Trace Metal and Chlorinated Hydrocarbon Concentrations in Shellfish from Irish Waters, 2001

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ABSTRACT

Major shellfish growing areas were sampled in accordance with the monitoring requirements of Council Directive 79/923/EEC, on the quality required of shellfish waters, and Council Directive 91/492/EEC, laying down the health conditions for the production and placing on the market of live bivalve molluscs. Data for physicochemical parameters in water, trace metal levels and chlorinated hydrocarbon concentrations in shellfish are presented.

In 2001, a total of 23 samples from 20 different shellfish sites were analysed for trace metals and chlorinated hydrocarbons. The median concentration of mercury in shellfish sampled in 2001 was <0.03 mg kg^{-1} wet weight, with a maximum of 0.04 mg.kg^{-1} wet weight which is well within the maximum limit of 0.50 mg kg^{-1} wet weight for mercury in bivalve molluscs set by the EU. The levels of lead and cadmium detected were low, with means of 0.20 and 0.24 mg kg^{-1} wet weight and maxima of 0.37 and 0.74 mg.kg^{-1} wet weight respectively, also within the respective maximum levels of 1.50 and 1 mg kg^{-1} wet weight set by the EU. There are no internationally agreed standards or guidelines available for the remaining trace metals and chlorinated hydrocarbons in shellfish. However these results were compared with the strictest standard or guidance values for shellfish, which are applied by contracting countries to OSPAR, and were found to be well below the strictest values listed. This is evidence of the clean, unpolluted nature of Irish shellfish and shellfish producing waters.

As in previous years, the water quality from shellfish growing areas was good and conformed to the requirements of the Directive. Petroleum hydrocarbons were not visible in any of the shellfish waters or as deposits on the shellfish. This survey confirms previous studies (Glynn *et al.*, 2003; McGovern *et al.*, 2001; Bloxham *et al.*, 1998; Smyth *et al.*, 1997 and Nixon *et al.*, 1995, 1994, and 1991), which show that contamination from trace metals and chlorinated hydrocarbons is low in Irish shellfish aquaculture.

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INTRODUCTION

The determination of water quality, trace metal and chlorinated hydrocarbon concentrations in shellfish from Irish waters is carried out by the Marine Institute in part fulfilment of the monitoring requirements of various EU legislation, including:

- EU Council Directive 79/923/EEC on the quality required of shellfish growing waters, as implemented in Ireland by Statutory Instrument (SI) No. 200 of 1994,
- EU Directive 91/492/EEC laying down the health conditions for the production and placing on the market of live bivalve molluscs,
- Commission Regulation 466/2001/EC (as amended by Regulation 221/2002/EC),

This information also contributes to the Joint Assessment and Monitoring Programme (JAMP) as required by the 1994 OSPAR convention.

Trace metals exist naturally in the environment and many including chromium, cobalt, copper, iron, manganese, molybdenum, vanadium, strontium and zinc are essential elements for living organisms. However, some trace metals such as mercury, lead and cadmium are not required for metabolic activity and can be toxic at quite low concentrations.

Although mercury, lead and cadmium occur naturally in the earth's crust, they can also be introduced into the aquatic environment from anthropogenic activities such as mining, industry and agriculture. Once in the aquatic environment these metals can be bioaccumulated in fish tissues. Due to physiological differences, certain species will concentrate mercury more readily than others (Clark *et al.*, 1997).

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are man-made compounds that are ubiquitous air and water-borne contaminants. These are persistent pollutants with a tendency to bioaccumulate in fish tissue and biomagnify through the food chain (Clark *et al.*, 1997).

Council Directive 79/923/EEC requires that Member States designate shellfish growing areas. Monitoring of a range of physicochemical parameters in designated shellfish waters is undertaken to ensure that the quality of the edible species is maintained or enhanced. Directive 79/923/EEC was transposed into Irish legislation through SI No. 200 of 1994 and this also sets out designated shellfish waters in Ireland.

Sampling during 1993 and 1994 was carried out bi-annually for selected sites. The results of these surveys (Nixon *et al.*, 1994, 1995) showed that the quality of designated shellfish growing waters in Ireland was appreciably higher than required by the guidelines of the Directive, and therefore the frequency of monitoring was reduced to an annual basis in 1995, as is permitted under the Directive. Previous results were published by Glynn *et al.*, 2003; McGovern *et al.*, 2001; Bloxham *et al.*, 1998; Smyth *et al.*, 1997 and Nixon *et al.*, 1995, 1994 and 1991. This report presents the results of 23 shellfish samples (6 *C. gigas*, *6 O. edulis* and *11 M. edulis)* from 20 sites in 2001, including a number of areas not formally designated.

Analyses of mercury, cadmium, chromium, copper, lead, zinc and chlorinated hydrocarbons were carried out on shellfish from all of the sites. Based on previous results, special attention was given to sites that may be influenced by local anthropogenic sources (Bloxham *et al*., 1998; Smyth *et al.*, 1997 and Nixon *et al.*, 1995, 1994 and 1991).

With the exception of mercury, cadmium and lead (Commission Regulation 466/2001/EC) there are currently no applicable European standards for trace metals and chlorinated hydrocarbons in fishery products. Therefore in the absence of EU standards for other contaminants in shellfish, monitoring results have been compared to strictest guidance or standard values available in other OSPAR Convention contracting countries.

Other reports on residue and contaminants monitoring in farmed and wild finfish, as well as other food safety and environmental monitoring reports are available from the Marine Institute (www.marine.ie/chem).

MATERIALS AND METHODS

Sample collection and preservation

Shellfish samples were collected from September to November. Figure 1 shows the areas sampled in 2001. Detailed information on the locations, dates, species sampled, cultivation methods etc. are shown in Appendix 1.

Where possible, approximate to each site where shellfish were sampled, temperature, salinity and pH measurements were taken *in situ*, typically at 1m depth using a Hydrolab® multiparameter probe (Minisonde®). At each location the water surface was visually examined for evidence of hydrocarbon contamination. Collected water samples were returned to the laboratory for the determination of suspended solids. Typically, one litre of water was filtered through a 0.45 µm membrane, which was washed with purified water and dried at 105 °C. Results of the physico-chemical measurements are shown in Appendix 1.

Samples of the main shellfish species produced in each of the growing areas were collected; mussels consisting of 50 individuals and oysters of 25 individuals. Shellfish were depurated overnight in seawater collected from the growing area at the time of sampling. The lengths of individual shellfish were recorded prior to the soft tissue being removed from the shells to be washed and drained. The percentage meat and shell weights were calculated and recorded. The pooled soft tissue was then homogenised and approximately a 1g sub-sample taken from the homogenate and dried at 105ºC to constant weight to determine the moisture content. The remainder was divided into 2 sub-samples; one portion was freeze-dried for 16 hours and stored for metal analysis, the other stored at < -20ºC prior to mercury and chlorinated hydrocarbon analysis.

Mercury analysis

Concentrated nitric acid (4ml) was added to approximately 0.7g of wet tissue and digested in a laboratory microwave oven (CEM MARS 5). After cooling, potassium permanganate was added until the colour of the solution stabilised. Sufficient hydroxylamine sulphate/ sodium chloride solution was added to neutralise the potassium permanganate and 1ml of potassium dichromate was added as a preservative. The solution was diluted to 100ml with deionised water.

Following reduction of the samples with stannous chloride, the mercury was determined by Cold Vapour Atomic Fluorescence Spectroscopy (CV-AFS) using a PSA Merlin Analyser.

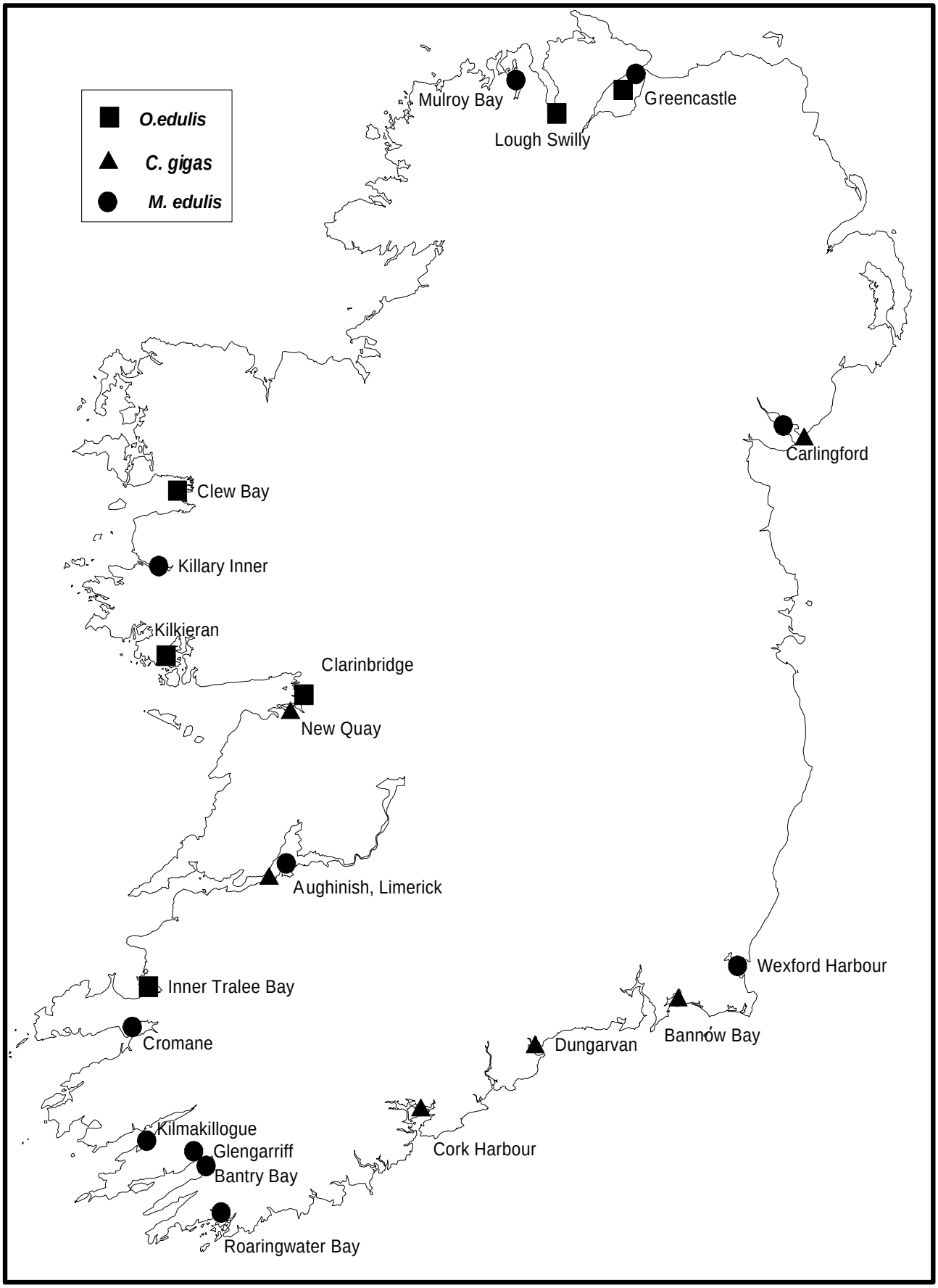

Figure 1. Location of shellfish-growing areas monitored during 2001.

Trace metal analysis (cadmium, chromium, copper, lead and zinc)

Nitric acid (4ml) and hydrogen peroxide (4ml) were added to approximately 0.2g of freeze dried tissue and digested in a laboratory microwave oven (CEM MARS 5). After cooling samples were diluted to 50mls with deionised water. Lead, cadmium, chromium and copper concentrations were determined using Graphite Furnace Atomic Absorption Spectrometry with Zeeman background correction (Varian SpectrAA 220Z). Zinc concentrations were determined using Flame Atomic Absorption Spectroscopy (Varian SpectrAA 20 Plus).

Chlorinated hydrocarbon analysis

Due to the lipophilic nature of PCBs and OCPs, lipid was extracted from tissue samples using the method developed by Smedes, (QUASH, 1998; QUASH, 1999). Chlorinated hydrocarbons were removed from the lipid by alumina column chromatography followed by separation of the majority of PCBs from the OCPs using silica column chromatography. Concentration levels were determined by gas chromatography with electron capture detection (GC-ECD) using a Hewlett Packard 5890 gas chromatograph fitted with two 50 metre 0.25mm i.d. fused silica capillary columns (CP-SIL 8CB, Chrompack) and a second column of different polarity as confirmation (CP-SIL 19CB, Chrompack).

Quality control

To ensure sufficiently high quality analytical data was produced during the 2001 shellfish monitoring programme, quality control samples, including reference materials (RMs), were analysed with each batch of samples. As the availability of appropriate marine certified reference materials (CRMs) is limited (de Boer and McGovern, 2001), reference materials supplied by QUASIMEME, (Quality Assurance of Information for Marine Environmental Monitoring), FRS Marine Laboratory, Aberdeen, were used to supplement the use of CRMs.

Although not certified, QUASIMEME provides materials of suitable matrix and analyte concentrations that have assigned values derived from intercalibrations involving many expert laboratories in this field. Obtaining a Z-score between -2 and +2 is considered satisfactory for environmental monitoring programmes.

Between 3 and 10 analyses were carried out on each RM used in this programme, the results of which are shown in Table 1. The quality assurance results obtained were considered sufficient for the purpose of the monitoring programme. However a negative bias was determined for PCB 105. This was not considered to affect the results as all levels are in the region of two orders of magnitude below strictest OSPAR human health standards. A correction factor was applied to determinants PCB 28, 31 and 52 based on recoveries for reference materials, which demonstrated consistent positive bias for these determinants. Notwithstanding, as levels are over 2 orders of magnitude less than the lowest (German) human health standard available, this bias is not considered of importance in relation to the results.

Table 1: Results of the analyses of reference materials obtained during the 2001 shellfish testing.

a) Certified Reference Materials

Reference Material	Certified Values	Measured Value (Mean ± SD)	No. of Analyses	Mean Z Score	No. |Z|<2
Mussel Tissue CRM 278R					
	µg g^{-1} dry wt.	***µg g^{-1} dry wt.***			
Cadmium	0.348	0.263 ± 0.056	8	-1.24	7
Copper	9.45	8.33 ± 0.68	7	-0.91	7
Chromium	0.78	0.64 ± 0.11	8	-1.11	7
Lead	2.00	1.95 ± 0.17	8	-0.20	8
Mercury	0.196	0.182 ± 0.017	7	-0.41	7
Zinc	83.1	82.5 ± 7.2	10	-0.05	10
Oyster Tissue CRM 1566a					
	µg g^{-1} dry wt.	***µg g^{-1} dry wt.***			
Cadmium	4.15	4.18 ± 0.21	4	0.05	4
Copper	66.3	53.0 ± 1.61	4	-1.60	4
Chromium	1.43	1.03 ± 0.02	4	-1.95	4
Lead	0.371	0.462 ± 0.038	5	1.28	5
Mercury	0.0642	0.079 ± 0.010	5	0.80	5
Zinc	830	873 ± 62.2	4	0.41	4

b) QUASIMEME Reference Materials

Reference Material	Assigned Values	Measured Value (Mean ± SD)	No. of Analyses	Mean Z Score	No. |Z| <2
QOR062BT (Wet mussel tissue)					
PCBs	***mg kg^{-1} wet wt.***	***mg kg^{-1} wet wt.***			
PCB 101	3.2	3.08 ± 0.06	4	-0.27	4
PCB 105	0.83	0.35 ± 0.13	4	-3.16	0
PCB 118	2.35	1.95 ± 0.04	4	-1.16	4
PCB 138	6.11	6.11 ± 0.87	4	0.00	4
PCB 153	9.04	8.32 ± 0.11	4	-0.61	4
PCB 156	0.42	0.28 ± 0.04	4	-1.34	4
PCB 180	0.81	0.69 ± 0.02	4	-0.81	4
Organochlorine Pesticides					
DDD- p,p'	0.61	0.29 ± 0.05	4	-2.53	1
DDE- p,p'	1.34	1.28 ± 0.30	4	-0.26	3
DDT- o,p'	0.20	0.34 ± 0.05	4	1.86	1
DDT- p,p'	0.50	0.20 ± 0.14	4	-2.65	1
HCB	0.19	0.16 ± 0.02	4	-0.38	4
Lindane	0.17	0.35 ± 0.12	4	2.57	1
trans-Nonachlor	0.16	0.10 ± 0.02	4	-0.81	4

RESULTS AND DISCUSSION

Shellfish survey

The results of the biological measurements and physicochemical monitoring carried out during 2001 are given in Appendix 1. Generally, the water quality in all areas is good and conforms to the Annex of Directive 79/923.

Parameters such as pH, temperature, suspended solids and salinity are typical of results from previous monitoring. During sample collection the water surface was examined for the presence of visible petroleum hydrocarbons. No visible hydrocarbon film or deposition was evident at any of the shellfish-growing areas.

The concentrations of mercury, trace metals and chlorinated hydrocarbon contaminants analysed in the shellfish tissue are presented in Appendix 1. The level of contaminants in shellfish is a good indicator of contaminant levels present in the water column and can provide valuable information on the quality of the shellfish and the waters in which they are grown. As such, Irish shellfish monitoring data has been used for environmental assessments (Boelens *et al.*, 1999; EPA, 2000) as well as for the protection of consumers of Irish seafood products.

EU Commission Regulation 466/2001/EEC (as amended by Regulation 221/2002/EC) came into effect on 5th April 2002. This provides maximum levels for mercury, lead and cadmium in foodstuffs, including bivalve mussels. For mercury in fisheries products, the provisions of a previous decision (Commission Decision 93/351/EC) were transferred into this regulation. However, the maximum limit of 0.5mg kg^{-1} wet weight is unchanged with respect to shellfish. A maximum level of 1 mg kg^{-1} and 1.5 mg kg^{-1} wet weight for cadmium and lead respectively in bivalve molluscs is specified in this regulation.

As there are no currently applicable European standards for contaminants in shellfish, with the exception of mercury, cadmium and lead, the levels were compared with the available standards and guidance values set for human consumption by various OSPAR contracting countries. Individual values differ between countries, but the strictest guidance and standard values are presented in Table 2.

Table 2: Synopsis of the strictest guidance and standard values applied by various OSPAR countries for contaminants in shellfish for the assessment of the possible hazards to human health, updated to incorporate new European legislation on mercury, cadmium and lead.

Contaminant	Values and Units (wet weight)	Qualifier	Country
Cadmium	1.0 mg kg^{-1}	Guidance	EC[1]
Copper	20 mg kg^{-1}	Standard	Spain[2]
Lead	1.5 mg kg^{-1}	Guidance	EC[1]
Mercury	0.5 mg kg^{-1}	Standard	EC[1]
p,p' DDT and metabolites	500 µg kg^{-1}	Standard	Finland
HCB	50 µg kg^{-1}	Guidance	Norway
α and β HCH	50 µg kg^{-1}	Guidance	Norway
Lindane	100 µg kg^{-1}	Standard	Finland
PCB 28	80 µg kg^{-1}	Standard	Germany
PCB 52	80 µg kg^{-1}	Standard	Germany
PCB 101	80 µg kg^{-1}	Standard	Germany
PCB 138	100 µg kg^{-1}	Standard	Germany
PCB 153	100 µg kg^{-1}	Standard	Germany
PCB 180	80 µg kg^{-1}	Standard	Germany

Notes: 1. Commission Regulation 466/2001/EC as amended by Commission Regulation 221/2002/EC

2. This value does not apply to Oysters for which a higher value of 60 mg kg^{-1} has been set.

Oysters are known to accumulate high levels of zinc with concentrations as high as 11,000 mg kg^{-1} wet weight being found in the digestive glands (Clark *et al.*, 1997). The UK is the only country at present to set down a guideline value of 50mg kg^{-1} for Zn in food; however this excludes shellfish. The level in shellfish is expected to be well in excess of 100 mg kg^{-1} wet weight, (Anon., 1993).

There are no published guidelines for acceptable concentrations of chromium in shellfish. Chromium contamination results mainly from human activities.

Assessment of data for individual shellfish growing areas

Data obtained during monitoring in 2001 is examined below for each sampling location and considered with respect to human consumption standards and guidance values and also to previous years monitoring data. This data is available in Fisheries Research Centre (FRC) fisheries leaflets and Marine Institute (MI) Marine Environmental Health Services publications (Glynn *et al*., 2003; McGovern *et al*., 2001; Bloxham *et al*., 1998; Smyth *et al*., 1997 and Nixon *et al.*, 1995, 1994 and 1991).

Aughinish, New Quay, Co. Clare

A sample of *C. gigas* was collected from Aughinish Bay during 2001. Trace metal concentrations were well below human consumption tolerance values as compiled by OSPAR (Table 2). Cadmium was determined at 0.74 mg kg^{-1} wet weight, which is below the EU maximum limit (1.0 mg kg^{-1}). Copper levels were found to be 22.2 mg kg^{-1} wet weight, well below the Spanish standard of 60 mg kg^{-1} set for oysters. The level of mercury present in the *C. gigas* sample (0.03 mg kg^{-1} wet weight) was more than 10 times lower than the EU maximum limit for mercury in fisheries products. Analysis of the sample for organochlorine substances indicated that levels were very low with respect to human consumption standards.

Aughinish, Limerick

M. edulis and *C. gigas,* were sampled from Aughinish, Limerick. The level of mercury was low at 0.03 and <0.03 mg kg^{-1} wet weight for *M. edulis* and *C. gigas* respectively. Copper levels for *C. gigas* sample were found to be 27.0 mg kg^{-1} wet weight, well below the Spanish standard of 60 mg kg^{-1} set for oysters. Results for other trace metals were very similar to previous years monitoring. Levels of PCBs and organochlorine pesticides in 2001 were comparable with previous years and were well within tolerance levels compiled by OSPAR (Table 2).

Bannow Bay

C. gigas were tested for organics and trace metals in 2001. Trace metal concentrations in shellfish were found to be very similar to previous years and well within the tolerance levels given in Table 2. Analysis of the sample for chlorinated hydrocarbons indicated levels far below strictest tolerance levels as compiled by OSPAR.

Bantry Bay

A sample of *M. edulis* was collected from Bantry Bay in 2001. The level of mercury in the soft tissues of *M. edulis* grown in Bantry Bay was <0.03mg kg^{-1} wet weight, well below the EU 0.5mg kg^{-1} maximum limit (Table 2). Other trace metal levels analysed in 2001 were well within the guideline concentrations and were similar to previous years. Chlorinated hydrocarbon levels were very low and comparable with previous values.

Carlingford Lough

C. gigas and *M. edulis* were sampled from Carlingford Lough. The level of mercury was low at 0.03 and 0.04 mg kg^{-1} wet weight for *M. edulis* and *C. gigas* respectively. Copper levels were found to be 24.0 mg kg^{-1} wet weight for *C. gigas* and 1.46 mg kg^{-1} wet weight for *M. edulis*, which were well below the Spanish standard of 60 mg kg^{-1} set for oysters and 20 mg kg^{-1} set for mussels. Analyses for other trace metals were carried out and results were very similar to previous years monitoring. Chlorinated hydrocarbons were measured and levels were low and well within the strictest standards available for PCBs.

Clarinbridge

Clarinbridge native oysters, *O. edulis* were sampled for this programme in 2001. Trace metal levels including mercury (<0.03 mg kg^{-1} wet weight) were low and compared favourably with the strictest tolerance levels available (Table 2). Levels of PCBs and organochlorine pesticides in 2001 were comparable with previous years and were well within tolerance levels compiled by OSPAR (Table 2).

Clew Bay

A sample of native oysters, *O. edulis*, collected in 2001was analysed for trace metals. Trace metal levels in the shellfish were low as in previous years and mercury was determined as <0.03 mg kg^{-1} wet weight, well within the strictest tolerance levels available (Table2). Chlorinated hydrocarbons were measured and levels were low and well within the strictest standards available.

Cork Harbour

Samples of Cork Harbour oysters, *C. gigas* were collected in 2001. Water and shellfish quality were similar to previous years and conformed to the requirements of the Directive. Copper levels were found to be 11.1mg kg^{-1} wet weight for *C. gigas*, well below the Spanish standard of 60mg kg^{-1} set for oysters. Levels for other trace metal and chlorinated hydrocarbon levels continues to be very low.

Cromane

A sample of *M. edulis* was collected from Cromane during 2001. Trace metal concentrations, including mercury continue to be low and within the tolerance levels set out in Table 2. Levels of PCBs and organochlorine pesticides in 2001 were comparable with previous years and were well within tolerance levels compiled by OSPAR (Table 2).

Dungarvan

A sample of Pacific oyster, *C. gigas*, collected in 2001 was analysed for trace metals. Trace metal levels including mercury (<0.03mg kg^{-1} wet weight) were low and compared favourably with the strictest tolerance levels available (Table 2). Chlorinated hydrocarbon levels continued to be very low.

Glengarriff

A sample of blue mussels, *M. edulis* was collected from Glengariff during 2001. Trace metal concentrations were comparable with previous years and were well below human consumption tolerance values as compiled by OSPAR (Table 2). Levels of PCBs and organochlorine pesticides in 2001 were comparable with previous years and were well within tolerance levels compiled by OSPAR.

Greencastle

O. edulis and *M. edulis* were sampled from Greencastle. The level of mercury was low at <0.03 mg kg^{-1} wet weight for both *M. edulis* and *O. edulis*. Copper levels were found to be 18.8 mg kg^{-1} wet weight for *O. edulis* and 1.16 mg kg^{-1} wet weight for *M. edulis*, which were well below the Spanish standard of 60 mg kg^{-1} set for oysters and 20 mg kg^{-1} set for mussels. Analyses for other trace metals were carried out and results were very similar to previous years monitoring. Chlorinated hydrocarbons were measured and levels were low and well within the strictest standards available for PCBs.

Kilkieran

A sample of native oysters, *O. edulis*, collected in 2001was analysed for trace metals. Trace metal levels in the shellfish were low as in previous years and mercury was determined as 0.03 mg kg^{-1} wet weight, this is well within the strictest tolerance levels available (Table 2). Chlorinated hydrocarbons were measured and levels were low and well within the strictest standards available for PCBs.

Killary Harbour, Inner

Mussel samples, *M. edulis*, were collected from Killary Harbour in 2001. The shellfish produced at this location contained levels of trace metals and chlorinated hydrocarbons well within the human consumption guidelines and standards set by OSPAR countries and in close agreement with previous years.

Kilmakillogue, Kenmare Bay

M. edulis were collected at Kilmakillogue and analysed for both trace metals and organochlorine substances. Trace metal levels in the shellfish were low as in previous years and mercury was determined as <0.03 mg kg^{-1} wet weight, this is well within the strictest tolerance levels available (Table 2). Chlorinated hydrocarbon analysis was carried out and results were well within the strictest standards set by OSPAR countries (Table 2).

Lough Swilly

Trace metals were determined for *O. edulis* sampled from Lough Swilly in 2001. The level of mercury was below the limit of quantitation (<0.03 mg kg^{-1} wet weight). Copper levels for *O. edulis* sample was found to be 12.2 mg kg^{-1} wet weight, well below the Spanish standard of 60 mg kg^{-1} set for oysters. Analyses for other trace metals were carried out and results were very similar to previous years monitoring.

Mulroy Bay

A sample of blue mussels *M. edulis*, collected in 2001 was anlaysed for trace metals and chlorinated hydrocarbons. The level of trace metals measured in *M. edulis* from Mulroy Bay were low and comparable with previous years and was well within human consumption guidelines and standards set by OSPAR countries (Table 2). Chlorinated hydrocarbon levels were low and comparable with previous values.

Roaringwater Bay

Mussel samples, *M. edulis*, were collected from Roaringwater Bay during 2001. Trace metal levels including mercury (<0.03 mg kg^{-1} wet weight) were low and compared favourably with the strictest tolerance levels available (Table 2). Chlorinated hydrocarbon analysis was carried out also and results were well within strictest standards available.

Tralee Bay, Inner

Analysis of *O. edulis* collected in 2001 conformed to previous years and results were within the values set out in Table 2. Water and shellfish qualities were similar to previous years and conformed to the requirements of the Directive. The level of chromium (0.42 mg kg^{-1} wet weight) conformed with previous monitoring and was considerably lower than the exceptional elevated value observed for 2000 sample (3.11 mg kg^{-1} wet weight).The level of mercury in the soft tissues of *O. edulis* was below the limit of detection, well below EU 0.5mg kg^{-1} maximum limit (Table 2). Chlorinated hydrocarbons were measured and levels were low and well within the strictest standards available for PCBs.

Wexford Harbour

Samples of *M. edulis* were collected from Wexford Harbour in 2001 and were analysed for both trace metals and organochlorine substances. As in previous years the mercury concentration measured in the mussels was very low at <0.03 mg kg^{-1} wet weight when compared with the EU maximum limit of 0.5mg kg^{-1} wet weight (Table 2). In 2001 a concentration of 1.22 mg kg^{-1} wet weight for copper in mussels was detected which is well below the Spanish standard of 20 mg kg^{-1} set for mussels. Similarly, the lead concentration of 0.37 mg.kg^{-1} wet weight was well within the EU maximum limit of 1.5 mg.kg^{-1} wet weight. Other trace metal levels in mussel tissue continues to be low. Analysis indicated organochlorine levels to be very low with respect to human consumption standards.

CONCLUSIONS

The water quality monitored in the shellfish growing areas in 2001 was good and conformed to the guidelines of the 1979 Council Directive 79/923/EC.

Based on the analyses of the 2001 samples, total mercury and trace metal concentrations in shellfish from shellfish growing areas were low, which agreed with previous studies (Glynn *et al*., 2003; McGovern *et al*., 2001; Bloxham *et al*., 1998; Smyth *et al.,* 1997 and Nixon *et al.,* 1995, 1994 and 1991). All shellfish samples tested for mercury, cadmium and lead were well within the respective limits of 0.5 mg kg^{-1}, 1 mg kg^{-1}, and 1.5 mg kg^{-1} wet weight, as set by European Commission Regulation 466/2001/EC, (as amended by Regulation 221/2002/EC).

Chlorinated hydrocarbon concentrations continue to be very low in Irish shellfish, which again confirmed previous studies (Glynn *et al*., 2003; McGovern *et al*., 2001; Bloxham *et al*., 1998; Smyth *et al.,* 1997 and Nixon *et al.,* 1995, 1994 and 1991). All results were well within the strictest standards and guidance values of OSPAR member states.

The analytical results presented in this report are indicative of the unpolluted nature of Irish waters and fisheries products with respect to environmental contaminants.

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Appendix 1 (Page 1 of 3): Results of monitoring of shellfish-growing areas - 2001.

Sample Site	Aughinish, New Quay Clare	Auginish, Limerick	Auginish, Limerick	Bannow Bay	Bantry Bay	Carlingford Lough	Carlingford Lough	Clarinbridge
M.I. Reference No.	ENV2001/ 393	ENV2001/ 414	ENV2001/ 415	ENV2001/ 383	ENV2001/ 411	ENV2001/ 352	ENV2001/ 351	ENV2001/ 394
Sampling date	22/10/01	15/11/01	15/11/01	15/10/01	13/11/01	06/09/01	06/09/01	22/10/01
Species sampled	*C. gigas*	*M. edulis*	*C. gigas*	*C. gigas*	*M. edulis*	*C. gigas*	*M. edulis*	*O. edulis*
Number individuals	25	50	25	25	50	25	50	25
Method of cultivation	trestle	bed	trestle	trestle	rope	trestle	bed	bed
Water Parameters								
Temperature (ºC)	12.2	10.6	10.6	14.0	12.3	15.9	16.9	12.2
Salinity (psu)	34.3	18.9	18.9	6.54	33.9	34.2	34.0	25.3
pH	7.98	8.11	8.11	8.01	8.27	8.18	8.21	8.29
Suspended Solids (mg L^{-1})	8.30	34.6	36.4	118	8.80	4.20	13.9	148
Shellfish								
Shell length range (mm)	78.8-133	52.0-75.1	81.4-113	77.0-126	47.8-64.3	101-134	41.5-58.1	70.9-110
Shell mean length (mm)	104	62.0	94.4	97.7	55.6	113	48.7	94.7
Shell length std dev (mm)	11.8	5.03	8.04	10.1	3.51	23.1	3.80	9.52
Meat weight (%)	12.7	20.2	10.3	21.8	35.1	7.80	31.3	12.9
Shell weight (%)	87.3	79.8	89.7	78.2	64.9	92.2	68.7	87.1
Meat water content (%)	79.5	80.3	81.7	79.5	75.7	76.7	74.9	81.7
Metals mg kg^{-1} (ppm) wet wt.								
Cadmium	0.74	0.24	0.42	0.10	0.13	0.33	0.13	0.24
Chromium	<0.19	0.23	0.22	nd	<0.19	<0.19	0.17	<0.19
Copper	22.2	1.74	27.0	3.91	1.62	24.0	1.46	7.37
Lead	0.25	0.26	0.14	0.16	0.15	0.26	0.69	0.13
Mercury	0.03	0.03	<0.03	<0.03	<0.03	0.04	0.03	<0.03
Zinc	680	15.4	315	104	29.3	473	18.2	200
PCB's µg kg^{-1} (ppb) wet wt.								
CB Congener 28*	0.29	0.20	0.18	0.26	0.16	0.29	N/A	0.20
CB Congener 52*	0.56	0.51	0.43	0.67	0.38	0.70	N/A	0.48
CB Congener 101	0.55	0.54	0.48	0.63	0.44	0.75	0.55	0.40
CB Congener 118	0.22	0.19	0.21	0.23	0.17	0.47	0.30	0.11
CB Congener 138	0.23	0.22	0.22	0.23	0.32	0.45	1.35	0.13
CB Congener 153	0.42	0.41	0.58	0.41	0.76	0.99	0.58	0.25
CB Congener 180	0.03	0.04	0.04	0.03	0.12	0.05	0.03	0.02
CB Congener 31*	0.67	0.20	0.16	0.27	0.16	0.28	nd	0.20
CB Congener 105	0.18	0.08	0.08	0.18	0.09	0.19	0.09	0.09
CB Congener 156	0.03	0.02	0.01	0.02	0.02	0.14	0.04	N/A
Organic pesticides µg kg^{-1} (ppb) wet wt.								
DDD - p,p'	0.51	0.12	0.27	0.16	0.06	0.24	0.17	0.17
DDE - p,p'	0.61	0.32	0.54	0.94	0.18	0.74	0.42	0.50
DDT - p,p'	0.43	0.05	0.51	0.21	0.34	0.32	0.12	0.43
HCB	0.07	0.04	0.04	0.06	0.04	0.06	0.04	0.02
gamma- HCH	0.40	0.44	0.40	0.47	0.45	0.70	0.54	0.42
trans-Nonachlordane	0.35	0.03	0.13	0.04	0.15	0.20	0.03	0.29
Aldrin	0.02	0.01	0.04	0.04	0.03	0.07	nd	0.02
Isodrin	0.12	0.04	0.04	0.06	0.03	0.15	nd	<0.03
trans-Chlordane	0.15	0.03	0.07	0.03	0.06	0.11	0.03	0.04
cis-Chlordane	0.16	0.03	0.03	0.02	0.03	0.02	0.02	0.02
Endrin	0.10	<0.03	0.07	nd	0.08	<0.04	0.04	0.06
Lipid Smedes (%)	2.62	1.46	1.68	2.98	1.95	3.32	1.86	1.89

Notes : N/A: Samples not analysed
nd: Substances were not detected above the Limit of Detection (LOD) (Appendix 2)
< value: value = Limit of Quantitation (LOQ) for the relevant determinand
***: Correction factor applied to PCB 28, 31 and 52 based on recoveries for reference materials. Values reported are indicative.**

Appendix 1 (Page 2 of 3): Results of monitoring of shellfish-growing areas - 2001.

Sample Site	Clew Bay	Cork Harbour	Cromane	Dungarvan	Glengarriff	Greencastle	Greencastle	Kilkieran
M.I. Reference No.	ENV2001/ 395	ENV2001/ 406	ENV2001/ 412	ENV2001/ 381	ENV2001/ 410	ENV2001/ 372	ENV2001/ 374	ENV2001/ 392
Sampling date	23/10/01	12/11/01	14/11/01	16/10/01	13/11/01	11/10/01	11/10/01	24/10/01
Species sampled	*O. edulis*	*C. gigas*	*M. edulis*	*C. gigas*	*M. edulis*	*M. edulis*	*O. edulis*	*O. edulis*
Number individuals	25	25	50	25	50	50	25	25
Method of cultivation	bed	bed	bed	trestle	rope	bed	bed	bed
Water Parameters								
Temperature (ºC)	12.8	12.4	N/A	15.1	12.5	N/A	13.3	N/A
Salinity (psu)	10.1	28.8	N/A	2.4	34.0	N/A	32.0	N/A
pH	8.26	8.64	N/A	7.66	8.23	N/A	8.02	N/A
Suspended Solids (mg L^{-1})	52.1	47.0	2.30	51.4	7.10	19.7	N/A	5.70
Shellfish								
Shell length range (mm)	70.5-89.9	81.1-117	44.3-64.9	85.7-112	50.5-63.1	42.9-55.6	63.5-112	69.2-95.1
Shell mean length (mm)	78.4	94.2	53.7	101	55.6	48.0	78.0	81.9
Shell length std dev (mm)	5.26	7.24	5.30	7.01	2.95	2.53	10.4	6.39
Meat weight (%)	9.10	14.9	29.4	16.0	45.9	25.1	11.8	7.20
Shell weight (%)	90.9	85.1	70.6	84.0	54.1	74.9	88.2	92.8
Meat water content (%)	75.5	75.3	74.5	76.4	74.5	77.2	73.0	76.7
Metals mg kg^{-1} (ppm) wet wt.								
Cadmium	0.50	0.23	0.14	0.22	0.10	0.09	0.34	0.43
Chromium	0.28	0.23	0.33	<0.19	<0.19	0.58	<0.19	<0.19
Copper	3.48	11.1	1.93	11.8	1.75	1.16	18.8	5.07
Lead	<0.06	0.45	0.14	0.29	0.09	0.13	0.10	0.10
Mercury	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.03
Zinc	337	165	23.7	226	25.9	15.9	439	421
PCB's µg kg^{-1} (ppb) wet wt.								
CB Congener 28*	0.17	N/A	0.19	0.23	0.18	0.19	0.25	0.13
CB Congener 52*	0.43	N/A	0.48	0.49	0.46	0.42	0.43	0.51
CB Congener 101	0.35	1.10	0.53	0.55	0.49	0.61	0.54	0.39
CB Congener 118	0.09	0.63	0.15	0.34	0.17	0.30	0.28	0.14
CB Congener 138	0.11	1.17	0.16	0.33	0.24	0.44	0.43	0.17
CB Congener 153	0.22	1.18	0.29	0.65	0.59	0.61	0.61	0.29
CB Congener 180	0.01	0.04	0.03	0.03	0.05	0.05	0.03	0.02
CB Congener 31*	0.17	N/A	0.19	0.20	0.12	0.13	0.13	0.14
CB Congener 105	0.08	0.18	0.09	0.12	0.05	0.11	0.09	0.10
CB Congener 156	<0.01	0.03	0.01	0.03	0.02	0.03	0.06	<0.01
Organic pesticides µg kg^{-1} (ppb) wet wt.								
DDD - p,p'	0.08	0.31	0.05	0.13	0.03	0.28	0.38	0.15
DDE - p,p'	0.16	1.30	0.19	0.51	0.19	0.65	0.78	0.19
DDT - p,p'	0.25	0.34	<0.03	0.35	0.18	0.22	0.12	0.21
HCB	0.03	0.03	0.05	0.03	0.05	0.03	0.04	0.04
gamma- HCH	0.31	0.47	0.46	0.38	0.48	0.44	0.35	0.59
trans-Nonachlordane	0.29	0.09	0.07	0.19	0.06	0.04	0.05	N/A
Aldrin	0.03	nd	0.01	N/A	0.05	<0.01	0.02	0.02
Isodrin	0.08	<0.03	0.14	0.06	nd	nd	nd	0.13
trans-Chlordane	<0.01	0.04	0.10	0.06	0.03	0.03	0.05	N/A
cis-Chlordane	0.04	0.04	0.05	0.05	0.04	0.02	0.04	N/A
Endrin	0.12	0.09	<0.03	0.05	0.07	0.04	nd	0.17
Lipid Smedes (%)	1.91	2.73	1.90	2.94	2.36	1.86	2.20	2.12

Notes : N/A: Samples not analysed
nd: Substances were not detected above the Limit of Detection (LOD) (Appendix 2)
< value: value = Limit of Quantitation (LOQ) for the relevant determinand
***: Correction factor applied to PCB 28, 31 and 52 based on recoveries for reference materials. Values reported are indicative.**

Appendix 1 (Page 3 of 3): Results of monitoring of shellfish-growing areas - 2001.

Sample Site	Killary Inner	Kilmakillogue	Lough Swilly	Mulroy Bay	Roaringwater Bay	Tralee Bay, Inner	Wexford Harbour
M.I. Reference No.	ENV2001/ 396	ENV2001/ 416	ENV2001/ 373	ENV2001/ 371	ENV2001/ 405	ENV2001/ 413	ENV2001/ 382
Sampling date	23/10/01	14.11.01	11/10/01	11/10/01	12/11/01	15/11/01	15/10/01
Species sampled	*M. edulis*	*M. edulis*	*O .edulis*	*M. edulis*	*M. edulis*	*O. edulis*	*M. edulis*
Number individuals	50	50	25	50	50	25	50
Method of cultivation	rope	rope	trestle	rope	rope	bed	bed
Water Parameters							
Temperature (ºC)	13.4	11.9	13.5	14.5	11.9	9.50	14.6
Salinity (psu)	32.7	33.4	27.1	33.8	33.0	28.4	17.5
pH	8.20	8.33	8.01	8.36	N/A	8.29	7.82
Suspended Solids (mg L^{-1})	5.50	9.30	N/A	12.7	2.00	56.6	29.0
Shellfish							
Shell length range (mm)	38.0-61.7	48.5-59.4	72.7-124	46.1-66.7	43.4-60.1	67.7-77.0	37.3-59.1
Shell mean length (mm)	52.8	54.6	102	51.6	52.6	73.3	51.3
Shell length std dev (mm)	4.57	3.20	11.7	3.63	2.96	2.32	4.00
Meat weight (%)	41.4	40.0	13.2	41.9	31.5	12.2	39.8
Shell weight (%)	58.6	60.0	86.8	58.1	68.5	87.8	60.2
Meat water content (%)	75.9	76.4	78.9	73.7	77.1	74.8	77.9
Metals mg kg^{-1} (ppm) wet wt.							
Cadmium	0.12	0.10	0.26	0.11	0.06	0.42	0.04
Chromium	0.23	<0.19	<0.19	<0.19	<0.19	0.42	<0.19
Copper	1.70	1.18	12.2	1.45	1.55	20.4	1.22
Lead	0.08	0.08	0.11	0.08	0.15	0.08	0.37
Mercury	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Zinc	22.2	18.8	198	21.7	18.4	366	15.1
PCB's µg kg^{-1} (ppb) wet wt.							
CB Congener 28*	0.26	0.16	0.19	0.23	0.18	0.13	N/A
CB Congener 52*	0.53	0.43	0.47	0.50	0.47	0.39	N/A
CB Congener 101	0.47	0.40	0.46	0.47	0.54	0.41	0.58
CB Congener 118	0.12	0.15	0.15	0.16	0.21	0.19	0.32
CB Congener 138	0.15	0.15	0.15	0.18	0.21	0.17	0.64
CB Congener 153	0.24	0.27	0.33	0.28	0.36	0.33	0.44
CB Congener 180	0.02	0.02	0.02	0.02	0.03	0.03	0.03
CB Congener 31*	0.18	0.17	0.13	0.29	0.19	0.07	nd
CB Congener 105	0.11	0.09	0.05	0.11	0.08	0.10	0.12
CB Congener 156	<0.01	0.05	0.03	0.03	0.02	<0.01	0.02
Organic pesticides µg kg^{-1} (ppb) wet wt.							
DDD - p,p'	0.35	nd	0.14	0.10	0.11	0.12	0.36
DDE - p,p'	0.22	0.25	0.41	0.38	0.28	0.34	1.42
DDT - p,p'	0.07	nd	0.18	0.20	0.39	0.11	0.18
HCB	0.05	0.08	0.03	0.08	0.07	0.03	0.04
gamma- HCH	0.41	nd	0.41	0.49	0.92	0.51	0.43
trans-Nonachlordane	0.05	nd	0.16	0.08	0.07	0.10	0.04
Aldrin	0.04	0.07	0.01	0.03	0.05	<0.01	nd
Isodrin	0.06	0.06	0.17	0.06	0.05	nd	0.05
trans-Chlordane	0.04	nd	0.07	0.07	0.07	0.06	0.03
cis-Chlordane	0.04	nd	0.03	0.03	0.04	0.03	0.01
Endrin	nd	nd	0.05	0.13	0.09	0.07	nd
Lipid Smedes (%)	1.94	2.23	2.22	2.48	2.02	2.07	1.67

Notes : N/A: Samples not analysed
nd: Substances were not detected above the Limit of Detection (LOD) (Appendix 2)
< value: value = Limit of Quantitation (LOQ) for the relevant determinand
***: Correction factor applied to PCB 28, 31 and 52 based on recoveries for reference materials. Values reported are indicative.**

Appendix 2: Metal Detection Limits (mg kg^{-1} wet weight).

Metal	LOD
Cadmium	0.004
Chromium	0.07
Copper	0.16
Lead	0.02
Mercury	0.01
Zinc	1.21

Glossary and Abbreviations

Determinants

DDD	4,4'-dichlorodiphenyldichloroethane
DDE	1,1'-dichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethene
DDT	4,4'-dichlorodiphenyl-1,1,1-trichloroethane
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
OCPs	Organochlorine pesticides
PCBs	Polychlorinated biphenyls
Cd	Cadmium
Cr	Chromium
Cu	Copper
Hg	Mercury
Pb	Lead
Zn	Zinc

Species

M. edulis	*Mytilis edulis*	Blue mussel
O. edulis	*Ostrea edulis*	Native/flat oyster
C. gigas	*Crassostrea gigas*	Pacific oyster

Others

QUASH	Quality assurance of sampling and sample handling (in marine environmental monitoring)
QUASIMEME	Quality assurance of information for marine environmental monitoring
RM	Reference material
CRM	Certified reference material
N/A	Not analysed
LOD	Limit of detection
nd	Not detected
SI	Statutory Instrument
EU	European Union
AA	Atomic absorption (spectroscopy)
GC-ECD	Gas chromatography with electron capture detection