

Stable carbon and nitrogen isotopic variations in latest Pleistocene to Holocene organic matter from Lake Ontario, Canada

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We have examined the variations in organic carbon (OC) and nitrogen (TN) contents, C/N ratios (7-10) and stable carbon and nitrogen isotopic compositions of bulk organic matter (OM) from Lake Ontario (the easternmost Great Lake) since 12.3 ka BP. Samples were obtained from three piston cores that contain sediments from each of Lake Ontario's major sub-basins. These data indicate low primary productivity during glacial times (12.3-10.8 ka BP), consistent with the cold and dry period proposed for this region by Lewis et al. (2008) [1]. That said, the carbon isotopic compositions of OM in glacial sediments display different upward variations in cores from west to east across the Lake Ontario sub-basins: Niagara sub-basin (west), an increase from -29 to -27 per mil (VPDB); Mississauga sub-basin (central), a decrease from -27 to -28.5 per mil (VPDB); Rochester sub-basin (east), an increase from -28 to -27 per mil (VPDB). These differences likely arise from greater contributions of terrestrial OM both in the west and the east as glacial meltwater entered the lake via the Niagara River (west) and directly from the Laurentide Ice Sheet (east). A short-lived influx of glacial meltwater from 10.8-10.5 ka BP is indicated by increased mass accumulation rates (MARs) during this interval of time. Upon cessation of glacial meltwater supply at 10.5 ka BP, the carbon-isotope composition of Lake Ontario OM decreased to -29.5 per mil across the basin. With hydraulic closure of Lake Ontario during the early Holocene, rising lacustrine productivity is indicated by progressively increasing OC and TN concentrations and OM carbon- and nitrogen-isotope compositions. Return of upper Great Lakes water to Lake Ontario during the region's Nipissing Rise at 5.0 ka BP correlates well with a temporary lowering of primary productivity in Lake Ontario. This decrease is followed shortly thereafter by a return to increasing OC, TN and OM carbon- and nitrogen-isotope compositions as modern Lake Ontario emerged. This history of lacustrine productivity for Lake Ontario is similar to that reported for Lake Superior [2], the deepest and largest of the Laurentian Great Lakes. Such comparisons may facilitate future regional synthesis of primary productivity in the Great Lakes during their changing histories from the latest Pleistocene to the present.

[1] Lewis et al. (2008) *EOS* **89**, 541-542. [2] Hyodo and Longstaffe (2011) *Quaternary Science Reviews* **30**, 2988-3000.

Mineralogical and Geochemical Investigation of Tungsten in natural environments: An Emerging Contaminant

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W is one of the most widely used and poorly understood elements today [1][2]. A lack of knowledge about its biogeochemistry coupled with its unique and advantageous properties have led to an explosion of W based products for domestic, military, and industrial applications [1]. Recently W has come under scrutiny following a CDC investigation of a leukemia cluster in Fallon, Nevada which implicated high levels of W in the drinking water as a probable cause [1][2]. Besides W's potential health hazards, recent studies have shown that the WO_4^{2-} oxyanion is soluble in water, capable of moving through soils. Also, dissolution of W metal leads to decreases in bacterial biomass in soils and increases in fungal biomass, also having adverse effects on plant life [2][3][4].

The hypothesis to be tested is that the physical and chemical changes from chemical weathering, mineral dissolution and precipitation, and/or redox reactions catalyzed by microbial activity control W transport and sequestration. These parameters control W by means of adsorptive/desorptive reactions, reductive/oxidative mineral dissolution or aqueous complexation with sulfide. Three sites have been chosen for geochemical and mineralogical analysis; two sites of high W concentrations (Fallon and Hoisington, KS) and one site of low concentration (Carrizo aquifer, Texas). Surface samples from within the town of Fallon and in-lake sediments from Cheyenne Bottoms Refuge in Hoisington have both shown high levels of W. The first step used in understanding the W-sediment association is x-ray microprobe aided speciation and bulk XANES, utilizing synchrotron radiation. This is done with μ XRF mapping accompanied by μ XANES and μ XRD on mineral/sediment grains and also elucidates the association of W with other elements (Ca, Fe, Mn, Fe, As, Cu, Mo, Ti, Zn). Sediment samples from Fallon were analyzed for bulk W speciation, and the data showed predominately W-VI, though the presence of minor shoulders in the spectra may indicate the presence of other species. The μ XRF map revealed that the highest density of W hotspots was in samples nearest the hard-metal facility, and good correlations were found with Fe. Sequential extractions are also being done to understand the partitioning of sediment fractions and preference of W to bind with various fractions.

[1] Koutsospyros, Braid, Christodoulatos, Dermatas, Strigul (2006) *J. Hazard. Mat.* **136**, 1-19. [2] Strigul, Koutsospyros, Arienti, Christodoulatos, Dermatas, Braid (2005) *Chemo* **61**, 248-258. [3] Johnson, Inouye, Bednar, Clarke, Winfield, Boyd, Ang, Goss (2009) *Land Cont. & Reclam.* **17**, 141-151. [4] Ringelberg, Reynolds, Winfield, Inouye, Johnson, Bednar (2009) *J. Environ. Qual.* **38**, 103-11