OSPAR COMMISSION

Protecting and conserving the North-East Atlantic and its resources

Metals in sediment and biota: status and trend of copper burden

Radioactive Substances Series

2016

OSPAR Convention

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

Convention OSPAR

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

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Metals in sediment and biota: status and trend of copper burden

Contents

Executive Summary

Copper is a naturally occurring substance which is highly toxic in the aquatic environment, and hence is used as a major component in antifouling paints to avoid fouling of ship hulls and marine installations. Increasing concentrations of copper are now found in sediments mainly close to harbours and shipping lanes, but not so much in marine fish and shellfish.

Copper comes from many sources, e.g. use as building material and in electronic products. Although large scale efforts have been made to reduce riverine inputs, direct discharges and atmospheric inputs of copper since the 1980s, it has not stopped the increase in copper concentrations in sediments. Whereas marine fish and shellfish tend to regulate their uptake, sedimentation is the main sink of copper in the ocean. Further legislation and research on antifouling substances containing copper is probably needed to achieve the two goals of copper being at “concentrations … not giving rise to pollution effects” (2008/56/EC) and copper being close to background concentrations (OSPAR Agreement 2010-03) in coastal waters with high shipping intensity. Also, further investigation is needed of possible copper inputs to the marine environment via run-off from soils and roads.

Récapitulatif

Le cuivre est une substance naturelle qui est fortement toxique dans le milieu aquatique, et c'est donc un des principaux constituants des peintures antifouling, qui évitent la salissure des coques des navires et des installations marines. On trouve maintenant des concentrations croissantes de cuivre dans les sédiments, essentiellement à proximité des ports et des voies de navigation, à un moindre niveau toutefois dans les poissons de mer, les mollusques et les crustacés.

Le cuivre provient de nombreuses sources ; par exemple, il est utilisé comme matériau de construction et dans les produits électroniques. Malgré les vastes efforts déployés pour réduire les apports en provenance des rivières, les rejets directs et les apports atmosphériques de cuivre depuis les années 1980, l'augmentation des concentrations de cuivre dans les sédiments n'a pas été enrayée. Tandis que les poissons de mer, les mollusques et les crustacés ont tendance à réguler leur absorption, la sédimentation est le principal mécanisme d'accumulation du cuivre dans l'océan. Il est probablement nécessaire de mettre en place une législation supplémentaire et de conduire des recherches additionnelles sur les substances antifouling contenant du cuivre pour atteindre les deux objectifs pour le cuivre, à savoir pour celui-ci des « concentrations… ne produisant pas d'effets dus à la pollution » (2008/56/CE[1]) et des concentrations de cuivre proches des teneurs ambiantes (Accord OSPAR 2010-03[2]) dans les eaux côtières très fréquentées par la navigation. Il faut également étudier davantage les apports potentiels de cuivre dans le milieu marin en provenance des eaux de ruissellement des sols et des routes.

[1] Art. 9.1 de la Directive 2008/56/CE du Parlement européen et du Conseil du 17 juin 2008 établissant un cadre d'action communautaire dans le domaine de la politique pour le milieu marin (MSFD). JO L 164, 25.6.2008, p. 19

[2] Stratégie Substances dangereuses d'OSPAR

Background to the assessment sheet

Policy issue

Many man-made and naturally occurring chemicals end up in the North-East Atlantic as a result of land-based and sea-based human activities.

Policy objectives

- EU – Marine Strategy Framework Directive:
  - Aims to achieve good environmental status of the EU's marine waters by 2020;
  - Concentrations of contaminants are at levels not giving rise to pollution effects.
- OSPAR – North-East Atlantic Environment Strategy:
  - Cessation of discharges, emissions … of hazardous substances by 2020;
  - Hazardous substances in the marine environment:

    (i) achieve concentrations near background values for naturally occurring substances; and

    (ii) close to zero for man-made substances.

Specific Questions/Background

Copper (Cu) is an extensively used metal in a variety of applications. Since the early 1980s measures have been taken to reduce riverine inputs, direct discharges and atmospheric inputs. As a result there were important downward trends in concentrations in both sediment and biota. Recently, however, increasing Cu levels have been observed, in contrast to most other metals and organic substances.

Sources of Cu in the environment

Cu is used for many purposes, both in the metal form directly, mainly for building materials and electrical wires, and as chemicals (oxide, sulphide and chloride mainly but also other formulations). The sources to the marine environment are both as metal, in e.g. copper plating and brass propellers, or as chemicals added to antifouling paints. About 18 million tonnes are mined on a yearly basis (USGS, 2015), with 43% used for building construction, 19% in electric and electronic products, 19% in transportation equipment, 12% for general consumer products and 7% used in industrial machinery and equipment.

The total use of copper chemicals in EU 1999 was 32 400 tonnes, broken down into categories as shown in Figure 1 (Hansen et al., 2014). Note that cattle feed includes all type of animal feeds. It should be noted that Cu-chemicals are only a small part of the total Cu (3% of the Danish Cu imports in 1992).

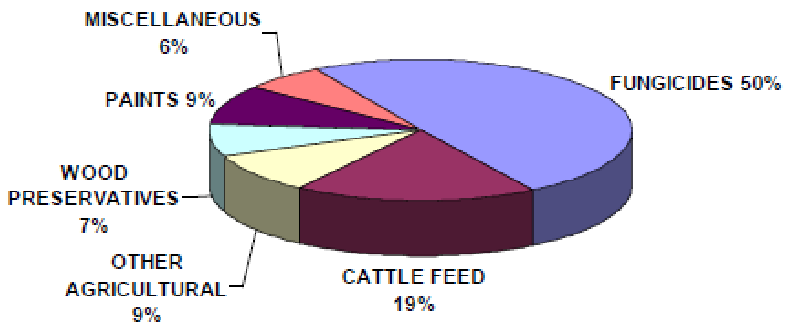

Figure 1: Consumption of copper chemicals in EU in 1999 in different categories, total used 32400 tonnes

The main use of copper chemicals varies by country. In Table 1 some examples of the main uses in Denmark and Sweden are shown (given as imported tonnes in the year investigated). The main uses in Denmark are for feed additives especially in pig feeds, whereas the main use in Sweden is for wood preservation (Hansen et al., 2014). In both countries around 15% is used for antifouling paints, and in 1992 it was estimated that this was the main source of Cu to the (marine) water in Denmark, accounting for 18-28 tonnes of the 20-38 tonnes emitted directly to the water, i.e. 75-90% of the total losses to water from copper chemicals (Lassen et al., 1996).

Table 1: Use of copper chemicals in Nordic countries (metric tonnes)

Copper compounds imported for use in	**Imported** tonne**s of copper compounds in the year investigated**		
	Denmark 1992 (Lassen, 1996)	*Denmark 2012 (Hansen, 2014)*	*Sweden 2009 (Hansen, 2014)*
Wood preservative coatings	200-250	47	823
Feed additives	300-400	365	no data
Antifouling Paints	27-40	46-85	183
Dyestuffs, pigments	100-200	no data	44
Fertilisers	125-140	32	25
Total	800-1100	490-531	1140

Shipping

Cu has been used in antifouling treatments since ancient times (Yebra et al., 2004), but especially so from the end of the 18th century, where it was used together with other metals (mainly lead, arsenic and mercury) as an antifouling agent. Notably, the fastest sail ship in its time, the Cutty Sark from 1869, was clad in brass sheeting (Muntz-metal, alloy of 60% Cu, 40% Zn and trace amounts iron) on the bottom, preventing fouling (Taylor, 2013). Cu-based paints are usually not used on aluminium hulls as contact between the two metals can form a galvanic element and lead to damage of the hull.

Since a ban on the most efficient antifouling agent TBT (OSPAR Assessment Sheet for TBT, http://www.ospar.org/site/assets/files/7413/ospar_assessment_sheet_cemp_imposex_2014.pdf), substitution to Cu-based paints with Irgarol 1051 (Cybutryne) or Diuron booster biocides, started on smaller vessels and has now continued for over a decade. These two booster biocides are either not approved or banned in several EU countries (for example UK, Denmark, Sweden, Holland). Danish legislation placed limits on the release rate of Cu from antifouling paints on pleasure crafts to 200 µg cm^{-2} in the first 14 days and 350 µg cm^{-2} after 30 days (Danish Ministry of the Environment, 2011).

The new antifouling components, though not causing as detrimental effects as TBT, can have certain adverse effects on biota and be concentrated in sediments, especially in harbour areas (e.g. Briant et al., 2013 and Dafforn et al., 2011). Banning metals in antifouling paints can lead to increased fuel consumption, the use of TBT has been estimated to decrease CO_2 emission from ships with 23 million tonnes (Dafforn et al., 2011).

In harbours, leaching of Cu antifouling from ships' hulls is also of importance, as shown by Cu leaching from the introduction of boats to marinas in San Diego Bay (Biggs and D'Anna, 2012), where Cu concentrations rapidly increased in water to concentrations above chronic and acute toxicity levels. Some of the Cu is sequestered into the sediments, but also exchanged with the area outside the harbour. A management model, restricting the number of boat introductions per time, can keep the Cu levels in the harbour waters under the toxic levels (Biggs and D'Anna, 2012). Another source of metallic Cu is from polishing the brass propellers from ships by diving companies in the surface water, which can contribute to elevated concentrations of Cu in harbour water, and transport of fine Cu particles to the sediment, introducing up to 150 g of Cu per propeller to the environment (Berbee, pers. comm.). Other maintenance work typically done around the harbour, like cleaning of Cu-containing antifouling paints and re-painting, can also add to the inputs in the harbour waters.

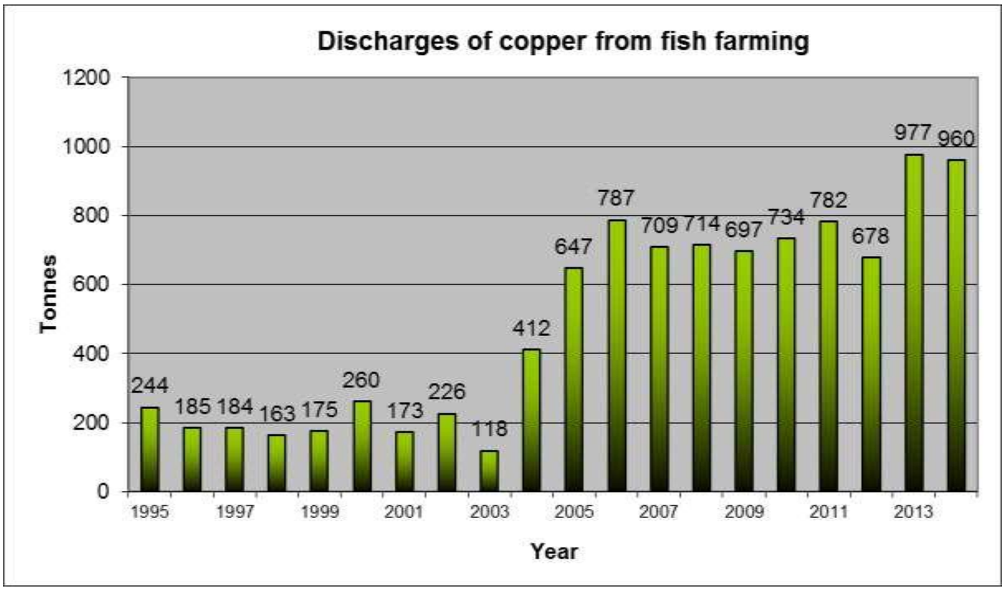

Figure 2. Estimate of discharge from fish farming in Norway, based on 85% of the sales statistic for Cu in regularly used antifouling paint (Skarbøvik, 2015). The estimate is considered uncertain.

Aquaculture

The rapid growth in the use of Cu-based antifouling systems in aquaculture over the past decade has markedly increased the inputs of Cu to the sea in northern Scotland and west and north Norway (OSPAR Commission, 2011). The total use of Cu in Norwegian fish farms was estimated to be 261 tonnes of Cu in 2005 by (Fitridge et al., 2012), the same range as the 75-311 tonnes of Cu estimated to have been used on UK pleasure boats in 1998 (UK Marine SACs project). The latest estimate from the Norwegian RID report are 960 tonnes in 2014 (figure 2, Skarbøvik*, 2015*), but the estimates are considered very uncertain as it is based on sales statistics for a number of common antifouling products, assuming 85% of the Cu is lost to the environment. However, the estimate correlates fairly well with the fish production in Norway. Particularly the EU classification of Cu as a R50/R53 as very toxic and may cause long term adverse effects in the aquatic environment (EEC directive 67/548, 1967), and public awareness of chemical antifouling use, may change the focus to other non-chemical means of protection against fouling instead of Cu and chemicals. Despite this, nets made of Cu alloy wire are being used and tested for their effectiveness in keeping predators like sea lions, seals and sharks out, and improve the health of fish (ICA, 2012), currently mainly outside of the EU.

Trace metal concentrations were measured in sediment collected from Scottish sea lochs in 2005 and 2006. Cu concentrations in sediment beyond 25 m from the farms were below those that cause benthic effects (Russell et al., 2011). In Norway a study focussed on cadmium (Cd) contamination from fish farms, but also included other metals like Cu (Falk, 2014).The Cu concentrations in crab brown meat was higher than reference concentrations in crabs, but no correlation to distance to the fish farm was evident. The general conclusion was that fish farm contributed Cu and zinc (Zn) to the environment, but it was not possible to determine if the impact was higher than other sources of Cu in the environment.

Land based inputs

Figure 3. Copenhagen City hall seen from ICES HQ – with copper roofing and traffic on H.C. Andersen Boulevard as sources of Cu.

The importance of Cu in brakes and tyres, and the losses from railway current supply, was mentioned in the QSR 2000. A major source of Cu to the environment is brake pad wear, and a recent estimate suggests that this contribution is at the same level as other sources of airborne Cu pollution (Hulskotte et al., 2006). Under Californian law Cu concentrations in brake-pads should be reduced to 5% by 2021 and to below 0.5% by 2025 (DTSC, 2010). Another significant input of Cu to the environment is from the corrosion of Cu materials, such as drinking water tubing and Cu roofs, gutters (ER, 2014). Although a large part of the corrosion products is removed by adsorption on wastewater treatment sludge the remaining part flows via effluents into surface waters. Other important sources are the runoff and leaching of agricultural soils containing livestock manure, especially from pigs where Cu and Zn is used in the production (Bak et al., 2015) and, in some countries, due to application of sewage sludge as fertiliser (Nicholson et al., 2003). In France, the use of Cu as a fungicide is also of concern (Babcsańyi, 2014), giving rise to increased soil concentrations and run-off to wetlands during high-flow conditions.

The direct inputs to the OSPAR area have been estimated in the RID program (OSPAR 2015a) to between 2460 and 2700 tonnes yr^{-1}, with the majority to the central North Sea (970 tonnes yr^{-1}) and Norwegian Sea (588 tonnes). The areas where increases in Cu concentrations are found are receiving ~154 tonnes yr^{-1} (Channel) and ~80 tonnes yr^{-1} (each of the Celtic and Irish Sea).

Airborne input

Input in aerosols and precipitation are reported by the CAMP program (OSPAR 2015b), but no time trends were shown for Cu. The highest aerosol concentrations were found around at the border between the Channel and the North Sea (>3µg m^{-3}) and the central Channel (1.5-3 µg m^{-3}), whereas precipitation showed the highest concentrations south of Ireland and the Bay of Biscay (>6 µg l^{-1}), and also relatively high levels 3-6 and 1-3 µg l^{-1} at the channel/North Sea border and south-east England respectively. Same levels are found in precipitation around Denmark (North Sea, Skagerrak and Belt Sea). Levels are low <0.8 µg l^{-1} at the Channel-Celtic Sea border in both UK and French samples.

Fate of Cu in the water

The fate of Cu entering the marine environment is complex and the freshwater/sewage sources can be transferred to sediments at the freshwater/seawater interface due to flocculation and binding to settling particles, or by complexation with natural ligands (e.g. humic substances) or exudates of algae before dispersion over larger areas (Sunda and Lewis, 1978; Leal et al., 1999). The increasing concentrations in sediments, but not in mussels, should be investigated further, and the sources and pathways into the sediment clarified.

Findings from the 2015 assessment of OSPAR datasets update at MIME 2015

Cu concentrations in sediment, fish, blue mussels and pacific oyster were evaluated for the whole OSPAR convention area in 2015. For sediments, mussels and oysters OSPAR background assessment concentrations (BAC) were used as an indicator of levels being close to background, no BAC was available for fish species. To assess if concentrations in sediment were causing biological effects, the Effect Range Low (ERL) was used (Long et al., 1995; Buchman, 2008). However no assessment criteria for detrimental effects were available for fish or shellfish. This is partly due to the fact that Cu is a micronutrient and an essential element, and as such many organisms have some biological control over the uptake and release of Cu.

Sediments

Overall, the metal burden of Hg, Cd, Pb, Cu and Zn in sediments were mostly found to be decreasing in the North Sea, with 6% of 1931 assessed sediment time-series showing downward trends compared to 1.6% showing an increasing trend. There were more significant downward trends for mercury than for any other metal: of the 387 mercury time-series, 39 showed a downward trend and just 1 an upward trend, probably an indication of the huge effort to decrease release of Hg into the environment from the 1990s and onwards. Also Cadmium with 20 downward trends and 1 upward trend was indicating generally improving conditions, whereas Pb and Zn was both had 5 upward trends. The metal with the most upward trends was Cu, for which 19 of the 388 time-series in sediment were increasing and 35 were decreasing. Sites with increasing trends tended to be located in the vicinity of harbours, marinas and major shipping lanes. The general pattern for Cu is (Figure 4) that sites with concentrations above ERL are further increasing. The colour codes used are the same as in the OSPAR assessment web-tool (http://dome.ices.dk/OSPARMIME2015/main.html), blue for values below BAC, green for values ERL for sediments, orange when below food criteria and no exotoxicological criteria are available, black when no assessment criteria are available for the species. Triangles indicate significant trends, pointing upward for increasing and downward for decreasing trends, circles indicate no trends. In the southern UK below the latitude 55^{o}, 9 of the 20 time-series above ERL (red) showed an upward trend. Along the coast of the Netherlands, most stations are also above ERL, and 3 of these stations with increasing trends. For the whole assessment, very few trends of stations below ERL (green) and BAC (blue), showed an upward trend, all 4 stations in the sound of Jura at the Scottish west coast and 1 of two station. Upward trends in Cu concentrations in sediment have also been found on the southern Spanish Atlantic coast. In the German Bight and central North Sea concentrations are generally low and decreasing, and only stations in the German rivers are above the ERL, based on single measurements.

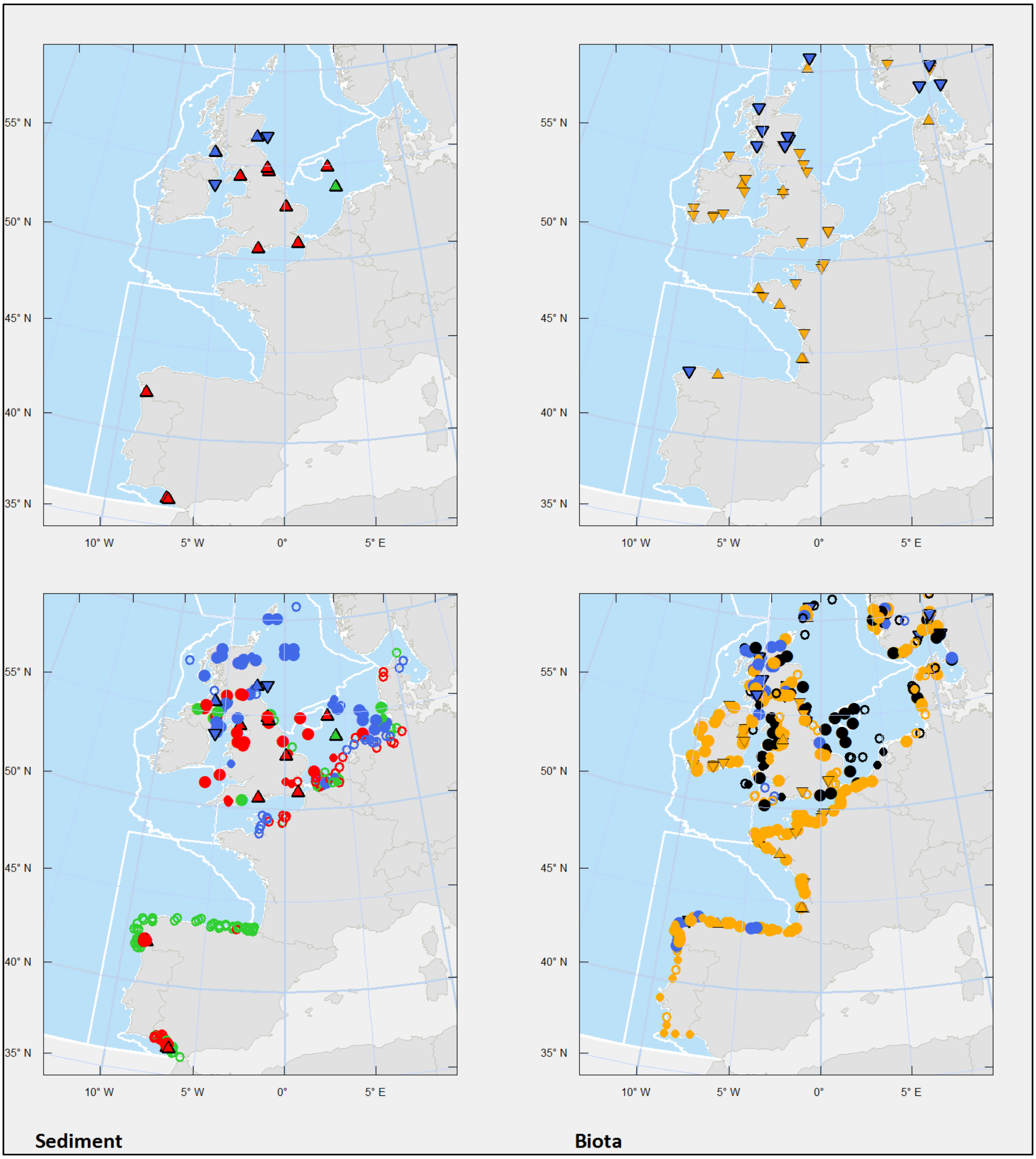

Figure 4: trend and status for Cu in sediment (left) and biota (right). Most trends are not significant and only for significant time trends the assessment class is shown with the symbol colour in the upper pane. In the lower pane, the status assessment is shown with the edge colour indicating the assessment class for stations where no time trend was available.

Biota

In biota, 420-440 time trends were assessed, with 21% significant time trends found for Cd and Pb, and only half the number of significant time trends for Hg and Zn (13-15% significant trends), and only 10% significant trends for Cu. The majority of the trends for metals were downward, but for Cd and Hg, the number of increasing trends was more than half of the number of downward trends, a much higher proportion than for Pb and Zn (10-17%), for Cu 29% were increasing.

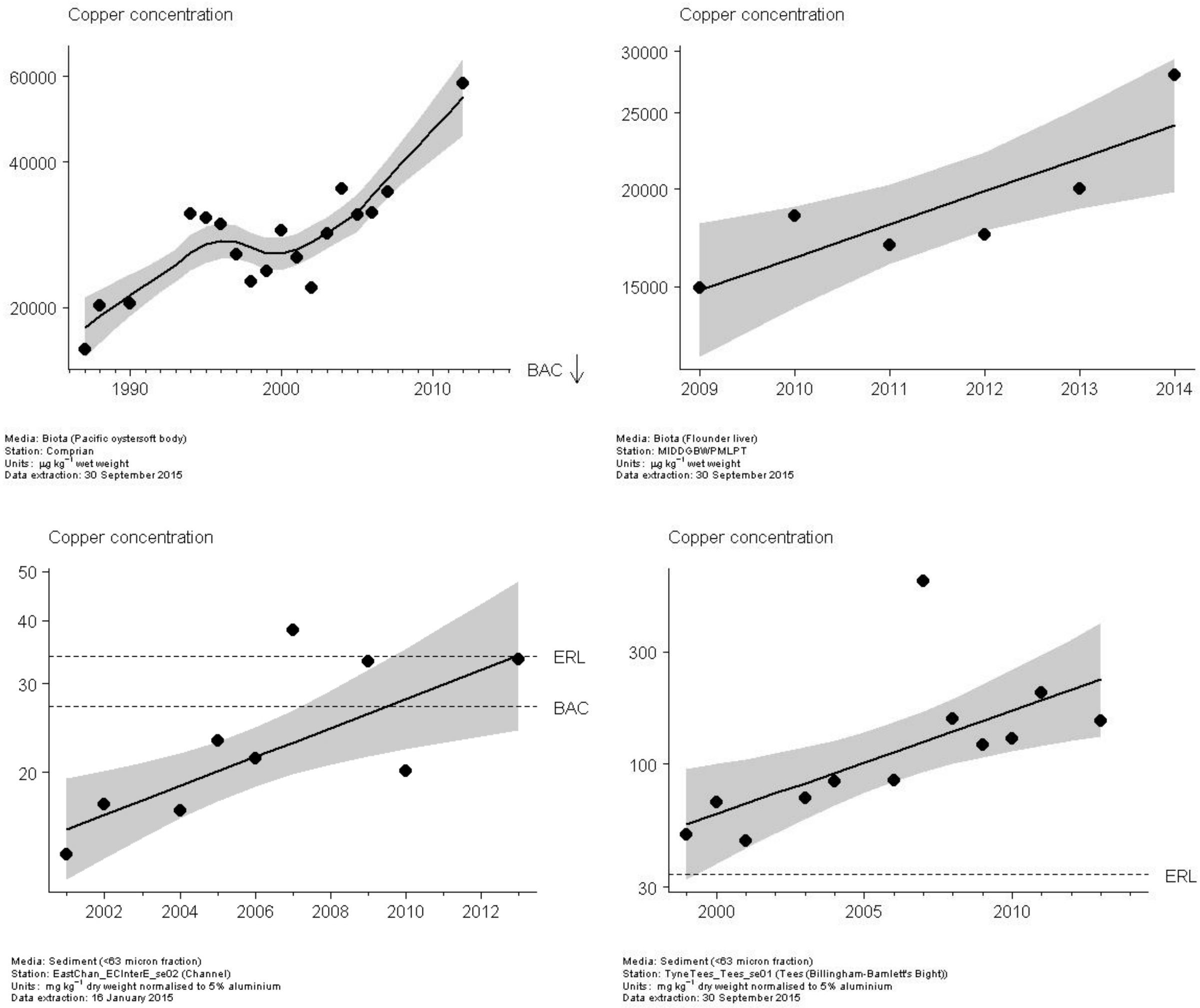

Figure 5: Increasing trends in Pacific oyster (Crassostrea gigas), Blue mussels (Mytilus edulis) and sediments. Recent data from Comprian (not reported to ICES yet) show continuing increase after 2010

Trends in Cu concentrations of 421 biota time-series have been observed in 10 time-series for three fish and seven shellfish stations, and 34 downward trends (four fish, the rest shellfish). Some of the increasing trends were observed in Blue mussels (*Mytilus edulis*) around the UK, in the Irish Sea, the English Channel, on the English east coast and south of the Shetland Islands, all at sites where concentrations were already above BAC. The Pacific oyster (*Crassostrea gigas*) accumulates Cu to a much larger degree than Blue mussels (Phillips and Yim, 1988; Larsen, 2011), leading to concentrations in tissues a factor 10-100 higher than in Blue mussels. Cu uptake is generally controlled by bivalves, but with different efficiency from species to species (Pan and Wang, 2012). The upward time trends of Pacific oysters along the French coast in Bay of Biscay were already noticed in relation to monitoring after the ban on TBT on pleasure boats in France in the 1980s (Claisse and Alzieu, 1993). Interestingly, of the four Pacific oyster stations examined by Claisse and Alzieu, three (Cap Ferret, Comprian and Les Jacquets) are still monitored, and two of them (Comprian and Les Jacquets) show increasing trends after a dip around 1998 to 2003 (Figure 5). No direct geographical link was observed between Cu in biota and sediment samples.

Comparison of levels with other parts of the world

The levels of Cu in sediments the OSPAR assessment ranges from 1-355 mg kg^{-1}, with median value 22 mg kg^{-1} and average of 33 mg kg^{-1}. In comparison, a recent review of Chinese data (Pan and Wang 2012) indicated average values of 8-753 mg kg^{-1} with measured concentrations ranging from 1-4000 mg kg^{-1} (both around Hong Kong), and though no assessment was made of time trends, the major sources were expected to be riverine inputs and industrialised areas, which caused "alarmingly high" levels of metals in sediment, water and biota. Metal mining is widespread, resulting in both air pollution in the form of dust, and leakage from mine-tailing, resulting in levels of up to 4540 mg kg^{-1} in sediments of the Nanyang River. The highest average concentrations were found in Jinzhou Bay and Hong Kong, at 417 mg kg^{-1} respectively 119 mg kg^{-1}, whereas 19 of 29 areas were at the level or below the OSPAR average concentration. In Auckland, New Zealand (Mills et al., 2012), evaluation of sediment monitoring from 1998 to 2010 for both harbours, regional discharges and "state of the environment" stations indicated upward trends in harbours, especially at Chelsea (Central Waitemata Harbour), but mixed signals were obtained as some areas of the Manuku harbour was both upwards and downwards, in different parts of the harbour. In general the number of downward trends was higher than upward trends, and concentration levels were low at 1-42 mg kg^{-1}.

Conclusion

The Cu concentrations in coastal and near-harbour sediments in the OSPAR area are at levels far above ERL. Furthermore, increasing trends were observed in some of these coastal areas. This indicates a problem that needs to be taken into consideration if the EU MSFD target for Descriptor 8 of 'contaminant concentrations not giving rise to pollution effects' is to be met and good environmental status achieved. In the open waters, the OSPAR target of concentrations being close to background is fulfilled for Cu. The problem of elevated Cu concentrations in coastal and near-harbour sediments is most likely connected to antifouling paints and ship maintenance procedures in harbours, but in general also run-off from agricultural soils and roads can attribute to the negative impact on coastal areas. Further legislation and research into antifouling systems and cleaner harbours is probably needed to achieve the goals of close to background concentrations in coastal waters with high shipping intensity.

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