North Sea marine matrices under high surveillance: a preliminary study of dioxins and dioxin-like compounds

V. Debacker (1), P. Huart (1), A.-C. Massart (2), G. Eppe (2), T. Jauniaux (3), J.M. Bouquegneau (1), and E. De Pauw (2)

(1) Oceanology, University of Liège, B6c Sart Tilman B-4000 Liège

(2) Laboratory of Mass Spectrometry, Centre for the Analysis of Residues in Traces (CART) University of Liège, B6c, B-4000 Liège

(3) Pathology Department of the Veterinary College, University of Lièg, B43 Sart Tilman, B-4000 Liège

E-mail : Virginie.Debacker@ulg.ac.be

The general objective of a sustainable development of the marine ecosystem and in particular of the North Sea has led the Belgian federal authorities to launch several short and long-term action programmes. Among those, the determination of organic pollutant levels, their distribution and effects on the marine ecosystem are of particular concern. Such a scheme should help the authorities to establish a general ecotoxicological assessment of different marine matrices representing a marine trophic chain.

In addition, the recent Quality Status Report of the greater North Sea (QSR, 2000) clearly identifies the need of reliable techniques and monitoring programmes for a better understanding of the distribution and effects of dioxin and dioxin-like compounds (PCDDs/Fs) in the marine environment. Those lipophilic compounds bioaccumulate through the food chain to top predators and humans. However, very little information on levels of dioxins, furans and dioxin-like PCBs in marine invertebrates, fishes, birds and marine mammals is available. Preliminary measurements performed in our laboratory (SSTC Report, MN/12/85, 2001) and others indicated that levels in seafood often exceed by far the regulatory prescriptions that have been established for farm terrestrial animals (Focant et al., 2001a).

During this project, a three level strategy of analysis, developed at the Laboratory of Mass Spectrometry, is proposed:
at the screening level with the use of two bioassays both responding to PCDDs/FS and coplanar PCBs compounds (a competitive binding enzyme immuno-assay or EIA and the chemically activated luciferase expression or CALUX);
a semi-quantitative level using tandem mass spectrometry (MS-MS) (Focant et al., 2001b);
a reference quantitative method using the high resolution mass spectrometry (HRMS) which allows unambiguous detection and quantification of all isomers (Beltest accredited) (Windal et al., 2000; Pirard et al., 2002).
Furthermore, EROD (7-ethoxyresorufin-O-deethylase) activity, a biomarker of cytochrome P450A1 ("CYP1A1") induction, will be monitored in the biological samples in order to determine whether this effect assessment is correlated to the measured concentrations in "dioxin-like" contaminants (ULB, Marine Laboratory).

These analytical techniques will be applied to different marine matrices representing both ecotoxicological and public health targets, namely sediments, invertebrates (starfishes and mussels), commercial fishes (plaice), seabirds (common guillemots) and marine mammals (harbour porpoises). These samples will be collected along known gradient of pollution:
mussels, starfishes, and sediments in intertidal locations along the Belgian coast and mouth of the Scheldt River;

plaices, starfishes, and sediments from the mouth of the Scheldt River to offshore stations outside the river plume;
beached birds and mammals will be assessed as well, as they are local top-predators in the North Sea and consequently bio-indicators of the health of the global ecosystem.
Finally the project aimed at extending the scope of developed methods to other organic pollutants of high concern such as the known 'flame retardants' or polybromated diphenyls ethers (PBDEs) which have been recently added to the OSPAR list of priority contaminants.

Analyses are currently undertaken for most of the above-mentioned marine matrices. However, preliminary results obtained on seabirds (the common guillemot, *Uria aalge*), collected stranded at the Belgian coast, showed that high levels of dioxin and dioxin-like compounds tend to accumulate in these marine top predator (Huart, 2001). Most of these individuals presented a long and chronic debilitating pathology referred to as 'cachexia' which is characterised by a mild to severe atrophy of the pectoral muscle and depletion of subcutaneous and abdominal fat reserves (Jauniaux et al. 1996, 1998). Previous studies have demonstrated that higher levels of heavy metals are associated to this debilitating cachectic status (Debacker et al. 1997, 2000). As other pollutants such as the dioxin and dioxin-like compounds are clearly suspected to enhance such a pathology, tissues levels of dioxins and dioxin-like compounds were thus related to the general health status of the guillemots. Preliminary results indicated that these contaminants tend to increase with increasing cachexia severity. In addition, levels were clearly higher in individuals collected at the Belgian coast compared to those detected in guillemots collected stranded on the Brittany coasts after the Erika oil spill.

For the top predators such as the common guillemots, dioxin and dioxin-like compounds alike other contaminants such as heavy metals, could adversely affect the individuals with degrading body condition.

REFERENCES

Debacker et al. 1997. Dis. Aquat. Org. 29:159-168.
Debacker et al. 2000. Env. Res. A 84 (3):310-317.
Focant et al. 2001a. Chemosphere, In press.
Focant et al. 2001b. Chemosphere 43 (4-7): 417-424.
Huart, P. 2001. Unpublished graduation thesis, University of Liège.
Jauniaux et al. 1996. Ann. Med. Vet. 140:149-159.
Jauniaux et al. 1998. Vet. Rec. 143:387-390.
Pirard et al. 2002. Ana. Bioana. Chem. 372: 373-381.
Windal et al. 2000. Anal. Chemistry 72 : 3916-3921.