

## Theme Session G

### Human health risks and marine environmental quality

#### ICES CM 2006/G:01

##### **The role of northeast monsoon seasons in the dilution of heavy metal concentrations in sediments off Pahang, South China Sea**

B. Y. Kamaruzzaman, N. A. M. Shazili, K. Y. S. Willison, M. C. Ong, and H. A. G. Norhiezzam

A geochemical study was conducted in the Pahang waters of the South China Sea with samples collected in pre-monsoon and post-monsoon seasons. Surface sediments collected from 48 stations were analyzed for concentrations of heavy metals (Pb, Cu, Mn and Zn) using a sensitive inductively coupled plasma mass spectrometry (ICP-MS). In general, the concentration of studied metals in both seasons show considerable variation spatially, which largely appears to be controlled by natural processes. This was proved by their enrichment factors (EF) which have values significantly about unity and are considered to be dominantly terrigenous in origin. In this study, it is interesting to note that the concentrations of all studied metals are relatively high in the pre-monsoon season and become much lower after the post-monsoon season. In the pre-monsoon season, Pb has an average value of 24.5 µg/g dry weight, Cu 19.2 µg/g dry weight, Mn 1.15 µg/g dry weight, and Zn 93.6 µg/g dry weight. However, during the post-monsoon season, the concentrations of Pb, Cu, Mn, and Zn were significantly decreased to 13.1 µg/g dry weight, 6.31 µg/g dry weight, 1.06 µg/g dry weight, and 51.4 µg/g dry weight, respectively. These findings indicate that the annual seasonal changes that occur in Pahang waters of the South China Sea play an important role in regulating the concentrations of heavy metals.

Keywords: Heavy metal, Northeast monsoon, South China Sea.

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#### ICES CM 2006/G:02

##### **Sources, consumer exposure and risks of organotin contamination in seafood**

Jan-Willem Wegener and Frank Willemsen

The European project 'Sources, consumer exposure and risks of organotin contamination in seafood' (OT-SAFE, contract number QLK1-CT-2001-01437) was aimed to establish the risk of the anti-fouling agent TBT (tribu-

tylin) for the European seafood consumer. Although the use of TBT is now restricted, TBT can still be found in the marine environment and, as a consequence, in seafood for human consumption.

Seafood samples were taken in eleven European countries. The distribution of samples was weighed according to consumption and the expected TBT level. The consumption data were compiled from food consumption surveys or, lacking these, more crude data such as market data and catches and landings data. The expected TBT levels were derived from the (limited) existing data on TBT in seafood and from ecotoxicological studies. In order to guarantee the quality of the data, sample collection was based upon ICES protocols and TBT concentrations were determined to the highest analytical standard using a certified reference material BCR-477 (tin species in mussel tissue).

Based on the analyses and the consumption data, intake levels were calculated and compared with the known TDI (tolerable day index).

To be at risk of exceeding the TDI for TBT as a result of seafood consumption, one has to be a high consumer of seafood and one has to consume seafood containing higher-than-average concentration of TBT. Therefore, there must be some concern about sardines in Greece; molluscs are a cause for concern in Portugal and, especially, Italy.

Keywords: organotin, seafood, consumption, risk assessment.

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#### ICES CM 2006/G:03

##### **Proliferation of the Pacific oyster *Crassostrea gigas* in Dutch coastal waters and its consequences for human use**

Aad Smaal, Jeroen Wijsman, and Marnix Poelman

Since the introduction of the Pacific oyster in 1964 in the Oosterschelde estuary (SW Netherlands) for oyster culture a rapid proliferation has occurred. The species is now abundant in all Dutch coastal waters. The extended oyster reefs nowadays cause problems for various functions of the estuaries. The wild oyster population competes with other shellfish species for food and space, hence the commercial exploitation of mussels, cockles, and oysters is threatened by the wild oysters. Also the

function for wintering birds is threatened as they depend on the availability of shellfish and the oysters are not a useful prey. Recreational use is impacted as oyster reefs are dangerous for human health: sharp shell edges cause serious injuries if people touch reefs during swimming, diving, surfing, and sailing. Another human health aspect is the consumption of wild fresh oysters that are not under sanitary control.

For management of the expanding oyster populations various measures are under development. In the Oosterschelde experimental fishery has been carried out to test the effectiveness in reducing the oyster stock and also to evaluate environmental impacts of fishery. The extension of the oyster impacts and the results of the experimental fishery will be discussed.

Keywords: invasive species, oysters, injuries, management.

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#### ICES CM 2006/G:04

##### Contaminants in marine food chains: old patents and new pollutants

Jacob de Boer and Pim E. G. Leonards

Since the 1960s the marine environment has been contaminated by a multitude of organic contaminants, most of them complex mixtures of polychlorinated substances. Well-known examples are the DDT group, the drins (dieldrin, endrin, etc.), hexachlorocyclohexanes (HCHs), toxaphene, and PCBs. Most of these have been regulated during the last decades of the previous century. That has resulted in decreasing trends of most of these contaminants in marine biota and sediment top layers. However, other less known contaminants, often used as alternatives for the compounds that have been banned, have taken their place. A well-known example is the group of brominated flame retardants. Nowadays perfluorinated compounds such as PFOS and PFOA are being found in marine biota. These fluorinated compounds differ in behavior from most other organic contaminants, as they are less lipophilic and tend to concentrate in livers and blood of fishes rather than in the fat tissue.

Where authorities feel that the problem of persistent organic pollutants has been solved by banning chlorinated pesticides and PCBs, environmental scientists see a similar process taking place again, now with brominated and fluorinated compounds. Apparently, it is still possible to produce these environmental harmful substances, due to the fact that they are based on relatively old patents, which have not been subjected to environmental risk assessments.

Keywords: Organic contaminants, flame retardants, perfluorinated compounds.

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#### ICES CM 2006/G:05

##### Perfluorinated alkylated substances in the marine environment

Pim de Voogt

Perfluorinated alkylated substances (PFAS) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have recently gained scientific and regulatory interest because of their finding in marine mammals from remote areas. Until to date, the transport routes of PFAS from their sources to the remote areas have not been explained satisfactorily. Long-range air transport of precursors and oceanic transport have been proposed as possible mechanisms. Because of their intrinsic polar or even ionic character, several of the PFAS can dissolve in appreciable amounts in water. In oceanic waters PFOA is usually the major representative of the PFAS detected, followed by PFOS.

There are very few data on PAS in sediments of marine origin. Available data suggest widespread occurrence of PFAS in sediments at the low ng/g to sub-ng/g level. Also substances that may be transformed to PFOS or PFOA are present in sediments.

PFAS accumulate in the liver and serum of biota. Concentrations in marine fish appear to be on average one order of magnitude lower than those in freshwater fish. Significantly higher PFOS concentrations have been reported in marine mammals, suggesting a biomagnification effect. In marine mammals substantial variations in concentrations have been observed. This may partly be caused by differences in location or by differences in habitat. Concentrations found in biota range from the low ng/g to the low µg/g (ww) level. Those found in biota from Northern America tend to be higher than those reported in biota from Europe.

Temporal trends based on data from fish, marine mammals and bird eggs showed an increase between the 1970s and 2002. There are contradictory reports about temporal trends of PFOS and PFOA in human blood.

Food is an important route of exposure for PFAS in non-occupationally exposed humans. Based on current knowledge a provisional estimate of human intake has been made. This has led to the tentative conclusion that a major intake route is probably from fish consumption, although possible routes of exposure other than food ingestion (e.g. dermal contact and inhalation) have not been fully quantified yet.

Keywords: perfluorinated alkylated substances, PFOS, PFOA, exposure, biomagnifications.

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## ICES CM 2006/G:06

### Distribution of PCBs compounds in *Bivalve molluscs* coming from the Galician coast (N.W. Spain)

N. Carro, I. García, M. Ignacio, and A. Mouteira

Polychlorinated biphenyls (PCBs) are a group of synthetic halogenated hydrocarbons (209 congeners) that present low vapour pressure, high chemical and thermal stability, and high dielectric constant. These properties make them very useful as constituents in a wide range of industrial products, such as in dielectric fluids of transformers and capacitors, heat exchange and hydraulic fluids, fire retardants, lubricants and other materials. On the contrary, their general inertness and lipophilicity can cause serious problems to estuarine and marine environment.

The high filtration power of some bivalve molluscs involves they can be considered like bioindicators of micropollution. However, some biological factors and environmental conditions can influence the bioaccumulation.

Galicia in northwest Spain is an important shellfish producing region so it is necessary to carry out an analytical control of these contaminants (PCBs) in the estuarine bays (Rías) which are the main production areas for molluscs.

The objective of this work is to study the distribution and levels of PCBs in some species of bivalve mollusc, clams (*Venerupis pullastra* and *Ruditapes decussatus*), and cockle (*Cerastoderma edulis*) coming from several Rías of Galicia (A Coruña, Camariñas, Muros, Arousa, Pontevedra and Vigo), for this purpose 10 PCB congeners (IUPAC nº 31, 28, 52, 101, 118, 153, 105, 138, 156 and 180) recommended by the International Council for the Exploration of the Sea (ICES)<sup>1</sup> have been extracted by using Soxhlet and determined by Gas Chromatography (ECD) and Gas Chromatography coupled to Mass Spectrometry. Univariate and Bivariate statistical techniques have been applied to PCB data concentration in order to learn the spatial trends and possible influences of species on PCB distribution and bioaccumulation.

<sup>1</sup>Duinker, J. C., Schulz, S. E., Patrick, G. 1988. Selection of chlorinated biphenyl congeners for analysis in environmental samples. *Marine Pollution Bulletin* 19:19-25.

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## ICES CM 2006/G:07 – Poster

### An assessment of risks of bream (*Abramis brama* L.) from the Russian EEZ of the Vistula and the Curonian Lagoons (the South-East Baltic Sea) for human food using

Natalia Chukalova

20 bream with visible pathological skin symptoms and 20 fish with no signs of disease from the Curonian and the Vistula Lagoons (the South-East Baltic Sea) were examined with standard bacteriological and parasitological methods in October 2005. A total of 198 bacterial cultures from 10 genera were detected in bream from both Lagoons. The microflora composition of fish with external diseases and healthy bream was different. Several of the bacteria were also more prevalent in fish with external diseases. Six species of opportunistic bacteria from 3 genera were found in muscles of fish. The pathogenic behavior of the detected bacteria was clarified.

23 parasitic species from 8 systematic groups were noted in bream from the Curonian Lagoon and the Vistula Lagoon. Pathogenic parasites for human *Paracoenogonimus ovatus* mtc. (P=5%, A= 0,05 sp., I= 1sp.) and *Contracaecum* sp. 1. (P= 85%, A= 22,65, I= 26,65) were only found in fish from the Curonian Lagoon. *Methacercariae* were found in bream muscles and larvae of nematodes only in the fish abdominal cavity. Muscles of all investigated bream corresponded to requirements of the Russian Sanitary Code and were suitable for human consumption. The presence of high virulent cultures of opportunistic bacteria in fish muscles indicates that bream can cause human infectious diseases.

Keywords: human pathogens, bream, *Abramis brama*, parasites, opportunistic bacteria, South- Eastern Baltic Lagoons.

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## ICES CM 2006/G:08

### Food web transfer of dioxins and other contaminants in the Western Scheldt: implications for human and environmental health

Martine van den Heuvel-Greve, Pim Leonards, and Dick Vethaak

In 2005 a baseline study was conducted to assess the occurrence of dioxins and other contaminants in the estuarine environment of the Western Scheldt in the southwest of the Netherlands. Sediment was sampled at five locations and samples from two simple food chains were collected near the city of Terneuzen. The samples were

analysed for both consumption of fish products and environmental quality. Dioxin concentrations in fish products did not exceed current EU standards, although they came very close. A new standard for both dioxins and dioxin-like PCBs will come into effect on 4 November 2006 and shine a new light on the outcome of this study. Some contaminants showed a clear trend with higher concentrations in the eastern part of the Western Scheldt and lower sediment concentration in the western side. Contaminants that accumulated in both the benthic and pelagic food chain were PCBs, lower brominated flame retardants, and PFOS. Potential benefits of simultaneous sampling for environmental and human health will be discussed.

Keywords: dioxins, food web transfer, human health, environmental health.

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### ICES CM 2006/G:09 – Poster

#### Parasitological assessment of the commercial fishes from the Russian EEZ of the South Baltic Sea

Galina Rodjuk and A. Eliseev

Parasitological research of commercial fish in the Russian EEZ of the South Baltic Sea (including the Vistula and Curonian Lagoons) has been carried out in Atlant-NIRO since 1996. The main aim of these investigations was assessment of fish for human consumption. Six fish species were studied in 1996–2005 by the total parasitological dissection method: Baltic herring (5642 specimens), cod (556), flounder (728), sprat (1830), smelt (111), and zander (15). Five human pathogenic parasite species representing the following higher taxa were found: Cestoda – *Diphyllobothrium sp.* (smelt), Nematoda – *Anisakis simplex* L. (herring, cod, flounder, zander), *Contracaecum osculatatum* L. (herring, sprat, cod, flounder) Acanthocephala – *Corynosoma semerme* L. (herring, sprat, cod, flounder, smelt), *C. strumosum* L. (herring, cod, flounder, smelt). *Plerocercoids Diphyllobothrium sp.* were found in the Curonian Lagoon only. Nematodes were found in the Baltic Sea and in the Vistula Lagoon. Cystacanths of the genera *Corynosoma* were found in all investigated regions. The correlation between the incidences of fish infestation of these parasites and fish body length, sex; as well as season and region was studied. The highest indices of infestation were observed for *A. simplex* L. in herring and cod. All pathogenic parasites were found on the surface of the internal organs of the fish abdominal cavity. In herring only *A. simplex* L. was found in the abdominal muscles (0.2%, 1-3 sp.).

Keywords: human pathogenic parasites, fish parasites, the Baltic Sea, Vistula and Curonian Lagoon.

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### ICES CM 2006/G:10 – Withdrawn

### ICES CM 2006/G:11

#### Assessing nation-wide distributions of contaminant levels in selected finfish and shellfish from the Estuaries of the United States

J. Kevin Summers

The U.S. EPA Environmental Monitoring and Assessment Program (EMAP) through its National Coastal Assessment (NCA) has collected and analyzed fish and shellfish samples from over 646 estuarine locations along the Atlantic and Gulf of Mexico coastlines in 1991–1996 and from over 2000 estuarine locations along all coasts in 1998–2002. Fillet tissue was analyzed from all samples from 1990–1996 and whole body samples were analyzed for the samples from 1997–2000. Cumulative distribution frequencies for total fish and selected species' tissue and whole body concentrations were compared to the U.S. EPA Fish Advisory Guidelines for recreational and subsistence fishers. For 1990–1997, tissue concentrations ranged from 0.004–1.63 µg/g with 54% and 51% of the fish exceeding the subsistence fishers' criterion in Atlantic estuaries and Gulf of Mexico estuaries, respectively. Twenty-three percent of the fish exceeded the lower limit of the recreational fishers' guidance (four 8-ounce meals per month) for mercury in Atlantic estuaries during the same period, while 21% of the fish in Gulf of Mexico estuaries exceeded this criteria. During 1997–2000, whole body concentrations for mercury from fish throughout the United States exceeded the recreational fishers' guidelines described above in only 1% of fish. This large reduction would be expected when comparing whole body concentrations with fillet concentrations. Mercury is almost completely sequestered within muscle tissue in fish. Estimations of fillet concentrations in muscle tissue for the 1998–2000 period showed 42% of fish exceeding the lower limit of the recreational fishers' guidance for mercury listed above with 48% exceedance in fish from Northeastern estuaries, 42% in West Coast estuaries, 18% in Gulf of Mexico estuaries, and 10% in Southeastern estuaries. Tissue and whole body samples were also analyzed for total PAHs, total PCBs, selected metals, and pesticides. Data are available from the EMAP/NCA website: [www.epa.gov/emap](http://www.epa.gov/emap)

Keywords: tissue contaminants, mercury, monitoring, estuarine.

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## ICES CM 2006/G:12 – Poster

### Automated determination of Hg-species in marine biota by means of GC-CVAFS<sup>1</sup> after TMAH digestion<sup>2</sup> and solvent stripping as serial sample preparation procedure

Reinhard Kruse

Cold Vapour AFS can be run with high sensitivity, is easily to be handled and – last but not least – is one of the definitely low budget techniques. These characteristics make it the detection method of choice in the special field of gas chromatographic speciation analysis of mercury in marine biota.

In order to complete this method's advantages, we made some effort to find a convenient serial digestion procedure and to make the GC sampling mode fit for liquid injection. Complete speciation can be achieved in one unique procedure in which methyl- and ethyl-Hg, inorganic and elementary Hg, as well as other derivatives can be separated and quantified. By varying some experimental details all Hg-species can furthermore be summarized and quantified as total mercury via common GC signals.

Our analytical procedures include the following steps:

#### **Speciation:**

Digestion by TMAH, alkylation by STEB<sup>3</sup> (alt.: STPB<sup>4</sup>), solvent-thermo stripping by N<sub>2</sub> into n-decane, GC on a 5 µ wide-bore capillary column after automatic liquid injection, AFS-detection as Hg<sup>0</sup> via pyrolysis in a 920°C quartz cell.

#### **Total mercury:**

Digestion by TMAH, alkaline reduction by NaBH<sub>4</sub>, internal solvent focussing into n-decane, GC as above.

Limits of detection and quantification can be established in the sub-ng/g range. Thus the mercury burden of nearly every type of marine biota can be speciated. The method used up to now of measuring mercury contents in fish merely as total Hg can thus be replaced or completed, providing more detailed analytical and toxicological information.

However, due to the time consuming (because necessarily moderate) digestion conditions the total procedure of our speciation analysis takes all in all 18 hours time. This demand should be no problem for measuring in scientific activities, e.g. monitoring programmes. But in some cases 18 hours may be too long time for checking fresh fish that is bound for the market.

<sup>1</sup> GC-CVAFS: cold vapour atomic fluorescence spectrometry

<sup>2</sup> TMAH: tetra methyl ammonium hydroxide

<sup>3</sup> STEB: sodium tetra ethyl borate

<sup>4</sup> STPB: sodium tetra n-propyl borate

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## ICES CM 2006/G:13

### Is the use of biological approaches for diarrhetic shellfish poisoning testing still justifiable?

Stefan Effkemann

The occurrence of harmful algal blooms, followed by the accumulation of algal toxins in mussels poses a threat to human consumers. In addition the presence of these compounds in mussels can lead to significant economic consequences for the mussel fishery. According to decision 2002/225/EG chemical analytical techniques (e.g. HPLC, LC-MS) can be used as well as biological methods (e.g. mouse bioassay) for DSP (diarrhetic shellfish poisoning) toxin testing purposes, while they guarantee a comparable consumer protection. Since biological methods failed in many cases and due to animal protection issues, the application of these testing methods has to be critically scrutinized.

In Germany exclusively modern chemical analytical techniques are applied for routine analysis of DSP-toxins. A new LC-MS/MS method for the simultaneous determination of okadaic acid, dinophysistoxins, pectenotoxins, azaspiracid, and yessotoxins was developed. The new method enables an accurate and reliable determination of DSP toxins. Furthermore it is characterized by detection limits in the lower ppb range. In contrast to biological methods the requirements of community decision 2002/225/EG can be fulfilled.

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