

O₂ controls the Biogeochemical cycling of Cd, Fe and Mn along 85° 50' W in the Oxygen Minimum Zone of the Eastern Tropical South Pacific

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Oxygen Minimum Zones (OMZs) in the Eastern Tropical South Pacific (ETSP) is formed via a complex interplay of weak ocean ventilation (oxygen supply) and biological respiration (oxygen consumption). Dissolved oxygen (O₂) concentrations are a critical controlling parameter for the partitioning between redox states for a number of bio-essential metals such as Fe and Mn. Under low O₂ conditions (< 10 μM) the more soluble lower oxidation states are stabilized leading to longer residence times for these elements in the water column with implications for the distribution of these elements in these waters. Potential feedbacks may also occur whereby enhanced Fe concentrations, fuel surface water productivity resulting in higher fluxes of sinking organic matter which when respired further decreases O₂ in the OMZ.

In early 2009 we undertook a meridional transect across the ETSP OMZ from 14° S to the equator along 85° 50' W using the German research vessel Meteor (Expedition M77-4). During this expedition we focused on the relationships between the location of the OMZ, the absolute O₂ concentrations and the concentrations and distributions of the redox sensitive metals Fe and Mn in order to assess the current state of this OMZ with regard to redox sensitive metals. We also estimate here fluxes for Fe and Mn to the 85° 50' W transect supplied by upwelling, aeolian deposition or via the transport of Fe and Mn rich waters from the Peruvian shelf to the study area.

In this work we also observed that OMZs can influence the biogeochemistry of non-redox sensitive elements. Most notably for Cd, as our data suggested changes in the remineralization length for Cd was most likely linked to changes in Zooplankton diel migration due to the depth of the OMZ.

Organic Geochemistry and Toxicology of Fluids from Shale Gas Wells

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Background

Hydraulic fracturing frees energy resources previously thought uneconomical to produce, allowing contemporary industrial and societal needs to be met. Fluids resulting from this process (frac fluid and produced water) are complex chemical mixtures that contain various additives used for hydrofracturing and naturally-occurring substances extracted from the shale. A list of hydrofracturing additives used can be found in publically available registries such as FracFocus, www.fracfocus.org and additives are disclosed in a growing number of states. However, scientific research on this issue is still lacking and few studies have been published regarding the geochemistry of these fluids or their possible effects on human cell lines.

Results and Conclusion

In the present work we quantified and identified the dichloromethane-extractable organic constituents in the fluids (frac and produced waters) using gas chromatography/mass spectrometry. We also used short term *in vitro* bioassays with human lung (A549) and liver (HepG2) cells to assess the toxicity of fluids (frac and produced waters) from several hydraulic fracturing wells (HFX) at dilutions ranging from full strength to 1:1000 and exposure times from 36 hr - 2 weeks. Major organic constituents included: C10-C17 branched alkanes, ethylene glycol monododecyl ethers, di-n-octyl-phthalate, and 2,2,4-trimethyl-1,3-pentanediol. Using the fluids at full strength 50-75% of cells were killed after 36-60 hr. After 72 hr 4 of 8 HFX samples killed ≥92% of HepG2 cells (p<0.05) and the other 4 killed 50-80% of the cells. After two weeks, 100% of A549 cells initially plated in HFX at full strength were dead. We also examined HFX waters collected from 1 - 10 days following hydraulic fracturing in order to assess whether toxicity would abate. Toxicity in HFX waters remained significantly higher than in laboratory pure water (p<0.05) without a clear trend. Future studies will determine whether the observed toxicity was due to these organic compounds, inorganic constituents, hypersalinity or a combined effect.