

Matrix in-situ sensing of fluorescent dissolved organic material

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The UN considers ocean waters, seas and rivers as ecosystems highly under pressure. The sustainable development goal SDG14 describes the need for environmental monitoring of sensitive multiple-scales ecosystems (UN). Therefore, in-situ sensors of key environmental parameters installed on autonomous platforms are of high relevance, as they increase the spatial-temporal resolution, while at the same time reducing operation expenses (Pearlman and Zielinski, 2017). Chromophoric dissolved organic matter (CDOM) is one of these highly relevant parameters, as it is influencing the light availability and is related to the pool of dissolved organic matter (DOM) in the water column (Helms et al, 2008; Kirk, 2011). Optically active components of DOM can be detected by inherent optical properties like absorption and fluorescence (Moore et al, 2009; Carstea, 2012; Massicotte et al, 2017). A rather complete “optical fingerprint” can be derived by excitation-emission-matrix (EEM) spectroscopy through benchtop fluorimeters (Drozdowska et al, 2013; Miranda et al, 2018). However disadvantages occur, like time consuming sample preparation, large time duration of measurement, and an overall time delay between sampling and measuring.

Matrix optical fluorescence sensors have been recently developed and tested introducing this technique for long-term monitoring (Ferdinand et al, 2017). Using essential wavelength combinations in a 3-by-4 matrix, parameters of interest are directly addressed and measured. The sensor MatrixFlu-UV detects different FDOM components in separated optical channels simultaneously (mainly 254nm excitation and 460nm emission for peak humic-like A, and 320nm/460nm for humic-like C peak). For field testing including reference measurements, this sensor has been deployed on an expedition of RV Heincke in July 2017 along the Norwegian coastlines and adjacent fjords, especially within Sognefjord and Trondheimsfjord (Figure 1). The MatrixFlu-UV showed stable long-term performance and similar dynamics as compared to the flow through system. Here we present an analytical comparison of derived data sets with full EEM references. Thereto absorption and fluorescence data were collected from reference samples by standard fluorescence benchtop detector systems like Horiba AquaLog and Perkin-Elmer LS55 spectrometer (FDOM), deriving full excitation-emission-matrix data, and Shimadzu UV-2700 photometer (CDOM) for absorption measurements.

Additionally, considering also annual variation (Makarewicz et al, 2018), data from two previous cruises along similar coastal transects and seasons were taken into account (RV Heincke cruises HE431 in 2014 and HE448 in 2015). Principle component analysis via PARAFAC allowed identifying the different fluorescent components of FDOM for comparison with the newly developed MatrixFlu-UV.

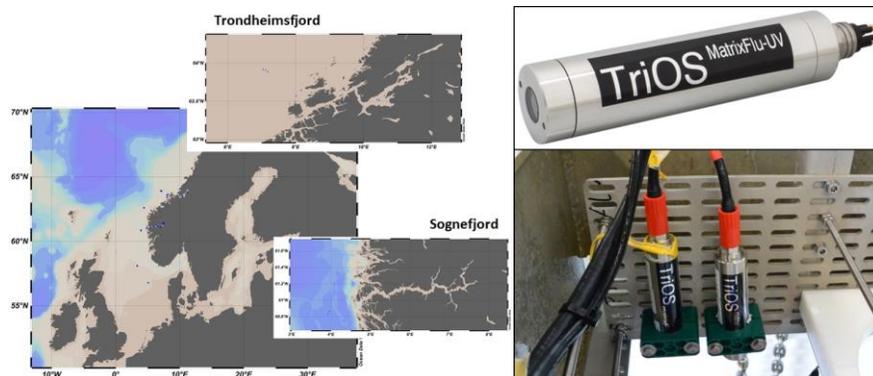


Figure 1. Left: Area of investigation during RV Heincke cruise HE491 in 2017. Dots indicate the location of sampling at stations. Right: Sensor MatrixFlu-UV (top) deployed in ship moon-pool (bottom).

References:

Cârstea, E. M. (2012). Fluorescence Spectroscopy as a Potential Tool for In-Situ Monitoring of Dissolved Organic Matter in Surface Water Systems. In: Nuray Balkis (Ed.), Water Pollution. InTechOpen. <http://doi.org/10.5772/1418>

Drozdowska, V., Freda, W., Baszanowska, E., Rud'z, K., Darecki, M., Heldt, J.R., Toczek, H. (2013). Spectral properties of natural and oil polluted Baltic seawater – results of measurements and modeling. *Eur.Phys.J.Spec.Top.*, 222 (9), 2157–2170. <http://doi.org/10.1140/epjst/e2013-01992-x>

Ferdinand, O.D., Friedrichs, A., Miranda, M.L., Voß, D., & Zielinski, O. (2017). Next generation fluorescence sensor with multiple excitation and emission wavelengths — NeXOS MatrixFlu-UV. *IEEE OCEANS 2017 - Aberdeen*. <http://doi.org/10.1109/OCEANSE.2017.8084809>

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., et al. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnol.Oceanogr.*, 53(3), 955-969. <http://doi.org/10.4319/lo.2008.53.3.0955>

Kirk, J.T.O. (2011). *Light and photosynthesis in aquatic ecosystems*. Third Edition ed. New York, USA: Cambridge University Press.

Makarewicz, A., Kowalczyk, P., Sagan, S., Granskog, M.A., Pavlov, A.K., Zdun, A., Borzycka, K., & Zabłocka, M. (2018). Characteristics of Chromophoric and Fluorescent Dissolved Organic Matter in the Nordic Seas. *Ocean Sci.Discuss.*, 1–41. <http://doi.org/10.5194/os-2017-100>

Massicotte, P., Stedmon, C., & Markager, S. (2017). Spectral signature of suspended fine particulate material on light absorption properties of CDOM. *Marine Chemistry* 196, 98–106. <http://doi.org/10.1016/j.marchem.2017.07.005>

Miranda, M.L., Mustafa, N.I.H., Robinson, T.B., Stolle, C., Ribas-Ribas, M., Wurl, O., Zielinski, O. (2018). Influence of solar radiation on biogeochemical parameters and fluorescent dissolved organic matter (FDOM) in the sea surface microlayer of the southern coastal North Sea. *Elem.Sci.Anth.*, 6(1), 15. <http://doi.org/10.1525/elementa.278>

Moore, C., Barnard, A., Fietzek, P., Lewis, M.R., Sosik, H.M., White, S., Zielinski, O. (2009). Optical tools for ocean monitoring and research. *OceanSci.*, 5(4), 661–684. <http://doi.org/10.5194/os-5-661-2009>

Pearlman, J., & Zielinski, O. (2017). A new generation of optical systems for ocean monitoring - matrix fluorescence for multifunctional ocean sensing. *SeaTechnology*, 2017(2), 30-33.

UN - <https://sustainabledevelopment.un.org/sdg14>.