Biogeochemical characterization of dissolved organic matter by fluorescence spectroscopy in mud volcano area in the Gulf of Cadiz.

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In this study the use of spectrofluorometric technique was used for the first time to assess the dynamics of dissolved organic matter (DOM) in mud volcanoes in the Gulf of Cadiz (GC). DOM was assessed in two oceanographic cruises (June and December 2016) in three mud volcanoes of the GC: Anastasya (AN, 452 m), Pipoca (PI, 635 m) and San Petersburg (SP, ~ 1000 m). Water column samples between ~ 5 to 850 m and pore water from sediments core every one-centimeter (n=12) were analyzed in each volcano. Fluorescence DOM (FDOM) was analyzed combining emission-excitation matrixes and multivariate parallel factor analysis (n=110, PARAFAC, Murphy et al. 2013).

Six PARAFAC components/fluorophores were identified (Table 1); a terrestrial humic-like widely distributed (C1), a marine humic-like (C2), two protein-like that resembles the amino acids tyrosine (C3) and tryptophan (C5), a possibly polycyclic aromatic hydrocarbon-like (PAH) (C4) and a fulvic-like component (C6). The latter has been described as highly resistant to biodegradation, found in Holocene core sediments and proposed as an ecological marker for warmer climates in the Earth (D'Andrilli et al. 2017).

Seasonal differences were observed in the distribution of FDOM components, especially in AN, with higher intensities during summer. Tyrosine-like C3 was the most abundant component (41-57%), both in water and sediment, except in AN. Fluorescence intensity for all volcanoes was almost two orders of magnitude higher in sediments than in the water column, however the relative contribution for each component varies. For example, % C6 (resistant fulvic-like) was always higher in the water column than in the pore water and was depleted in half of sediments samples measured in SP. On the other hand, differences in the distribution of FDOM between volcanoes showed an opposite trend during winter between AN and PI, while FDOM increased with depth in AN, it decreased in PI.

As far as we know there are no studies focused on the characterization of the diagenesis of DOM in mud volcanoes in the GC. This is the first analysis of DOM in mud volcanoes employing fluorescence spectroscopy. Moreover, our results in the GC reveal the presence of PAH-like compounds and one distinctive of the Holocene (D'Andrilli et al. 2017), besides differences in the process that control the production and degradation of DOM in mud volcanoes. The biogeochemical implications of these results will be discussed.

Table 1. Characteristics of the PARAFAC components observed in the mud volcanoes and comparison to published components using OpenFluor database (Murphy et al. 2014, Tucker's congruence $p > 0.96$, except for C4, Coble's characterization and literature.

	Ex peak	Em peak	Coble's peaks	Openfluor matching	Description
C1	270	454	A/C	C1, Cawley et al. 2012 C1, Yamashita et al. 2010	Terrestrial Humic like
C2	320	407	M	C2, Catalá et al. 2015	Marine humic-like
C3	275	300	B	C1, Murphy et al. 2006	Protein-like tyrosine
C4	280	323, 360 374	-	C5, Kothawala et al. 2012 (0.92) C5, Dainard et al. 2015 (0.9).	Protein-like Humic-like PAH-like (Gonnelli et al. 2018). A combination of protein-like and tannins-like markers (C2, D'Andrilli et al. 2017)
C5	300	359	T	C3, Catalá et al. 2015 C3, Brogi et al. 2018	Protein-like tryptophan
C6	270	414-419	-	C2, Brogi et al. 2018 C3, D'Andrilli et al. 2017	Fulvic-like. Terrestrial Humic-like, characteristic of the Holocene, and ecological marker of warmer climate.

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