



Oil detection with ferrybox system: project GRACE

Tarmo Kõuts*, Siim Pärt* and Leonie Nüsser**

*Tallinn University of Technology

** Aachen University

GRACE objectives

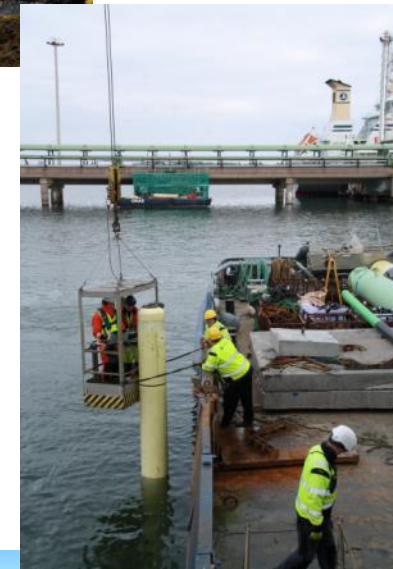
- Improve the observation and predictions of oil movements in the sea using **novel on-line sensors** on vessels, fixed structures, smart buoys or gliders, and smart data transfer to operational awareness systems;
- Explore the true environmental impacts and benefits of a suite of marine **oil spill response technologies** in the cold climate and ice-infested areas in the northern Atlantic Ocean and the Baltic Sea. Methods included are:
 - **mechanical collection** in water and below ice,
 - **in situ burning**,
 - use of **chemical dispersants**,
 - natural **biodegradation**
 - and combinations of these;
- Assess in particular the **impacts on fish, invertebrates** (e.g., mussels, crustaceans) and macro algae of naturally and chemically dispersed oil, in situ burning residues and non-collected oil using highly sensitive biomarker methods, and to develop specific methods for the rapid detection of the effects of oil pollution on biota
- Develop a **strategic Net Environmental Benefit Analysis tool (sNEBA)** for oil spill response strategy decision making in cold climate and ice-infested areas.

GRACE period 1

1.3.2016-31.8.2017



- Consortium works well together – all partners dedicated
- Much field and laboratory work initiated
- Unique possibilities to perform field tests e.g with in situ burning in Greenland, Smart buoy trials in oil harbour, FerryBox on passenger ship, electrokinetic treatment in the heart of Helsinki
- Successful communication of the project to the right end users



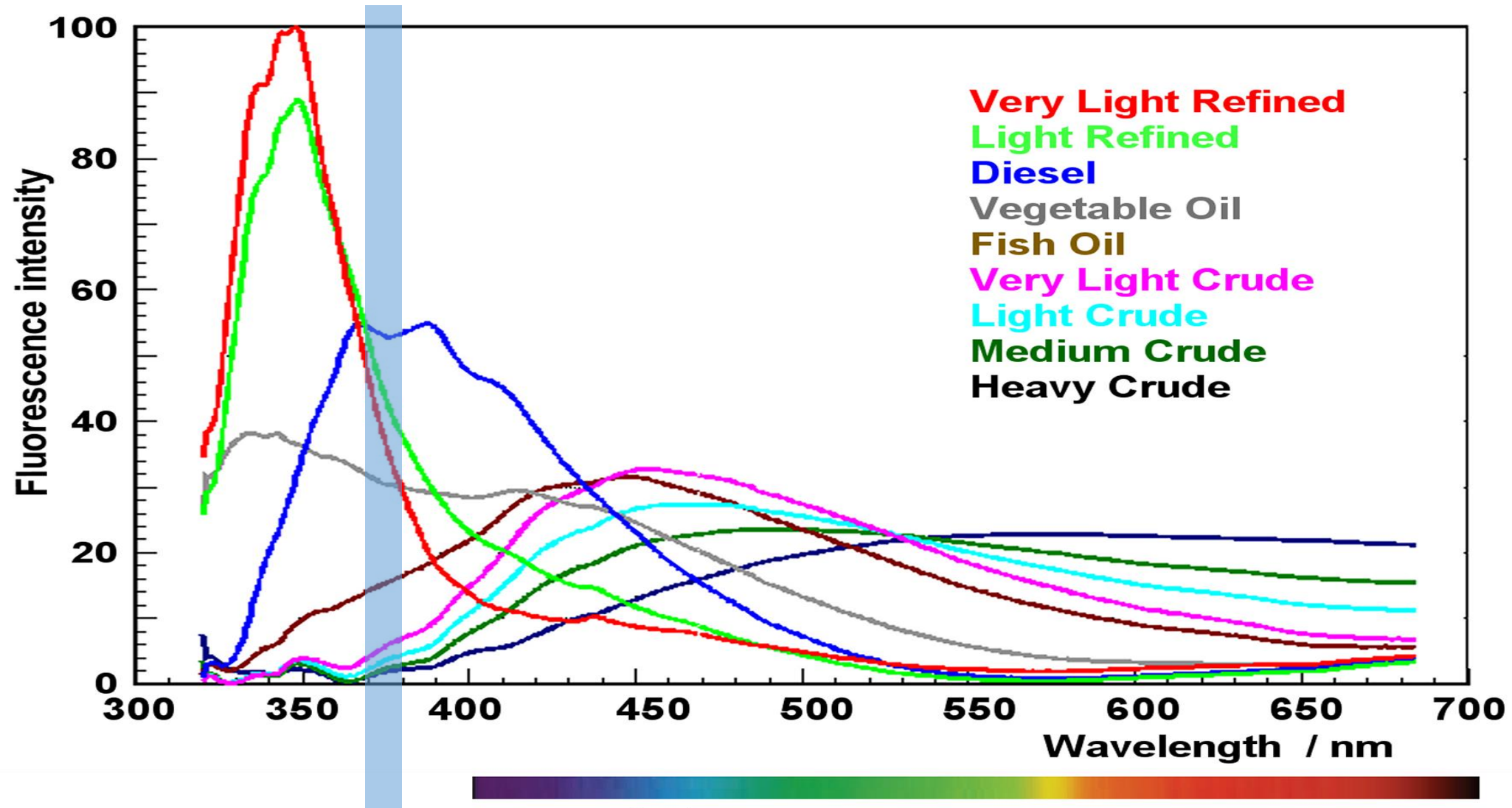
FerryBox on M/S BALTIC QUEEN



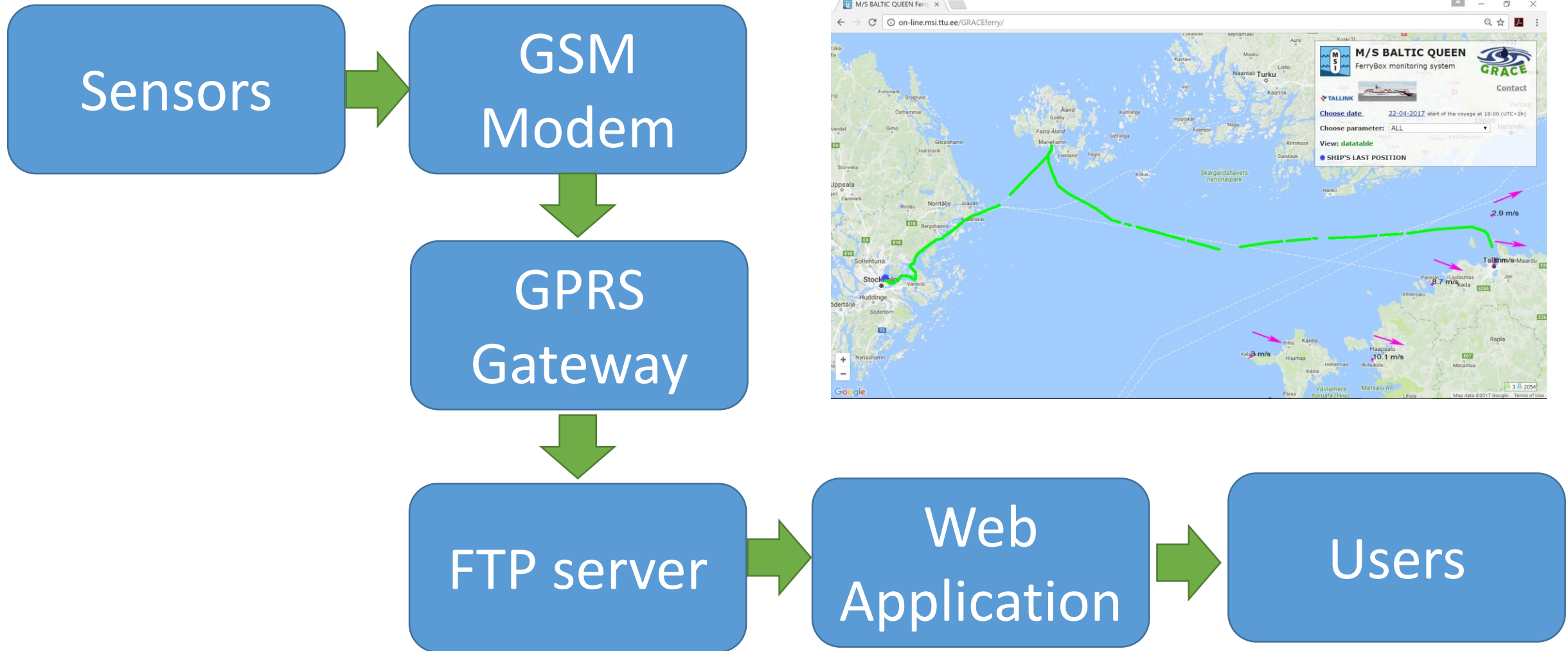
Measurement of Polycyclic Aromatic Hydrocarbons (PAH-s)

- Crude oil and other fossil fuels contain polycyclic aromatic hydrocarbons (PAHs).
- PAHs are hydrocarbons containing only carbon and hydrogen—they are composed of multiple aromatic rings.
- Most PAHs are also fluorescent, emitting characteristic wavelengths of light when they are excited (when the molecules absorb light)
- Ultra-violet fluorescence (UVF) is considered to be a highly sensitive, reasonably selective, simple, rapid and straight-forward method to determine oil-based aromatic compounds in seawater. The method is based on the similarities between the fluorescence excitation and emission spectra of nonpolar organic compounds.

Measurement of Polycyclic Aromatic Hydrocarbons (PAH-s)



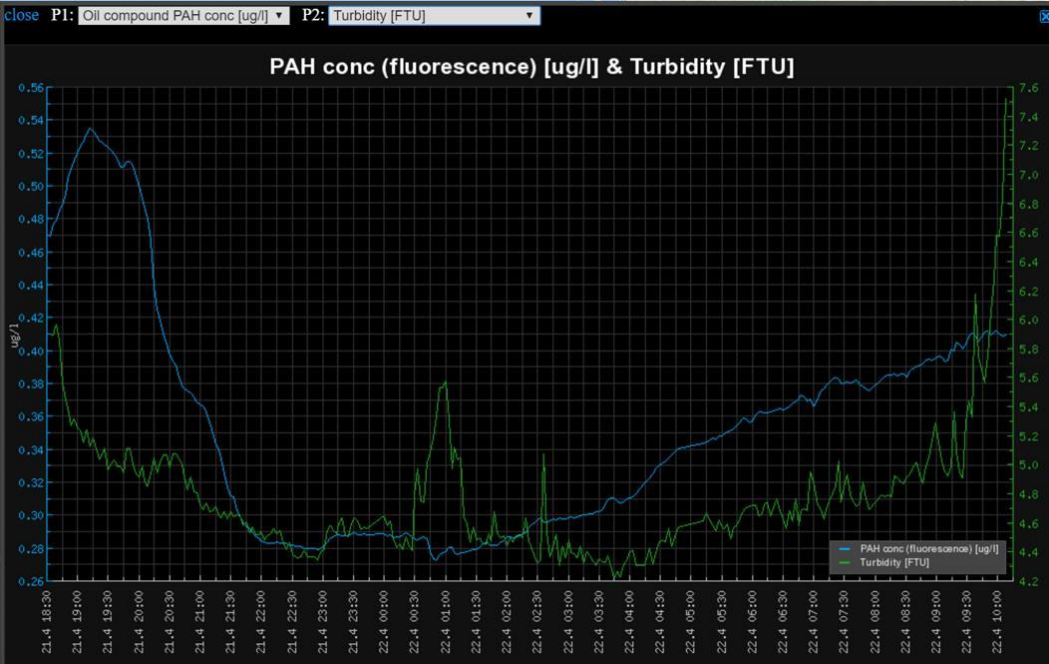
On-line data management and user interface







Data management and visualisation via web-based user interface

<http://on-line.msi.ttu.ee/GRACEferry/>





M/S BALTIC QUEEN
FerryBox monitoring system



Contact

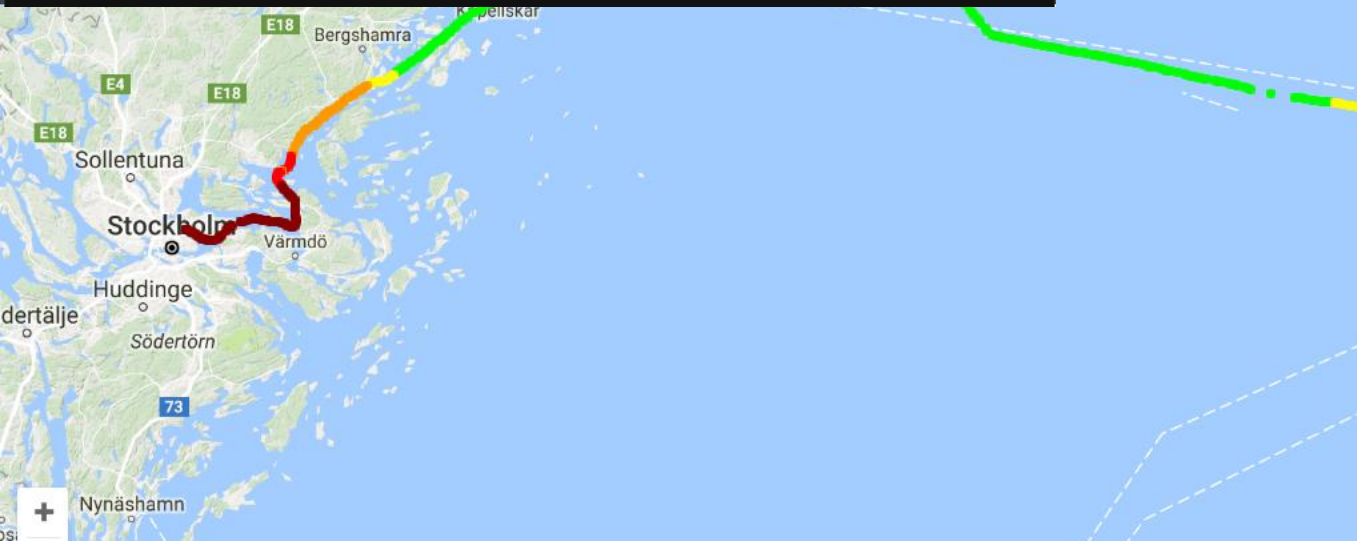
Choose date: 05-04-2017 start of the voyage at 18:00 (UTC+2h)

Choose parameter: Oil compound PAH conc [ug/l]

View: **datatable, graph**

SHIP'S LAST POSITION

- 0,15..0,18 ug/lrg
- 0,18..0,21 ug/l
- 0,21..0,25 ug/l
- 0,25..0,28 ug/l
- 0,28..0,31 ug/l

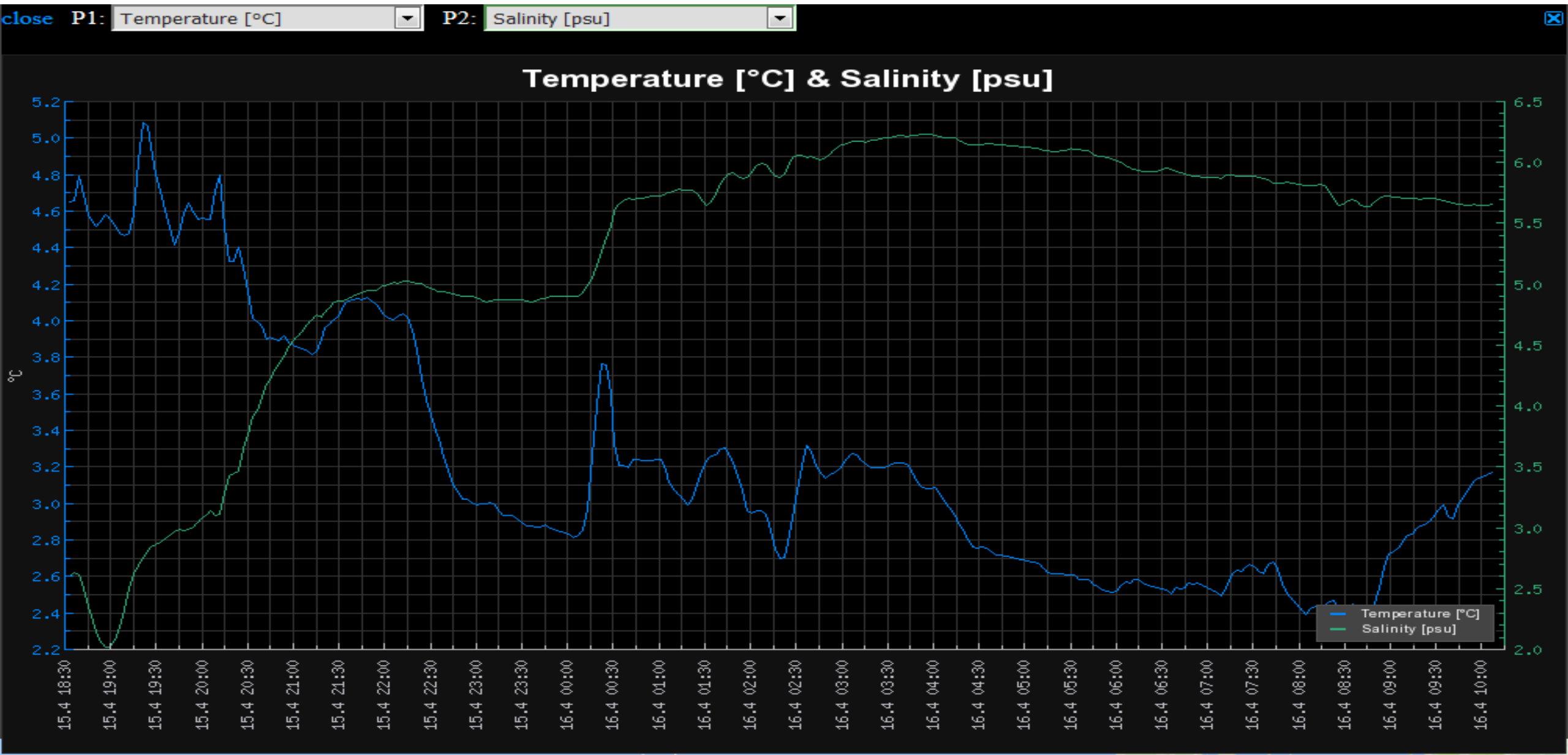


GRACEferrybox (close window)

Time (local)	Latitude	Longitude	Temperature [°C]	Conductivity [mS/cm]	Salinity [psu]	Turbidity [FTU]	PAH conc [ug/l]	CO ₂ conc [ppm]	H ₂ O [ppt]	Pressure [mbar]	Signal strength [dBm]	Current GSM/GPRS provider	Battery voltage [V]
21.04.2017 17.00	59° 21' 0288"	18° 6' 7671"	18.57	0.1	0.06	2.33	-0.08	581.73	22.0	1004.22	-51	24001	14.5
21.04.2017 17.01	59° 21' 0284"	18° 6' 7662"	18.57	0.1	0.06	2.32	-0.08	582.22	22.0	1004.22	-51	24001	14.7
21.04.2017 17.02	59° 21' 0283"	18° 6' 7671"	18.59	0.1	0.06	2.32	-0.08	583.02	22.0	1004.16	-51	24001	13.7
21.04.2017 17.03	59° 21' 0284"	18° 6' 7662"	18.59	0.1	0.06	2.32	-0.08	584.29	22.02	1004.09	-51	24001	14.6
21.04.2017 17.04	59° 21' 0282"	18° 6' 7673"	18.59	0.1	0.06	2.29	-0.08	584.76	22.02	1004.1	-51	24001	14.2
21.04.2017 17.05	59° 21' 0294"	18° 6' 7665"	18.59	0.1	0.06	2.32	-0.08	585.56	22.02	1004.09	-51	24001	14.1
21.04.2017 17.06	59° 21' 0284"	18° 6' 7662"	18.59	0.1	0.06	2.32	-0.08	586.29	22.03	1003.98	-51	24001	14.3
21.04.2017 17.07	59° 21' 0285"	18° 6' 7675"	18.6	0.1	0.06	2.29	-0.08	587.21	22.04	1003.96	-51	24001	14.4
21.04.2017 17.08	59° 21' 0271"	18° 6' 7673"	18.6	0.1	0.06	2.32	-0.08	587.82	22.04	1004.03	-51	24001	14.8
21.04.2017 17.09	59° 21' 0266"	18° 6' 7666"	18.6	0.1	0.06	2.32	-0.08	588.55	22.04	1004.09	-51	24001	13.8
21.04.2017 17.10	59° 21' 0251"	18° 6' 7641"	18.6	0.1	0.06	2.32	-0.08	589.49	22.05	1004.03	-51	24001	14.6
21.04.2017 17.11	59° 21' 0253"	18° 6' 7651"	18.61	0.1	0.06	2.29	-0.08	590.14	22.05	1004.03	-51	24001	14
21.04.2017 17.12	59° 21' 0275"	18° 6' 7658"	18.6	0.1	0.06	2.32	-0.08	590.85	22.05	1004.14	-51	24001	14.6
21.04.2017 17.13	59° 21' 0253"	18° 6' 7669"	18.6	0.1	0.06	2.32	-0.08	591.62	22.05	1004.09	-51	24001	14
21.04.2017 17.14	59° 21' 0256"	18° 6' 7693"	18.61	0.1	0.06	2.32	-0.08	592.2	22.05	1004.24	-51	24001	13.8
21.04.2017 17.15	59° 21' 0259"	18° 6' 7686"	18.61	0.1	0.06	2.32	-0.08	592.97	22.05	1004.14	-51	24001	14.3
21.04.2017 17.16	59° 21' 0287"	18° 6' 7682"	18.61	0.1	0.06	2.29	-0.08	593.89	22.06	1004.25	-51	24001	13.7
21.04.2017 17.17	59° 21' 0273"	18° 6' 7685"	18.61	0.1	0.06	2.29	-0.08	594.51	22.06	1004.09	-51	24001	13.7
21.04.2017 17.18	59° 21' 0275"	18° 6' 7691"	18.61	0.1	0.06	2.29	-0.08	595.41	22.06	1004.19	-51	24001	13.8
21.04.2017 17.19	59° 21' 0289"	18° 6' 7699"	18.61	0.1	0.06	2.28	-0.08	596.06	22.07	1004.13	-51	24001	14.8
21.04.2017 17.20	59° 21' 0288"	18° 6' 771	18.61	0.1	0.06	2.28	-0.08	596.92	22.07	1003.93	-51	24001	13.7
21.04.2017 17.21	59° 21' 0288"	18° 6' 7708"	18.61	0.1	0.06	2.33	-0.08	597.48	22.07	1003.94	-51	24001	14.7
21.04.2017 17.22	59° 21' 0281"	18° 6' 7685"	18.61	0.1	0.06	2.32	-0.08	598.41	22.08	1003.94	-51	24001	13.7
21.04.2017 17.23	59° 21' 0267"	18° 6' 7674"	18.61	0.1	0.06	2.28	-0.08	599.16	22.08	1003.94	-51	24001	13.8
21.04.2017 17.24	59° 21' 0278"	18° 6' 7669"	18.61	0.1	0.06	2.32	-0.08	599.86	22.08	1003.84	-51	24001	14.4
21.04.2017 17.25	59° 21' 0265"	18° 6' 7657"	18.61	0.1	0.06	2.32	-0.08	600.77	22.08	1003.82	-51	24001	13.9
21.04.2017 17.26	59° 21' 0266"	18° 6' 7667"	18.61	0.1	0.06	2.33	-0.08	601.32	22.08	1003.89	-51	24001	13.8
21.04.2017 17.27	59° 21' 0284"	18° 6' 7677"	18.61	0.1	0.06	2.32	-0.08	602.3	22.09	1003.89	-51	24001	14.1



General distribution pattern of physical properties on Stockholm-Tallinn route





General distribution pattern of PAH and turbidity on Stockholm-Tallinn route

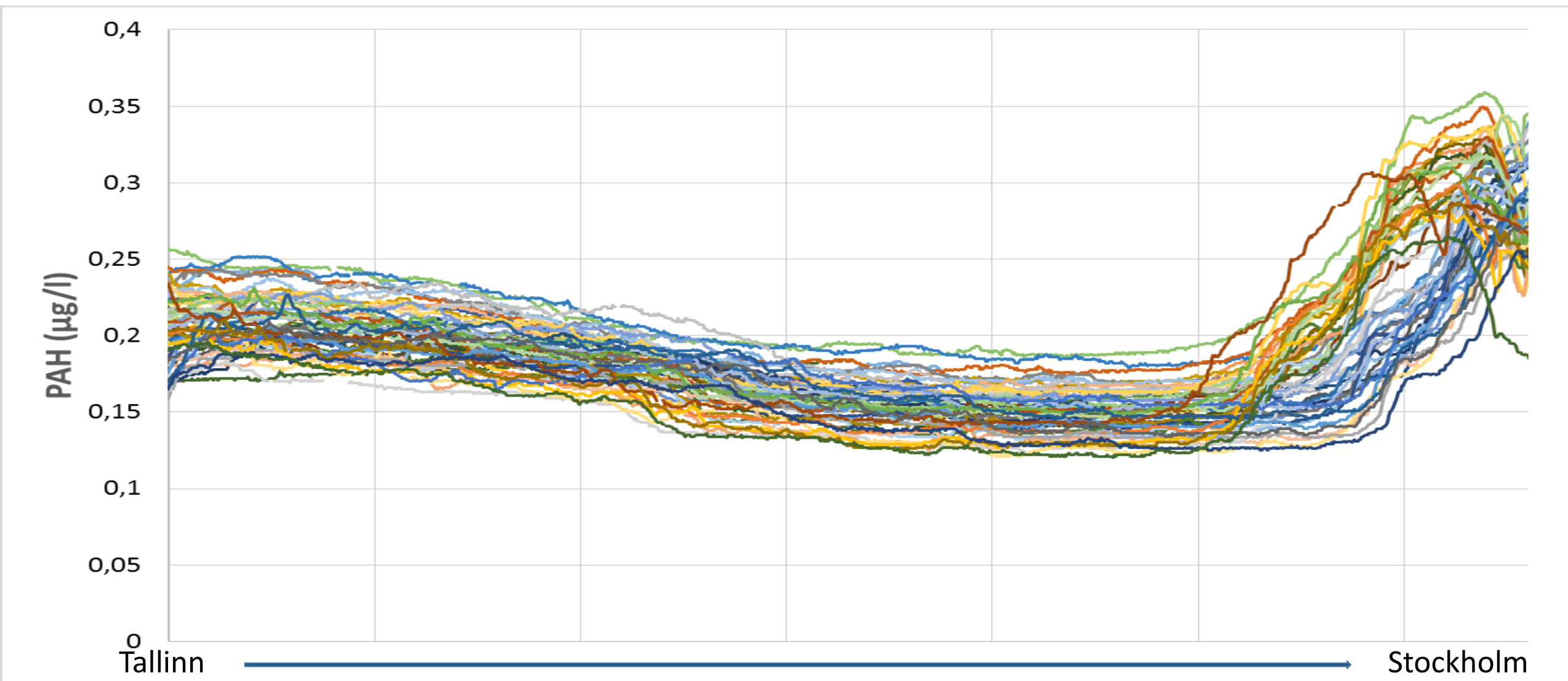
close P1: Oil compound PAH conc [ug/l] P2: Turbidity [FTU]

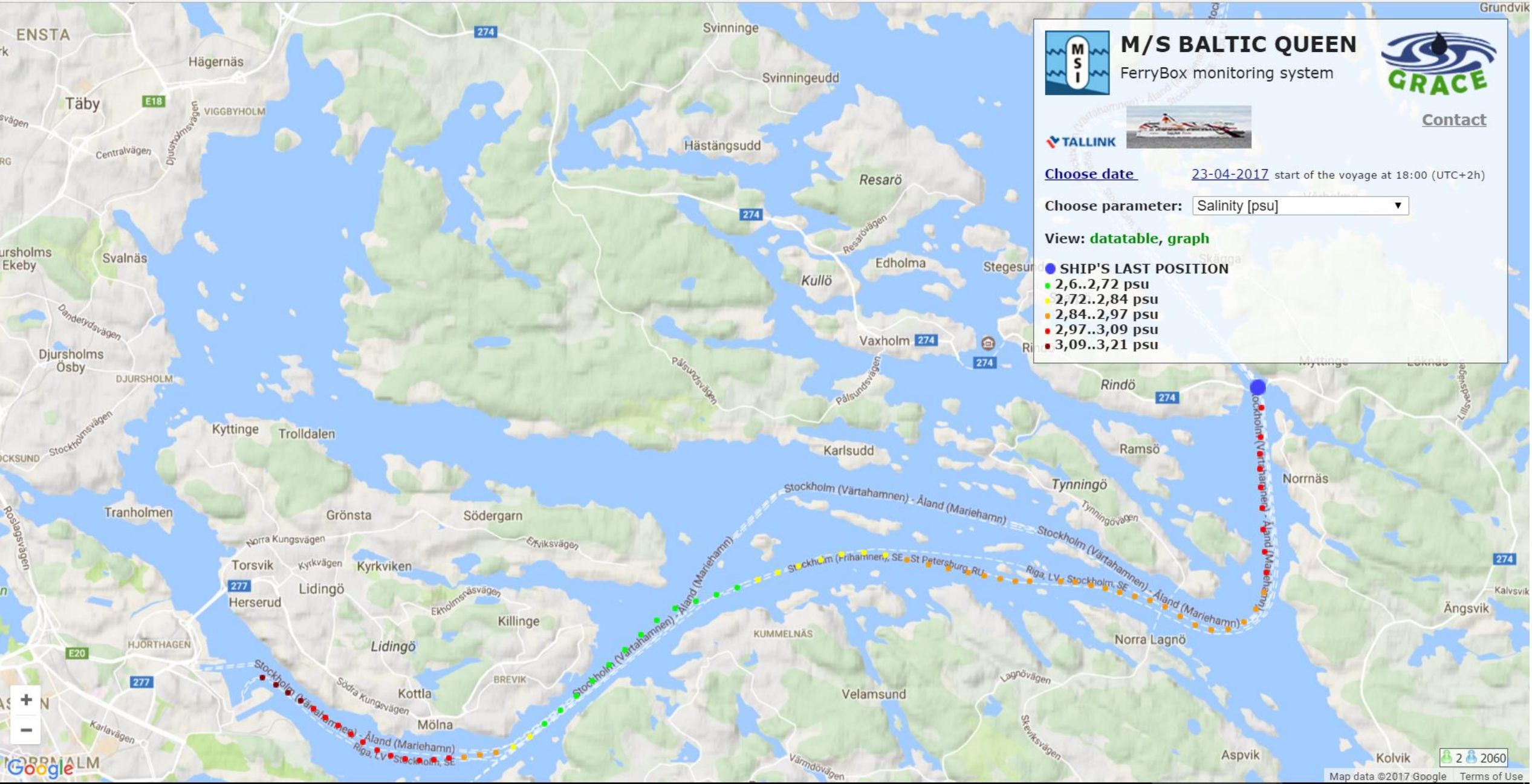
PAH conc (fluorescence) [ug/l] & Turbidity [FTU]



Variability of oil compound PAH concentrations

16.02.2017 – 11.04.2017







M/S BALTIC QUEEN

FerryBox monitoring system



[Contact](#)




[Choose date](#) 23-04-2017 start of the voyage at 18:00 (UTC+2h)

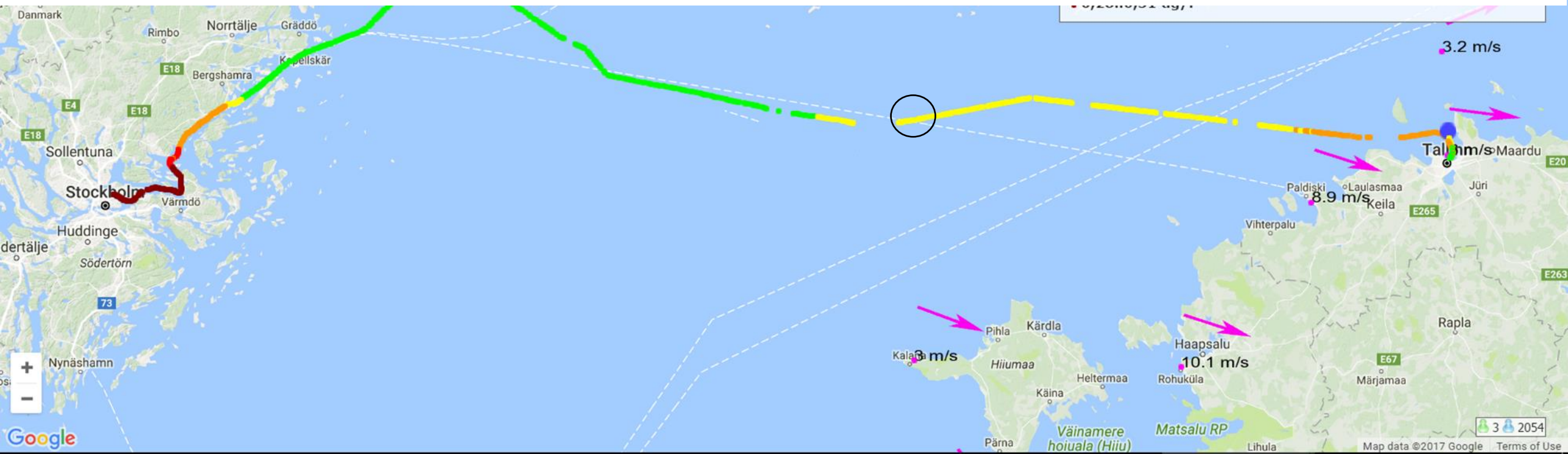
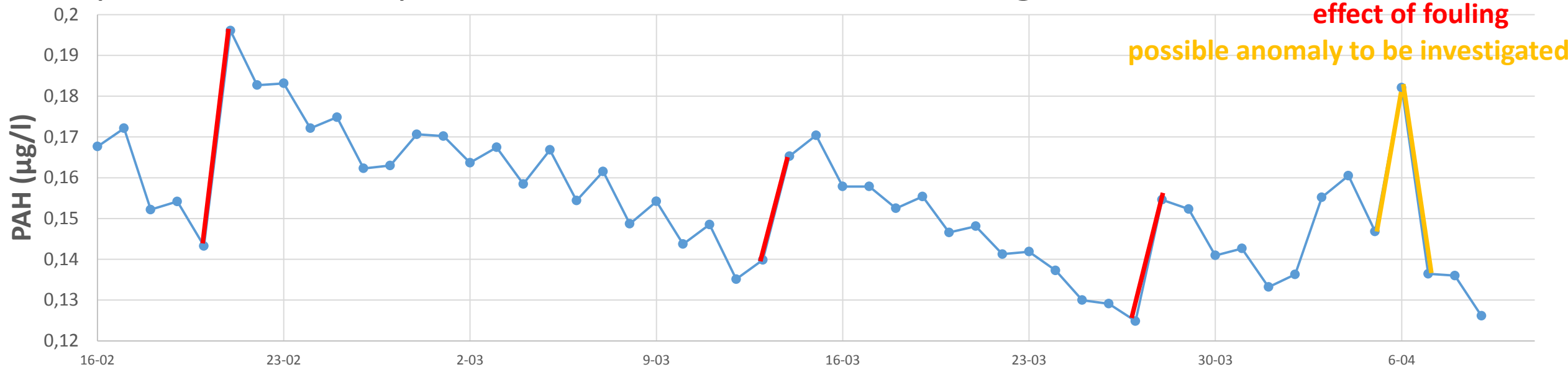
Choose parameter:

View: [datatable](#), [graph](#)

SHIP'S LAST POSITION

- 2,6..2,72 psu
- 2,72..2,84 psu
- 2,84..2,97 psu
- 2,97..3,09 psu
- 3,09..3,21 psu

Temporal variability of PAH concentrations in single locations



Comparison of UV fluorescence sensors

- UviLux UV-fluorometer measures oil compounds polycyclic aromatic hydrocarbons (PAH) concentrations (in terms of Carbazole). Sensitivity of the sensor is 0,005 $\mu\text{g/l}$ or 5ppt (**Carbazole**), calibrated range 0,005 – 2000 $\mu\text{g/l}$, excitation light 255nm and emission light 360nm.
- enviroFlu-HC measures PAH concentrations, in terms of Phenantrene. Sensitivity of the sensor is 0,3ppt (**Phenant** 500 ppb, excitation light 254nm and emissi

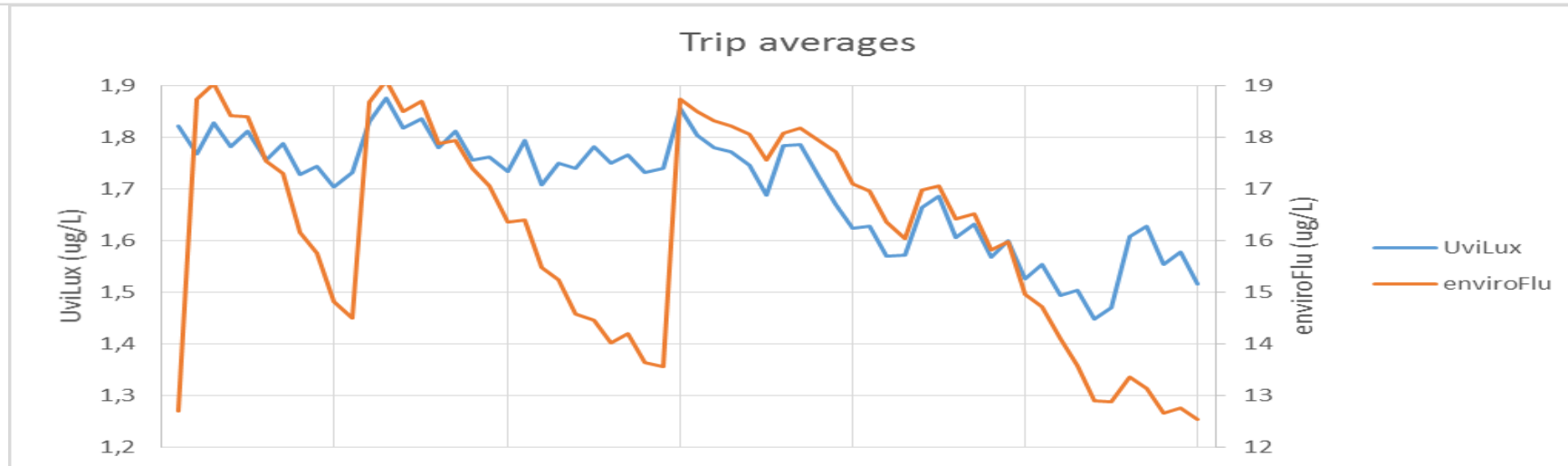
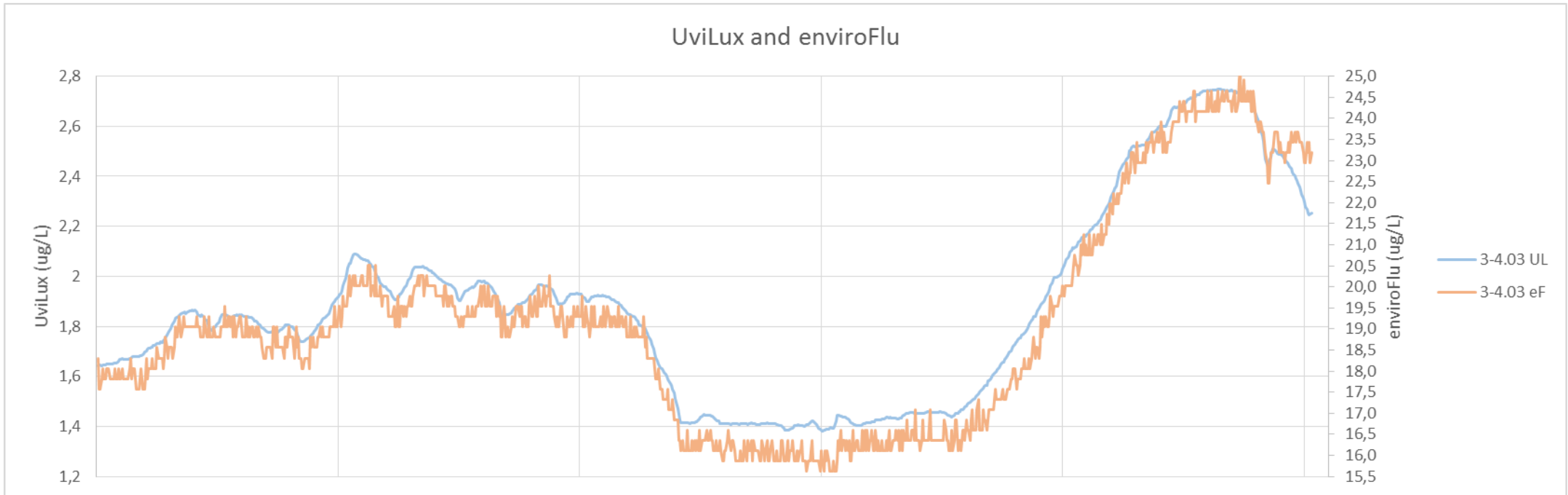


UviLux

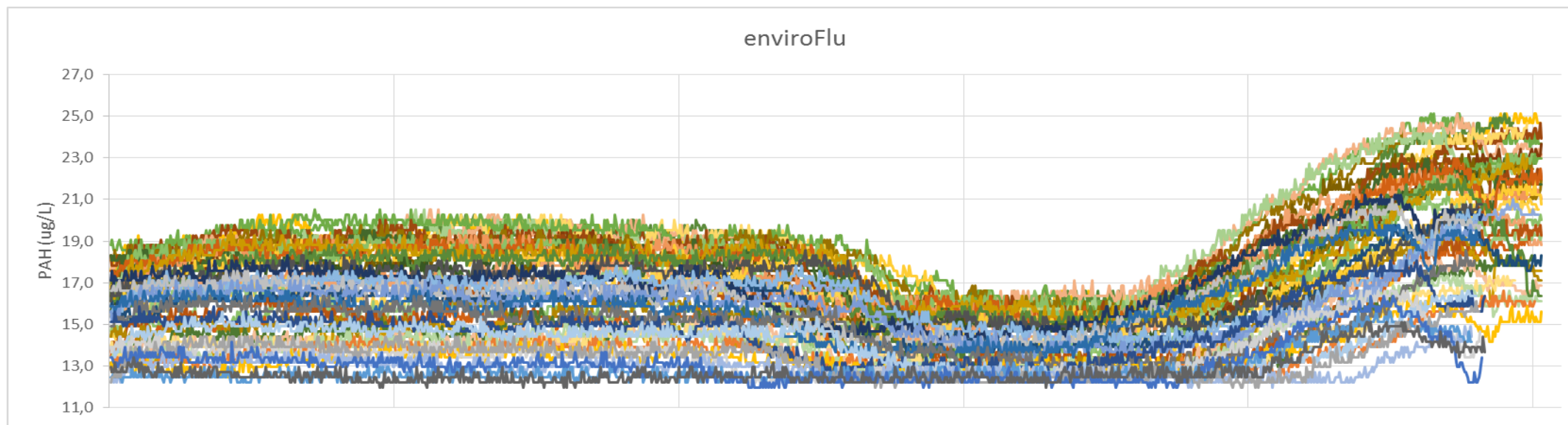
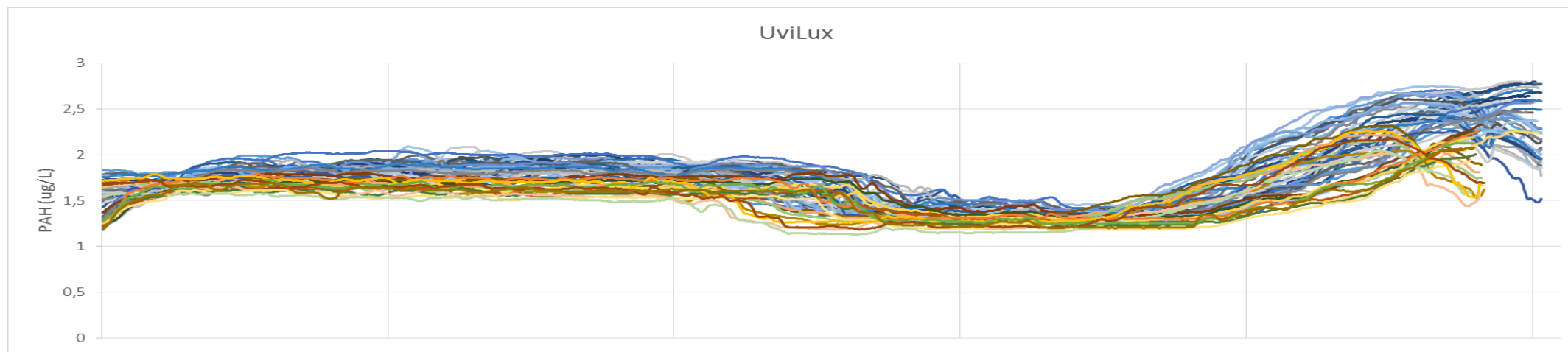


enviroFlu-HC

PAH concentration measurements with UviLux and Trios sensors

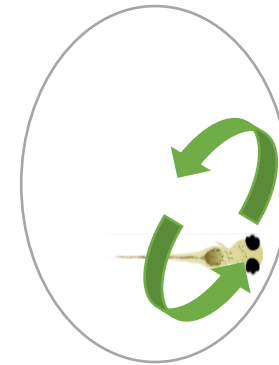
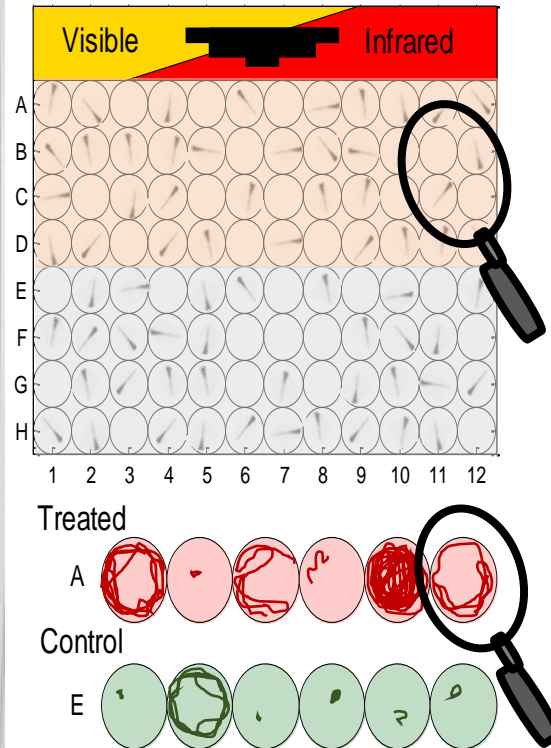
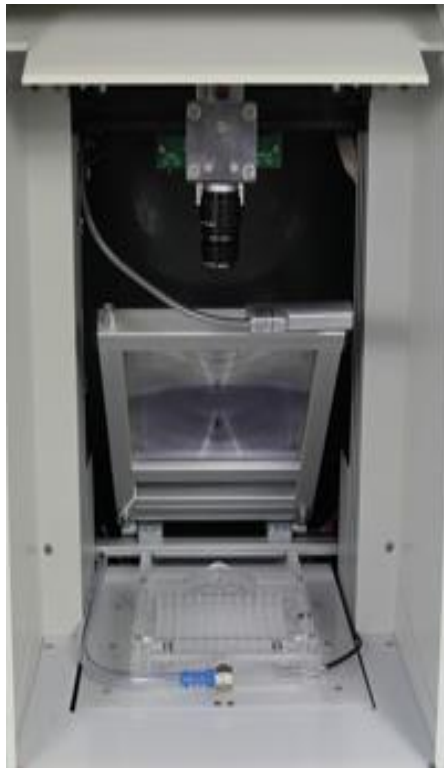


PAH concentration measurements with UviLux and Trios sensors

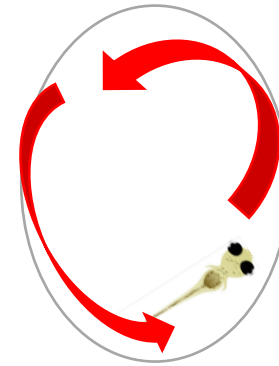


Tallinn  Stockholm

Novel Biosensor for FerryBox systems – Zebrafish embryo behavior



Control embryo

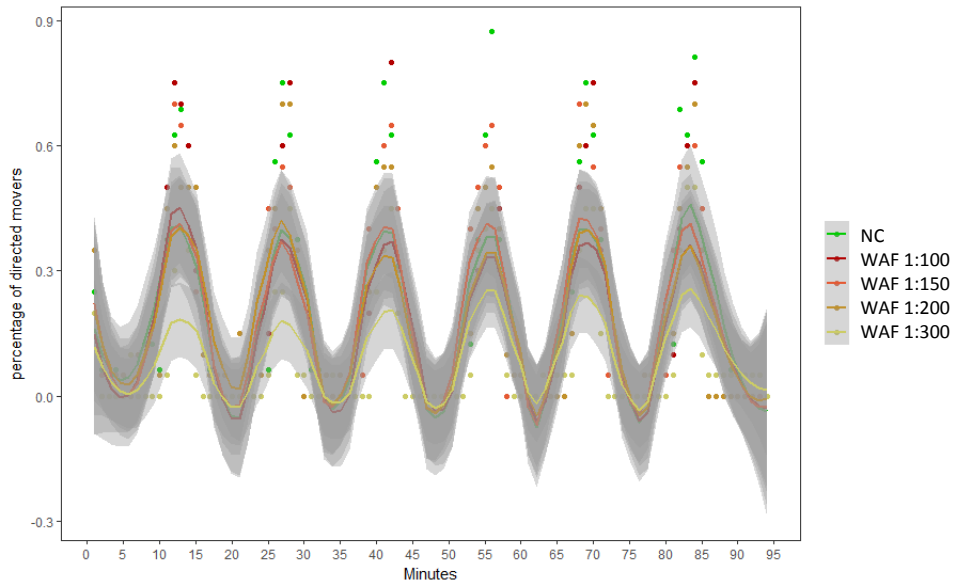


Embryo treated with toxicant show elevated movement levels

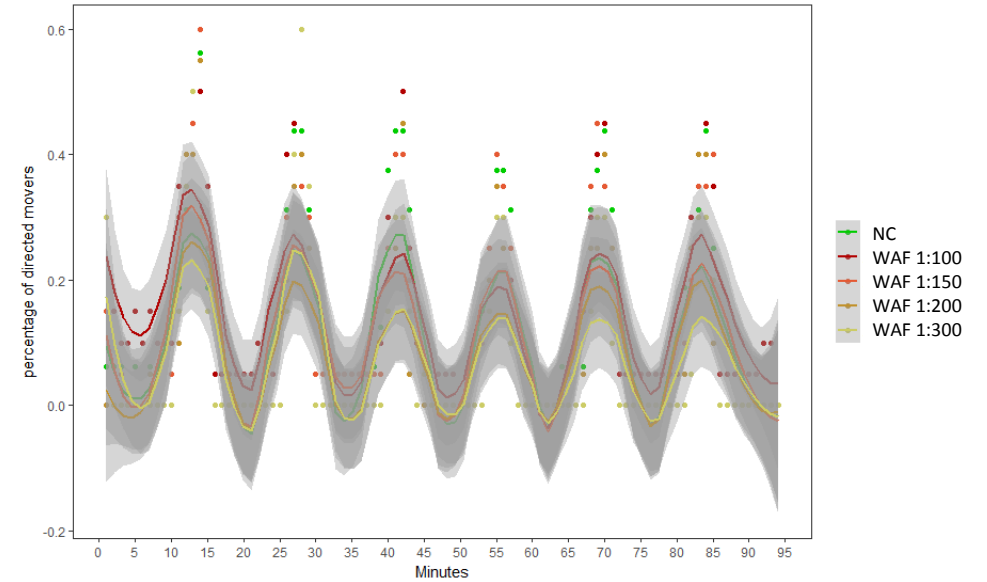
WAF exposure – effects on behavior

- Zebrafish embryos exposed to different WAF dilutions were tested
- Effects not clearly distinguishable from control activity
- Highest tested dilution 1:100
- Refined tests will be applied to test higher WAF levels

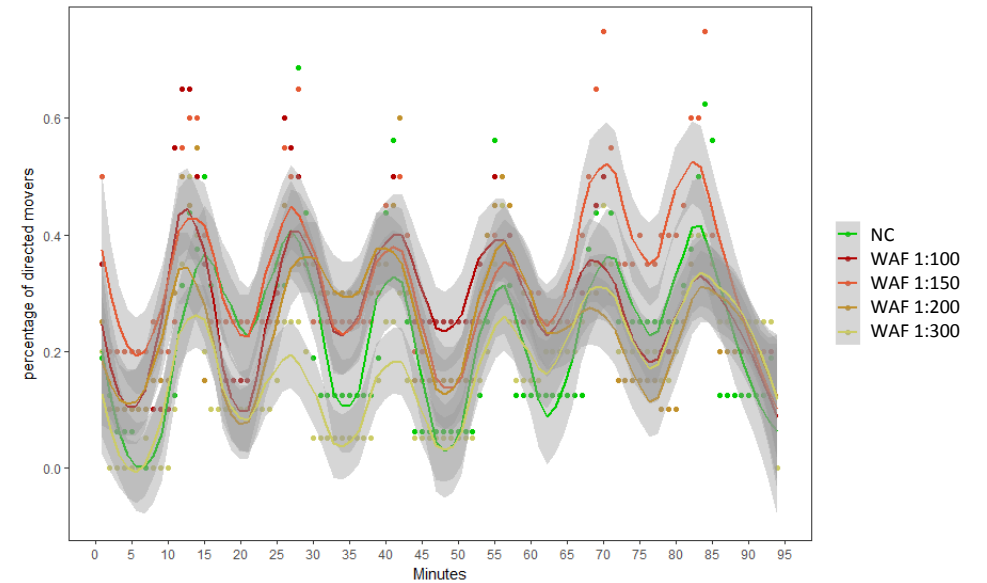
WAF replicate 3



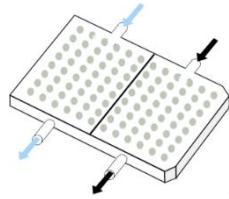
WAF replicate 1



WAF replicate 2



Biosensor – next steps



First prototype of customized flow through well plate available beginning of 2018

1. testing of salinity threshold under flow-through conditions
2. testing of WAFs under flow-through conditions
3. testing of model substances under flow-through conditions

-> Determination of sensitivity of the system

Summary

- All together 60 ship voyages were analysed (19.02 – 19.04.2018). PAH concentrations varied between 1-2,6 µg/L (**Carbazole**) and 12,4-25,5 µg/L (**Phenanthrene**)
- Measured PAH concentrations are not absolute values, but rather relative, still variability patterns can be estimated
- UviLux and enviroFlu Trios showed similar variability patterns
- No sudden concentration rises which directly would indicate the oil spills, have been detected during the test period, all PAH concentrations stayed below those defining an oil spill
- Pilot version of novel biosensor going to be integrated in MS BALTIC QUEEN FerryBox