

ImpEx Project – Environmental Impacts of Exhaust Gas Cleaning Systems for Reduction of SO_x on Ships

Sampling and analysis protocol

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Abbreviations

BDN: Bunker Delivery Note

BfG: German Federal Institute of Hydrology (*Bundesanstalt für Gewässerkunde*)

BSH: Federal Maritime and Hydrographic Agency (*Bundesamt für Seeschifffahrt und Hydrographie*)

CEMS: Continuous Emission Monitoring System

CL: Closed loop

EGCS: Exhaust Gas Cleaning System (scrubber system)

HU: Hamburg Institute for Hygiene and Environment (*Institut für Hygiene und Umwelt Hamburg*)

OL: Open loop

PAH: Polycyclic aromatic hydrocarbon

PPE: Personal protective equipment

PTFE: Polytetrafluoroethylene

UBA: German Environment Agency (*Umweltbundesamt*)

WWU: University of Münster (*Westfälische Wilhelms-Universität*)

1. Introduction

On behalf of the German Environment Agency (UBA), the Federal Maritime and Hydrographic Agency (BSH) and a consortium of German public institutions, are conducting the research project “*ImpEx – Environmental Impacts of Exhaust Gas Cleaning Systems for the Reduction of SOx on Ships*” (2020 – 2023, Project No. (FKZ) 3719 57 101 0). The project is focused on the analysis of exhaust gas cleaning systems (EGCS) discharge water and the revision of the quality criteria set in the EGCS Guidelines of the International Maritime Organization. For this purpose a sampling and analysis campaign on board ships is carried out, which includes chemical composition and ecotoxicological effects of EGCS discharge water. For further information about the project, please contact the BSH.

The present protocol provides the procedures for sampling and analysis of water from EGCS as well as fuel and lubricating oil to be carried out within the ImpEx project. The purpose of the protocol is to preserve quality assurance and quality control, ensure reproducibility within the sampling and analysis campaign and prevent possible uncertainties. The document will be provided in advance to the ship operators as well as ship agencies collaborating in the ImpEx project and will be shared publicly by reporting of the results to ensure transparency and comparability with different data sets. Any deviation from the procedures described below will be recorded accordingly. It should be noted that the present protocol takes into consideration the guidance on discharge water data collection provided in the “2021 EGCS Guidelines” and the general principles of the standard ISO 5667-1, as appropriate.

2. Sampling procedures

2.1 Preparation for water sampling

2.1.1. Sampling points location

Data template in Annex 1 should be filled out by the ship operators before going onboard and sent to project's contact person. In order to evaluate the potential environmental impact, discharge water from EGCS will be sampled. Within the sampling and analysis campaign, both open loop (OL) and closed loop (CL) systems will be sampled. If the ship is equipped with hybrid EGCS, the system will be sampled in both operation modes. Additional water streams part of the scrubbing process will be sampled to determine the enrichment and origin of pollutants as well as the efficiency of water treatment units (if provided). Thus, at least following water streams will be sampled:

In OL systems (Figure 1)

- Inlet water (for background)
- Water after scrubbing, after treatment system (if applicable) but before dilution
- Discharge water (after treatment system and dilution)

In CL systems (Figure 2)

- Seawater (for background), e.g. from inlet to EGCS coolers
- Water after scrubbing and before treatment system
- Discharge water (after treatment system but before dilution)

The minimum sampling points in OL systems are as recommended in the “2021 EGCS Guidelines”. In cases where no dilution exists, only two sampling points would remain as minimum. The minimum sampling points in CL systems differ from the sampling points in OL systems. Unlike OL systems, where treatment systems are relatively rare and dilution for pH control is more common, CL systems usually include a treatment system and do not require dilution. In order to assess the removal efficiency of treatment systems in CL systems, sampling upstream and downstream the treatment system are considered. For hybrid systems in cases where water after treatment is sent to a holding tank (“zero discharge mode”) for later discharge, sampling will be carried out during CL operation before and after treatment, sampling of seawater (for background) might be omitted if inlet water sampled from OL operation is considered to have a similar composition (e.g. sampling of OL operation timely close to discharge from holding tank), and discharge from holding tank might be sampled. If necessary, further sampling points will be considered within the scope of the project. For instance, if a treatment system is present in an OL system, the stream after scrubbing and prior to treatment could be sampled to assess the efficiency of the treatment system. Figure 1 and Figure 2 depict the minimum water streams and potential further points to be sampled.

For the determination of the sampling points, technical information about the EGCS installed on board (e.g. piping and instrumentation diagrams and operation and maintenance manual) as well as photographs and specifications of the sampling pipe and valve should be delivered from the ship operator in advance. ImpEx project workers should carried out an inspection of the system and pipelines prior to conducting the sampling. The sampling point should have a location that is representative of the main water stream and accessible to personnel. Additionally, the sampling point should fulfill the requirements in the section below.

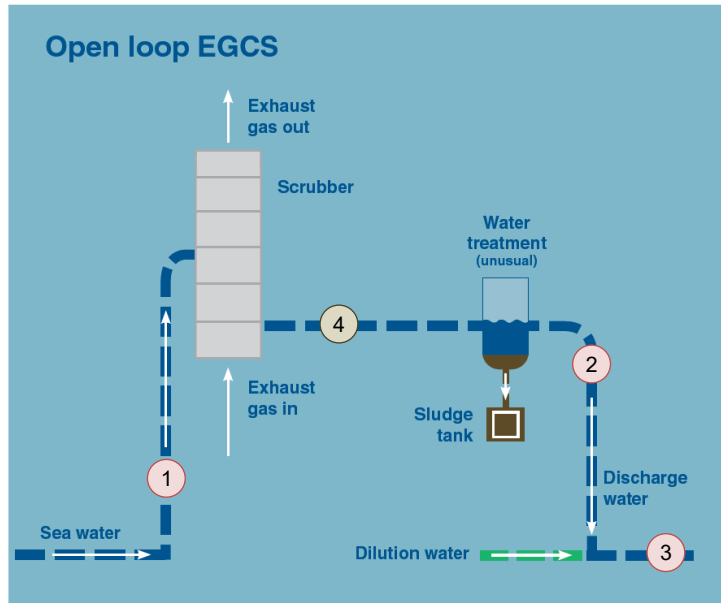


Figure 1. Process diagram of open loop systems and identification of sampling points (1: Inlet water, 2: Water before dilution, 3: Discharge water, 4: Potential additional point)

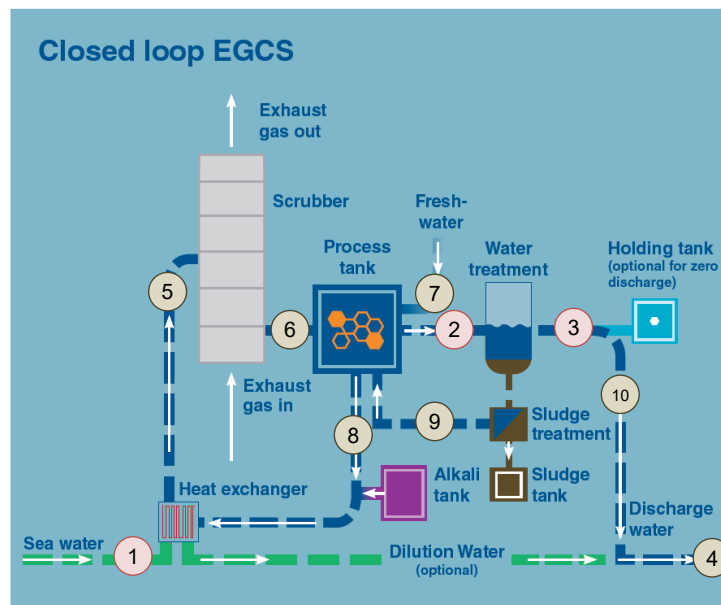


Figure 2. Process diagram of closed loop systems and identification of sampling points (1: Inlet water, 2: Water after EGC unit, 3: Discharge water, 4-10: Potential additional points)

2.1.2. Specifications of the sampling point

By the selection of sampling points, following requirements for the sampling valve and tubing will be considered:

- Cleanliness of the sampling point to avoid contamination.
- The material of the valve and the pipe should be stainless steel (quality grade suitable for warm and acidic seawater medium) or plastic (preferably inert material, such as PTFE), but not copper, brass or lead, in order to avoid contamination.
- It should be labeled for clear identification.
- It should be easily accessible with sufficient space (at least 35 cm) to place a sample bottle underneath.

The selected sampling points should be clearly identified and described as required in Annex 3. In the case of missing or inadequate sampling points directly located nearby the main water pipelines, it could be considered to take water samples from the measuring cabinet (discharge water monitoring equipment). A measuring cabinet is known that, besides having inlet and outlet water connections, includes a third connection to enable sampling.

2.1.3. Sampling equipment

The sampling equipment and prepared sample containers should be made ready prior to sampling. For the chemical and ecotoxicological analyses carried out in the laboratories, sampling equipment will be prepared and delivered by the laboratories. Sample bottles should be labeled before sampling taking into consideration the nomenclature in Annex 3. It is crucial to know the itinerary of the ship in advance, so that preparation arrangements can be completed before going on board.

2.1.4. Preparation for storage and holding of samples

To ensure proper storage and holding, ship's personnel needs to appoint an appropriate space on board for samples and ice packs, preferably in an enclosed container in a cool space without direct sunlight.

2.1.5. Preparation for transport

In cases where samples need to be transported with ice packs, these should be deep-frozen (at -20 °C or as cold as possible) at least 48 hours prior to sampling. Arrangements for shipping of the samples should be done in advance with the port agent of the destination port.

2.1.6. Health and safety requirements

Persons conducting the sampling should be aware about the potential hazards of the water. Personal protective equipment (PPE) should be used in accordance with requirements of the ship, of the shipping company and of BSH. It is recommended the wear protective eyeglasses/goggles, ear protection, protective gloves, protective clothing and safety shoes.

2.1.7. Personnel qualifications and responsibilities

The sampling should be supervised by trained ImpEx project workers in order to ensure a consistent quality. It is important that the person taking the samples is instructed. As mentioned above, based on the technical specifications and the prior inspection of the system, ship's personnel and project workers will determine the locations to be sampled. Ship's personnel should inform project workers where and how to safely dispose the collected flushing water.

2.1.8. Documentation and information to be provided prior to sampling

The ship's personnel or company should provide specific information and related documentation about the ship, combustion units, EGCS and monitoring systems. The specific information to be provided corresponds to Annex 1. Supporting documents are listed below:

- International Air Pollution Prevention Certificate (IAPP Certificate)
- SOx Emission Compliance Plan (SECP)
- Exhaust Gas Cleaning System - Technical Manual (ETM)
- EGCS Record Book
- Onboard Monitoring Manual (OMM), including
 - Exhaust Gas Continuous Emission Monitoring System (CEMS) and
 - Water Monitoring System
- Material Safety Data Sheet (MSDS) of chemicals added (e.g. alkali, flocculant)

2.2 Collection of water samples

2.2.1 Sampling schedule

A sampling schedule will be prepared in advance in agreement with the crew, considering when the samples latest need to be analyzed at laboratory. The sampling should preferably be undertaken with the EGCS operating above 50% of its maximum capacity and/or with load above 50% of aggregated maximum continuous rating of all fuel oil combustion units connected to the EGCS. For this reason, sampling should be carried out during transit.

The sampling should be carried out under stable operating conditions (stable engine load, same fuel oil and stable water flow). The ship route should allow having at least one hour of stable conditions for every EGCS operation mode. Ship's personnel and project workers should agree the sampling schedule based on that requirement. In addition, the sampling should be carried out after the system has been running in stable conditions for a sufficient time. For this purpose, a simple estimation of sufficient time can be calculated as described:

- For OL operation. The water inside the EGCS needs to be exchanged twice. The required time for exchange can be calculated from the total water volume inside the system and the pump rate. Note: This information should be provided by the ship's personnel. The total water volume should be known for stability calculations. If the information is not available, it is assumed that sampling can be started 5 minutes after operation in stable conditions.
- For CL operation. Due to the recirculation, the sufficient time cannot be calculated easily. The re-circulated water inside a closed loop system and bleed-off will be representing a mixture from the last operation hours.

2.2.2 Filling up of sampled water

In order to ensure representativeness and prevent contamination during sampling, following practices will be followed:

- Sample bottles for chemical and ecotoxicological analyses will be prepared by the laboratories.
- Sample bottles will be labeled with the sample point identification number as described in Annex 3. Labeling should be completed before the sampling is conducted, as the bottle might get wet during the filling. Date and time of sampling as well as the person taking the samples should be written immediately prior to the sampling.
- Sampling of the different sampling points should be timely executed following the water process flow. In OL systems, the sequence should be "inlet", "after scrubbing" and "discharge" sampling point. In CL systems, the sequence should be "after scrubbing", "discharge" and "seawater" sampling point.
- The water flow and the engine load(s) should be steady before and during the sampling.
- Suitable PPE should be used during sampling and manipulation of the samples all the time.
- Sampling valve should be flushed with at least 10 liters before taking the sample and the water being flushed should have reached a stable level of clarity and flowrate. The configuration of the sampling point should be considered, i.e. estimated water volume in sampling tubing should be fully flushed. After that, the

valve should not be closed between flushing and taking the samples. If filling more than one bottle, the sampling valve will not be closed in between.

- It is recommended to wash three times all sample bottles with sampling water (except for the sample bottles prepared with chemicals for sample preservation). This step should be definitely carried out with the sample bottles for determination of alkalinity.
- All sample bottles should be filled up to the brim and closed firmly to avoid air in the bottles.
- Further specific instructions provided by the laboratories should be considered.

2.2.3 Field sampling report and monitoring data

The ship's personnel should provide data recorded from the CEMS in the exhaust gas and from water monitoring systems as well as other relevant operational parameters for the evaluation of the analysis results. The data could be submitted as .xls or .csv file and should cover at least three hours before sampling and the whole sampling. During the sampling campaign, the EGCS should be operated under stable conditions. Some parameters might not be available due to operational reasons, e.g. inlet water during closed loop operation. Report form in Annex 2 should be filled out after completion of sampling. It includes data of the ship, combustion unit(s) and EGCS during sampling. Parameters recorded automatically in the data logger and provided as file are not required to be filled out in report form in Annex 2.

2.3 Amount, storage, preservation and transportation of water samples

2.3.1 Sample amount

Table 1 indicates the required volumes to be sampled for every parameter and the standard that specifies the requirements for the sampling bottle. For the parameters to be measured on board and chemical analyses to be carried out in the laboratories single sampling is required. Double sampling is required only for the determination of mercury and for the ecotoxicological assays. Sample bottles required for the chemical analyses and the ecotoxicological assays should be provided by the laboratories.

2.3.2 Storage and preservation

Table 1 lists the physical properties of the sample bottles to be used according to the analysis to be performed. It takes into account ISO 5667-3 and the appropriate standard method. In addition, preservation and storage conditions are specified. As the water samples will have an elevated temperature, the filled sample bottles should be cooled down to room temperature before packed together with the cool packs inside the transportation container.

2.3.3 Transportation

Sampling equipment to be used during transportation should meet provisions under Table 1. The maximum allowable time between sample drawing and the actual analysis is indicated in Table 1 as well. To ensure that the given period is not exceeded, also taking into account transit time, arrangements to be made for transportation and the sample time schedule, as described in section 2.2, have to be considered as well. A close communication with the laboratories will help ensuring certainty further.

Transportation container. For transportation, an insulated and leak proof container should be used. The transportation container should be provided by the laboratories. It should be able to receive a sufficient quantity of ice packs. The transportation container should be packed tight and in a way that prevents movement of sample bottles.

Storage of filled transportation container on board. The packed transportation container with the unfrozen samples should be stored leakage-proof in a cold place, above 0°C (e.g. the cold garbage room or an empty provision room). If the storage on board extends 12 hours, the cool packs should be exchanged before shipping.

Shipping of samples. Shipping of the samples to the laboratories should take place as soon as possible to avoid overrun of maximum storage times indicated in Table 1. Labeling of the transportation container should be in accordance with local requirements for shipping and handling of water samples. Immediately before handing over the samples to the port agent, the ice packs should be replaced in the transportation container. Temperature inside the transportation container should be monitored (e.g. by using loggers) until samples are stored in appropriate temperature controlled spaces in the laboratory. Usually it is not necessary to include a customs declaration as these are water samples of zero commercial value, but customs requirements should be clarified beforehand.

Chain of custody. A formal chain of custody process is required, with records.

2.4 Fuel and lubricating oil

Fuel and lubricating oil used in the engine system, which is connected to the EGCS being sampled, should be sampled for potential chemical analysis including sulphur content, metals and polycyclic aromatic hydrocarbons (PAHs). The results of the analysis should allow to better trace/identify the source of pollutants in the EGCS discharge water. As for water samples, Table 1 indicates the required volumes to be sampled and further requirements for potential analysis of fuel and lubricating oil. The selection of the sampling point for oil fuel should be following the conditions of the Commission Implementing Decision (EU) 2015/253, as appropriate. For instance, the sampling point should be as close to the fuel inlet of the fuel-oil combustion machinery item as feasible and safely possible. The information in Annex 2 (Table A-10) and the documentation listed below should be provided by the ship's personnel:

- Copy of bunker delivery note (BDN)
- Copy of fuel analysis report (if available)
- Safety data sheet (lubricating oil)

Table 1. Requirements for sampling amounts, storage and preservation

No.	Parameter	Bottle material	Volume	Method specifying sampling bottle requirements	Preservative	Storage temperature	Maximum time until analysis
Measurements on board on water samples							
1	pH	PP, beaker	1 L	-	-	-	-
2	Temperature						
3	Conductivity						
4	Turbidity						
5	pH	HDPE	5 L	-	-	-	-
6	Turbidity						
7	PAH _{phe}						
8	Nitrogen compounds						
Chemical analysis on water samples							
9	pH	PE, wide-neck	200 mL	-	-	-	-
10	Alkalinity (acid capacity, K _s)	Schott-glass	500 mL ⁱ	DIN 38409-7:2005-12	-	Cooled at 4°C	48 hours
11	Suspended solids	Schott-glass	500 mL	DIN EN 872:2005-04	-	Cooled at 4°C	48 hours
12	TOC	PE, wide-neck	50 mL	DIN EN 1484: 1997-08	0.5 mL HCl 2M	Cooled at 4°C	1 week
13	TN _b			DIN EN 12260: 2003-12			
14	DOC	PE, wide-neck	100 mL	DIN EN 1484: 1997-08	-	Cooled at 4°C	1 week
15	Nitrate	PE, wide-neck	50 mL	DIN EN ISO 13395:1996-12 (CFA)	-	Cooled at 4°C	24 hours
16	Nitrite						
17	Sulphur ⁱⁱ	LDPE, wide-neck	125 mL	DIN EN ISO 11885:2009-09	3.1 mL HNO ₃ 3.6M supra pure	Room temperature	2 weeks
18	Metals [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn]			DIN EN ISO 17294-2:2017-01			

No.	Parameter	Bottle material	Volume	Method specifying sampling bottle requirements	Preservative	Storage temperature	Maximum time until analysis
19	Hg ⁱⁱ	Borosilicate glass	2 x 100 mL	DIN EN ISO 12846:2012-08	-1 mL HCl (supra pure), 2 mL KBr-KBrO ₃ -solution (Titrisol)	Room temperature	2 weeks
20	Metals (dissolved) [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn]	LDPE, wide-neck	500 mL	DIN EN ISO 17294-2:2017-01	-	Cooled at 4°C	48 hours
21	Hg (dissolved) ⁱⁱ	Borosilicate glass	2 x 100 mL	DIN EN ISO 12846:2012-08	-	Cooled at 4°C	48 hours
22	16 EPA PAHs	Amber glass with joint stopper, narrow-neck	1 L	DIN 38407-F39: 2011-09	-	Cooled at 4°C	24 hours
23	Indicator PCB ^{ii, iv}						
24	GC-MS Screening ⁱⁱ						
25	16 EPA PAHs (dissolved)	Amber glass with joint stopper, narrow-neck	1 L	DIN 38407-F39: 2011-09	-	Cooled at 4°C	24 hours
26	Indicator PCB (dissolved) ^{ii, iv}						
27	GC-MS Screening (dissolved) ⁱⁱ						
28	HOI – Hydrocarbon oil index	Amber glass with joint stopper, narrow-neck	1 L	DIN EN ISO 9377-2: 2001-07	-	Cooled at 4°C (if possible)	4 days
29	HOI – Hydrocarbon oil index (dissolved)	Amber glass with joint stopper, narrow-neck	1 L	DIN EN ISO 9377-2: 2001-07	-	Cooled at 4°C (if possible)	4 days

No.	Parameter	Bottle material	Volume	Method specifying sampling bottle requirements	Preservative	Storage temperature	Maximum time until analysis
30	VOC (HVHH/BTEX) ⁱⁱ	Glass with joint stopper, narrow-neck	250 mL ⁱⁱⁱ	DIN 38407-43: 2014-10	-	Cooled at 4°C (if possible)	2 days
31	Dioxins (PCDDs/PCDFs) ⁱⁱ	Green glass	1 L	ISO 18073:2004-04	-	Cooled at 4°C (if possible)	2 days
32	Dioxins (PCDDs/PCDFs) (dissolved) ⁱⁱ	Green glass	1 L	ISO 18073:2004-04	-	Cooled at 4°C (if possible)	2 days
33	Extended list of PAHs (dissolved) ⁱⁱ	Amber glass with screw caps (Teflon seals)	2.5 L	-	-	Frozen	Months
34	Extended list of PAHs (particulate) ⁱⁱ						
Ecotoxicological assays on water samples							
35	Luminescent bacteria (WET)	Brown/amber Schott screw-cap bottles OR brown HDPE bottles (wide neck)	4 x 1 L	-	non, if possible (chemical stability provided)	Cooled at 0°C to 4°C (<8°C max); Storage at -20°C preferred if shipment within 24h is not possible ^{vii}	12h at room temperature; 24h > 5°C and < 8 °C; 48h at 0°C to 4°C; two months at -20 °C (in compliance with ISO 5667-16) ^{vii}
36	Marina algae (WET)						
37	Zooplankton crustacean - copepod test (WET)						
38	Recombinant yeast assay (hAHR-binding): (Dioxin-like effect)						
39	Ames test (Mutagenicity)						
40	Fish egg test						
Fuel and lubricating oil							

No.	Parameter	Bottle material	Volume	Method specifying sampling bottle requirements	Preservative	Storage temperature	Maximum time until analysis
41	Sulphur content in (only in fuel oil)	Glass (wide neck)	250 mL	-	-	Preferably cooled (<4°C)	Months
42	Metals [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn] ⁱⁱ	Glass (wide neck) ^v HDPE (wide neck) ^{vi}	250 mL ^v 1 L ^{vi}	-	-	Ambient temperature	Months
43	Hg ⁱⁱ						
44	16 EPA PAHs ⁱⁱ						

Abbreviations: 16 EPA PAHs, Priority PAH listed by the US Environmental Protection Agency; Ah, Aryl hydrocarbon; As, Arsenic; BTEX, Benzene, toluene, ethylbenzene and xylene; Cd, Cadmium; Cr, Chromium; Cu, Copper; DOC, Dissolved organic carbon; Fe, Iron; GC-MS, Gas chromatography – Mass spectrometry; Hg, Mercury; HVHH, Highly volatile halogen hydrocarbons; Mn, Manganese; Ni, Nickel; PCB, Polychlorinated biphenyl; PCDDs/PCDFs, Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; Pb, Lead; PAH_{phe}, Polycyclic aromatic hydrocarbons – phenanthrene equivalents; Sb, Antimony; Se, Selenium; TNb, Total nitrogen bound; TOC, Total organic carbon; V, Vanadium; VOC, Volatile organic carbons; WET, Whole effluent toxicity; Zn, Zinc.

- i. According to the norm, the sample bottle should be washed with sampling water prior to fill up the bottle.
- ii. Analyses will not be carried out in all sampled ships and sampling points.
- iii. Filled without air bubbles.
- iv. Indicator PCB: CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180.
- v. For fuel oil samples.
- vi. For lubricating oil samples.
- vii. Refer to Annex 8 for the detailed protocol on sample storage, preparation and processing for bioassays.

3. Analyses

3.1 Measurements on board on water samples

The parameters listed in Table 2 will be analyzed on board. Temperature, pH and conductivity will be determined in all samples immediately after sampling using a calibrated portable electronic measuring device (HI98195, Hanna Instruments, Romania). Likewise, turbidity will be determined with a portable turbidimeter (2100IQis, Hach Lange, China).

A calibrated measuring cabinet EGC Water Analyzer (Model 11A10001X, TriOS Mess- und Datentechnik GmbH, Germany), equipped with the sensors listed in Table 2 (No. 5-7), will be taken on board for determination of turbidity, pH and PAH_{phe} in inlet and outlet samples. The measuring cabinet model is actually covering a great share of the market of water monitoring systems on board ships for the mandatory continuous monitoring EGCS discharge water quality. The results from the measurements of turbidity, pH and PAH_{phe} will be compared to the values reported from the on-board online monitoring data from the ship. Samples from further sampling points might be analyzed to observe the changes in the parameters across the EGCS. Additionally, a separated calibrated spectral sensor (OPUS-UV, TriOS Mess- und Datentechnik GmbH, Germany) will be used for measurement of nitrogen compounds.

Both measuring cabinet EGC Water Analyzer and sensor OPUS-UV will be integrated into a measuring system loop, arrayed as depicted in Figure 3. Samples will be analyzed following the sequence from the cleanest to the dirtiest sample (i.e. “inlet” prior to “outlet” samples) in order to prevent cross contamination. Every sample will be circulated in the system for at least five minutes after the measured values are stable. The system will be flushed with clean water prior to every measurement.

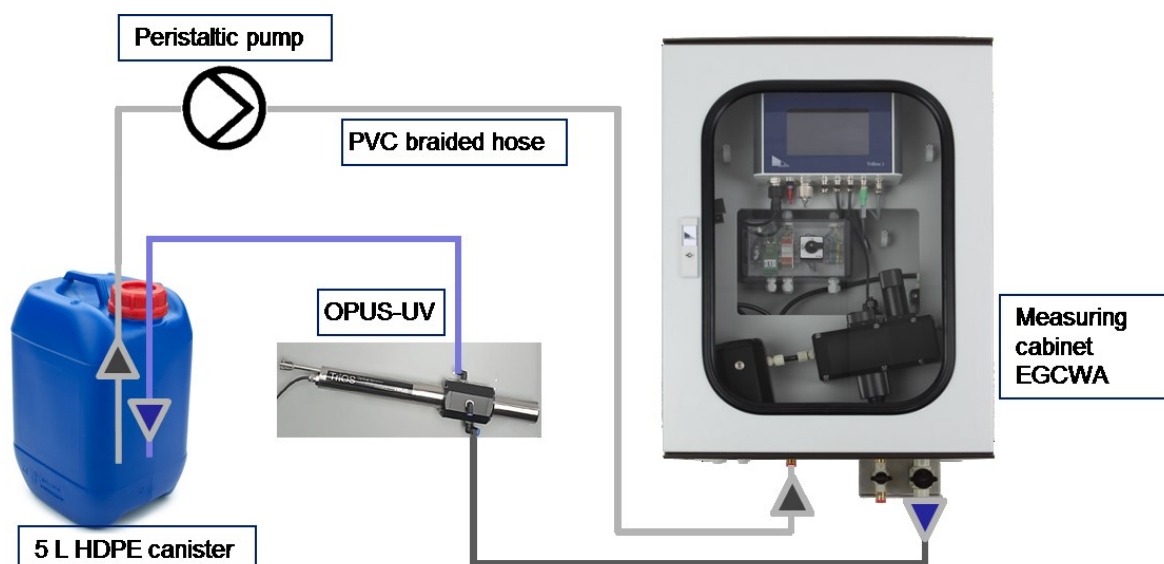


Figure 3. Measuring system taken on board for pH, turbidity, PAH_{phe} and nitrogen compounds

Alternatively, it will be discussed with the ship crew if the measuring cabinet EGC Water Analyzer and the sensor OPUS-UV are possible to be hydraulic connected to the EGCS water streams to be sampled. In that case, measurements could be carried out continuously for longer time periods. Technical specifications, safety and space availability should be evaluated. A connection downstream the existing water monitoring units on board may be a possibility.

Table 2. Methods for sample preparation and analysis for parameters to be measured on board

No.	Parameter	Analysis method	Preparation and conditioning
1	pH	Sensor HI7698194-1 (Hanna, Romania)	-
2	Temperature		-
3	Conductivity	Sensor HI7698194-3 (Hanna, Romania)	-
4	Turbidity	ISO 7027 Turbidimeter 2100Qis (Hach, China)	
5	pH (EGCWA)	DIN EN 60746-2:2003-09 TpH-D sensor (TriOS, Germany)	-
6	Turbidity (EGCWA)	DIN EN ISO 7027-1:2016-11 TTurb sensor (TriOS, Germany)	-
7	PAH _{phe} (EGCWA)	MEPC.184(59) enviroFlu sensor (TriOS, Germany)	-
8	Nitrogen compounds	OPUS-UV sensor (TriOS, Germany)	-

Abbreviations: EGCWA, Measuring cabinet EGC Water Analyzer; PAH_{phe}, Polycyclic aromatic hydrocarbons – phenanthrene equivalents.

3.2 Chemical analysis on water samples

The samples will be shipped for chemical analysis to the laboratories of the Hamburg Hygiene and Environment Institute (HU) and of the Institute of Geology and Palaeontology of the University of Münster (WWU). Most of the parameters will be determined by HU except for dioxins (PCDDs/PCDFs), which will be assigned to the partner laboratory Umwelt Control Labor GmbH. The determination of the extended list of PAHs will be undertaken by WWU. Table 3 indicates the methods for analysis as well as the preparation and conditioning procedures for determination of the chemical composition on water samples.

Table 3. Methods for sample preparation and analysis for chemical composition of water samples

No.	Parameter	Analysis method	Preparation and conditioning
9	pH	DIN EN ISO 10523:2012-04	-
10	Alkalinity	DIN 38409-7:2005-12	Cooled at 4°C
11	Suspended solids	DIN EN 872:2005-04	Cooled at 4°C
12	TOC	DIN EN 1484: 1997-08	0.5 mL HCl 2M/50mL
13	TN _b	DIN EN 12260: 2003-12	
14	DOC	DIN EN 1484: 1997-08	Filtration on 0.45 µm + 0.5 mL HCl 2M
15	Nitrate	DIN EN ISO 13395:1996-12 (CFA)	Filtration on 0.45 µm
16	Nitrite		
17	Sulphur	DIN EN ISO 11885:2009-09 (ICP-OES)	LDPE bottles prefilled with 3.1 mL HNO ₃ 3.6M supra pure
18	Metals [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn]	DIN EN ISO 17294-2:2017-1 (ICP-MS/MS)	LDPE bottles prefilled with 3.1 mL HNO ₃ 3.6M supra pure

No.	Parameter	Analysis method	Preparation and conditioning
19	Hg	DIN EN ISO 12846:2012-08 (CV-AAS) If required: DIN EN ISO 17852:2008-04 (CV-AFS)	1 mL conc. HCl (suprapur) + 2 mL potassium bromide bromate digestion reagent (KBr-KBrO ₃ -solution)
20	Metals (dissolved) [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn]	ISO 17294-2:2017-1 (ICP-MS/MS)	Filtration on 0.45 µm + decanting into 125 mL LDPE + addition of 3.1 mL 3.6M HNO ₃ suprapur
21	Hg (dissolved)	ISO 12846:2012-08 (CV-AAS) If required: ISO 17852:2008-04 (CV-AFS)	Filtration on 0.45 µm + decanting into 2x100mL borosilicate bottles + 1 mL conc. HCl (suprapur) + 2 mL potassium bromide-bromate digestion reagent (KBr-KBrO ₃ -solution)
22	16 EPA PAHs	DIN 38407-F39: 2011-09	-
23	Indicator PCB ^{i, iv}	DIN EN ISO 6468: 1997-02 DIN 38407-37:2013-11	
24	GC-MS Screening ⁱ	DIN 38407-F39: 2011-09 (NIST-Data base)	
25	16 EPA PAHs (dissolved)	DIN 38407-F39: 2011-09	
26	Indicator PCB (dissolved) ^{i, iv}	DIN EN ISO 6468: 1997-02 DIN 38407-37:2013-11	Filtration on 0.45 µm + (if required, previous centrifugation)
27	GC-MS Screening (dissolved) ⁱ	DIN 38407-F39: 2011-09 (NIST-Data base)	
28	HOI	DIN EN ISO 9377-2: 2001-07	
29	HOI (dissolved)	DIN EN ISO 9377-2: 2001-07	Filtration on 0.45 µm + (if required, previous centrifugation)
30	VOC (HVHH/BTEX) ⁱ	DIN 38407-43: 2014-10 ⁱⁱⁱ	-
31	Dioxins (PCDDs/PCDFs) ⁱ	ISO 18073:2004-04	-
32	Dioxins (PCDDs/PCDFs) (dissolved) ⁱ	ISO 18073:2004-04	Filtration on 0.45 µm + (if required, previous centrifugation)
33	Extended list of PAHs (dissolved) ⁱ	Internal laboratory method (GC-MS) ⁱⁱ	Centrifugation (18,000 g for 30 min) + LLE with n-hexane + sample evaporation ⁱⁱ
34	Extended list of PAHs (particulate) ⁱ	Internal laboratory method (GC-MS) ⁱⁱ	Centrifugation (18,000 g for 30 min) + ultrasonic extraction with 1) dichloromethane + 2) toluene/methanol,

No.	Parameter	Analysis method	Preparation and conditioning
			combining extracts, sample evaporation ⁱⁱ

Abbreviations: 16 EPA PAHs, Priority PAH listed by the US Environmental Protection Agency; AAS, Atomic absorption spectrometry; AFS, Atomic fluorescence spectrometry; APLI, Atmospheric-pressure laser ionization; As, Arsenic; BTEX, Benzene, toluene, ethylbenzene and xylene; Cd, Cadmium; CFA, Continuous flow analysis; Cr, Chromium; Cu, Copper; CV, Cold vapor; DOC, Dissolved organic carbon; Fe, Iron; GC, Gas chromatography; Hg, Mercury; HOI, Hydrocarbon oil index; HVHH, Highly volatile halogen hydrocarbons; ICP, Inductively coupled plasma; Mn, Manganese; MS, Mass spectrometry; Ni, Nickel; OES, Optical emission spectrometry; PCB, Polychlorinated biphenyl; PCDDs/PCDFs, Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; Pb, Lead; Sb, Antimony; Se, Selenium; TNb, Total nitrogen bound; TOC, Total organic carbon; V, Vanadium; VOC, Volatile organic carbons; Zn, Zinc.

- i. Analyses may not be carried out in all sampled ships.
- ii. Refer to Annex 6 for the description of the analysis method for the extended list of PAHs.
- iii. Refer to Annex 7 for the list of volatile organic compounds to be determined.
- iv. Indicator PCB: CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180.

3.3 Ecotoxicological assays on water samples

The samples will be shipped for ecotoxicological analysis to the laboratories of the German Federal Institute of Hydrology (BfG) and UBA. BfG works together with two contracting laboratories (Institut Dr. Nowak GmbH & Co. KG and Noack Laboratorien GmbH) for the conduction of selected whole effluent toxicity tests. Table 4 indicates the methods for analysis as well as the preparation and conditioning procedures for determination of ecotoxicological effects on water samples.

Table 4. Methods for sample preparation and analysis for ecotoxicological effects of water samples

No.	Parameter	Analysis method	Preparation and conditioning
35	Luminescent bacteria (WET) ⁱ	<i>Aliivibrio fischeri</i> (ISO 11348-2)	Samples tested as native samples if compatible with the bioassay test requirements. Filtration and pH-adjustment of the samples may be required prior to testing. Additionally, samples will be extracted for enrichment of contaminants ⁱⁱⁱ and subsequently retested in the bioassays.
36	Marina algae (WET) ⁱ	<i>Phaeodactylum tricornutum</i> (ISO 10253:2006)	
37	Zooplankton crustacean - copepod test (WET) ⁱ	<i>Acartia tonsa</i> (ISO 14669)	
38	Recombinant yeast assay (hAHR-binding): (Dioxin-like effect) ⁱ	Recombinant Yeast-based Assay (according to Miller et al. 1999)	
39	Ames test (Mutagenicity) ⁱⁱ	ISO 11350	Samples will be extracted for enrichment of contaminants ⁱⁱⁱ and removal of salt water, because fish egg test is incompatible with saline water, and subsequently tested in the bioassays.
40	Fish egg test ⁱⁱ	DIN EN ISO 15088	

Abbreviations: hAHR, Human aryl hydrocarbon receptor; WET, Whole effluent toxicity.

- i. Analysis carried out by BfG
- ii. Extracts of the samples will be tested by UBA; the extraction procedure will be carried by BfG.
- iii. Refer to Annex 8 for the detailed protocol on sample preparation and processing for bioassays.

3.4 Fuel and lubricating oil

The analytical methods for chemical characterization of fuel and lubricating oil are indicated in Table 5. Sulphur content will be carried out at the BSH laboratory (with ISO 17025:2017 accreditation). Metals and PAHs will be carried out by the laboratory of Bureau Veritas.

Table 5. Methods for sample preparation and analysis for chemical composition of fuel and lubricating oil samples

No.	Parameter	Analysis method	Preparation and conditioning
41	Sulphur content	XRF spectroscopy (EN ISO 8754)	Centrifugation (fuels of low viscosity); additional heating and homogenization beforehand (fuels of high viscosity)
42	Metals [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn]	IP 501 - modified for determination of additional elements (ICP-OES)	-
43	Hg	UOP 938	-
44	16 EPA PAHs	CMA/3/B ⁱ	-

Abbreviations: 16 EPA PAHs, Priority PAH listed by the US Environmental Protection Agency; As, Arsenic; Cd, Cadmium; Cr, Chromium; Cu, Copper; Fe, Iron; Hg, Mercury; ICP, Inductively coupled plasma; IP, Institute of Petroleum; Mn, Manganese; Ni, Nickel; OES, Optical emission spectrometry; Pb, Lead; Sb, Antimony; Se, Selenium; UOP, Universal Oil Products Company; V, Vanadium; XRF, X-ray fluorescence; Zn, Zinc.

- i. CMA method was developed by the Flemish Institute for Technology Research and is comparable to EN 16143 (for extender oils) but has broader range of application.

4. Results

Ship operators will be provided with the results of the analyses corresponding to their ship without data evaluation or conclusions. Within the framework of the project all results, their evaluation and conclusions will be published keeping ship operators and sampled ship anonymously.

References

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OSPAR Commission (2007): WEA Guidance Document. Publication Number: 316/2007. ISBN 978-1-905859-55-9

PPR (2020): Annex 9 – Draft MEPC Resolution. 2020 Guidelines for Exhaust Gas Cleaning Systems. Report to the Marine Environment Protection Committee. Document PPR 7/22/Add.1

Miller, C. A. (1999). "A Human Aryl Hydrocarbon Receptor Signaling Pathway Constructed in Yeast Displays Additive Responses to Ligand Mixtures." *Toxicology and Applied Pharmacology* 160(3): 297-303.

Annex 1 Information prior to sampling

Table A-1. Information prior to sampling: **Ship information**

No.	Parameter	Specification/Value
1	Ship's name	
2	IMO number	
3	Ship build date	dd.mm.yyyy
4	Ship type	
5	Flag	
6	Gross tonnage	
7	Dead weight tons	

Table A-2. Information prior to sampling: **EGCS – General**

No.	Parameter	Specification/Value
1	Manufacturer	
2	Model	
3	EGCS type (operation mode)	OL / CL / hybrid
4	Construction form	U-type / I-type
5	Water distribution in scrubber tower	packed bed / spray layers _ / combination
6	Serial number	
7	Design capacity (MW)	
8	Design capacity (kg _{exhaust gas flow} /h)	
9	Number of streams	single / multiple
10	Installation type	retrofit / newbuilding
11	Installation date	dd.mm.yyyy
12	Approval scheme	scheme A / B
13	Approval date	dd.mm.yyyy
14	Estimated yearly operation time (h)	
15	Type of water treatment system (if any)	
16	Added chemicals	
16.1	Alkali (chemical, concentration and dosage)	
16.2	Flocculant (chemical, concentration and dosage)	
16.3	Others (chemical, concentration and dosage)	
17	Additional notes:	

Table A-3. Information prior to sampling: **EGCS – Water monitoring**

No	Parameter	Specification/Value	
		Inlet	Outlet
1	pH sensor		
1.1	Manufacturer		
1.2	Model		

No	Parameter	Specification/Value	
		Inlet	Outlet
1.3	Date of last maintenance	dd.mm.yyyy	dd.mm.yyyy
1.4	Date of last calibration	dd.mm.yyyy	dd.mm.yyyy
1.5	Discharge limit value	-	
2	Turbidity sensor		
2.1	Manufacturer		
2.2	Model		
2.3	Date of last maintenance	dd.mm.yyyy	dd.mm.yyyy
2.4	Date of last calibration	dd.mm.yyyy	dd.mm.yyyy
3	PAH_{phe} sensor		
3.1	Manufacturer		
3.2	Model		
3.3	Date of last maintenance	dd.mm.yyyy	dd.mm.yyyy
3.4	Date of last calibration	dd.mm.yyyy	dd.mm.yyyy
3.5	Discharge limit value	-	
4	Measuring cabinet (if applicable)		
4.1	Manufacturer		
4.2	Model		
5	Additional notes:		

Table A-4. Information prior to sampling: **EGCS – Exhaust gas monitoring (CEMS)**

No.	Parameter	Specification/Value
1	CO₂ sensor	
1.1	Manufacturer	
1.2	Model	
1.3	Date of last maintenance	dd.mm.yyyy
1.4	Date of last calibration	dd.mm.yyyy
2	SO₂ sensor	
2.1	Manufacturer	
2.2	Model	
2.3	Date of last maintenance	dd.mm.yyyy
2.4	Date of last calibration	dd.mm.yyyy
3	Measuring cabinet (if applicable)	
3.1	Manufacturer	
3.2	Model	
4	Zero gas (for calibration)	
4.1	Manufacturer	
4.2	Substance	
4.3	Expiry date	dd.mm.yyyy
4.4	Calibration concentration (SO ₂ in ppm; CO ₂ in %)	
5	Span gas (for calibration)	
5.1	Manufacturer	
5.2	Substance	
5.3	Expiry date	dd.mm.yyyy

No.	Parameter	Specification/Value
5.4	Calibration concentration (SO ₂ in ppm; CO ₂ in %)	
6	Additional notes:	

Table A-5. Information prior to sampling: **Combustion unit(s) connected to EGCS**

No.	Parameter	Specification/Value
1	Manufacturer	
2	Model	
3	Serial number	
4	Type of combustion unit	ME / AE / boiler
5	Rated power (kW)	
6	Rated speed (rpm)	
7	Cycle	2-stroke / 4-stroke
8	Estimated yearly operation time (h)	
9	EGCS connected	As identified in Table A-2
10	NOx Tier	Tier I / II / III
11	De-NOx technology	EGR / SCR / None
12	Additional notes:	

Annex 2 Field sampling report – Ship information, operation conditions and monitoring data

Information to be provided by the ship's personnel in conjunction with sampling for each operation mode (OL and/or CL): conditions during sampling period.

Table A-6. Field sampling report: **Ship information**

No.	Parameter	Specification/Value
1	Cruise speed (knots)	
2	Start of sampling date and time (UTC)	dd.mm.yyyy hh:mm
3	Stop of sampling date and time (UTC)	dd.mm.yyyy hh:mm
4	Ship's position at start of sampling (GPS)	
5	Ship's position at end of sampling (GPS)	
6	Weather conditions	calm / rough
7	Notes:	

Table A-7. Field sampling report: **EGCS – General**

No.	Parameter	Specification/Value
1	System operation mode	OL / CL
2	Approx. EGCS load (%)	
3	Average washwater flowrate (m ³ /h)	
4	Average dilution water flowrate (if applicable) (m ³ /h)	
5	Average/Estimated make-up water flowrate (in CL system) (m ³ /h)	
6	Average/Estimated bleed-off flowrate from process tank (in CL system) (m ³ /h)	
7	Average/Estimated sludge produced from water treatment (in CL system) (kg/h)	
8	Average/Estimated water flowrate from water treatment to be discharged or to be stored in holding tank (in CL system) (m ³ /h)	
9	Type of water treatment system (if any)	
10	Added chemicals: alkali (chemical, concentration and dosage)	
11	Added chemicals: flocculant (chemical, concentration and dosage)	
12	Added chemicals: others (chemical, concentration and dosage)	
13	Energy consumption of pumps for washwater and dilution water (A)	
14	Additional notes:	

Table A-8. Filed sampling report: **EGCS – Water monitoring unit**

No.	Parameter	Specification/Value	
		Inlet	Outlet
1	pH, average (-)		
2	PAH _{phe} , average (µg/L)		
3	Turbidity, average (NTU/FTU)		
4	Time in monitoring record system also UTC? (Yes/No)		
5	Additional notes: <i>If dilution exists, pH value to be reported is from the stream after dilution.</i>		

Table A-9. Field sampling report: **EGCS – Exhaust gas monitoring (CEMS)**

No.	Parameter	Specification/Value
1	SO ₂ (ppm), after EGCS	
2	CO ₂ (%), after EGCS	
3	SO ₂ /CO ₂ ratio (ppm/%)	
4	Exhaust gas flowrate (Nm ³ /h)	
5	Temperature (°C), before EGCS	
6	Temperature (°C), after EGCS	
7	Pressure (mbar), before EGCS	
8	Pressure (mbar), after EGCS	
9	Additional notes:	

Table A-10. Field sampling report: **Combustion unit(s) in operation and connected to sampled EGCS and fuel oil in use**

No.	Parameter	Specification/Value
1	Combustion unit(s) in operation and connected to sampled EGCS	ME / AE / boiler
2	Approx. total combustion unit(s) load (MW)	
3	Approx. total combustion unit(s) load (%)	
4	Total fuel consumption rate (t/h)	
5	Specific fuel oil consumption (kg/MWh)	
6	Fuel classification (according to ISO 8217)	
7	Fuel sulphur content (according to BDN)	
8	Fuel viscosity (if available)	
9	Fuel ash content (if available)	
10	Fuel density (if available)	
11	Additional notes:	

Annex 3 Field sampling report – Sampling points details, sample bottles identification and on-board measurements

Information to be gathered and filled out by the project workers in conjunction with sampling for each operation mode (OL and/or CL).

Table A-11. Field sampling report: **Identification of sampling points**

1	Sampling point ID (or sample code) <i>[Sampling point ID is composed by ship number, EGCS operation mode (OL: open loop; CL: closed loop) and water stream identification (IN: inlet or background; BT: before treatment; AT: after treatment; BD: before dilution; OU: outlet). For example: S3/CL/OU]</i>
2	Detailed description of water process stream <i>[Including: inlet/background, before/after treatment, before/after dilution]</i>
3	Physical location of sampling point/valve <i>[Deck, frame, next to]</i>
4	Design and material of sampling point/valve <i>[In order to identify potential contamination sources, a detailed description of the sampling point/valve configuration, including manufacturer and model of sampling valve, is required]</i>
5	Graphical description <i>[To ensure that the sampling point can be found for following sampling programs, additional graphical material, such as process diagrams, piping and instrumentation diagrams, drawings or photographs, can be attached. The attached material should be listed below]</i>

Table A-12. Field sampling report: **Sample bottles identification**

No.	Bottle code	Sample code	Parameter(s)	Bottle volume and material	Box Nr.	Notes
1	e.g. S1/HU/001	e.g. S1/OL/IN	e.g. TSS			
2						
3						
4						
5						
6						
7						
8						
9						

i. Bottle code is composed by ship number, laboratory and bottle number. Sample code is composed by ship number, EGCS operation mode and process water stream.

Table A-13. Field sampling report: **Onboard measurements**

No.	Parameter	Sampling point				Notes
1	Sampling date					
2	Sampling time					
Onboard measurements with handheld device, immediately after sampling						
3	pH (-)					
4	Temperature (°C)					
5	Conductivity (mS/cm)					
6	Salinity (PSU)					
Onboard measurements with TriOS measuring system						
7	pH (-)					
8	Turbidity (NTU)					
9	PAH _{phe} (µg/mL)					
10	Nitrogen compounds (mg/mL)					
11	Measurement (1) date/time					
12	Measurement (2) date/time					

Abbreviations: IN, Inlet; BT, Before treatment; AT, After treatment; BD, Before dilution; OU, Outlet.

Annex 4 Example timeline during ships visit for BSH sampling exercise

BSH personnel will supervise the sampling to ensure a consistent and high quality. On board, the protective measures due to the COVID-19 pandemic must be followed (see also BSH occupational safety concept). After the sampling is completed, BSH personnel will disembark the ship together with the samples. In order to ensure this, a detailed planning is important.

Prior to the sampling campaign:

Sampling equipment will be sent to the ship in advance or if arriving by car directly.

Shipping will be organized by BSH in cooperation with ship operator.

Equipment is properly packed, labeled and secured. Equipment will be packed on euro pallets, maximum 2-3 euro pallets.

Equipment needs to be stored on board until personnel embark the ship.

BSH personnel embark the ship:

Embarking at the last port prior to disembarkation port in or near Germany.

BSH personnel will need a cabin (double cabin no window).

Shortly after embarkation BSH personnel will ask for short opening meeting with Chief Engineer and/or Captain for planning of sampling and discussion of open questions.

Safety introduction to BSH personnel by ship crew.

Preparation of equipment and sampling points.

Sampling starts as agreed and scheduled in opening meeting.

Samples and BSH personnel disembark the vessel:

Samples are packed securely and leakage-proofed.

Samples will be picked up by BSH Crew ashore.

BSH will organize customs clearance for pick-up.

Annex 5 Equipment list

The equipment list will be used for custom declaration and will be sent to the ship prior embarkation.

<u>Equipment list</u>	Amount	Weight [kg]
Sum		0

Annex 6 Description of analysis method for extended list of PAHs

Method for PAH analysis by gas chromatography – atmospheric pressure laser ionization – mass spectrometry (target PAH, PAH screening, alkylated PAH)

University of Münster

The applied method is based on the procedure used by Dohmann et al. (2019) with some modifications described here. Standard compounds for target analysis are listed in Table 1. All standards are combined to two stock solutions of 1 ng/μl in toluene, knowing that not all compounds can be ionized using APLI. As internal standards a 16 deuterated EPA PAH mixture (Chiron, Norway) is used. Dichloromethane, n-hexane, cyclohexane and methanol (all GC ultra-grade, Roth, Germany) are used.

Dichloromethane, n-hexane, cyclohexane and methanol (all GC ultra-grade, Roth, Germany) are used. Deionized water (MilliQ Integral 5, Millipore, Germany) is taken from a reservoir (2.5 L amber glass bottle) *on-site* as a field blank and further treated equally to the other samples. All samples should be immediately sealed in pre-cleaned amber glass bottles (2.5 L, heated up to 300°C for at least 12 hours) and frozen the same day until extraction to prevent biodegradation.

All samples and field blanks are slowly defrosted over night at room temperature, followed by centrifugation at 18,000 g for 30 min. During centrifugation, particulate matter present in the water samples accumulated at the bottom of the centrifugation tubes. Liquid-liquid extraction with n-hexane (3 cycles with 20 mL, horizontal shaking device for 15 min per cycle) is applied for PAH extraction. Afterwards the samples are reduced to 1.0 mL using a rotary evaporator (Heidolph, Germany). Three recovery rate samples are prepared by spiking deionized water (1000.0 g each, Merck Millipore, Germany) with the custom-made PAH-mixture, resulting in an overall analyte concentration of 50 ng L⁻¹ for each analyte.

GC-APLI-MS measurements of the extracts is carried out according to Große Brinkhaus et al. (2017) using a gas chromatograph (GC2010Plus, Shimadzu, Germany) equipped with a RXI-PAH column (40 m, 0.18 mm i. d., 0.07 mm film thickness, Restek, USA). The temperature program starts at 80 °C (hold for 1 min) is raised at a rate of 100 °C/min to 110 °C and afterwards raised at a rate of 3 °C/min first to 240 °C (hold for 5 min), then to 250 °C (hold for 5 min), and finally to 340 °C (hold for 30 min). Helium (99.999 % purity, Westfalen AG, Germany) serves as carrier gas with linear velocity of 40 cm/s. Split/splitless high pressure injection is used at 340 °C (398.9 kPa hold for 1 min). The GC is coupled to a time-of-flight mass spectrometer (Maxis 3 G UHR QTOF MS, Bruker Daltonik, Germany) using a multipurpose ion source (iGenTraX, Germany). The ion source setup is used according to Schiewek (Schiewek et al., 2007) using a heated transfer line and an APCI-vaporizer for additional gas supply.

Laser ionization is performed by use of a KrF excimer laser (ATLEX SI laser, ATL Lasertechnik, Germany). The excimer laser emits photons with 248 nm wavelength (5.0 eV) with 5 mJ beam energy at a repetition rate of 100 Hz. Using this analytical setup, limits of detection between 5 and 50 fg/μl injection volume could be obtained (benzo[a]pyrene: 25 fg/μl) leading to a 100 - 3,500-fold higher sensitivity compared to common GC-MS (Stader et al., 2013; Große Brinkhaus et al., 2017). The concentrations are corrected considering recovery rates and dilution effects. Naphtho[1,2-*b*]fluoranthene and naphtho[2,3-*a*]pyrene are quantified as a sum parameter due to coelution. For the screening, a feature list (peaks with corresponding mass-to-charge ratio, retention time and intensity) of features with a minimum intensity is provided which shows only aromatic compounds due to the aromatic-selective ionization process.

GC-MS measurements of the extracts is carried out according to Große Brinkhaus et al. (2017) using a gas chromatograph – mass spectrometer (GCMS-QP-2010Plus, Shimadzu, Germany) equipped with a RXI-PAH column (60 m, 0.25 mm i. d., 0.10 mm film thickness, Restek, USA). The temperature program starts at 80 °C (hold for 1 min) is raised at a rate of 100 °C/min to 100 °C and afterwards raised at a rate of 3 °C/min first to 238 °C (hold for 3 min), then to 242 °C (hold for 5 min), then to 249 °C (hold for 7 min) and finally to 340° C (hold for 10 min). Helium (99.999 % purity, Westfalen AG, Germany) serves as carrier gas with linear velocity of 40 cm/s. Split/ splitless high pressure injection is used at 340 °C (350.0 kPa hold for 1 min). The GC is coupled to a EI quadrupole MS and Single Ion Monitoring (SIM) is used.

Table 1: Target PAH of standard mix (custom made)

No	Substance	m/z	No	Substance	m/z
1	Naphthalene	128	41	Benzo[b]fluoranthene	252
2	2-Methylnaphthalene	142	42	Benzo[k]fluoranthene	252
3	2,6-Dimethylnaphthalene	156	43	7,12-Dimethylbenzo[a]anthracene	256
4	1,3-Dimethylnaphthalene	156	44*	Benzo[j]fluoranthene*	252
5*	Acenaphthylene*	152	45	Benzo[a]fluoranthene	252
6	1,8-Dimethylnaphthalene	156	46	Benzo[e]pyrene	252
7	Acenaphthene	154	47	Benzo[a]pyrene	252
8	2,3,6-Tri methylnaphthalene	170	48	Perylene	252
9	Fluorene	166	49	3-Methylcholantrene	268
10	1-Methylfluorene	180	50	6-Methylbenzo[a]pyrene	266
11	Phenanthrene	178	51*	Indeno[1,2,3-cd]fluoranthene*	276
12	Anthracene	178	52	Dibenzo[a,j]anthracene	278
13	3-Methylphenanthrene	192	53	Indeno[1,2,3-cd]pyrene	276
14	2-Methylphenanthrene	192	54	Dibenzo[a,c]anthracene	278
15	9-Methylphenanthrene	192	55	Dibenzo[a,h]anthracene	278
16	1-Methylphenanthrene	192	56	Benzo[b]chrysene	278
17	9-Methylanthracene	192	57	Benzo[ghi]perylene	276
18	Fluoranthene	202	58	Anthanthrene	276
19	9,10-Dimethylanthracene	206	59	Naphtho[1,2-b]fluoranthene	302
20	Pyrene	202	60	Naphtho[1,2-k]fluoranthene	302
21	Retene	234	61*	Naphtho[2,3-j]fluoranthene*	302
22	2-Methylfluoranthene	216	62	Naphtho[2,3-b]fluoranthene	302
23	1-Methylfluoranthene	216	63	Dibenzo[a,e]fluoranthene	302
24	3-Methylfluoranthene	216	64	Dibenzo[a,l]pyrene	302
25	Benzo[a]fluorene	216	65	Naphtho[2,3-k]fluoranthene	302
26	Benzo[b]fluorene	216	66	Naphtho[2,3-e]pyrene	302
27	1-Methylpyrene	216	67	Dibenzo[a,e]pyrene	302
28	7H-Benzo[c]fluorene	216	68	Coronene	300
29	Benzo[ghi]fluoranthene	226	69	Naphtho[2,3-a]pyrene	302
30	Benzo[c]phenanthrene	228	70	Dibenzo[a,i]pyrene	302
31	Benzo[a]anthracene	228	71	Dibenzo[a,h]pyrene	302
32*	Cyclopenta[cd]pyrene*	226			
33	Triphenylene	228			
34	Chrysene	228			
35	6-Methylbenzo[a]anthracene	242			
36	2-Methylchrysene	242			
37	5-Methylbenzo[a]anthracene	242			
38	6-Methylchrysene	242			
39	5-Methylchrysene	242			
40	4-Methylchrysene	242			

Coelution in GC-APLI-MS

* not ionized by APLI

Coelution in GC-MS

References

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Annex 7 Supplementary information on volatile organic compounds

List of volatile organic carbons to be determined under the methodology applied by the Hamburg Institute for Hygiene and Environment

Institut für Hygiene und Umwelt Hamburg

Table 1: List of volatile organic carbons to be determined

No.	Substance	No.	Substance
1	Trichlormethan	33	1.4-Xylol
2	Tetrachlormethan	34	1.3.5-Trimethylbenzol (Mesitylen)
3	1.1-Dichlorethan	35	1.2.4-Trimethylbenzol
4	1.2-Dichlorethan	36	1.2.3-Trimethylbenzol
5	1.1.1-Trichlorethan	37	1.2.3.4-Tetramethylbenzol
6	1.1.2-Trichlorethan	38	1.2.3.5-Tetramethylbenzol
7	Dibrommethan	39	1.2.4.5-Tetramethylbenzol (Durol)
8	Bromdichlormethan	40	p-Isopropyltoluol
9	Dibromchlormethan	41	Inden
10	Bromchlormethan	42	Indan
11	1.2-Dibromethan	43	Naphthalin
12	1.1.2-Trichlortrifluorethan	44	1-Methylnaphthalin
13	Chlorethen (Vinylchlorid)	45	2-Methylnaphthalin
14	1.1-Dichlorethen	46	Chlorbenzol
15	1.2-Dichlorethen cis	47	1.2-Dichlorbenzol
16	1.2-Dichlorethen trans	48	1.3-Dichlorbenzol
17	Trichlorethen	49	1.4-Dichlorbenzol
18	Tetrachlorethen	50	1.2.3-Trichlorbenzol
19	2,3-Dichlorpropen	51	1.2.4-Trichlorbenzol
20	Benzol	52	1.3.5-Trichlorbenzol
21	Toluol	53	2-Chlortoluol
22	2-Ethyltoluol	54	3-Chlortoluol
23	Summe 1.3/1.4-Ethyltoluol	55	4-Chlortoluol
24	Ethylbenzol	56	Dichlormethan
25	Styrol	57	Methyl-t-butylether
26	Isopropylbenzol (Cumol)	58	3-Chlorpropen (Allylchlorid)
27	n-Propylbenzol	59	Ethyl-t-butylether
28	1.2-Diethylbenzol	60	Tribrommethan
29	1.3-Diethylbenzol	61	1.3-Dichlorpropen cis
30	1.4-Diethylbenzol	62	1.2.3-Trichlorpropan
31	1.2-Xylol	63	1.2-Dichlorpropan
32	1.3-Xylol	64	1.3-Dichlorpropen trans

Annex 8 Supplementary information on ecotoxicological analysis

Bundesanstalt für Gewässerkunde

Storage and transportation of water samples prior to ecotoxicological analysis

The water samples are to be delivered to the BfG at the earliest 24 hours and at the latest 96 hours after sampling. The samples are to be stored refrigerated directly after sampling and also cooled during transport using cooling packs. Immediately after the arrival of the samples at the BfG, they should be divided: one part to be sent cooled to contract laboratories (see Table below) and the other part to be frozen at -20 °C until further processing. When the samples arrive at the contract laboratories, they are either directly to be tested or frozen at -20 °C as well. The testing of the native samples should be conducted at the same time in the contract laboratories and at the BfG in order to keep the storage time of the samples the same. Accordingly, the frozen samples should be thawed at the same day and then either be fed directly to the test or be concentrated 1000-fold by solid phase extraction (SPE). Half of the extracts will be sent to UBA to be used for the fish-egg and Ames tests. The extracts should be shipped unrefrigerated by courier service with a maximum shipping time of 24 hours.

Table A.8. Distribution of the samples between the laboratories.

Laboratory	Sampling action 1		Sampling action 2		Sampling action 3		Sampling action 4	
	Native sample (WE)	Extract	Native sample (WE)	Extract	Native sample (WE)	Extract	Native sample (WE)	Extract
UBA	-	~350 µl MeOH ~250 µl DMSO	-	~600 µl MeOH ~400 µl DMSO	-	~600 µl MeOH ~400 µl DMSO	-	~600 µl MeOH ~400 µl DMSO
BfG	-	<400 µl DMSO	1.0 l	1000 µl DMSO	1.0 l	1000 µl DMSO	1.0 l	1000 µl DMSO
Contract laboratory 1	0.5 l	-	0.5 l	-	0.5 l	-	0.5 l	-
Contract laboratory 2	0.5 l	-	0.5 l	-	0.5 l	-	0.5 l	-

Abbreviations: DMSO, Dimethyl sulfoxide; MeOH, methanol; WE, Whole effluent. Extracts are to be dissolved either with MeOH or with DMSO.

Preparation and conditioning of water samples prior to ecotoxicological analysis

The evaluation of the ecotoxicological potential of water samples from EGCS generally follows the principles of whole effluent assessment (WEA), keeping the EGCS water samples as unchanged as possible for the testing (OSPAR Commission 2007, WEA Guidance Document). Thus, EGCS effluent samples are tested as native samples and the only adjustment applied were of the pH-value, in cases the pH of a native sample deviates from the acceptable pH-range of the corresponding bioassay (according to the test standard or guideline used). Further processing procedures on the sample are required dependent on the water samples properties and bioassay standard requirements.

Differences in water sample quality parameters, such as pH and turbidity, are expected, varying dependent on the sampling point (e.g. before or after scrubbing) and EGCS operation

mode (open loop, OL or closed loop, CL). For instance, the water samples from CL systems taken after the scrubbing but before the treatment unit can be very turbid and contain variable amounts of precipitates and suspended material of different nature (e.g. flocculants). In these cases, a filtration step is required to remove suspended and precipitated particles from the native samples, which could otherwise interfere with the bioassay performance. After filtration, the samples can either directly applied to the bioassays (after pH-adjustment in case of deviation from acceptable range between pH 6 and 8) or are subjected to solid phase extraction.

Filtration

- a. Prior to the conduct of the *in-vitro* ecotoxicity assays, EGCS water samples should be filtered using glass fibre filters (type A/C borosilicate glass without binder, pore size: 1 µm, thickness 254 µm; Pall Life Sciences, Dreieich) followed by solid-phase extraction (see 2. Extraction procedure).
- b. Prior to the conduct of the WEA in-vivo and in-vitro bioassays, turbid and precipitating EGCS water samples are filtered using glass fibre filters (borosilicate glass micro fibres with binder, retention capacity 0.4 µm, thickness 1 mm; Macherey Nagel, Düren).

Extraction procedure

Solid-phase extraction is performed using Oasis HLB cartridges (pore size 80 Å, particle size 30 µm, capacity 6 ml, 200 mg) from Waters (Milford, Massachusetts, USA). These are conditioned with 1×2 mL n-heptane, 1×2 mL acetone, 3×2 mL methanol and 4×2 mL H₂O applying ~400 mbar pressure. Double-distilled water is to be extracted in parallel to provide a procedural blank. After extraction, cartridges are suction dried under vacuum (~ 40 min). Samples are eluted with methanol, with the final volume of the eluent adjusted to the targeted enrichment factor. Commonly, 1000-fold concentrated extracts are applied. Since methanol is not compatible with most *in-vitro* bioassays, the solvent is evaporated and exchanged by dimethyl sulfoxide (DMSO) (volume according to the targeted enrichment factor) prior to testing.

Relative enrichment factor of the samples

The relative enrichment factor (REF) is the combination of the enrichment of the extraction and the dilution in the bioassay and represents the enrichment or dilution of the original sample in each bioassay. The REF is equivalent to a concentration and is expressed in the units [L_{water sample}/L_{bioassay}].

$$REF = enrichment\ factor_{SPE} * dilution\ factor_{bioassay}$$