Towards operational monitoring of ship emissions using Long Path Differential Optical Absorption Spectroscopy

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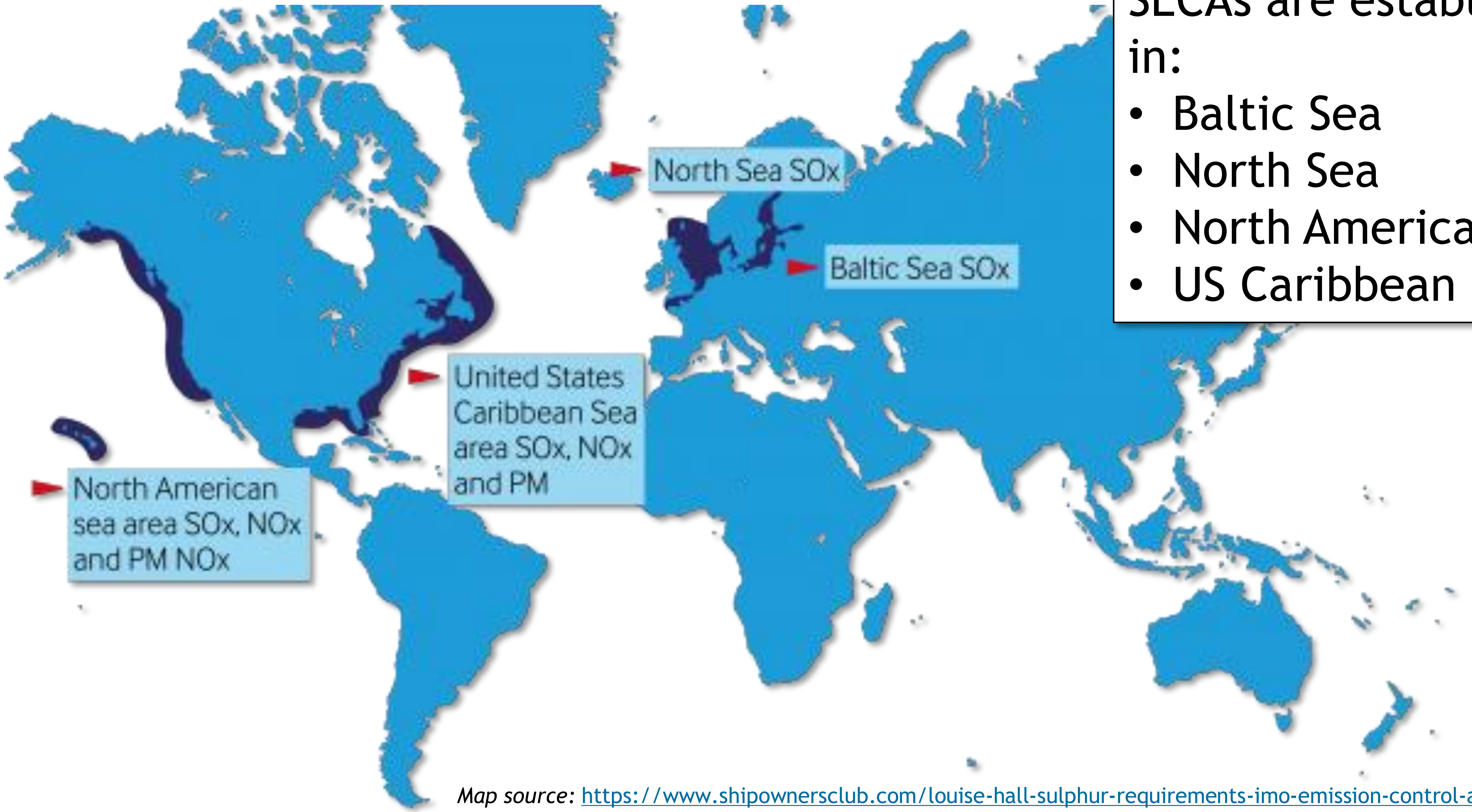
Emission Control Aeras (ECAs)



SECAs are established in:

- Baltic Sea
- North Sea
- North American Area
- US Caribbean Sea

Map source: https://www.shipownersclub.com/louise-hall-sulphur-requirements-imo-emission-control-areas/

Emission Control Aeras (ECAs)

- MARPOL Annex IV by IMO regulates the emission of air pollutants by ships [1]
- Ship emissions of Sulphur compounds SO_x (mainly SO2) are limited within Sulphur (S)ECAs
- Implies limitation of Sulphur fuel content (SFC) to **0.1% m/m inside** and to **0.5% m/m** outside of SECAs [2]
- Limitation of NO_x emissions for diesel engines of over 130kW output within ECAs depending on ship construction date

Table source [2]

Tier	Ship construction date on or after	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		n < 130	n = 130 - 1999	n ≥ 2000
I	1 January 2000	17.0	$45 \cdot n^{(-0.2)}$ e.g., 720 rpm – 12.1	9.8
II	1 January 2011	14.4	$44 \cdot n^{(-0.23)}$ e.g., 720 rpm – 9.7	7.7
III	1 January 2016	3.4	$9 \cdot n^{(-0.2)}$ e.g., 720 rpm – 2.4	2.0

Tier III limits apply within NO_x ECAs, Tier II outside of ECAs

[1] www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Air-Pollution.aspx
[2] www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)---Regulation-14.aspx
[3] www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Nitrogen-oxides-(NOx)---Regulation-13.aspx

Controlling ECA compliance

Compliance with MARPOL regulations demands:

- Use of refined **expensive marine diesel oil** (low Sulphur content) instead of heavy fuel oil
- Upgrading ships with scrubber units to reduce Sulphur emissions (need to be continuously washed with sea water)
- Application of Selective Catalytic Reduction (SCR) for removal of NOx in exhaust gas (needs ammonia as additional consumable)

➢ ECAs increase ship operation costs

➢ Reliable evidence for violations only possible by fuel sample

  - Expense limits efficient control

➢ **Alternative continuous monitoring can increase control efficiency for suspicious ships**

Sulphur fuel content (SFC) from exhaust gases

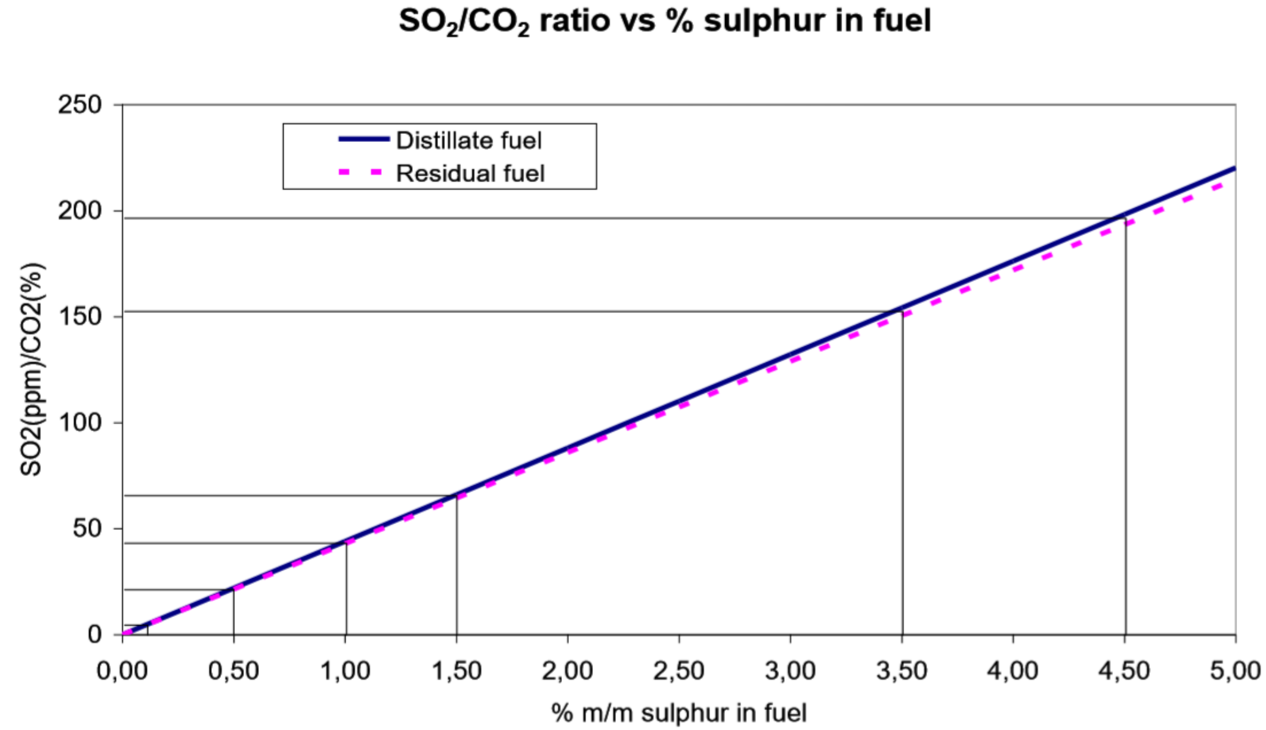
CO_2 in plume is correlated to the amount of burned fuel (carbon fuel content 87%, [1])

→ SO_2/CO_2 ratio indicates SFC (Sulphur per burned fuel (mass/mass))

$$\mathrm{SFC}\,[\%] = \frac{\mathrm{S}\,[\mathrm{kg}]}{\mathrm{fuel}\,[\mathrm{kg}]} = \frac{\mathrm{SO_2}\,[\mathrm{ppm}] \cdot \mathrm{A(S)}}{\mathrm{CO_2}\,[\mathrm{ppm}] \cdot \mathrm{A(C)}} \cdot 87\,[\%] = \frac{\mathrm{SO_2}\,[\mathrm{ppb}]}{\mathrm{CO_2}\,[\mathrm{ppm}]} \cdot 0.232\,[\%],$$

A(S), A(C) = atomic weight of S and C, resp.

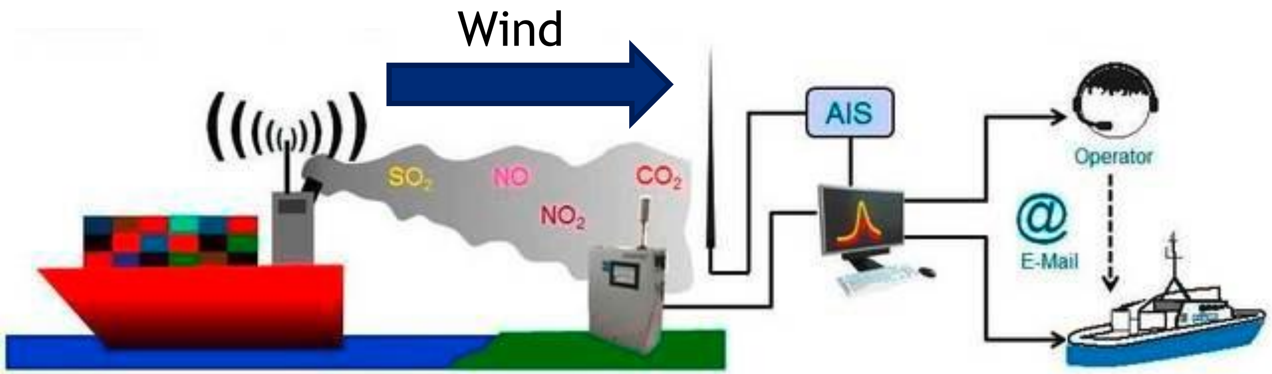
Adapted from [2]



Taken from ANNEX 1 RESOLUTION MEPC.259(68) (adopted on 15 May 2015) 2015 GUIDELINES FOR EXHAUST GAS CLEANING SYSTEMS

[1] Cooper et al.: Exhaust emissions from ships at berth, Atmos. Environ., 37, 3817–3830, 2003
[2] Kattner, L. et al.: Monitoring compliance with sulfur content regulations of shipping fuel by in situ measurements of ship emissions, Atmos. Chem. Phys., 15, 10087–10092, 2015.

SFC monitoring using in situ instruments on shoreline



https://www.bsh.de/DE/THEMEN/Beobachtungssysteme/Schiffsabgasmessnetz/schiffsabgasmessnetz_node.html

Currently applied by Federal Hydrographic agency (BSH) and IUP Bremen (MESMART project www.mesmart.de)

Advantage

- Multi-component measurements (SO_2, NO_x, CO_2, O_3).

▫ Direct monitoring of:

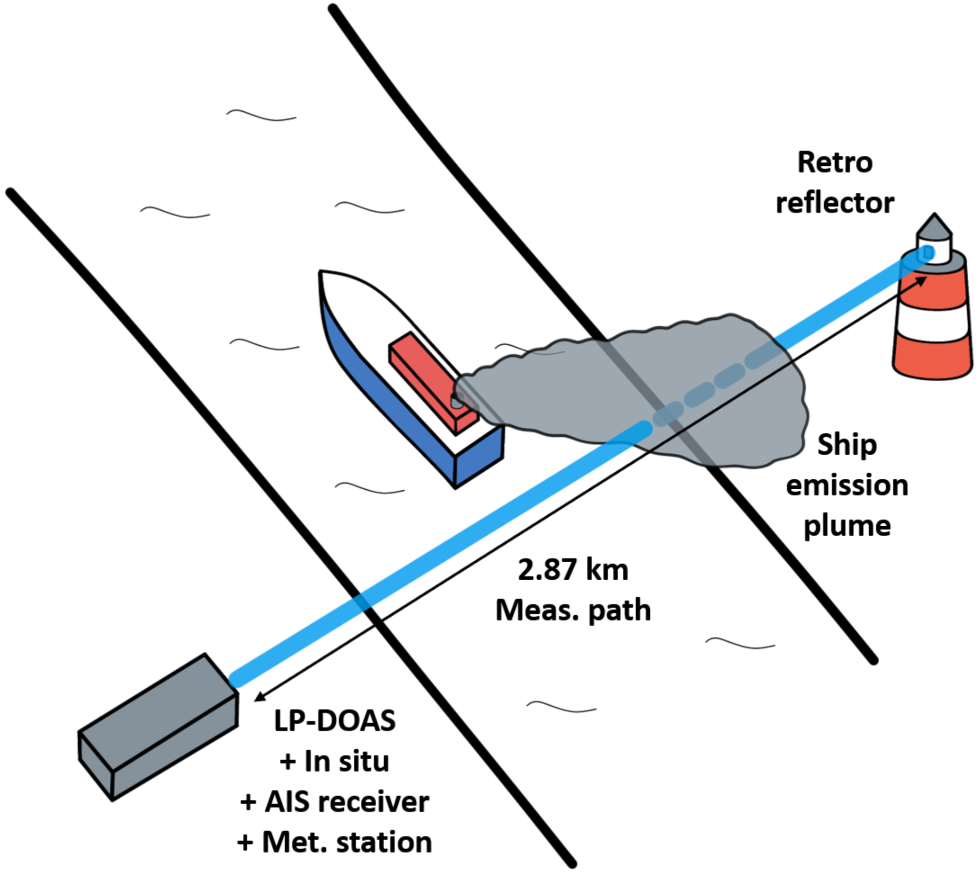
- Sulphur fuel content (SO_2/CO_2)
- Emission factors for NO_x (NO_x/CO_2)

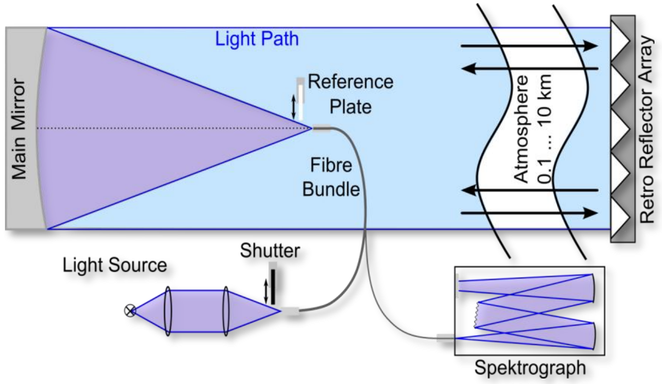
Disadvantage

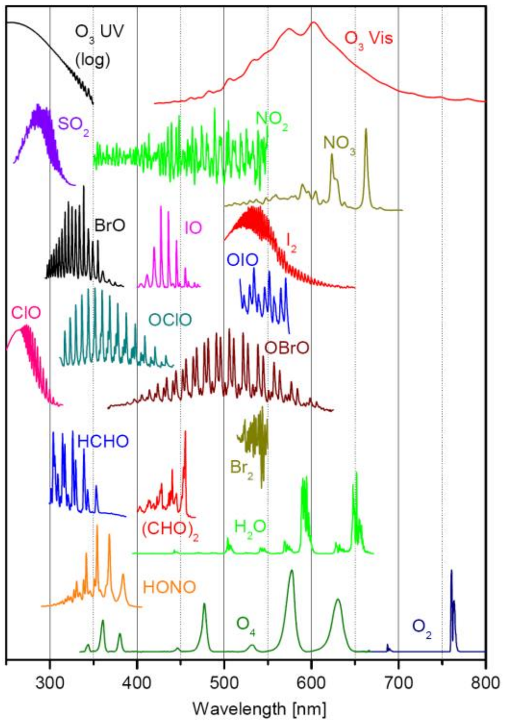
- Relies on meteorological transport of emission plume (backward trajectories), limitation by wind direction and speed
- Plume dilution during travel time reduces signal strength

→ Valid signal only for few passing ships

Using Long Path-DOAS for ship plume monitoring







Top: Scheme of an LP-DOAS instrument.

Right: Trace gases with differential absorption features which can be detected with the DOAS method.

- **Remote sensing** of atmospheric trace gases like NO2, SO2, O3 using Differential Optical Absorption Spectroscopy (DOAS) [1]

[1] Nasse et al., 2019, https://doi.org/10.5194/amt-12-4149-2019

- Measurements of ship plumes in **close proximity to point of emission**
- Application at harbour entrances (usually 500 to 1000m width) or rivers (for inland shipping)

Introduction of novel commercial LP-DOAS instrument

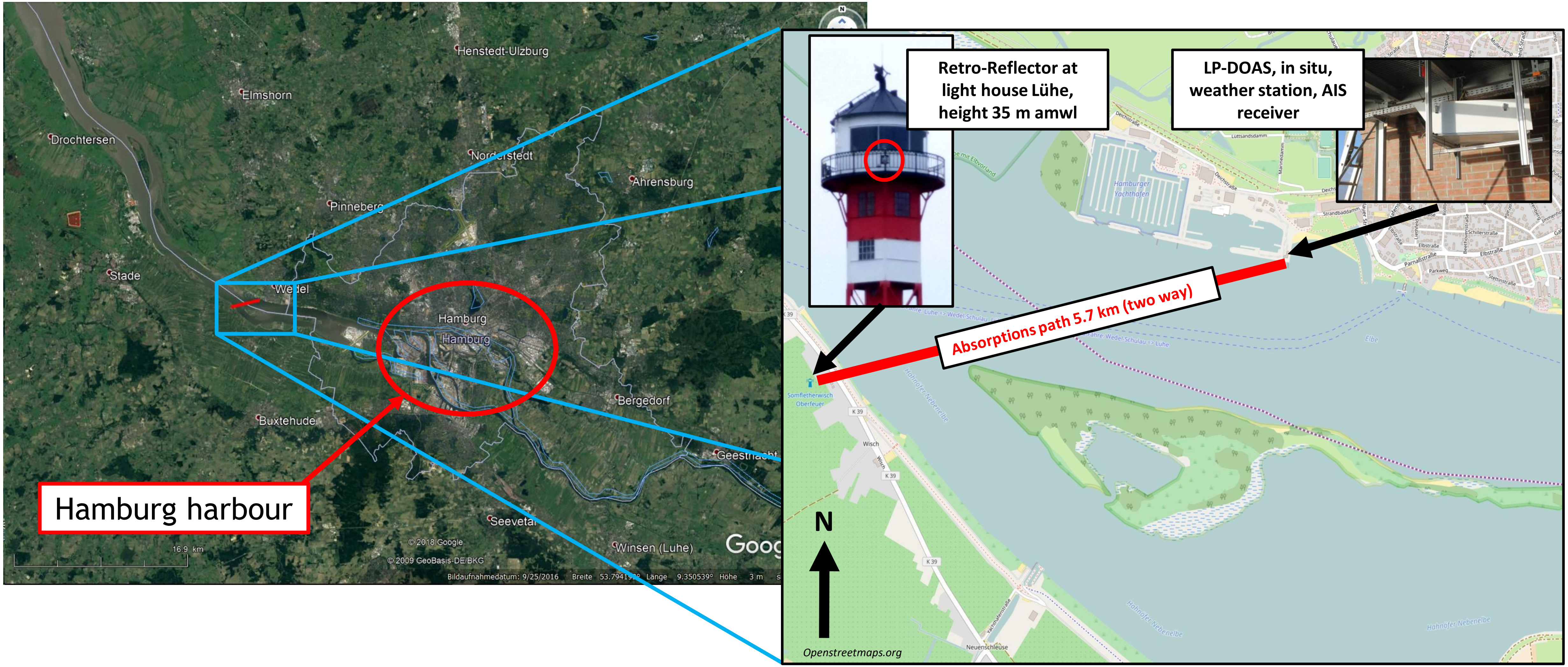
- Spin-Off from Institute of environmental Physics, University of Heidelberg (https://airyx.de/).
- Focused on development of commercial DOAS instruments.

Instrument specifications:

Dimensions	70x35x60 cm^3
Weight	<10 kg
Power consumption	<100W
Detectable species (simultaneous)	NO_2, SO_2, O_3, HCHO, HONO, H_2O
Light source	High power broadband laser driven xenon arc lamp
Time resolution	1-3 seconds
Meas. Path lengths	100 – 3000 m
Spectral range / resolution	310-465 nm / 0.8 nm
Calibration gases	Not required
Telescope adjustment	Automatic path alignment

Airyx LP-DOAS at Elbe river currently operated by K. Krause and F. Wittrock of IUP Bremen in cooperation with BSH (Federal Hydrographic Agency, Germany).

Six weeks of LP-DOAS measurements of ship plumes near Hamburg harbour



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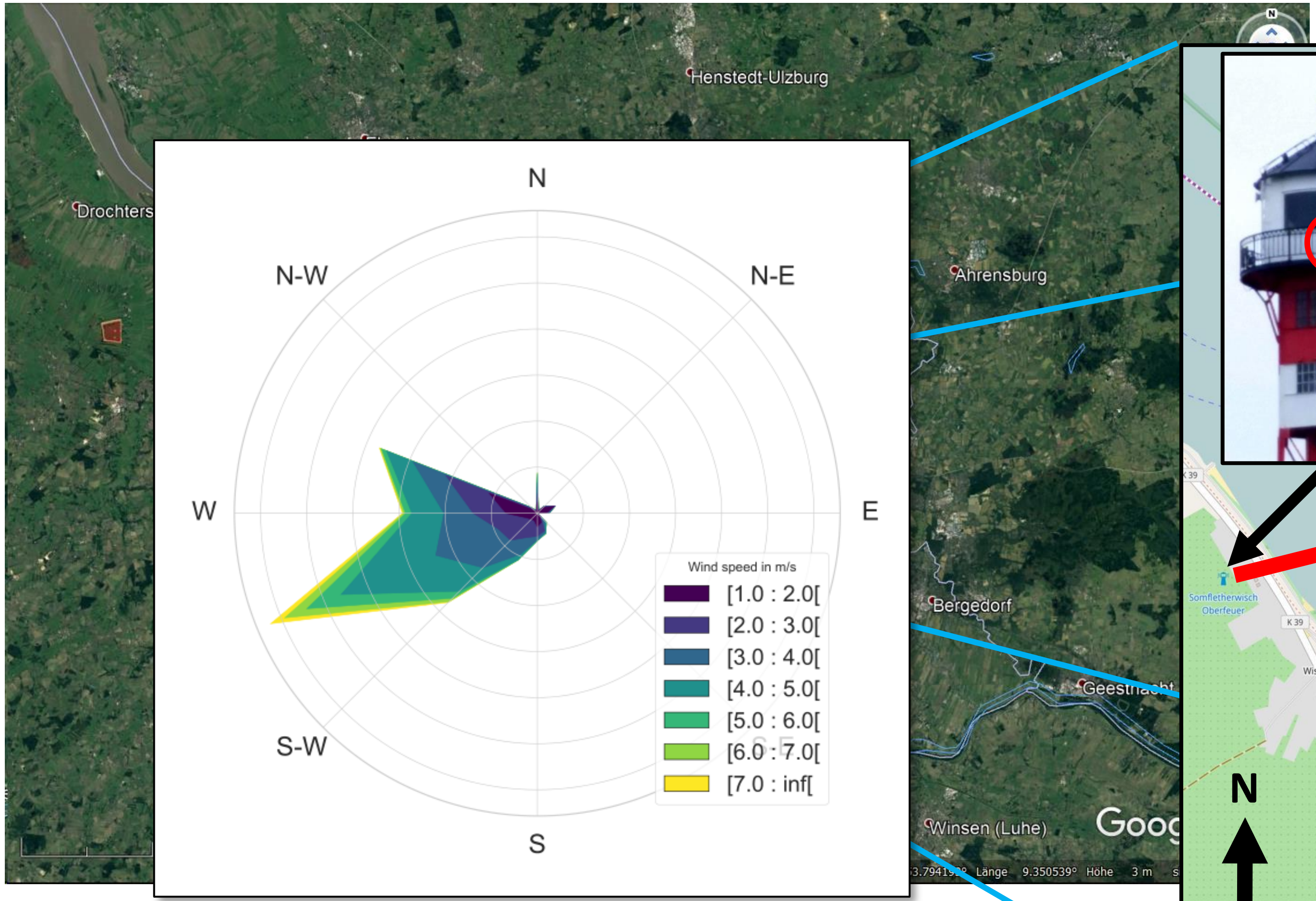
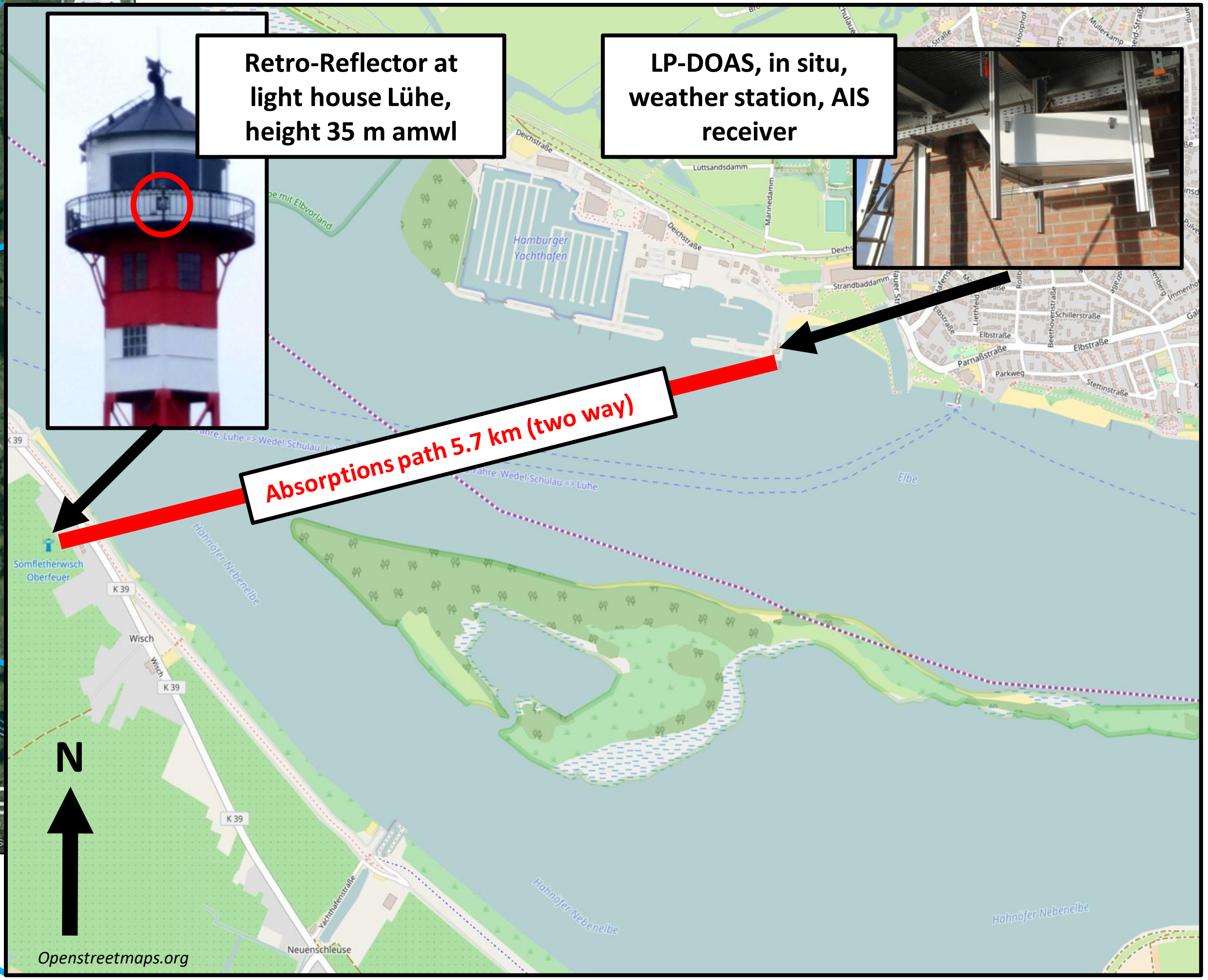
Six weeks of LP-DOAS measurements of ship plumes near Hamburg harbour





Wind conditions during measurement period.

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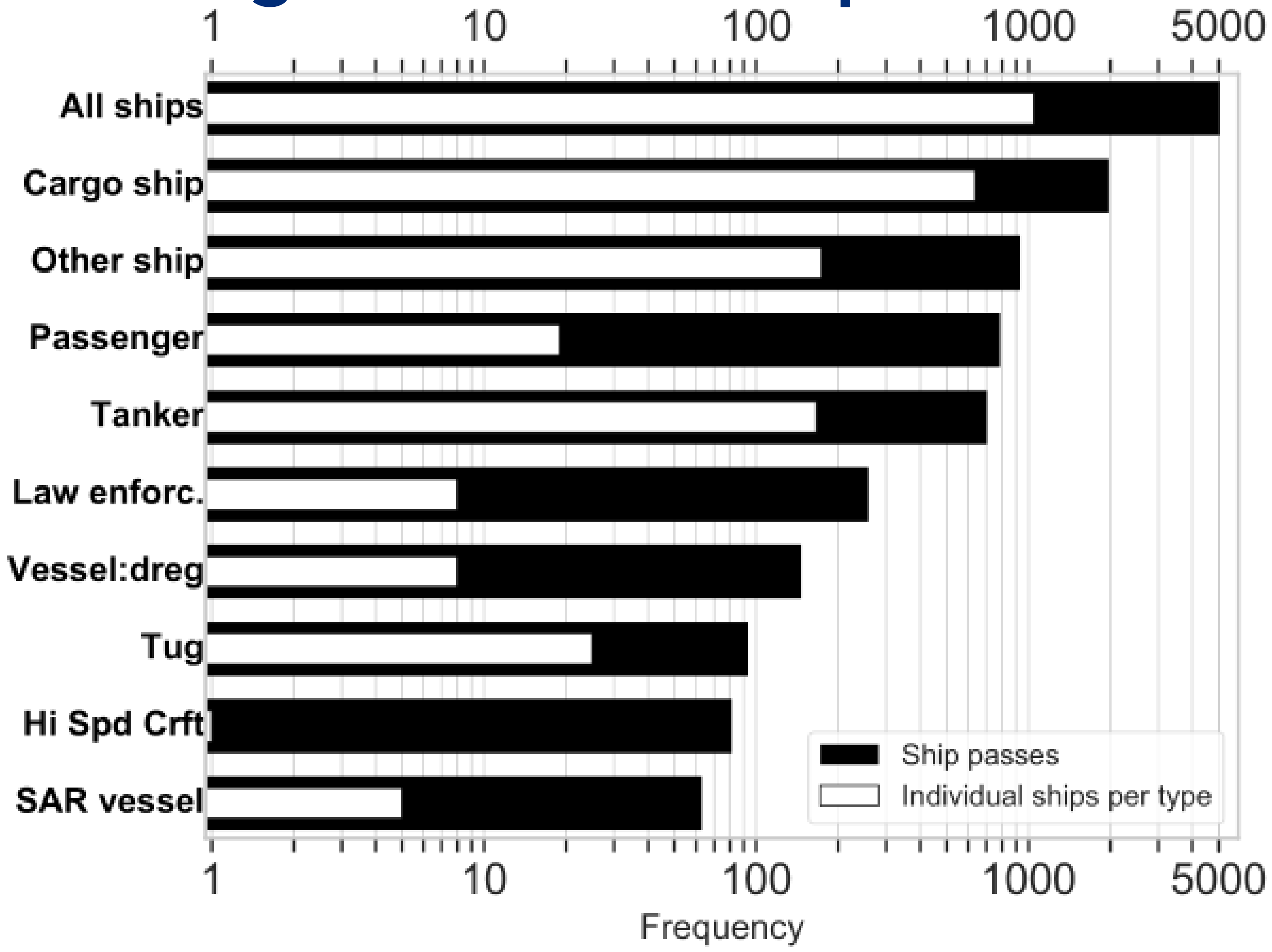
Distribution of ship types passing the measurement site during measurement period



- Frequency distribution of ships separated by types passing the instruments during the measurement period.
- Occurrences are displayed on a log-scale for the sake of readability.
- **Black bars** represent the total number of **ship passes** while white bars represent the total number of individual ships. (Some ships frequently passed the measurement site during the measurement period, e.g. ferries)

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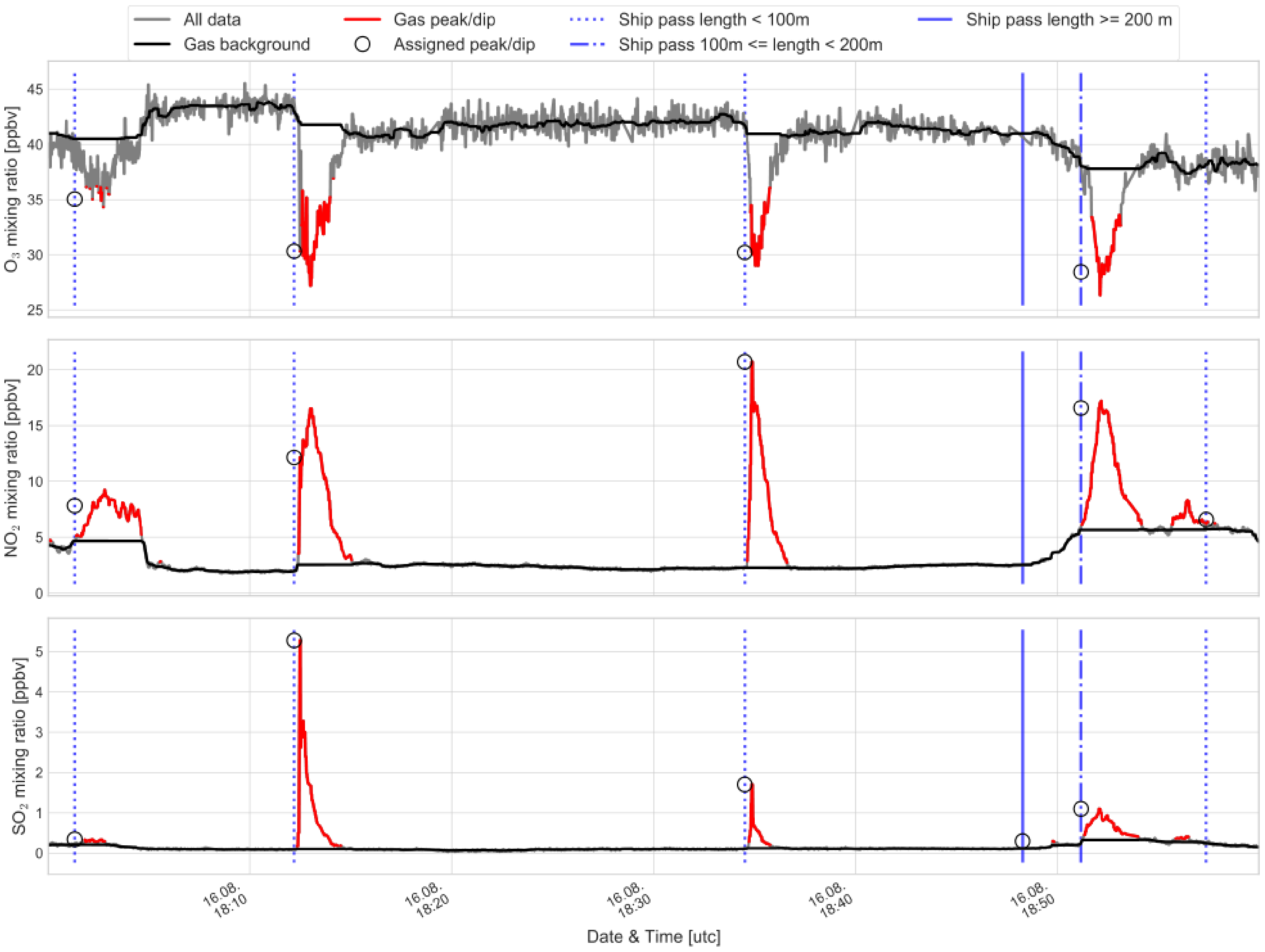
Assignment of LP-DOAS data to ship emission plumes



- Identification of background concentrations (low pass filtered data □ running median with appropriate window size)
- If data differs 2*sigma from background □ plume data (red)
- If peak data is within time window prior (30sec) or posterior (60 sec) of a single ship pass, it is assigned to that particular ship.
- Ozone dips correlate with NO_2 peaks and indicate strong NO to NO_2 titration while plume dilutes (Diesel engine NO_x emissions are dominated by NO)

➢ **Quantification of NO_x using NO_2 is problematic since depending on plume travel time and O_3 availability!**

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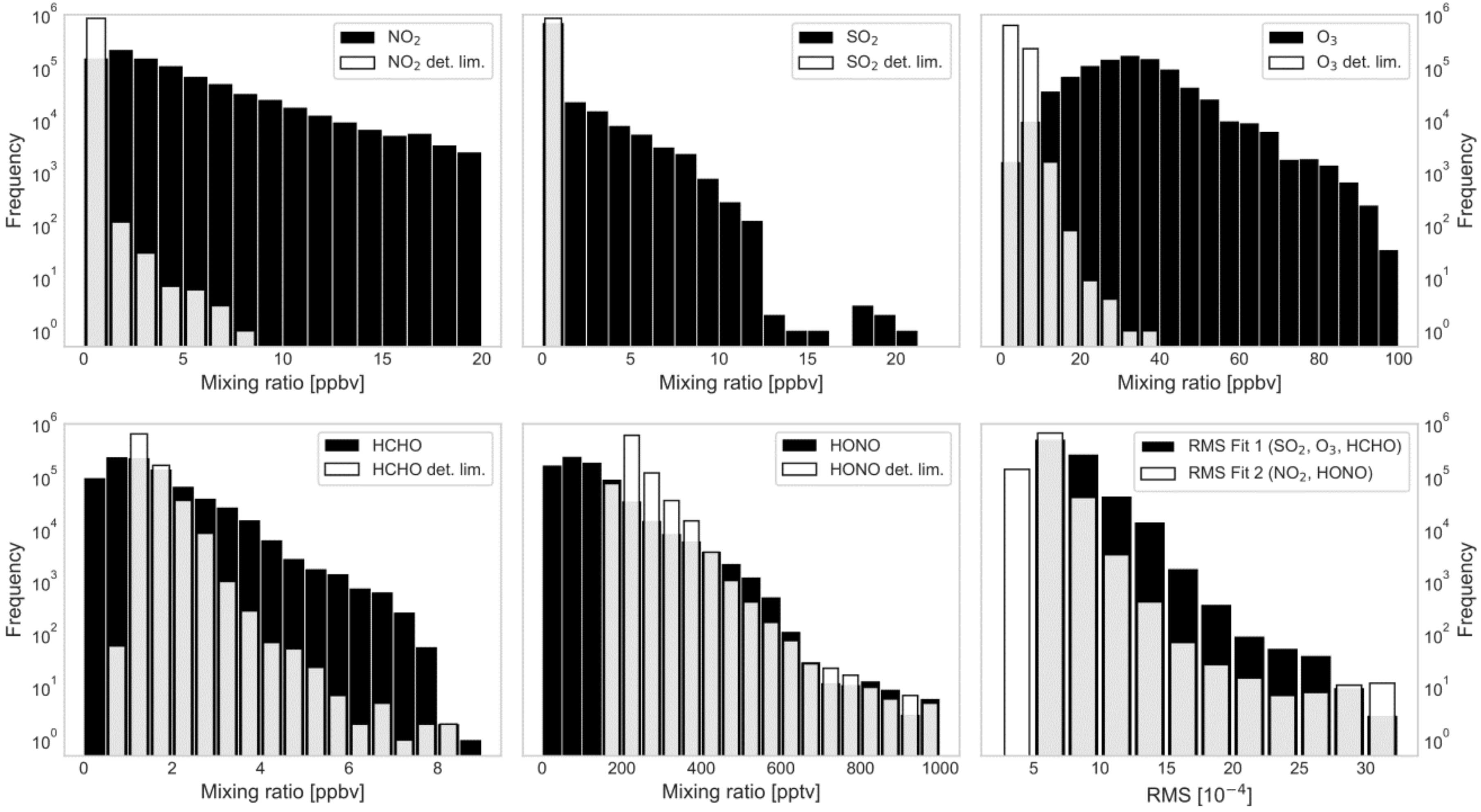
Performance of the LP-DOAS instrument



Histograms of 6 weeks of LP-DOAS data. RMS from DOAS fit of two spectral windows (297-309 and 334.5-356.6 nm)

- Time resolution: 1 to 3 seconds
- Total measurement path length: 5.74 km
- SO_2, NO_2 signal to noise ratio meets requirements of plume monitoring
- No significant detection of HCHO in plumes

Average detection limits [ppbv]

SO_2	0.08
NO_2	0.44
O_3	4.85
HCHO	1.44
HONO	0.24

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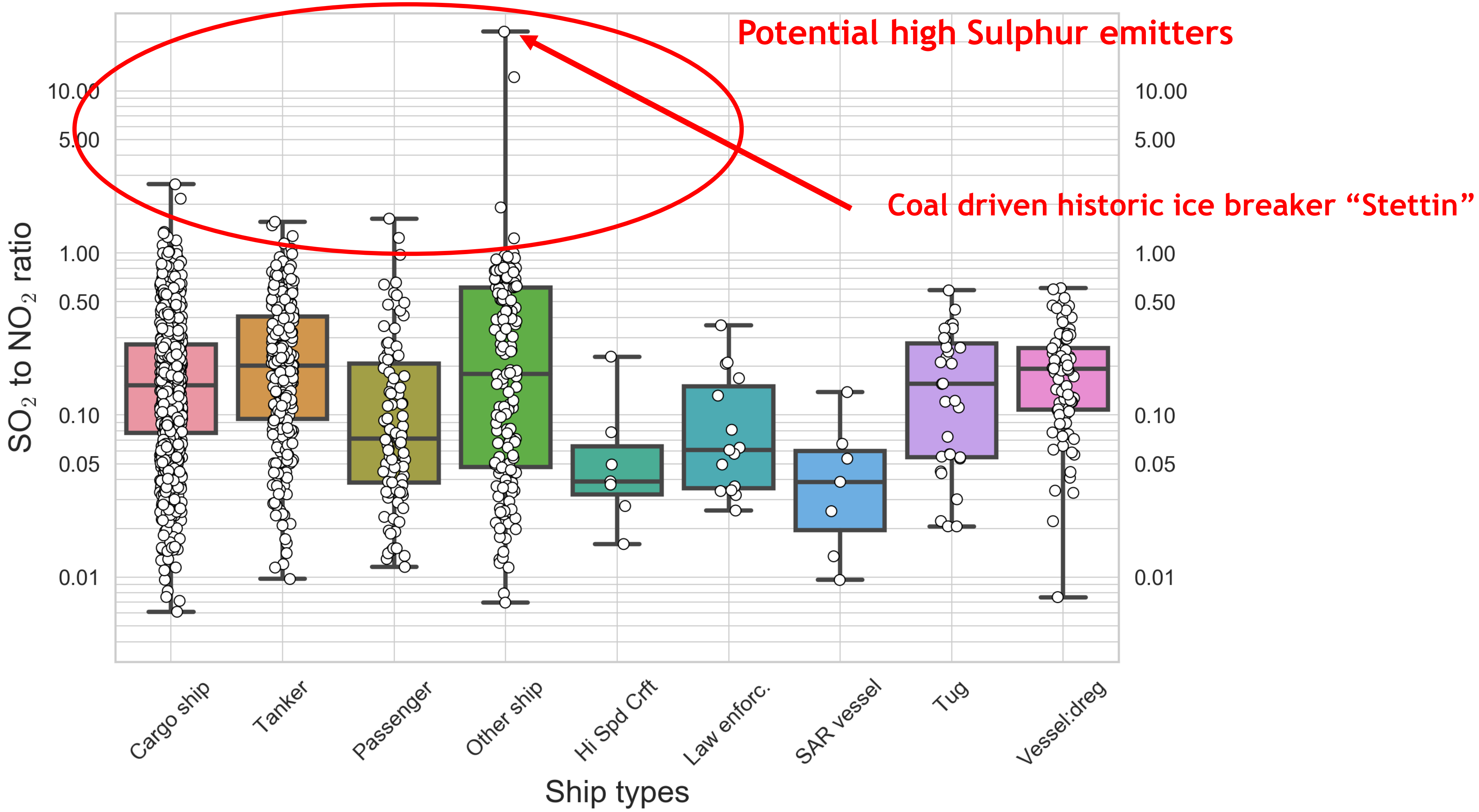
SO2 / NO2 ratios from LP-DOAS data



Each point represents a particular ship. Boxes show median and 25 and 75 percentile.

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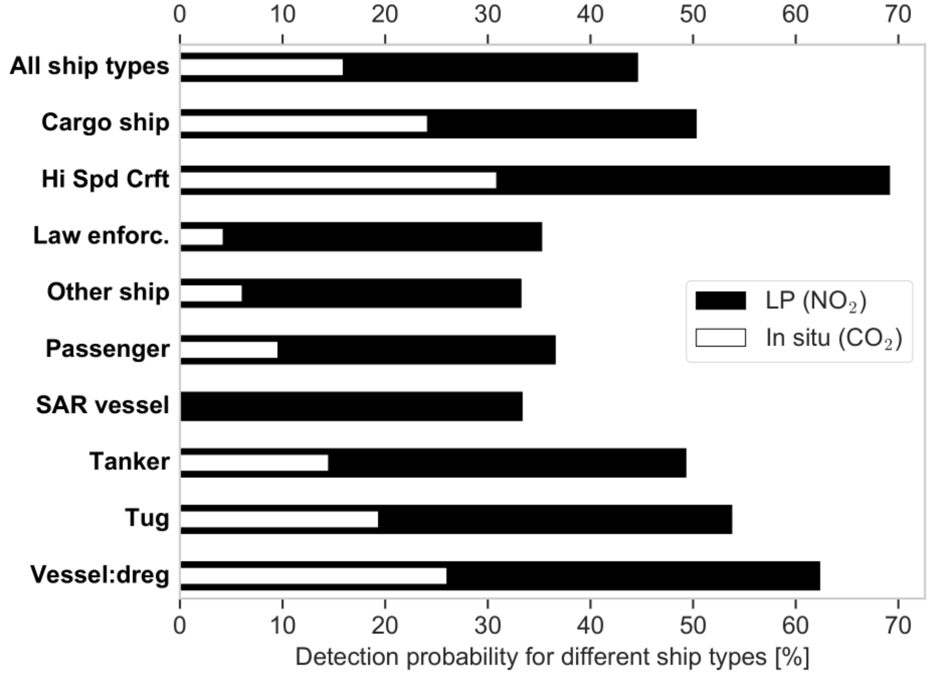
Plume detection yield - LP-DOAS vs in situ

- Using ships with high number of passes as "benchmark" ships
- Detection yield = ratio of successful ship detections (via NO_2 for LP and CO_2 for in situ) and total number of ship passes for each benchmark ship
- For larger ships (length>50m) the yield for LP-DOAS is approx. three times higher than for in situ
- Smaller ships are barely detected by in situ
  → Smaller engines, weaker emission signature
  → Plume transport/dilution leads to insignificant signal, thus no ship assignment
- **Averaged detection yields for all ship types:**
  - **In situ: 16%**
  - **LP-DOAS: 44%**

Benchmark ship [type]	Ship Length [m]	Ship passes	Det. yield [%] IS CO_2	Det. yield [%] LP NO_2
Dredging vessel	152	109	29	64
Dredging vessel	95	92	27	56
High Speed Craft	51	71	30	69
Dredging vessel	40	72	0	27
Passenger	34	590	7	35
Law enforcer	30	90	3	36
Law enforcer	24	75	3	31



Bar plot: Detection yields for LP (black bars) and in situ (white bars) for all ships

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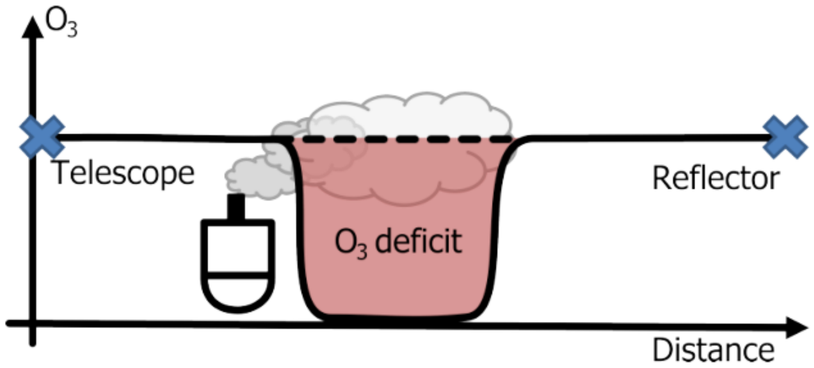
Estimation of emission strengths from LP-DOAS

NO excess in plume → Plume is O3 free



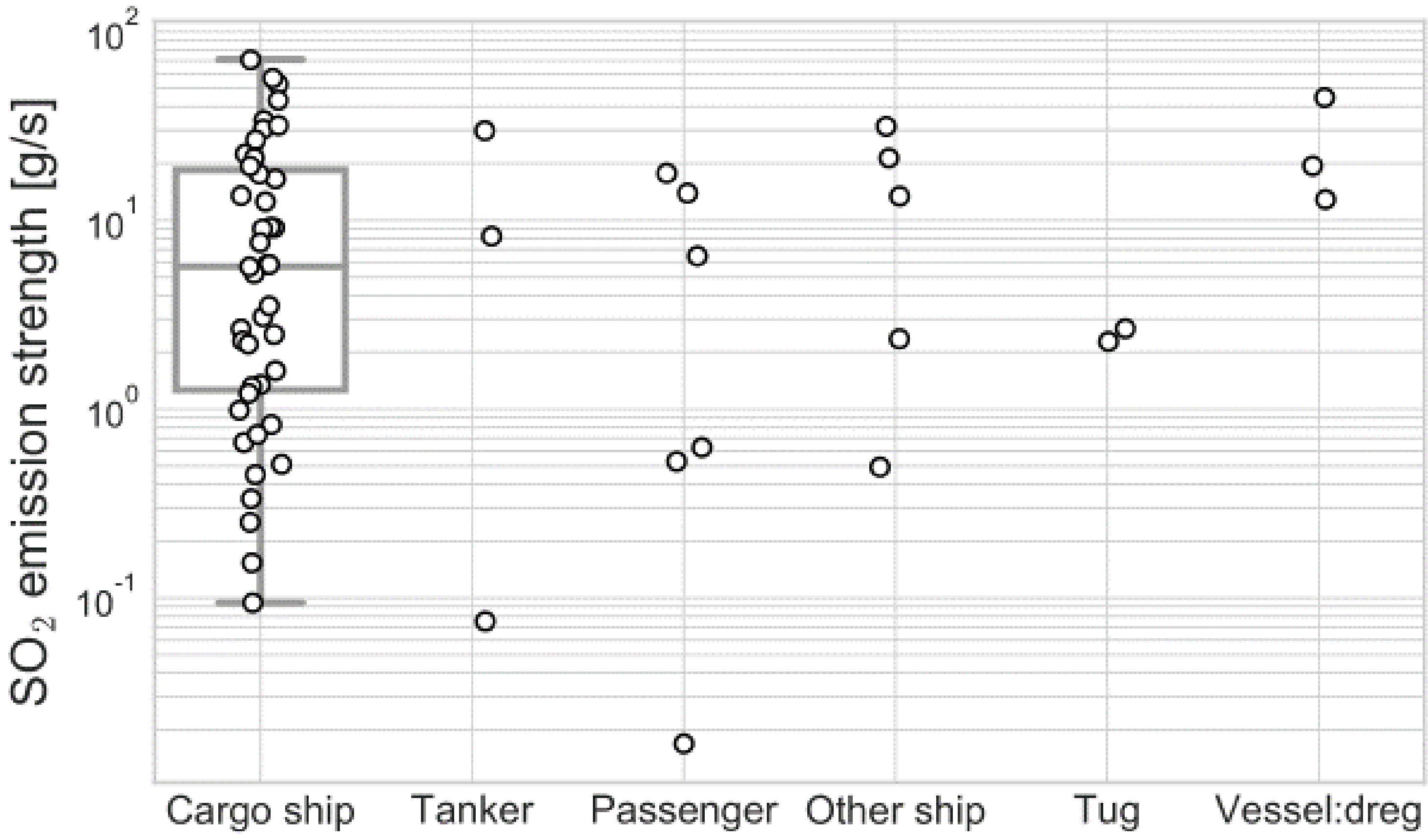
- Estimate plume width P from ozone decrease dO3 (see slide #12) using: P = L (dO3 / O3_bg)

- Apply simple gaussian dispersion model to estimate source strength Q:

$$C(x,y,z;H) = \frac{Q}{2\pi\sigma_y\sigma_z\,\mathrm{u}_r}\exp\left(-\frac{y^2}{2\sigma_y^2}\right)\cdot$$
$$\left\{\exp\left(-\frac{(z-H)^2}{2\sigma_z^2}\right)+\exp\left(-\frac{(z+H)^2}{2\sigma_z^2}\right)\right\}$$

$\Rightarrow Q$

Method under development.



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Conclusion

- **Operational monitoring** of ship emissions with LP-DOAS is feasible
- No dependency on meteorological plume transport enables **higher detection yields compared with in situ (44% vs 16%)**
- Measurement path lengths (2-3 km) suitable for most harbour entrance widths
- Fast measurement response of 2-3 seconds sufficient fast for passing ships
- Automatic measurement with low maintenance and no required consumables (no calibration gases needed) allow simple long term monitoring

- Planed system extensions: **derive precise emission factors**
  - **simultaneous measurement of CO_2 and NO** (not possible with current LP-DOAS setup)