

1.5.5.5 Update of JAMP guidance on normalisation of contaminant concentrations in sediment

Request

Update of JAMP guidance on normalisation of contaminant concentrations in sediment (OSPAR 8-2009)

To update the technical annex on normalization of contaminant concentrations in sediments contained in the JAMP Guidelines for monitoring of contaminants in sediments. The update should ensure that the technical annex is fully applicable across the OSPAR maritime area.

Source of information

ICES 2009. Report of the Work Group on Marine Sediments in Relation to Pollution (WGMS, 2009)

Summary

Ideally monitoring of contaminants in sediments would be based on the analysis of samples with similar composition with respect to grain size, organic content, etc. This situation will seldom occur therefore new temporal trend programs should be carried out where possible using fine-grained sediments or a fine-grained fraction, isolated by sieving. Contaminant concentrations in whole sediments can be subjected to normalisation using cofactors for organic matter, clay minerals etc., if one takes into account the presence of both cofactors and target contaminants in the mineral structure of the sand fraction of the sediment. ICES recommends that normalization should be applied if this results in a reduction in the residual variation in temporal data but it should not be applied if the residual variance is not reduced.

To facilitate data interpretation, analytical data for field samples should be accompanied by information on limits of detection and long term precision. In order to contribute to environmental assessment, data for field samples should include the grain size distribution, as a minimum the proportion of the analysed fraction in the original whole sediment. Aluminium (Al) and total organic (TOC) concentrations should be reported for use as potential cofactors. In order to take into consideration potential regional differences in sediment composition in monitoring contaminants in sediments and its assessment, cofactors others than those mentioned in Sections 3 and 4 may be used. Furthermore, regionalised pivot points for calculating normalised contaminant concentrations as well as regionalised Background (Assessment) Concentrations may be derived for different regions. Specifically, ICES recommends that OSPAR invite its Contracting Parties to present proposals for pivot values, Background Concentrations, and associated cofactor values that they consider appropriate to particular parts of the Convention area. Similarly it is recommended that the current assessment procedure using EACs/ERLs be revisited with a view to introducing a degree of flexibility in the expression and testing of data against these criteria.

ICES Response

Taking into consideration experience of the application of normalisation in OSPAR data assessments and the current objectives of the OSPAR JAMP, the Technical Annex 5 of the JAMP Guideline has been updated/ revised. The updated JAMP guidance on normalisation of contaminant concentrations in sediment is attached in Annex 1.

Background information

Normalisation of the concentrations of contaminants in sediments is described in the current Annex on normalisation in the JAMP Guidelines for Monitoring Contaminants in Sediment as a procedure to correct or adjust contaminant concentrations for the influence of the natural variability in sediment composition; in particular for grain size, organic matter content and mineralogy.

The need for normalisation arises from the observation that most natural and anthropogenic substances, metals and organic contaminants, show a much higher affinity to fine-grained particulate matter than to the coarse fraction. Constituents such as organic matter and clay minerals show the strongest adsorption capacity for these contaminants. Therefore it is commonly found that, if the pollution level in the overlying water is held constant, there is a correlation between the concentration of contaminants in sediments and the cofactors that act as proxies for the phase or phases in the sediment which show high affinity for the contaminants. For example, in sediment samples that are in equilibrium with the same water, the concentrations of organic contaminants such as PAHs or CBs can show correlations with the concentration of organic carbon in the sediment. The organic matter shows a high affinity for these contaminants, and the organic carbon acts as a proxy for organic matter in the sediments; some workers have used organic nitrogen as the proxy. It should be noted that the nature of organic matter can differ between samples both temporally and spatially and therefore its affinity for contaminants can also vary.

In the case of metals such as lead, cadmium and mercury, good correlations with the concentrations of aluminium and lithium have been reported, indicating that these metals are primarily associated with clay minerals. Good correlations between metals and organic carbon have also been reported. In some cases, this may indicate that the metals are also associated with organic matter, but the situation is complicated by correlations between the concentrations of aluminium and total organic carbon (TOC) or % fine-grained material in the sediment, for example.

The linear correlations found between concentrations of contaminants and cofactors such as aluminium, lithium or organic carbon or measures of grain size is the basis of normalisation procedures that have been used to aid the interpretation of monitoring data in OSPAR programmes (Annex 1, Figure 1). If normalisation is not applied, the variations in bulk sediment properties add to the overall variance in the contaminant data, and in some cases can be a dominant source of the variation. Patterns of concentrations within time series, or in spatial surveys in small geographical areas can largely reflect differences in particle size distribution between samples and thus reduce the power of monitoring programmes to address the objectives of the JAMP.

The slopes of the correlations between contaminant concentrations and cofactor concentrations are greater in locations/areas where anthropogenic contamination occurs than in areas that can be considered as uncontaminated or background areas. These slopes could be used as an expression of the degree of contamination, but the amount of field and laboratory work required to establish the correlations routinely in monitoring programme would be very high. Therefore, advantage has been taken of the expected linear correlations to make use of the ratios between contaminant and cofactor concentrations as a measure of the slope.

So as to simplify comparisons between areas, normalised concentrations have been expressed as the equivalent concentrations that would be found in sediment with the same degree of contamination but of a standard composition, a sediment with a high proportion of fine grained material. The concentrations of cofactors in such fine-grained sediments typically are 5% aluminium, 50 ppm lithium, or 2.5% organic carbon content. These concentrations are also typical of the sieved fraction < 63 and < 20 µm.

As discussed in the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediment, the isolation of a fine fraction (e.g. <20 µm, <63 µm) of sediment by sieving can be regarded as a physical normalisation to reduce the differences in granulometric composition between sediment samples. This normalization is applicable to both metals and organic contaminants (Ackermann *et al.*, 1983; Klamer *et al.* 1990). Consequently the coarse particles, which usually do not bind anthropogenic contaminants but generally act to dilute their concentrations, are removed from the sample. The degree of normalisation achieved by sieving is such that it may be possible to directly compare contaminant concentrations measured in these fine fractions. In addition, the differences in sediment composition due to geochemical nature remaining after sieving can be further normalised by the use of cofactors such as aluminium, lithium or TOC. Thus, sieving is a first powerful step in normalisation.

There are a number of practical benefits that may result from the sieving of sediments prior to analysis. Firstly, the concentrations of both contaminants and cofactors are greater in the sieved fraction than in the bulk sediment. This can often increase analytical precision. Sieving will be particularly important for sediments that are dominated by sand grade material, since concentrations of contaminants in the whole sediment can be very low and difficult to measure with precision.

Secondly, differences in analytical methods applied for the determination of metal concentrations, are less important for sieved fine fractions than for whole sediments. Some laboratories use total digestion methods or apply X-ray fluorescence techniques, while other laboratories use partial digestion methods. The differences in analytical results will be greater for very sandy sediments. The differences in analytical results obtained are much smaller for the analyses of the sieved fraction whether total or partial extraction methods are used.

Finally, the pivot values, i.e. the concentration of metals and cofactors in the coarse fraction of the sediment samples, have much less importance in the normalisation for sieved fractions than for whole (< 2mm) sediments.

Critical comments concerning normalisation

The critical components of the conceptual model of normalisation and its use in relation to OSPAR objectives are:

- a) The existence of useful correlations between contaminant and cofactor concentrations
- b) The degree to which a single set of pivot values, varying only with broad categories of analytical method, e.g. total extraction/digestion methods versus partial strong acid extractions for metals, can be applied across the Convention area
- c) The degree to which a single set of background concentrations and associated values of cofactors should be applied across the Convention area

- d) The use of the same cofactors across the Convention area, mainly aluminium concentrations for metals and TOC content for organics.

Experience of the application of normalisation in OSPAR data assessments has led to all these aspects of normalisation being criticised. ICES therefore reviewed the bases of the criticisms, and developed proposals for modifications to the way in which normalisation is applied in OSPAR programmes to accommodate, where possible, the criticisms that have been made.

It has been observed in some areas that the correlations between contaminant and cofactor concentrations may be weak or even absent. A number of reasons might give rise to this observation, including that the cofactor used is inappropriate for the contaminant of concern, that the degree of contamination or environmental quality is very variable with time or space, or that there is significant additional variance arising from the measurements of the concentration of the chosen cofactor.

The purpose of normalisation is to reduce the variability between samples arising from differences in bulk sediment properties. In the situations outlined above, the use of normalisation would not have the desired effect. ICES therefore recommend that the decision as to whether to apply normalisation to a time series of data should be based upon the apparent effectiveness of the normalisation. Current procedures applied by OSPAR MON in assessing time series of data involve the application of smoothers or linear regressions for short time series. Use of an effective cofactor should reduce the residual variance around the fitted smoother or regression. ICES therefore recommend that normalisation should be applied if this results in a reduction of the residual variance in time series, but should not be applied if the residual variance is not reduced.

Pivot values represent the concentrations of contaminants and cofactors in sediment containing no fine-grained material, i.e. in sand. The concentrations of some cofactors have often been found to be zero or undetectable in sand, for example, TOC. Other cofactors, such as aluminium, are commonly present at measureable concentrations in sand, e.g. from inclusion in the sand fraction of minerals other than quartz, for example feldspars. Also there can be measureable concentrations of metals in the sand fraction from these minerals or from coatings on sand grains. The degree to which for example aluminium is extractable from such minerals is dependent upon the analytical method, chemical extraction/digestion method used. Strong acid partial digestions will extract less aluminium than a total digestion procedure.

The main concern expressed regarding pivot values is that the composition of sand-sized material may differ significantly between different parts of the Convention area. The use of inappropriate pivot values could have significant impact on the calculated normalised concentrations, particularly for sediment samples containing relatively small proportions of fine-grained material. ICES therefore recommend that Contracting Parties be invited to present proposals for pivot values appropriate to particular parts of the Convention area. Such regionalised pivot values should be applicable over large parts of the Convention area, for example across entire Regions.

Most of the data currently available to OSPAR assessment groups are from inshore or shelf sea areas. In some parts of the Convention area, the shelf is rather narrow, and monitoring programmes can extend into relatively deep water on the continental slope. The implementation of the EU Marine Strategy Framework Directive, which covers large areas of European Seas beyond the continental shelf, is also likely to increase the pressure for survey and monitoring activity in deeper water. ICES notes that sediments in deep water tend to have different characteristics from those in shallow and inshore areas. ICES therefore advises that it may be necessary to define pivot values or BCs applicable to different depth zones. ICES suggest that two depth zones be considered; shelf and inshore areas including estuaries in less than 200m water depth, and deep-water sediments in more than 200m depth. ICES notes that some current sediment monitoring data from Spain and Portugal are obtained from locations deeper than 200m. As a preparatory step, the ICES Data Centre will be asked to use the information on station location in the Station Dictionary to complete the available data field for depth of water at the sampling stations. At present, the database contains a reasonable amount of records for which this information has been provided.

Background Concentrations and associated Background Assessment Concentrations are required to address the OSPAR objective that concentrations of hazardous substances should be at or close to background. Background concentrations of man-made synthetic substances, such as PCBs should, by definition, be zero. However, background concentrations of naturally occurring substances, such as metals and PAHs, need to be defined. Generally, they reflect concentrations found in sediment laid down in pre-industrial times, determined using core samples, or from surface sediments in areas considered to be remote from significant anthropogenic inputs of the contaminants of concern.

Two main concerns have been expressed in relation to Background Concentrations. They are both related to the degree to which the current Background Concentrations are appropriate for application throughout the Convention area. Firstly, it has been suggested that the current values, derived from a data set that emphasises the northern part of the Convention area, may not be immediately applicable elsewhere. Secondly, the Background Concentrations are

currently expressed as normalised values to 5% aluminium or 50 ppm lithium for metals and 2.5% TOC for organic contaminants, and it has been suggested that these “reference” values of the cofactors may not be appropriate for all areas. The use of inappropriate values for Background Concentrations could lead to misleading assessments as to whether concentrations in sediment are at or close to background.

ICES therefore recommends that OSPAR invite its Contracting Parties to present proposals for Background Concentrations and associated cofactor values that they consider to be appropriate to particular parts of the Convention area. The combinations of Background Concentrations and associated cofactor values should be consistent with the way in which pivot values to be used in the assessment of the field data are expressed, to allow the construction of straight lines joining pivot values and Background Concentrations. Such regionalised Background Concentrations should be applicable over large parts of the Convention area.

The current data assessment methods used by OSPAR MON apply aluminium as a cofactor for metals and TOC as a cofactor for organic contaminants. It has been suggested that this harmonised approach may not be appropriate for all parts of the Convention area. In some areas, other cofactors may be more effective than Al, Li or TOC for some contaminants. For example, in some areas it might be more effective to use TOC as a cofactor for mercury.

ICES therefore recommends that OSPAR invite its Contracting Parties to present proposals for the specification of cofactors to be used for the normalisation of concentrations of particular contaminants in their monitoring data. The effectiveness of the normalisation would be assessed through the effect of application of normalisation on the residual variance about time series, as described above. When making proposals, it will be necessary for Contracting Parties to ensure that pivot values and Background Concentrations expressed in relation to the same cofactors are also available. Such regionalised approaches to specification of cofactors should be applicable over large parts of the Convention area, for example across entire Regions

Upper assessment criteria – EACs etc.

The 2008 OSPAR MON assessment of contaminant concentrations in sediment employed two types of assessment criteria. One of these, termed T_0 in their report, was used to assess whether concentrations were at or close to background, i.e. the T_0 criteria were the Background Assessment Criteria.

The upper type of assessment criteria, termed T_1 in their report, were used to assess whether the concentrations observed were below levels that were likely to result in unacceptable biological effects. The appropriate OSPAR criteria are EACs, but MON found that EACs were not available for all the contaminants of interest. Specifically, EACs for sediment were available for PCBs but not for metals or PAHs. In order to have a complete set of criteria, MON applied effects range - low (ERL) values for metals and PAHs. MON used the normalised concentrations of all contaminants for the purpose of trend assessment, and for comparison with BACs, which are also expressed as normalised concentrations. For consistency, MON made comparisons between normalised concentrations and EACs/ERLs. While EACs for PCBs are expressed as concentrations normalised to TOC, ERLs are expressed simply as concentrations, i.e., not normalised. It has been argued that comparison of normalised field data with non-normalised ERLs is inappropriate.

ICES recommends that the MON assessment procedure be amended to allow for increased flexibility in the application of normalisation procedures, pivot values and BCs. It may also be appropriate to revisit the current assessment procedure against EACs/ERLs with a view to introducing a parallel degree of flexibility in the expression and testing of data against these T_1 criteria.

ANNEX 1: Technical annex on normalisation

Normalisation of contaminant concentrations in sediments

1. Introduction

The purposes of the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediment is to address OSPAR objectives for hazardous substances in Convention waters, namely:

Preventing pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances, and that

Hazardous substances should not give rise to unexpected or unacceptable biological effects.

Environmental monitoring is carried out, and monitoring data have been used to address these objectives. Studies of temporal trends in concentrations express the environmental response to control measures applied to inputs of contaminants to the sea and to assess progress towards background concentrations. Comparisons of observed concentrations with Background Concentrations (BCs) through the use of Background Assessment Concentrations (BACs) are used to determine whether concentrations are at or close to background. Comparisons of observed concentrations with OSPAR Environmental Assessment Criteria (EACs) or similar assessment criteria are used to indicate whether concentrations are at levels that are not expected to give rise to unacceptable biological effects. Monitoring for spatial distributions is discussed in Section 10 below.

As contaminant concentrations may vary due to differences in bulk sediment composition, e.g. differences in particle size distribution, organic matter content, results from comparisons of observed data to assessment criteria or trend assessments may be obscured. In order to reduce variances of contaminant concentrations due to differences in bulk sediment composition and to increase the power of monitoring programmes to address the objectives of the JAMP, procedures for normalisation of the concentrations of contaminants in sediment have been developed and used in OSPAR assessments of monitoring data.

2. Purposes

This annex provides guidance on the application of methods to normalise contaminant concentrations in sediments. Normalisation is defined here as a procedure to adjust contaminant concentrations for the influence of the natural variability in sediment composition, grain size, organic matter and mineralogy. Most natural and anthropogenic substances, metals and organic contaminants, show a much higher affinity to fine particulate matter compared to the coarse fraction. Constituents such as organic matter and clay minerals contribute to the affinity to contaminants in this fine material.

Fine material, both inorganic and organic, and associated contaminants are preferentially deposited in areas of low hydrodynamic energy, while in areas of higher energy, fine particulate matter is mixed with coarser sediment particles which are generally have weaker binding capacity for contaminants. This dilution effect will cause lower and variable contaminant concentrations in the resulting sediment. Obviously, grain size and organic matter are important factors controlling the distribution of natural and anthropogenic components in sediments. It is, therefore, essential to normalise for the effects of grain size or organic carbon in order to provide a basis for reliable assessments of temporal trends and for meaningful comparisons of the occurrence of substances in sediments of variable bulk properties with background (assessment) criteria and environmental assessment criteria derived for a defined sediment composition.

In sediment of varying bulk properties, contaminant concentrations will be closely related to the distribution of fine grained material, and any effects of other sources of contaminants, for example anthropogenic sources, will be at least partly obscured by grain size differences. Also in temporal trend monitoring, differences in sediment bulk properties can obscure trends. If samples have a considerable and constant percentage of fine material, the influence of grain size distribution is of minor importance and may probably be neglected.

3. Normalisation procedures

Two different approaches to correct for variable sediment compositions are widely used:

- a) Isolation of the fine fraction by sieving, e.g. $< 20 \mu\text{m}$, $< 63 \mu\text{m}$, can be regarded as means to reduce the differences in sediment granulometric compositions and is applicable to both metals and organic contaminants (e.g. Ackermann *et al.*, 1983; Klamer *et al.*, 1990; QUASH, 2000). Consequently the coarse particles, which usually do not bind anthropogenic contaminants and dilute their concentrations, are

removed from the sample. Then, contaminant concentrations measured in these fine fractions can be directly compared. Subsequently, the differences in sediment composition due to geochemical nature remaining after sieving can be further corrected for by the use of cofactors. Thus, sieving is a powerful first step in normalisation.

- b) Normalisation can be performed by relating the contaminant concentration with components of the sediment that represents its affinity for contaminants, i.e. binding capacity. Normalisation of contaminant concentrations can be performed by linear regression against cofactors (Cato, 1977; Smedes, 1997; Smedes *et al.*, 1997). Another procedure takes into account that the coarse sediment fraction contains natural metal concentrations in the crystal structure before the normalisation is performed (cf. Section 4). Combinations of cofactors, possibly identified from multiple regression analysis, can be used;

4. Normalisation using cofactors

- a) The binding capacity of the sediments can be related to the content of fines, primary factor, in the sediments. Normalisation can be achieved by calculating the concentration of a contaminant with respect to a specific grain-size fraction such as $< 2 \mu\text{m}$, i.e. the clay fraction, $< 20 \mu\text{m}$ or $< 63 \mu\text{m}$;
- b) As the content of fines is represented by the contents of major elements of the clay fraction such as aluminium (Windom *et al.*, 1989) or an appropriate trace element enriched in that fraction such as lithium (Loring, 1991), these can also be used as cofactors, secondary factors. Both, aluminium and lithium behave conservatively, as they are not significantly affected by, for instance, the early diagenetic processes and strong redox effects frequently observed in sediments. Problems may occur when the sediment is derived from glacial erosion of igneous rocks, with significant amounts of aluminium present in feldspar minerals contributing to the coarse fraction. In such cases, lithium may be the preferable cofactor (Loring, 1991);
- c) Organic matter, usually represented by organic carbon, is the most common cofactor for organic contaminants due to their strong affinity to this sediment component. In some environments, trace metal concentrations can also be normalised using organic carbon content, especially in surface sediments (Cato, 1977).

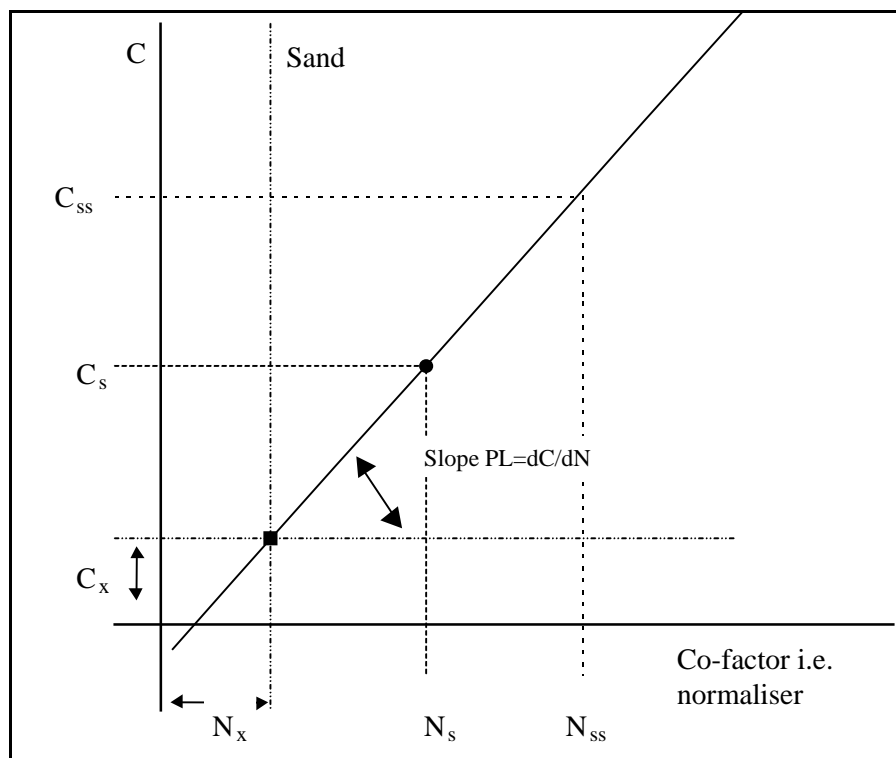


Figure 1 Relationship between the contaminant C and the co-factor N (from Smedes, 1997).

5. Theory

The general model for normalisation taking into account the possible presence of contaminants and cofactors in the coarse material is given in Figure 1 (Cato, 1977; Smedes *et al.*, 1997; Kersten and Smedes, 2002). C_x and N_x represent the co-factor and the contaminant contents, respectively, in pure sand. These “intercepts” can be estimated from samples without fines and organic material. The line of regression between the contaminant and co-factor will originate from that point. That means that regression lines of sample sets with a different pollution level and consequently different slopes

will have this point in common (i.e. pivot point) (OSPAR, 2008). When this pivot point is known, only one sample is required to estimate the slope. This allows determination of the contaminant content for any agreed (preselected) cofactor content (N_{ss}) by interpolation or extrapolation. The slope for a sample with a contaminant content C_s and a cofactor content of N_s can be expressed as follows:

$$PL = \frac{dC}{dN} = \frac{C_s - C_x}{N_s - N_x} \quad (1)$$

The extrapolation to an agreed cofactor content, N_{ss} , follows the same slope:

$$PL = \frac{dC}{dN} = \frac{C_s - C_x}{N_s - N_x} = \frac{C_{ss} - C_x}{N_{ss} - N_x} \quad (2)$$

Rewriting gives the contaminant content, C_{ss} , that is normalised to N_{ss} :

$$C_{ss} = (C_s - C_x) \frac{N_{ss} - N_x}{N_s - N_x} + C_x \quad (3)$$

Results of different samples normalised to the agreed N_{ss} can be compared directly.

Normalisation by this model can be applied with different cofactors. Here primary and secondary cofactors can be distinguished. A primary cofactor like the clay fraction or organic carbon is not present in the coarse fraction and consequently has no intercept ($N_x=0$). Al and Li are present in the coarse fraction and therefore are considered to be secondary cofactors. Provided N_x and C_x are known, the model allows recalculation of total samples to a cofactor content usually found in sieved fractions, either < 20 or $< 63\mu\text{m}$. However such an extrapolation for a coarse grained sample will be associated with a large error due to the uncertainty of the intercepts and the analysed parameters. For a more fine grained sample, the uncertainty of the normalised result is much lower than for normalisation of a sieved fraction to the agreed cofactor content and will result in a more accurate result. The model presented also applies to the normalisation of organic contaminants using organic carbon but in that case the intercepts N_x and C_x will not differ significantly from zero.

Principally, the result allows comparison of data of total and sieved samples, irrespective the sieving diameter but the error has to be taken into account. Through propagation of errors the standard error of the result can be calculated from the analytical variation and the natural variation of the intercept N_x . (Smedes *et al.*, 2005). Results can therefore always be reported with a standard deviation.

6. Considerations on cofactors

The **clay mineral content** is the most important cofactor for trace metals. In the model above the N_x will be zero for clay and only the intercept due to the content of the trace metal in the coarse fraction (C_x) has to be taken into account. However, current inter-comparison exercises do not include this parameter. Presently other parameters such as aluminium or lithium are used to represent the clay content.

The **aluminium** content in the sandy fraction may vary from area to area. For some areas aluminium contents in the sandy fractions are found at the same level as found in the fines (Loring, 1991) and therefore the intercept N_x becomes very high. In equation (3) this implies that the denominator is the result of subtracting two large numbers, that is the normaliser content in the sample (N_s) and the normaliser content in only sand (N_x). Consequently, due to their individual uncertainties, the result has an extremely high error. Obviously, normalisation with low intercepts is more accurate. Much lower intercepts are found if partial digestion methods are used that digest the clay minerals, but not the coarse minerals. Using partial digestion, the spatial variability of the results of aluminium analyses in the sandy fraction has been found to be much smaller than with total methods. Although normalising concentrations of contaminants in fine grained material will always give more accurate results, an error calculation will identify whether using coarse samples (and total methods, e.g. HF, X-ray fluorescence, lithium tetraborate fusion) allows the requirements of the program to be met.

For most areas the **lithium** content in the sandy fraction is much lower than in the fine fraction. In addition, results from partial digestion and total methods do not differ significantly. There is only little spatial variability of the lithium content in the sandy fraction. Generally, compared to aluminium, more accurate normalised data can be expected using lithium.

As for clay, no intercept (N_x) applies for organic matter, which is usually represented by **organic carbon**. Organic matter also occurs in the coarse fraction but is even then a cofactor that contributes to the affinity for contaminants, whereas the aluminium in the coarse fraction does not. Furthermore, organic matter in a sample is not always well

defined as it can be composed of material with different properties. The most variable properties will be found in the organic matter present in the coarse fraction, i.e. that not associated with the fines. In **fine sediments** or in the sieved fine fractions the majority of the organic matter is associated with the mineral particles and it is assumed to be of more constant composition than in the total sample. In addition, the nature of the organic matter may vary. For samples with low organic carbon content close to the detection limit, normalisation using this cofactor suffers from a large relative error. This results from the detection limit and the insufficient homogeneity that cannot be improved due to the limited intake mass for analysis.

For further interpretation of data, the **proportion of fines** determined by sieving can be useful. Provided there are no significant amounts of organic matter in coarse fractions, the proportion can be used as a cofactor, particularly for organic contaminants. The error in the determination of fines has to be taken into account and will be relatively high for coarse samples.

7. Considerations on contaminants

Almost all trace metals, except mercury and in general also cadmium, are present in the coarse mineral matrix of samples. The metal concentrations show a spatial variability depending on the origin of the sandy material. In sandy sediments, partial digestion techniques result in lower values than are obtained from total digestion techniques. This implies that partial digestion results in lower intercepts (pivot point is closer to the zero). However, the partial digestion must be strong enough so the clay will be totally digested as is the case with HF digestion techniques, and the measured aluminium content remains representative for the clay. It was demonstrated that analyses of fine material gave similar results for several trace elements using both total and strong partial methods (Smedes *et al.*, 2000; Kersten and Smedes, 2002, cf. Technical Annex 6).

For organic contaminants the situation is more complex. In general, correlations of organic contaminants with organic carbon have no significant intercept, i.e. the contaminants are primarily associated with organic matter. Thus for sediment samples that contain low concentrations of organic carbon (e.g. very sandy sediments), concentrations of these contaminants can be below or very close to the analytical detection limit. Application of the normalization procedure using organic carbon to such samples is inappropriate, since it will greatly magnify the analytical error. The influence of these errors can be minimised by analysing muddy sediments, or by analysing a fine fraction sieved from the bulk sandy sediment.

In some cases, PAHs in sediment are found associated with materials such as soot or ash. Concentrations of PAHs can be quite high in these materials, and this can result in high concentrations of PAHs in grain size fractions where soot, ash etc are concentrated. These materials generally are present in small quantities, and the PAHs associated with them have little biological activity, and therefore are of limited environmental significance. Although the available data are not comprehensive, existing information indicates that PAH concentrations in sieved fine fractions (e.g. <63 µm) are not significantly affected by the presence of small amounts of soot, ash etc.

8. Isolation of fine fractions for analyses

The Sample preparation

Samples should be sieved at 2 mm as soon as possible after sampling to remove large detritus and benthic organisms. Otherwise during further sample handling like storage, freezing or ultrasonic treatment, biotic material will deteriorate and become part of the sediment sample. Until the final sieving procedure that isolates the fines, the sample can be stored at 4°C for about a week and up to 3 months when frozen at -20°C, although direct wet sieving is preferred. For prolonged storage freeze-drying of samples can be considered. In this case contamination and losses of contaminants during freeze-drying have to be checked. Air-drying may also not be appropriate due to high contamination risks, and checks are needed. Besides, samples may be difficult to disaggregate and mineral structures may be affected.

Requirements for Sieving

A wet sieving procedure is required to isolate the fine-grained fractions, < 63 µm or < 20 µm. Wet sieving re-suspends fine particles that would otherwise remain attached to coarser particles in the sample. Sediments should be agitated during sieving to disaggregate agglomerates of fines and to prevent clogging of the mesh. Freeze-dried samples need to be re-suspended using ultrasonic treatment. Seawater, preferably from the sampling site, should be used for sieving as it reduces the risk of physico-chemical changes in the sample i.e. losses through leaching or contamination. Furthermore seawater assists the settling of fine particles after the sieving. If water from the sampling site is not available, then seawater of an unpolluted site, diluted with deionised water to the required salinity, can be used. The amount of water used for sieving should be kept to a minimum and be reused for sieving subsequent batches.

To minimise or prevent contamination it is recommended to use large sample amounts of sediment for sieving. No significant contaminant losses or contamination was detected when at least 25 g of fine fraction is isolated.

Methodology

Both automated and manual methods are available for sieving. A video presentation of these methods can be provided by the QUASH Project (QUASH, 1999).

- The automatic sieving method pumps seawater over a sieve that is clamped on a vibrating table (Klamer *et al.*, 1990). The water passing the sieve is lead to a flow-through centrifuge that retains the sieved particles and the effluent of the centrifuge is returned to the sieve by a peristaltic pump. Large sample amounts, up to 500 g, can be handled easily.
- The second method is a manual system sieving small portions 20–60 g using an 8-cm sieve in a glass beaker placed in an ultrasonic bath (Ackermann *et al.*, 1983). Particles are isolated from the water passing the sieve by batch wise centrifugation. The water can be reused for a subsequent batch of sediment. In case of sandy samples, when large amounts of sediments have to be sieved, removal of the coarse material by a pre-sieving over e.g. 200- μm mesh can facilitate the sieving process.

Isolated fine fractions have to be homogenised thoroughly, preferably by a ball mill, as centrifugation produces inhomogeneous samples due to differences in settling speed of different grain-size fractions.

9. Limitations of normalisation

The purpose of normalisation is to reduce the variability between samples arising from differences in bulk sediment properties. However, it has been observed in some areas that the correlations between contaminant and cofactor concentrations may be weak or even absent. This may happen, e.g., if the cofactor used is inappropriate for the contaminant of concern, the degree of contamination is very variable with time or space, or there is significant additional variance arising from the measurements of the concentration of the chosen cofactor.

Contracting Parties may specify cofactors other than Al, Li or TOC to be used for the normalisation of concentrations of particular contaminants in their monitoring data. The effectiveness of the normalisation should be assessed through the effect of application of normalisation on the residual variance about time series, as described above. When making proposals, it will be necessary for Contracting Parties to ensure that pivot values and Background Concentrations expressed in relation to the same cofactors are also available.

Current procedures applied by OSPAR MON in assessing time series of data include the application of smoothers or, for short time series, linear regressions. Normalisation using cofactors should be applied if this results in a reduction of the residual variance around the fitted smoother or regression in time series, but should not be applied if the residual variance is not reduced. In case the residual variance can be reduced for time series, normalisation should also be applied to check whether observed concentrations of contaminants are at or close to Background (Assessment) Concentrations and whether they comply with the Environmental Assessment Criteria.

Furthermore, as the composition of sand-sized material may differ significantly between different parts of the Convention area, **pivot values** (cf. Section 5) can vary too. In addition, they can vary with the analytical method, i.e. with partial or total digestion for metals analysis. The use of inappropriate pivot values could have significant impact on the calculated normalised concentrations (cf. Section 5), particularly for sediment samples containing relatively small proportions of fine grained material. Therefore, Contracting Parties may derive pivot values appropriate to particular parts of the Convention area. Such regionalised pivot values should be applicable over large parts of the Convention area, for example across entire Regions

The current **Background (Assessment) Concentrations** may be inappropriate for application throughout the Convention area, as they were derived from a data set that emphasises the northern part of the Convention area. In addition, the Background Concentrations are currently expressed as normalised values (to 5% aluminium for metals and 2.5% TOC), and these “reference” values for the cofactors may not be appropriate for all areas. The use of inappropriate values for Background Concentrations could result in misleading assessments, e.g., as to whether concentrations in sediment are at or close to background. Therefore, Contracting Parties may derive Background Concentrations and associated cofactor values that they consider to be appropriate to particular parts of the Convention area. The combinations of Background Concentrations and associated cofactor values should be consistent with the way in which pivot values to be used in the assessment of the field data are expressed, to allow the construction of straight lines joining pivot values and Background Concentrations. Such regionalised Background Concentrations should be applicable over large parts of the Convention area, for example across entire Regions

10. Spatial monitoring in the CEMP

Historically, OSPAR has on occasion organised large scale spatial monitoring programmes to describe the spatial distribution of contaminants in the marine environment. However, such programmes have not been undertaken for many years for the more established contaminants.

The 2007 revision of the OSPAR Coordinated Environmental Monitoring Programme describes the role of spatial monitoring in CEMP. There are two primary roles:

- i) “if an area of concern is identified in a spatial programme, a temporal trend programme may be implemented at a limited number of representative sites;”

A purpose of spatial monitoring is therefore to identify areas for more thorough temporal trend monitoring. An example of this could be a proposal for “one-off” surveys of a group of emerging contaminants. A possible survey design would be to measure these contaminants (mainly in sediment) in a series of major river estuaries to detect the important areas of input for potential future monitoring. Such exploratory scoping programmes will usually lack underlying knowledge of the behaviour of the new contaminants.

A second purpose for spatial monitoring is:

- ii) if a temporal trend changes unexpectedly, a spatial programme may be used to identify contaminant sources or the extent of the problem.”

This is a form of investigative monitoring, by which an unexpected problem or feature of data is identified and a programme is subsequently designed to investigate the cause and scale of the effect.

Both of these purposes are rather specialised, and it is difficult to give reliable guidelines on the need for, or nature of, appropriate normalisation of concentrations of contaminants in sediment. For example, it is unlikely that there will be enough underlying information concerning emerging contaminants to be able to specify the best normalisation methods, and almost by definition there will be insufficient data to establish BACs or EACs.

In the second case, the nature of investigative programmes will be very dependent on the problem being investigated, and details of its geographical location. The objective will be to answer the specific issue that made the investigation necessary. Investigative programmes will need great flexibility and will be specifically designed to address unexpected features in local data. It is therefore difficult to specify how data from such an investigation should be handled.

In both cases, therefore, the group managing the programme must be aware of the potential of differences in bulk sediment properties to influence their data and to take account of this in their data interpretation. However, the variable and unpredictable nature of these surveys and their results mean that rigid definition of approaches to data interpretation would be inappropriate.

11. Recommendations

1. For monitoring, it would be ideal to analyse samples with equal composition. This could be confirmed by determination of cofactors Al, Li, TOC and parameters of the grain size distribution (e.g. clay content, proportion < 20µm, proportion < 63µm). However, this situation will seldom occur.
2. New temporal trend programs should be carried out by the analysis of fine sediments or a fine-grained fraction, isolated by sieving. Existing temporal trend programs could be continued using existing procedures, provided that assessment of the data indicates that the statistical power of the programs is adequate for the overall objectives.
3. Contaminant concentrations in whole sediments can be subjected to normalisation using cofactors for organic matter, clay minerals etc., by taking into account the presence of both cofactors and target contaminants in the mineral structure of the sand fraction of the sediment. Taking into account these non-zero intercepts of regressions of contaminant concentrations with cofactors, normalisation to preselected cofactor content will reduce the variance arising from different grain sizes. Normalised values for sandy sediments will have greater uncertainties than for muddy sediments. The propagated error of the variables used for normalisation may be unacceptably high for sandy sediments, if both contaminant and cofactor concentrations are low, particularly when approaching detection limits. In that case, in order to reduce the overall uncertainty, alternative procedures, such as sieving, need to be used to minimise the impact of this error structure.
4. The natural variance of sample composition will be smaller in the fraction < 20 µm than in the fraction < 63 µm. Therefore, for trace metals, the fraction < 20 µm should be preferred over the fraction < 63 µm. However, separation of the fraction < 20 µm can be considerably more laborious than the separation of the fraction < 63 µm and this may prove to be an obstacle to its wide application. For this practical reason, the

fraction < 63 µm is an acceptable compromise for monitoring programmes. For organic contaminants, the fraction < 63 µm should be used for analyses, as it may be difficult to incorporate the organic matter with the highest binding capacity for organic contaminants in the fine grained fraction < 20 µm completely. Thus, variances due to separating the fine fraction can be reduced.

5. There will still be some residual variance arising from differences in the composition (mineralogy and organic carbon content) of the sediments. Therefore, the preferred approach is analyses of contaminants in fine sediments or in the fraction < 63 µm, followed by normalisation of analytical results using cofactors (see section 3). Current scientific knowledge indicates that this procedure minimises the variances arising from differences in grain size, mineralogy and organic matter content. Application of this two-tiered approach to fractions < 20 µm gives results that can be directly compared to results found by normalisation of concentrations measured in fractions < 63 µm.
6. In order to clarify aspects of data interpretation, analytical data for field samples should be accompanied by information on limits of detection and long term precision. In order to contribute to environmental assessment, data for field samples should include the grain size distribution, as a minimum the proportion of the analysed fraction in the original whole sediment. Aluminium (Al) and total organic (TOC) concentrations should be reported for use as potential cofactors. If possible, the determination of Li as an additional potential cofactor is recommended.
7. In order to take into consideration potential regional differences in sediment composition in monitoring contaminants in sediments and its assessment, cofactors others than those mentioned in section 3 may be used. Furthermore, regionalised pivot points for calculating normalised contaminant concentrations as well as regionalised Background (Assessment) Concentrations may be derived for different regions.
8. In order to take into consideration potential regional differences in sediment characteristics and normalisation procedures, it is recommended that the current assessment procedure using EACs/ERLs be revisited with a view to introducing a degree of flexibility in the expression and testing of data against these criteria.
9. In the case of spatial monitoring, exploratory scoping programmes will usually lack underlying knowledge of the behaviour of the new contaminants, and of assessment criteria such as BACs or EACs. Investigative programmes will be very dependent on the problem being investigated, and details of its geographical location, and will need great flexibility to be able to effectively address unexpected features in local data. It is therefore difficult to specify how data from either kind of programme should be handled. In both cases, the group managing the programme must be aware of the potential of differences in bulk sediment properties to influence their data and to take account of this in their data interpretation. However, the variable and unpredictable nature of these surveys and their results mean that rigid approaches to data interpretation would be inappropriate.

12. References

- Ackermann, F., Bergmann, H., and Schleichert, U. 1983. Monitoring of heavy metals in coastal and estuarine sediments - A question of grain-size: <20 µm versus <60 µm. *Environmental Technology Letters*, 4: 317–328.
- Cato, I. 1977. Recent sedimentological and geochemical conditions and pollution problems in two marine areas in south-western Sweden. *Stria*, 6. 158 pp. Uppsala.
- Gobeil, C., MacDonald, R. W., and Sundby, B. 1997. Diagenetic separation of cadmium and manganese in suboxic continental margin sediments. *Geochim. Cosmochim. Acta*, 61: 4647–4654.
- Kersten, M., and Smedes, F. 2002. Normalisation procedures for sediment contaminants in spatial and temporal trend monitoring - a critical review, *J. Environ. Monit.*, 4: 109–115.
- Klamer, J. C., Hegeman, W. J. M., and Smedes, F. 1990. Comparison of grain size correction procedures for organic micropollutants and heavy metals in marine sediments. *Hydrobiologia*, 208: 213–220.
- Loring, D. H. 1991. Normalization of heavy-metal data from estuarine and coastal sediments. *ICES Journal of Marine Science*, 48: 101–115.
- OSPAR. 2008. CEMP Assessment Manual. Co-ordinated Environmental Monitoring Programme Assessment Manual for contaminants in sediment and biota.
- QUASH. 1999. Sediment Sieving Techniques, QUASH Project Office, FRS Marine Laboratory, PO Box 101, Victoria Road, Aberdeen, AB11 9DB, Scotland.
- Smedes, F. 1997. Grain size Correction Procedures, Report of the ICES Working Group on Marine Sediments in Relation to Pollution. *ICES CM 1997/Env:4*, Annex 6.
- Smedes, F., Lourens, J., and Wezel, van A. 1997. “Zand, Slib en Zeven, Standardisation of contaminant contents in marine sediments, Report RIKZ-96.043 (Dutch), ISSN 0927-3980, RIKZ, PO Box 20907, 2500 EX, The Hague.
- Smedes, F., Davies, I. M., Wells, D., Allan, A., Besada, V. 2000. Quality Assurance of Sampling and Sample Handling (QUASH) - Interlaboratory study on sieving and normalisation of geographically different sediments; QUASH round 5 (sponsored by the EU Standards, Measurements and Testing Programme).
- Smedes, F., Davies, I. M., and Fryer, R. J. 2005. Pragmatic estimation of uncertainty in normalized concentrations of contaminants in sediments. *ICES CM 2005/Z:04*.

Windom, H. L., Schropp, S. J., Calder, F. D., Ryan, J. D., Smith, R. G. Jr., Burney, L. C., Lewis, F. G., Rawlinson, C. H. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the south-eastern United States. *Environ. Sci. Technol.*, 23: 314–320.

Appendix

Testing normalisation methods

As normalisation should correct for sediment composition, a criterion for an adequate normaliser is that after normalisation of equally polluted sediment samples with different grain size distributions, the results should not differ significantly. However, sample sets to test normalisation approaches for this criterion are scarce. An alternative approach is to take one sample and to produce subsamples with varying grain size distributions (Smedes, 1997; Smedes *et al.*, 1997; Smedes *et al.*, 2000). Both the fine and coarse subsamples are analysed for contaminants and potential normalisers. In this way a higher variability for the normaliser concentrations, i.e. a worst case than ever will occur in nature, can be obtained which provides a sensitive test for the effectiveness of potential normalisers.

Normalisation is intended to correct for sediment composition for sediments that are equally polluted. Here equally polluted means that the sediments are in equilibrium with the same water. Normalised results should not significantly differ for sediment samples with different grain size distributions

To test which parameters, i.e. co-factors, are suitable for a certain area, a set of equally polluted samples should be collected. In practice this is often problematic as often pollution is not homogeneous in the area and/or the range in grain-size that can be collected is too limited to properly demonstrate relations between co-factors and contaminants.

However, this can also be addressed through an active approach which is applicable to all areas, excepting areas where sediment is dominated by only sand or gravel. Smedes *et al.* 1997 used pairs of sieved and un-sieved samples to test co-factors. In the EU QUASH project, survey and intercalibration samples were actively separated in different grain-size fractions (Smedes *et al.*, 2000). To adopt this approach, the following procedure is suggested. A large sediment sample, 3 litre or more, containing sand as well as fine material, is taken. This sample is transferred to a glass bottle and liquefied using local water and then shaken, tumbled or mixed for at least one month. The sediment is then separated into subsamples with different grain-size compositions by sieving and decantation. A range of fractions can be separated, for example <20 μ m, <63 μ m, >63 μ m etc and, of course, also the un-fractionated sediment is part of the set.

A decantation procedure will give another type of sample. Suspend the sediment in the local water used for shaking and wait a short time to allow the coarse material to settle. Then quickly pour off part of the upper water into a second container. Let the particles settle and pour the water back, with the residual coarse material, and repeat until sufficient fine material has been separated for analysis. It is also possible to sieve only at 20 μ m and mix the <20 μ m and the >20 μ m in different proportions creating a series of equidistant compositions.

It is suggested that the approach described above also includes the estimation of pivot values. Therefore a portion of coarse sediment, i.e. >63 μ m, is treated with ultrasonic so fine material attached to the coarse sediment is released. This fine material is washed out and if sufficient can be analysed also. The coarse sample is added to the sample set.

Results from such an exercise are given below. Here 10 kg sediment from 6 different positions was equilibrated by tumbling for 3 months in excess water. In this research project, organotin compounds were added to investigate their distribution over grain-size fractions (Smedes and Nummerdor, 2003¹). In Figure 1–4, the relations of co-factors and some metals are given for several stations. The extreme differences in composition caused by the separation process allow demonstration of the relations over large concentration ranges. Also, some rather extreme samples (like very coarse floating material that was sometimes present in low quantities, typically 0.1–0.5%) were isolated when present. This material had a very high organic carbon content, very low mineral cofactors and a higher OC/N ratio than the rest of the fractions. In Figure 4, this sample is the outlier (open symbols) in the relations. Basically these fractions have no meaning as they are of very low abundance but they give some indication of whether target elements or compounds show a preference for organic carbon, although it should be considered it is not the typical OC as is normally found from humic and fulvic residues.

Values close to the origin also allow derivation of pivot values, although this was not the focus of the QUASH project. Figure 5 shows cofactor and zinc data for all stations in the fraction >63 μ m; only a few of these were ultrasonically treated. For the Dutch coastal area, the pivot value for Zn can be estimated at about 14–15 mg/kg and for Al and Li at around 4 g/kg and 4 mg/kg respectively.

¹ Smedes, F., and Grietje, A., and Nummerdor, N. 2003. Grain-size correction for the contents of butyl compounds in sediment. RIKZ/2003.035. ISBN 03693477x, National Institute of Coastal and Marine Management (Rijksinstituut voor Kust en Zee), RIKZ, PO Box 20907, 2500 EX, The Hague, The Netherlands.

Application of this process will provide robust information and allow optimization of normalisation for a certain location and will show what bias or variability may be expected from the use of non-regionalised values for pivot points in the procedure for normalisation.

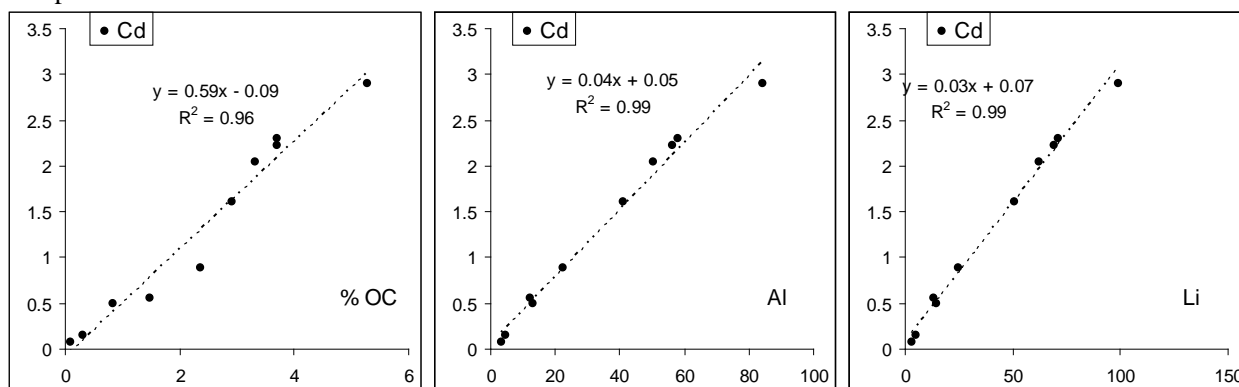


Figure 1 Cd and cofactors in Rotterdam harbour area.

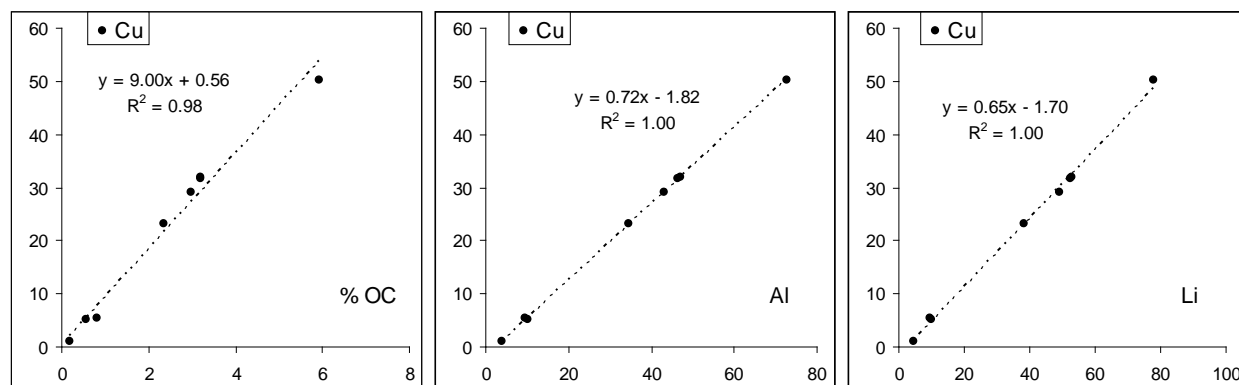


Figure 2. Cu and cofactors in Nieuwe Waterweg towards Sea.

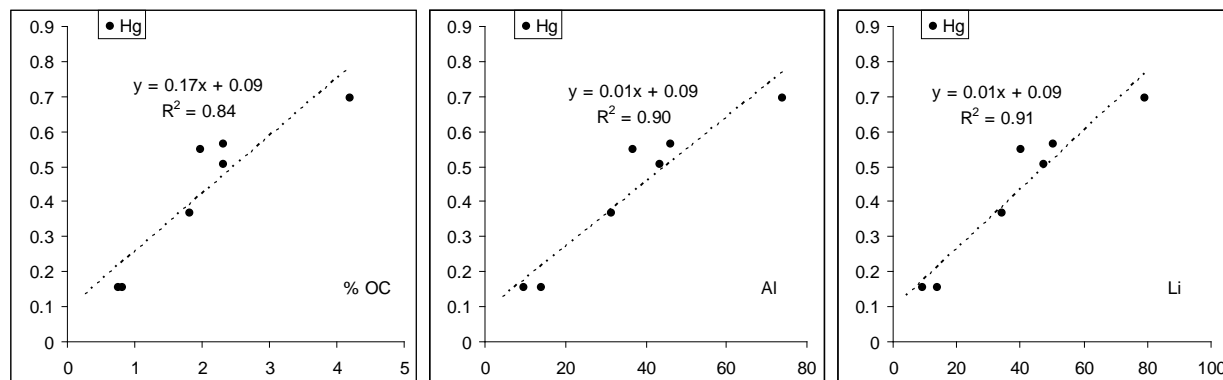


Figure 3. Hg and cofactors in sludge dump site at Sea.

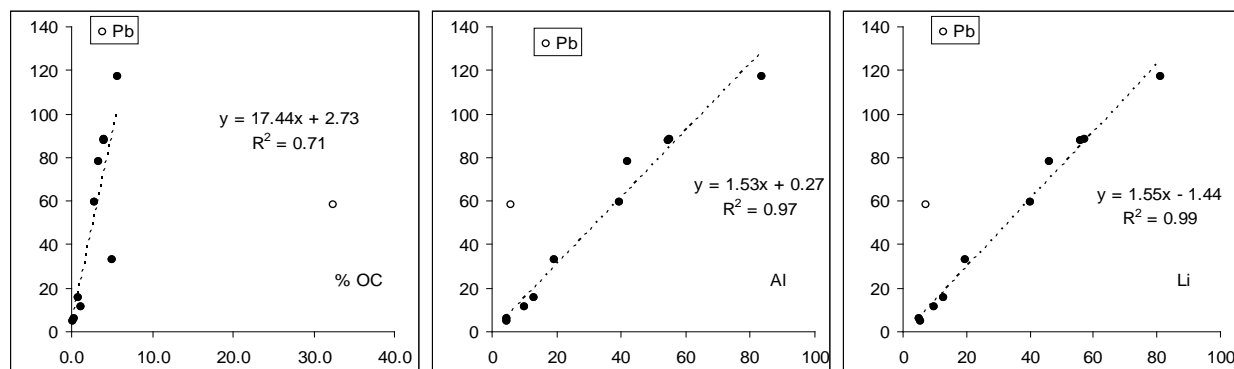


Figure 4. Pb and cofactors in front of IJmuiden Harbor. Note that one outlier is omitted. This is from coarse floating material with high OC content and representing less than 0.2% of the sample weight.

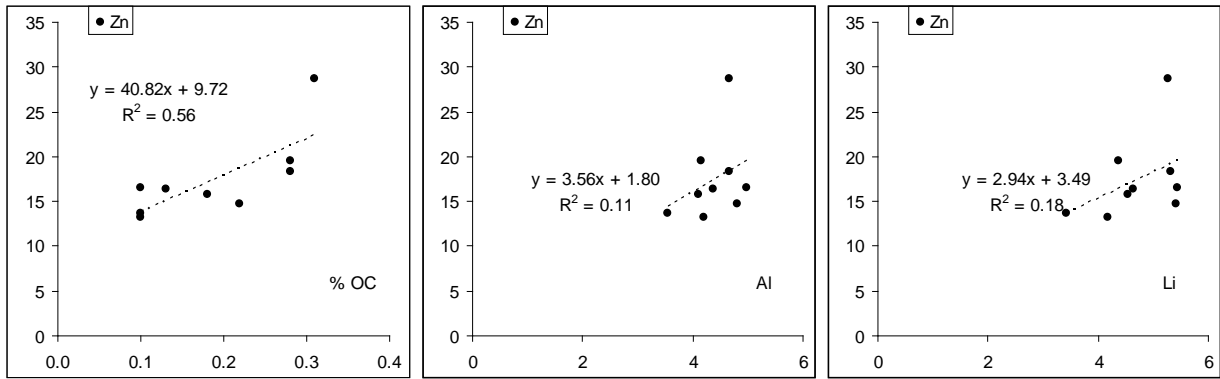


Figure 5. Zn and cofactors in only the >63 samples.