Evaluation of the correlation of oceanic water parameters unmasked by representative sampling and sample analysis uncertainty

Carlos Borges[1], Carla Palma[1], Ricardo Silva[2]

[1] Instituto Hidrográfico, R. Trinas 49, 1249-093 Lisboa, Portugal; carlos.borges@hidrografico,pt; carla.palma@hidrografico.pt

[2] Centro de Química Estrutural – Faculdade de Ciências da Universidade de Lisboa, Edifício C8, Campo Grande, 1749-016 Lisboa, Portugal; rjsilva@ciencias.ulisboa.pt

Problem Identification:

Oceanic water masses present conservative oceanographic parameters like temperature and salinity.

Correlations between nutrients and some of these parameters have been identified. However, these correlation can be masked by system heterogeneity and measurement uncertainty. This masking will be larger when large, heterogeneous systems are studied.

Methodology:

Sampling:

Portuguese Continental Platform, between 40.12° N and 40.46° N and 8.96° W and 9.30° W
Sampling dates: October 2018 and April 2019
Number of samples, n = 20
Grid of 15 x 20 nautical miles
Distance between samples, d = 5 x 5 nautical miles
Sampling level: 25 m

Analysis:

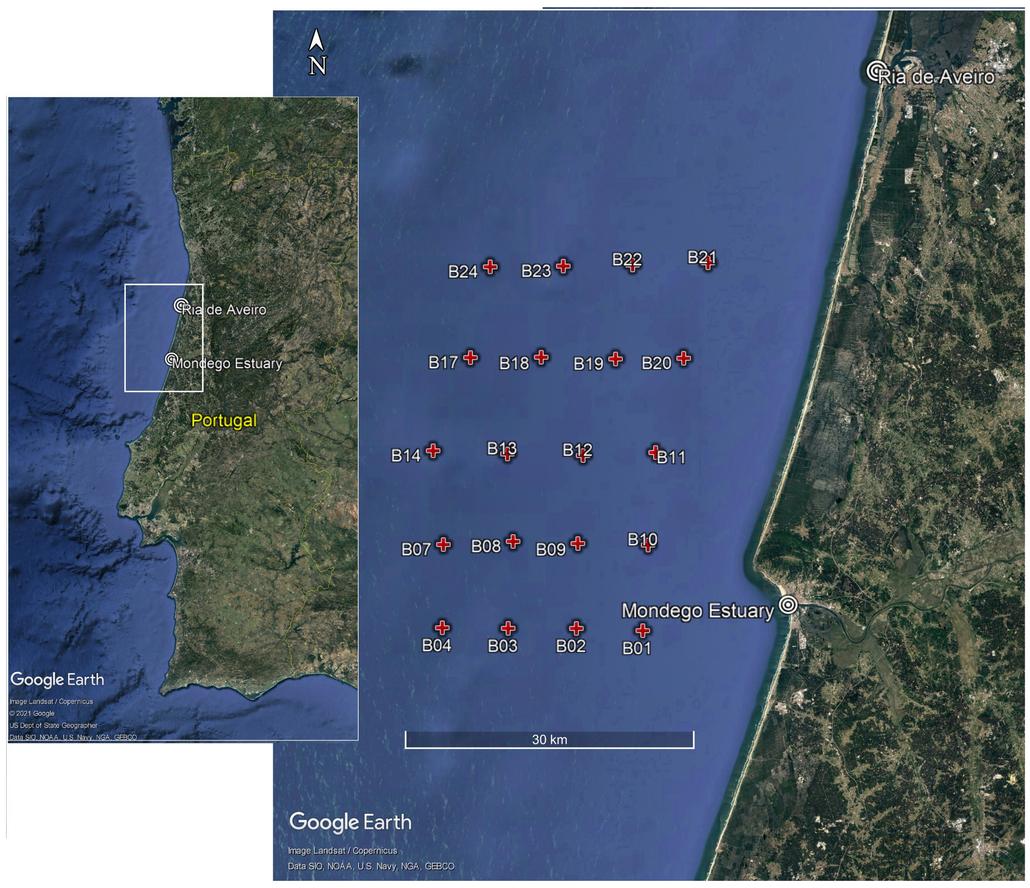
Segmented Flow Analysis

Uncertainty Modelation:

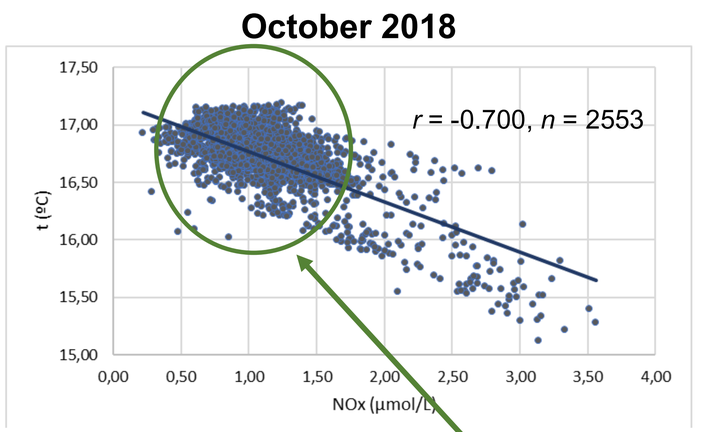
Monte Carlo Simulations of georeferenced information applied to Temperature and NO_x
Single Sampling (SS) modeling strategy used

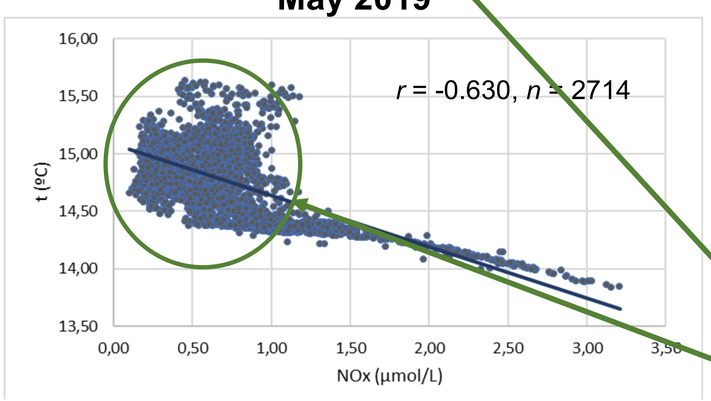
Purpose:

Estimate the correlation between pairs of parameters, considering the impact of system heterogeneity, sampling uncertainty and sample analysis uncertainty



Location of the sampling positions (B01 to B24) where water samples were collected, at 25 m depth, on two sampling occasions (October 2018 and May 2019), implanted over Google Earth images.





Correlations between NO_x and *t* for the two sampling occasions (r_{crit} ≈ 0.40 for n = 2500)

Results:

Simulated uncertainty of the measurement of NO_x and *t*, from random sampling, in the studied area for 95% confidence level on two sampling occasions and relevant uncertainty components. (§ - Value obtained by the Monte Carlo Method; Analytical components of uncertainty are, for NO_x: s'_I= 1.21% (Oct2018), s'_I= 6.10% (May2019) and u'_T= 3.09%). s'_S, s'_r, s'_I and u'_T are, respectively, the sampling, repeatability, interm. precision and veracity standard uncertainties and *Ú'* is the relative expanded uncertainty (*k*=2, ≈95 % conf. Level)

Parameter	October 2018				May 2019			
	Mean §	s'_S (%) §	s'_r (%)	U' (%)	Mean §	s'_S (%) §	s'_r (%)	U' (%)
NO_x / µmol L^{-1}	1.18	34.9	1.02	70.0	0.789	57.0	4.61	115
t / °C	16.7	1.60	0.009	3.19	16.7	1.60	0.009	3.21

- the total uncertainty main contributor is the uncertainty arising from sampling;
- the relative expanded uncertainty associated with NO_x is 1 to 2 orders of magnitude higher than that of *t*;
- an agglomerate of points at lower concentrations of NO_x, more evident in May 2019, is observed.

Conclusions:

- A stronger temperature stratification in May 2019 can explain a somewhat weaker correlation between studied parameters than the one determined for October 2018 ⇒ A more heterogeneous water mass masks temperature and NO_x correlation;
- The correlation is slightly affected by system heterogeneity;

Nevertheless, it can be stated that the correlations are meaningful

References

Iwata, T.; Shinomura, Y.; Natori, Y.; Igarashi, Y.; Sohrin, R.; Suzuki, Y. *J. Oceanogr.*, **2005**, 61, 721-732.
Borges, C.; Palma, C.; Silva, R. B. *Anal. Chem.*, **2019**, 91, 5698–5705.
Borges, C.; Palma, C.; Dadamos, T.; Bettencourt da Silva, R.J.N. *Chemosphere*, **2021**, 263, 128036.

Acknowledgements

This work was financed by the Operational Program Mar2020 through project "AQUIMAR – Caracterização geral de áreas aquícolas para estabelecimento de culturas marinhas" and Fundacão para a Ciência e Tecnologia (FCT) through the multiannual financing program 2020-2023 of Centro de Química Estrutural.