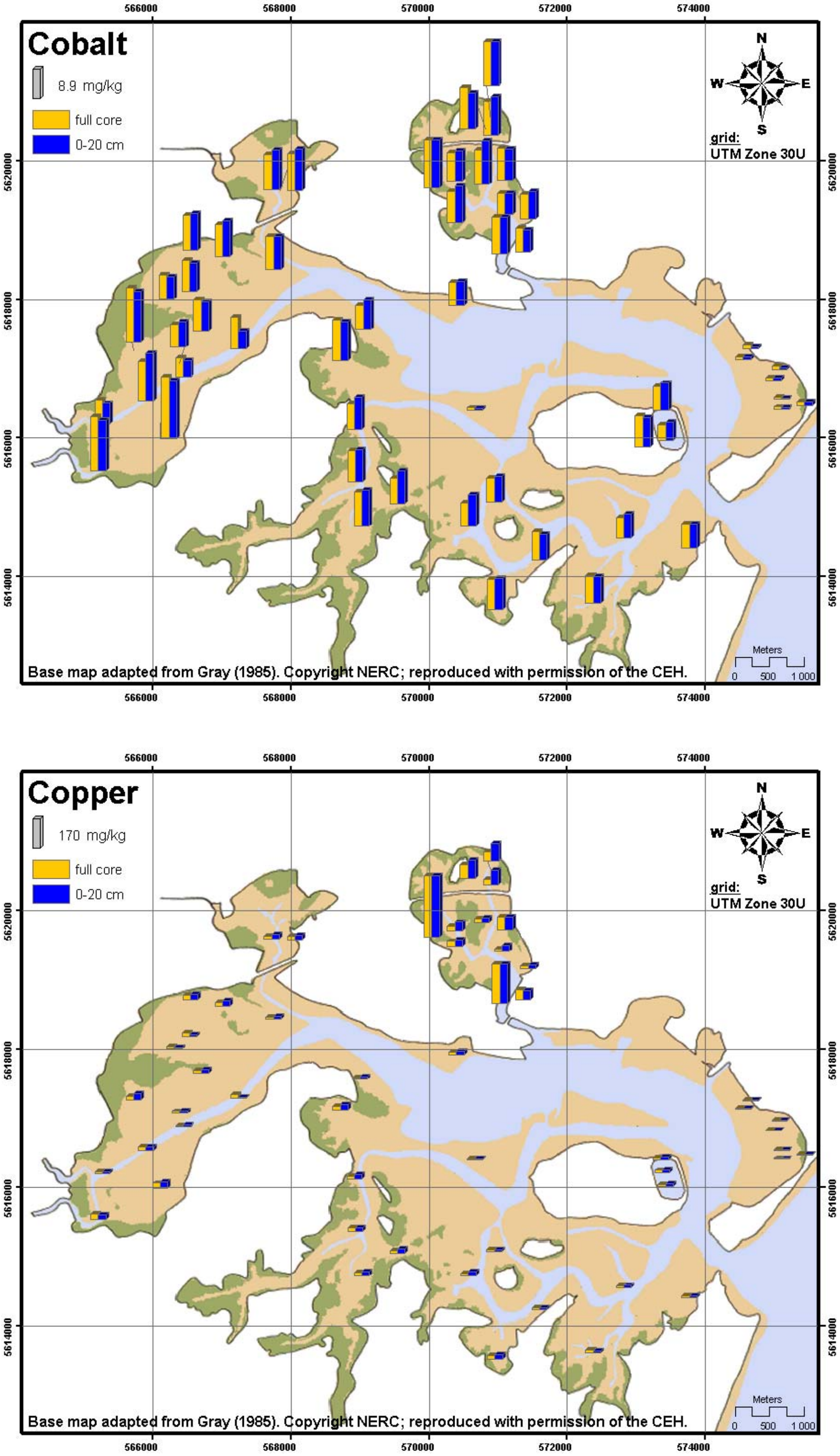


Figure 26: **Average concentrations (means calculated over the complete cores and over the topmost 20 cm) of cobalt and copper in Poole Harbour**

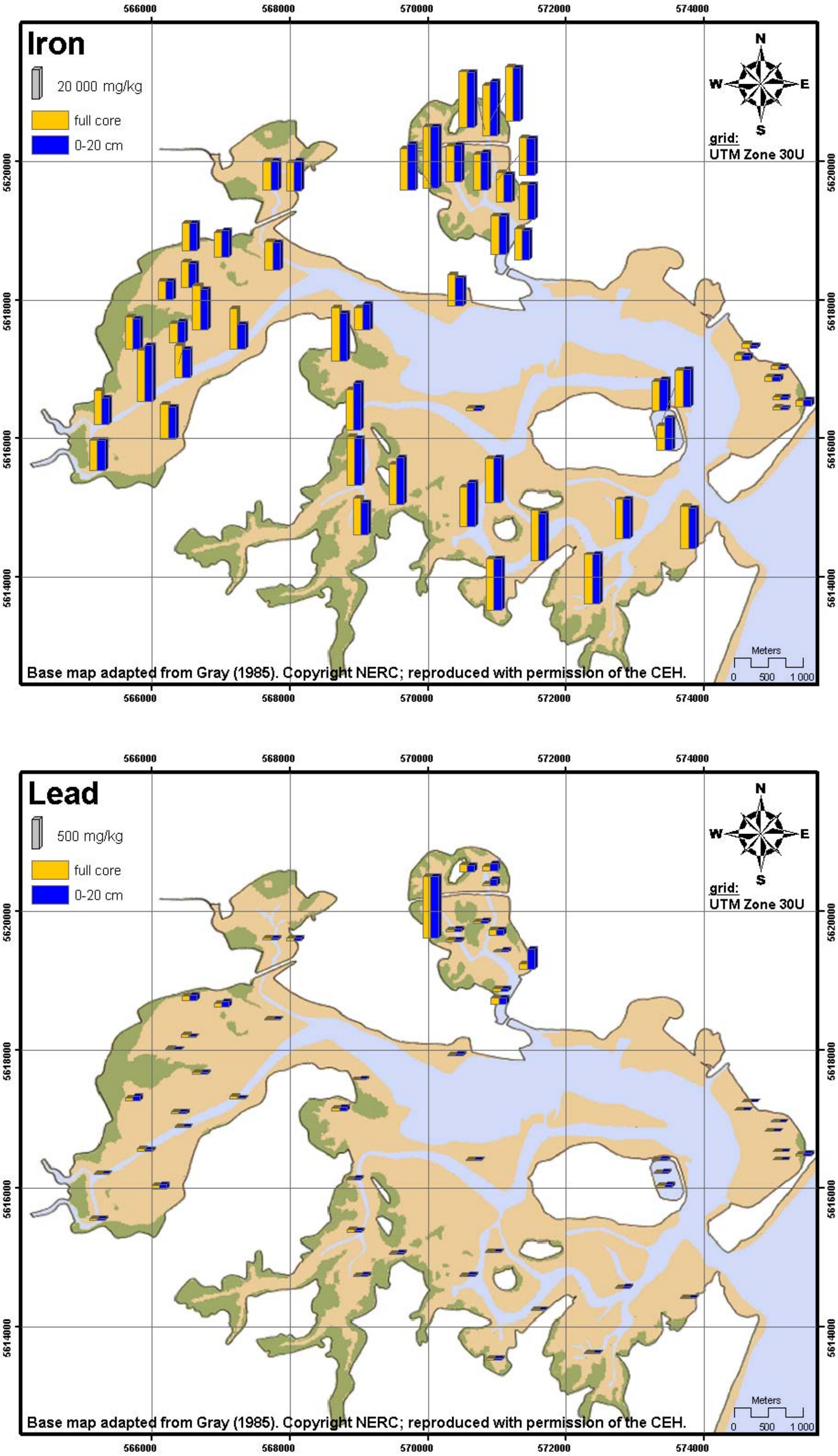


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Figure 27: Average concentrations (means calculated over the complete cores and over the topmost 20 cm) of iron and lead in Poole Harbour

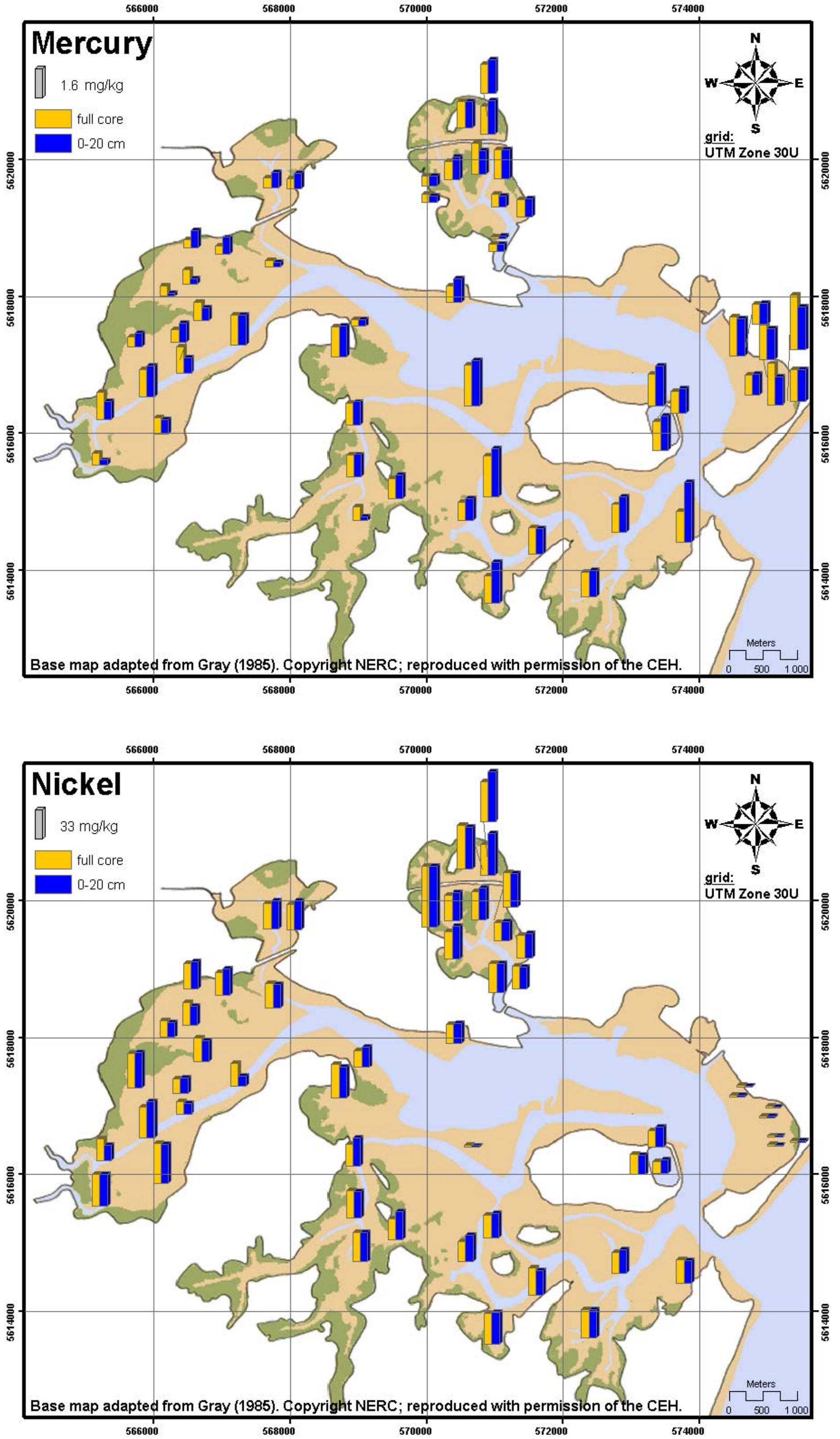


Figure 28: **Average concentrations (means calculated over the complete cores and over the topmost 20 cm) of mercury and nickel in Poole Harbour**

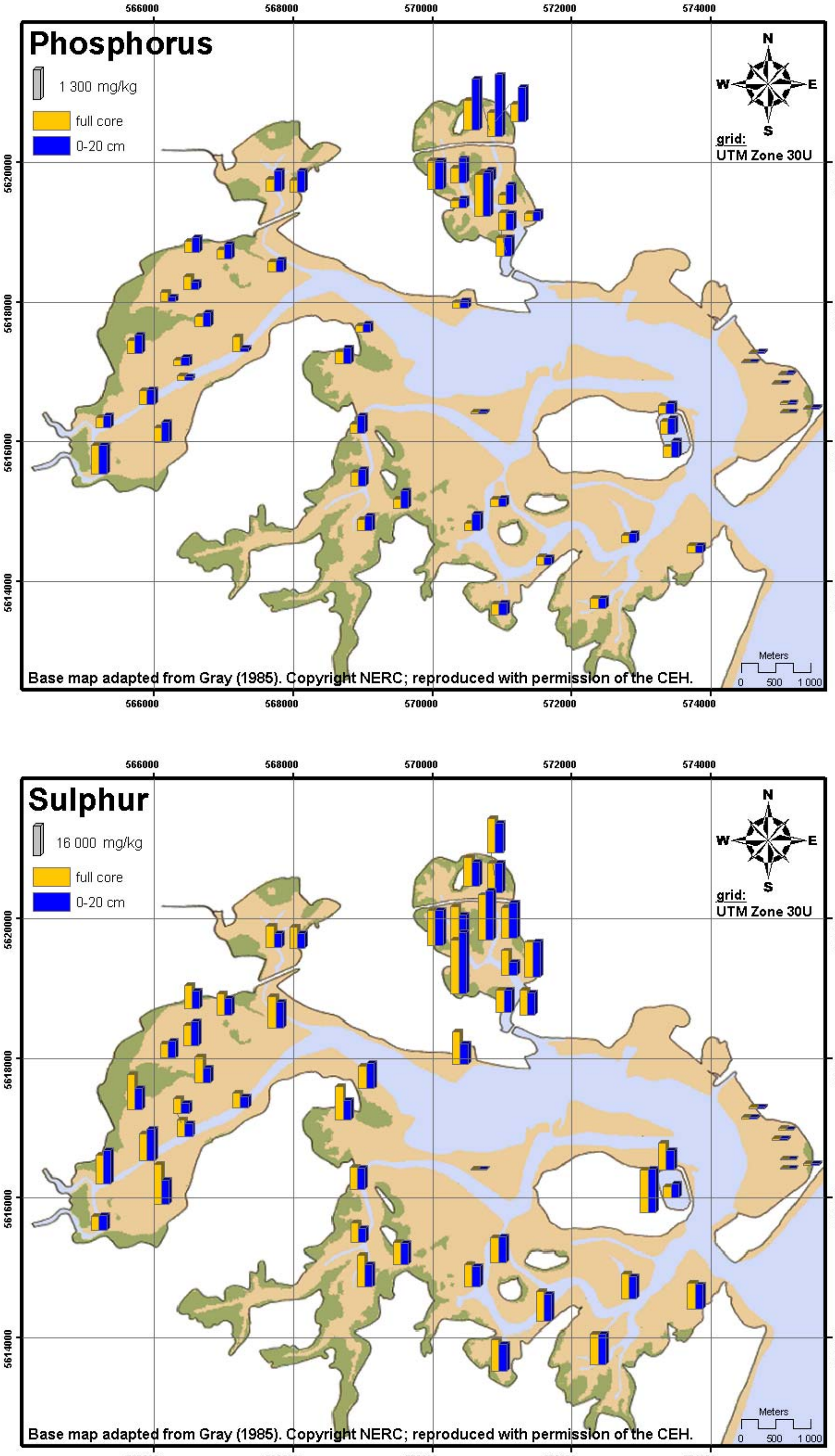
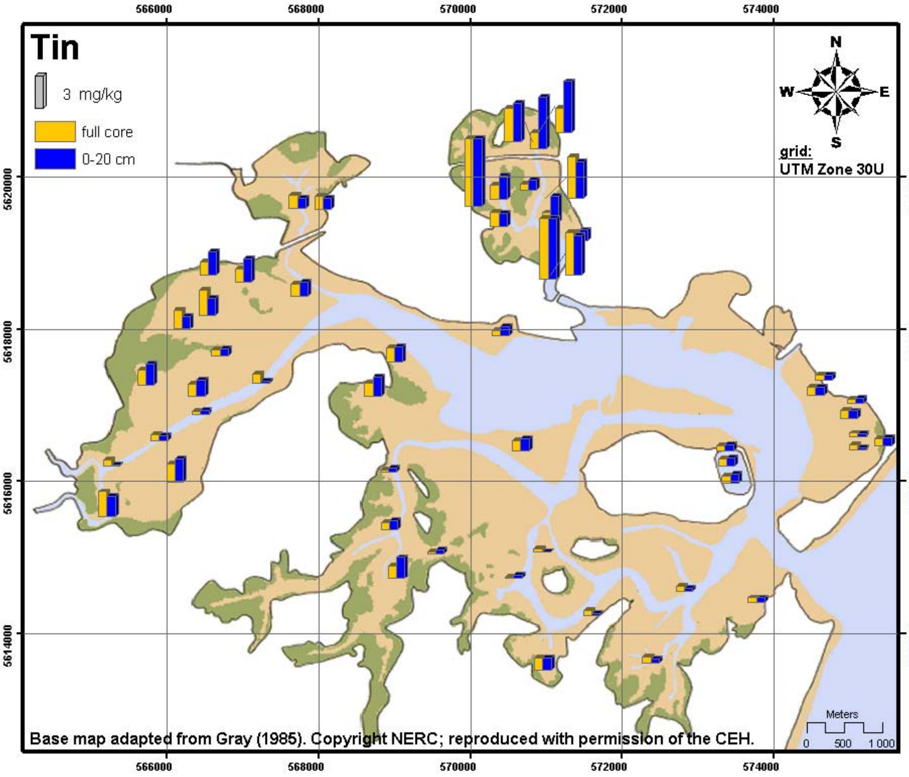


Figure 29: **Average concentrations (means calculated over the complete cores and over the topmost 20 cm) of phosphorus and sulphur in Poole Harbour**



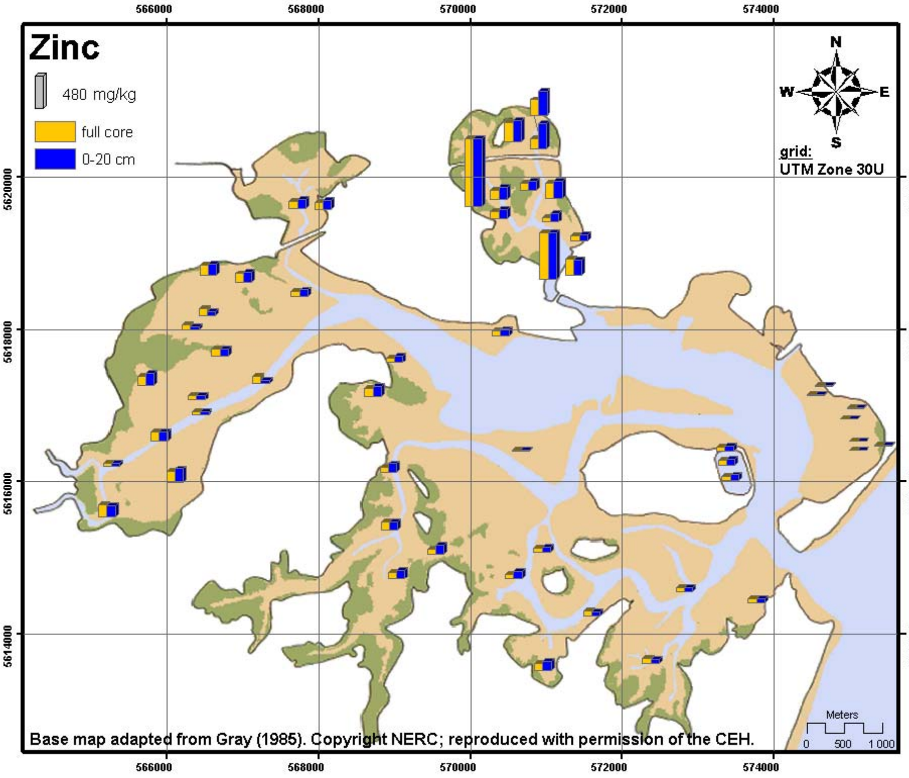


Figure 30: **Average concentrations (means calculated over the complete cores and over the topmost 20 cm) of tin and zinc in Poole Harbour**

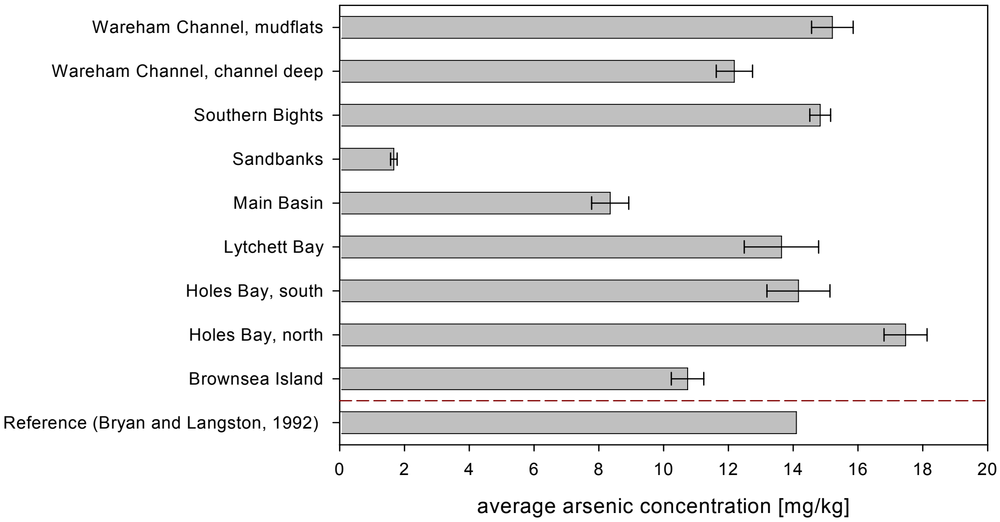
Phosphorus, a very mobile element, can usually be found only in the upper, *i.e.* more recent, sections of the sediment column. Especially the PSTW appears to be a major source of this element. In addition, elevated levels were measured at the mouth of the river Frome in the south-western reach of Wareham Channel; however, these were found to disperse shortly after the entrance and are much more equally distributed throughout the depths of the sediment (Figure 29).

Most elements show very clear differences in the concentration levels between the different zones of the estuary (Figure 31-Figure 34). Most notably, Eastern Sandbanks and the Brownsea Island lagoon have for nearly all analyses low to very low concentrations, while Holes Bay shows the highest loads (especially pronounced for cadmium, copper and zinc in the north), followed by the Wareham Channel and Lytchett Bay. In Wareham Channel, the mudflats typically have much higher concentrations compared to the cores of the channel deep, except for mercury (Figure 33).

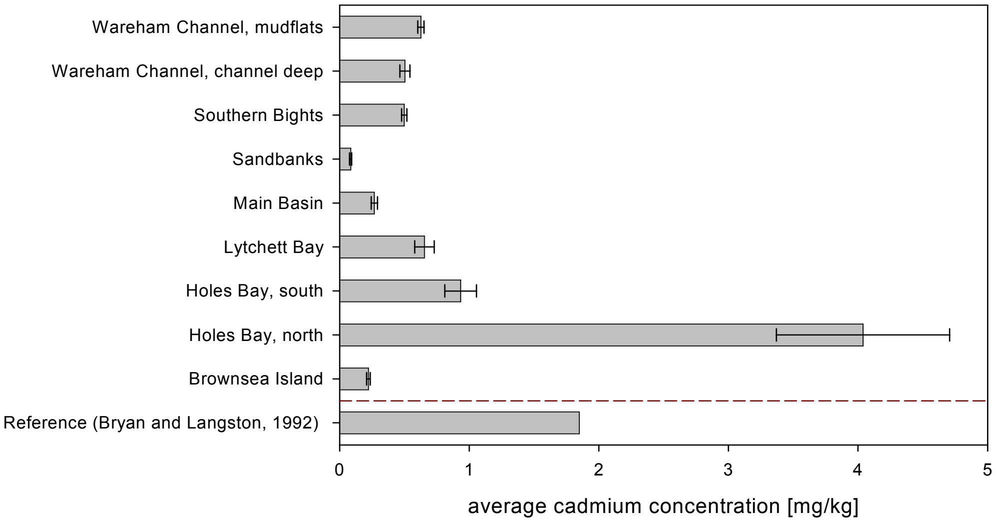
The values by Bryan and Langston (1992), which have been used for reference purposes (*cf.* Chapter 5.2), have been inserted below the values measured in this study, separated by a dashed line. The number of cores can be found in Table 8.

Table 8: Total number of cores per zone

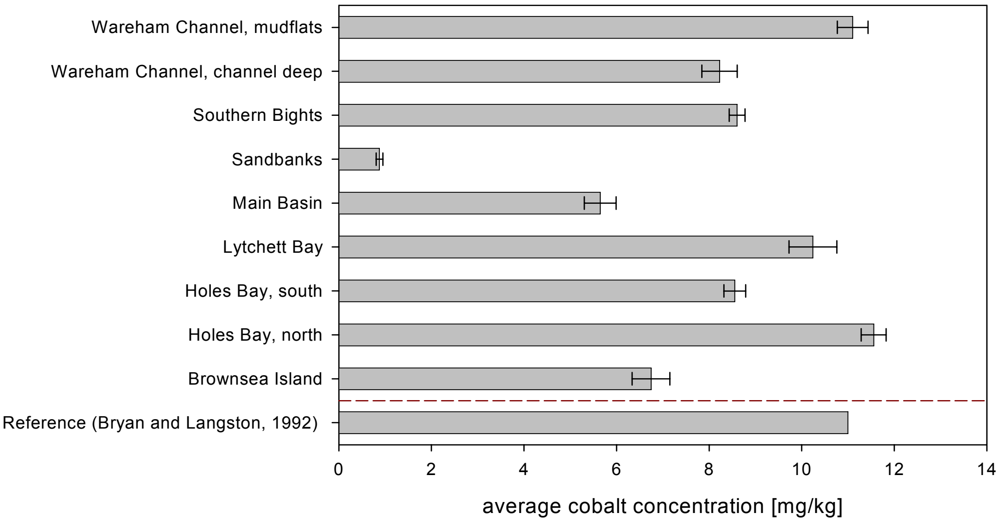
zone	number of cores
Wareham Channel, mudflats	10
Wareham Channel, deeps	4
Southern Bights	11
Eastern Sandbanks	7
Main Basin	4
Lytchett Bay	2
Holes Bay, north	3
Holes Bay, south	9
Brownsea Island	3



(a)



(b)



(c)

Figure 31: **Comparison of the average concentrations of arsenic (a), cadmium (b) and cobalt (c) in the major sampling zones; whiskers indicate standard error of the mean**

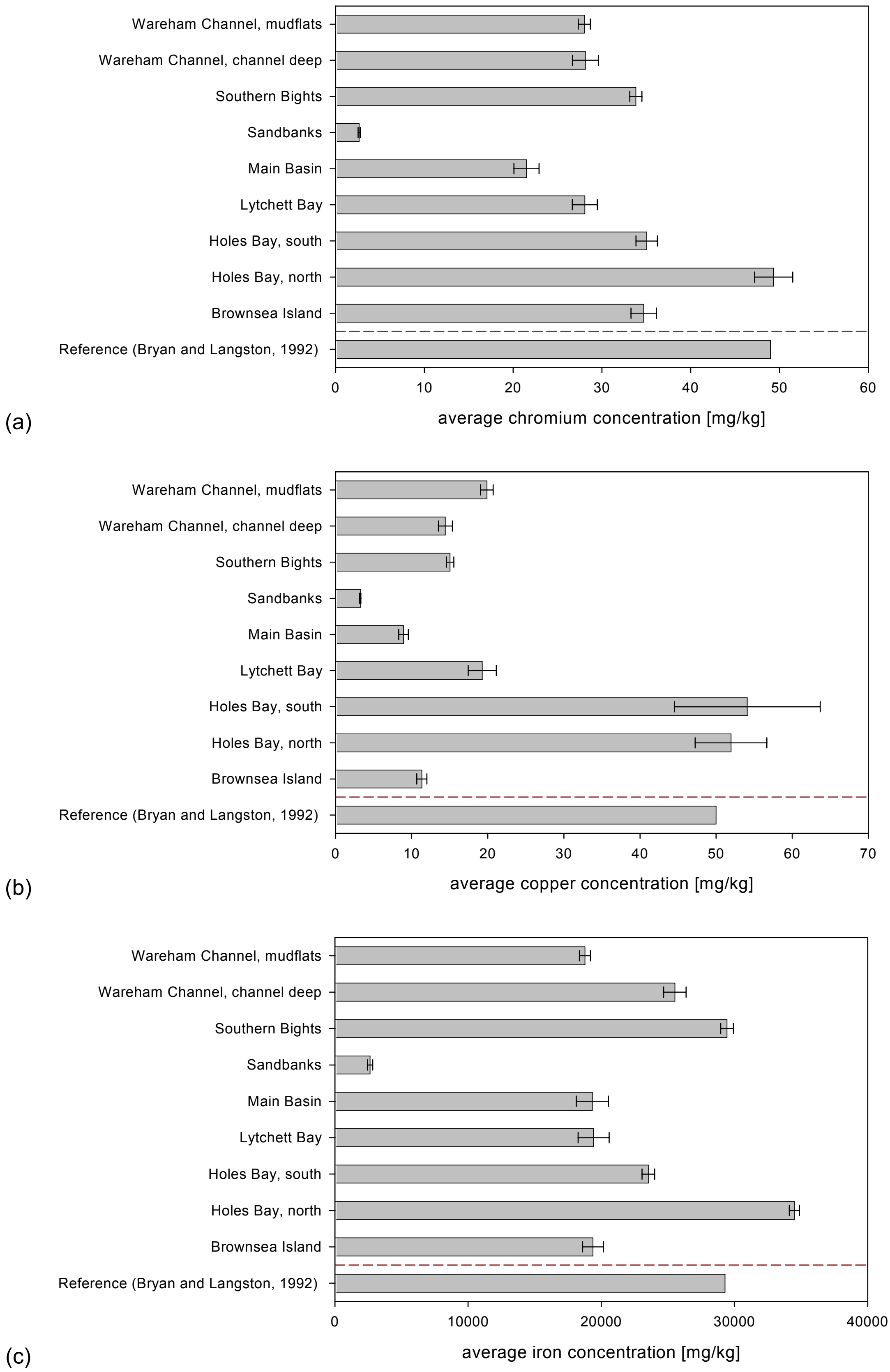


Figure 32: **Comparison of the average concentrations of chromium (a), copper (b) and iron (c) in the major sampling zones; whiskers indicate standard error of the mean**

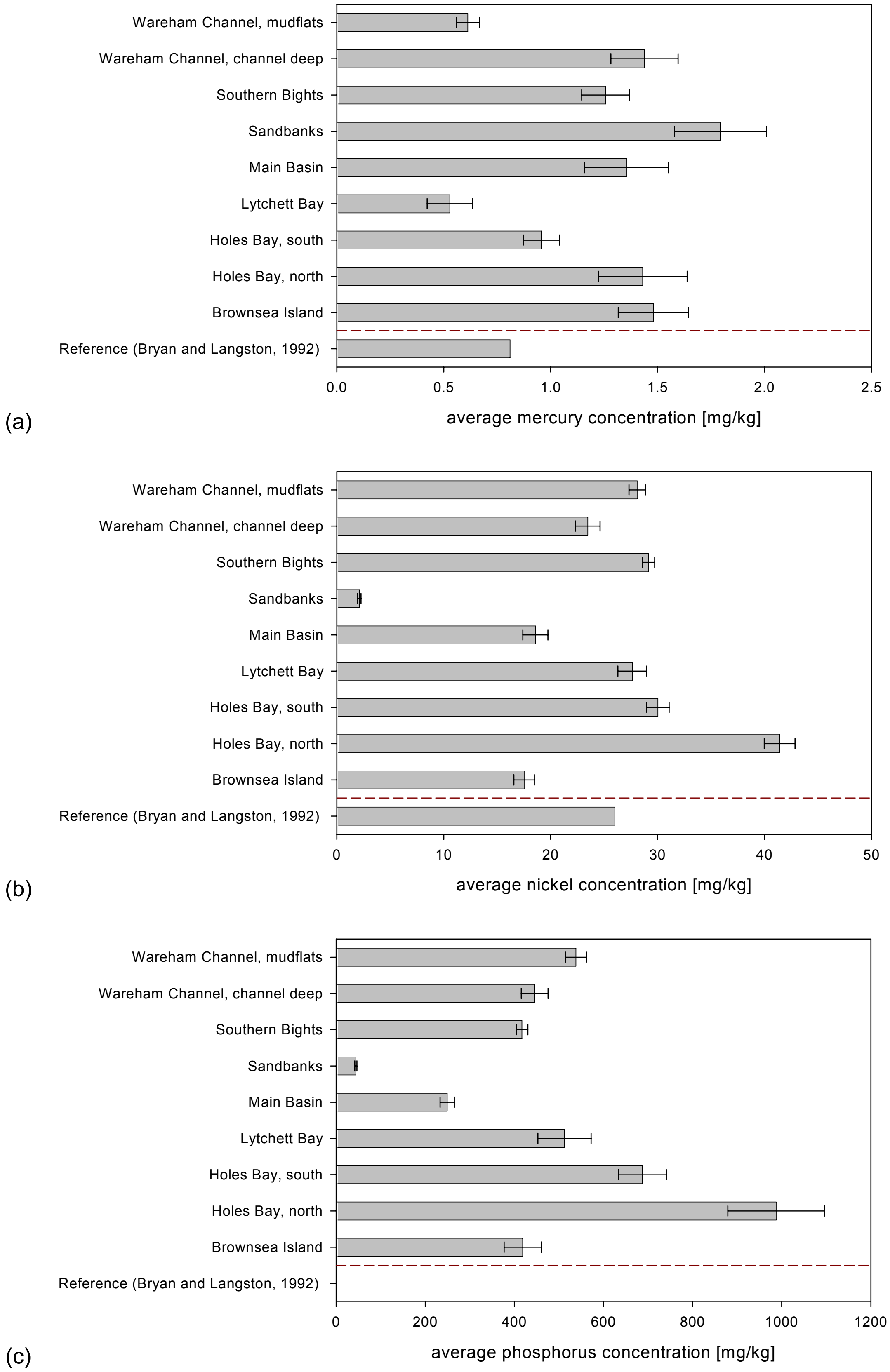
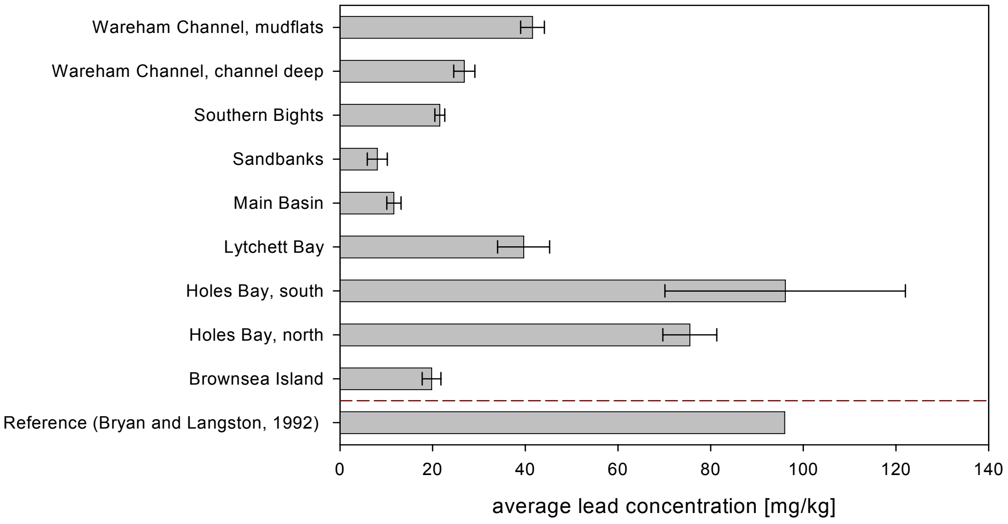
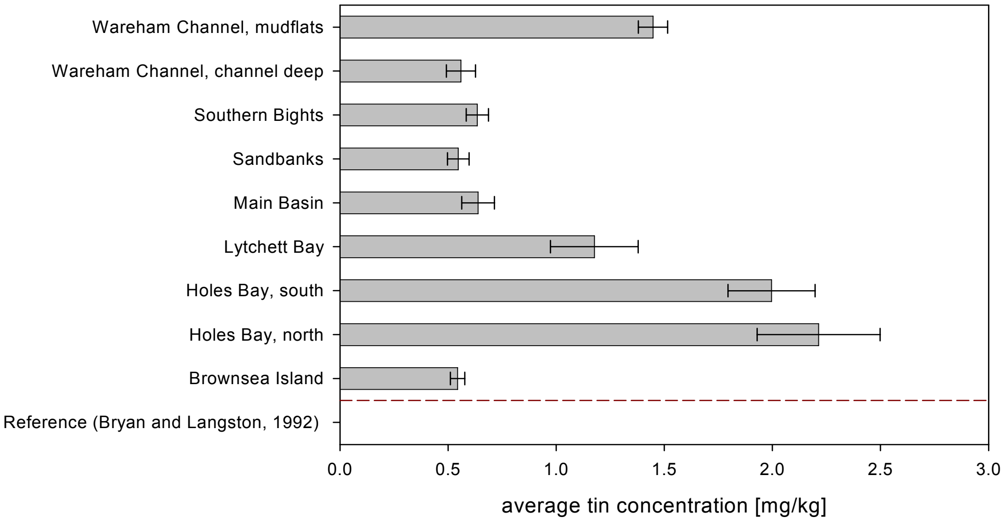


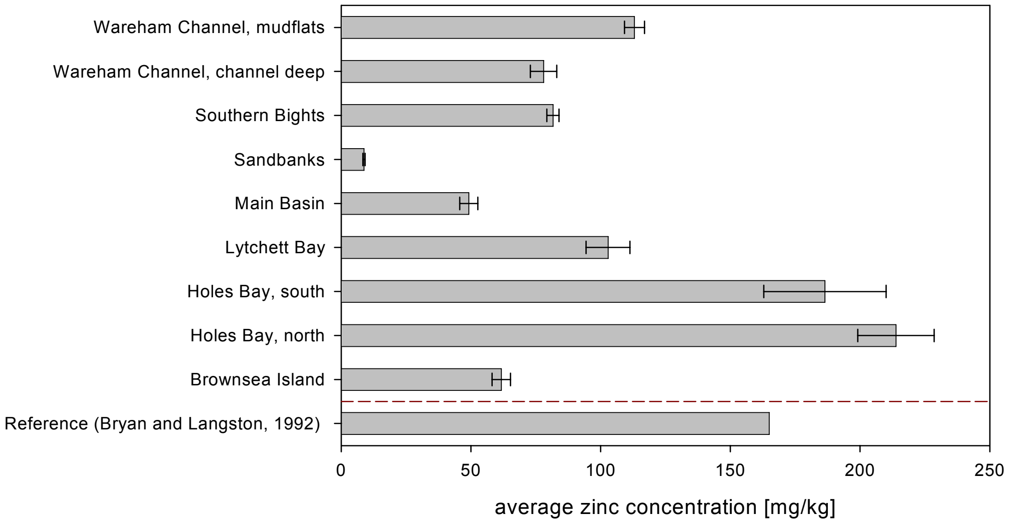
Figure 33: **Comparison of the average concentrations of mercury (a), nickel (b) and phosphorus (c) in the major sampling zones; whiskers indicate standard error of the mean**



(a)



(b)



(c)

Figure 34: Comparison of the average concentrations of lead (a), tin (b) and zinc (c) in the major sampling zones; whiskers indicate standard error of the mean

The results of the ANOVA tests (Table 9) show a very high significance ($p<0.05$) for nearly all analysed contaminants. The null-hypothesis that all zones in Poole Harbour have similar contamination profiles can consequently be rejected. Such results were entirely to be expected, given the extreme concentrations in Holes Bay versus the negligible concentrations in the Eastern Sandbanks (Figure 31-Figure 34).

Table 9: Comparison (one-way ANOVA tests) of the contamination in the regions Holes Bay, Lytchett Bay, Wareham Channel, Eastern Sandbanks, Brownsea Island, Southern Bights and Main Basin)

		sum squares	**df**	**mean square**	**F**	***p***
Al	between groups	1912832910.1	6	318805485.0	26.671	<0.0001
	within groups	549846207.7	46	11953178.4		
As	between groups	1294.9	6	215.8	50.46	0.0005
	within groups	1967.2	46	42.8		
Cd	between groups	16.0	6	2.7	2.494	0.0357
	within groups	49.2	46	1.1		
Co	between groups	505.6	6	84.3	13.188	<0.0001
	within groups	293.9	46	6.4		
Cr	between groups	6931.5	6	1155.2	15.924	<0.0001
	within groups	3337.2	46	72.5		
Cu	between groups	39321.7	6	6553.6	2.786	0.0214
	within groups	108213.4	46	2354.5		
Fe	between groups	3545019275.7	6	590836546.0	17.256	<0.0001
	within groups	1575052469.6	46	34240271.1		
Hg	between groups	5.8	6	1.0	3.828	0.0035
	within groups	11.6	46	0.3		
Ni	between groups	5374.3	6	895.7	12.814	<0.0001
	within groups	3215.4	46	69.9		
P	between groups	2675288.6	6	445881.4	6.900	<0.0001
	within groups	2972737.0	46	64624.7		
Pb	between groups	122716.9	6	20452.8	1.136	0.3568
	within groups	828013.2	46	18000.3		
S	between groups	1159855316.4	6	193309219.4	11.296	<0.0001
	within groups	787226632.2	46	17113622.4		
Sn	between groups	29.6	6	4.9	4.970	0.0005
	within groups	45.6	46	1.0		
Zn	between groups	378667.7	6	63111.3	1.478	0.0064
	within groups	834675.5	46	18145.1		

5.3.2 Holes Bay

A closer investigation showed that while the majority of cores showed substantial metal/metalloid concentrations, two cores had typically lower levels: P08 in the very shallow parts directly adjacent to the supratidal part in the middle of Holes Bay, and P09 in the south-eastern end. Particularly the latter (which is the core located closest to the former BDH factory) had usually very low concentrations in all analyses. This core did, however, show elevated levels of lead in the most recent layers.

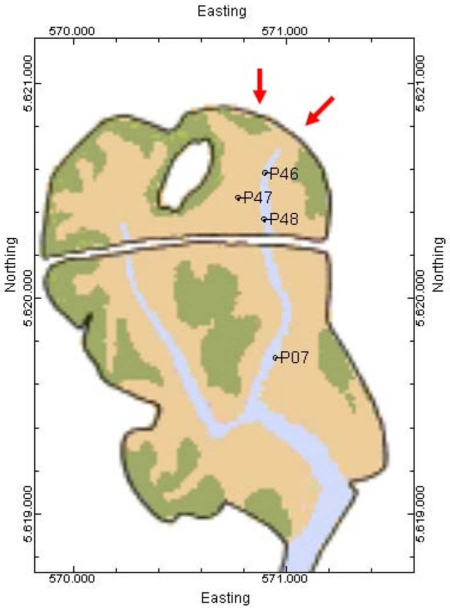
Table 10: Average *aqua regia* extractable fraction [TCA; mg·kg^{-1}] and ammonium nitrate leachable fraction [PES; %] in Holes Bay

	0-20 cm		20-40 cm		40-60 cm		60-80 cm		80-100 cm	
	TCA	**PES**	**TCA**	**PES**	**TCA**	**PES**	**TCA**	**PES**	**TCA**	**PES**
As	17.31	30.20	15.32	27.95	13.39	28.67	13.89	33.56	16.12	39.42
Cd	2.32	49.42	2.23	37.74	2.42	38.37	1.51	46.83	1.19	42.19
Cr	45.90	37.88	40.60	14.83	37.25	20.14	35.71	16.81	37.19	15.86
Co	10.24	26.53	9.47	26.82	9.14	24.30	9.11	27.64	10.02	26.51
Cu	105.12	24.41	46.80	22.56	31.68	21.08	25.77	26.09	24.25	26.04
Hg	1.01	12.66	0.91	11.21	1.25	12.50	1.15	13.29	1.58	32.39
Ni	38.73	22.18	33.25	44.08	32.74	15.77	30.22	18.54	33.04	16.93
P	1214.14	54.04	725.94	49.96	630.48	27.74	568.62	52.62	568.94	44.08
Pb	171.42	18.38	91.35	16.41	45.53	16.23	39.52	20.25	38.63	18.85
Sn	3.44	24.74	2.09	23.48	1.24	23.07	1.50	25.80	1.10	25.22
Zn	331.74	30.44	191.85	32.44	134.39	28.74	112.66	11.39	120.23	35.52

In the first 20 cm depth, all average concentrations except chromium exceeded the TELs substantially; especially the concentrations of copper (99 % PEL) mercury (144 % PEL) lead (153 % PEL) and zinc (122 % PEL) are a cause for concern, as there is based on the SQGs, a substantial risks of adverse effects on aquatic life. These are averages over Holes Bay, including the low concentration cores P08 and P09.

For the analyses of the impact of the PSTW four cores have been selected. Two cores in the channel in which two major outputs of the PSTW are discharging (P46 and 48), one core in the intertidal next to the channel (P47) and one core downstream for reference purposes (P07; *cf.* Figure 35).

Figure 35: The cores presumed to be mainly affected by the Sewage Treatment Works in Holes Bay (base-map adapted from Gray, 1985, used grid is UTM Zone 30U; primary PSTW-outputs marked with red arrows)



Core P48 has much lower contamination levels than the ones closer to the PSTW plant. The distance between P46 and P48 is about 250 metres. The core next to the channel (P47) has nearly exactly the same concentration levels as the one closest to the PSTW, but the peak is not in a depth of ~13 cm, but ~47 cm. If it is the same peak, the sedimentation rate in the channel can be assumed to be three times lower than in the intertidal marshland. The most remote core, on the other hand, also extracted in the channel, shows a similar pattern as the first, but with much lower concentrations. The reference core in the south shows a different pattern, the concentrations are decreasing, indicating that this core was subjected to a very different contamination regime. There is a small peak at the same depth as the channel cores north of the bridge, however it is negligible. These data reinforces the suggestions of previous studies (*cf.* Chapter 5.1.2) that the PSTW has indeed been a major point source of contamination in Poole Harbour, with considerable impact on the poorly flushed secondary embayment Holes Bay.

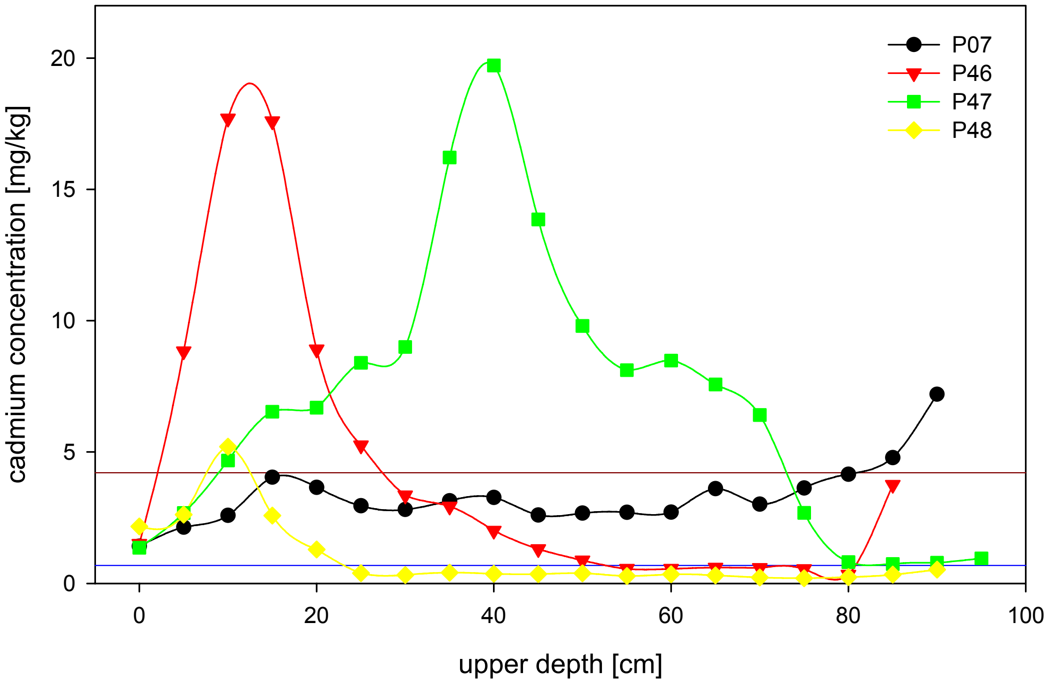


Figure 36: **Cadmium concentration in the four cores directly affected by the two outputs of Sewage Treatment Works in Holes Bay [blue reference line indicates TEL, dark red reference line PEL-value]**

Unlike most of the metals/metalloids, phosphorus (Figure 37) showed mostly recent contaminations (not particularly high, though, only at about 0.35 %) and had a comparable pattern in all cores north of the bridge. As for cadmium, the core extracted next to the channel showed elevated levels in the middle of the core, but not comparable to the cadmium peaks. Again, the reference core in the south shows a different pattern and seems to have been subjected to a very different contamination regime. In addition, there was either a much more constant influx of phosphorus which only decreased in recent times, or an anthropogenic removal of phosphorus in the topmost 20 cm of sediment by, for example, effects of dredging. Natural post depositional mobility would have, owing to the homogenous structure of the sediment, likely affected all cores to a comparable degree, and only the cores close to the PSTW show a significant different concentration in the top 20 cm (p<0.001).

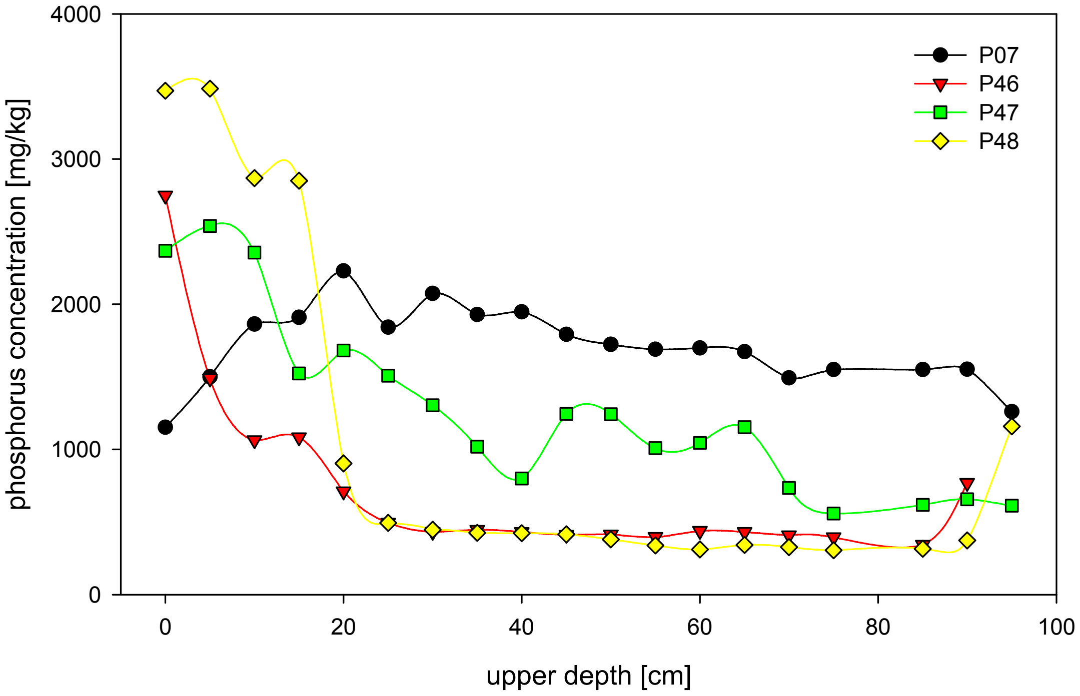


Figure 37: **Phosphorus concentration in the three cores closest to the Sewage Treatment Works in Holes Bay**

The remaining contaminants showed no clear picture, concentrations varied without clear trends. All analysed metals, except chromium (95 % TEL), were clearly well above the threshold effect levels, most notably cadmium with 620 %. Phosphorus concentrations in the first 20 cm were the highest measured in the estuary, reaching 3.5 g·kg^{-1}, which was more than 7 times the estuary's average. It was, atypically for this element, still present in high concentrations in greater depths in core P07.

Table 11: Metal/metalloid concentrations [mg·kg^{-1}] in the three cores in the northern part of Holes Bay

	P46			P47			P48		
	0-30 cm	**30-60 cm**	**60-90 cm**	**0-30 cm**	**30-60 cm**	**60-90 cm**	**0-30 cm**	**30-60 cm**	**60-90 cm**
Al	20850.80	21481.72	22912.49	23349.00	21278.23	21125.71	19635.40	18990.34	16996.65
As	19.00	23.63	17.73	16.08	14.36	24.32	16.51	11.49	11.36
Cd	9.97	1.84	1.06	5.22	12.79	4.45	2.04	0.35	0.27
Co	13.22	12.53	12.89	10.50	11.55	13.34	10.98	9.31	8.01
Cr	68.80	40.93	40.46	66.69	64.79	49.74	52.56	33.65	29.35
Cu	90.30	36.22	26.03	98.40	83.16	50.79	71.03	11.51	9.52
Hg	1.67	1.39	1.40	1.42	0.77	1.44	1.46	1.84	0.51
Ni	52.62	38.33	39.17	45.30	55.45	43.17	43.51	29.07	24.88
P	1264.69	421.59	463.87	1996.19	1069.92	794.22	2212.56	404.60	323.09
Pb	117.03	77.45	44.90	102.38	113.96	111.76	89.54	13.43	12.52
Sn	4.42	1.43	0.59	3.27	3.44	3.15	3.91	0.05	0.22
Zn	332.36	190.85	138.91	295.06	306.73	224.61	316.63	73.33	63.34

A second major point source was the Poole Power Plant Station (PPPS) in the south-western end of Holes Bay. Cores here were limited to a depth of approximately 40 cm, with a massive layer of solid, white chalk stopping any further penetration. This was expected, as the layer is well known and was essential for the construction of the PPPS (BEA, 1949). The layer itself could only be penetrated approximately 2 cm, but all samples from this layer showed elevated concentrations of selenium (14.1 mg·kg^{-1}) and very high concentrations of strontium (697.8 mg·kg^{-1}). The other metals, which were originally targeted, typically showed very low metal concentrations (except for copper and lead well below TEL-values).

Table 12: Comparison of the chalk with the immediately overlying sediment layer

	concentrations [mg·kg^{-1}]							
	Co	Cr	Cu	Ni	Pb	Zn	Sr	Se
white clay layer	1.4	3.9	18.3	3.9	6.4	34.2	697.8	14.1
overlaying sediment	7.9	33.3	83.6	29.9	108.4	434.4	153.7	0.3

5.3.3 Wareham Channel

The loads in Wareham Channel are typically between the values observed in Southern Bights and Holes Bay. Concentrations are usually below TEL or in the PER (Table 13). Mobilities are slightly lower compared to Holes Bay, but arsenic showed a much larger ammonium nitrate leachable fraction.

A major point source in the Wareham Channel was the former Royal Navy Cordite Factory (RNCF). However, unlike the other major point sources (PPPS, BDH, PSTW); this weapons facility is located in a region with much lower concentration levels (Table 13). In addition, there are no railway tracks leading through the area, therefore a geochemical normalisation is possible. This point source has therefore been considered in the subsequent case study (*cf.* Chapter 6).

Table 13: Average *aqua regia* extractable fraction [TCA; mg·kg^{-1}] and ammonium nitrate leachable fraction [PES; %] in Wareham Channel

	0-20 cm		20-40 cm		40-60 cm		60-80 cm		80-100 cm	
	TCA	**PES**	**TCA**	**PES**	**TCA**	**PES**	**TCA**	**PES**	**TCA**	**PES**
As	12.12	41.24	18.32	32.25	15.26	26.42	12.03	25.25	11.96	29.76
Cd	0.55	52.59	0.62	31.83	0.62	43.70	0.56	31.84	0.58	47.50
Cr	25.86	11.57	29.63	9.88	27.58	7.39	27.95	7.09	30.65	7.02
Co	9.74	30.05	10.48	24.55	10.36	17.03	9.93	18.88	10.68	19.68
Cu	18.44	22.78	19.60	17.19	17.43	13.50	15.54	14.40	20.84	13.49
Hg	0.79	11.94	0.82	9.43	0.84	6.93	1.05	14.94	0.90	8.34
Ni	24.97	17.59	28.09	16.81	26.64	11.70	26.00	11.50	28.19	15.75
P	542.39	55.09	450.35	28.49	475.08	49.04	500.04	54.69	650.94	55.29
Pb	33.75	20.31	53.45	16.40	36.30	11.79	27.03	11.62	27.35	18.25
Sn	1.20	35.40	1.30	19.65	1.12	15.32	1.03	14.06	1.17	15.03
Zn	101.88	21.27	114.18	25.61	96.45	26.86	91.79	23.00	106.47	24.16

5.3.4 Southern Bights

As expected, concentrations in the Southern Bights zone were very low and all values except mercury remained well below their respective TEL-value (Table 14).

Table 14: Average *aqua regia* extractable fraction [TCA; mg·kg^{-1}] and ammonium nitrate leachable fraction [PES; %] in the Southern Bights

	0-20 cm		**20-40 cm**		**40-60 cm**		**60-80 cm**		**80-100 cm**	
	TCA	**PES**	**TCA**	**PES**	**TCA**	**PES**	**TCA**	**PES**	**TCA**	**PES**
As	13.41	33.99	15.14	26.37	13.63	24.00	12.11	20.48	13.74	21.03
Cd	0.52	27.15	0.54	17.44	0.39	37.47	0.36	42.13	0.43	12.17
Cr	34.00	14.17	34.82	21.53	30.58	9.02	28.35	8.15	33.24	14.67
Co	8.39	14.91	8.42	11.63	7.41	9.66	6.99	9.37	8.02	8.56
Cu	18.09	24.02	14.35	18.71	11.60	15.85	10.67	15.22	12.11	15.67
Hg	1.81	9.72	1.14	7.63	1.11	20.41	1.37	5.44	1.01	12.57
Ni	28.60	27.24	29.56	17.96	26.20	8.67	24.22	8.25	28.30	3.79
P	534.31	58.53	394.11	53.67	331.92	46.61	298.88	107.1[ђ]	363.05	47.74
Pb	26.79	13.23	21.54	9.88	15.66	12.66	12.90	10.35	12.88	7.64
Sn	0.63	13.51	0.56	11.12	0.31	15.07	0.55	8.51	0.68	7.59
Zn	93.20	26.99	77.17	17.41	65.10	16.08	58.68	14.16	67.65	7.29

[ђ] likely caused by cross-contamination

Copper concentrations decreased with depth in the majority of cores. However, in some cores there was a considerable variation. Both grain size profiles (*cf.* Chapter 10.4.5) and iron distribution showed no noteworthy variations. To address local discrepancies for the Southern Bight zone, the averages for each depth were calculated for the depths 0-60 cm (to compensate for different core lengths). This resulted in a much clearer trend (Figure 38): on average, copper concentrations rose steadily, until they levelled out just above the threshold effect level; although in the topmost 10 cm the deviation between the cores was strongest.

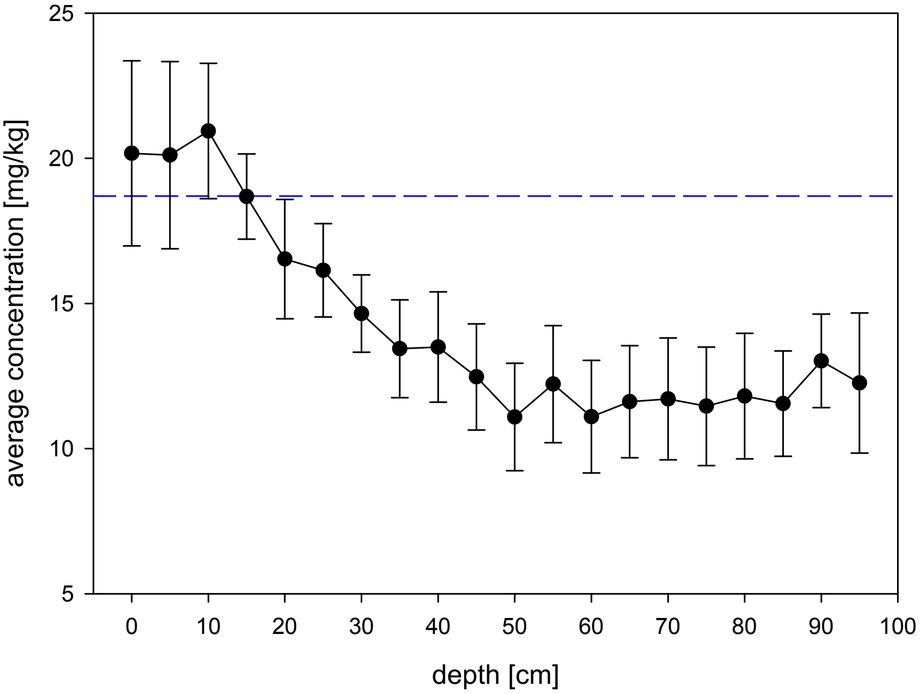


Figure 38: **Copper concentrations in the Southern Bights as averages for each depth (whiskers indicate standard error of the mean, reference line the TEL)**

5.3.5 Brownsea Island lagoon

Three cores were extracted in the Brownsea Island lagoon (P51-53) in accordance with bird protection regulations and the approval of the Dorset Wildlife Trust (pers. comm. Thain[13], 2006). The cores had different lengths (Table 7), but showed identical concentrations and trends, therefore only the longest core, P53, was presented in detail. Only phosphorus showed differences between the three cores: in all cores clearly the highest concentrations were in the topmost part of the sediment column; however, concentrations were significantly decreasing northwards, *i.e.* closer to the wall (Figure 29): core P51 (south) had a concentration of 1416 mg·kg^{-1}, P52 (middle) of 1285 mg·kg^{-1} and P53 (north) of 630 mg·kg^{-1}.

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[13] Chris Thain, Reserve Manager Dorset Wildlife Trust

The metal data showed a small peak for all metals in a depth of 65 cm, which coincides with the peaks observed close to the RNCF (*cf.* Chapter 5.3.3). Concentrations were very low, with only arsenic, mercury and lead reaching the TEL-values; and lead only in the topmost layer. Based on the sediment accretion rates by Cundy and Croudace (1996) the small peak would be linked to a time frame of 1918-1931, *i.e.* shortly after WW1. The second peak is more recent and much stronger, in a depth of approximately 20-25 cm, *i.e.* originating from 1974-1986. While the other concentrations returned to average concentrations afterwards, lead concentrations are increasing further until the present day and exceeded the TEL and copper is levelling out below TEL.

Owing to the relevance of this lagoon as a reference area (water exchange with the main basin, but very limited turbation) the complete profile of P53, including absolute and normalised data, was included as ancillary data (*cf.* Chapter 10.4.3).

5.3.6 Eastern Sandbanks and Lytchett Bay

In Lytchett Bay the concentrations were typically just below TEL-values or in the lower possible effects-range (Table 15). There are no trends regarding contamination load and depth, contamination influxes appear to be constant. In Lytchett Bay random samples have been analysed with partial extraction schemes, these samples indicate very similar mobilities compared to Southern Bights.

Table 15: Average metal/metalloid concentrations [mg·kg^{-1}] in Lytchett Bay

depth [cm]	As	Cd	Co	Cr	Cu	Hg	Ni	P	Pb	Sn	Zn
0-20	12.06	0.59	11.14	31.76	25.14	0.86	30.08	814.95	39.56	0.62	135.62
20-40	14.76	0.98	11.70	33.19	28.36	1.03	32.41	809.89	54.06	1.18	135.71
40-60	16.92	0.98	10.05	29.58	22.41	0.41	27.97	376.77	73.98	1.73	120.41
60-80	15.06	0.42	11.39	27.34	12.71	0.29	29.31	322.29	20.95	0.71	114.41
80-100	14.76	0.98	11.70	33.19	28.36	1.03	32.41	809.89	54.06	1.18	135.71
0-100	13.64	0.66	10.24	28.08	19.28	0.53	27.64	512.52	39.66	1.18	102.89

The concentrations in Eastern Sandbanks were usually negligible. Most metals, particularly arsenic, zinc and lead, have the highest concentrations in the upper parts of the cores, indicating contamination of recent origin. The values in the sandy sediments show hardly any concentrations, only mercury and tin exceed the TEL-values (Table 16). However, the observed tin concentrations are still fairly low and the few published guideline values for this element (Crommentuijn *et al.*, 2000; Buchman, 2004) are inconsistent, therefore it is unlikely to pose any threat in the observed concentrations. Furthermore, these concentrations are consistent with levels observed outside Poole Harbour (Hübner, 2009). Mercury, on the other hand, showed higher concentrations in this region of the Harbour; concentrations were even higher than in Holes Bay. Partial extraction outcomes were inconclusive and showed substantial variations.

Table 16: Average metal/metalloid concentrations [mg·kg^{-1}] in sediments of Eastern Sandbanks

depth [cm]	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Ni**	**P**	**Pb**	**Sn**	**Zn**
0-20	1.64	0.08	0.61	2.40	3.42	1.44	1.54	56.84	11.43	0.48	9.96
20-40	1.79	0.10	1.11	2.98	3.26	2.21	2.62	37.77	6.16	0.66	8.33
40-60	1.38	0.03	0.99	2.49	2.73	1.55	2.21	25.50	3.33	0.36	6.65
0-60	1.60	0.07	0.90	2.62	3.13	1.73	2.13	40.03	6.97	0.50	8.31

5.3.7 Risk potential

The risk potential was calculated over 20 cm depth intervals for all regions with sufficient PES-data using RPI_1 (Equation 4; Table 17) and RPI_2 (Equation 5; Table 18).

Table 17: **Risk potential index of the analysed elements in the three major zones, using formula RPI_1**

	depth	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	$\overline{X}$
Holes Bay	0-20 cm	11.18	17.47	14.00	13.43	14.15	4.57	24.40	7.35	13.32
	20-40 cm	9.52	9.67	11.73	5.75	11.90	5.54	12.29	4.39	8.85
	40-60cm	8.43	10.34	12.83	3.76	17.28	3.26	6.09	2.89	8.11
	60-80 cm	9.46	9.05	8.89	3.40	16.46	3.26	5.90	1.53	7.24
	80-100 cm	11.89	9.16	6.65	3.20	36.36‡	3.41	5.57	2.88	6.11
Southern Bights	0-20 cm	9.19	7.91	2.33	2.29	22.15	3.74	3.24	1.94	6.60
	20-40 cm	9.14	9.99	1.94	1.60	12.30	3.14	2.25	1.29	5.21
	40-60cm	7.85	5.68	2.04	1.19	19.69	1.93	1.85	1.05	5.16
	60-80 cm	6.44	5.01	2.03	1.08	12.50	1.74	1.38	0.89	3.88
	80-100 cm	7.40	7.87	1.27	1.24	14.07	1.38	1.18	0.73	4.39
Wareham Channel	0-20 cm	9.15	5.44	3.42	2.28	10.73	2.63	5.05	1.89	5.07
	20-40 cm	12.23	5.76	2.99	2.10	9.93	2.89	7.19	2.32	5.68
	40-60cm	9.22	4.64	3.51	1.66	8.72	2.29	4.14	2.01	4.52
	60-80 cm	7.10	4.60	2.73	1.52	15.92	2.21	3.06	1.77	4.86
	80-100 cm	7.67	5.02	3.45	1.98	10.19	2.81	3.88	2.10	4.64

‡ outlying value based on insufficient data, not included in mean

Table 18: **Risk potential index of the analysed elements in the three major zones, using formula RPI_2**

	depth	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	$\overline{X}$
Holes Bay	0-20 cm	0.55	0.97	0.31	1.16	1.20	0.70	1.26	1.00	0.92
	20-40 cm	0.47	0.81	0.17	0.49	1.01	0.85	0.64	0.60	0.60
	40-60cm	0.41	0.89	0.18	0.32	1.46	0.50	0.32	0.39	0.57
	60-80 cm	0.46	0.61	0.16	0.29	1.39	0.50	0.31	0.21	0.49
	80-100 cm	0.58	0.46	0.16	0.28	2.99‡	0.52	0.29	0.39	0.74
Southern Bights	0-20 cm	0.45	0.16	0.14	0.20	1.87	0.57	0.17	0.26	0.46
	20-40 cm	0.45	0.13	0.18	0.14	1.04	0.48	0.12	0.18	0.32
	40-60cm	0.38	0.14	0.10	0.10	1.66	0.30	0.10	0.14	0.38
	60-80 cm	0.32	0.14	0.09	0.09	1.06	0.27	0.07	0.12	0.27
	80-100 cm	0.36	0.09	0.14	0.11	1.19	0.21	0.06	0.10	0.29
Wareham Channel	0-20 cm	0.45	0.24	0.10	0.20	0.91	0.40	0.26	0.26	0.34
	20-40 cm	0.60	0.21	0.10	0.18	0.84	0.44	0.37	0.32	0.37
	40-60cm	0.45	0.24	0.08	0.14	0.74	0.35	0.21	0.27	0.31
	60-80 cm	0.35	0.19	0.08	0.13	1.35	0.34	0.16	0.24	0.36
	80-100 cm	0.38	0.24	0.09	0.17	0.86	0.43	0.20	0.29	0.32

‡ outlying value based on insufficient data, not included in mean

The risk potentials were clearly highest in Holes Bay ($\bar{x}_{RPI1}$=8.73; $\bar{x}_{RPI2}$=0.66) for all metals, especially lead has a high risk potential in the topmost layer. Wareham Channel ($\bar{x}_{RPI1}$=4.95; $\bar{x}_{RPI2}$=0.34) and Southern Bights ($\bar{x}_{RPI1}$=5.05; $\bar{x}_{RPI2}$=0.34) varied around a mutual average with a slightly increasing trend, while Holes Bay showed a clear trend. All three zones show a decrease of the risk potential with increasing depth, although the increase is by far the strongest in Holes Bay (Figure 39). While both RPI-calculation methods show very comparable outcomes, there are differences: trends were stronger pronounced with RPI_2, which is, unlike RPI_1, purely based on up-to-date effect-levels and is has a slightly different approach. The variances for Wareham Channel and Southern Bights were stronger; furthermore, a lower risk is indicated in the deep layer of Holes Bay, and a higher risk in the topmost layer.

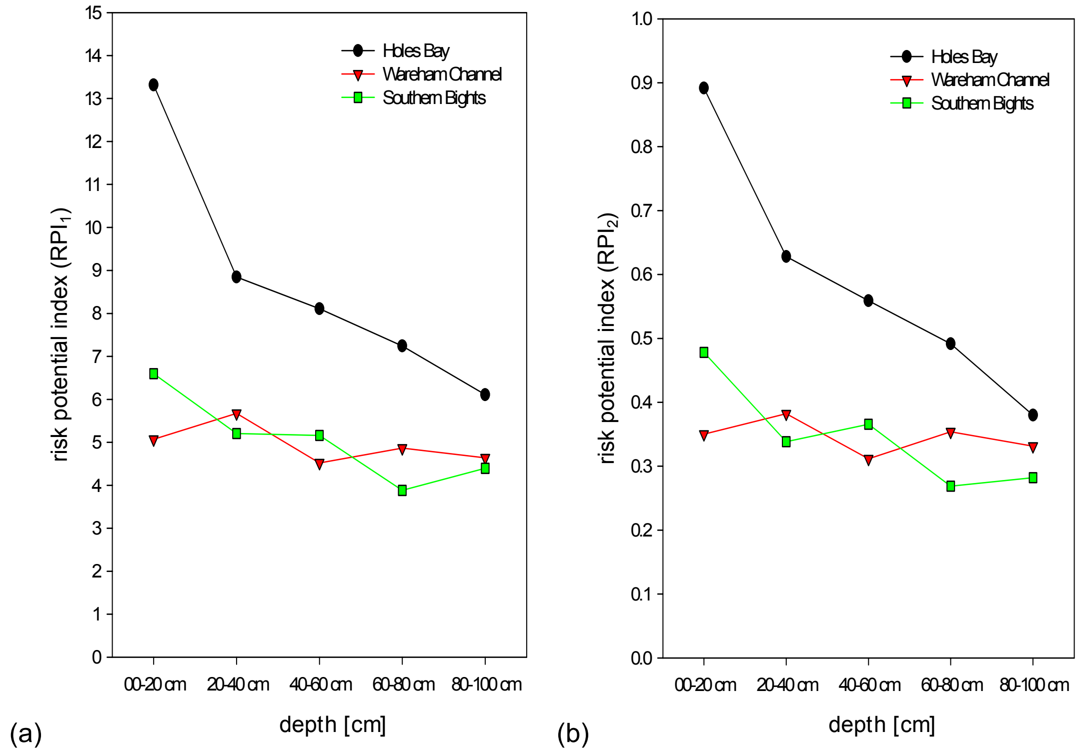

Figure 39: Risk potential index calculated with formula RPI_1 (a) and RPI_2 (b) in the three major zones

5.4 Discussion

5.4.1 Absolute concentrations

Observed mean values of this study correspond well with these general reference values for Poole Harbour (Bryan and Langston, 1992).

The null hypothesis that there are no significant differences between the sampling zones (*cf.* Chapter 5.1) must be rejected. A comparison of all major regions shows significant differences between the metal/metalloid and phosphorus concentrations.

The second null hypothesis that the metal/metalloid concentrations are below the threshold effect levels must be rejected as well. In fact, most concentrations clearly exceeded the TELs and were typically in the PER. Especially in Holes Bay, the heavily industrialised secondary embayment, elevated concentrations have been detected.

The PSTW is considered a major offender in Poole Harbour (Langston *et al.*, 2003). Elevated phosphorus concentrations of recent origin were detected in the three north-eastern cores, and the data clearly reinforces the finding that it is the main source of phosphorus input (Langston *et al.*, 2003; Wardlaw, 2005). Typically, phosphorus had the highest concentrations in the topmost layers, particularly in areas with high ongoing phosphorus input. As the Christchurch Harbour case study indicated, a large percentage of this element is typically washed out rapidly and only insoluble fractions remain behind. In addition to phosphorus, the PSTW also appears to be a major source of cadmium, with additional influxes of copper, nickel and zinc. Chromium concentrations are also highest in these cores, although the concentration remained below TEL.

Lead was only found in a single core (P04) in considerable concentrations. The core average was 999.3 mg·kg^{-1} (~9x PEL); highest concentration was measured in 15-20 cm depth with 1691.6 mg·kg^{-1} (~15x PEL). It is assumed that this was caused by a localised source – very likely some of the old and unmaintained trawlers rusting in the close vicinity of that core. As lead reacts with clays, phosphates, sulfates, carbonates, hydroxides and organic matter its solubility is greatly reduced (McLean and Bledsoe, 1996) and it is not easily remobilised from sediments (Förstner, 1983), therefore the high lead concentrations have hardly spread. Elevated levels were also found in the channel leading from the PSWT southwards, but levels are much lower and remain typically within the PER.

While the report by PDE (1992) described sediments from the south east of Holes Bay as chemically clean sandy silt; Langston *et al.* (2003) suggested that these sediments may not be typical and that much of the silt in Holes Bay could not be accurately classed as chemically clean. The findings of the present study clearly reinforce the conclusions of Langston *et al.*, as the concentrations in Holes Bay showed substantially elevated levels for all targeted metals and metalloids (except chromium), with a small number of cores showing significantly lower overall concentrations: For example, cores in the south-eastern end (P09) and those extracted closely to the former power plant (P01-P02) showed significantly lower concentrations for most metals. Very high strontium concentrations have been found in the chalk layer in south-western Holes Bay. Samples showed no activity; therefore, the ^{90}Sr isotope can be ruled out. Sabine *et al.* (1982) found equally high strontium concentrations (up to 749 $mg \cdot kg^{-1}$) in "metamorphosed and metasomatised limestone" (chalk) in studies in Northern Ireland; it is therefore assumed that the observed concentrations are of geological origin. The chalk is not native and was arranged there for the building of the PPPS (BEA, 1949), but it is uncertain as to where the chalk was imported from. In the overlying sediment layers concentrations were, unlike the rest of the embayment, comparably low, indicating that the remediation measures in the area have been successful, although limited to a small margin around the PPPS.

A report to Wessex Water by Emu Ltd in 2003 reported a significant increase of aluminium concentrations in Holes Bay from 1991 on, but without ascribing any reason for this (Underhill-Day, 2008). This observation could not be confirmed, the aluminium concentrations in that sub-region did not show any significant changes (mean: 19680 mg·kg^{-1}, standard error: 276) and appear to be stable in the cores extracted.

Since the core closest to the former chemical factory BDH typically had the lowest concentrations observed within Holes Bay, it is assumed that the facilities output since 1946 and the catastrophic fire in 1988 have not resulted in a lasting environmental damage in its immediate vicinity, at least not concerning metals/metalloids or phosphorus. The degree to which specific organic compounds were involved has not been assessed in this study; however, it is assumed that the majority of non-conservative contaminants has been broken down in the last three decades. For a targeted analysis of remaining contamination, the original, so far untraceable report would be necessary. That core did, however, show elevated lead concentrations in the most recent layers (Figure 27); presumably owing to its close proximity to the major motor traffic routes.

High concentrations have been measured for tin, with the highest values again clearly in Holes Bay, followed by the Wareham Channel mudflats and Lytchett Bay. Much lower concentrations were observed in the Wareham Channel deep transect (cores P29-P32; Figure 30), Southern Bights, Eastern Sandbanks and Brownsea Island. Although the methodology did not yield a very high recovery for that element, most levels are clearly exceeding acceptable values, even in some cores of the Southern Bights; especially Wytch Farm. The observed concentrations of tin are likely caused by two inputs: the PSWT in the North of Holes Bay, where the contamination is predominantly located in the top 20 cm and gradually decreases in southerly direction, and by the gradual degradation of TBT to elemental tin. Langston *et al.* (1987) found elevated TBT-loads in areas of Poole Harbour with high levels of boating activities, particularly in and around the marinas; with TBT concentrations in much of Poole Harbour exceeding environmental quality targets. According to Bergmann and Grünwald (2006), TBT concentrations that are 1,000 times higher than the NOEL-level of sediment organisms can be found close to ship assembly points like harbours and docks. However, only few published guideline values (*cf.* Chapter 2.2.6) are available for this element, and these are largely inconsistent. Following the discovery of the high toxicity of TBT, the use of this anti-fouling agent has been regulated in the UK since 1987 (Langston, 1990). In the late 1980s large quantities of TBT were present in Poole Harbour (Langston *et al.*, 1987) and it was unlikely that the concentrations have returned to NOEL-levels at certain locations, although there was still uncertainty as to the actual levels (Langston *et al.*, 2003). The vast majority of vessels are stationed in Holes Bay or its direct vicinity, and that embayment has on average small particle sizes and extremely poor flushing characteristics, both factors facilitating a contaminant build-up. Along the banks of the river Frome a large number of yachts have been anchored over the years, which together with the presence of isolated wrecks (Figure 40) is likely to have increased contamination levels in Wareham Channel. Although the EA tries to remove such wrecks as soon as possible, it is sometimes difficult to ensure the cooperation of the owners, leading to considerable delays in their removal (pers. comm. Kingston-Turner[14], 2008).

Figure 40: A wreck in the Frome, photographed October 2008

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[14] Stuart Kingston-Turner, Fisheries Officer, Environment Agency

Mercury shows a very different pattern from tin, this is particularly evident in Wareham Channel. While loads in the mudflats are low and typically below PEL, in the channel deep transect the measured concentrations were clearly highest (Figure 30). In addition, there is a clear increasing trend towards the harbour entrance, where all other tested contaminants show significantly lower concentrations owing to the larger grain sizes. This different pattern can be explained by the fact that mercury concentrations are directly associated (over a strong logarithmic relationship) with organic matter rather than sediment type (Langston, 1982). Mercury has been used commonly by a variety of industries and contamination in surface waters may be significant due to combustion of fossil fuels (Kennish, 1997). For example, 1 kg coal typically can only release 0.03-0.3 mg of mercury; however, the annual combustion is estimated to be $2 \cdot 10^8$ t (Bliefert, 1994) – consequently 6-60 t of mercury may reach the atmosphere each year. The Minamata's disaster in 1950's, described, for example, in Tsuda *et al.* (2009), led to increased global awareness (LaGrega *et al.*, 1994) and eventually to decreasing emissions. In the samples, extracted mercury concentrations were usually clearly above the PEL-value of 0.7 $mg \cdot kg^{-1}$, but with a clear decreasing trend. In Holes Bay concentrations decreased from 1.6 to 1.0 $mg \cdot kg^{-1}$, in Wareham Channel from 1.1 to 0.8 $mg \cdot kg^{-1}$. Cores in Southern Bights showed no clear trend.

Eastern Sandbanks had, except for mercury (see above), the lowest concentrations in all tests. Cundy and Croudace (1995) suggest a stronger association of metals with organic phases in that region, whereby the organic material is speculated to represent debris from adjacent salt marsh. This would explain the inconsistent DIN 19730 outcomes observed for this region. The die-back of vegetation and associated release of sediments is also discussed in case study 5 (*cf.* Chapter 7). According to Cundy and Croudace the highest metal concentrations (tested for Cu, Pb and Zn) in this particular region are associated with the grain size fractions <8 µm. Such fine grain sizes could not be analysed separately within the scope of this study. The total content, however, was shown to be negligible for all tested contaminants except mercury.

5.4.2 Mobilities and risk assessment

Compared with Christchurch Harbour the ammonium nitrate extractable fraction is significantly lower throughout the Poole Harbour estuary, usually ranging between 11 and 35 % for most metals and 23-52 % for cadmium, which is more in line with literature values (*e.g.* Bauer *et al.*, 1996).

Although Wareham Channel shows much lesser loads than Holes Bay, the concentrations should be monitored carefully nevertheless, especially as the toxicity of metals such as Cd, Cr, Pb, Hg, Ni and Zn, can be increased by the reduced salinity and increased temperatures (Langston, 1990). While the area of Eastern Sandbanks has a salinity similar to that of seawater (median 29.8), the salinity in Wareham Channel is approximately half that value (median 15.7; Humphreys, 2005); in addition it is typically warmer owing to the high standing time and larger quantities of shallows, although no precise figures are currently available.

The risk potential, a dimensionless index which takes both total concentrations and the mobility of an element into account to estimate the potential hazardous nature of sediment contamination, was successfully adapted by using the newest available values of the SQuiRTs tables (Buchman, 2008). Both RPI equations showed nearly identical outcomes, but RPI_2 slightly amplified the visible trends. If the total available concentration in the sediment equals the probable effect levels and the mobile (*i.e.* easily available and migrating) fraction equals the threshold effect level, the dimensionless RPI_2 would assume a value of 1. This critical value, indicating a substantial risk associated with the contaminant load, was only exceeded for a few elements, and typically only in the topmost layers. This modified formula worked well and its application, in combination with the latest NOAA effect levels, is recommended for an assessment and comparison of the potential risk of adverse effects in different regions.

5.5 Conclusions

The danger for contamination redistribution in the Southern Bights is, owing to both the comparably low concentrations and the low mobility of the elements in that region, considered low. In Wareham Channel the total concentrations are higher, but the mobilities are comparably low, resulting in a slightly higher risk potential. In Holes Bay, however, the situation differs, especially in the topmost part of the sediment both the concentrations and the mobilities are high. Large scale dredging measures, like the planned operation for the construction of a new bridge (the “Twin Sails Ahead” project; GPL, 2004), could easily remobilise these elements. The funding for this project is unsure and start of work has been postponed several times. Early September 2009, dredging operation began with a grab system, resulting in a considerable washing out effect. There is a high risk that this will lead to a considerable redistribution of contamination, as such activities are reported to cause the release of chemical contaminants in waters used for recreational, rearing or fishery activities, consequently representing a threat to human health (*e.g.* Donati and De Angelis, 2003; Karlsson *et al.*, 2008). Together with the associated oxygenation processes, such a redistribution could lead to a considerable increase of contamination throughout Holes Bay, with the potential for adverse effects in the estuary.

In Eastern Sandbanks hardly any contamination could be detected. Concentrations were comparable to the values in the approaches to Poole Harbour (Hübner, 2009; *cf.* Chapter 10.4.6), which had similar grain size distributions.

6 Case study 4: Distribution patterns in Poole Harbour (UK) – Part 2: Normalised concentrations

6.1 Introduction

Between different sites the geophysical factors, especially the grain size distribution, vary strongly. The grain size of the sediment has a pronounced effect on the spatial distribution of metals (Lakhan *et al.*, 2002), since metals have a strong affinity with silt and clay fractions (Bliefert, 1994; Langston and Spence, 1998; Roussiez *et al.*, 2005) and the variability in grain size imposes considerable spatial and temporal variance on sediment-derived chemical data (Loring, 1991; Birch *et al.*, 2008). Fine grained sediments have a high sorptive capacity for contaminants, by contrast, environments containing primarily coarse grained sediments are non-cohesive and have a low sorptive capability (Kersten and Smedes, 2002). While the total concentration of potentially toxic metals increases generally with the size of the clayey fraction, the bioavailability decreases on average by circa 2 % per weight-% clay (Kuntze *et al.*, 1988). Apart from their higher sorptive capability, sediments with a wider range of grain sizes will be better flushed and therefore less vulnerable to contaminant build-up (Langston *et al.*, 2003).

The metal concentrations alone allow no safe differentiation between anthropogenic and natural sources and a determination of distribution patterns may be unreliable (for example, an area rich in clay might result in a false positive, while the analysis can easily underestimate the contamination in sandy sediments). A comparatively recent development in research into metal distributions is to compensate for this effect by the introduction of a normalising scheme. Such a normalising element (often referred to as normalizer, normalizing factor or, misleadingly, as chemical ratio) is “*the attempt to compensate for the natural variability of trace metals in sediments so that any anthropogenic metal contributions may be detected and* *quantified*" (Loring, 1991). The application of a normalisation scheme should have, in theory, two connected effects. Firstly, differences introduced by different grain sizes should be substantially reduced. The concentrations throughout the samples of an unpolluted environment should become very homogenous; while single contamination events should stand out clearly.

A normalisation approach must be selected very carefully, since a poorly chosen normalisation could invalidate the results. Luoma (1990) defined three quality criteria: the normalising element must (1) covary in proportion with the natural concentrations of the metals of interest; (2) be insensitive to anthropogenic sources; (3) not be influenced by changes in the geochemical conditions such as variations of the redox potential. Nevertheless, and despite its importance, there are no clear rules regarding the procedure and the choice is still subjective (Roussiez *et al.*, 2005). Consequently, numerous approaches have been proposed; the most common techniques can be subdivided into the following groups: physical segregation, granulometric normalisation, elemental normalisation and post-extraction normalisations (Birch *et al.*, 2008).

For example, normalisations have been proposed based on ^{133}Cs and lead isotope measurements (Roussiez *et al.*, 2005), or expressing concentrations as ratios of organic carbon, cobalt, iron, lithium, scandium or aluminium. Iron and aluminium are commonly used in literature (*e.g.* Hirst, 1962; Bruland *et al.*, 1974; Bertine and Goldberg, 1977; Helz *et al.*, 1985; Hornung *et al.*, 1989; Carral *et al.*, 1995; Daskalakis and O'Connor, 1995). Both are well suited, as they are abundant in nature, and aluminium is not commonly associated with anthropogenic inputs (Birch *et al.*, 2008). There are differences between the elements, though; for example, it was shown that more than 50 % of the variation in concentration of As, Cr, Cu, Ni, Pb, Sn and Zn is accounted for by Fe or Al normalisation, while concentrations of Ag, Cd, Hg, Sb, and Se where not strongly correlated (Daskalakis and O'Connor, 1995).

Another frequently used approach is the consideration of only the clay fraction in the analyses. The analysis of the ≤2 µm fraction alone is considered to be an ideal, yet rather impractical normalisation procedure (Kersten and Smedes, 2002). Hence, most studies utilise 63 µm sieves. The disadvantage of all grain size based approaches is that they double the necessary time in the laboratory (analysis of the whole sample for total content analysis/risk assessment plus the separate analysis of the <63 µm fraction for the determination of distribution patterns). In addition, simply using a single sieve holds the danger of not taking all factors into account; such a method does not fully consider the variability of the mineralogical composition and of the clay content between two areas (Roussiez *et al.*, 2005). For this reason, Kersten and Smedes (2002) recommended a two-tiered normalisation scheme, including sieving (using the common 63 µm sieves) and geochemical correction. However, there is little agreement over which geochemical approach leads to the best outcome. Standardisation of normalisation techniques was found to be one of the most critical aspect in the overall sediment monitoring strategy (Herut and Sandler, 2006).

In this study, different approaches have been compared. Firstly, the established approach analysing for each sample the <63 µm fraction separately. Secondly, an approach has been utilised which analyses six different grain sizes of several samples from key areas and establishes the average recovered concentrations for each fraction. The latter approach is much quicker and economic, as it requires substantially less samples. It is, however, based on the assumption that the random samples sufficiently reflect the distribution patterns. Lastly, both granulometric normalisation schemes were tested as two-tiered approaches with geochemical normalisation schemes (iron and aluminium).

6.2 Material and methods

In order to analyse the effects of both sediment size and grain structure on the metal concentrations, laser based grain size measurement data and scanning electron microscope (SEM) pictures have been processed in addition to the methodology described in Chapter 2.

SEM-pictures were taken using a SEM model Jeol 5300, equipped with the capability for secondary electron imaging (SEI). This instrument is supplemented with an Oxford Instruments INCA energy-dispersive x-ray analysis (EDXA) system. Both qualitative and quantitative microanalyses have been undertaken simultaneously during SEM observation. As well as being able to operate as a conventional high-vacuum SEM, the Jeol 5300 is capable of operating under low vacuum conditions, thus allowing the imaging of uncoated samples, moist samples and samples prone to sample charging (*i.e.* dusty materials). The pictures allowed the evaluation of differences in the surface structure of different grain size fractions.

A SCOPAC report (SCOPAC, 2004b) pointed out that the available data on sediment grain sizes in Poole Harbour (*e.g.* Green, 1940; Green *et al.*, 1952) is old and the used recovery methods may have significantly underestimated the fine sand and silt fractions. The report itself gives general gradients horizontal trends, but no vertical profiles. Similarly, most studies tested, often repeatedly, the top layer (*e.g.* Parker and Pinn, 2005), instead of providing a long vertical profile. Basically, while the sheltered embayments and creeks usually consist of fine silts and clays, sediments subjected to wave activity and tidal currents show a wider range of grain size (Langston *et al.*, 2003). As no vertical profiles could be found in the literature, grain size distributions were analysed in a number of cores. These measurements were performed with a Fritsch Analysette 22eco, courtesy of ICBM-Terramare (Wilhelmshaven, Germany). Wet samples were dispersed ultrasonically for 1 min before laser-diffraction analysis with a convergent laser beam. The grain size fraction 0-63 µm, 64-125 µm, 126-140 µm, 141-200 µm, 201-300 µm and 301-1000 µm have been analysed (*cf.* Chapter 10.3.3).

Between the results of laser diffractometry measurements and manual sieving obviously certain differences exist, as even a scientific sieve will not reach a comparable accuracy. However, it was shown for fine- and medium-grained samples that both approaches show good agreements with regard to mean grain size, sorting, and central cumulative mass/volume percentages (Rodríguez and Uriarte, 2009).

Concentrations have then been analysed using different normalisation schemes:

a) granulometric correction:
  (1) using solely the <63 µm fraction for analysis,
  (2) using all above stated fractions, incorporating total concentrations [mg·kg^{-1}], quantity of each grain sizes fraction [%], and average recovery rate for each grain size fraction [%],

b) elemental corrections:
  (3) using an elemental correction with iron, expressing the concentration as dimensionless ratio,
  (4) using an elemental correction with aluminium,
  (5) using an elemental correction with iron and aluminium,

c) two-tiered approaches:
  (6) approaches incorporating one normalisation scheme each from the two previous groups.

Recently, the element cobalt has also been used as a normalising element itself (*e.g.* by Matthai and Birch, 2001). One of its main advantages is a good relationship to size-normalised data (Birch *et al.*, 2008). However, if cobalt normalised and grain size normalised data are related, it can consequently be assumed that any effective normalisation scheme should yield fairly homogenous cobalt concentrations in turn. Accordingly, for each normalisation procedure the coefficient of variation (CV) of cobalt was calculated, in order to evaluate the efficiency of the normalisation scheme.

6.3 Results

Grain size data was not available for all cores: only in Wareham Channel was the coverage of fully grain size analysed cores sufficiently high. However, Holes Bay and Southern Bights showed a very uniform distribution, and in no case did less than 92 % of the sample belong to the <63 µm fraction. Consequently, neither the commonly used <63 µm normalisation scheme, nor the 6-fractions approach used in the present study would have yielded a noteworthy effect.

6.3.1 Grain size measurements

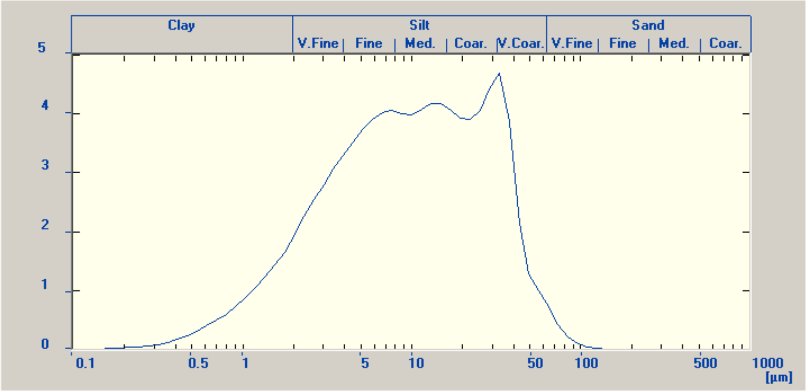
The lower part of the sediment is generally homogenous, containing clay, silt and sand fraction (ranging from 0.3 to >500 µm). With decreasing depth in the column, the sand fraction becomes smaller while the amount of silt and clay increases, until in a depth of 40 cm and higher virtually all material can be attributed to the 1-50 µm size fraction. On average, 91.1 % of the sample material in the channel deep and 82.6 % of the sample material in the shallows/mudflats belonged to the <63 µm grain size fraction (Table 19).

Table 19: Average grain size fraction in the cores [% of total sample material]

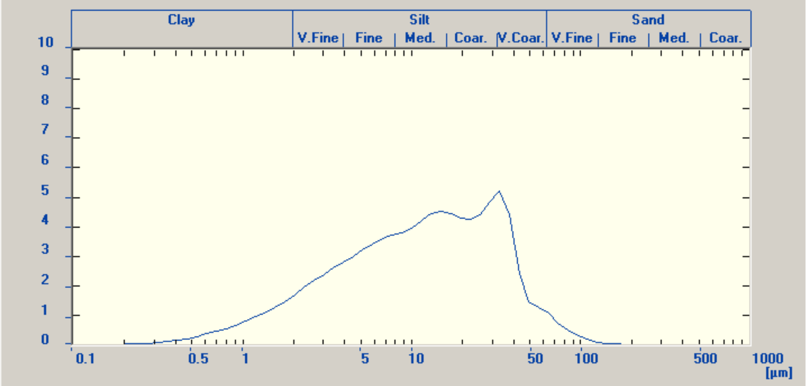
	channel deep		shallows/mudflats	
	$\bar{x}$	s^2	$\bar{x}$	s^2
0-63 µm	91.13	15.18	82.55	5.80
64-125 µm	4.49	5.09	7.95	4.49
126-140 µm	0.58	1.50	4.30	1.74
141-200 µm	1.97	6.25	1.95	0.52
201-300 µm	1.12	3.16	1.38	0.88
301-1000 µm	0.72	2.73	1.88	0.39

Figure 41 shows representative layers of sample core 11 and full profiles can be found in Chapter 10.4.5.

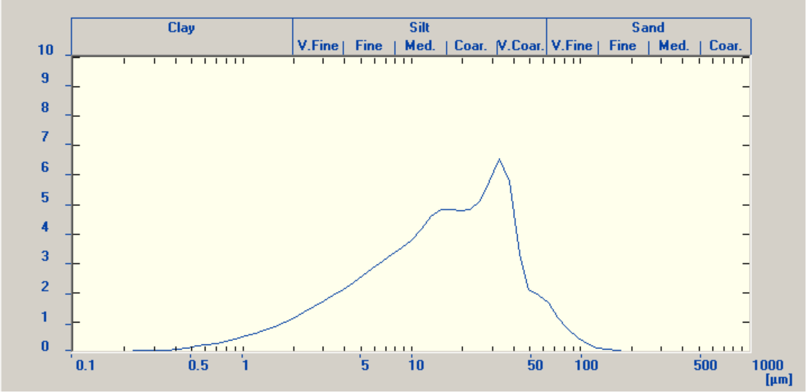
0-10 cm



30-40 cm



60-70 cm



90-100 cm

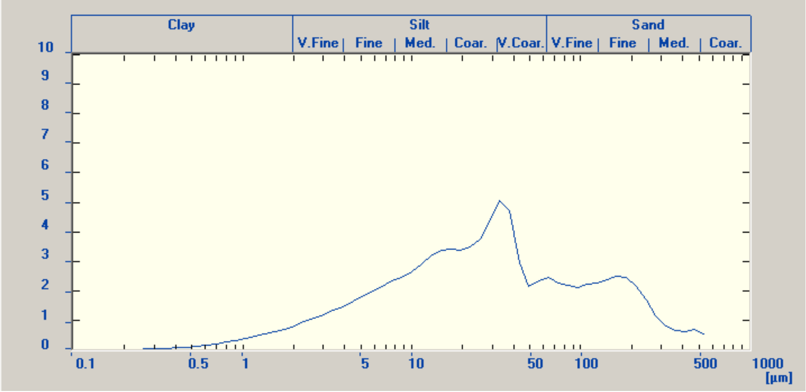
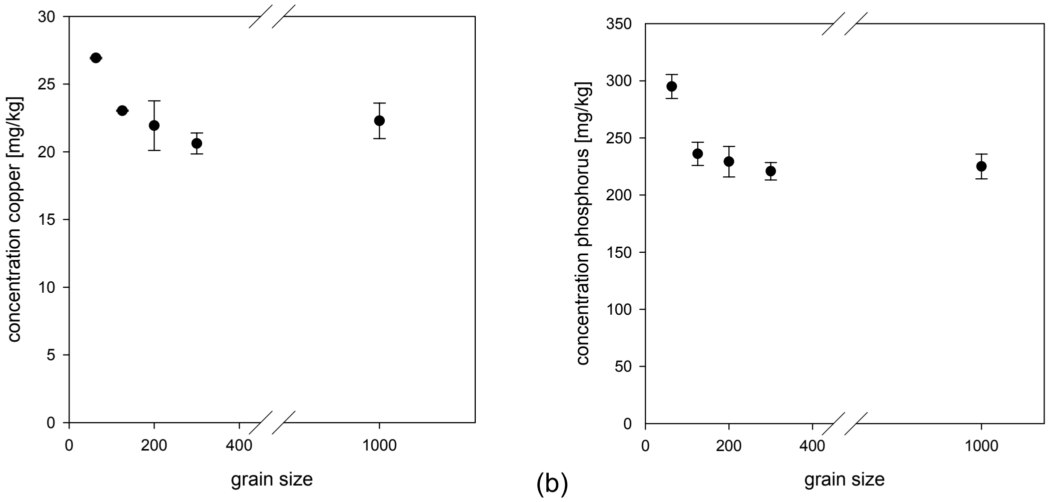


Figure 41: Typical grain size distribution throughout a core, here core P14: grain size versus distribution proportion $dQ_3(x)$

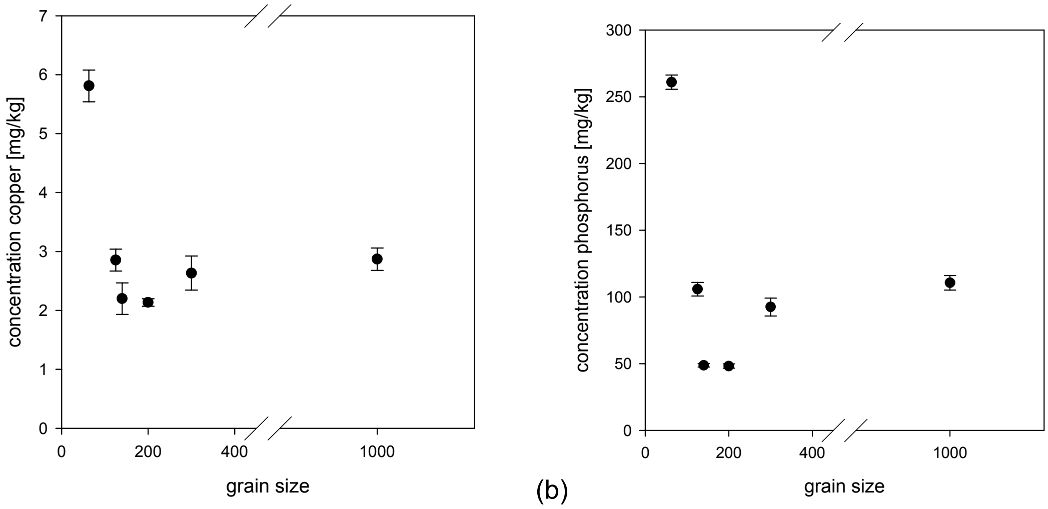
6.3.2 Chemical differences of the grain size fractions

As expected the recoveries are much higher with small grain sizes; particularly the smallest fraction (0-63 µm) leads to very high recoveries. However, unlike the rest of Wareham Channel (Figure 42), the channel deep itself (cores P29-32; Figure 43) showed two important differences: (a) the difference between the recoveries of <63 µm and the other fractions was considerably larger and (b) the recoveries unexpectedly rose again between 200 and 300 µm, particularly clearly visible for phosphorus (Figure 43b). This is consistent throughout all the elements analysed.



(a) (b)

Figure 42: Copper (a) and phosphorus (b) loads in a typical sample from core P11 (Wareham Channel, shallows), sample consisting of 7 replicates)



(a) (b)

Figure 43: Copper (a) and phosphorus (b) loads in a typical sample from core P31 (Wareham Channel, deep, sample consisting of 7 replicates)

Based on these tests the average recoveries for each grain size fraction have been calculated (Table 20). The smallest analysed grain size fraction (<63 µm) typically, although not always, yielded the highest recoveries; it was therefore defined as maximal possible recovery rate (*i.e.* 100 %).

Table 20: Average recovery rates [%] of the different grain size fractions in the Wareham channel shallows, defining 63 µm as 100 %

	63 µm	125 µm	140 µm	200 µm	300 µm	1000 µm[‡]
aluminium	100.00	95.81	93.32	90.83	87.92	94.07
arsenic	100.00	90.14	80.68	71.22	63.79	76.64
cadmium	100.00	98.76	96.07	93.37	100.81	101.67
cobalt	100.00	83.86	81.43	79.00	82.86	79.29
chromium	100.00	85.56	83.52	81.47	76.58	82.77
copper	100.00	85.22	84.25	83.28	82.01	81.56
nickel	100.00	81.86	79.95	78.04	76.02	80.63
phosphorus	100.00	80.00	78.84	77.68	74.84	76.24
lead	100.00	86.69	81.59	76.49	83.41	74.20
zinc	100.00	87.31	86.04	84.77	81.59	84.26
$\bar{x}$	100.00	87.52	84.57	81.61	80.98	83.13

[‡] based on very little sample material

Table 21: Average recovery rates [%] of the different grain size fractions in the Wareham channel deep (cores P29-32), defining 63 µm as 100 %

	63 µm	125 µm	140 µm	200 µm	300 µm[‡]	1000 µm[‡]
aluminium	100.00	23.24	13.11	14.47	22.85	23.48
arsenic	100.00	20.01	16.46	16.93	20.25	20.27
cadmium	100.00	12.01	23.21	33.15	25.73	10.53
cobalt	100.00	45.27	21.21	26.92	50.84	47.83
chromium	100.00	31.51	16.76	18.13	30.33	32.36
copper	100.00	29.52	22.75	22.09	27.23	29.68
nickel	100.00	27.83	14.80	16.90	29.20	28.41
phosphorus	100.00	35.87	16.53	16.35	31.35	37.49
lead	100.00	46.53	27.39	25.20	52.53	48.11
zinc	100.00	36.40	20.38	21.28	37.24	38.94
$\bar{x}$	100.00	30.82	14.82	21.14	37.75	31.71

[‡] based on very little sample material

6.3.3 Comparison of the normalisation schemes

The previous tests provided two key elements: the grain size distribution, *i.e.* percentage of each grain size fraction per cores (*cf.* Chapter 6.3.1) and the relative recovery rate which was obtained for each grain size fraction for each element (*cf.* Chapter 6.3.2). Based on these data a normalisation scheme has been applied for the Poole Harbour estuary.

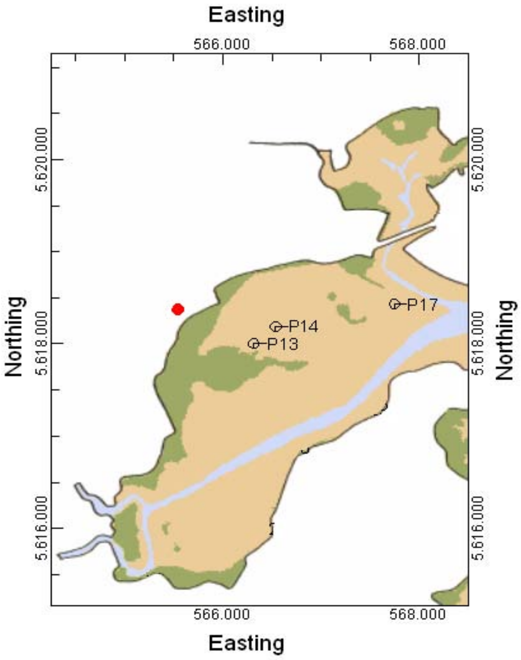
Table 22: Comparison of the efficiency of the applied normalisation schemes, using coefficients of variations of cobalt [%] as an indicator

		all	channel	shallows
without a normalisation		22.16%	30.59%	18.79%
granulometric corrections	<63 µm approach	22.04%	26.66%	20.88%
	6 fraction approach	22.50%	30.53%	19.29%
elemental corrections	ratio of iron	12.92%	15.16%	12.03%
	ratio of aluminium	22.19%	24.43%	21.29%
	ratio of iron and aluminium	40.37%	42.14%	39.66%
two-tiered approaches	<63 µm + iron	14.49%	12.54%	14.97%
	<63 µm + aluminium	23.02%	22.41%	25.68%
	<63 µm + iron and aluminium	41.61%	28.84%	44.80%
	6 fractions + iron	13.34%	15.29%	12.56%
	6 fractions + aluminium	21.48%	24.29%	20.35%
	6 fractions + iron and aluminium	39.15%	41.94%	38.03%

6.3.4 Normalisation applied on the Wareham Channel sediment data

The vast majority of significant point sources are located in the heavily industrialised Holes Bay area. The concentrations in that embayment are much higher, plumes are largely overlapping owing to marginal flushing characteristics and sediments are considerably mixed in certain regions owing to intensive shipping. In addition, railway tracks are running through the middle of the area leading, consequently, a much higher anthropogenic iron load (Burkhardt *et al.*, 2007) is rendering a geochemical normalisation with iron completely inoperative. The Royal Navy Cordite Factory (RNCF), however, is situated in the Wareham Channel area and therefore ideally suited for a comparison of absolute and normalised data.

Figure 44: The cores selected for the analysis of impact by the Royal Navy Cordite Factory in Wareham channel (base-map adapted from Gray, 1985, used grid is UTM Zone 30U; facility location is marked by red dot)



Between 1915 and 1957 the Royal Navy Cordite Factory (RNCF) manufactured naval gun propellant, explosives and associated ammunition. Peak production was reached during WW2, in 1959 the facility was shut down; however, the Admiralty Materials Laboratory (AMF) conducted corrosion research on the facilities grounds afterwards (*cf.* Capter 5.1.2). Contamination in these areas tends not to be dispersed over a large area and may lead to some heterogeneity; owing to the sheltered, low-energy conditions in Poole Harbour (Langston *et al.*, 2003). Consequently, a comparably clear, undisturbed profile can be expected, at least in cores P13 and P14 (Figure 23). In these two cores, which are directly adjacent to the RNCF grounds, all analysed metals/metalloids showed a massive peak between 30 and 60 cm depth, in particular phosphorus, tin, cadmium, lead and copper (Figure 45).

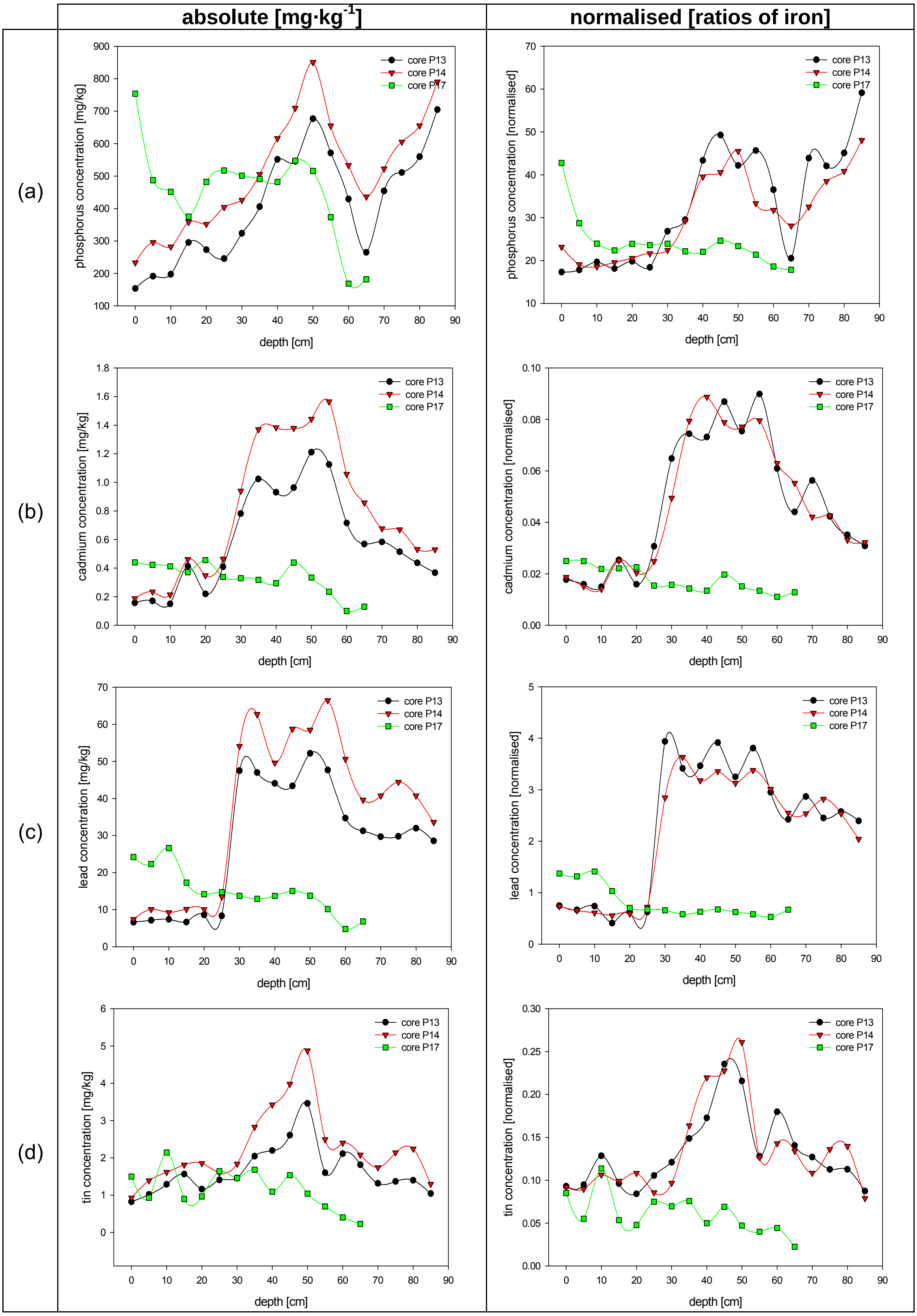


Figure 45: Absolute and normalised concentrations of phosphorus (a), cadmium (b), lead (c) and tin (d) in the cores adjacent to the former Royal Navy Cordite Factory

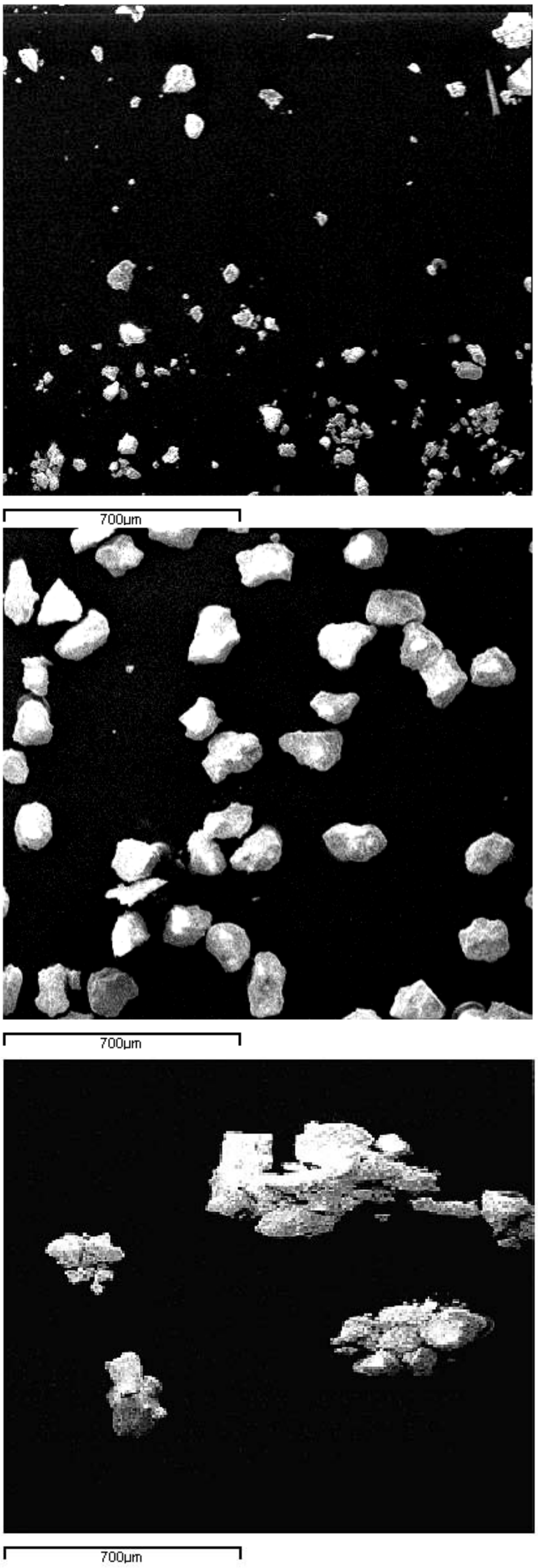
Core P17, about 1400 metres further downstream, shows similar patterns for zinc, lead and nickel (although with partly much lower concentrations), while most of the other elements, and particularly copper and phosphorus, show no comparable trend. From a depth of approximately 35 cm on all values rapidly returned to average concentrations.

After applying the normalisation scheme, the difference between the contamination profiles in cores P13 and P14 (which are close to each other and directly adjacent to the facility), decreased substantially for all analysed elements (Figure 45), especially cadmium. For phosphorus, the normalisation caused a strong effect for the observed peaks in 0-5 and 40-60 cm depth respectively, which became much less pronounced.

6.4 Discussion

6.4.1 Normalisation schemes

While the 0-63 µm, 64-125 µm, 126-140 µm and 141-200 µm grains are predominantly very smooth, the 201-300 µm and 301-1000 µm grains are heavily structured (Figure 46) and have therefore an increased surface:mass relationship, thus explaining the unexpected rise in concentrations for the channel transect. Compared to the intertidal cores the gap between the concentrations in the 0-63 µm fraction is much higher in that transect, too. Presumably, the higher current speeds lead to a washing out effect in the larger grain sizes, while in the smallest grain size fraction contaminants can build up easier.



<63 µm fraction

64-140 µm fraction

141-1000 µm fraction

Figure 46: SEM pictures of different grain size fraction

Regarding the choice of a normalisation scheme no approach which is based on grain sizes alone led to any considerable difference. This caused by the generally very fine material (*cf.* Table 19; Figure 41; Chapter 10.4.5): on average approximately 91 % of the material in the channel deep and 83 % of the material in the shallows/mudflats belonged to the <63 µm fraction.

Although the average particle size in the channel deep transect was slightly smaller, the <63 µm granulometric approach led to a slightly better result (variance decreased by 4 %), compared to the intertidal cores. This can be explained by the substantially larger difference between this and the larger fractions. Nevertheless, the measured variance was still unacceptably high, especially considering the effort necessary for this approach.

Both aluminium and iron are present in the estuary (except of the Eastern Sandbanks sub-region) in large quantities: aluminium between 1 and 3 % and iron between 2 and 3.5 % (*cf.* Chapter 5.3). A normalisation with aluminium, one of the oldest normalisation schemes and "the most basic geochemical approach" (Birch *et al.*, 2008), did not yield any measurable effect, either. This could be, in part, owing to the inadequate recoveries for this element (*cf.* Table 2). Approaches using a combination of aluminium and iron failed completely. The normalisation with iron on the other hand reduced the variance in the normalising element cobalt substantially. It lead to the lowest variance and can therefore be assumed to be best suited for Wareham Channel.

6.4.2 Royal Navy Cordite Factory / Admiralty Materials Laboratory

Regarding the analyses of the Royal Navy Cordite Factory (RNCF) and Admiralty Materials Laboratory (AML) respectively, all contaminants in cores P13 and P14 showed a steady increase until a depth of approximately 60 cm and a considerable peak in the depth between 35 and 60 cm. These two cores, lying directly next to the area (P13 and P14) showed some discrepancies, with P13 typically having lower concentrations. As both cores are directly adjacent to each other, they must be assumed to be effected to a comparable degree. When the normalisation scheme was applied, the differences between them decreased considerably, both plots became much more comparable for all metals/metalloids. This showed that the normalisation scheme has worked well, while none of the two granulometric normalisation schemes had any noticeable effect on these plots.

In core P17, the reference core downstream, hardly any concentrations could be detected. Only phosphorus showed comparable loads; however, the peaks in the same depth layer were eliminated by the normalisation scheme and can consequently be assumed to be unrelated. This core indicates a recent input of phosphorus through Lytchett Bay, which is consistent with the observations in that embayment (*cf.* Chapter 5.3.6).

Two major studies analysed the sediment accretion rates in Poole Harbour. The work by Cundy and Croudace (1996) was based on ^{210}Pb dating and stated a rate of 4.6-7.2 mm·yr^{-1} for the saltmarshes and 8.4 mm·yr^{-1} for the mud flats. Warneke's (2002) study on the other hand, which is primarily based on isotope analyses of weapons fallout data with evidence of tropospheric fallout from the Nevada tests in the early 1950s, reported values of 10.3-12.1 mm·yr^{-1}. The differences could partly be caused by high organic contents, as this tends complicate age determinations (Rosenbaum-Mertens, 2003), but the substantial difference makes an accurate determination impossible. Based on the accumulation rates reported by Cundy and Croudace (1996), the depth of the peaks is linked to the period between 1936(±6) and 1966(±6), which coincides approximately with the time between the preparation for WW2, when the RNCF had its highest production output, and the closure of the facility in 1959. Based on accumulation rates reported by Warneke (2002), however, these peaks are associated with the years 1950-1979(±4), which would suggest that the anti-corrosion research of the AML caused the high loads; which would explain particularly well the elevated levels of copper, lead, cadmium, sulphur and tin, although not the observed levels of phosphorus. It could be argued that the data on *Spartina anglica* (*cf.*

Chapter 7) suggests that Warneke's data describes the sedimentation regime better, but more data is required to clarify this issue.

6.5 Conclusions

The generalisation that the smaller the grain size, the higher the associated metal concentrations are, cannot be confirmed for the Wareham Channel. Nevertheless, it had little impact on the outcomes of the normalisation schemes in this study, as the sediment was too fine grained.

Cobalt proved to be not only a valid normalisation approach, but it was also a suitable tool for the assessment of normalisation schemes. Normalisations based on the grain size alone had little effect in the study area. Although it was consequently not possible to assess whether or not the simplified method, based on fewer samples, would have resulted in a reasonable estimation of the contaminant distribution, it is clear that a granulometric normalisation approach, which is typically requiring significantly more time and effort, is unnecessary in environments like Wareham Channel, where the sediment is very fine grained. The analyses showed that a fast and simple normalisation based on iron ratios, requiring no additional sample processing, led clearly to the best outcomes. Comparable tests will be necessary in order to assess if this normalisation scheme is the appropriate option for Wareham Channel only, or for any area with comparable, very fine grain size distributions.

Two previous studies came to substantial different sediment accretion rates in Poole Harbour, which impairs the evaluation of the age of a sediment layer. Without reliable data it is impossible to draw a conclusion and determine the contamination origins with certainty. In order to make more reliable connections between depth of the sediment and the age, an accurate sedimentation rate is indispensable. Consequently, intensive research will be required to evaluate the differences between the age determination approaches, and to define a reliable, proven procedure.

7 Case study 5: The saltmarsh cord grass *Spartina anglica* C. E. Hubbard in Poole Harbour

7.1 Introduction

The perennial *Spartina anglica* C. E. Hubbard, despite having several evolutionary advantages over other plants in this environment, has died back in the harbour (Gray, 1985; SCOPAC, 2004b; Raybould, 2005; Diaz and May, n.d.). The reasons for this process are insufficiently understood (Raybould, 2005), and the hypothesis that it may be caused by climate change have been disproved (Loebl *et al.*, 2006): owing to rising sea level and storm frequency a decrease or steady state of *S. anglica* was expected, but despite this and a significant shift in the local temperature regime, many new sites were colonised instead.

It was therefore decided to evaluate whether a relationship between the metal contamination and the die-back could be established.

7.1.1 Development of *Spartina anglica* in the UK

In the early 19th century seeds of the smooth cord grass *Spartina alterniflora* Loisel were accidentally imported from the USA into the UK in shipping ballast (Thompson, 1991). In the UK it was first collected in 1829 in Southampton (Hubbard, 1965). This plant was originally native to the East and Gulf coasts of the USA (Ayres and Strong, 2001; Baumel *et al.*, 2003) and is *"one of the most widespread and locally abundant North American, intertidal, salt marsh plants"* (Thompson, 1991).

This plant was the seed parent in an interspecific hybridization with the native small cord grass *Spartina maritima* (Curtis) Fernald. The outcome is the sterile F1 hybrid *Spartina* x *townsendii* H. & J. Groves (Ayres and Strong, 2001), first collected in 1872 (Thompson, 1991) or 1900 (Hubbard, 1965). In the 1890s a chromosome doubling resulted in the fertile amphiploid English cordgrass, *Spartina anglica* C. E. Hubbard (in the following *Spartina* will be abbreviated as *S.*). It is possible that the emergence of *S. anglica* occurred immediately after the one of *S.* x *townsendii* (Thompson, 1991). According to Ferris *et al.* (1997) it is a "*textbook example of a natural amphiploid*". An amphiploid is defined as a hybrid with two sets of chromosomes, each set coming from a different species. *S. x townsendii* and *S. anglica* are morphologically very similar and were not recognised as different plants until 1957 (Gray *et al.*, 1991; Thompson, 1991). This led to inconsistent information concerning its introduction in the UK.

S. anglica was introduced in, or shortly after, the 1890s. Hubbard (1965) and Gray (1985) state that it was first recorded around 1890. Hammond (2005) rejected this estimate because Hubbard's conclusion is based solely on anecdotal evidence in personal correspondence with local residents, he states that the plant was not introduced until 1899.

Table 23: Overview of the discussed *Spartina* species

Latin name	common name	dis-covered	first record in the UK	remarks
Spartina maritima	small cord grass	(Curtis) Fernald	1666 (Merrett, 1666, cited in Marchant and Goodman, 1969)	formerly known as *Spartina stricta* (Ait.) Roth
Spartina alterniflora	smooth cord grass	Loisel	early 1800s (Baumel *et al.*, 2003) 1829 (Hubbard, 1965)	imported accidentally from the USA
Spartina x townsendii	Townsend's cord grass	H. & J. Groves	1870 (Goodman *et al.*, 1959) 1872 (Thompson, 1991) 1900 (Hubbard, 1965)	not recognised as different species until 1957 (Thompson, 1991)
Spartina anglica	English cordgrass, rice grass	C. E. Hubbard	~1890 (Gray, 1985) 1890 (Thompson, 1991) ≥1899 (Hammond, 2005)	

While its predecessors had a rather limited distribution, *S. anglica* characteristically spreads fast and becomes a dominant component of a saltmarsh (Thompson, 1991). The plant colonised zones in the mudflats that have so far not been occupied by *Spartina* spp., but scattered populations of *Salicornia* (Goodman *et al.*, 1969; Ferris *et al.*, 1997). Another evolutionary advantage of *S. anglica* in intertidal marshlands is that this species can sustain 241 days per year under tidal submergence (Diaz and May, n.d.). *Spartina* is typical for the lower, or pioneer, marshes between mean high water neap and mean high water tides, where only a few species can withstand the high salinity (Williams *et al.*, 1994). There is also considerable morphological variation in *S. anglica*, possibly due to its hybrid origins (WSNWCB, n.d.). Another reason for the success of this plant is its greater ability to oxidise toxins (*e.g.* sulphide and ferrous compounds) and tolerate salinity (Raybould, 2005). Loebl *et al.* (2006) suggest that warmer spring seasons could promote germination, growth and accelerated colonisation by *S. anglica*. *Spartina* usually occurs in form of patches (Figure 47).

Figure 47: *Spartina anglica* patch in Poole Harbour at high water conditions

Lee and Partridge (1983) reported higher sediment accretion rates for *S. anglica* than for other salt marsh vegetation, including other *Spartina* species. *S. anglica*'s ability to trap large volumes of tidal sediments worldwide has led to its deliberate introduction for land reclamation (Ranwell, 1967; Baumel *et al.*, 2003). *S. anglica* tends to strongly accumulate cadmium (Otte *et al.*, 1991), while Padinha *et al.* (2000) reported a relationship between metal contamination in the sediment and stress-indices of *Spartina*-plants, and that higher metal concentrations are being stored in the underground plant-structures except cadmium, which is stored equally throughout the whole plant. Such metal accumulating plants are often deliberately planted for decontamination purposes (Beier, 1994). *Spartina*-species are also considered potentially useful for the biomonitoring of coastal systems (Padinha *et al.,* 2000).

7.1.2 Impact of *Spartina anglica* on the sediment distribution

S. anglica plays a crucial role in the context of redistribution of chemicals (Hübner *et al.*, *submitted*). Millions of cubic metres of sediment have been released due to the die-back of *S. anglica* cultures; it is completely unclear to what degree this sediment contains contamination, and what, if any, are the long-term results of the release.

Thompson (1991) defines the success of an invasive species "*if it colonizes a wide geographical range, exists over a range of localized environmental conditions, and/or forms a dominant component of the habitat into which it spreads*". According to this definition, *S. anglica* has been extremely successful in Poole Harbour for a quarter of a century. It reached its maximum extent of approximately 8 km² in 1924 (Raybould, 2005) and 7.7 km² in 1925 (Diaz and May, n.d.) respectively. In Holes Bay it covered approximately 63 % of the intertidal area at that time (Gray and Pearson, 1984). Since 1924/25, however, this plant died back in many areas of the harbour (Gray, 1985; Diaz and May, n.d.). Aerial photographs indicate that 38.6 % of the total saltmarsh had been lost between 1947 and 1993 (Born, 2005). According to Corkhill and Edwards (2006), approximately 350 of the 8 km² in the harbour remains today, *i.e.* 56.3 % has been lost. CASI (Compact Airborne Spectrographic Imager) images between 1998 and 2005 confirmed that this trend is ongoing (Witt, 2008).

This resulted in a great amount of sediment being released (SCOPAC, 2004b; Raybould, 2005). At least 4 million of the about 7 million cubic metres of sediment accumulated by *Spartina* growth in Poole Harbour have already been released (Gray *et al.*, 1995; Diaz and May, n.d.), and the approximately 3 million m³ remaining are in the process of further decline as well (May, 2005). Swales *et al.* (2005) determined the sediment remobilisation rates following herbicide-induced *S. anglica* die-back and predicted complete sediment loss for their test-patches within 6-10 yr. It is unclear to what degree this sediment contained contamination, and, if contaminated, what the long-term consequences of the release are.

Many hypotheses have been given for the reason of the die-back, for example the rising sea-level (Corkhill and Edwards, 2006) or that the plant is reaching the end of its natural life (Drake, 2006). It is assumed that the die-back is partly caused by erosion of the salt-marsh edges, anaerobic conditions causing the death of the rhizomes, and the invasion of other species; however, the mechanisms of the die-back are complex and still not completely understood (Raybould, 2005).

The rising sea-levels will also effect this development. The interplay of sea-level rise and population density is expected to shape the saltmarshes of the future (Edwards, 2005). It is sometimes assumed that the rising sea-level will inevitably accelerate the die-back (Corkhill and Edwards, 2006). It was, for example, expected that *S. anglica* would decrease or reach an equilibrium near Sylt (Germany) owing to rising sea level and storm frequency, but contrary to that hypothesis an investigation of Loebl *et al.* (2006) showed that many new sites have been colonised instead. If the sea-level rises too much however, it must be expected that the die-back will increase. This would release even more potentially contaminated sediment, which would form a significant part of any newly generated marshlands.

The null hypotheses are:

(1) the metal concentrations had no measurable impact on the *S. anglica* distribution; and

(2) the die-back of *S. anglica* had no measurable effect on the metal concentrations in Poole Harbour.

7.2 Material and methods

To compare fairly faint concentration differences, the analyses are limited to a single zone of Poole Harbour, as concentrations in the six major zones of the estuary differ significantly (*cf.* Chapter 5.3.1). Approximately 63 % of the Holes Bay intertidals have once been covered by *S. anglica* and would therefore have been an ideal ground; however, the very high concentration throughout this embayment (*cf.* Chapter 5.3.2) ruled it out for this case study. In this contaminant cocktail it would be difficult to establish clear trends. The Southern Bights were selected, as both sufficient chemical and biological data were available for this area.

Chemical data from the previous case studies have been used and the methodology described previously (*cf.* Chapter 2) has been applied. Suitable samples (*e.g.* at least 80 cm core lengths, complete metal coverage with no calibration problems) were grouped by three different criteria: (1) zones where *S. anglica* has never been reported, (2) zones where it has died back, and (3) zones where it is still growing (Table 24). Considering that the plant is already dying back and sampling induces a considerable stress on the plant, only two cores have been extracted from such areas in order not to further increase the pressure.

Table 24: Core grouping for case study 5

	cores (*cf.* Figure 23)
group 1: no records of *S. anglica*	P27, P37, P38
group 2: *S. anglica* died-back	P24, P25, P33
group 3: still existing *S. anglica* patches	P26, P36

The length of the shortest core (90 cm) in the analyses was used as the maximum value, *i.e.* data below that depth was not taken into account, in order to avoid a bias caused by different core lengths. The three groups were then analysed by comparing their means and standard errors and by analysing the variance (t-tests and one-way ANOVA; Davies and Goldsmith, 1972; Landau and Everitt, 2004; De Veaux *et al.*, 2005). In addition, Levene's Test for Equality of Variances was executed, which indicates whether the variances from two samples are different. A value of greater than 0.05 indicates that the assumption of equal variances is met.

The die-back of *S. anglica* started in 1924/1925. As the cores used in this case study have been extracted in late 2008, the time frame of die-back in this study is circa 83.5 years. Based on a sediment accumulation rate of 7.2 mm per year (Cundy and Croudace, 1996), in 83.5 years 601.2 mm of sediment will consequently build up. In the extracted cores the depth of approximately 0-60 cm can consequently be assumed to be influenced by the die-back. According to Warneke’s (2002) sediment accumulation rates of 10.3-12.1 mm sediment per year, approximately 93.5(±8) cm can consequently be assumed to be influenced by the die-back. This is outside the study’s range of 90 cm (see above).

Cadmium is of special interest as it tends to be strongly accumulated by *S. anglica* and additionally has a very high mobility, *i.e.* it can be assumed to be released rapidly after die-back. Additionally, arsenic, copper, nickel and zinc have been included in this case study, as these elements are typical contaminants, cover a high range of mobilities (*cf.* Chapter 4.3.2) and yielded very good outcomes in the CRM-analyses (*cf.* Chapter 2.2.5).

7.3 Results

7.3.1 Average concentrations in the three groups

The observed concentrations were relatively low; the means were typically around or below the TEL-values. However, when comparing the three groups (Table 25) the data also showed that metal concentrations are elevated in places where *S. anglica* either grows or used to grow.

Except for cadmium, the highest concentrations of metals/metalloids have been measured in the cores of group 2, *i.e.* in the cores where *Spartina anglica* died back. Cadmium clearly has the highest concentrations in the areas where *S. anglica* is still growing and lowest where it was never recorded. In the depth range which is assumed to be widely unaffected by the die-back (*i.e.* deeper than 60 cm), cadmium concentrations were generally much lower; group 1 had concentrations of 0.32, group 2 of 0.37 and group 3 of 0.57 $mg \cdot kg^{-1}$. In the depth-layers which are assumed to be affected by the die-back (*i.e.* 0-60 cm depth), the concentrations in the cores where *S. anglica* never grew have slightly increased (0.39 $mg \cdot kg^{-1}$), while concentrations increased considerably in the other two groups: in the areas where it died back to 0.58 $mg \cdot kg^{-1}$ and where the plant is still growing to 0.81 $mg \cdot kg^{-1}$.

Table 25: Average concentrations of the metals arsenic, cadmium, copper, nickel and zinc [mg·kg^{-1}] in the three groups before and after the start of the die-back

		group 1: no records of *S. anglica*		**group 2:** *S. anglica* died-back		**group 3:** still existing *S. anglica* patches	
		mean	st. error	mean	st. error	mean	st. error
complete cores	Arsenic	13.32	0.40	17.54	0.71	14.82	0.66
	Cadmium	0.36	0.02	0.50	0.04	0.73	0.04
	Copper	12.42	0.61	18.08	0.85	16.22	1.29
	Nickel	27.00	0.90	33.54	0.77	27.89	1.36
	Zinc	67.56	2.94	100.09	3.79	85.38	5.82
shallower than 60 cm (assumed affected)	Arsenic	13.38	0.50	18.89	0.93	15.89	0.73
	Cadmium	0.39	0.03	0.58	0.04	0.81	0.06
	Copper	13.41	0.80	20.01	1.02	18.40	1.50
	Nickel	26.95	0.99	33.23	0.97	29.54	1.15
	Zinc	72.08	3.89	107.94	4.64	96.84	6.39
deeper than 60 cm (assumed unaffected)	Arsenic	13.21	0.66	14.84	0.46	12.68	1.14
	Cadmium	0.32	0.01	0.37	0.04	0.57	0.05
	Copper	10.49	0.76	14.21	0.74	11.86	2.01
	Nickel	27.11	1.85	34.15	1.28	24.59	3.26
	Zinc	58.71	3.63	84.39	3.64	62.46	9.01

Results of the ANOVA tests showed that the assumption of equal variances must be rejected for cadmium. While the four other analysed metals/metalloids (arsenic, zinc, nickel, copper) do not show a significant (defined as p<0.05) difference in concentrations between the three *S. anglica* growth patterns; the differences between the means of cadmium are significant (p=0.005; Table 26) between the three groups.

Table 26: Comparison of the means per core of the targeted metals/metalloids (one-way ANOVA on the three *S. anglica* growth patterns)

		Sum of Squares	df	Mean Square	F	Sig.
arsenic	Between Groups	23.350	2	11.675	2.466	.180
	Within Groups	23.675	5	4.735		
	Total	47.025	7			
cadmium	Between Groups	.183	2	.092	18.086	.005
	Within Groups	.025	5	.005		
	Total	.209	7			
copper	Between Groups	48,659	2	24.329	1.878	.246
	Within Groups	64.761	5	12.952		
	Total	113.419	7			
nickel	Between Groups	58.791	2	29.396	1.397	.330
	Within Groups	105.222	5	21.044		
	Total	164.013	7			
zinc	Between Groups	1487.926	2	743.963	3.557	.109
	Within Groups	1045.835	5	209.167		
	Total	2533.762	7			

7.3.2 Analyses of the different depth groups

In order to look at the results more closely, a t-test has been performed, analysing separately the depth which are assumed to be affected and unaffected by the die-back. For this purpose, the samples of the three groups were rearranged into two groups: samples with and without *S. anglica* presence (Figure 48). Between 0-60 cm cases of the die-back group were added to group 1 (*i.e. S. anglica* presence not assumed); between 60-90 cm cases of the die-back group were added to group 3 (*i.e. S. anglica* presence assumed).

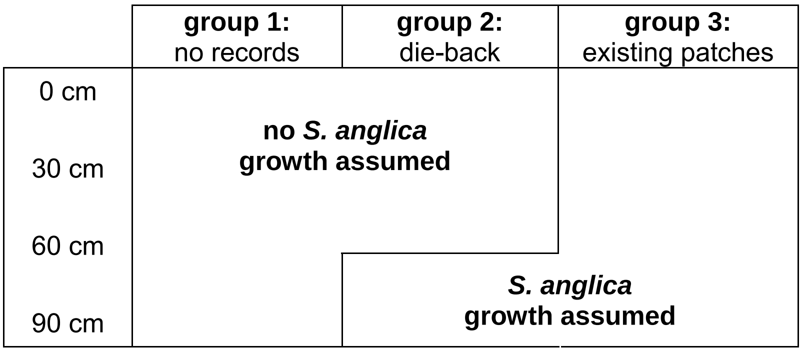


Figure 48: Regrouping used for the t-test

Regarding the Levene's Test for Equality of Variances tests, all analysed metals/metalloids had value of greater than 0.05, indicates that the assumption of equal variances is met (Table 27 and Table 28).

In the first independent sample t-test (Table 27), the depth layers which are assumed unaffected by the die back have been compared. As it can be assumed that group 2 at this time still contained *S. anglica* patches, samples of groups 2 and 3 (*S. anglica* presence assumed) have been compared with group 1 (*S. anglica* absence assumed). The results showed that in the depth layers before the die-back, the means are not significantly different for any metal/metalloid tested.

Table 27: T-test on the different *S. anglica* growing patterns: present/absent in the time before the die-back began

Independent Samples Test: 60-90 cm, comparing group 1 (*S. anglica* assumed absent) with groups 2+3 combined (*S. anglica* assumed present)

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
arsenic	Equal variances assumed	,072	,798	-,255	6	,807	-,5458	2,13760	-5,77630	4,68475
cadmium	Equal variances assumed	2,615	,157	-1,339	6	,229	-,1334	,09961	-,37715	,11031
copper	Equal variances assumed	,672	,444	-,741	6	,486	-2,5488	3,43803	-10,96131	5,86379
nickel	Equal variances assumed	,074	,795	-,325	6	,757	-2,2576	6,95675	-19,28021	14,76492
zinc	Equal variances assumed	,646	,452	-,889	6	,408	-14,7102	16,53954	-55,18100	25,76058

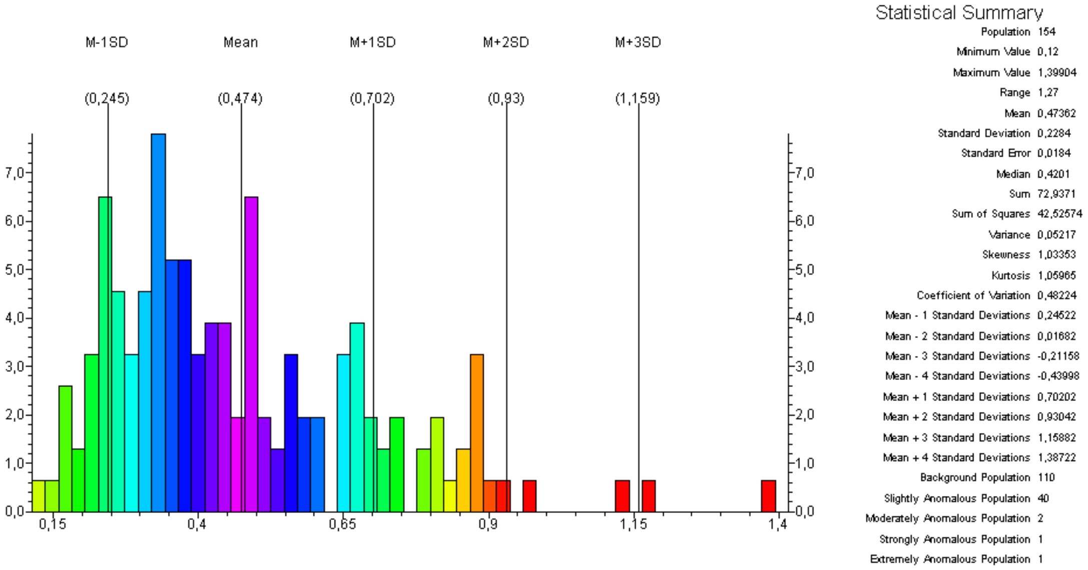
In the second independent sample t-test (Table 28), the depth layers which are assumed to be affected by the die back have been compared. Based on the assumption that the die-back group (group 2) lost its *S. anglica* patches, samples of groups 1 and 2 (*S. anglica* absence assumed) have been compared with group 3 (*S. anglica* presence assumed). The results now showed that the means are not significantly different for any metal/metalloid tested, except for cadmium. The means of cadmium is significantly (*p*=0.025; two-tailed) different in the areas where *S. anglica* patches are present and where it is not growing.

Table 28: T-test on the different *S. anglica* growing patterns: present/absent in the time after the die-back began

Independent Samples Test: 00-60 cm, comparing group 1+2 combined (*S. anglica* assumed absent) with group 3 (*S. anglica* assumed present)

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
arsenic	Equal variances assumed	,534	,492	-,442	6	,674	-1,0798	2,44220	-7,05562	4,89608
cadmium	Equal variances assumed	5,230	,062	2,968	6	,025	,2477	,08344	,04349	,45183
copper	Equal variances assumed	5,041	,066	,032	6	,976	,1315	4,14738	-10,01674	10,27981
nickel	Equal variances assumed	1,535	,262	-,619	6	,559	-4,8633	7,85616	-24,08666	14,36000
zinc	Equal variances assumed	2,461	,168	-,238	6	,820	-4,8132	20,22294	-54,29698	44,67051

The cadmium concentrations were analysed more closely. Figure 49 describes the basic statistics for this element: observed concentrations in Southern Bights are between 0.12 and 1.4 mg·kg^{-1}, with a mean concentration of 0.47 mg·kg^{-1}. Approximately 71 % of the cases are within a range of one standard deviation of the mean and 97 % within a range of two standard deviations, meaning that the data is normally distributed.



Statistical Summary

Population	154
Minimum Value	0,12
Maximum Value	1,39904
Range	1,27
Mean	0,47362
Standard Deviation	0,2284
Standard Error	0,0184
Median	0,4201
Sum	72,9371
Sum of Squares	42,52574
Variance	0,05217
Skewness	1,03353
Kurtosis	1,05965
Coefficient of Variation	0,48224
Mean - 1 Standard Deviations	0,24522
Mean - 2 Standard Deviations	0,01682
Mean - 3 Standard Deviations	-0,21158
Mean - 4 Standard Deviations	-0,43998
Mean + 1 Standard Deviations	0,70202
Mean + 2 Standard Deviations	0,93042
Mean + 3 Standard Deviations	1,15882
Mean + 4 Standard Deviations	1,38722
Background Population	110
Slightly Anomalous Population	40
Moderately Anomalous Population	2
Strongly Anomalous Population	1
Extremely Anomalous Population	1

Figure 49: Histogram and basic statistics of cadmium in the tested cores

The graphical output (Figure 50) illustrates the measured pattern (Table 25): the highest concentrations have been measured where the plant is still growing, followed by the areas where it died back, and lowest in the cores where it never grew. Only in the depth layer 90-100 cm the cadmium concentrations were equally high in groups 2 and 3.

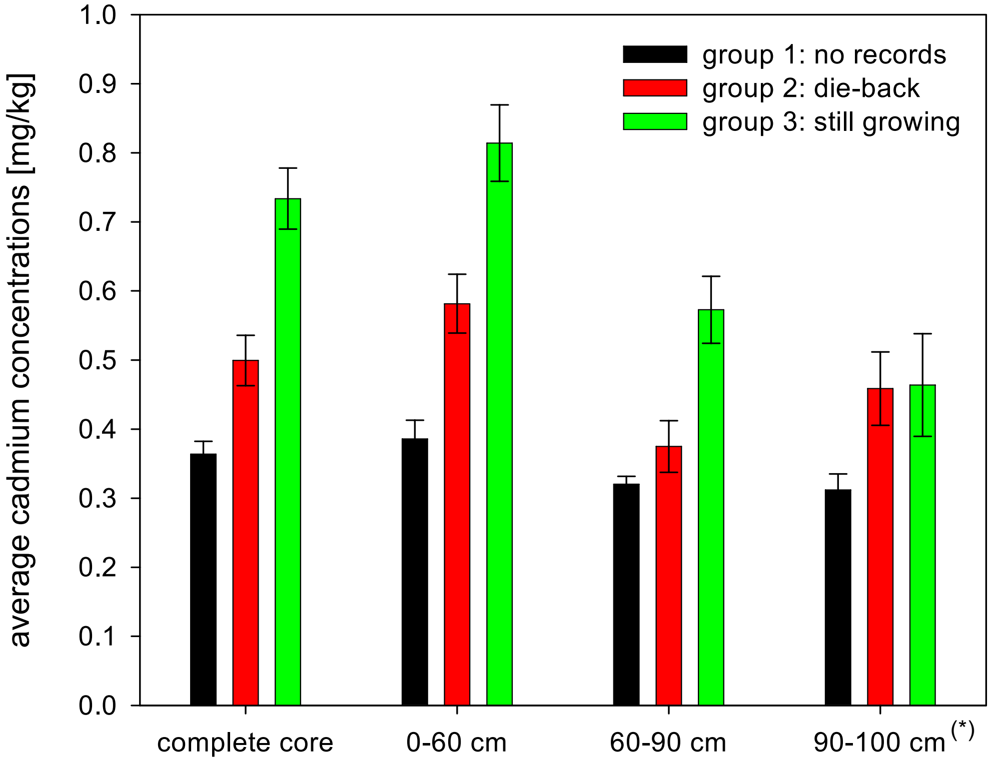


Figure 50: Average concentrations in the three groups (*S. anglica* growth patterns); whiskers indicate the standard error of the mean; the asterisk indicates reduced data safety

7.3.3 Sediment release

The analyses are based on dry weight (mg contaminant per kg dry sediment; equal to ppm or $\mu g \cdot g^{-1}$); the weight-volume relationship consequently had to be established in order to assess the extent of a possible cadmium release.

In the analyses of Southern Bights, the sediment weighted between 320 and 1200 kg per cubic metre with an average of 672 mg·kg^{-3}. When analysed per depth layer, there was a strong linear increase in dry weight with depth until a depth of 15 cm (r²=0.89, mean: 582 mg·kg^{-3}; Figure 51).

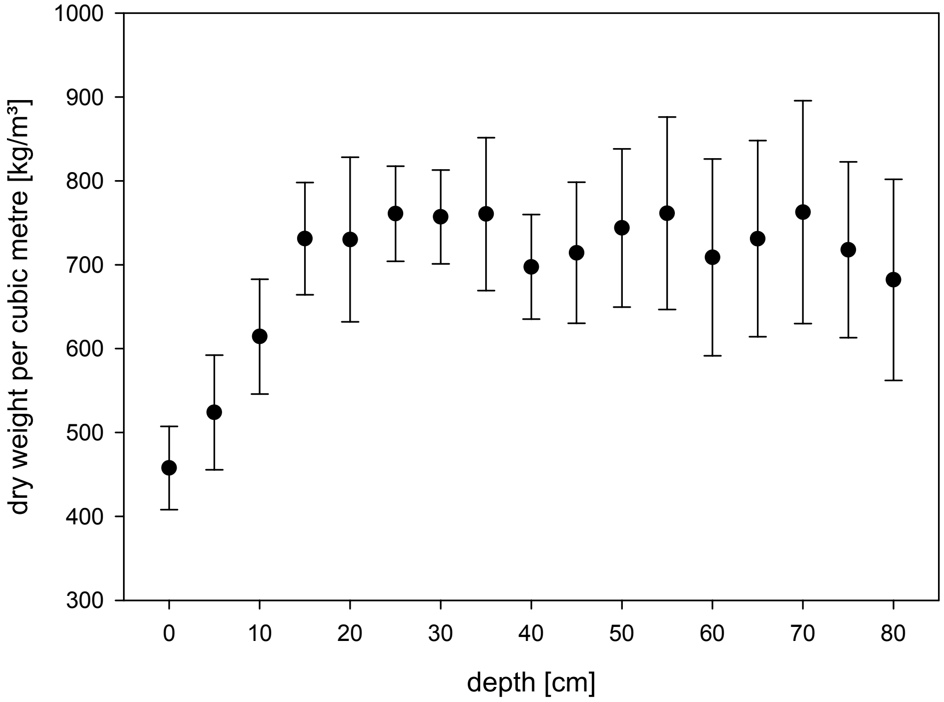


Figure 51: Average sediment density in the Southern Bights, whiskers indicate standard error of the mean

With the collected data, three scenarios could be established, one based on very conservative values, a second working with the values observed for the topmost layers only and a third one using the most adverse values possible with the acquired data, *i.e.* a worst-case scenario (Table 29).

Table 29: Calculated amount of released cadmium, following the die-back of *S. anglica*

	conservative scenario		primary scenario		worst-case scenario	
sediment loss:	400,000	m³	1,000,000	m³	3,000,000	m³
density:	458	kg·m^{-3}	582	kg·m^{-3}	672	kg·m^{-3}
sediment weight:	183,200,000	kg	581,803,025	kg	2,016,000,000	kg
total cadmium:	0.60	mg·kg^{-1}	0.81	mg·kg^{-1}	0.94	mg·kg^{-1}
mobility:	22	%	27	%	38	%
mobile fraction:	0.132	mg·kg^{-1}	0.219	mg·kg^{-1}	0.3572	mg·kg^{-1}
release:	24,182,400	mg	127,240,322	mg	720,115,200	mg
≙	24.2	kg	127.2	kg	720.1	kg
≙	~13·10^{-6}	%	~22·10^{-6}	%	~38·10^{-6}	%

7.4 Discussion

Considering the difficulties of locating suitable *S. anglica* patches in the estuary during the fieldwork, it is likely that the die-back has continued since Edward's (2005) work. However, it must be taken into account that unlike surveying, sampling in these shallow areas had to take place during high tide events, increasing the possibility of overlooking completely submerged *Spartina* patches.

In addition, it should be noted that, presumably owing to the die-back, only a limited amount of patches suitable for sample location could be located. Each sampling within a *Spartina* patch inevitably induces considerable stress to the plant. Consequently, only a single region of the estuary could be analysed in more detail. It cannot be completely ruled out that in a different region, for example Wareham Channel, a different pattern may have evolved in similar analyses.

7.4.1 Impact of contamination on the die-back of *S. anglica*

Regarding a possible influence of metals on the die-back, the null hypothesis could neither be rejected nor accepted; as the data did not demonstrate any reasonable pattern. In group 2 (areas where the plant died back) the concentrations of most were highest; however, the differences were not significant (0.11≤*p*≤0.33). In addition, the loads were still very low; in all cases concentrations were well below the threshold effect levels. It can be assumed that an exceptional high metal/metalloid-intolerance of this plant would already have been reported, and additionally it is very unlikely that the plant could, if intolerant to such low concentrations, have been so successfully in Holes Bay until 1924/1925 (Gray and Pearson, 1984), and, at least to some degree, still be (Witt, 2008).

7.4.2 Impact of *S. anglica* die-back on contamination

The analyses of the means showed no significant difference in concentrations for any analysed metal/metalloid except cadmium. Regarding cadmium, however, the data showed very clearly that concentrations were highest where the plant is still growing, followed by areas where it used to grow, and lowest where it was never recorded. The null hypothesis that the die-back of *S. anglica* had no measurable effect on the metal concentrations in Poole Harbour must be rejected. Evidence suggests that die-back is likely to have had an influence on cadmium concentrations in the harbour: where the plant grows, considerable amounts of cadmium are accumulated compared to the unpopulated areas. The concentrations in the unaffected cores increased only slightly, while concentrations increased steadily in the areas where it is growing (Figure 50).

The previous analyses (case study 3; *cf.* Chapter 5, especially Figure 25) suggested that the majority of the recent cadmium loads originate from the northern part of Holes Bay, *i.e.* the PSWT; while Underhill-Day (2008) suggested that the former industries in Poole have been a major source of less recent loads. Cadmium has a high mobility (*cf.* Chapters 4.3 and 5.3) and its adsorption rate is lower than for example zinc (Förstner, 1983). It is, in addition, inhibited by chloride (Salomons, 1980) and is (unlike other metals like zinc, copper, nickel and lead) persistently remobilised by increased salinity levels (Salomons *et al.*, 1982). It forms a soluble chloride complex in seawater and is, as the only metal, considered to be persistent in the columns of marine water bodies (Di Toro and Paquin, 2000). Consequently, it is washed out of Holes Bay more readily than the other metals/metalloids, but is accumulated by *S. anglica* growth in the south.

Concerning the differentiation between the depth layers (0-60 cm→assumed affected and 60-90 cm→assumed unaffected) only in regard to relative concentrations could a difference be observed (concentrations are much higher in the more recent layers), but no substantially different patterns emerged. This only changed in a depth exceeding 90 cm (although a depth bias can not be entirely ruled out here, as not all cores in the analyses reached that depth). This is probably caused by the reference data: no reliable sediment accumulation exists. The two data sets covering this area (Cundy and Croudace, 1996; Warneke, 2002) are contradictory, probably caused by the high organic matter content (Rosenbaum-Mertens, 2003). Assuming Cundy and Croudace's data is accurate, the die-back began in a depth of 60 cm, assuming Warneke's data is accurate, the die-back began in a depth of 93 cm. That groups 2+3 (*S. anglica* assumed present) had comparable concentrations only below 90 cm could be an indication that Warneke's data describes the sedimentation regime better. Also, the very similar patterns of the two major depth layers (00-60 cm and 60-90 cm), which, based on Cundy and Croudace’s data, have been assumed to be different, reinforce Warneke's accumulation rates. However, although the presented data gives a first indication in that regard; a high degree of uncertainty remains and there is a considerable need for more information, for example including the implications of the organic matter content, that may reconcile these differences.

In addition, analyses have confirmed (*cf.* Chapters 4.3 and 5.3) that the mobility of cadmium, which *S. anglica* tends to store, is very high and typically ranges between 30 and 50 %, although it was considerably lower in the Southern Bights (*cf.* Chapter 5.3.4). Compared to group 3 (still growing), group 2 (die-back) shows comparable cadmium concentrations in a depth below 90 cm, *i.e.* the depth which is assumed to be unaffected by the die-back. However, in all other depth layers group 2 typically has lower concentrations (Figure 50), namely they are lower by 35.1 % (60-90 cm) and 28.4 % (0-60 cm) respectively. There is a good agreement of these percentages with the mobile fractions determined for the corresponding depth layers: 32.1 % (60-90 cm) and 27.35 % (0-60 cm). This means that the difference in cadmium concentrations between the two groups (affected/unaffected by die-back) corresponds to 94±3.5 % of the mobile fraction.

Consequently, it is reasonable to conclude that (a) Warneke's data is more accurate than the data by Cundy and Croudace, at least for this region; and (b) the die-back did not only cause a ceasing of the cadmium accumulation, but additionally that the full mobile fraction of the cadmium has been released in the process.

7.4.3 Possible contamination release caused by the die-back

Cadmium concentrations did not exceed the TELs considerably and were in all cases well below the PELs. However, the *S. anglica* patches have significantly (p=0.05) higher concentrations, and in addition the large amount of sediment, which could be released owing to the die-back, must be taken into account as well.

The dry weight of samples obviously varies considerably between different sample sites. Consequently, different values can be found in the literature. According to Jain and Singh (2003) weights of 500-2000 kg per cubic metre have been observed for submerged sediments. Measurements in Poole Harbour varied significantly ($p<0.0001$) between sample locations as well, but were on average 672 $\mathrm{kg \cdot m^{-3}}$ in the Southern Bights. In the first 15 cm of the sediment the dry weight increased linearly ($r^2=0.89$; Figure 51) with depth, which is reasonable given that in the topmost layers the sediment is less compressed and consequently has a higher water content.

According to Gray *et al.* (1995), Diaz and May (n.d.) and May (2005), up to 3 million cubic metres of sediment accumulated by *Spartina* growth in Poole Harbour could under adverse conditions be released. Even based on a conservative calculation, an amount of 24 kg pure cadmium could still be released – in the scenario which is based on the most probable values an amount of 127 kg. Considering the mass of sediment replaced, these concentrations are fairly low. Given a steady nature of *S. anglica*'s die-back, comparably low concentrations would be released over a prolonged period of time. Together with the high persistence of cadmium in the water column, the contamination can be expected to disperse fairly rapidly and a large quantity would eventually be washed out of the estuary completely. In that case, it would likely not pose a considerable strain on the aquatic life. This also explains why the recent die-back (estimated to have caused the release of >4 million cubic metres) did not yield a measurable effect in the cores downstream.

However, if the die-back of *S. anglica* were to accelerate, for example triggered by the rising sea-level, the cadmium would be released in a much shorter time span, leading to a considerable peak of highly bioavailoable cadmium concentrations over a much shorter time span (compared to the previous szenario). This could cause a severe impact on the estuary, including nearby mussel farming. Cadmium can be deleterious to a vide variety of marine organisms (Kennish, 1997); for example, phytoplankton (Kayser and Sperling, 1980), zooplankton (Paffenhöfer and Knowles, 1978) or fish (*e.g.* Westernhagen *et al.*, 1980; Vetillard and Bailhache, 2005). Hence, the redistribution would have to be carefully monitored.

7.5 Conclusion

It appears that the metal contamination had no measurable impact on the *S. anglica* growth/die-back in Poole Harbour. However, it is probable that the die-back does, in turn, influence the cadmium concentrations in the harbour. Although there is a high uncertainty concerning which exact depth layers are affected by the die-back and which not, the data showed for the sample area that existing *Spartina* patches had clearly the highest cadmium concentrations, followed by areas where the plant used to grow. While the overall contamination in the Southern Bights rose only slightly in the last 80-100 years, areas where *S. anglica* still grows accumulated cadmium, while in the areas where *S. anglica* died back the cadmium accumulation ceased.

The data furthermore indicates that considerable amounts of cadmium have been released, typically the full mobile fraction. It can be assumed that the remaining patches are potentially at risk of further cadmium release as well, since they still store elevated cadmium concentrations (with an average of 0.81 $mg \cdot kg^{-1}$ in the first 60 cm approximately 120 % TEL-value). The quantity of sediment which could be released by *S. anglica*'s die-back is very high. If the die-back would be accelerated, for example triggered by the climate change, the cadmium concentrations in the estuary should be carefully monitored.

8 Summarising conclusions and outlook

The analysis of risks from metal contamination is severely limited by its diversity of approaches, and inconsistency is apparent in virtually all aspects in this field. Metal data is consequently too often incompatible. This study proposes a harmonised approach; both in regard to analytical procedures and environmental monitoring tools.

The absence of uniform guideline values makes it difficult to put the results of a particular study into context, since for the estimation of potential adverse effects sediment chemistry data alone are not sufficient. In North America researchers and environmental regulators have been working on sediment monitoring and controlling methods for some time. The research undertaken outside America is much less systematic; and the implementation of uniform and mandatory European SQGs in the near future is considered extremely unlikely. Multiple sediment quality guidelines have been proposed (at least 12 sets in Northern America alone). Various sets in use were evaluated and their suitability and limitations described in detail. SQGs of the TEL/PEL-subgroup are based on the scientifically defendable weight-of evidence approach and show a very low degree of variation; studies utilising appropriate methodology and either one of them are therefore to a high degree comparable. The most appropriate set (NOAA SQuiRTs) was selected for use in this study (*cf.* Chapter 2.2.6).

Various methods have been evaluated. For total pseudo concentrations, on which the quality standards of most European countries are based, the simple yet effective hotplate *aqua regia* delivers accurate and precise results (*cf.* Chapters 2.2.2 and 2.2.5). Regarding sequential and partial extraction schemes, the diversity of methods is even more significant. Owing to the different leaching strengths of the numerous suggested extractants, it is nearly impossible to compare different studies and a greater homogeneity of methods is urgently required. There is substantial amount of evidence indicating that sequential extraction schemes are generally unsuitable for precise analyses; while the faster, simpler and less error-prone partial extraction schemes have recently become more common (*cf.* Chapter 2.2.3-2.2.4). Such procedures can target the fractions which are potentially mobile (or bioavailable; depending on the chosen extractant) and are a vital supplement to stronger extraction procedures which are used for the more refractory forms. It should also be kept in mind that elements in different speciations might not be extractable by ammonium nitrate. However, although such schemes only indicate the theoretical mobility at a specific time and not the actual long-term migration in the sediment, it was demonstrated that an ammonium nitrate extraction, based on the standardised protocol DIN 19730, can predict the actual migration in the homogenous structure of the marshland rather well. In the vicinity of a linear channel, however, no correlation between the mobility and dispersion could be detected and the actual movement is much higher than the partial extractions generally indicated. The channel in the Christchurch study acts as an effective drainage system for both the landfill itself and the intertidal marshland in its sphere of influence. As mobile fractions are washed out very rapidly, leaving only the low mobile fractions behind, the DIN-procedure is only limitedly able to predict the migration of contaminants in the ground (*cf.* Chapter 4). In addition, it should not be misunderstood as a tool for the potentially bioavailable fraction, for which other PES procedures are available. However, if these limitations are appropriately considered, DIN 19730 constitutes a reliable method for the assessment of mobile fractions.

In previous studies, elevated levels of dissolved copper and zinc have led to a lower classification of the watercourses Bigge and Olpe (Germany), which are the main tributaries of the lake Biggesee. However, the concentrations in the sediment, which have been insufficiently considered in these studies, are also high and in some locations exceed probable effect concentrations. As these metals could, for example following an acidification of the water, easily get into solution again and superimpose on the already elevated concentrations in the watercourses, there is a risk that the annual environmental monitoring reports, which are based on analyses of water and suspended particles, could underestimate the hazardous potential of metals and metalloids in this region (*cf.* Chapter 3).

To evaluate the hazardous nature of the metal concentrations in Poole Harbour, a risk potential index, a dimensionless indicator incorporating both total concentrations and mobile fractions; has been calculated (*cf.* Chapter 5.3.7). In order to make it compatible with freshwater, marine and estuarine environments a modification to the original method is proposed. Although compared to the Southern Bights, the Wareham Channel subsection typically showed higher concentrations in the total content analyses, the risk potential was comparable in both subsections of the estuary. Typically, the concentrations of all analysed contaminants were clearly highest in the secondary embayment Holes Bay (*cf.* Chapter 5.3.2), where intense industrialisation combined with poor flushing characteristics led to threshold effect levels being exceeded for all metals except chromium. Some limited areas in Holes Bay, however, showed surprisingly low concentration, which explains the disputed outcomes in the study by PDE (1992). As Langston *et al.* (2003) suggested, these sediments are indeed not typical. The vast majority of sediments in Holes Bay cannot be classified as chemically clean.

The management and monitoring of dredging activities is critical (Sofonia and Unsworth, 2010). Since initial dredging work in Holes Bay has just started, systematic testing will be of great importance in the near future to evaluate the degree of environmental impact, in particular when these works will eventually intensify and construction of the bridge itself commences. It is clear that a considerable redistribution of contamination will probable take place owing to elevated turbidity, washing out and oxidisation processes. Therefore, the extent as well as the effects on aquatic life should be carefully monitored, both regarding immediate impacts (for example, by monitoring of the water column and biota tests based on short-term reactions like bioluminescence of bacteria) as well as long-term effects over a prolonged period (for example, by continued sediment sampling and long-term biota tests based on strong bioaccumulating species like mussels). Close collaboration between the Poole Harbour Commissioners, Bournemouth University, Environment Agency, Dorset Wildlife Trust and other environmental protection agencies operating in the estuary would help monitoring and reducing possible adverse effects on aquatic life.

Furthermore, this study found elevated levels of some contaminants in the topmost layers. Although the measured mobility is comparably low, small changes of the pH-value can have a profound effect on the adhesion to the sediment. Extensive tests of the likelihood of an acidification as well as its effects on the contamination in the complete sampling area would be a beneficial continuation of this research project. The data delivered by this project can also been implemented in sedimentation transport models, like those produced by the SCOPAC, or the TELEMAC simulation models used by HR Wallingford (2004). A hydrodynamic model updated in that way, could predict the redistribution of contamination under implementation of various factors, including, for example, dredging operations and/or various degrees of *S. anglica* die-back and/or climate change. In addition, it would also be advantageous to conduct a similar survey for organic contaminants in the estuary. Although not as persistent as metals, contaminants like pesticides, herbicides and hormones have recently gained increasing attention in the scientific community.

Two studies came to substantial different sediment accretion rates in Poole Harbour: A study by Cundy and Croudace (1996), based on ^{210}Pb analyses, stated a rate of 8.4 mm·yr^{-1}, while the more recent study by Warneke (2002), based on nuclear power plant and weapons residue, stated a rate between 10.3 and 12.1 mm·yr^{-1}. If both rates were applied to the only singular, clearly localisable point source in Poole Harbour, they came to reasonable, yet very different explanations: Cundy and Croudace’s data coincides very well with the time between the beginning of World War 2 and the closure of these facilities 20 years later. The data by Warneke on the other hand suggest that the contaminations are caused by the subsequent research on anti-corrosive agents, which would explain the elevated levels of cadmium, tin and lead. Data from the *Spartina anglica* study suggests that the sedimentation rate provided by Warneke is more accurate, but without more data it is difficult to reliably determine origins. In order to make a connection between depth of the sediment and the age, and so to determine the origins and sources of contaminations which a greater certainty, an accurate and proven sedimentation rate is indispensable. Consequently, intensive research will be required to evaluate the differences between the age determination approaches, and to define a reliable, proven procedure.

Cobalt proved to be a valid tool for the evaluation of the efficiency of normalisation schemes. It was found that in such finely grained environments, granulometric normalisation schemes did not yield any substantial effect, while normalisations based on iron-ratio reduced the variance considerably. Further studies will have to quantify which grain size distributions warrant the application of a granulometric approach and from which grain size distributions the application of such a time intensive scheme becomes unnecessary; which will safe considerable amount of time and effort in future projects dealing with very fine grained sample materials (*cf.* Chapter 6).

No impact of the metal contamination on the *S. anglica* growth/die-back could be detected in Poole Harbour. However, the die-back, in turn, appears to have influenced the cadmium concentrations in the harbour: while the overall contamination in the harbour rose in the last 80 years, with most of the cadmium appearing to have entered the estuary through Holes Bay, a large quantity of the cadmium stored in the sediment by *S. anglica* was washed out rapidly after release. It must furthermore be assumed that the remaining patches are potentially at risk of further cadmium release as well, as the die-back continues. A precise catalogue of the vanishing species (like *Spartina anglica* along England’s south coast or *Avicennia marina* in Australia) and the content of the accumulated sediment will help determining the degree of potential secondary contamination (*cf.* Chapter 7).

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10 Appendices

10.1 Appendix I – list of definitions

term	**definition**	**source**
accuracy [of the methodology]	conformity of the measured results with the actual concentrations in the sediment, determined by the →recovery rates of →certified reference materials	Hübner and Haslam, *submitted*
anthropogenic	substances or effects introduced by human activities	--
bioavailability	"a relative measure of that fraction of the total ambient metal that an organism actually takes up when encountering or processing environmental media"	Luoma and Rainbow, 2008
certified reference material (CRM)	"reference material, accompanied by an authenticated certificate, having for each specified quantity a value, measurement uncertainty, and stated metrological traceability chain"	ISO, 2004
climate change	"a change in the state of the climate that can be identified (…) by changes in the mean and/or the variability of its properties, and that persists for an extended period, typically decades or longer."	IPCC, 2007
conservative pollutants	stable chemicals which are not, or only on a very large timescale, subject to bacterial attack	Clark *et al.*, 1997
comparability	"the ability to compare results meaningfully wherever they originate"	Ellison *et al.*, 2003
contaminant	"an undesirable substance not normally present, or an unusually high concentration of a naturally occurring substance, in water, soil, or other environmental medium."	Horton, n.d.
contamination	"the presence of a substance where it should not be or at concentrations above background"	Chapman, 2005
dispersion index	a relative measure of dispersion of an element through a transect, under ideal conditions correlated with the →mobility of that element	Hübner *et al.*, *in press*
ecological risk assessment (ERA)	"a process that evaluates the potential for adverse ecological effects occurring as a result of exposure to →contaminants or other stressors"	Chapman and Wang, 2000

term	**definition**	**source**
estuary	“a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage.”	Cameron and Pritchard, 1963
heavy metals	“there is no authoritative definition to be found in the relevant literature”	Duffus, 2002
load	“mass of metal (in units of g or kg, for example) within a reservoir (*e.g.* atmosphere, sediment, water, *etc.*)”	Luoma and Rainbow, 2008
managed realignment	“a form of soft engineering in which land is allowed to flood at each high tide to generate new salt marsh”	French, 1997
metal	“an element that has a lustrous appearance (high reflectivity for light), is a good conductor of electricity and heat, and usually enters chemical reactions as a positive ion (cation)”	Luoma and Rainbow, 2008
metalloid	“an element with chemical properties intermediate between those of a metal and non-metal, as defined by its location in the periodic table”	Luoma and Rainbow, 2008
mobile fraction	the amount of the total concentration, which is electrostatically weakly bound to the sediment and therefore easily remobilised, measured with →partial extraction schemes	Schramel *et al.*, 2000
no observed effect level (NOEL)	“Greatest concentration or amount of a substance, found by experiment or observation, that causes no alterations of morphology, functional capacity, growth, development, or life span of target organisms distinguishable from those observed in normal (control) organisms of the same species and strain under the same defined conditions of exposure.”	Nic *et al.*, 2006
normalisation	“the attempt to compensate for the natural variability of trace metals in sediments so that any anthropogenic metal contributions may be detected and quantified”	Loring, 1991
partial extraction scheme (PES)	a weak or diluted acid or a chelating agent is used to remove metals from a single particular fraction	Haslam and Tibett, 2004
precision [of the methodology]	consistency of the results within the applied methodology, defined by the variation between the →replicates	Hübner and Haslam, *submitted*
probable effect level (PEL)	“value (…), above which adverse biological effects are usually or always observed”	CCME, 1995

term	definition	source
pollution	“→contamination that results in or can result in adverse biological effects to resident communities. All pollutants are →contaminants, but not all contaminants are pollutants.”	Chapman, 2005
pollution [marine]	“the introduction by man, directly or indirectly, of substances or energy into the marine environment, resulting in such deleterious effects as to harm to living resources, hazards to human health, hindrance to marine activities including fisheries, impairment of quality for use of seawater, and reduction of amenities”	GESAMP, 1982
possible effects range (PER)	values “between the →TEL and the →PEL, within which adverse effects are occasionally observed”	EC and MDDEP, 2007
recovery rate	the percentage of the →total concentration, which is extractable with a given method from a →sample or →certified reference material	--
replicates	identical sub-samples of the original →sample, undergoing identical analytical processes	--
risk [ecological]	“the probability of an adverse effect/event occurring to humans or the environment following exposure to a →trace metal, under defined conditions”	Luoma and Rainbow, 2008
risk potential index (RPI)	a dimensionless index describing the potential for adverse effects associated with an element; based on →total concentrations, →mobile fractions and →sediment quality guideline values	Bauer *et al.*, 1996
sample	sediment extracted from a given depth at a given location	--
sediment quality guidelines (SQG)	“numerical limits or narrative statements recommended to support and maintain designated uses of the aquatic environment.”	CCME, 1995
semi-metal	→ metalloid	--
sequential extraction scheme (SES)	at least two, usually more, consecutively applied →partial extraction schemes, sorted increasingly by their dissolving ability	NCR, 2003
success [of an invasive species]	“if it colonizes a wide geographical range, exists over a range of localized environmental conditions, and/or forms a dominant component of the habitat into which it spreads”	Thompson, 1991
threshold effect level (TEL)	value above which “adverse biological effects are occasionally observed”	EC and MDDEP, 2007

term	definition	source
total concentration	the amount of an element in a given →sample, including both natural and →anthropogenic sources	--
trace metal	“often used loosely without strict definition, although there is the implication that the metal is present in only ‘trace’ concentrations” (*cf.* →heavy metals)	Luoma and Rainbow, 2008
validation	"Confirmation by examination and provision of objective evidence that the particular requirements of a specified intended use are fulfilled."	King, 2002
weight-of-evidence approach	a statistical procedure to match biological effects with chemical concentrations, based on data from analyses of field-collected samples	Hübner *et al.*, 2009
wetlands	“whatever a competent expert says it is”	Haslam, 2003
	“The minimum essential characteristics of a wetland are recurrent, sustained inundation or saturation at or near the surface and the presence of physical, chemical, and biological features reflective of recurrent, sustained inundation or saturation.”	NRC, 1995

10.2 Appendix II – Corer

A wide range of coring devices has been developed, tested and recommended by various authors (University of Arizona, n.d.). Most corers are variations of a limited number of designs, most commonly the gravity-, piston- and vibro-corer (Smol, 2002). During this project three different corer designs have been used, each carefully selected to deliver the best result for the according environment (*cf.* Chapter 2.1.2, particularly Table 1).

10.2.1 Beeker sampler (type 04.29.SA)

The Beeker sampler is based on the piston corer design by Wright *et al.* (1984), and has an additional inflatable valve at the bottom, minimising disturbances and the loss of sample material (Temmerman *et al.*, 2004). In soft sediments core-compression is a severe problem with many designs (Blomqvist, 1985; Crusius and Anderson, 1991); the Beeker sampler has a core compression of only 4-5 % (Eijkelkamp, n.d.), which is very important for the later dating process (*cf.* Chapter 5.2). This design also provides a free water flow though the core-tube and avoids the common problem of many designs that a bow-wave disperses the top sediments before the corer hits the bottom (Cumming *et al.*, 1993; Glew *et al.*, 2001).

10.2.2 Russian peat corer, Russian auger

This is a semi-open, side-filling design. The corer is inserted into the sediment to the desired depth. The chamber is then rotated clockwise 180°, the cutting edge of the chamber cuts a sediment core and closes the chamber. The design is very robust and can gently be hammered into the sediment. This sampler design is ideally for dry or saturated, but not dripping wet samples. Additionally, the hinge is likely to jam in sandy environments.

10.2.3 Bigge corer

This design is a simple self-made auger nicknamed Bigge corer, owing to its first successful application in sediments of the Bigge (Germany). The corer proved to be very suitable for sandy wet sediments and works best under slightly flooded conditions (5-30 cm depths). Its main compartment is a slender, but stable tube with a sharp lower end. The head has been reinforced to allow the application of pressure (*i.e.* hammering) and also includes an O-ring. Like the Russian auger, the Bigge corer can be forced into the sediment even if it consists of very hard sandy fractions.

The whole construction weights less than 1 kg (excluding the hammer). Similar to the Beeker corer the free water flow in the tube prevents a bow wave and the dispersion of the top sediment, but friction can cause core compression during insertion. After full insertion the head can be sealed airtight, the resulting vacuum in the upper part as well as frictional resistance prevent sample loss except in the deepest part (depending on sediment characteristics 1-4 cm). This design does not work with extremely sandy sediments and only to a limited degree with dry samples. The corer's main areas of application are wet clay-sand mixtures in the intertidals and – owing to its weight – remote and difficult to reach sampling locations. It was primarily used were the other corers could not operate due to unfavourable bottom conditions and/or logistical limitations. This design has also been successfully used diver-operated in a smaller version; however, while core compression was very low, sample loss at the lower end may be substantial under water.

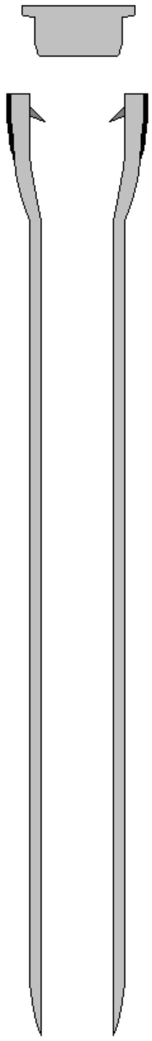


Figure 52: The Bigge corer design

10.3 Appendix III – Further details on analytical methodology

10.3.1 *Aqua regia*-extraction protocol

Based on McGrath and Cunliffe (1985), ISO (1995), Anon. (2005), Hübner and Haslam (*submitted*).

step	**original procedure** *(volume-based approach, lower sample:solvent relation)*	**modified procedure** *(weight-based approach, higher sample:solvent relation)*
1	weigh 0.500 g sample material into test tube	weigh 0.250±0.010 g sample material into test tube, record precise weight
2	add 8 ml HCl (36 %) and 2 ml HNO_3 (70 %)	add 9 ml HCl (36 %) and 3 ml HNO_3 (70 %)
3	allow to digest overnight at room temperature or for 2-3 h at 60 °C	allow to digest for at least 6 h at 60 °C (for reactive samples temperature must be increased very slowly), mix regularly during the first hour
4	increase temperature to 105 °C for 1 hour	increase temperature to 105 °C for 1 hour
5	increase temperature to 140 °C until samples are dry	increase temperature to 130 °C until samples are dry
6	allow to cool	allow to cool and record weight
7	add 12.5 ml of HCl (20 %)	add 5 ml of HCl (25 %)
8	increase temperature to 80 °C for 20 min, afterwards mix solution with a vortex mixer	increase temperature to 80 °C for 20 min, mix regularly during the process
9	--	add 10 ml of deionised water

10	--	heat at 80 °C for 20 min, mix afterwards
11	--	allow to cool and record weight
12	filter mixture through a Whatman no. 40 filter paper into a volumetric flask	filter mixture through a Fisher scientific no. 210 filter paper into sealable tubes
13	make up volume with deionised water	calculate dilution factor based on the recorded weights
14	analyse solution with an ICP	analyse solution with an ICP

10.3.2 Ammonium nitrate extraction protocol

Based on DIN (1993), DIN (1997) and Traub and Scharf (2001).

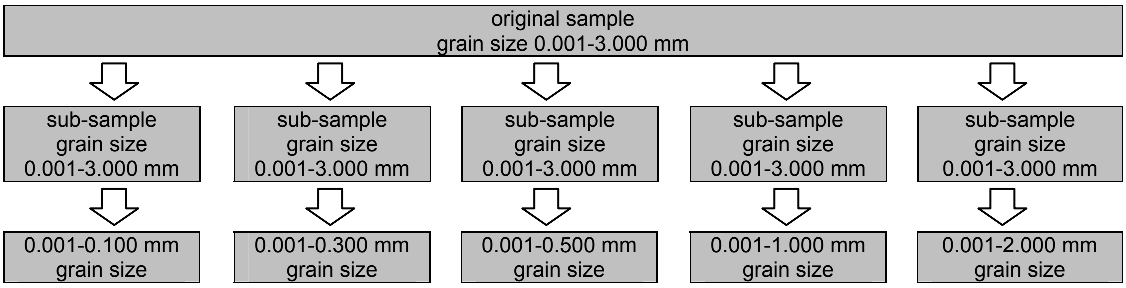
step	**procedure**
1	weigh 2.0 g sample material into test tube
2	add 5 ml 1 mol/L ammonium nitrate solution (NH_4NO_3)
3	shake for 2 h
4	allow the undissolved residue to settle
5	filter supernatant into sealable tubes
6	acidify with 50 µl nitric acid
7	analyse solution in ICP

10.3.3 Application of different sieving regimes

Type 1: Impact of mesh-size on effectiveness of *aqua regia*

The complete sample is separated into 5 identical sub-samples; each sub-sample is grinded until (nearly) all material fits through the according mesh-size (100, 300, 500, 1000, 2000 µm).

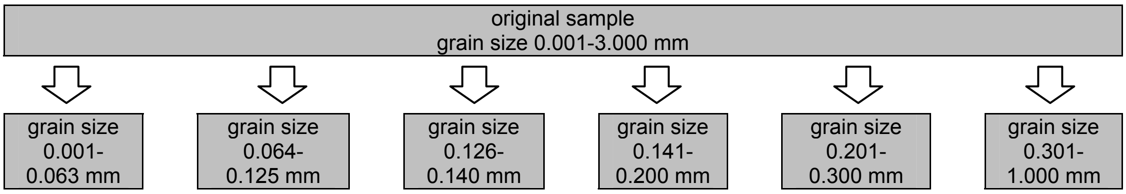
➔ Used for the determination of optimal mesh size (which mesh size yields highest accuracy and precision for the subsequent *aqua regia* extraction).



Type 2: Analysis of the different size fractions

Unlike type 1 the complete sample is separated without any force into 5 different grain size fractions (using 63, 125, 140, 200 and 300 µm and 1000 µm mesh sizes), so analysing the different sizes independently.

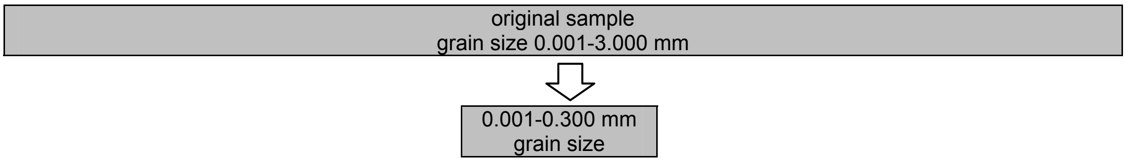
➔ Used for the normalisation procedure (which quantities are bound to a specific grain size fraction).



Type 3: Total content analyses

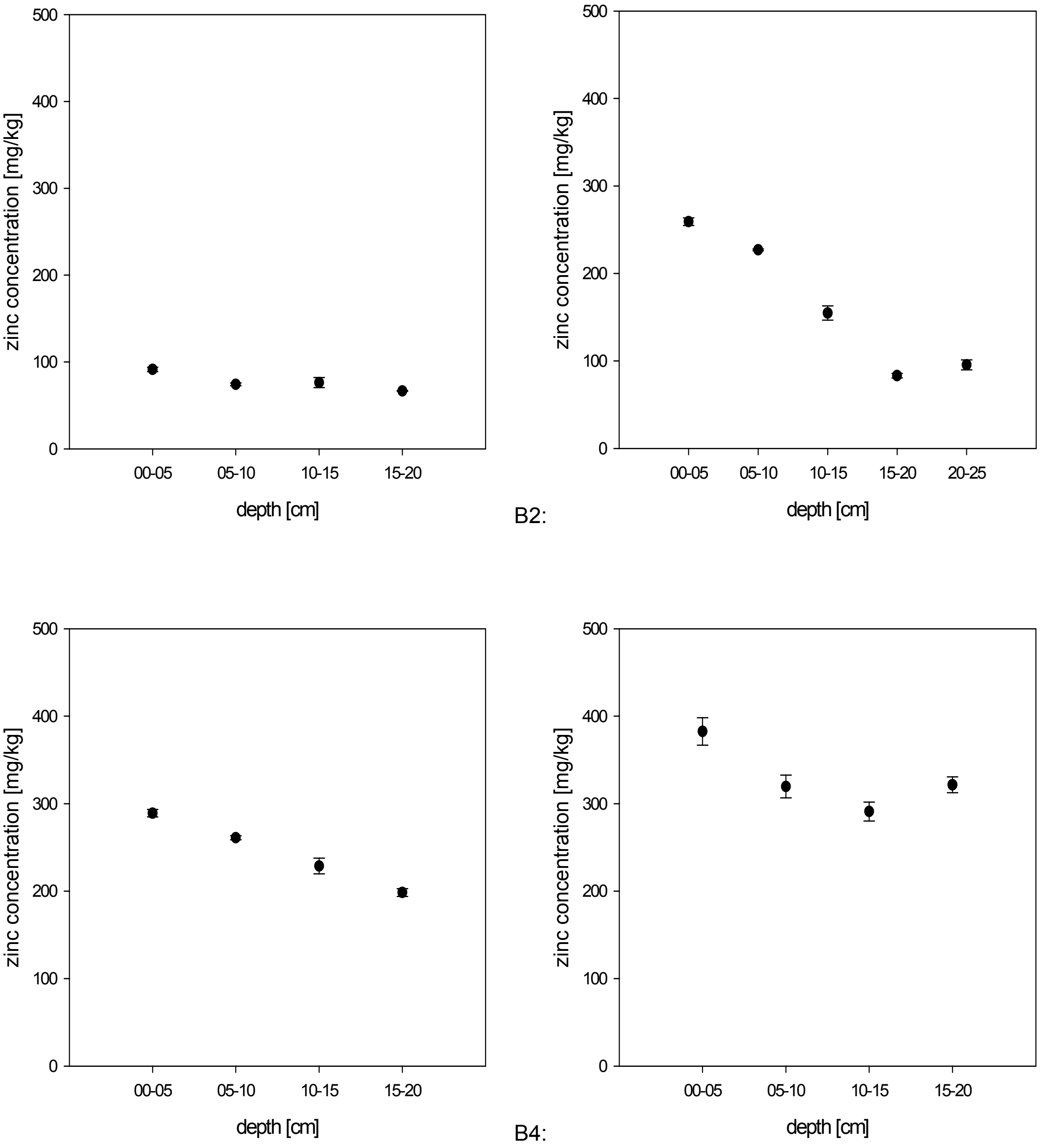
All samples are grinded until the complete sample material fits through a 300 µm mesh, which has shown the best efficiency in the first test (type 1).

➔ Used for the determination of total contamination (TCA; *cf.* Chapter 2.2.2).



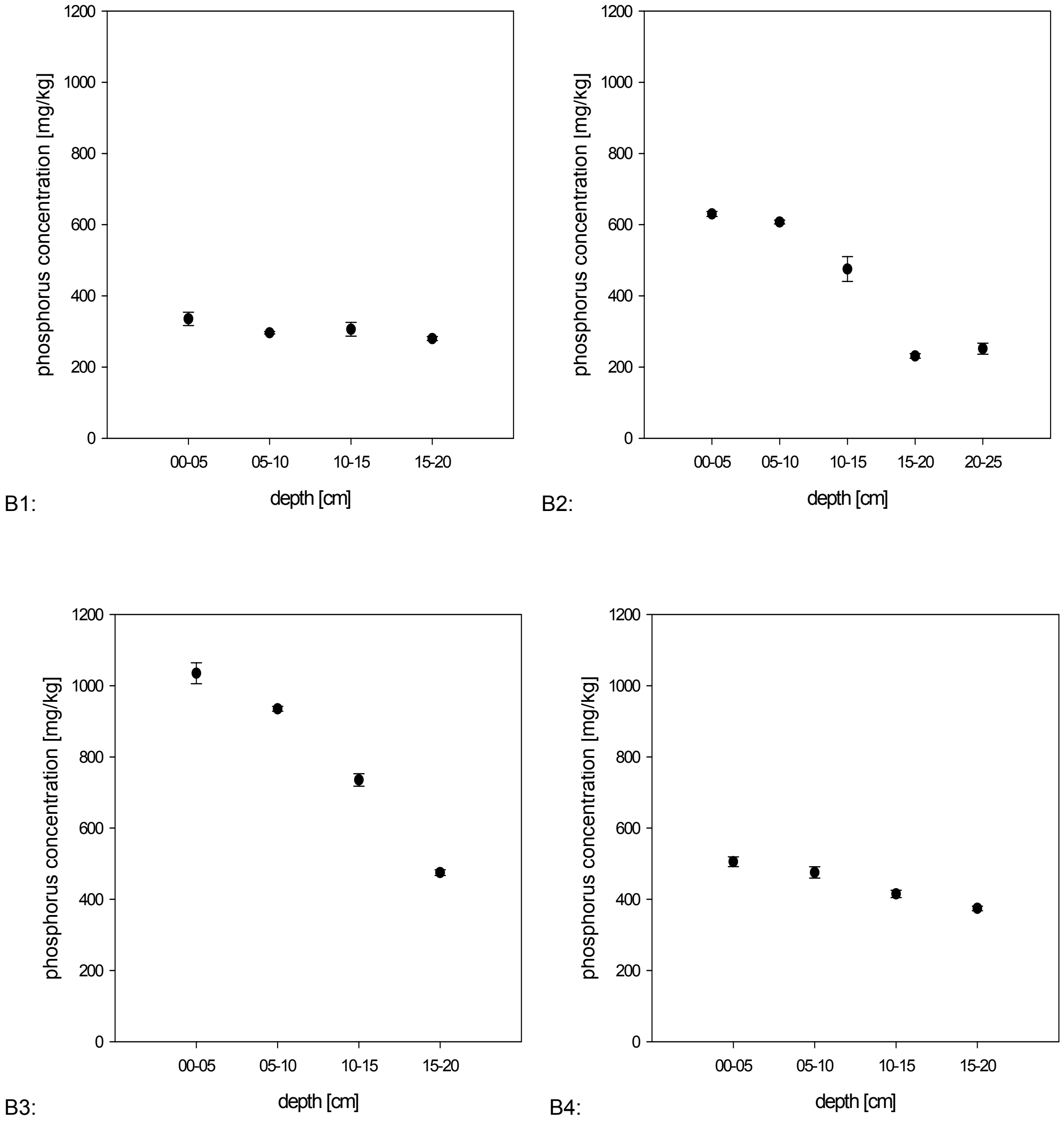
10.4 Appendix IV – Ancillary data

10.4.1 Depth profiles of contaminants in the Bigge



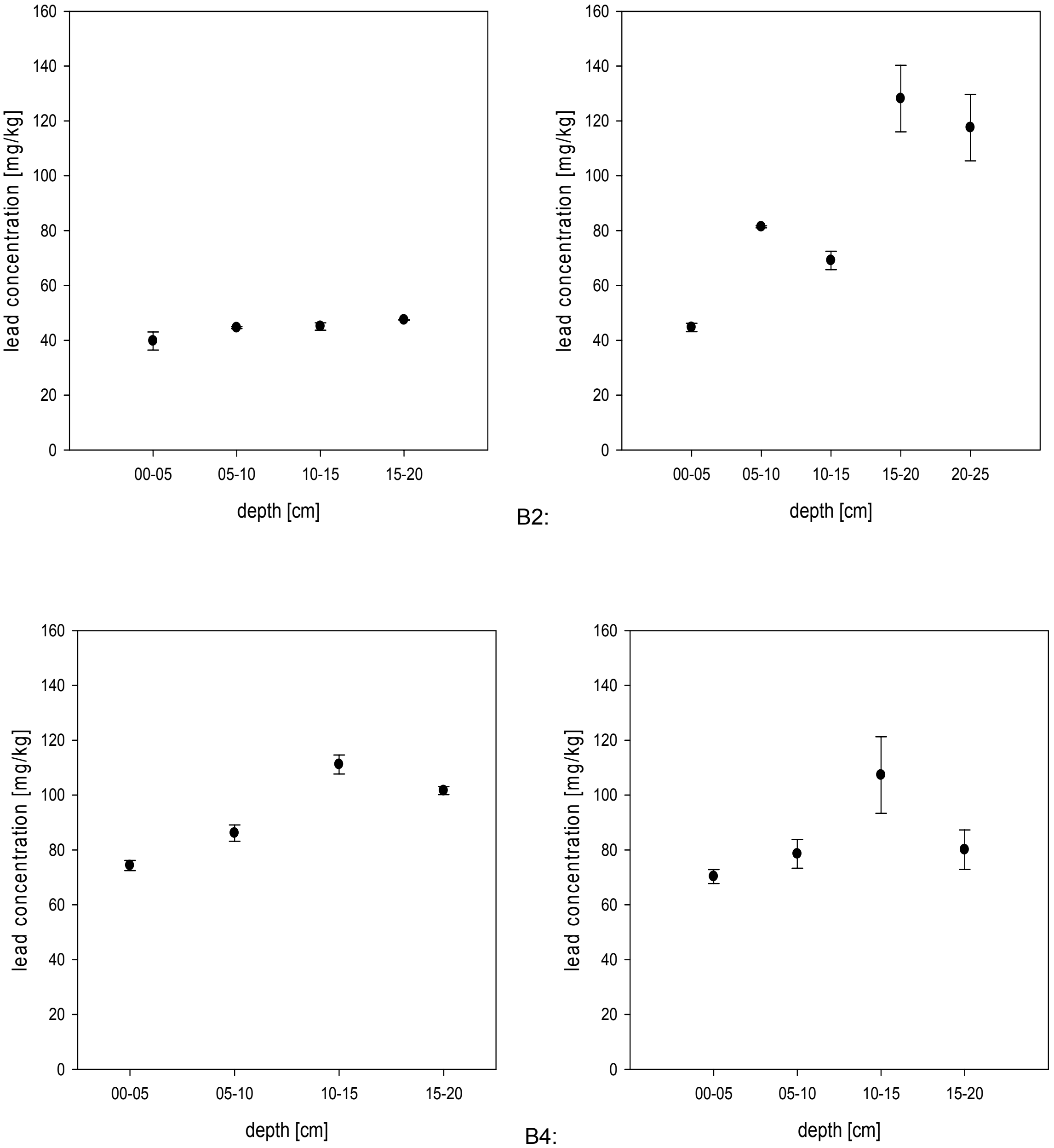
B1: B2: B3: B4:

Figure 53: Concentration of zinc [mg·kg^{-1}] in the Bigge, whiskers indicate standard error of the mean



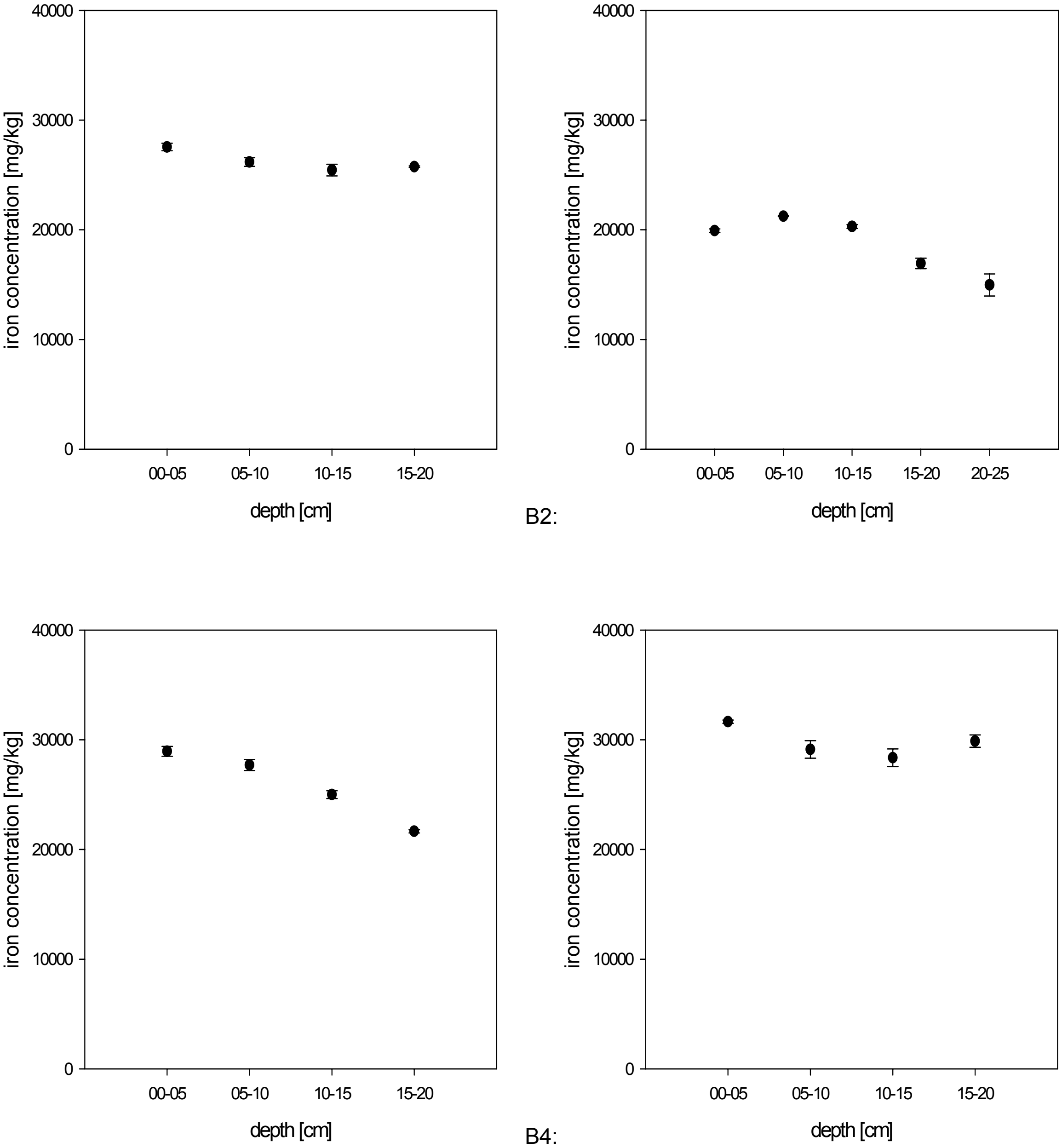
B1: B2: B3: B4:

Figure 54: **Concentration of phosphorus [mg·kg^{-1}] in the Bigge, whiskers indicate standard error of the mean**



B1: B2: B3: B4:

Figure 55: **Concentration of lead [mg·kg^{-1}] in the Bigge, whiskers indicate standard error of the mean**



B1:

B2:

B3:

B4:

Figure 56: Concentration of iron [mg·kg^{-1}] in the Bigge, whiskers indicate standard error of the mean

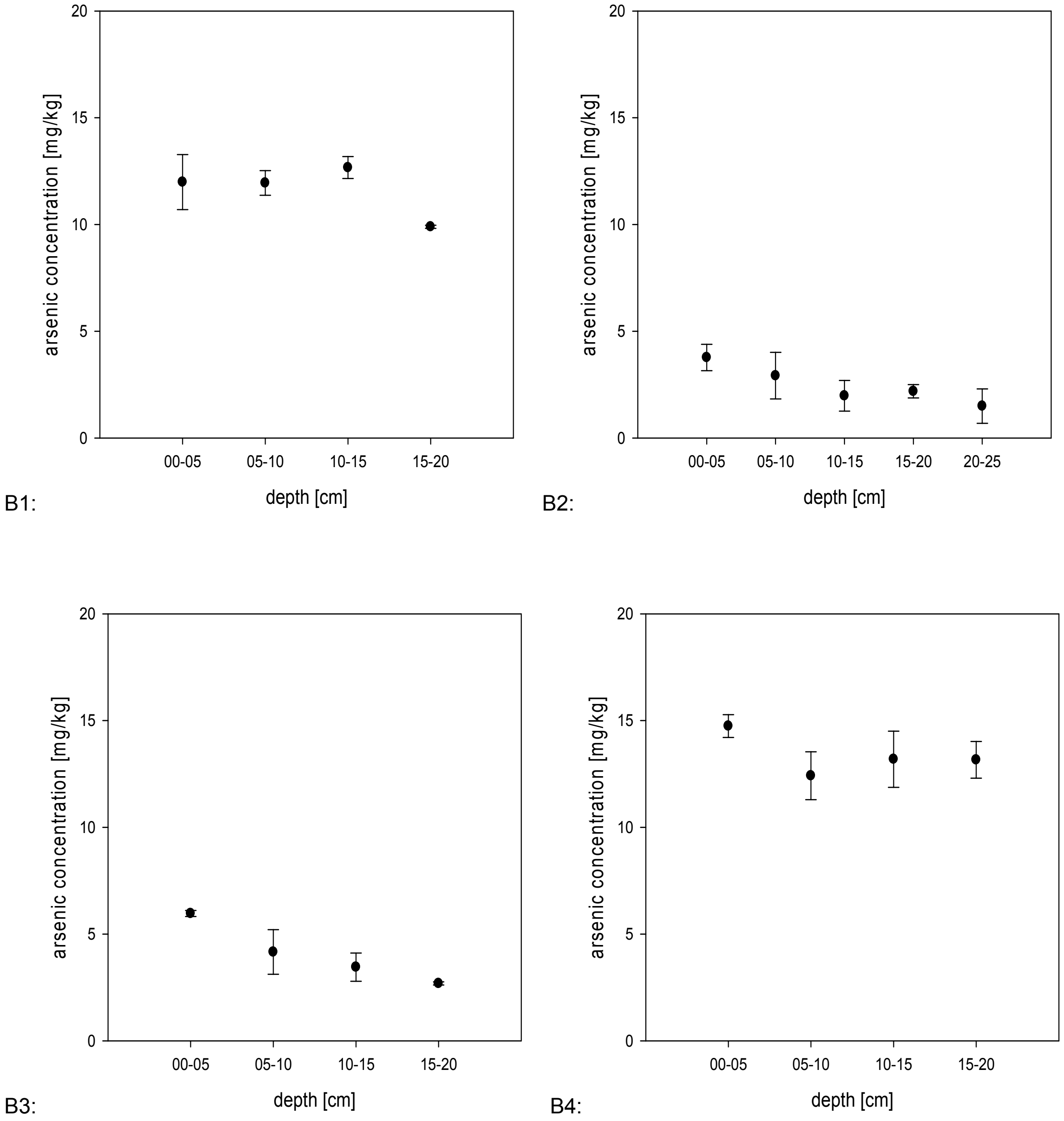
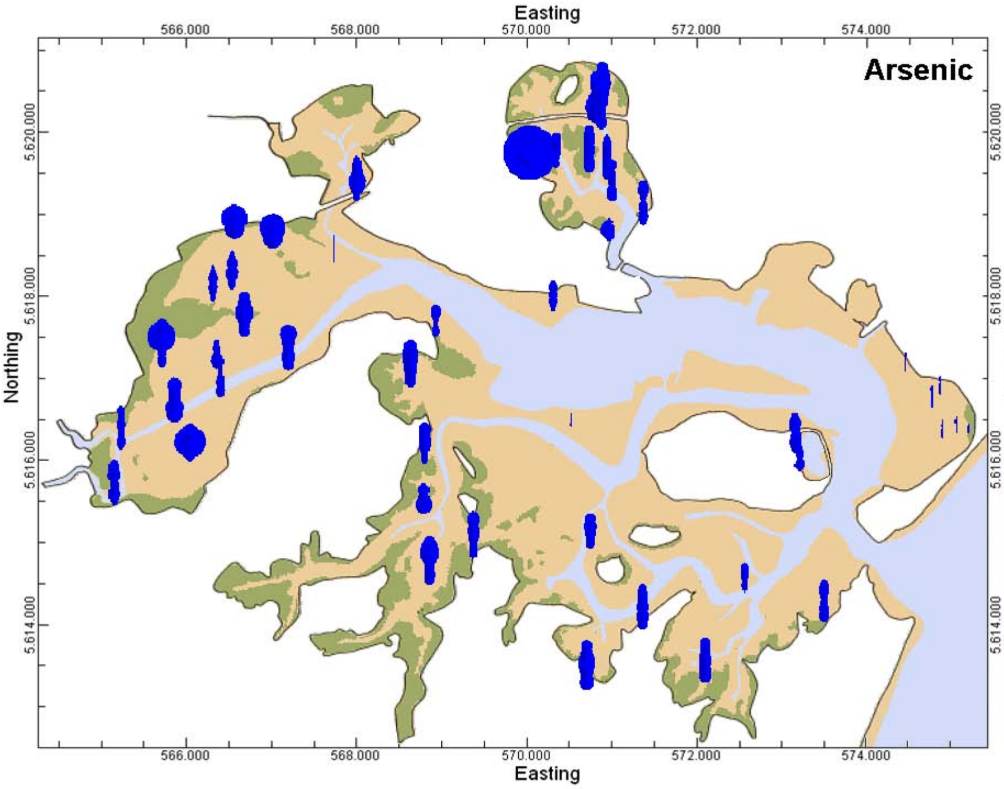
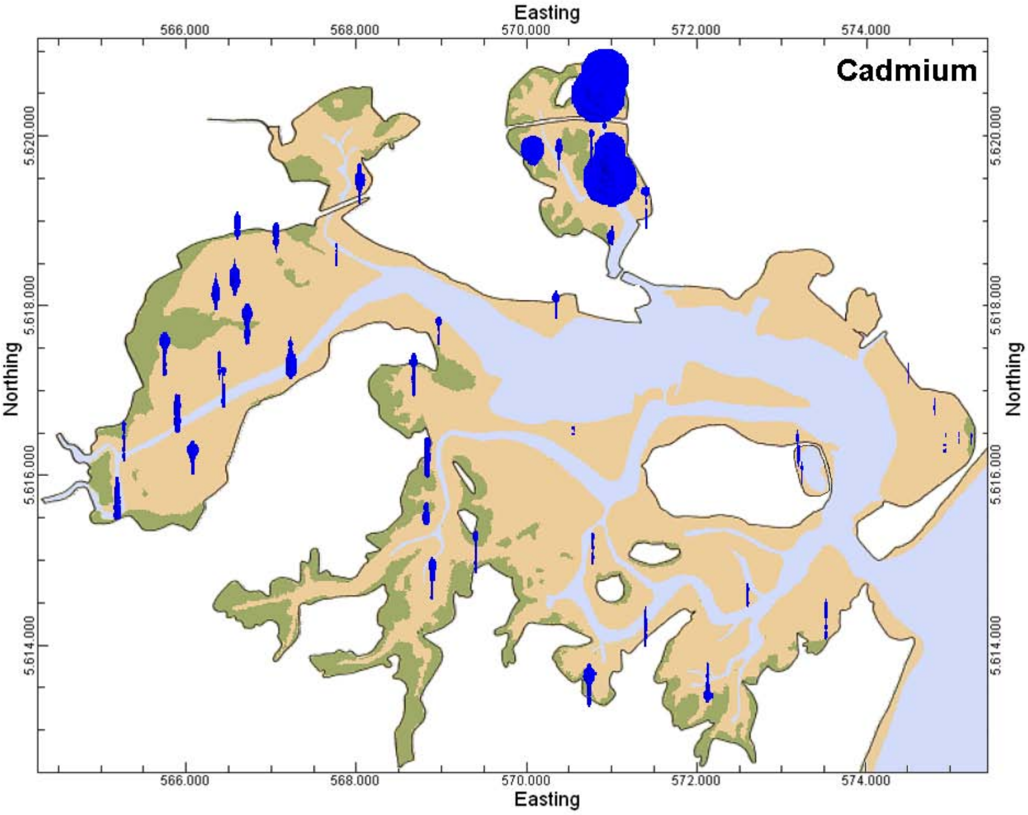


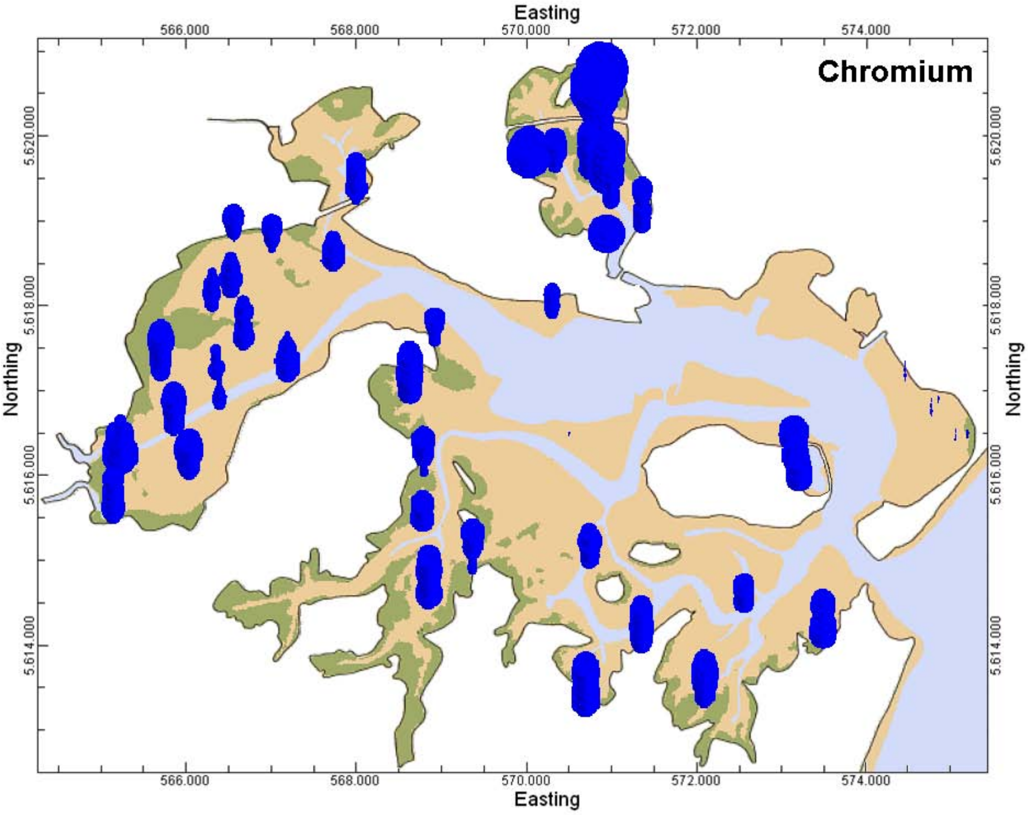
Figure 57: **Concentration of arsenic [mg·kg^{-1}] in the Bigge, whiskers indicate standard error of the mean**

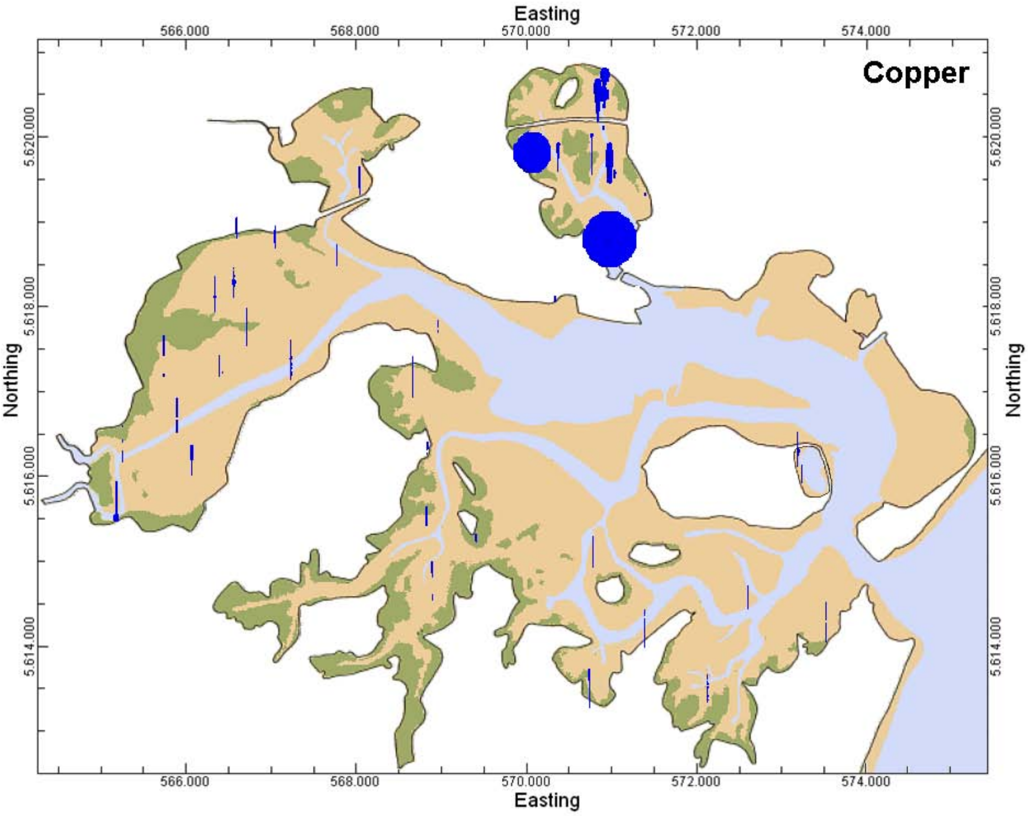
10.4.2 Three dimensional concentrations profiles of Poole Harbour

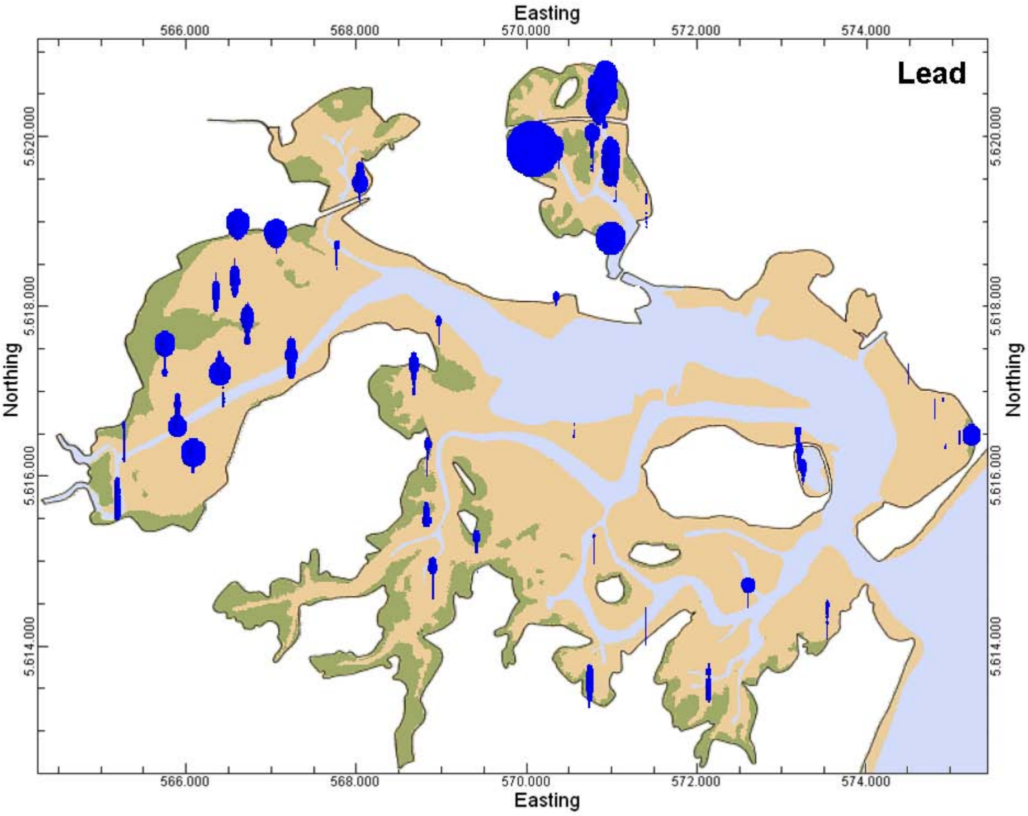
The following maps (base map based on UTM Zone 30U and adapted from Gray, 1985; copyright NERC and reproduced with permission of the CEH) show the relationship with depth (5 cm resolution) and represent a variation of the maps in case study 3 (Figure 24-Figure 30). Similar to the format used in case study 2 (Figure 15), the radius of the column indicates the concentration in the according depth layer; while the maps used in case study 3 show the average concentration per core. Compared to the plots below that format includes fewer details, but maintains a high degree of clarity and replicability. Therefore, it was implemented in the main study. While the plots below provide more detail, they can partly be very difficult to read out, particularly in areas where concentrations vary strongly (either between depth layers of the same core or between different cores in the sampling zone). For example, the high cadmium concentrations in the top layers of certain cores in Holes Bay (*cf.* Figure 36) cover the lower concentrations observed in greater depths.

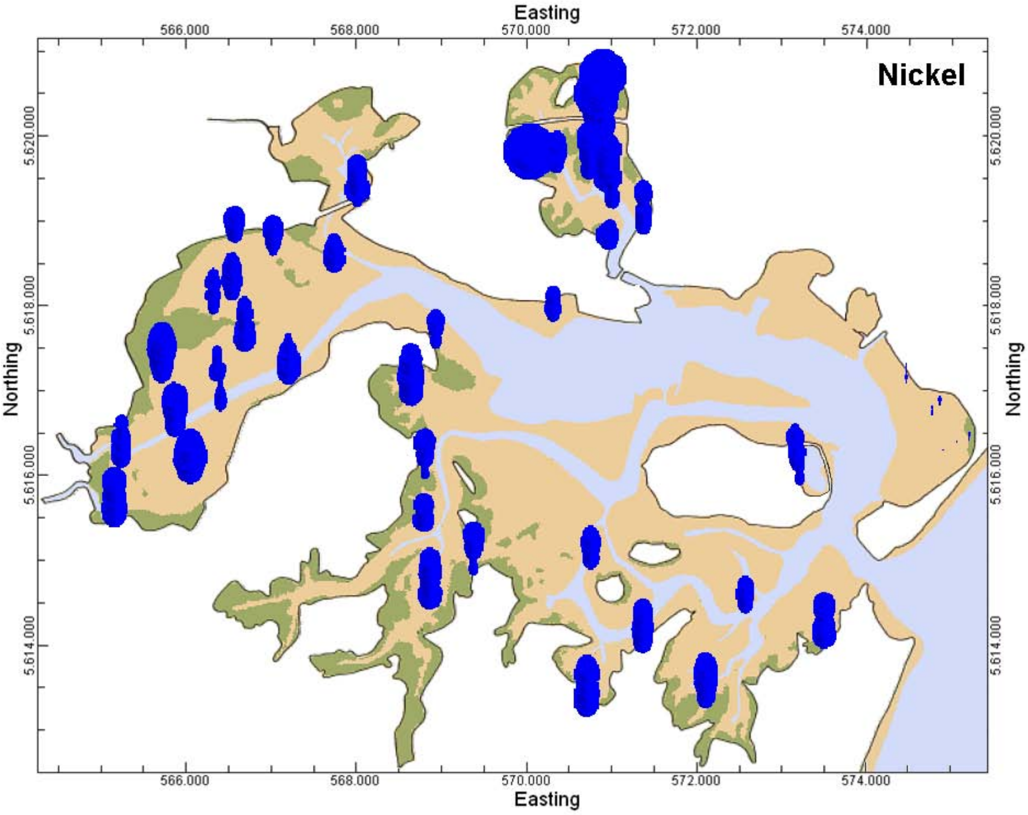


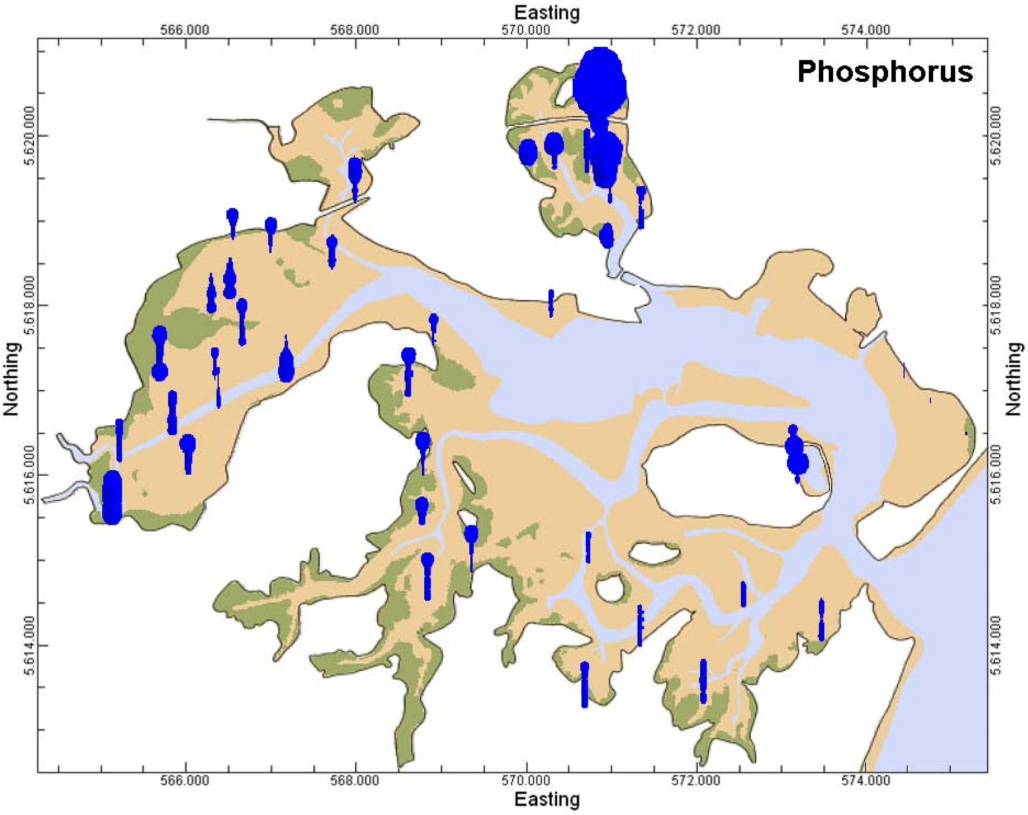

Cadmium
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000

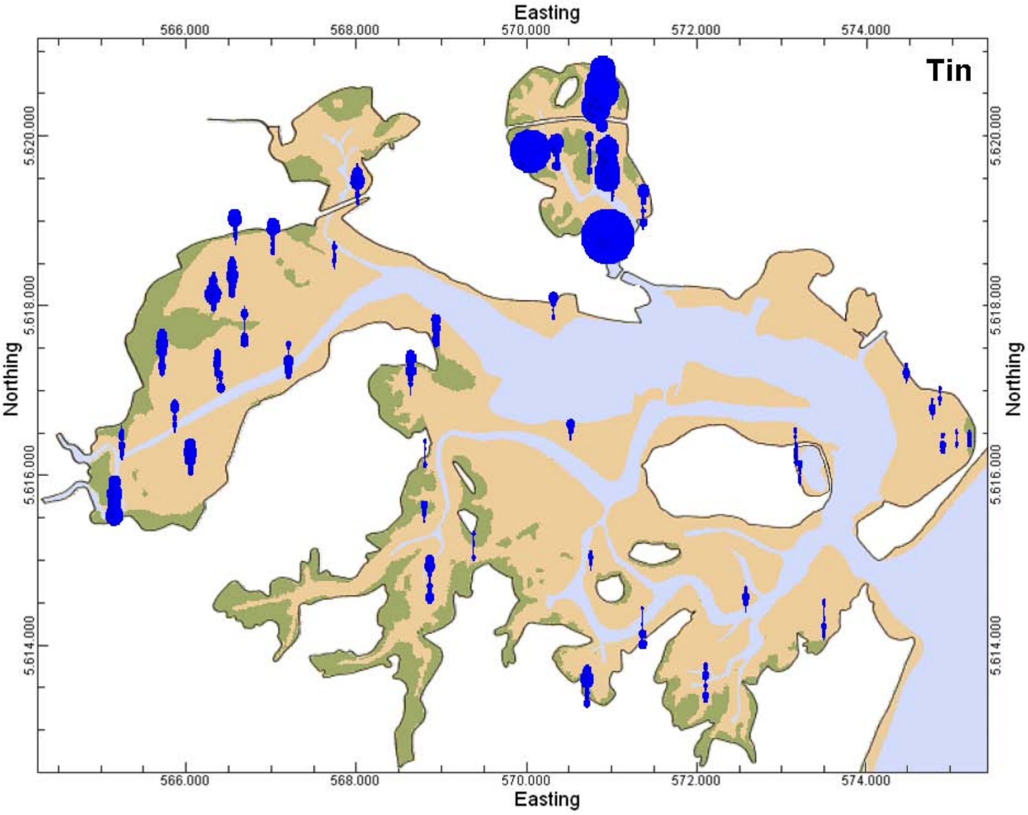

Chromium
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000

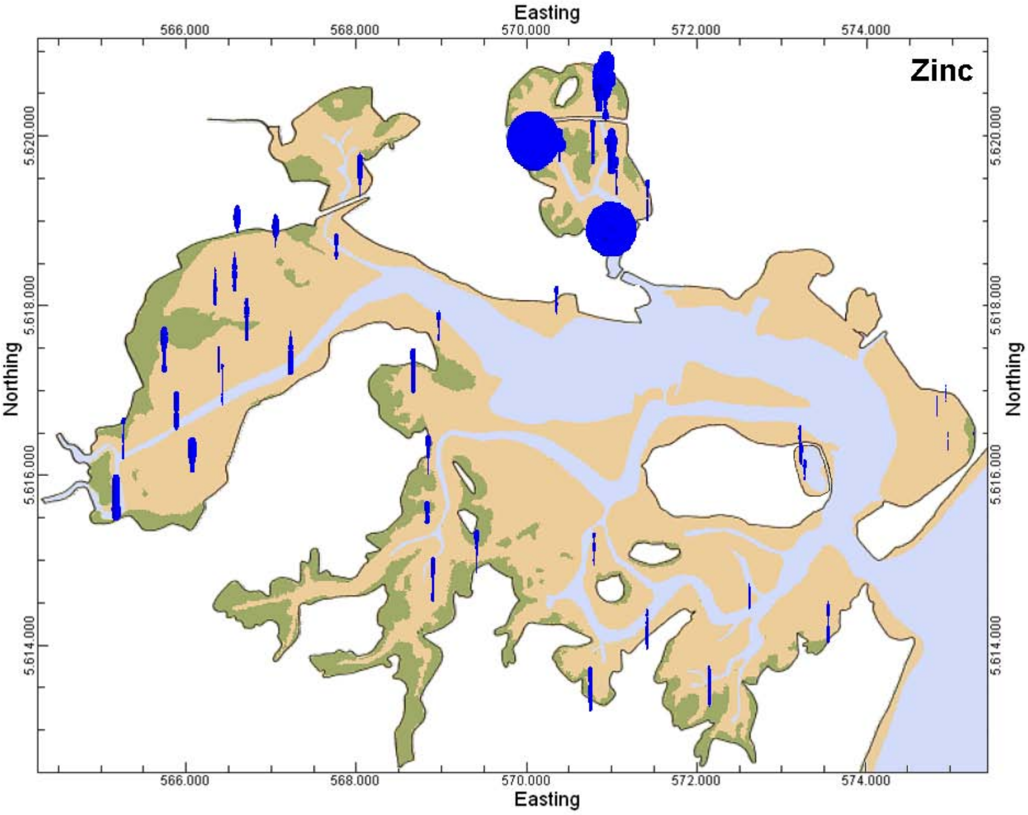

Copper
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000


Lead
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000


Nickel
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000


Phosphorus
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000


Tin
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000


Zinc
Easting
566.000
568.000
570.000
572.000
574.000
Northing
5.620.000
5.618.000
5.616.000
5.614.000

10.4.3 Complete contamination profiles of Brownsea Island

The literature recommends using sites with low turbation to get reference samples with a clear profile (Smol, 2002). Only one site offered such conditions: Brownsea Island lagoon. A sea wall was constructed on the eastern side of in order to drain St Andrew's Bay. The map-material shows that at least a provisional construction was already existing in 1811 (Makenzie and Hurd, 1829).

The area sheltered by this wall resulted in undisturbed reference samples; therefore, the complete processed data of core P53 was included in the appendix, both absolute and normalised.

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Survey map with
the permission of
the Controller of
Her Majesty's
Stationery Office
© Crown Copyright

Figure 58: Brownsea Island (sampling location of core P53 marked as red dot)

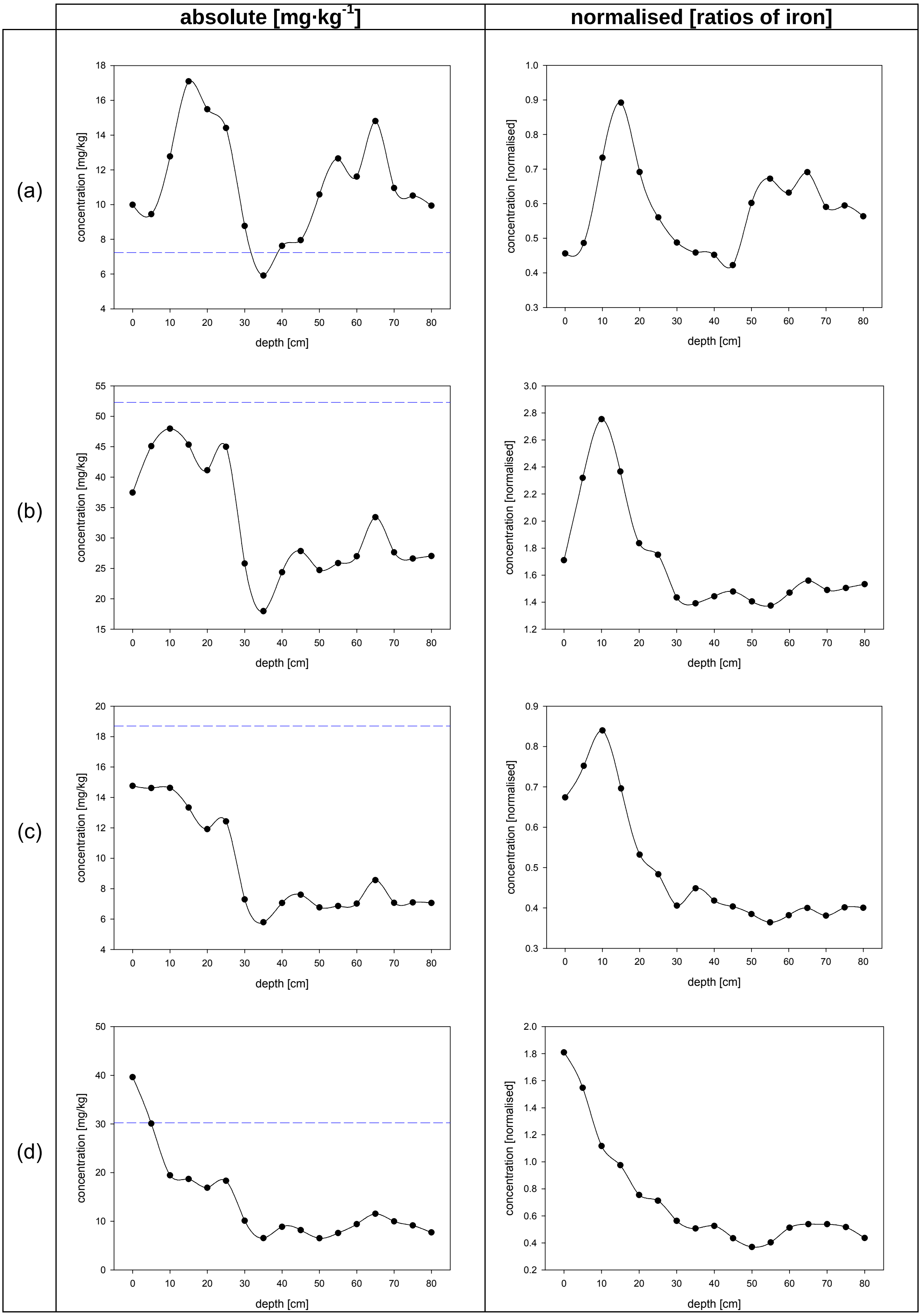


Figure 59: Absolute and normalised concentrations of arsenic (a), nickel (b), copper (c) and lead (d) in the Brownsea Island lagoon (reference lines indicate TEL-values)

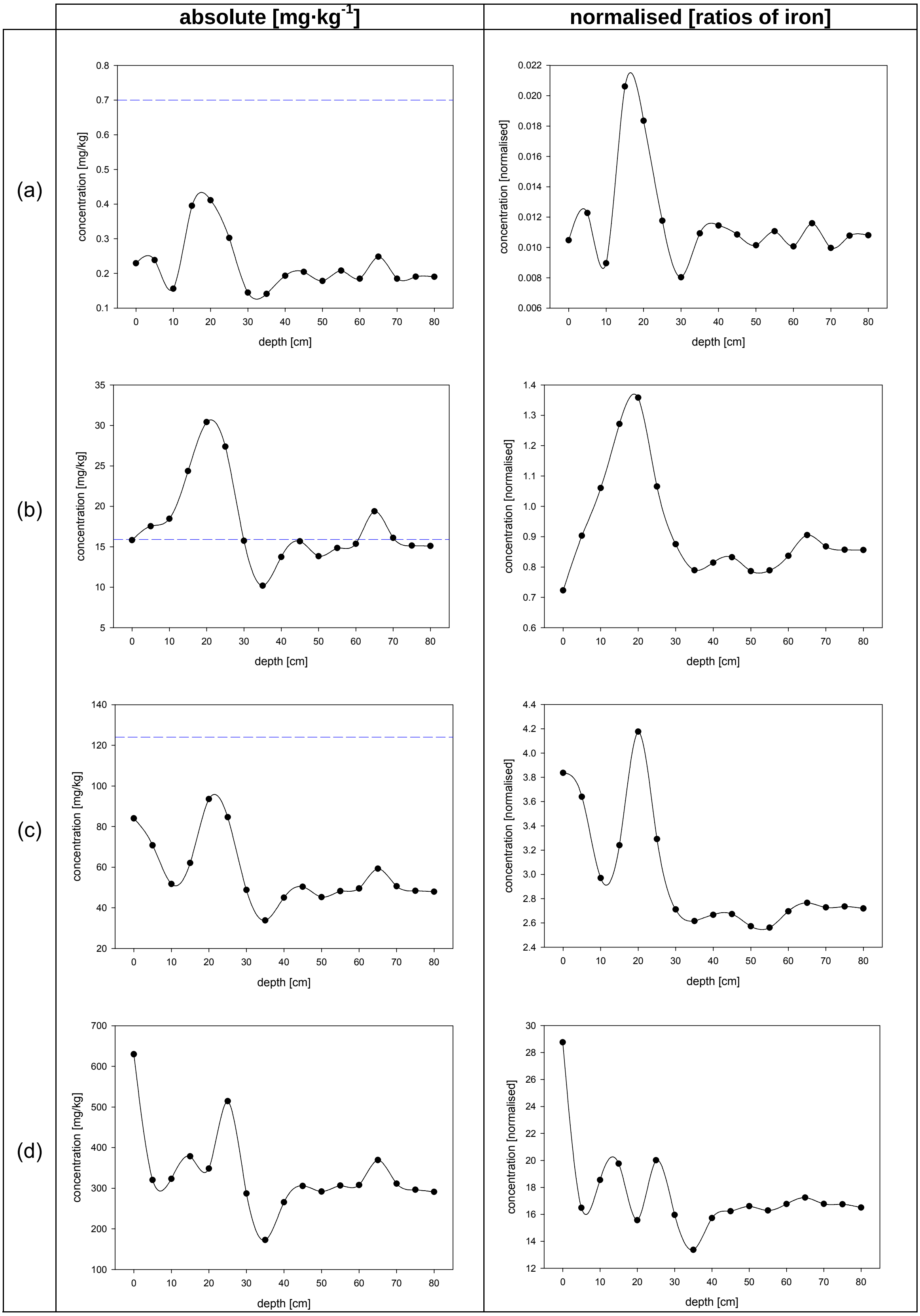
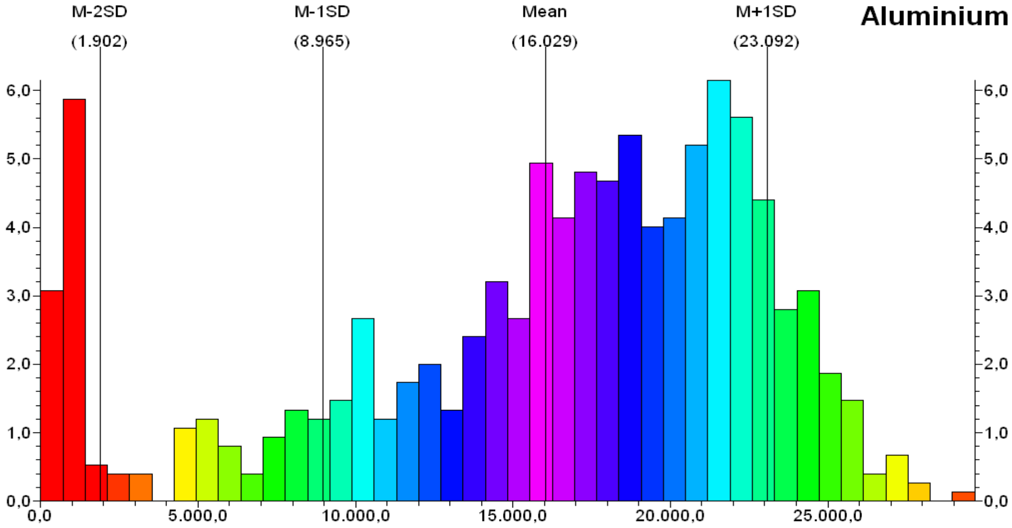
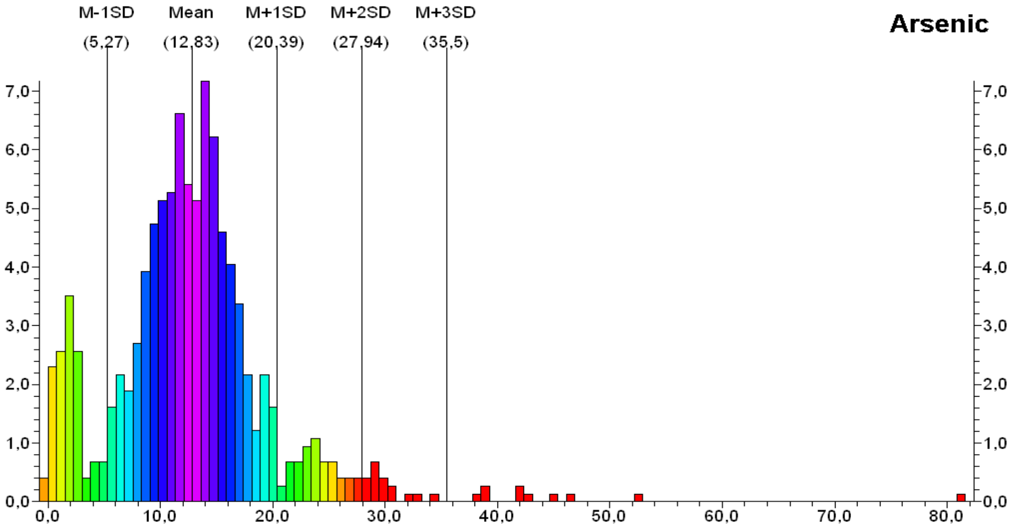


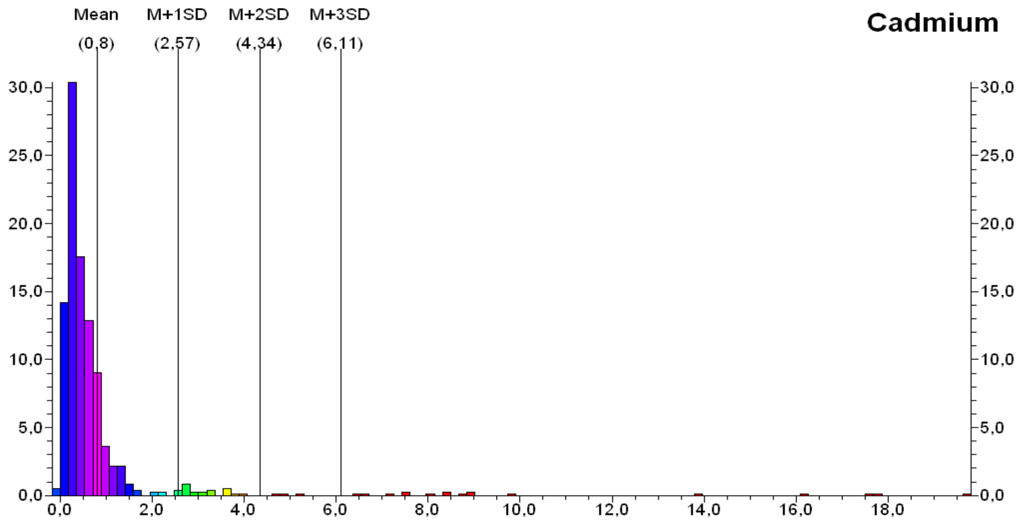
Figure 60: **Absolute and normalised concentrations of chromium (a), cadmium (b), zinc (c) and phosphorus (d) in the Brownsea Island lagoon (blue reference lines indicate TEL-values)**

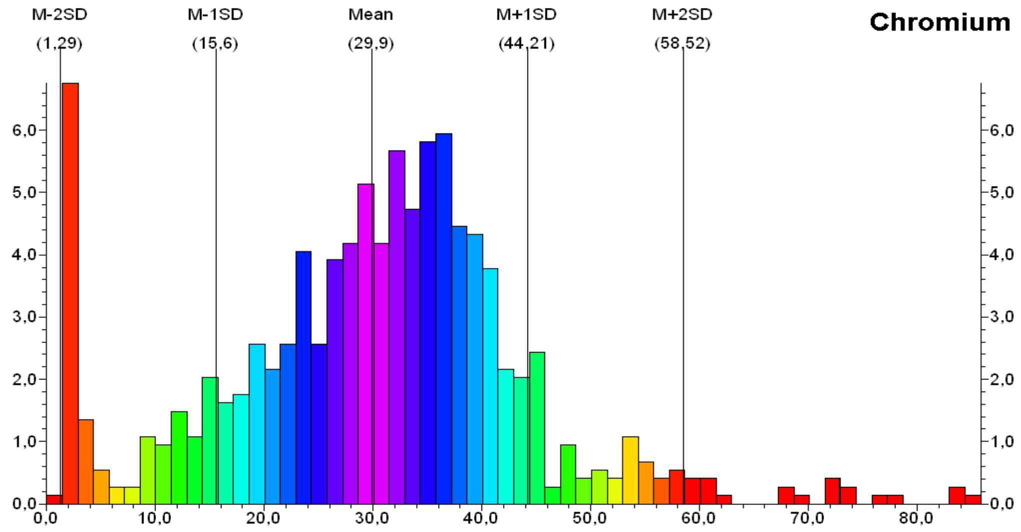
10.4.4 Concentration frequency histograms; Poole Harbour

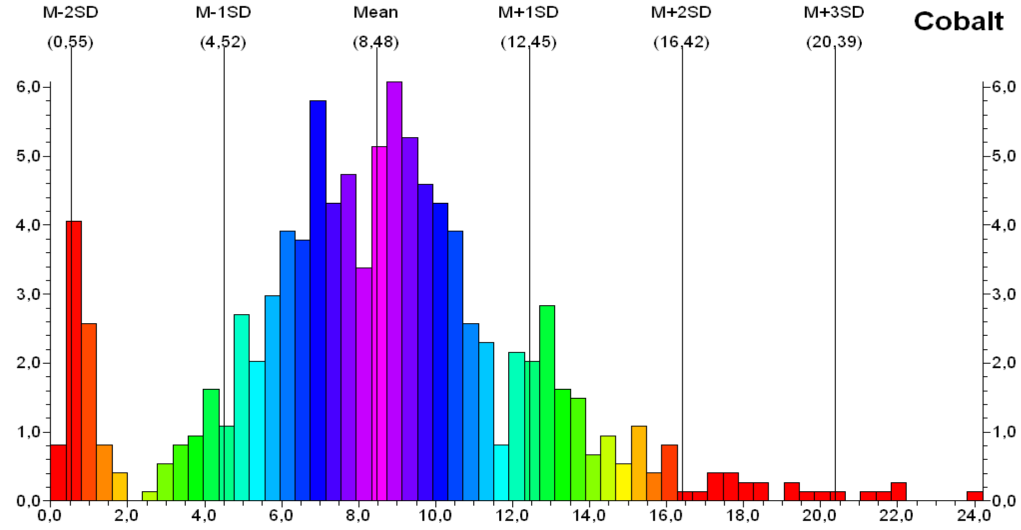
The following plots show histograms of the concentrations in Poole Harbour under inclusion of all cores and depth layers.

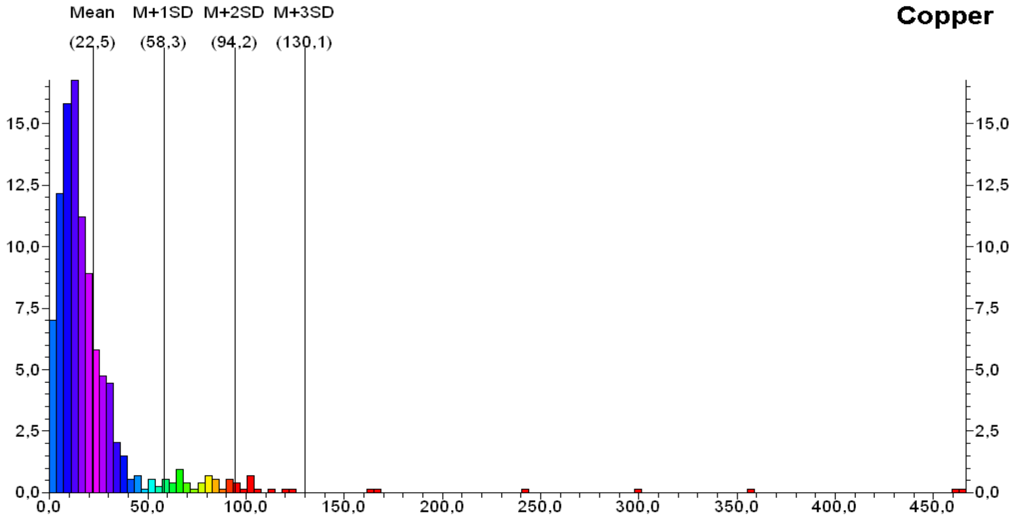




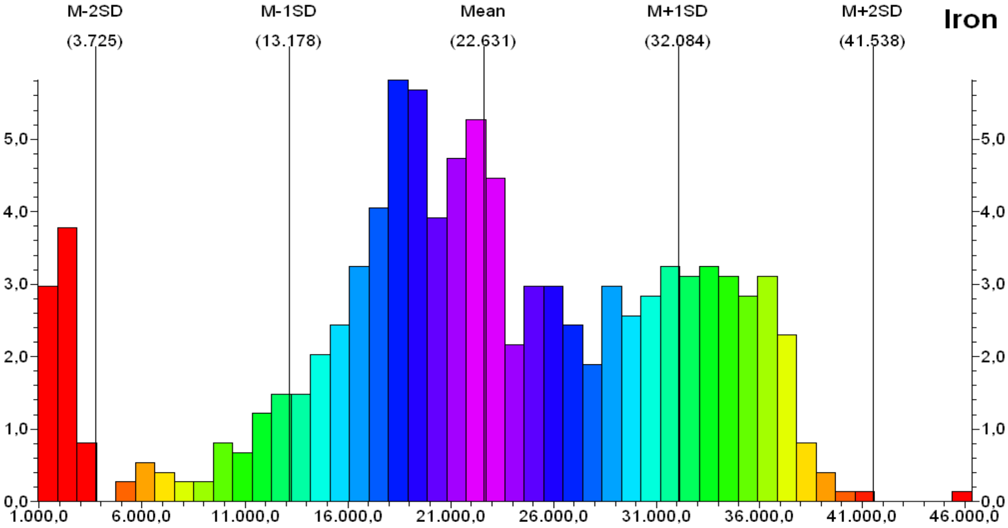

Cadmium
Mean
(0,8)
M+1SD
(2,57)
M+2SD
(4,34)
M+3SD
(6,11)
30,0
25,0
20,0
15,0
10,0
5,0
0,0
0,0
2,0
4,0
6,0
8,0
10,0
12,0
14,0
16,0
18,0


Chromium
M-2SD
(1,29)
M-1SD
(15,6)
Mean
(29,9)
M+1SD
(44,21)
M+2SD
(58,52)
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0,0
10,0
20,0
30,0
40,0
50,0
60,0
70,0
80,0

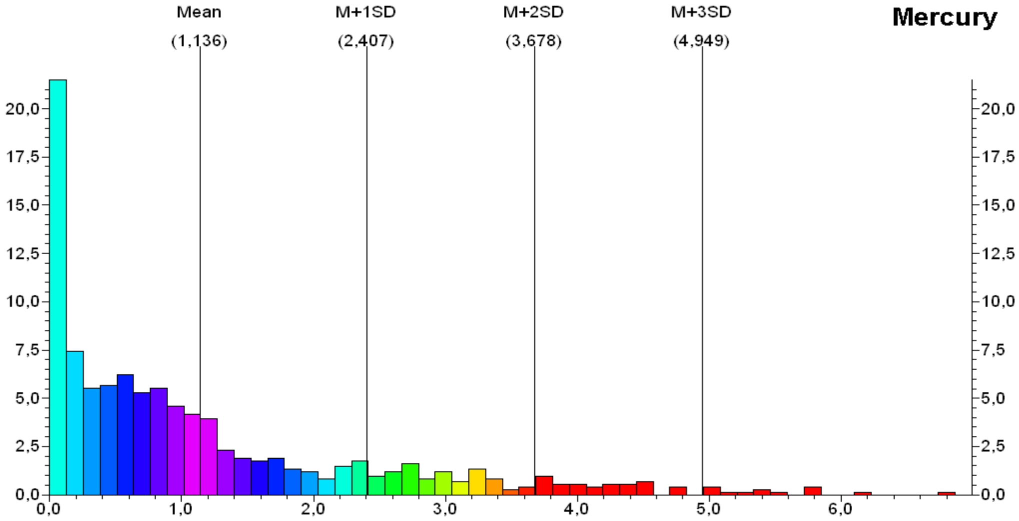

Cobalt
M-2SD
(0,55)
M-1SD
(4,52)
Mean
(8,48)
M+1SD
(12,45)
M+2SD
(16,42)
M+3SD
(20,39)
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0,0
2,0
4,0
6,0
8,0
10,0
12,0
14,0
16,0
18,0
20,0
22,0
24,0



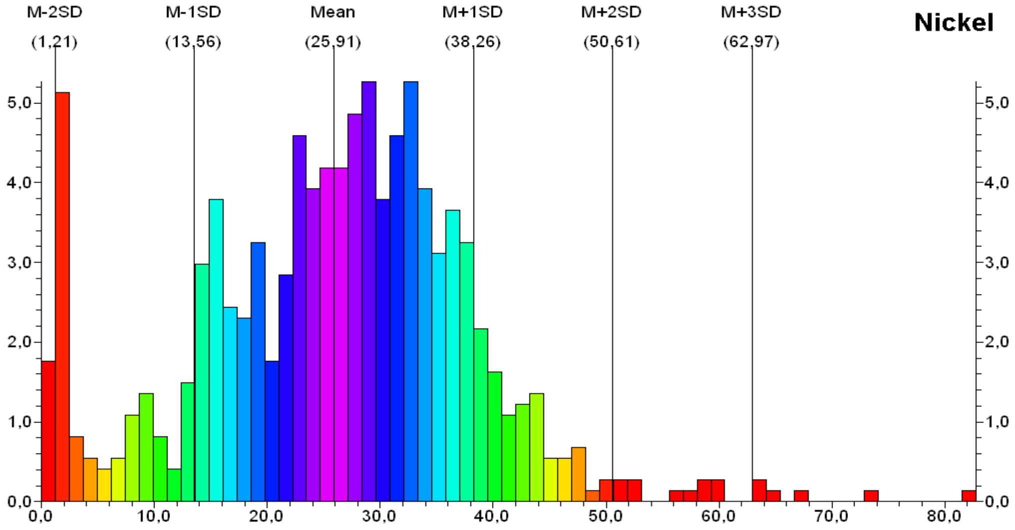
Copper

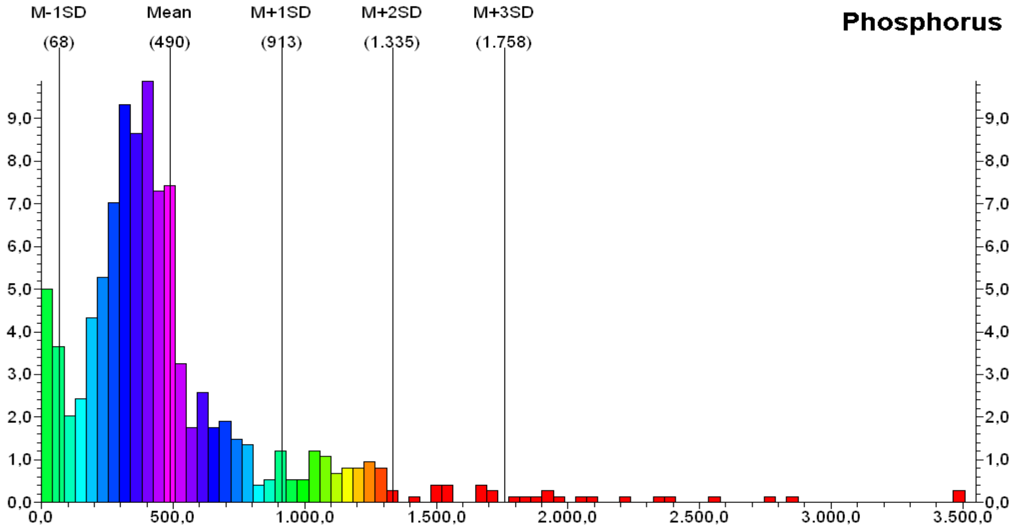


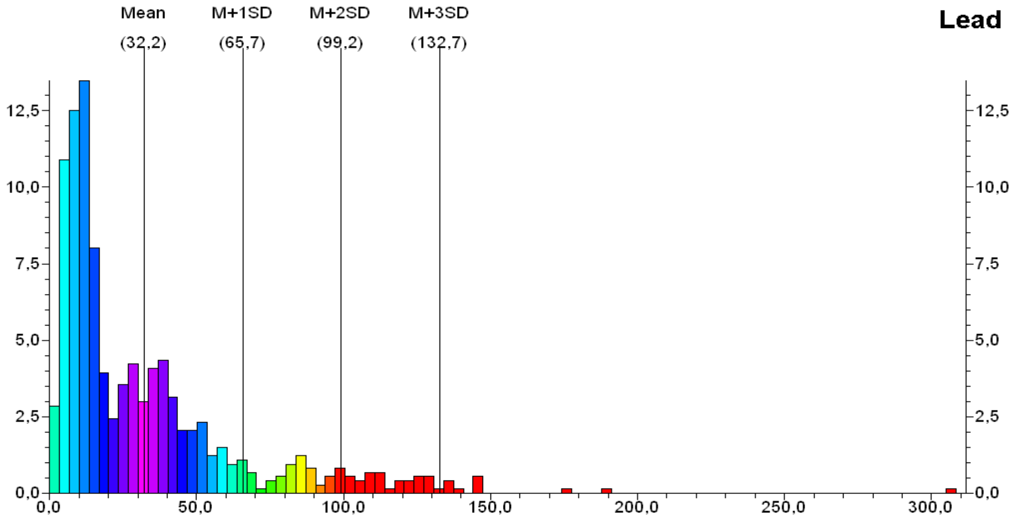
Iron

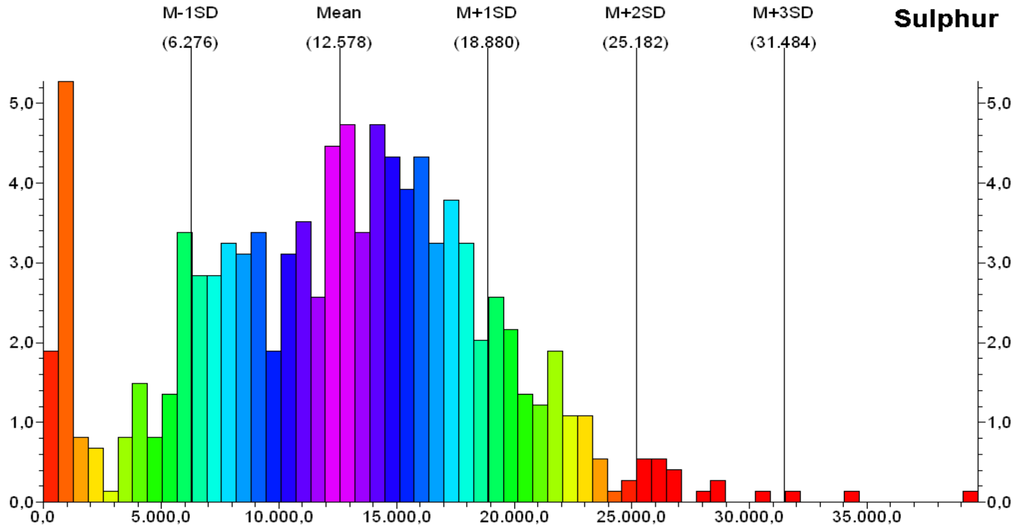


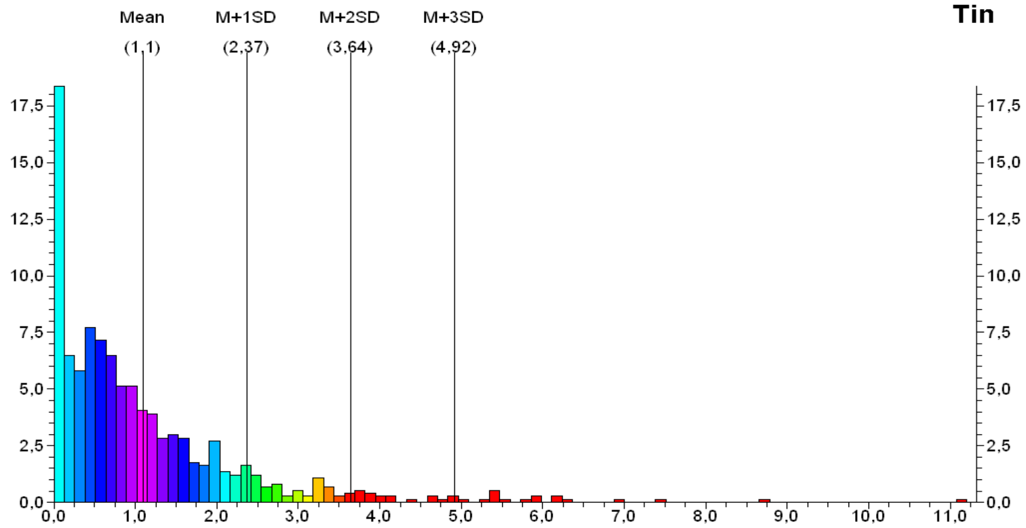
Mercury

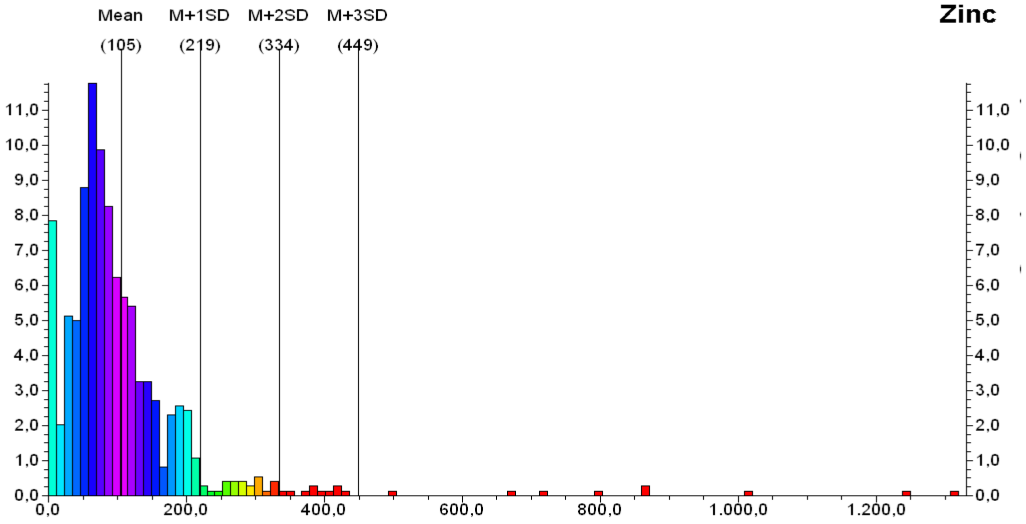

Nickel
M-2SD (1,21)
M-1SD (13,56)
Mean (25,91)
M+1SD (38,26)
M+2SD (50,61)
M+3SD (62,97)
0,0
1,0
2,0
3,0
4,0
5,0
0,0
10,0
20,0
30,0
40,0
50,0
60,0
70,0
80,0


Phosphorus
M-1SD (68)
Mean (490)
M+1SD (913)
M+2SD (1.335)
M+3SD (1.758)
0,0
1,0
2,0
3,0
4,0
5,0
6,0
7,0
8,0
9,0
0,0
500,0
1.000,0
1.500,0
2.000,0
2.500,0
3.000,0
3.500,0


Lead
Mean (32,2)
M+1SD (65,7)
M+2SD (99,2)
M+3SD (132,7)
0,0
2,5
5,0
7,5
10,0
12,5
0,0
50,0
100,0
150,0
200,0
250,0
300,0


M-1SD
(6.276)
Mean
(12.578)
M+1SD
(18.880)
M+2SD
(25.182)
M+3SD
(31.484)
Sulphur
5,0
4,0
3,0
2,0
1,0
0,0
0,0
5.000,0
10.000,0
15.000,0
20.000,0
25.000,0
30.000,0
35.000,0


Mean
(1,1)
M+1SD
(2,37)
M+2SD
(3,64)
M+3SD
(4,92)
Tin
17,5
15,0
12,5
10,0
7,5
5,0
2,5
0,0
0,0
1,0
2,0
3,0
4,0
5,0
6,0
7,0
8,0
9,0
10,0
11,0


Mean
(105)
M+1SD
(219)
M+2SD
(334)
M+3SD
(449)
Zinc
11,0
10,0
9,0
8,0
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0,0
200,0
400,0
600,0
800,0
1.000,0
1.200,0

10.4.5 Grain size profiles

Equipment used for grain size profiles courtesy of the research centre ICBM-Terramare, Wilhelmshaven (Germany).

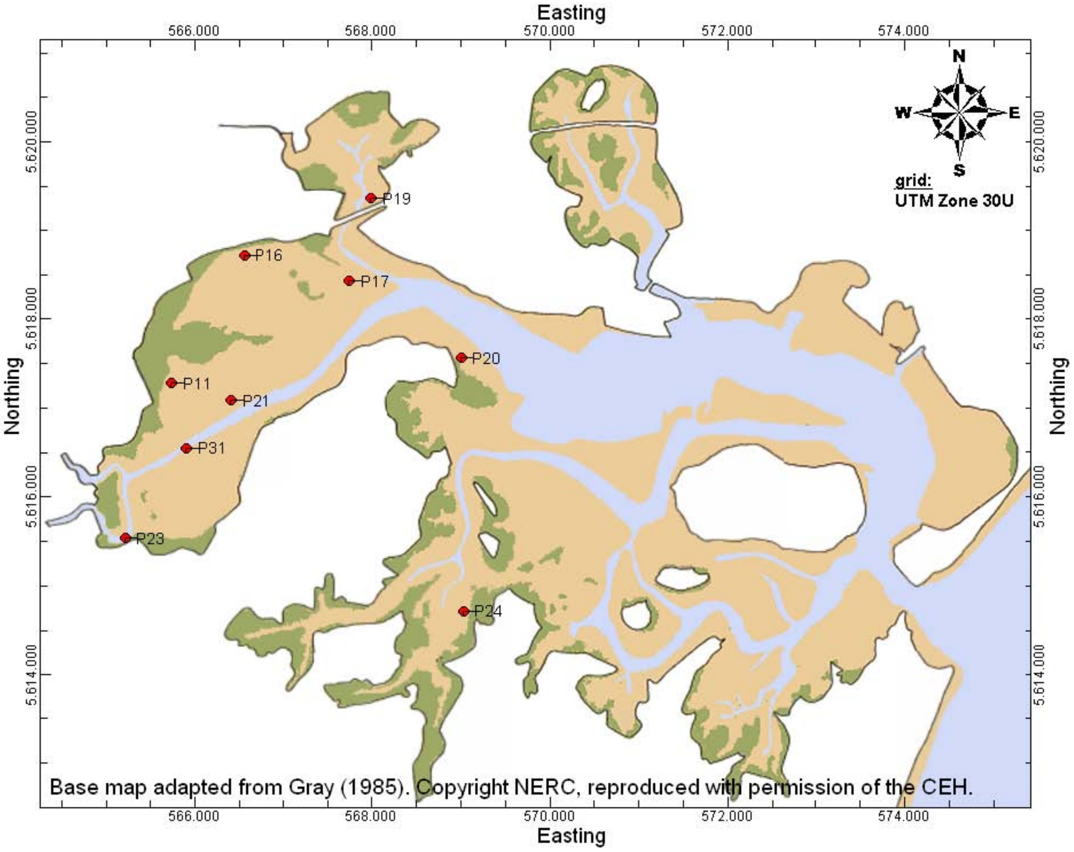
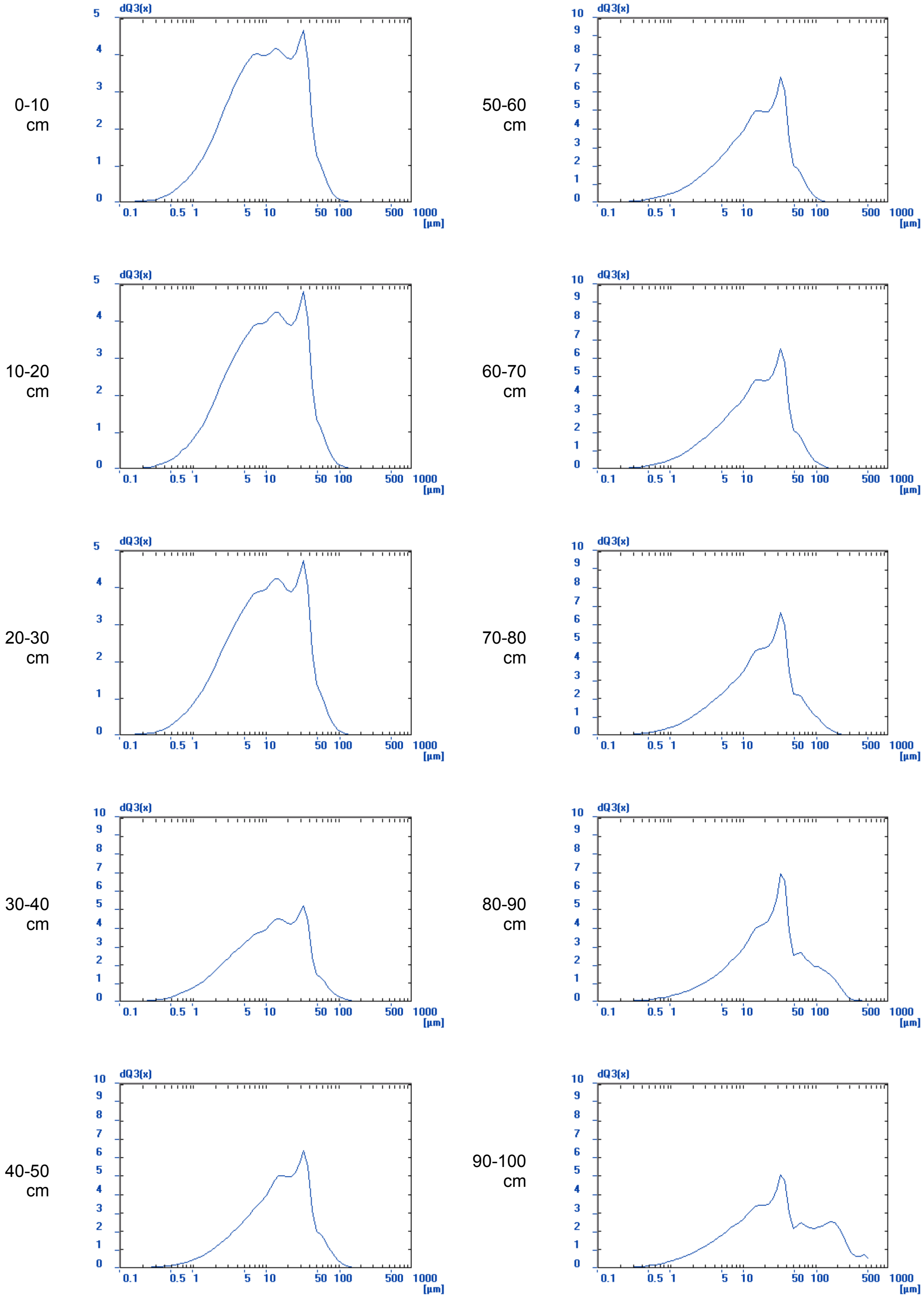


Figure 61: Cores with subsequently illustrated full sediment particle size profiles

Core P11 (Wareham Channel)



0-10 cm

50-60 cm

10-20 cm

60-70 cm

20-30 cm

70-80 cm

30-40 cm

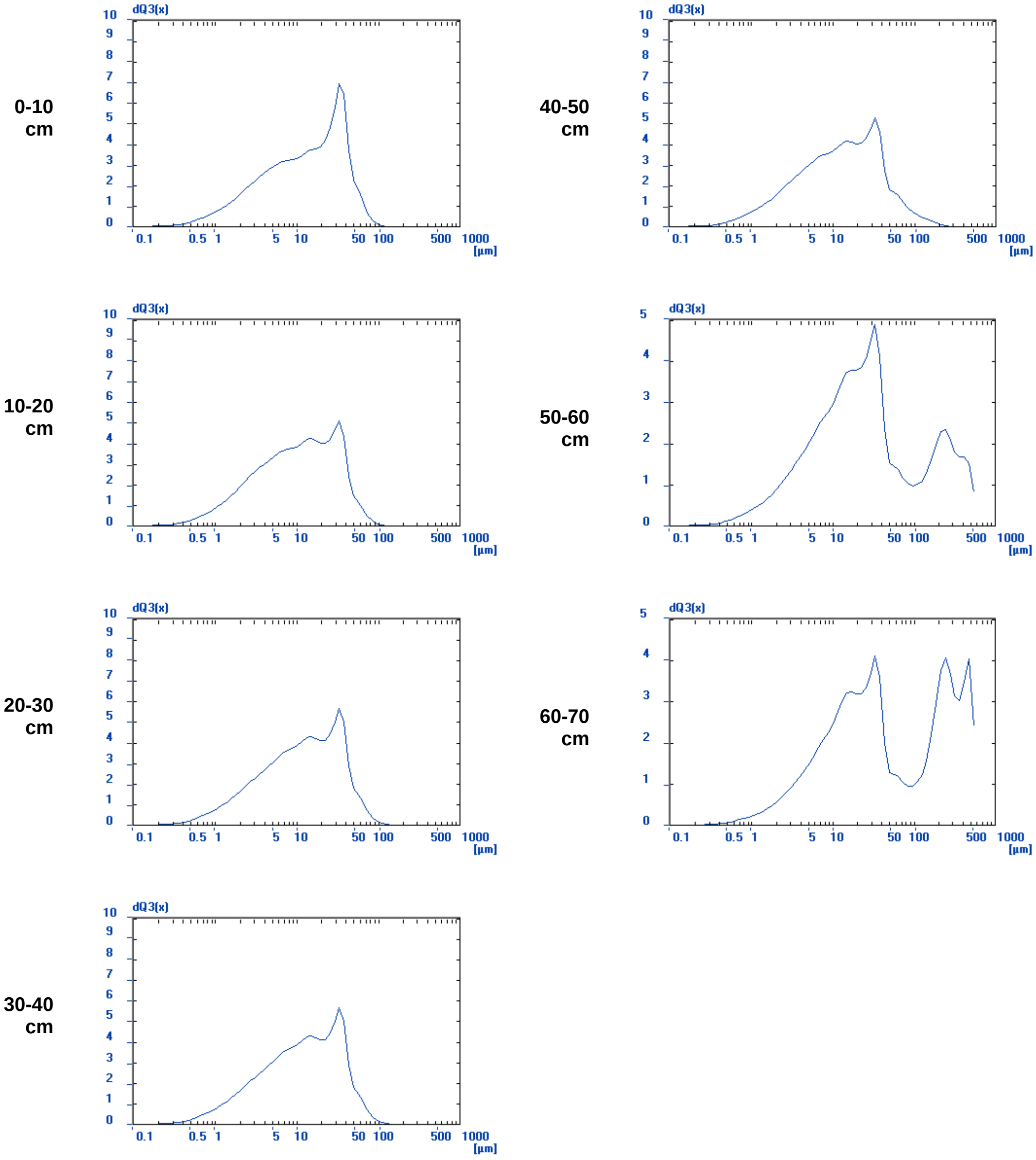
80-90 cm

40-50 cm

90-100 cm

Figure 62: Grain size distribution in core P11

Core P16 (Wareham Channel)



0-10 cm

40-50 cm

10-20 cm

50-60 cm

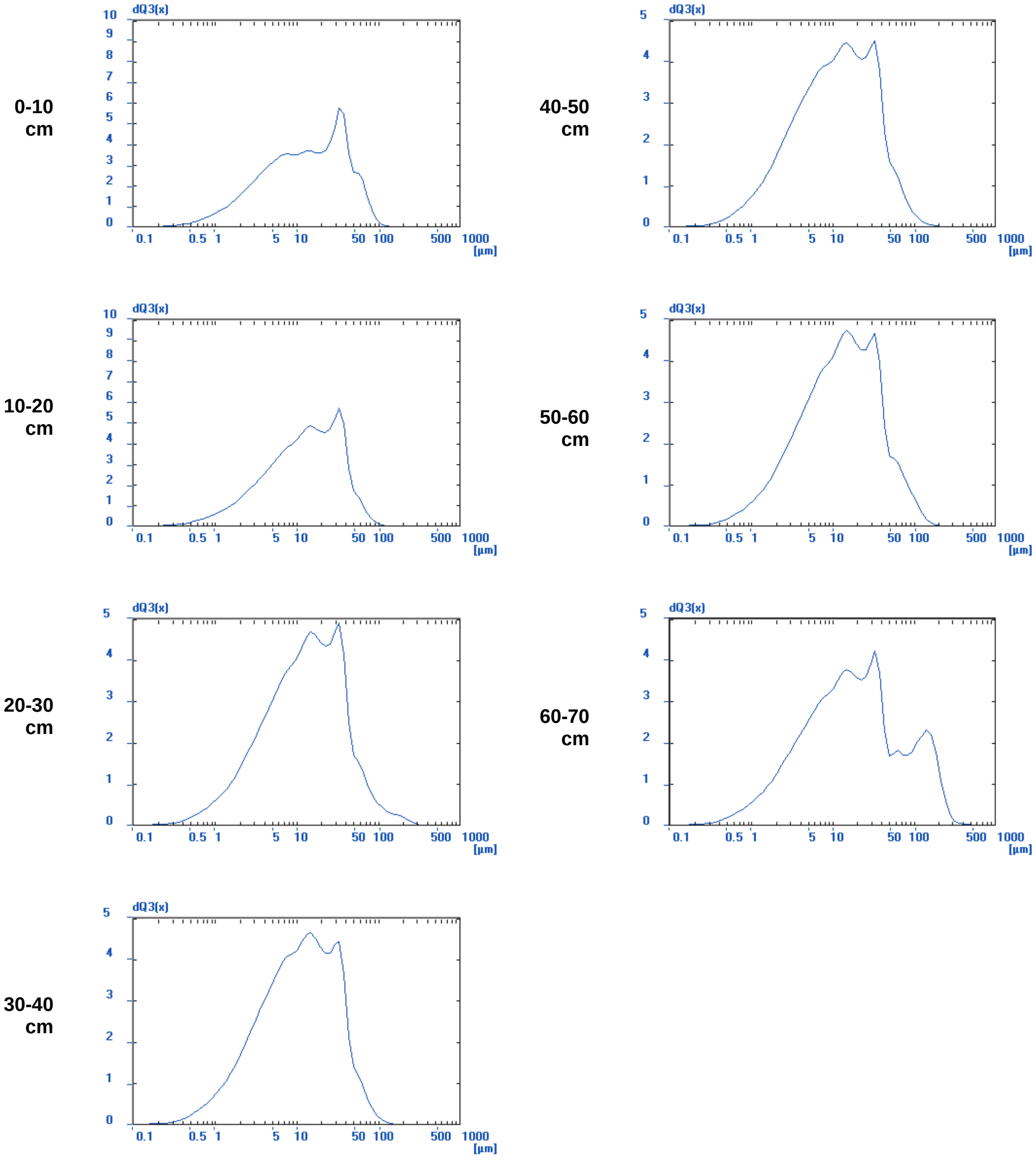
20-30 cm

60-70 cm

30-40 cm

Figure 63: Grain size distribution in core P16

Core P17 Wareham Channel, north-eastern end)



0-10 cm

10-20 cm

20-30 cm

30-40 cm

40-50 cm

50-60 cm

60-70 cm

Figure 64: Grain size distribution in core P17

Core P19 (Lytchett Bay)

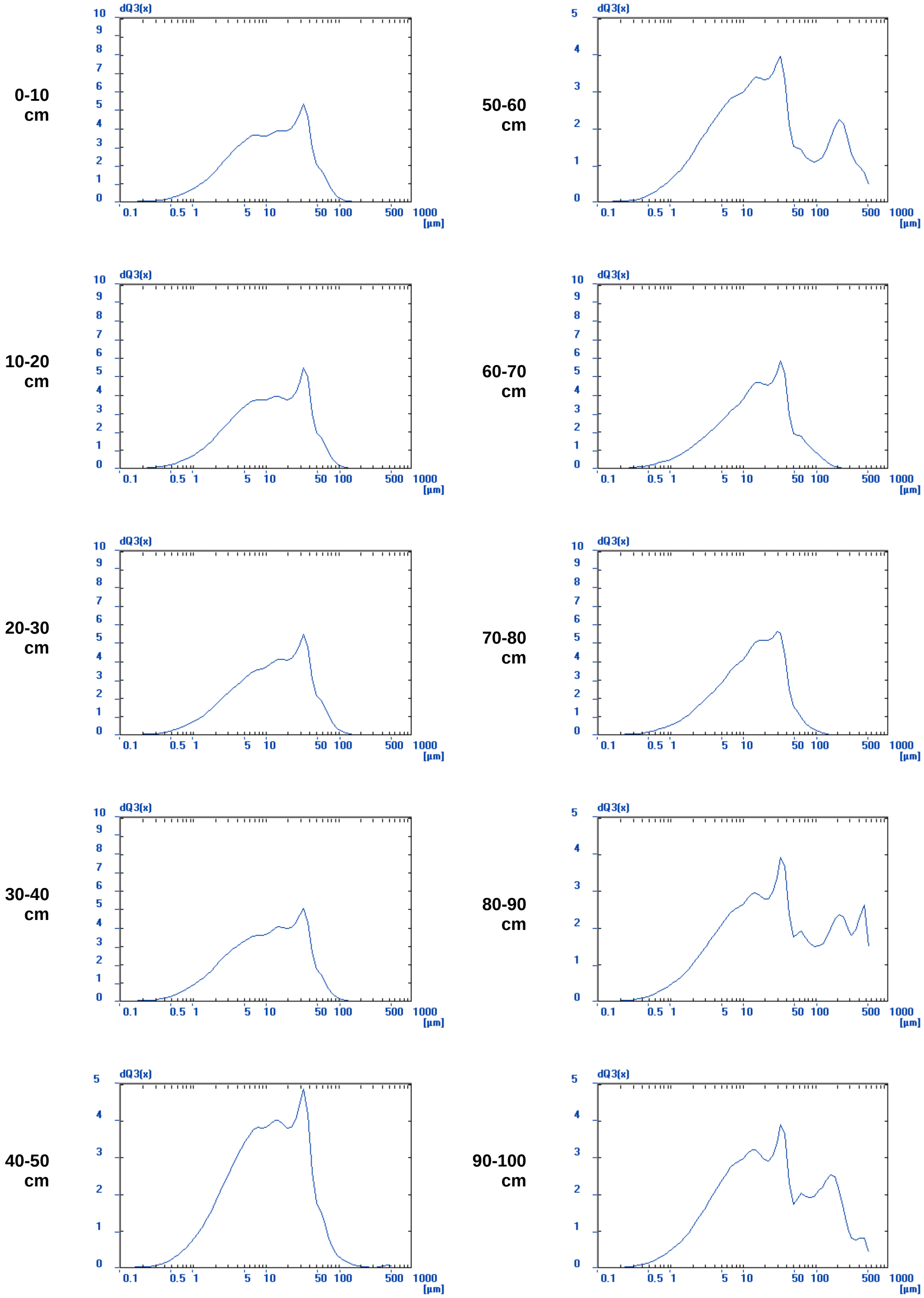
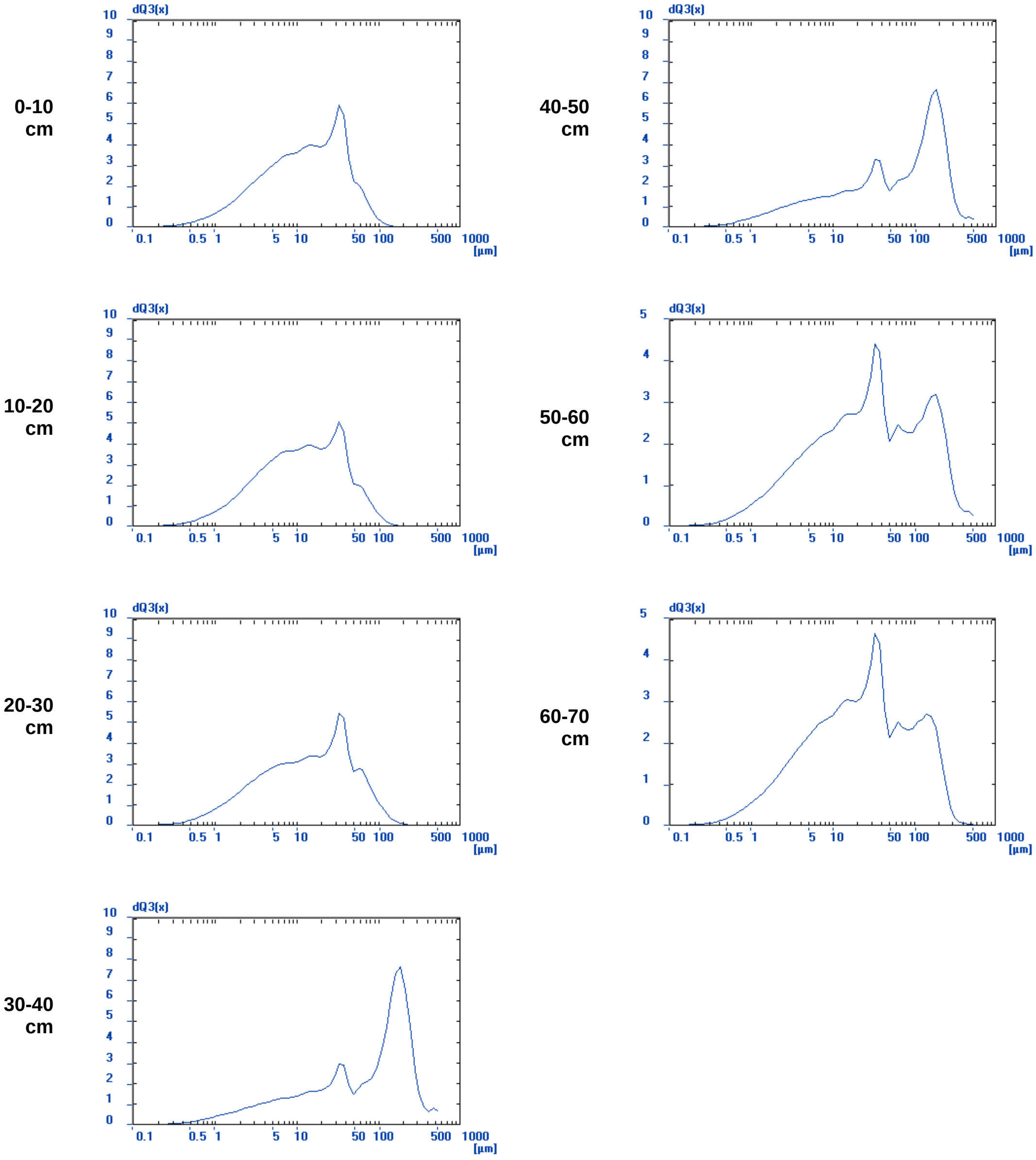


Figure 65: Grain size distribution in core P19

Core P20 (Arne; Gold Point)



0-10 cm

10-20 cm

20-30 cm

30-40 cm

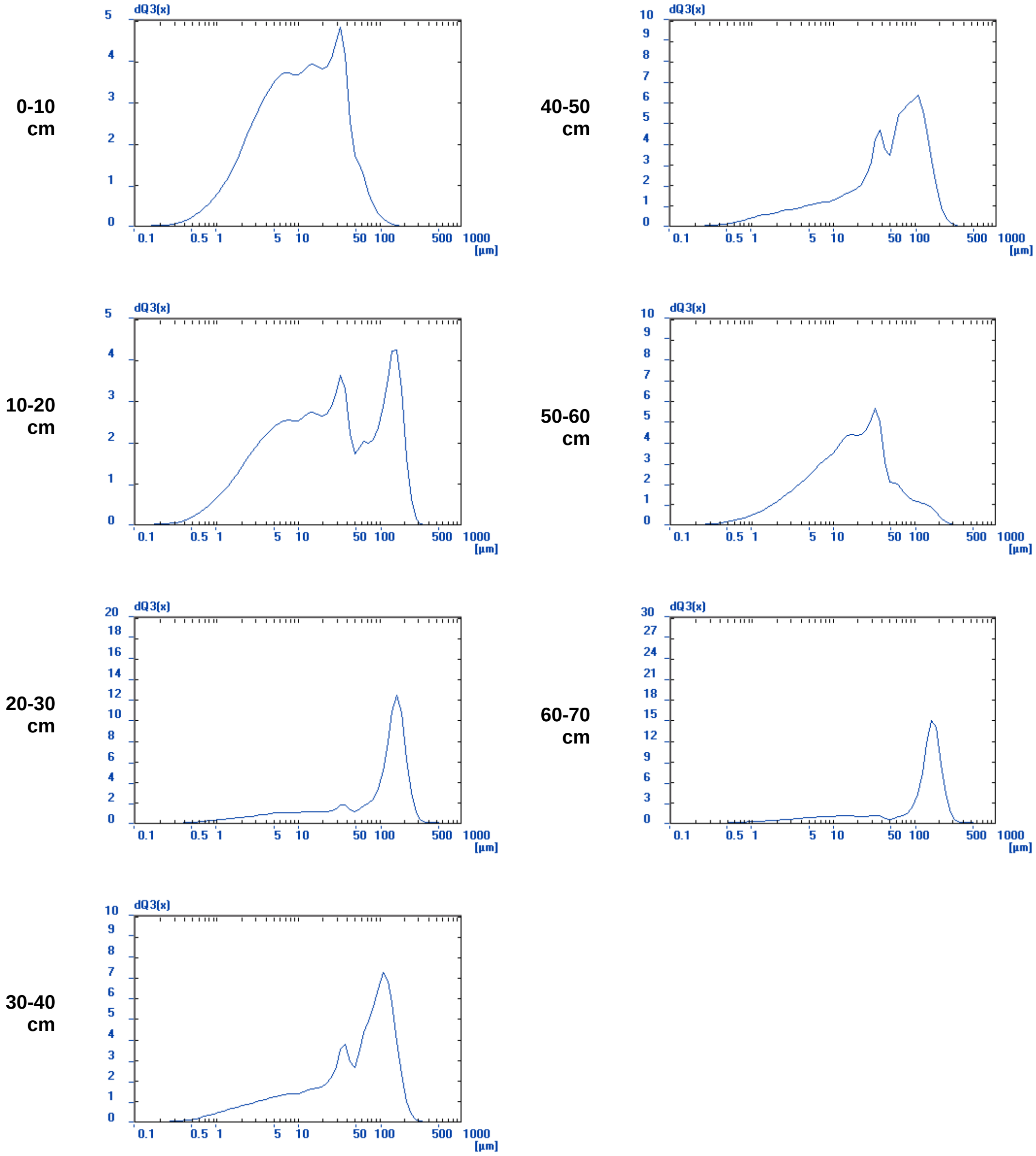
40-50 cm

50-60 cm

60-70 cm

Figure 66: Grain size distribution in core P20

Core P21 (Wareham Channel)



0-10 cm

10-20 cm

20-30 cm

30-40 cm

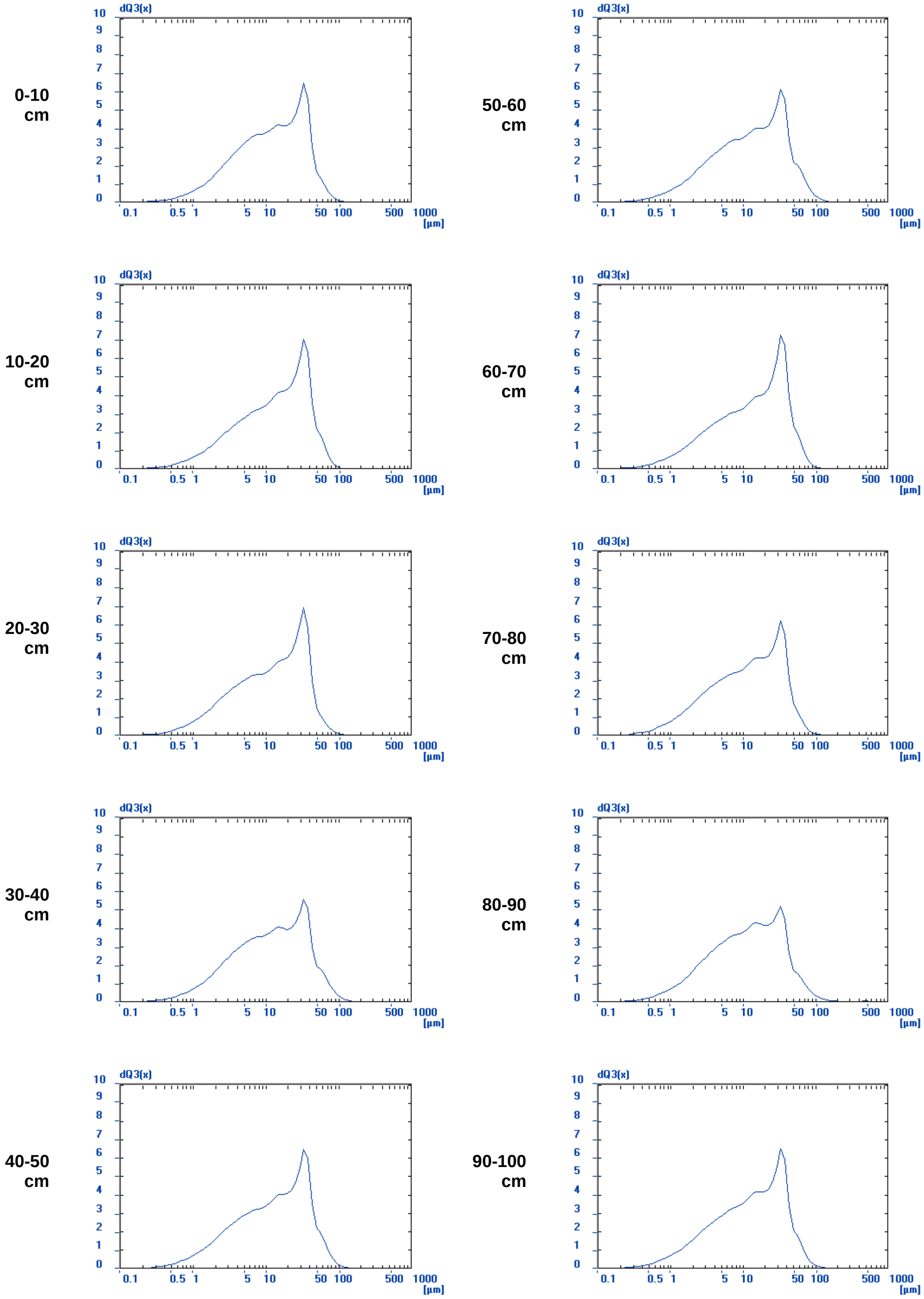
40-50 cm

50-60 cm

60-70 cm

Figure 67: Grain size distribution in core P21

Core P23 (Wareham Channel, south-western end)



0-10 cm

10-20 cm

20-30 cm

30-40 cm

40-50 cm

50-60 cm

60-70 cm

70-80 cm

80-90 cm

90-100 cm

Figure 68: Grain size distribution in core P23

Core P24 (Southern Bights, Wytch Lake)

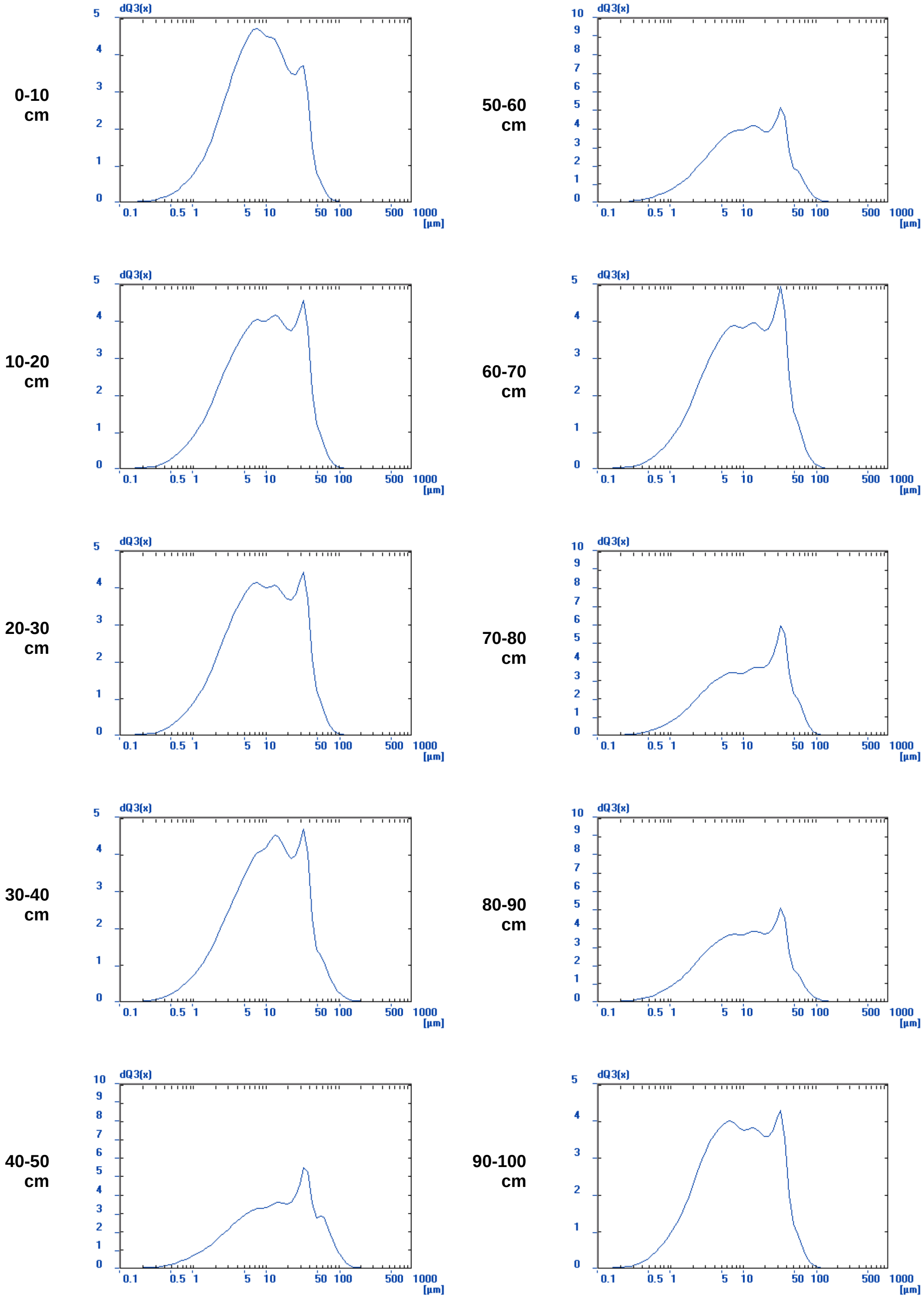


Figure 69: Grain size distribution in core P24

Core P31 (Wareham Channel)

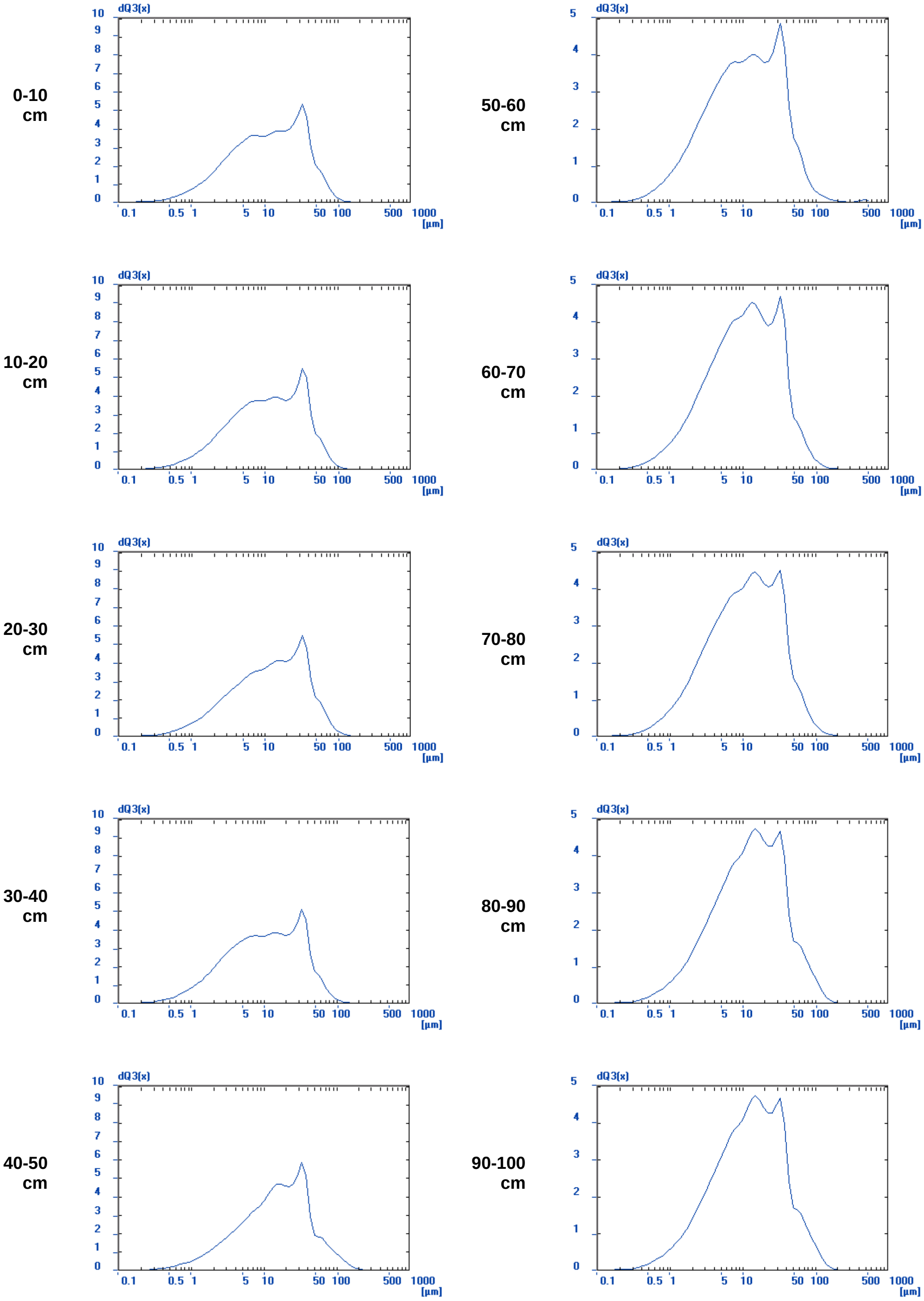


Figure 70: Grain size distribution in core P31

10.4.6 Metal concentrations in the Swash Channel

Table 30: Metal concentrations [all values in mg·kg^{-1}] in samples extracted in and around the historic Swash Channel Wreck

	Al	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sn	Zn
sample 1.1	570.52	4.66	0.08	0.88	2.69	2.86	0.09	2.26	3.12	0.55	6.26
sample 1.2	579.81	2.11	0.12	1.31	2.57	2.42	4.39	3.07	2.90	0.86	6.22
sample 2.1	663.52	1.97	0.01	0.47	2.06	2.28	0.26	1.17	2.01	0.27	7.05
sample 2.2	576.59	2.12	0.02	0.48	1.47	2.00	1.79	0.85	2.18	0.37	5.24
sample 2.3	631.38	1.66	0.01	0.47	1.36	2.11	0.73	0.84	1.74	0.32	4.74
sample 2.4	594.89	1.76	0.02	0.51	1.33	1.99	0.41	0.95	1.88	0.27	5.76
sample 2.5	664.78	1.95	0.01	0.50	1.58	1.78	1.43	1.06	1.84	0.35	5.30
sample 2.6	661.69	1.97	0.01	0.47	1.29	2.23	0.98	0.86	2.50	0.22	4.74
sample 2.7	661.69	1.97	0.01	0.47	1.29	2.23	0.89	0.86	2.50	0.22	4.74
TEL	--	7.24	0.68	--	52.30	18.70	0.13	15.90	30.24	0.05	124.00
PEL	--	41.60	4.21	--	160.00	108.00	0.70	42.80	112.00	--	271.00

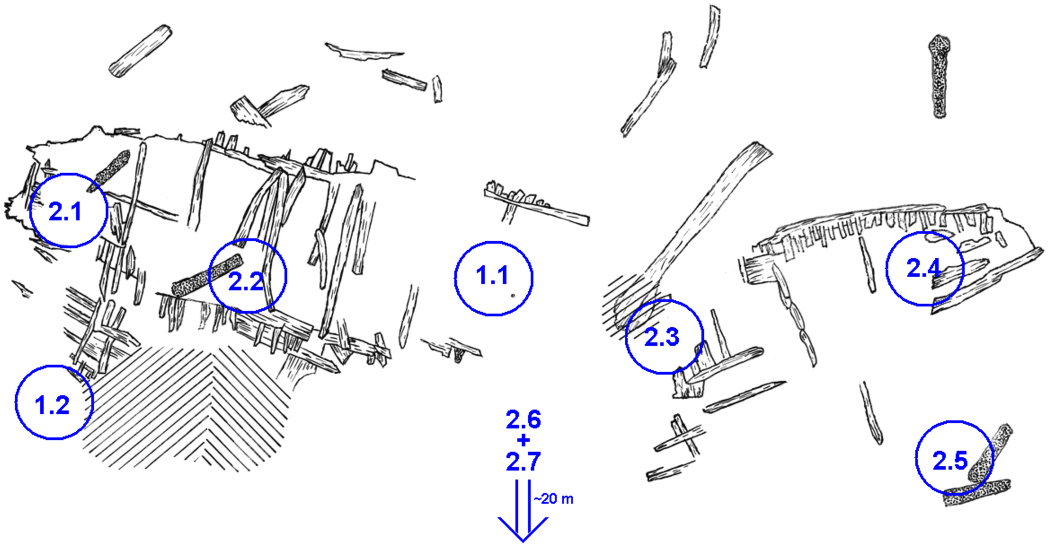


Figure 71: Sampling locations in and around the historic Swash Channel Wreck (map courtesy of Dave Parham)

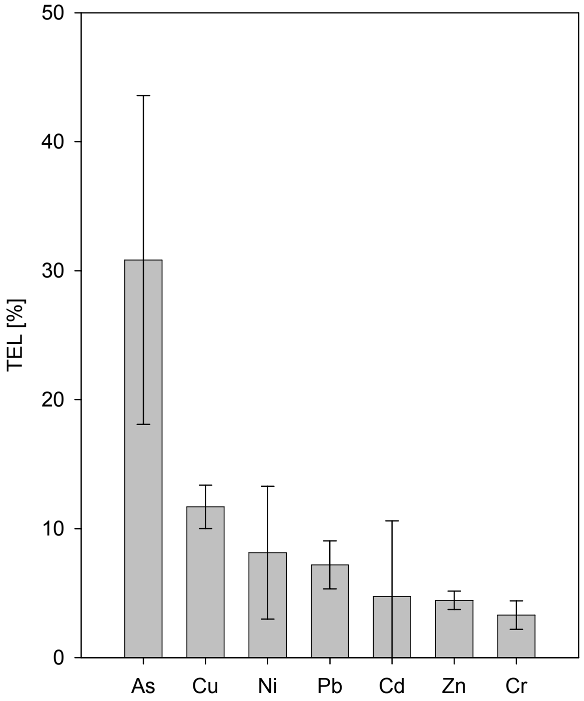


Figure 72: **The concentrations of seven metals in the sediments in and around the historic Swash Channel Wreck, values are the average percentages of their respective threshold effect level (TEL) concentrations**

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