



## Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature  
Conservation

STATE & CONSERVATION  
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<b>Document title</b>	Core indicator 'Polycyclic aromatic hydrocarbons (PAH) and their metabolites' – background on the metabolite GES-boundary derivation
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### Background

HELCOM HOD 50-2016 agreed on the GES boundary for the PAH indicator, pending a general study reservation by Germany and a study reservation by Denmark on proposed GES boundaries that are not environmental quality standards derived from EU directives or nationally agreed environmental quality standards (paragraph 4.48 of the outcome). For the PAH indicator the Danish study reservation concerns the GES boundary for metabolites and the secondary GES boundary for sediment.

HOD 48-2015 agreed on a Lead Country approach for the further development of core indicators (paragraph 3.64 of the outcome). The Lead Country for the PAH indicator is Germany (with lead on metabolites), with the Co-Lead Countries Finland and Sweden (with lead on PAH concentrations in sediment and biota).

When the GES-boundary was presented for adoption at HOD 50-2016, the GES boundary for the PAH metabolite 1-hydroxypyrene (483 ng/g fish bile) was reported as "Davies & Vethaak 2012" (Annex 4 of the outcome).

This document gives a more detailed description of the GES boundary for PAH metabolites and its derivation to be included in the relevant section as part of the update of the core indicator report.

The core indicator report for PAHs has previously been presented to STATE & CONSERVATION 2-2015 (paragraph 4J.12 point 17 of the outcome). At this time the metabolite GES boundary had not been agreed and is therefore not described in detail in the report. The [CORESET II version of the indicator report](#) is made available as reference material on the STATE & CONSERVATION 5-2016 meeting site.

### Action requested

The Meeting is invited to:

- take note of the attached information.

## Core indicator 'Polycyclic aromatic hydrocarbons (PAH) and their metabolites' – background on the metabolite GES-boundary derivation

### Background on the relevance of the parameter

1-Hydroxypyrene is the major metabolite of polycyclic aromatic hydrocarbons (PAH) in fish bile. 1-Hydroxypyrene in bile represents the exposure of the animal to PAH mixtures such as present in crude oil. Quantification of 1-hydroxypyrene in fish mirrors the measurement of PAHs in water or sediment. 1-Hydroxypyrene is a chemical substance measured in concentration units. Monitoring data of this parameter can be used for calculations with R-scripts as any other chemical contaminant.

### Good Environmental Station

The GES boundary for the PAH metabolite 1-hydroxypyrene measured in fish bile is

**483 ng/g (HPLC/GC-MS-method; derived for cod).**

### Background on GES boundary derivation

The GES was calculated on the base of Skadsheim (2004) and Skadsheim et al. (2009) by one of the authors of the respective publication during a meeting of the ICES working group of biological effects of contaminants (WGBEC). ICES WGBEC supports since this time the GES boundary for 1-hydroxypyrene (ICES, 2012). Skadsheim (2004) and Skadsheim et al. (2009) describe exposure experiments with fish and crude oil over a four week period and link the concentration of 1-hydroxypyrene in bile to PAH concentrations in water and toxic as well as behavioural effects to adult and larval cod caused by this PAH exposure. This GES of 1-hydroxypyrene in fish bile corresponds to a PAH concentration of crude oil in water causing unacceptable effects for adults and larvae of cod (ICES, 2012).

### GES application and quality assurance

The methods (mainly HPLC/GC-MS) have been intercalibrated (Kammann et al., 2013) with participation of 10 laboratories from 8 countries and lead to convincing results. So data of this parameter in databases produced by different laboratories can be used for an overarching assessment. Results produced with the methods HPLC or GC-MS are comparable. The high number of participating laboratories shows the broad acceptance and usage of the parameter in Europe.

The GES value itself was used in several publications to discuss whether a concentration of 1-hydroxypyrene found in fish bile reflects a PAH contamination which might be able to cause unacceptable effects in the organism (Kammann et al., 2014, 2016, Karl et al., 2016, Wariaghli et al., 2015). The GES values will also be used for evaluation of German monitoring results (publication in preparation) related to MSFD.

### References for GES establishment

- ICES, 2012. Integrated marine environmental monitoring of chemicals and their effects. In: Davies, I.M., Vethaak, D. (Eds.), International Council for the Exploration of the Sea, Cooperative Research Report No 315, p. 277pp. Copenhagen, Denmark.
- Skadsheim, A. 2004. Cod stocks exposed to crude oils: uptake, metabolism and biomarker effects. Technical Report AM-2004/005, Akvamiljo, Randaberg, Norway.
- Skadsheim, A., Sanni, S., Pinturier, L., Moltu, U-E., Buffagni, M., and Bracco, L. 2009. Assessing and monitoring long-range-transported hydrocarbons as potential stressors to fish stocks. Deep Sea Research Part II, 56: 2037–2043

**References for GES application and method quality assurance**

Kammann U, Akcha F, Budzinski H, Burgeot T, Gubbins MJ, Lang T, Le Menach K, Vethaak AD, Hylland K (2016) PAH metabolites in fish bile: from the Seine Estuary to Iceland, *Marine Environmental Research*, in press, doi:10.1016/j.marenvres.2016.02.014

<http://www.sciencedirect.com/science/article/pii/S0141113616300241>

Kammann U, Askem C, Dabrowska H, Grung M, Kirby MF, Koivisto P, Lucas C, McKenzie M, Meier S, Robinson C, Tairova ZM, Tuvikene A, Vuorinen PJ, Strand J (2013) Interlaboratory proficiency testing for measurement of the PAH metabolite 1-hydroxypyrene in fish bile for marine environmental monitoring, *Journal of AOAC International*. 96(3) 635-641

Kammann U, Brinkmann M, Freese M, Pohlmann J-D, Stoffels S, Hollert H, Hanel R, (2014) PAH metabolites, GST and EROD in European eel (*Anguilla anguilla*) as possible indicators for eel habitat quality in German rivers, *Environ Sci Pollut Res*, 21(4): 2519-2530

Karl H, Kammann U, Aust M-O, Manthey-Karl M, Lüth A (2016) Large scale distribution of dioxins, PCBs, heavy metals, PAH-metabolites and radionuclides in cod (*Gadus morhua*) from various fishing areas in Europe, *Chemosphere* 149:294-303

Wariaghli F, Kammann U, Hanel R, Yahyaoui A (2015) PAH Metabolites in Bile of European Eel (*Anguilla anguilla*) from Morocco, *Bulletin of Environmental Contamination and Toxicology*, 95(6):740-744