OSPAR COMMISSION

Protecting and conserving the North-East Atlantic and its resources

Background document on background assessment concentrations for Polybrominated Diphenyl Ethers (PBDE) in sediment report

Hazardous Substances and Eutrophication Series

2020

Background document on background assessment concentrations for Polybrominated Diphenyl Ethers (PBDE) in sediment

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OSPAR Convention

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the “OSPAR Convention”) was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. The Contracting Parties are Belgium, Denmark, the European Union, Finland, France, Germany, Iceland, Ireland, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Convention OSPAR

La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. Les Parties contractantes sont l'Allemagne, la Belgique, le Danemark, l’Espagne, la Finlande, la France, l’Irlande, l’Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d’Irlande du Nord, la Suède, la Suisse et l’Union européenne.

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1. Definitions/Glossary

AICc: Akaike Information Criterion corrected for small sample size.

BAC: Background Assessment Concentration – an assessment threshold for testing whether contaminant concentrations are ‘near background’.

BC: Background Concentration – the concentration of a compound in the pristine environment.

CEMP: Coordinated Environmental Monitoring Programme.

df: degrees of freedom.

EAC: Environmental Assessment Criteria – an assessment threshold for testing whether contaminant concentrations are likely to have adverse biological effects on the marine environment.

FEQG: Federal Environmental Quality Guideline.

ICES: International Council for the Exploration of the Sea.

LC: Low Concentration – the low, but measurable, concentration of a man-made substance used in the construction of a BAC.

MIME: Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment.

PAH: polycyclic aromatic hydrocarbon.

PBDE: polybrominated diphenyl ether.

PCB: polychlorinated biphenyl.

QSR: quality status report.

Quasimeme: Quality Assurance of Information for Marine Environmental Monitoring in Europe.

2. Executive Summary

To enable assessments of monitoring data for hazardous substances in marine sediment and biota, there is a need to have relevant assessment tools. OSPAR developed Background Assessment Concentrations (BACs) to assess contaminant concentrations in the environment. BACs are used to test whether concentrations are 'near background' or 'close to zero" in the case of man-made substances.

BACs for selected polybrominated diphenyl ether (PBDE) congeners in sediment were developed by MIME 2017 and trialled in the 2018 CEMP assessment (OSPAR, 2018). The BACs were updated by MIME 2018 and trialled in the 2019 CEMP assessment (OSPAR, 2019).

It is proposed that BACs of 0.05 µg kg^{-1} dw are adopted for CEMP assessments of BDE28, 47, 66, 85, 99, 100, 153, 154, 183 and 209 concentrations in sediment. The BACs should be used for the assessment of concentrations normalised to 2.5% organic carbon in all MIME regions apart from the Iberian Sea and the Gulf of Cadiz, and of non-normalised concentrations in the Iberian Sea and the Gulf of Cadiz.

Récapitulatif

Pour permettre l'évaluation des données de surveillance des substances dangereuses dans les sédiments et le biote, il est nécessaire de disposer d'outils d'évaluation pertinents. OSPAR a développé des concentrations d'évaluation de fond (BAC) pour évaluer les concentrations de contaminants dans l'environnement. Les BAC sont utilisées pour tester si les concentrations sont "proches des teneurs ambiantes" ou "proches de zéro" dans le cas des substances de synthèse.

Les BAC pour certains congénères de l'éther diphénylique polybromé (PBDE) dans les sédiments ont été développées par le MIME 2017 et testées dans l'évaluation du CEMP de 2018 (OSPAR, 2018). Les BAC ont été mises à jour par le MIME 2018 et testées dans l'évaluation du CEMP de 2019 (OSPAR, 2019).

L'on propose d'adopter les BAC de 0,05 µg kg 1 dw pour les évaluations CEMP des concentrations de BDE28, 47, 66, 85, 99, 100, 153, 154, 183 et 209 dans les sédiments. Les BAC devraient être utilisées pour l'évaluation des concentrations normalisées à 2,5 % de carbone organique dans toutes les régions du MIME, à l'exception de la mer Ibérique et du golfe de Cadix, et des concentrations non normalisées dans la mer Ibérique et le golfe de Cadix.

3. Introduction

Contaminant monitoring data form the basis of environmental assessments, which aim to characterise the status or quality of the marine environment with regard to chemical pollution. This means that measured concentrations are compared with assessment concentrations describing cut-offs for categories of environmental quality. These assessment concentrations have important implications as they are used to classify the status of a marine area.

OSPAR Background Assessment Concentrations (BACs) and Environmental Assessment Criteria (EACs) were primarily developed for the assessment of contaminant concentrations. BACs are used to make precautionary tests of whether observed concentrations are 'near background' or 'close to zero' in the case of man-made substances. Compounds with concentrations below the BAC fulfil the ultimate aim of the OSPAR Hazardous Substances Strategy of approaching the natural Background Concentration (BC). EACs were developed to assess whether concentrations of contaminants are likely to have adverse biological effects on the marine environment.

The concept behind BACs was first proposed by OSPAR (2004) and subsequently formalised by ICES (2004, Section 6.1). BACs were first used on a trial basis in the 2005 CEMP assessment (OSPAR, 2005a). Provisional BACs for selected metals in sediment, polycyclic aromatic hydrocarbons (PAHs) in sediment and mussels, and the polychlorinated biphenyl (PCB) CB153 in sediment, mussels and fish liver were then recalculated and agreed by OSPAR (2005b). Over the next few years, these were updated and added to, with the current set of BACs agreed by OSPAR (2009a, 2009b) in time for use in the 2010 Quality Status Report (QSR) (OSPAR, 2010). These BACs are for selected metals, PAHs and PCBs in sediment, fish and shellfish. BACs for polybrominated diphenyl ethers (PBDEs) were not developed at that time because insufficient monitoring data were available on which to base them.

The subject of BACs and EACs (or EAC equivalents) for PBDEs was revisited by MIME 2017. MIME developed BACs for selected PBDEs in sediment, fish and shellfish and trialled them in the 2018 CEMP assessment (OSPAR, 2018). The BACs were updated by MIME 2018 and used in the 2019 CEMP assessment (OSPAR, 2019). More work is required to develop satisfactory BACs for fish and shellfish. However, MIME 2019 proposed that the BACs for sediment be formally adopted for future CEMP assessments.

4. Synopsis of Background Information

4.1 Methodology for constructing Background Assessment Concentrations

BACs are used to test whether concentrations are at background levels for naturally occurring substances, or 'close to background' for man-made substances. This is done by testing the null hypothesis $H_0: \mu \geq BAC$ against the alternative hypothesis $H_1: \mu < BAC$ where μ is the mean concentration (in the most recent monitoring year). The test is precautionary since concentrations are considered to be above background (H_0) unless there is sufficient evidence to show otherwise (H_1).

The BAC is chosen to give a 90% power of rejecting H_0 when μ = BC, where BC is the Background Concentration. The BC of natural occurring substances is estimated using data from near-pristine locations (assuming they exist) and, for sediment concentrations, from cores. The BC of man-made substances is zero, and to construct the BAC it is necessary to replace the BC by a Low Concentration (LC) which is typically taken to be twice the Quasimeme standard error. This is typically taken to be twice the Quasimeme (Quality Assurance of Information for Marine Environmental Monitoring in Europe) external proficiency testing constant error, used in the calculation of Z-scores. The Quasimeme constant error was chosen as it is both measurable and ‘close to zero’, and is defined by the QUASIMEME Scientific Advisory Board. For the purposes of this section, the BC (or LC) is assumed known.

Power depends on the statistical test used, the number of years of data, and the variability in the data. It is necessary to standardise these to construct a BAC that can applied across the OSPAR area. Specifically, it is assumed that:

- there is a 10-year monitoring programme with the same sampling protocol followed every year (or equivalently, and more realistically, a 20-year monitoring programme with sampling every two years)
- the test is a one-tailed t-test at the 5% significance level based on the temporal trend regression model fitted to the monitoring data (as currently applied in CEMP assessments)
- the variability in the data is typical of that found in CEMP data; this is developed later, but for now it is assumed that the variability is characterised by a parameter ψ

The concentration measurements each year are assumed to be summarised by an annual index on the logarithmic scale (e.g. the median log concentration or the mean log concentration). Let **y** be the vector (length 10) of annual contaminant indices and assume that

$$\mathbf{y} = \mathbf{f} + \boldsymbol{\varepsilon}$$

where **f** represents a smooth systematic trend in contaminant levels over time and **ε** represents random variation, assumed to be independent between years and normally distributed with zero mean and standard deviation ψ. Let **X** be the design matrix used to estimate the systematic trend **f**. The choice of **X** is also discussed later, but it could correspond to a linear trend or a smooth on a fixed number of degrees of freedom. It is assumed that **X** estimates **f** with no bias. Let *r* be the rank of **X** and ν = 10 - *r* be the residual degrees of freedom associated with **X**. Let

$$\mathbf{H} = \mathbf{X}(\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}'$$

be the hat matrix. The fitted trend is then $\hat{\mathbf{f}} = \mathbf{H}\mathbf{y}$, which has variance $\mathbf{H}\psi^2$.

A one-tailed t-test at the 5% significance level is used to test H_0 vs H_1. Let

$$T = \frac{\hat{\mathbf{f}}_{10} - \log \mathrm{BAC}}{\hat{\psi}\sqrt{\mathbf{H}_{10,10}}}$$

where the 10 suffix picks out the fitted value and its variance in the most recent monitoring year, and where $\hat{\psi}^2$ is the usual unbiased estimator of ψ^2. Then H_0 is rejected in favour of H_1 if $T < t_{crit}$, where t_{crit} is the 0.05 quantile of a central t-distribution on ν degrees of freedom, denoted (t; ν). That is, the value such that

$$\mathrm{Prob}\left((t;\nu) < t_{crit}\right) = 0.05$$

When $\mathbf{f}_{10}$ = log BAC, T has a central t-distribution T ~ (t; v). More generally, T has a non-central t-distribution T ~ (t; v; δ) on v degrees of freedom and non-centrality parameter

$$\delta = \frac{\mathbf{f}_{10} - \log \text{BAC}}{\psi\sqrt{\mathbf{H}_{10,10}}}$$

The BAC is chosen to give 90% power when $\mathbf{f}_{10}$ = log BC. Let δ_{crit} be the value that satisfies

$$\text{Prob}\left((t;\nu;\delta_{crit}) < t_{crit}\right) = 0.90$$

Then the BAC is given by

$$\log \text{BAC} = \log \text{BC} - \delta_{crit}\psi\sqrt{\mathbf{H}_{10,10}}$$

or equivalently

$$\text{BAC} = \text{BC}\exp\left(-\delta_{crit}\psi\sqrt{\mathbf{H}_{10,10}}\right)$$

Two problems remain: choosing the appropriate form of **X** and hence **H** and estimating a suitable value of ψ. The methods for doing both have been updated since BACs were last constructed (in preparation for the 2010 QSR) to accommodate developments in the trend assessment methodology. A summary of the changes can be found in the discussions at MIME 2017.

First consider the choice of **X**. A time series with 10 years of data is assessed by fitting a linear trend and smooths on 2 and 3 degrees of freedom (df) and choosing the optimal model based on the Akaike Information Criterion corrected for small sample size (AICc). In practice, most time series reduce to a linear trend. However, the smooth on 2 df gives BACs that are closest to the previous approach and hence is used here. The corresponding values of δ_{crit} and **H** leads to BACs of the form:

$$\text{BAC} = \text{BC}\exp(2.51\psi)$$

Now consider the choice of ψ. The concentration measurements are modelled in a mixed modelling framework. This gives estimates of the between-sample and between-year random variation for each time series, denoted here as $\sigma^2_{i,\text{sample}}$ and $\sigma^2_{i,\text{year}}$ with the i used to index the time series. Analytical variability and the number of samples per year have tended to evolve in most time series (getting lower and fewer respectively) so, to characterise recent performance, the analytical variability $\sigma^2_{i,\text{analytical}}$ for time series is based on the median reported uncertainty in the last three monitoring years. Similarly, the number of samples per year n_i for time series i is taken to be the median number of samples in the last three monitoring years. The residual variance for time series i is then estimated to be

$$\psi_i^2 = \sigma^2_{i,\text{year}} + \frac{1}{n_i}(\sigma^2_{i,\text{sample}} + \sigma^2_{i,analytical})$$

The value of ψ typical of CEMP data is estimated by fitting a robust loess smoother (Cleveland et al., 1992) to the log ψ_i as a function of the fitted log mean concentration in the final monitoring year, with a span of 1 and weighted by the number of years in each time series. The (back-transformed) fitted value of the loess smoother at the BC (LC) is taken to be the typical ψ at background (low) concentration. When the BC (LC) is outside the range of the data, the fitted value at the closest observed mean concentration is used.

One final consideration: BACs are statistical constructs and there is no guarantee that they are environmentally relevant. They should be rejected if they are higher than the EAC or equivalent (if it exists) and if they are too high based on expert judgement. For PBDEs, the Canadian Federal Environmental Quality Guidelines (FEQGs) adapted for use in CEMP assessments (**HASEC 20/6/3**) were used as EAC equivalents.

4.2 Background Assessment Concentrations for PBDEs in sediment

The Quasimeme constant error is 0.05 µg kg^{-1} dw for PBDEs in sediment, so the standard choice of LC is 0.1 µg kg^{-1} dw. However, MIME 2017 considered this too high because many time series had mean concentrations around 0.1 µg kg^{-1} dw even in areas that would not be considered background. Instead, an LC of 0.01 µg kg^{-1} dw was used, a value typical of the lowest mean concentrations observed for most of the PBDEs considered (see Figure 1).

Figure 1 shows, by PBDE, the estimates of the residual standard deviation ψ from each time series plotted against the estimated mean concentration in the most recent monitoring year. They are taken from the 2019 CEMP assessment (OSPAR, 2019). There are systematic differences in variability between Contracting Parties which could be due to differences in the number of samples taken, analytical and reporting quality control, or natural variability in concentrations due to the choice of monitoring stations or other environmental drivers. A smoother, fitted to the data for each PBDE, was used to estimate the value of ψ typical of mean concentrations close to the LC. In Figure 1, this was usually the value of ψ where the smoother cut the LC (the grey vertical line). The two exceptions were BDE209, where the mean concentrations were all above the LC and the value of ψ at the lowest observed mean concentration was used, and BDE85, where there were too few data to fit the smoother and ψ was undefined. The value of ψ at the LC was then used to estimate the BAC (blue vertical line) for each PBDE. The BACs were all below the FEQGs (green vertical lines), typically well below (the FEQG for BDE183 is not shown because it is off the scale of the plot), with the smallest relative differences for the more toxic BDE99 and BDE100. The estimates of ψ at the LC, the resulting BACs and the FEQGs are given in Table 1.

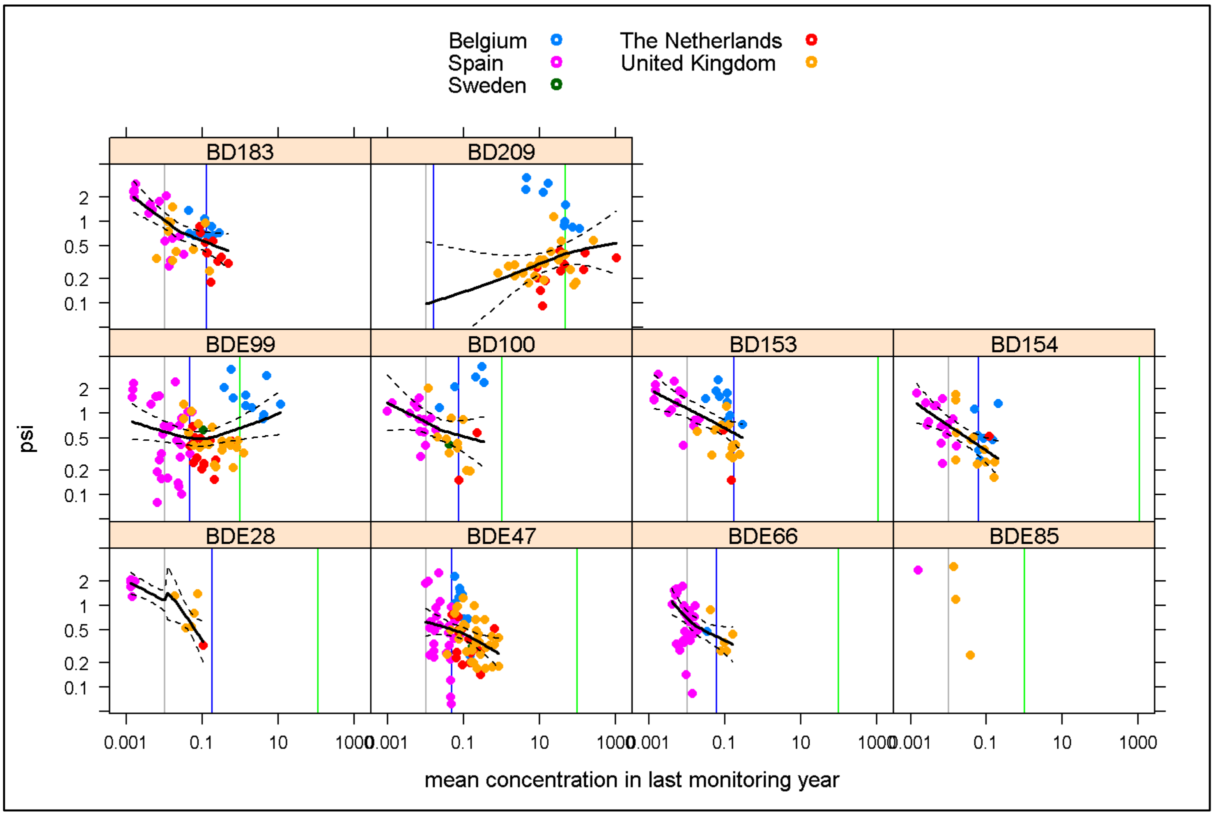

Figure 1. Estimates of the residual standard deviation ψ from each time series plotted against the estimated mean concentration (µg kg^{-1} dw) in the most recent monitoring year by PBDE congener. The points are coloured by Contracting Party. Concentrations are normalised to 2.5% organic carbon for Belgium, the Netherlands, Sweden and the United Kingdom but are not normalised for Spain. The fitted loess smoother (black line) with 95% pointwise confidence limits (dashed lines) is also shown. The three vertical lines are the LC (grey), the BAC (blue) estimated using the methodology described in Section 4.1, and the FEQG (green). A BAC could not be estimated for BDE85 and the FEQG for BDE183 is not shown as it is off the scale of the plot. Note that the BACs shown here are based on the monitoring and analytical characteristics of the individual congeners and, apart from BDE47, not the BACs eventually proposed for adoption.

Table 1. Estimates of ψ typical of CEMP data at concentrations close to the LC, with lower and upper 95% confidence limits, the BACs derived from them, and the FEQGs. Concentration units are µg kg^{-1} dw.

Congener	Ψ			LC	BAC	FEQG
	lower cl	estimate	upper cl			
BDE28	0.85	1.18	1.63	0.01	0.19	110.0
BDE47	0.42	0.62	0.92	0.01	0.05	97.5
BDE66	0.57	0.70	0.86	0.01	0.06	97.5
BDE85				0.01		1.0
BDE99	0.45	0.60	0.80	0.01	0.04	1.0
BDE100	0.57	0.79	1.08	0.01	0.07	1.0
BDE153	0.88	1.15	1.50	0.01	0.18	1100.0
BDE154	0.55	0.71	0.91	0.01	0.06	1100.0
BDE183	0.82	1.03	1.30	0.01	0.13	14000.0
BDE209	0.09	0.19	0.39	0.01	0.02	47.5

The BACs in Table 1 are environmentally acceptable in the sense that they are below the FEQGs. However, the wide variation in BACs between compounds (0.02 - 0.19 µg kg^{-1} dw) was considered unsatisfactory by MIME 2018, as it tended to reflect variation in analytical performance rather than environmental characteristics, and as it often resulted in higher BACs for compounds that would be expected to have lower concentrations based on a typical PBDE profile. MIME 2018 therefore agreed to use the BAC for BDE47 of 0.05 µg kg^{-1} dw for all the PBDE congeners in the 2019 CEMP assessment. The value for BDE47 was chosen because a) it was based on the most data; b) BDE47 had one of the lower values of ψ and hence one of the lower BACs; c) the BAC was below the mean concentration observed in most BDE47 time series, particularly in areas that would not be considered background; d) all Contracting Parties had monitoring data close to the BAC, so the value of ψ was representative of a wide range of CEMP data sources.

The BAC for BDE99 of 0.04 µg kg^{-1} dw was an alternative, more precautionary, candidate. However, the estimates of ψ for BDE47 and BDE99 were very similar (Table 1). In fact, before rounding, the point estimate of the BAC for BDE47 was 0.047 with 95% confidence intervals (0.029, 0.101) and the estimate for BDE99 was (slightly below) 0.045 with 95% confidence intervals (0.031, 0.074), so there was little to choose between them. In particular, 0.05 was well within the confidence intervals for both congeners. On balance, particularly considering points a) and d) above, MIME 2018 agreed that the value of 0.05 µg kg^{-1} dw based on BDE47 was a sensible choice. (Note that the rounding to 2 decimal places is consistent with the reporting resolution of most PBDE concentration measurements.)

MIME 2018 agreed to use the BAC of 0.05 µg kg^{-1} dw in all MIME regions. Concentrations normalised to 2.5% organic carbon were compared with the BAC in all regions apart from the Iberian Sea and the Gulf of Cadiz, and non-normalised concentrations were compared with the BAC in the Iberian Sea and the Gulf of Cadiz.

To illustrate, Figures 2 and 3 respectively show status assessments for BDE47 and BDE99 from the 2019 CEMP assessment using a BAC of 0.05 µg kg^{-1} dw. Points are coloured

- blue if the mean concentration is significantly ($p < 0.05$) below the BAC
- green if the mean concentration is significantly ($p < 0.05$) below the FEQG
- red if the mean concentration is not significantly below the FEQG

Status assessments for all the PBDE congeners considered in the 2019 CEMP assessment can be explored in more detail in the 2019 OSPAR contaminant app.

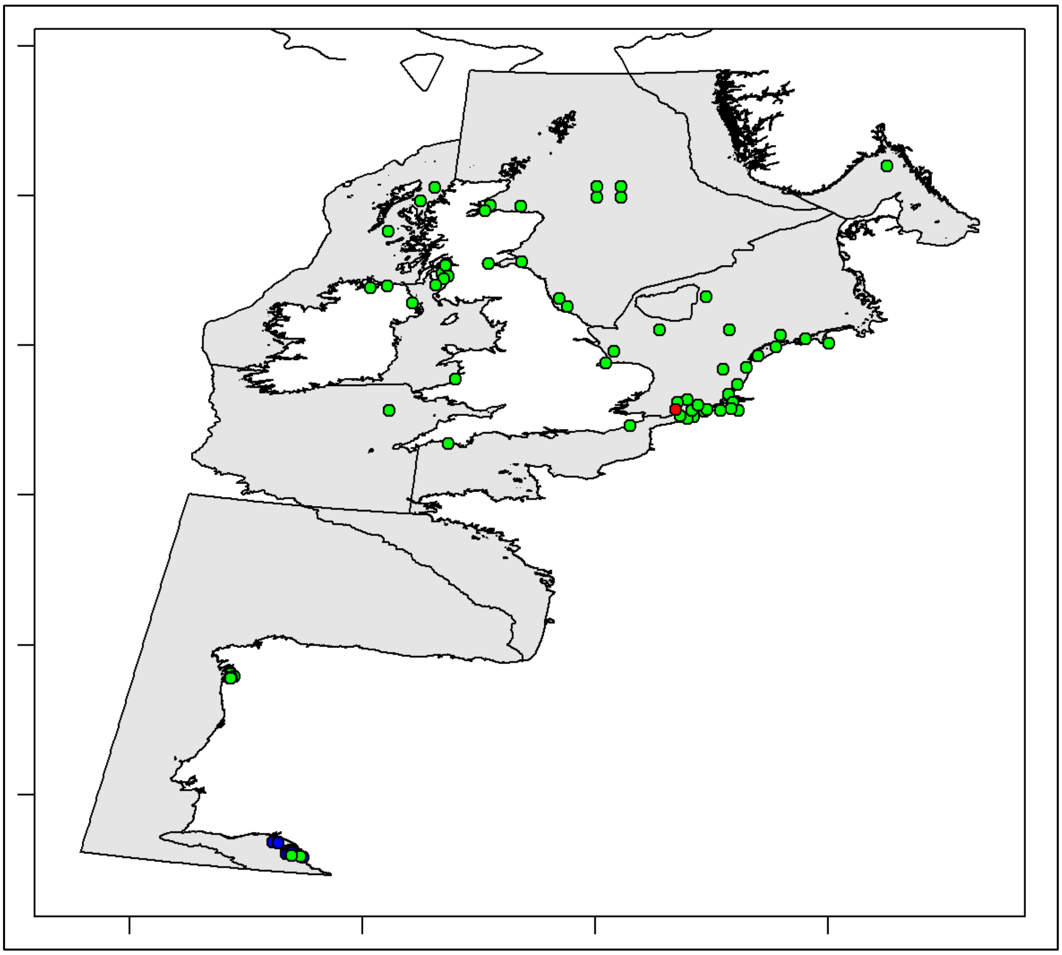

Figure 2. Status assessment of BDE47 from the 2019 CEMP assessment.

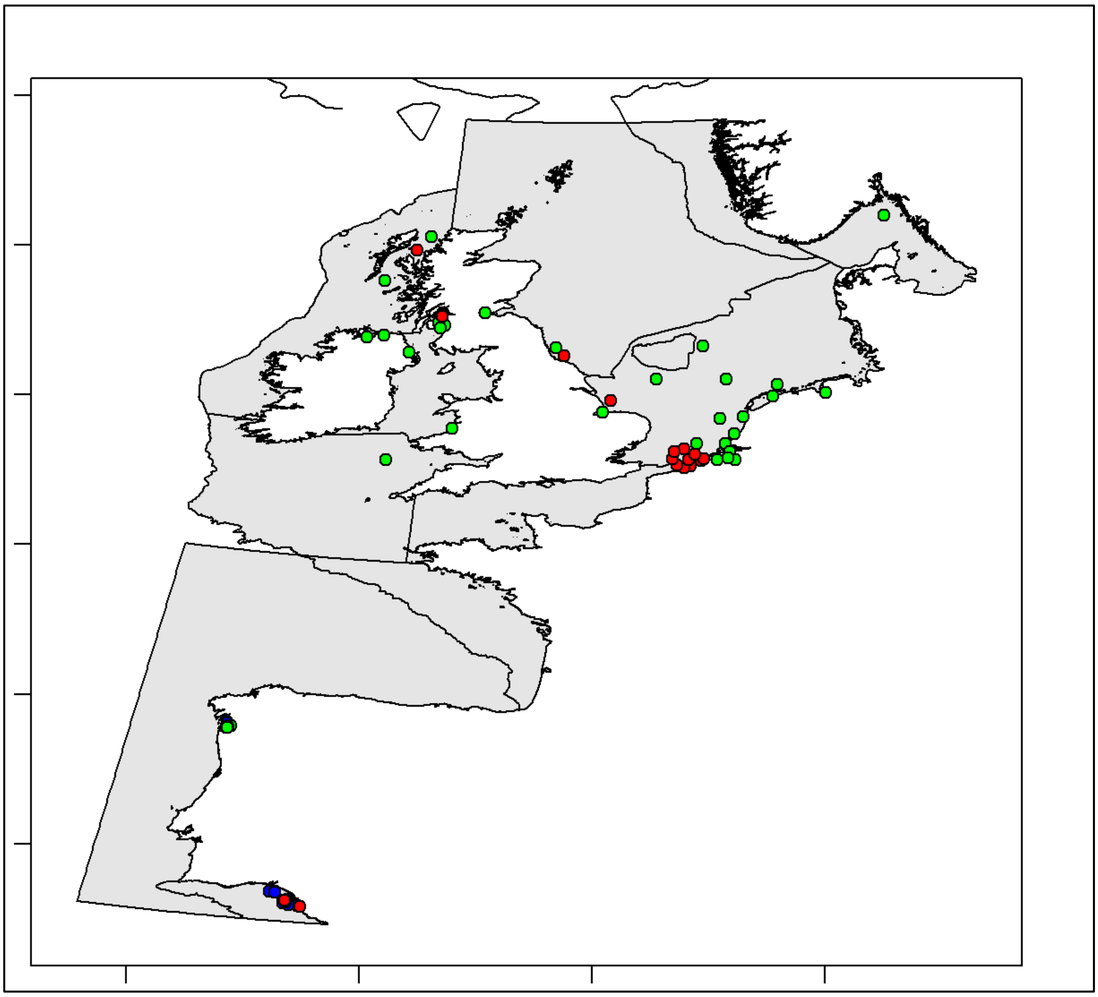

Figure 3. Status assessment of BDE99 from the 2019 CEMP assessment.

The PBDE congeners assessed in the 2019 CEMP assessment (BDE28, 47, 66, 85, 99, 100, 153, 154, 183 and 209) are only a selection of those measured and reported to the ICES database. If other congeners are considered in future assessments, then it is anticipated that analytical performance and sediment biogeochemistry for these compounds will be similar and a BAC of 0.05 µg kg^{-1} dw could be applied on a trial basis.

The BAC of 0.05 µg kg^{-1} dw should only be applied to the concentrations of individual PBDE congeners. If the sum of several PBDE congeners is to be assessed (for example, the sum BDE28, 47, 99. 100, 153 and 154) for comparison with the European Commission Environmental Quality Standard, then a new BAC appropriate for this sum would have to be calculated.

The BAC of 0.05 µg kg^{-1} dw should only be applied to concentrations normalised to 2.5% organic carbon in MIME regions apart from the Iberian Sea and the Gulf of Cadiz, and non-normalised concentrations in the Iberian Sea and the Gulf of Sea. If concentrations in future CEMP assessments are ever normalised to a different % organic carbon, then the choice of BAC will have to be reconsidered. There is no simple adjustment that could be made because of the mix of normalised and non-normalised concentrations used to construct the BAC (see Figure 1) and the use of a LC which is based on analytical performance rather than sediment characteristics.

5 Conclusions

BACs of 0.05 µg kg^{-1} dw should be adopted for OSPAR CEMP assessments of BDE28, 47, 66, 85, 99, 100, 153, 154, 183 and 209 concentrations in sediment. The BACs should be used for the assessment of concentrations normalised to 2.5% organic carbon in all MIME regions apart from the Iberian Sea and the Gulf of Cadiz, and of non-normalised concentrations in the Iberian Sea and the Gulf of Cadiz.

6 Proposals

BACs of 0.05 µg kg^{-1} dw should be adopted for OSPAR CEMP assessments of BDE28, 47, 66, 85, 99, 100, 153, 154, 183 and 209 concentrations in sediment. The BACs should be used for the assessment of concentrations normalised to 2.5% organic carbon in all MIME regions apart from the Iberian Sea and the Gulf of Cadiz, and of non-normalised concentrations in the Iberian Sea and the Gulf of Cadiz.

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OSPAR's vision is of a clean, healthy and biologically diverse North-East Atlantic used sustainably

ISBN: 978-1-913840-00-6
Publication Number: 761/2020