

SUB-COMMITTEE ON POLLUTION  
PREVENTION AND RESPONSE  
6th session  
Agenda item 11

PPR 6/11/2  
14 December 2018  
Original: ENGLISH

**REVIEW OF THE 2015 GUIDELINES FOR EXHAUST GAS CLEANING SYSTEMS  
(RESOLUTION MEPC.259(68))**

**Information on the options for standardization  
of the calibration of oil monitoring instruments**

**Submitted by CESA**

**SUMMARY**

*Executive summary:* This document provides information on PAH monitoring complementing the report of the Correspondence Group on Exhaust gas cleaning systems with reference to paragraph 10.1.3.2 of the *2015 Guidelines for exhaust gas cleaning systems* (resolution MEPC.259(68))

*Strategic direction, if applicable:* 1

*Output:* 1.12

*Action to be taken:* Paragraph 29

*Related documents:* PPR 6/11 and PPR 6/11/Add.1

**Introduction**

1 Paragraph 10.2.1 of the *2015 Guidelines for exhaust gas cleaning systems*, resolution MEPC.259(68), requires that the oil content of exhaust gas cleaning systems (EGCS) overboard discharges be controlled by continuous monitoring and recording of the concentration of polycyclic aromatic hydrocarbons (PAH).

2 The monitoring of oil in overboard discharges by PAH measurement and the concentration limits at various washwater flow rates were developed from a number of submissions to IMO, including document MEPC 55/4/5 (annex 1, section 7.2) and by subsequent working and correspondence groups. References include paragraph 8.3 of document BLG 12/6, section 10.1.3 of document BLG 12/6/Add.1, document BLG 12/WP.6/Add.4, annex 6 of document BLG 12/17 and annex 4 of document MEPC 57/21.

3 The rationale for measuring PAH as a surrogate for oil is that continuous monitoring instrumentation capable of directly measuring the very low concentrations of oil in EGCS discharges is not available. The concentrations are below the detection capabilities of traditional marine oil-in-water monitors, 15 and 5 parts per million. Oil, however, contains many species of hydrocarbons, including PAH, which fluoresce when exposed to ultra violet light energy, even at low parts per billion concentrations.

4 To limit the quantity of oil discharged to sea, the concentration of PAH at the EGCS overboard discharge is therefore compared with that at the EGCS seawater inlet.

### **Continuous PAH monitoring and reporting of PAH as phenanthrene equivalence**

5 Instruments for the continuous monitoring of PAH subject PAH molecules in the water to ultra violet light energy transmitted at the band of wavelengths absorbed by phenanthrene. This causes excitation of the molecules, which then fluoresce.

6 The concentration of PAH is determined by measuring the fluorescence at the band of longer wavelengths at which phenanthrene molecules fluoresce.

7 Phenanthrene was chosen because it is one of the most prevalent PAH species in petroleum and hydrocarbon fuel oils.

8 However, unlike exhaust gas emission sensors, in which wavelengths of light are selected to detect individual gas species, instruments for continuous monitoring of PAH cannot detect and quantify individual hydrocarbon species (and so cannot be compared with laboratory analysis, for example the US Environmental Protection Agency's 16 PAH). CESA would like to stress that it is not only phenanthrene that absorbs UV light energy and fluoresces at the selected bands of wavelengths, but also other PAH molecules. This is useful as it provides an overall measure of PAH concentration in the water and therefore oil.

9 In resolution MEPC.259(68), table 10.1.3.3 gives the maximum allowable PAH concentration (as phenanthrene equivalence ( $PAH_{pne}$ )), depending on the washwater flow rate after the inlet concentration has been deducted from the overboard concentration.

### **Instruments currently used for continuous monitoring of PAH in EGCS discharges**

10 The Exhaust Gas Cleaning Systems Association (EGCSA) has collectively engaged with seven suppliers of continuous PAH monitors in workshops aimed at ensuring the integrity and consistency of monitoring PAH in EGCS discharges.

11 Instruments from the suppliers are configured differently in terms of light sources for PAH excitation, geometry and arrangement of light transmission and fluorescence detection, and detector types, although all suppliers currently calibrate instruments using phenanthrene alone.

12 While all instruments transmit light within the band of wavelengths absorbed by phenanthrene, different central wavelengths, bandwidths and tolerances of light source are used.

13 Similarly, while all instruments detect fluorescence within the band of wavelengths at which phenanthrene fluoresces, different central wavelengths, bandwidths and tolerances of detector are used.

14 From a CESA perspective, the practical consequence is that while instruments from different manufacturers report a consistent PAH<sub>phe</sub> concentration during calibration when simply measuring phenanthrene in water, this is not so when monitoring real-world EGCS discharges, which contain a mixture of PAH; albeit in low concentrations.

### **Options for the consistent monitoring of oil in EGCS discharges**

15 CESA would like to report on four possible options for consistent measurement of the concentration of oil in EGCS discharges which have been explored by EGCSA.

#### ***Option 1: fixed wavelengths for continuous monitoring instruments and continuing with phenanthrene equivalence (PAH<sub>phe</sub>):***

16 A submission to the PPR Correspondence Group currently considering amendments to the 2015 EGCS Guidelines proposes a definition for phenanthrene equivalence (PAH<sub>phe</sub>). The definition has fixed wavelengths and bandwidths for PAH excitation and fluorescence detection that all monitors would have to use and a fixed multiplier that converts the concentration of PAH detected to a larger total number.

17 The first part of the proposed definition for PAH<sub>phe</sub> is: "The fluorescence signal produced by a PAH monitor with 254±10 nm excitation wavelength and 360±50 nm detection wavelength calibrated against a known phenanthrene concentration within the expected measurement range when exposed to EGCS discharge water containing a range of different PAH species.": Following discussions between EGCSA and PAH monitor suppliers, CESA does not support this part for the following technical and practical reasons:

- .1 it is assumed that the specification refers to a central wavelength (CWL) of 254 nm with a full width half maximum (FWHM) bandwidth of 20nm for the excitation and, similarly, a CWL and 360 nm and FWHM of 100 nm for the emission, however this is not defined;
- .2 there is no tolerance specified for either the position of the excitation and emission wavelengths nor their bandwidths;
- .3 the proposed wavelength for PAH excitation is positioned on the descending slope of the phenanthrene absorbance peak, which will lead to significant variation of reported concentrations when tolerances are considered;
- .4 the proposed bandwidth for monitoring the fluorescence emission is very broad and will lead to the detection of excess non-specific background fluorescence;
- .5 the definition takes no account of instrument geometry e.g. relevant position of light source to emission detector; and
- .6 in practical terms the proposal will limit the number of PAH monitor suppliers to the EGCS market to a small number of manufacturers and monitoring system assemblers. There is also potential for the range of light source and emission detector components to be limited. Non-compliant suppliers will need to change their instrument set-up, which will mean testing of those changes and instruments with type approvals will likely have to go through the process again. All of which stifles innovation and competition.

18 The second part of the proposed definition for PAH<sub>phe</sub> is: "As the PAH sensor measures the full range of PAH with different signal intensities, an internal factor of 6.2 should automatically convert the measured signal to calculate the total PAH concentration (e.g. 1 ppb phenanthrene equals 6.2 ppb  $\sum$ PAH = PAH<sub>phe</sub> (phenanthrene equivalence)."  
Sample analysis programmes (MEPC 73/INF.5) and discussions between EGCSA and PAH monitor suppliers do not support this part:

- .1 analyses and academic literature show that the ratio of phenanthrene to the other PAH in EGCS discharges and fuel oils is not firmly fixed. A multiplication factor, as proposed, is therefore not appropriate; and
- .2 the EGCS Guidelines have limits for PAH to be measured at the wavelengths that phenanthrene fluoresces i.e. PAH<sub>phe</sub> so that the quantity of oil in EGCS discharges is controlled. The multiplier deviates from this requirement as there is no reference to oil. The multiplier would also significantly increase PAH concentrations reported by continuous monitoring instruments, but no account has been taken of this in terms of appropriate discharge limits.

***Option 2: determination of PAH<sub>phe</sub> using a common industry agreed instrument configuration***

19 An example of determination of a parameter using a common, industry agreed instrument configuration is turbidity. There is an ISO standard cited in the EGCS Guidelines.

20 CESA would like to report that, following extensive group discussions between EGCSA and PAH monitor suppliers, this option is not recommended at the current time:

- .1 as stated above, instruments from the suppliers are configured differently and it has not been possible to reach agreement on a common configuration;
- .2 the time to reach a common standard through an organization such as ISO is likely to be lengthy, which does not suit the acceleration in EGCS deployment on ships in response to the global 0.50% sulphur limit; and
- .3 the need for PAH monitor manufacturers to change, test and regain approvals is similar to that in option 1.

***Option 3: determination of the concentration of oil using a certified standard mixture of PAH for calibration***

21 It has been proposed during group meetings between EGCSA and PAH monitor suppliers that a certified standard mix of PAH similar to that found in EGCS discharges be used for calibration rather than phenanthrene. The approach has a number of benefits:

- .1 Sample analysis programmes (MEPC 73/INF.5) indicate the profile of PAH species in EGCS discharges is petrogenic i.e. typical of petroleum and un-combusted fuel oil. Instruments calibrated using a PAH mix, typical of a fuel oil, will therefore enable the quantity of oil entering the sea to be closely monitored and controlled – a requirement of the EGCS Guidelines.

- .2 The wavelengths of light which are absorbed by phenanthrene have the profile of a sharp peak, which ultimately results in the inconsistent reporting of overall PAH concentrations in real-world EGCS discharges by different configurations of the instrument. The smooth profile of a PAH mixture will significantly reduce this inconsistency without the need for changes in existing instrument designs.
- .3 Although measured by PAH, instruments could readily report a concentration of oil; a parameter that is well-recognized and already used for the regulation of pollution from ships. It will also eliminate inconsistencies caused by different interpretations of phenanthrene equivalence.

22 Reporting the concentration of oil will require the limits given under resolution MEPC.259(68), table 10.1.3.3, to be re-defined.

23 CESA would like to underline that additional time will be required to finalize the choice of the certified standard based on a hydrocarbon fuel oil and the calibration framework, including how up to four concentrations relevant to the instrument range can be provided. Further, this methodology also needs to be tested in operation, however it is proposed that details of this option are submitted in time for consideration for incorporation into the EGCS Guidelines by MEPC 74.

***Option 4: regular sampling for laboratory analysis in place of continuous PAH monitoring***

24 Regular reporting of laboratory analysis of water samples could be used to monitor oil in EGCS discharges, rather than real-time measurement by PAH monitoring instruments. This would remove the need for standardization as described above and comparisons between laboratory analyses and measurements by continuous monitoring instruments would no longer arise.

25 Samples could be collected manually by ship's crew or by automated sampling, either of a full sample in individual sampling events or a composite sample over a defined sampling period. Automated sampling could be of water direct to a suitable sample container or by using for example, a solid phase extraction (SPE) cartridge suitable for collecting PAH.

26 Practical considerations for sampling include: availability and suitability of manual sampling points (EGCSA has developed a specification, which is freely available on its website), manual sampling technique, (again, EGCSA has developed a specification, which is freely available on its website), availability and shelf-life of suitably prepared sample containers, location and availability of accredited laboratory services to enable analysis within the required test method time frame, agreement on analytes to determine oil content and test methods.

27 In addition, considerations for automated sampling include: availability of systems suitable for shipboard use, availability and shelf-life of suitable SPE or similar cartridges and the effect of aging of analytes during composite sampling over a defined period.

28 In CESA's opinion, the feasibility and practicality of the sampling options will need to be confirmed and the schedule for regularly landing samples defined. In the case of automated sampling by SPE cartridge or similar, it is estimated that initial tests followed by shipboard trials could take up to 12 months.

**Action requested of the Sub-Committee**

29 The Sub-Committee is invited to note the options discussed in paragraphs 15 to 28 and take action as appropriate.

---