Trace Metal and Chlorinated Hydrocarbon Concentrations in Shellfish from Irish Waters, 2000

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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.

EU Commission Regulation 466/2001/EC (as amended by Regulation 221/2002/EC) came into effect on 5th April 2002. This set maximum levels for mercury, cadmium and lead in bivalve molluscs of 0.5mg kg⁻¹, 1mg kg⁻¹, and 1.5mg kg⁻¹ wet weight respectively. 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.

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. Levels of chlorinated hydrocarbons and trace metals in shellfish tissue were very low in all areas, which is evidence of the clean, unpolluted nature of Irish shellfish and shellfish producing waters.

This survey confirms previous studies (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 products.

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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 tissues 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 parameters in designated shellfish waters is undertaken to ensure that the quality of the edible species is maintained or enhanced. These include physical (pH, temperature, suspended solids, salinity and dissolved oxygen) and chemical parameters (organo-halogenated substances and heavy metals). 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 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 shellfish sampled from 19 sites in 2000, including a number of areas not formally designated.

The analysis of mercury, cadmium, chromium, copper, lead and zinc was carried out on shellfish from all of the sites. Chlorinated hydrocarbon analysis was carried out on shellfish from 11 sites in 2000. 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 the levels were compared with the available standards and guidance values for human consumption set by a number of European countries.

MATERIALS AND METHODS

Sample collection and preservation

Shellfish samples were collected during August and September. Figure 1 shows the areas sampled in 2000. Detailed information on the locations, dates, species sampled, cultivation methods etc. are shown in Appendix 1.

Where possible, at each site, temperature, salinity, pH and dissolved oxygen 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 μ m 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 before the soft tissue was 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 105° C 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 < -20^{\circ}C 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 hydrochloride was added to neutralise the potassium permanganate and 1ml of potassium dichromate was added as a preservative. The solution was diluted to 100ml with high purity water.

Following reduction of the samples with stannous chloride, the mercury was determined by cold vapour atomic fluorescence spectroscopy using a PSA Merlin Analyser.



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Figure 1. Location of shellfish-growing areas monitored during 2000.

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). Samples were diluted to 50mls with deionised water and trace metal concentrations were determined using a graphite furnace atomic absorption spectrometer (Varian SpectrAA-400 for copper and chromium, Varian SpectrAA Zeeman 220 for cadmium and lead) and a flame atomic absorption spectrometer (Varian SpectrAA 20 Plus) for zinc.

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 data was produced during the 2000 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 2 and 5 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 positive bias was noted for early eluting PCBs (PCBs 28, 31, 52) and a negative bias determined for DDT- o,p', DDT- p,p' and Dieldrin. 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

Table 1: Results of the analyses of reference materials obtained during the 2000 shellfish testing.

CRM	Certified Value	Measured Value	No. of
	(± 95 % confidence limit)	(Mean ± SD)	Analyses
Oyster Tissue SRM 1566a	$\mathbf{m} \mathbf{g}^{-1} dry wt.$	$\mathbf{mg} g^{-1} dry wt.$	
Mercury	0.06 ± 0.01	0.07 ± 0.01	2
Mussel Tissue CRM 278R	$\mathbf{mg} g^{-1} dry wt.$	$\mathbf{mg} \mathbf{g}^{-1} dry wt.$	
Cadmium	0.348 ± 0.007	0.319 ± 0.01	3
Copper	9.45 ± 0.13	9.35 ± 0.08	3
Chromium	0.78 ± 0.06	0.57 ± 0.04	3
Lead	2.00 ± 0.04	1.49 ± 0.08	3
Mercury	0.196 ± 0.009	0.21 ± 0.02	3
Zinc	83.1 ± 1.70	81.0 ± 0.46	4
Dogfish Muscle DORM2			
Cadmium	0.043 ± 0.008	0.044 ± 0.004	3
Copper	2.34 ± 0.16	2.25 ± 0.06	3
Lead	0.065 ± 0.007	0.087 ± 0.02	3
Zinc	25.6 ± 2.30	26.3 ± 2.00	4

b) QUASIMEME Reference Materials

Reference Material	Assigned Measured Values (Mean + SD)		No. of Analyses	Mean Z Score	No. -2 <z<2< th=""></z<2<>
OTM050BT (Wet mussel ti	ssue)	(112000 = 0.22)			
	mg kg ⁻¹ wet wt.	mg kg ⁻¹ wet wt.			
Mercury	0.049	0.054 ± 0.00	5	0.34	5
QOR062BT (Wet mussel tis	ssue)				
PCBs	ng kg ⁻¹ wet wt.	ng kg ⁻¹ wet wt.			
PCB 28	0.33	0.60 ± 0.07	4	2.95	0
PCB 31	0.27	0.58 ± 0.06	4	3.68	0
PCB 52	0.85	1.46 ± 0.04	4	3.89	0
PCB 101	3.2	3.42 ± 0.17	4	0.49	4
PCB 105	0.83	0.59 ± 0.05	4	-1.58	4
PCB 118	2.35	2.33 ± 0.10	4	-0.07	4
PCB 138	6.11	4.90 ± 0.24	4	-1.48	4
PCB 153	9.04	8.85 ± 0.59	4	-0.16	4
PCB 156	0.42	0.24 ± 0.01	4	-1.80	4
PCB 180	0.81	0.70 ± 0.05	4	-0.71	4
Organochlorine Pesticides					
DDD- p,p'	0.61	0.36 ± 0.01	4	-2.02	1
DDE- p,p'	1.34	1.35 ± 0.06	4	0.06	4
DDT- o,p'	0.20	0.03 ± 0.01	4	-2.31	0
DDT- p,p'	0.50	0.01 ± 0.01	4	-4.40	0
Dieldrin	0.90	0.09 ± 0.01	4	-4.98	0
HCB	0.19	0.19 ± 0.00	4	-0.02	4
ү-НСН	0.17	0.24 ± 0.10	4	1.02	3
trans-Nonachlor	0.16	0.08 ± 0.01	4	-1.09	4

RESULTS AND DISCUSSION

Shellfish survey

The results of the biological measurements and physico-chemical monitoring carried out during 2000 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, salinity and dissolved oxygen measurements met the criteria set out in the Directive in all cases.

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 1mg 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 by various OSPAR countries for human consumption. 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 (Anon, 1992), 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	$20 \mathrm{~mg~kg}^{-1}$	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	$500 \ \mu g \ kg^{-1}$	Standard	Finland	
НСВ	$50~\mu g$ kg $^{-1}$	Guidance	Norway	
α and β HCH	50 μ g kg $^{-1}$	Guidance	Norway	
Lindane	$100~\mu g$ kg $^{-1}$	Standard	Finland	
PCB 28	$80~\mu{ m g~kg}^{-1}$	Standard	Germany	
PCB 52	$80~\mu{ m g~kg}^{-1}$	Standard	Germany	
PCB 101	$80~\mu g~kg^{-1}$	Standard	Germany	
PCB 138	$100~\mu g$ kg $^{-1}$	Standard	Germany	
PCB 153	$100 \ \mu g \ kg^{-1}$	Standard	Germany	
PCB 180	$80 \ \mu g kg^{-1}$	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 2000 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 (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 2000. Trace metal concentrations were comparable with previous years and well below human consumption tolerance values as compiled by OSPAR (Table 2). The level of mercury in the meat (0.05 mg kg⁻¹ wet weight) was 10 times lower than the EU maximum limit for mercury in fisheries products. Water quality measurements taken conformed to the requirements of the Directive. Analysis indicated organochlorines levels to be very low with respect to human consumption standards.

Bannow Bay

C. gigas were tested for organics and trace metals in 2000. 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 (German) tolerance levels as compiled by OSPAR.

Bantry Bay

The water parameters measured at this site in 2000 were, as for all sites, typical of northern temperate waters and conformed to the Directive. 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). Trace metal levels in 2000 sample were well within the guideline concentrations and were similar to previous years. Chlorinated hydrocarbon levels were very low and comparable with previous values.

Bruckless

M. edulis were sampled for this programme from Bruckless in Donegal Bay for the first time in 1999. In 2000 trace metal concentrations in mussel tissue were low and well within the human consumption tolerance levels given in Table 2. The mercury concentration was below the limit of detection of the method. Chlorinated hydrocarbon analysis was carried out for this site and concentrations were also well within strictest guidelines.

Carlingford Lough

Oysters, *C. gigas*, were sampled from Carlingford Lough. Mussels are also produced in this area but to a lesser extent. Water quality parameters measured in 2000 conformed to the Directive. The level of mercury was low at 0.04mg kg⁻¹ wet weight. Copper levels were found to be 31.9mg kg⁻¹ wet weight, well below the Spanish standard of 60mg kg⁻¹ set for

oysters. Analyses for other trace metals were carried out and results were very similar to previous years monitoring. Levels of PCBs and organochlorine pesticides in 2000 were comparable with previous years and were well within tolerance levels compiled by OSPAR (Table 2).

Clarinbridge

M. edulis were sampled for this programme in 2000. The water quality parameters measured conformed to the Directive. Trace metal levels including mercury (0.04mg kg^{-1} wet weight) were low and compared favourably with the strictest tolerance levels available (Table 2). Analyses of organic contaminants were not carried out for this site.

Clew Bay

A sample of native oysters, *O. edulis*, collected in 2000 was analysed for trace metals. The mercury level was very low at <0.03mg kg⁻¹ wet weight. Concentrations of other trace metals were very low and well within human consumption guidelines (Table 2). Chlorinated hydrocarbon analysis was carried out and results were well within the strictest standards available.

Cork Harbour

Cork Harbour oysters, *C. gigas* were analysed. Water and shellfish quality was similar to previous years and conformed to the requirements of the Directive. Trace metal and chlorinated hydrocarbon levels continued to be very low.

Cromane

A sample of blue mussels, *M. edulis* was collected from Cromane. Water and shellfish qualities were similar to previous years and conformed to the requirements of the Directive. Trace metal concentrations, including mercury continue to be low and within the tolerance levels set out in Table 2. No organic analysis was carried out on the shellfish from this site.

Dungarvan

Analysis of *C. gigas* collected in 2000 conformed to previous years (1996-1999) and results were within the values set out in Table 2. Water quality measurements taken in 2000 satisfied the requirements of the Directive. Chlorinated hydrocarbons were measured and levels were low and well within the strictest standards available for PCBs.

Glengarriff

A sample of *M. edulis* was collected from Glengarriff during 2000. Trace metal concentrations were comparable with previous years and were well below human consumption tolerance values as compiled by OSPAR (Table 2). The level of mercury in the soft tissues of *M. edulis* was below the limit of detection, well below EU 0.5mg kg⁻¹ maximum limit (Table2). No organic analysis was carried out on the shellfish from this site.

Inner Tralee Bay

A sample of Pacific oyster, *C. gigas*, collected in 2000 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). The water quality parameters determined in 2000 conformed to the requirements of the Directive. No organic analysis was carried out on the shellfish from this site.

Killary Harbour, Inner

Trace metals were determined for *M. edulis* sampled from Killary Harbour in 2000. The level of trace metals measured was well within human consumption guidelines. No organic analysis was carried out on the shellfish from this site.

Kilmakillogue, Kenmare Bay

Mussel samples, *M. edulis*, were collected from Kilmakillogue. Water quality parameters in 2000 conformed to the requirements of the Directive. Again, the shellfish produced at this location contained levels of trace metals well within the human consumption guidelines and standards set by OSPAR countries and in close agreement with previous years. No organic analysis was carried out on the shellfish from this site.

Lough Foyle, Quigley's Point,

M. edulis were collected at Quigley's Point 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 0.03mg kg^{-1} wet weight, this is well within the strictest tolerance levels available (Table 2). Trace metal and chlorinated hydrocarbon concentrations in the mussels collected were well within the strictest standards set by OSPAR countries (Table 2).

Mulroy Bay

The levels of trace metals measured in *M. edulis* from Mulroy Bay were low and comparable with previous years. These were well within human consumption guidelines and standards set by OSPAR countries (Table 2). No organic analysis was carried out on the shellfish from this site.

Roaringwater Bay

Mussel samples, *M. edulis*, collected during 2000 had trace metal levels typical of those measured in previous years and were well within human consumption guidelines and standards set by OSPAR countries. Water quality parameters conformed to the requirements of the Directive. No organic analysis was carried out on the shellfish from this site.

Waterford Harbour, Arthurstown,

Samples of *M. edulis* were collected from Arthurstown in 2000. Lead was determined at 0.54 mg kg^{-1} wet weight, below the EU maximum limit (1.5mg kg⁻¹). This is below the lead levels determined in 1999 (0.77mg kg⁻¹ wet weight) however it was above the value measured in previous years (0.22mg kg⁻¹ in 1997, 0.24mg kg⁻¹ in 1996, 0.38mg kg⁻¹ in 1995). Levels of mercury and other trace metals were low and within the tolerance levels set out in

Table 2. Chlorinated hydrocarbons were detected at low levels and well within the strictest standards available in OSPAR countries.

Wexford Harbour

M. edulis sample collected from Wexford Harbour in 2000 was analysed for both trace metals and organochlorine substances. The water quality parameters determined in 2000 conformed to the requirements of the Directive. 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 0.5 mg kg⁻¹ wet weight (Table 2). In 2000 a concentration of 0.51 mg kg⁻¹ wet weight for lead in mussels was detected which is well within the new EU maximum limit (1.5 mg kg⁻¹). With the exception of a single uncharacteristic result in 1996 lead concentrations in mussels from this site have been within the strictest standard of 1.5 mg kg⁻¹ but have been elevated compared with other Irish shellfish growing areas (McGovern *et al.*, 2001 and Bloxham *et al.*, 1998). Other trace metal levels in mussel tissue continued 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 2000 was good and conformed to the guidelines of the 1979 Council Directive 79/923/EC with respect to pH, temperature, suspended solids, salinity and dissolved oxygen.

Total mercury and trace metal concentrations in shellfish from shellfish growing areas were low, which agreed with previous studies (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 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 (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 results of the analyses in this report are indicative of the unpolluted nature of Irish waters and fisheries products with respect to environmental contaminants.

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REFERENCES

- Anon, (1992). Monitoring Manual Principles and Methodology of the Joint Monitoring *Programme*. A compilation of standards and guidance values for contaminants in fish, crustaceans and molluscs for the assessment of possible hazards to human health. Oslo and Paris Commissions. Update 1992 - A7.2/92-E.
- Anon, (1993). Monitoring and Surveillance of Non-Radioactive Contaminants in the Aquatic Environment and Activities Regulating the Disposal of Wastes at Sea, 1991. Aquatic Environment Monitoring Report No. 36. Directorate of Fisheries Research, Lowestoft.
- Bloxham, M., A. Rowe, E. McGovern, M. Smyth and E. Nixon, (1998). Trace Metal and Chlorinated Hydrocarbon Concentrations in Shellfish and Fin-fish from Irish Waters – 1996. *Fishery Leaflet 179*. Marine Institute, Dublin.
- Boelens, R.G.V., D. Maloney, A. Parsons, A. Walsh, (1999). Ireland's Marine and Coastal Areas and Adjacent Seas: an Environmental Assessment. Marine Institute, Dublin.
- Bowman, J.J., K.J. Clabby, J. Lucey, M.L. McGarrigle and P.F. Toner, (1996). Water Quality in Ireland 1991-1994. *Environmental Protection Agency*, Ardcavan, Wexford.
- Clark, R.B., C. Frid and M. Attrill, (1997). Marine Pollution (4th ed.), Clarendon Press, Oxford.
- de Boer, J. and E. McGovern, (2001). Certified Reference Materials for Organic Contaminants for use in Monitoring of the Aquatic Environment. *Trends Anal. Chem.*, 20, 140–159.
- **EPA**, (2000). Ireland's Environment: a Millennium Report. Stapleton, L., M. Lehane and P. Toner. Environmental Protection Agency, Wexford. ISBN 1-84095-016-1
- McGovern, E., A. Rowe, B.McHugh, J. Costello, M. Bloxham, C. Duffy & E. Nixon (2001). Trace Metal and Chlorinated Hydrocarbon Concentrations in Shellfish from Irish Waters 1997-1999. *Marine Environment and Health Series*, No.2, 20001
- Nixon, E., D. McLaughlin, R.G. Boelens and G. O'Sullivan, (1991). Contaminants in marine biota 1990 monitoring programme. *Fishery Leaflet 151*. Department of the Marine, Dublin.
- Nixon, E., A. Rowe, M. Smyth, D. McLaughlin and J. Silke, (1994). Monitoring of Shellfish Growing Areas 1993. *Fishery Leaflet 160*. Department of the Marine, Dublin.

- Nixon, E., A. Rowe, M. Smyth, D. McLaughlin and J. Silke, (1995). Monitoring of Shellfish Growing Areas 1994. *Fishery Leaflet 166*. Department of the Marine, Dublin
- O'Sullivan, M.P., E.R. Nixon, D. McLaughlin, Ml. O'Sullivan and D. O'Sullivan, (1991). Chemical contaminants in Irish estuarine and coastal waters, 1978 to 1988. *Fisheries Bulletin No. 10.* Department of the Marine, Dublin.
- QUASH, (1998). Draft Report on the QUASH Interlaboratory Study; Determination of Lipid in Fish and Shellfish, Round 1 SBT-2 Exercise 1000, Sponsored by the EU Standards, Measurements and Testing Programme. QUASIMEME Project Office, Marine Laboratory, Aberdeen.
- QUASH, (1999). Report on the Proceedings of the QUASH Workshop on Lipid Determination and Biota Sample Handling. Sponsored by the EU Standards, Measurements and Testing Programme. Galway, Republic of Ireland, 30 September – 4 October 1998. QUASIMEME Project Office, Marine Laboratory, Aberdeen.
- Smyth, M., A. Rowe, E. McGovern and E. Nixon, (1997). Monitoring of Shellfish Growing Areas 1995. *Fishery Leaflet 174*. Department of the Marine, Dublin

Appendix 1 (Page 1 of 2): Results of monitoring of shellfish-growing areas - 2000.

Sample Site	Aughinish, New Quay Co. Clare	Bannow Bay	Bantry Bay	Bruckless	Carlingford Lough	Clarinbridge	Clew Bay	Cork Harbour	Cromane	Dungarvan
M.I. Reference No.	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000
Sampling date	/523 18/09/00	/538 27/09/00	/528 12/09/00	/379 17/08/00	/375 15/08/00	/524 06/09/00	/525 07/09/00	/526 11/09/00	/531 13/09/00	/537 26/09/00
Sampling time	16.45	13.40	13.10	11.30	12.00	17.45	15.00	15.22	14.30	18.00
Species sampled	C. gigas	C. gigas	M. edulis	M. edulis	C. gigas	M. edulis	O. edulis	C gigas	M. edulis	C. gigas
Number individuals	25	25	50	50	25	50	25	25	50	25
Method of cultivation	trestle	trestle	rope	rope	trestle	bed	bed	bed	bed	trestle
Water Parameters										
Temperature (°C)	17.0	N/A	16.9	N/A	16.3	18.2	N/A	18.9	16.2	15.7
Salinity (psu)	39.0	N/A	37.4	N/A	38.1	37.0	N/A	38.0	33.9	37.5
рН	6.96	N/A	8.16	N/A	7.74	8.18	N/A	7.87	8.12	7.00
Dissolved oxygen	100	N/A	95.2	N/A	95.0	153	N/A	121	92.3	92.7
(% saturation) Suspended Solids (mg l ⁻¹)	9.60	108	1.40	5.80	9.20	231	2.40	3.70	2.00	96.8
Shellfish			-			-	-			
Shell length range(mm)	85 1-122	109-150	41 7-59 7	50 7-65 5	78 0-105	49 7-62 6	64 4-86 7	72 8-109	55 4-81 8	74 1-108
Shell mean length(mm)	97.6	131	49.1	58.1	90.5	57.0	74.6	93.7	66.3	92.5
Shell length std dev (mm)	9.90	10.2	4.22	4.03	7.74	2.80	5.44	12.1	5.89	8.48
Meat weight(%)	11.2	21.5	43.1	22.7	8.20	15.5	10.6	16.9	26.8	15.7
Shell weight(%)	88.8	78.5	56.9	77.3	91.8	84.5	89.4	83.1	73.2	84.3
Meat water content (%)	76.9	76.2	76.7	75.4	77.5	76.1	76.3	75.0	76.6	75.6
Metals mg kg ¹ (ppm) wet	wt.									
Cadmium	0.37	0.10	0.18	0.10	0.42	0.26	0.44	0.25	0.19	0.30
Chromium	<0.19	nd	<0.19	<0.19	nd	0.22	0.24	<0.19	<0.19	<0.19
Copper	9.01	3.87	1.49	1.69	31.9	1.61	5.48	11.4	1.73	10.6
Lead	0.10	0.09	0.09	0.07	0.17	0.22	<0.06	0.25	0.08	0.19
Mercury	0.05	nd	<0.03	nd	0.04	0.04	<0.03	0.03	<0.03	nd
Zinc	263	127	25.6	10.7	216	21.9	254	169	15.0	173
PCB's µg kg ⁻¹ (ppb) wet w	rt.									
PCB 28	0.23	0.31	0.25	0.18	0.29	N/A	0.14	0.39	N/A	0.20
PCB 52	0.60	0.63	0.59	0.40	0.40	N/A	0.39	0.79	N/A	0.40
PCB 101	0.40	0.61	0.41	0.34	0.48	N/A	0.31	1.07	N/A	0.47
PCB 118	0.05	0.23	0.14	0.08	0.31	N/A	0.05	0.64	N/A	0.18
PCB 138	0.09	0.15	0.15	0.08	0.22	N/A	nd	0.61	N/A	0.19
PCB 153	0.37	0.61	0.58	0.30	0.92	N/A	0.32	1.53	N/A	0.64
PCB 180	0.04	0.05	0.06	0.03	0.06	N/A	0.03	0.11	N/A	0.06
PCB 31	0.24	0.34	0.28	0.17	0.27	N/A	0.18	0.39	N/A	0.17
PCB 100	0.07	0.06	-0.05	c0.02	-0.02	N/A	0.04		IN/A	0.08
$\mathbf{OCB}'_{2} u = k \mathbf{e}^{-1} (\mathbf{n} \mathbf{n} \mathbf{h}) u = \mathbf{e}^{-1} \mathbf{e}^$	<0.04	nu	<0.04	<0.05	<0.05	N/A	<0.02	<0.00	N/A	<0.03
	Λ ι.	0.25	NI/A	0.05	0.22	NI/A	0.05	0.20	NI/A	0.00
DDE - p,p	0.13	1.00	N/A	0.05	0.22	N/A	0.05	1 30	Ν/A N/A	0.09
DDL - p,p DDT - o p'	0.23 nd	0.03	~0.02	0.27 nd	~0.04	N/A	0.25 nd	0.04	N/A	0.07
DDT - 0,p DDT - n n'	0.19	0.03	<0.02 nd	nd	0.02	N/A N/Δ	0.09	0.04	N/A	0.02
Dieldrin	0.10	0.03	nd	0.11	0.10	N/A	0.05	0.10	N/A	0.00
HCB	0.05	0.07	0.11	0.07	0.04	N/A	0.04	0.07	N/A	0.05
γ-HCH	0.33	0.45	N/A	0.23	0.36	N/A	0.22	0.43	N/A	0.36
trans-Nonachlor	0.16	0.17	nd	0.05	0.13	N/A	0.08	0.07	N/A	0.29
Trans-Chlordane	nd	0.05	nd	nd	0.02	N/A	nd	0.05	N/A	nd
Cis-Chlordane	<0.01	0.03	N/A	nd	0.02	N/A	nd	0.03	N/A	<0.01
	0.01	0.00	0.01	0.40	0.07	N 1/2		0.00	N 1/A	o /=
Lipid Smedes (%)	2.64	3.63	2.64	2.19	2.35	N/A	1.77	2.90	N/A	2.47

Notes : N/A: Samples not analysed

nd: Substances were not detected above the Limit of Detection (LOD)

< value: value = Limit of Quantitation (LOQ) for the relevant determinand

Appendix 1 (Page 2 of 2): Results of monitoring of shellfish-growing areas - 2000.

Sample Site	Glengarriff	Inner Tralee Bay	Killary Harbour,	Kilmakillogue, Kenmare Bay	Lough Foyle, Quigleys	Mulroy Bay	Roaring Water Bay	Waterford Harbour, Arthurstown	Wexford Harbour
M.I. Reference	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000	ENV2000
No.	/527	/532	/522	/530	/378	/380	/529	/533	/539
Sampling date	14/09/00	13/09/00	15/09/00	16/09/00	19/09/00	17/09/00	20/09/00	27/09/00	21/09/00
Sampling time	15.30 M. odulio	18.00 C. aiaaa	T7.35	14.30	13.30	9.00	10.30	M. odulio	14.00 M. odulio
Species sampled	IVI. EQUIIS	C. yiyas	IVI. EQUIIS	IVI. EQUIIS	IVI. EQUIIS	IVI. EQUIIS	M. EQUIS	M. edulis	IVI. EQUIIS
Method of cultivation	50 rone	20 bed	50 rone	JU	UC bed	50 rone	50 rope	UC bed	UC bed
Water Parameters	торе	beu	торе	торе	beu	торе	торе	beu	beu
Temperature (°C)	17 1	16.7	N/A	16.4	N/A	N/A	17.5	N/A	16.0
Salinity (psu)	37.3	38.0	N/A	37.5	N/A	N/A	39.0	N/A	28.6
pH	8.15	8.13	N/A	8.17	N/A	N/A	7.96	N/A	8.04
Dissolved oxvaen									
(% saturation)	99.6	91.4	N/A	86.0	N/A	N/A	95.0	N/A	81.2
Suspended Solids (mg l ⁻¹)	3.40	13.4	1.40	9.30	6.70	1.60	1.30	629	11.9
Shellfish									
Shell length range (mm)	41.8-59.1	62.5-88.2	40.8-59.1	40.9-54.6	51.0-70.1	42.2-57.8	49.9-65.0	44.0-60.5	43.6-58.9
Shell mean length (mm)	51.4	73.3	49.3	46.2	58.9	50.6	56.4	54.0	51.6
Shell length std dev (mm)	3.91	6.11	3.85	3.22	4.26	4.21	3.76	4.09	3.59
Meat weight (%)	46.5	8.90	23.0	50.5	13.7	43.6	48.9	16.0	32.6
Shell weight (%)	53.5	91.1	77.0	49.5	86.3	56.4	51.1	84.0	67.4
Meat water content (%)	/6./	75.1	75.4	77.4	79.0	80.0	77.9	79.0	77.8
Metals mg kg ⁻¹ (ppm) wet	wt.								
Cadmium	0.18	0.63	0.10	0.13	0.20	0.20	0.11	0.31	0.11
Chromium	nd	3.11	<0.19	<0.19	0.36	<0.19	<0.19	0.86	<0.19
Copper	1.01	31.6	1.55	1.47	1.24	1.29	1.51	1.63	1.71
Lead	<0.06	0.08	<0.06	<0.06	0.09	<0.06	0.08	0.54	0.51
Mercury	nd	<0.03	<0.03	< 0.03	0.03	<0.03	<0.03	<0.03	< 0.03
	17.2	407	13.9	15.7	12.0	21.0	24.7	10.1	19.0
PCB's µg kg ' (ppb) wet w	/t.	N1/A	N1/A	N1/A	0.44	N1/A	N1/A	0.40	0.40
PCB 28	N/A	N/A	N/A	N/A	0.11	N/A	N/A	0.16	0.13
PCB 52	N/A	N/A	N/A	N/A	0.32	N/A	N/A	0.33	0.31
	IN/A	N/A	IN/A	N/A	0.28	N/A	N/A	0.54	0.36
	IN/A	N/A	N/A	N/A	0.14	N/A	N/A	0.21	0.10
PCB 153	N/Δ	N/A N/Δ	N/Δ	N/A	0.12	N/Δ	N/A N/Δ	0.34	0.50
PCB 180	N/A	N/A	N/A	N/A	0.03	N/A	N/A	0.04	0.04
PCB 31	N/A	N/A	N/A	N/A	0.11	N/A	N/A	0.12	0.13
PCB 105	N/A	N/A	N/A	N/A	0.05	N/A	N/A	0.11	0.03
PCB 156	N/A	N/A	N/A	N/A	0.02	N/A	N/A	0.03	<0.02
OCP's µg kg ⁻¹ (ppb) wet v	vt.								
DDD - p,p'	N/A	N/A	N/A	N/A	0.20	N/A	N/A	0.36	0.22
DDE - p,p'	N/A	N/A	N/A	N/A	0.35	N/A	N/A	0.74	0.77
DDT - o,p'	N/A	N/A	N/A	N/A	0.01	N/A	N/A	0.01	nd
DDT - p,p'	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.08	N/A
Dieldrin	N/A	N/A	N/A	N/A	0.05	N/A	N/A	0.08	0.09
HCB	N/A	N/A	N/A	N/A	0.03	N/A	N/A	0.04	0.04
γ -HCH	N/A	N/A	N/A	N/A	0.13	N/A	N/A	0.18	0.19
trans-Nonachlor	N/A	N/A	N/A	N/A	0.03	N/A	N/A	0.04	0.05
Trans-Chlordane	N/A	N/A	N/A	N/A	0.09	N/A	N/A	nd	nd
Cis-Chlordane	N/A	N/A	N/A	N/A	0.01	N/A	N/A	<0.01	nd
Lipid Smedes (%)	N/A	N/A	N/A	N/A	1.27	N/A	N/A	1.32	1.38

Notes : N/A: Samples not analysed

nd: Substances were not detected above the Limit of Detection (LOD)

< value: value = Limit of Quantitation (LOQ) for the relevant determinand

Metal	LOD
Cadmium	0.004
Chromium	0.074
Copper	0.16
Lead	0.021
Mercury	0.01
Zinc	1.21

Appendix 2: Detection Limits (mg kg⁻¹ wet weight) for metals

Glossary and Abbreviations

Determinants								
DDD	4,4'-dichlorodiphenyldichloroethane							
DDE	1,1'-dichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethene							
DDT	4,4'-dichlorodipheny	4,4'-dichlorodiphenyl-1,1,1-trichloroethane						
HCB	Hexachlorobenzene	Hexachlorobenzene						
HCH	Hexachlorocyclohexa	Hexachlorocyclohexane						
OCPs	Organochlorine pestio	Organochlorine pesticides						
PCBs	Polychlorinated biphe	Polychlorinated biphenyls						
Cd	Cadmium							
Cr	Chromium							
Cu	Copper	Copper						
Hg	Mercury	Mercury						
Pb	Lead	Lead						
Zn	Zinc							
DO	Dissolved Oxygen							
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 monitoring)	sampling and sample handling (in marine environmental						
QUASIMEME	Quality assurance of	Quality assurance of information for marine environmental monitoring						
RM	Reference material	Reference material						
CRM	Certified reference m	aterial						
NA	Not analysed							
LOD	Limit of detection	Limit of detection						
nd	Not detected							
SI	Statutory Instrument	Statutory Instrument						
EU	European Union	European Union						
AA	Atomic absorption (s	Atomic absorption (spectroscopy)						
GC-ECD	Gas chromatography with electron capture detection							