9. CONTAMINANTS

NIEA Research vessel RV Capitella

Key messages

- There is good information from key sites showing significant reductions in heavy metal contamination in sediments, almost to levels considered to be "background".
- There is less information on newer pollutants that may accumulate in the sediments.
- The pollution effects from the contaminant tributyl tin, commonly known as TBT, have dramatically declined.
- The evidence from seawater measurements is very encouraging. Inputs and concentrations of the most commonly monitored contaminants in seawater have fallen in recent years as a result of earlier controls placed upon their use. They are generally below UK environmental quality standard (EQS) limits.

What are hazardous substances and where do they come from?

Hazardous substances can be naturally occurring or man made. Examples of naturally occurring contaminants include heavy metals, crude oil and its derivatives, such as polycyclic aromatic hydrocarbons. These are more commonly known as PAHs.

Heavy metals and oil in the earths crust are natural resources that are exploited by man.

Hazardous substances may be released into the environment as a result of man's activities such as manufacturing, pest control and the burning of fossil fuels. They may also be released by leaching from rocks and soils.

PAHs are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, rubbish or other organic substances. PAHs generally occur as complex mixtures (for example, as part of combustion products such as soot), not as single compounds.

Organophosphates or organohalogens are examples of man-made or synthetic hazardous substances. These carbon-based chemicals, such as solvents and pesticides, may enter the marine environment from industrial discharges, run-off from agriculture and pollution events.

Most organophosphates are insecticides. Organophosphates were developed about 200 years ago, but their insecticidal properties were only discovered in the 1930s. Some are very toxic; however, they usually are not persistent in the environment.

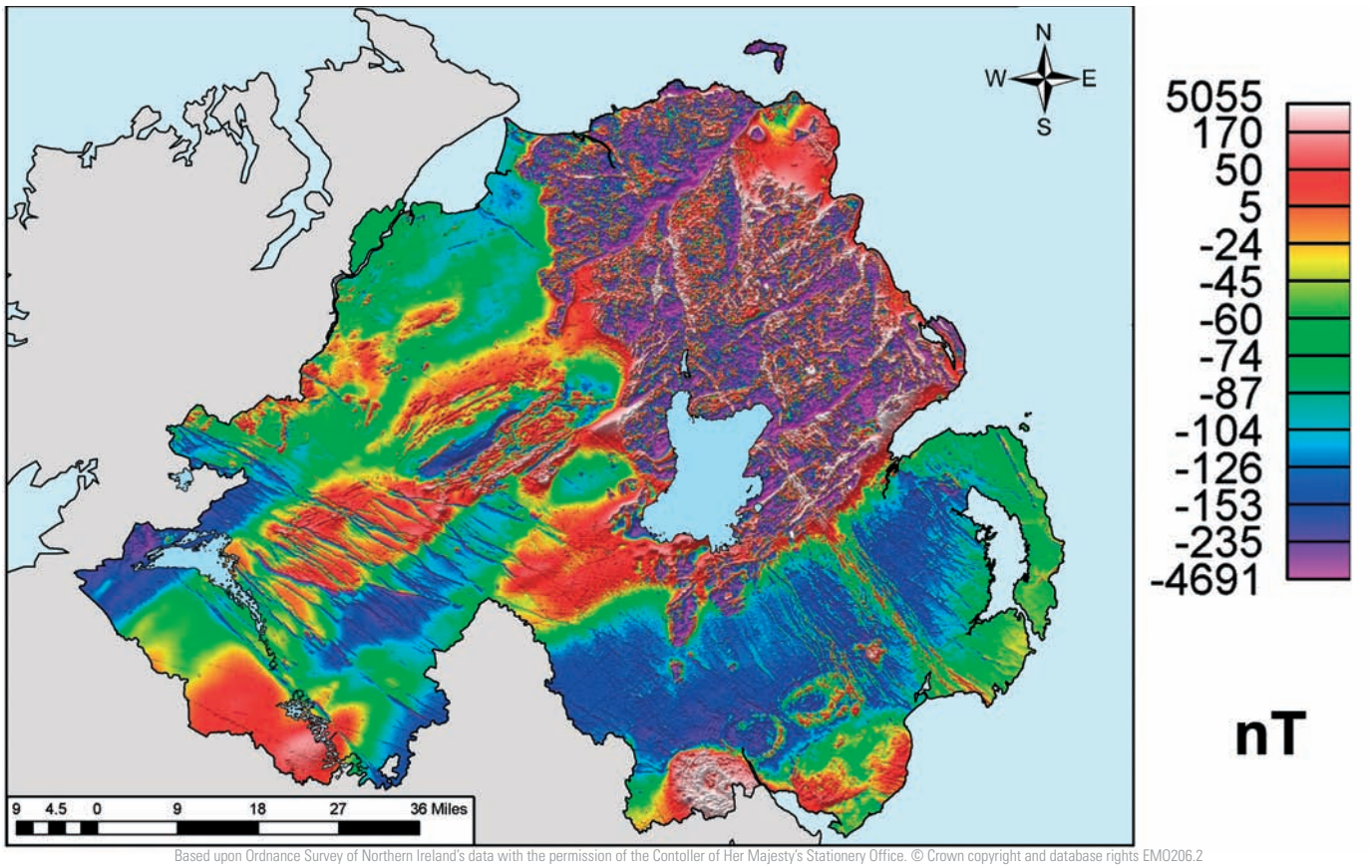


Figure 9.1 Aerial magnetic survey of Northern Ireland revealing the underlying geology.
(Map reproduced from data collected as part of the Tellus Project with the permission of the Geological Survey of Northern Ireland, ©Crown Copyright 2010.)

Chlorine organohalogens are very common and are called organochlorines. Some common uses for organohalogens are as solvents, pesticides, coolants, fire-resistant materials and components of adhesives and sealants.

Polychlorinated biphenyls, commonly referred to as PCBs, are a group of synthetic substances on the OSPAR List of Chemicals for Priority Action. They are toxic, highly accumulative in the marine food chain and very persistent in the environment. They are present in the environment as a result of widespread historical use of these products, mainly as insulation in electrical transformers and capacitors and for lubrication in gas pipeline systems. PCBs can be acutely toxic at high concentrations or chronically toxic at concentrations as low as parts per billion, an equivalent dilution of adding about a teaspoon into an Olympic sized swimming pool. They are endocrine disruptors, producing hormone-like responses in the body. Some are also carcinogenic. The sale and new use of PCBs was banned in 1981. Their use in existing equipment was prohibited in 2000.

Other organohalogen compounds, such as brominated flame retardants, are added to products in order to make them more fire-resistant.

The marine environment is the ultimate sink of these substances through transport via rivers and direct discharges or deposition from the atmosphere by solution at the surface or in rainfall. The potential hazard associated with the different organohalogen substances depends on their individual properties and behaviour following release.

Higher levels of contaminant concentrations are often associated with fine grained sediments. These fine grained sediments tend to accumulate where they can settle out, in undisturbed or less energetic environments. Inshore, these tend to be sheltered areas with low current velocities and offshore in deep water. Inputs of selected substances to the marine environment via rivers and direct discharges have been quantified for the OSPAR Riverine, Indirect and Direct Discharges (RID) programme annually since 1990.

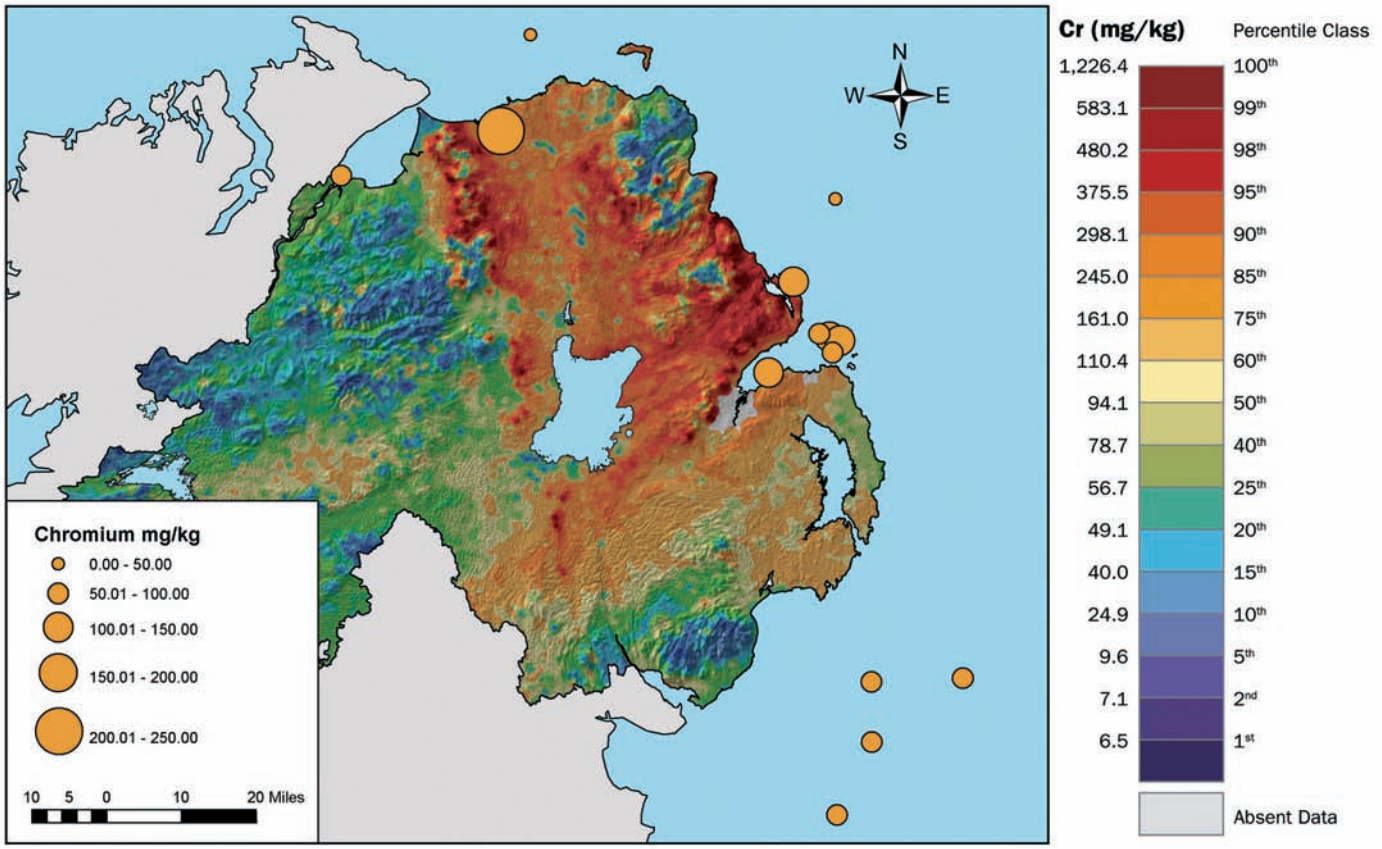


Figure 9.2 Soil geology showing chromium (Cr) concentrations. Coastal and estuarine seabed sediment chromium concentrations (mg/kg), collected at sampling sites around the Northern Ireland coastline, are overlaid on this map. (map reproduced from data collected as part of the Tellus Project with the permission of the Geological Survey of Northern Ireland, ©Crown Copyright 2010).

This programme measures contaminant concentrations and flow volumes for all inputs to the UK marine areas.

Currently our monitoring directly assesses only a limited number of hazardous chemicals. The monitored chemicals are selected on the basis of a risk assessment and the availability of appropriate methods of analysis.
The impact of other contaminants, such as tributyl tin (TBT), can be assessed their impacts by studying the biological affect they cause. The presence of contaminants can be measured in water, sediments and marine plants and animals.

Are our sediments contaminated?

For its size, Northern Ireland is recognised as one of the most geologically diverse areas in the world. The rocks underlying and protruding into the landscape of Northern Ireland underpin the chemical composition of the surface soils and coastal sediments (Figure 9.1). For instance, areas dominated by the Antrim basalts tend to show high levels of certain metals such as nickel and chromium. These concentrations are more commonly associated with man's activities.

In comparison to land-based sampling, data from estuarine, coastal and offshore surveying is extremely limited. This is in part due to the expense associated with sampling in the marine environment. However, in Northern Ireland a series of spatial surveys undertaken by NIEA and AFBI have provided the basis for the selection of a core set of 14 stations (Figure 9.2) [1-5].
They have been monitored for over 10 years and have been used to assess the current contaminant status for marine sediments. These surveys have shown there is a general reduction in the concentrations of metals, in line with the trend in inputs.

These sites form part of the UK monitoring network for the Clean Seas Environmental Monitoring Programme (CSEMP). This network of almost 500 sites around the UK measures the concentrations of specific chemicals which are persistent, toxic and have the ability to accumulate in food chains.

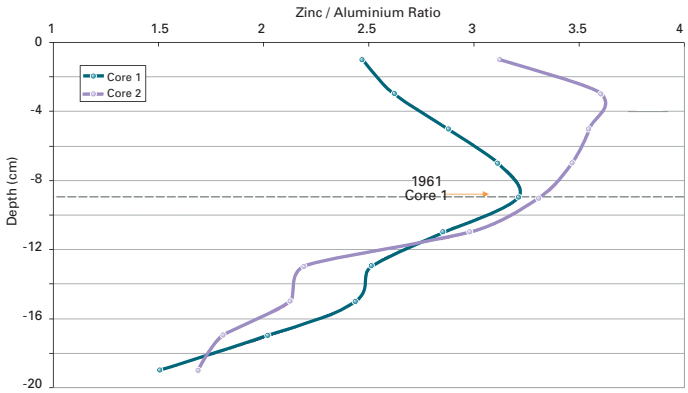


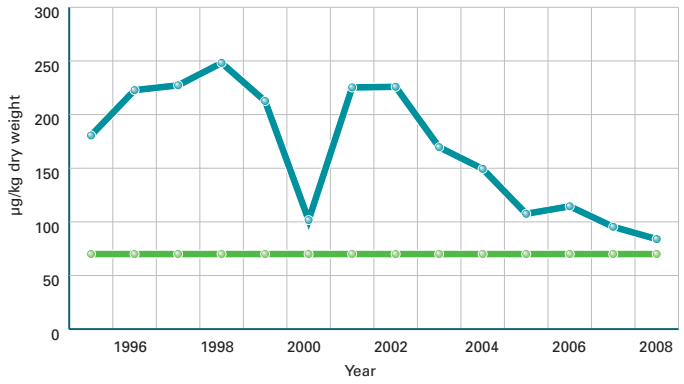
Figure 9.3 Normalised zinc concentrations in a core of sediment taken from Belfast Lough. Zinc increased steadily up to the layer representing 1961, then began to decrease again

Concentrations of metals in marine sediments have been assessed by normalising to a standard aluminium value to account for low level geological variations and then comparing the value to the background assessment concentrations[6]. Improved practices and better regulation, combined with the decline in some of the most polluting industries historically, have reduced the input of a range of contaminants into the marine environment. The most dramatic improvements have been observed in our most industrialised sea lough, Belfast Lough. These improvements are readily observed by taking long cores of sediment from the sea bed and looking at the contaminant burden in the descending layers. In the same way as a tree's annual rings are laid down over time, in undisturbed sediments, the depth below surface in a core can be related to past deposition, right back to pre-industrial times.

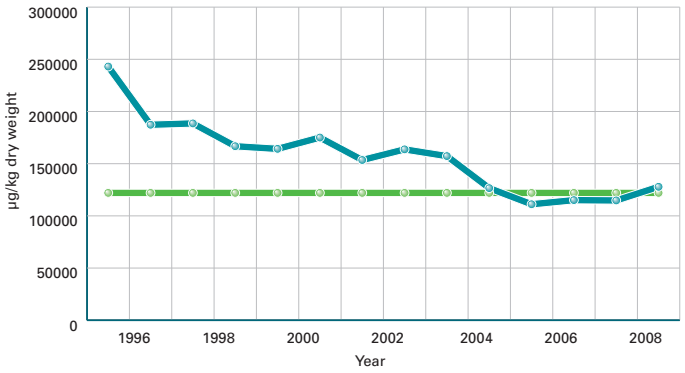
Two cores taken from separate sites in Belfast Lough (Figure 9.3) illustrate the dramatic changes in zinc concentration in the sediments linked to the introduction and subsequent closure of an industrial source[7].Both cores show a peak in zinc concentration at a depth in the sediment of about 10 centimetres. Radio isotope dating of sediment in the cores revealed that the maximum zinc concentration occurred in 1961.

The subsequent decrease in zinc can be linked directly to industrial closures in the 1980's. The length of the cores reflects the seabed composition at the core site, with pre-industrial sediments being those below about 100 centimetres.

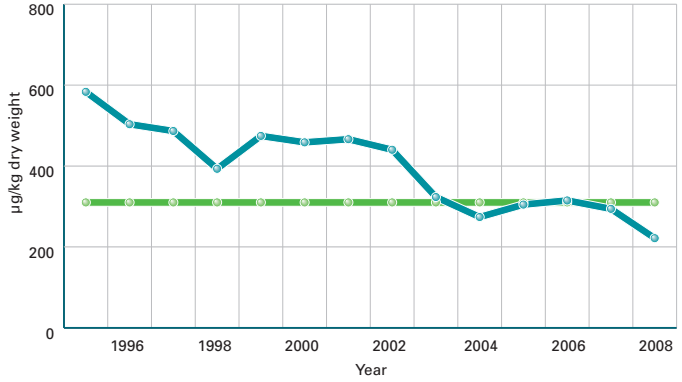
Hg (Mercury)



Zn (Zinc)



Cd (Cadmium)



Pb (Lead)

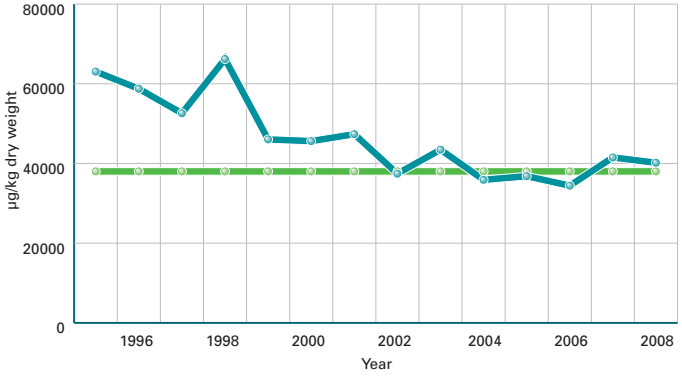


Figure 9.4 Decreases in metals concentration in sediments at a site, in Inner Belfast Lough (Station BL5), over time.

Metals Concentration in sediments, Belfast Lough
Background Assessment Concentrations

Alternatively, the current contaminant status can be assessed by analysing only the most recently deposited sediment, the surface layer. Over the past 14 years, monitoring in inner Belfast Lough has shown a steady and in some cases, significant decrease in the concentrations of most heavy metals analysed in the sediments (Figure 9.4).
Now 6 of the 8 heavy metals monitored have decreased to approximately background assessment concentrations.

Only chromium persists above the background assessment concentration and this may be due to the underlying geology. It is possible to attribute some of the step reductions in metals such as cadmium to the cessation of a specific discharge.

Unlike contaminants such as metals and PAHs, which occur naturally in the environment, for man-made substances such as PCBs the goal is to be at a measurable background concentration as close to zero as possible.

The analytical methods used to find such small concentrations in samples have proved challenging. Around the coast of Northern Ireland, the sites with the lowest recorded PCB levels were in Strangford Lough and off the north coast. Sites offshore tended to have concentrations 2 to 4 times the background concentration, with little change year on year. Inshore, the concentrations show more variation year on year, with values at about 4 times the background concentration. The highest values returned are from inner Belfast Lough, at about 10 times the background concentration over the past decade. However, results from the past 2 years, as displayed in Figure 9.5, have shown a reduction in concentration compared with those previously recorded. These results are encouraging although it is too early to establish a declining trend.

Are our sea waters contaminated?

Some metals occur naturally in coastal waters in trace amounts and can be toxic at high concentrations. Organisms like shellfish that filter water to feed, can be at particular risk because the metals may build up in their bodies. In our waters, the concentrations of chromium, cadmium, copper, mercury, nickel, lead and zinc usually fall below the recommended environmental quality standard values. The only exception was chromium at one site, in one year, possibly due to the local geology.

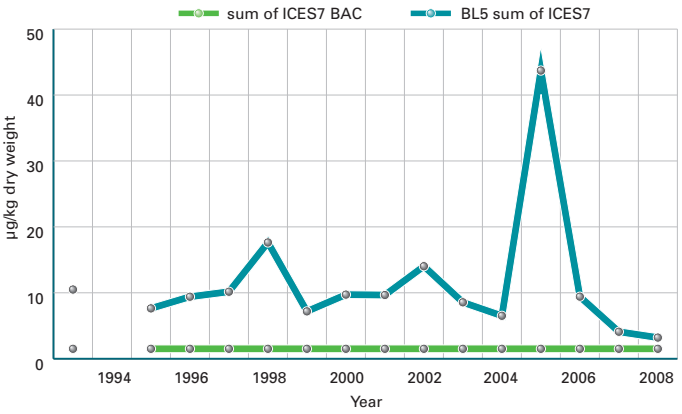
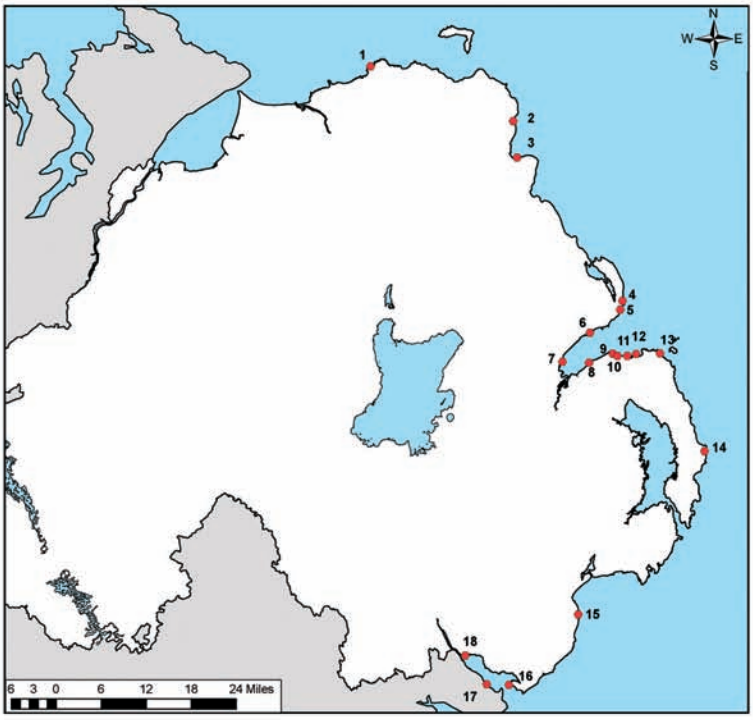


Figure 9.5 Sum of the ICES 7 priority Polychlorinated biphenols PCB's (CB28, CB52, CB101, CB118, CB138, CB153 and CB180).
Background Assessment Concentrations (BAC), are normalised to 2.5% Carbon (C) in Inner Belfast Lough.

NIEA has examined 5 years of data collected for a variety of monitoring programmes. There were very few occasions when organic determinands exceeded environmental quality standard values. One exceedance in lindane (gamma-HCH) was detected in 2006 in Lough Foyle. The organophosphorous compounds simazine, atrazine and diazinon are still being sporadically detected, especially in the River Bann. Atrazine and simazine have been banned for some time and should ultimately disappear from the environment. However, similar problems may arise with the products that will be used to replace them.

Some chlorinated solvents are still being detected on occasion, primarily due to the fact they are still in common use as degreasing agents and dry-cleaning solvents.

Other pollutants, like faecal contaminants, are examined in Chapter 14 on bathing water quality.



Site	Name	OSPAR Class 2004	OSPAR Class 2007
1	Giants Causeway	B	A
2	Cushendun	B	A
3	Redbay	C	B
4	Cloughfin Port	B	B
5	Claghan Rock	C	B
6	Carrickfergus	D	C
7	Ross Rock	C	C
8	Cultra	C	B
9	Helen's Bay	C	B
10	Swinley Point	C	B
11	Smelt Mill Bay	C	B
12	Lukes Point	C	C
13	Sandy Bay	C	C
14	Portavogie	C	C
15	Bloody Bridge	B	A
16	Greencastle	D	C
17	Carlingford	C	B
18	Warrenpoint	C	C

Figure 9.6 Imposex survey sites with comparative OSPAR classifications from 2004 and 2007 inset.

Are contaminants having biological impacts?

Biological impacts of contaminants are often hard to measure. However, the antifouling agent TBT was found to have an adverse effect on marine molluscs, causing shell thickening and recruitment failure in oysters. Another effect TBT has is that it has been shown to cause is the production of a non-functional male penis in female dogwhelks *Nucella lapillus*, a condition known as imposex[8]. Severe imposex may lead to sterility in females, which can be detrimental to whole populations. The use of TBT-based anti-fouling paints was banned on small vessels in 1987 and on all vessels after 2003.

The degree of induced imposex is measured using the Vas Deferens Sequence Index (VDSI) and classified according to an OSPAR classification scheme[9].
http://www.ni-environment.gov.uk/imposex_dec09.pdf.
A synoptic survey of imposex in dogwhelks along the Northern Ireland coast was undertaken in 2004 and again in 2007; 18 sites were sampled and results are presented along with the OSPAR classes for each year in Figure 9.6. Nearly 70% of sites have improved a full class over a 3 year period showing a marked improvement since the ban on use of TBT-based antifouling paints. The survey in 2007 revealed that 67% of the sites had improved ratings; the remaining sites being unchanged. Some 17% of the sites in 2007 were rated as class A, 44% were class B, and 39% were class C.

Further work

The chemicals and the way in which we monitor them will continue to change as new contaminants enter the marine environment and novel sampling and analytical techniques are developed. We need to understand more about the effects of mixtures of chemicals. Classical toxicology has provided information on the hazards of individual compounds but in their environment, animals are exposed to more than one compound at a time.
For endocrine disruptors, the effects of exposure to more than one compound are unknown.

Environmental quality standards values and development for some of the newer priority substances referred to in the Water Framework Directive are still under discussion. Once established, the full hazardous substances monitoring programme for organic compounds will be put in place.

Legislation	
Marine Strategy Framework Directive (2008/56/EC) Descriptor 8 Concentrations of contaminants are at levels not giving rise to pollution effects	
Other relevant EC Directives (full references and corresponding regulations – Appendix II)	
Urban Waste Water Treatment Directive	Driving tighter standards in sewage treatment & some industrial effluents
Water Framework Directive	Driving overall improvements in water quality
EQS's in the field of water policy	Control discharges that are likely to contain dangerous substances that go into water
Dangerous Substances Directive and its "daughter" directives	Control discharges that are likely to contain dangerous substances that go into water
Shellfish Waters Directive	Protect shellfish populations by maintaining water quality
International Agreements	
OSPAR Convention for the protection of the marine environment of the North-East Atlantic	Hazardous Substances Strategy
National and Local legislation	
Food and Environment Protection Act, 1985	Control the deposit of articles or substances in the sea
Water (Northern Ireland) Order 1999	Allowing NIEA to set appropriate consent conditions for sewage and industrial effluent treatment

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