

PROCEEDINGS OF THE TWENTY-SIXTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

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Pomona College, Claremont, CA

Dr. Robert J. Varga, Editor
Director, Keck Geology Consortium
Pomona College

Dr. Jade Star Lackey
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Pomona College

Carol Morgan
Keck Geology Consortium Administrative Assistant

Christina Kelly
Symposium Proceedings Layout & Design
Office of Communication & Marketing
Scripps College

*Keck Geology Consortium
Geology Department, Pomona College
185 E. 6th St., Claremont, CA 91711
(909) 607-0651, keckgeology@pomona.edu, keckgeology.org*

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Editor and Keck Director
Pomona College

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91711

Christina Kelly
Proceedings Layout & Design
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**Keck Geology Consortium: Projects 2012-2013
Short Contributions— Ireland Project**

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Faculty: *ANNA MARTINI*, Amherst College, *TIM KU*, Wesleyan University.

**PORE WATER AND SEDIMENT CARBON ISOTOPE GEOCHEMISTRY OF MARL LAKE
SEDIMENTS, LOUGH CARRA, IRELAND**

SARAH SHACKLETON, Wesleyan University

Research Advisor: Timothy Ku

**LATE HOLOCENE CLIMATE VARIABILITY FROM LOUGH CARRA, COUNTY MAYO, WESTERN
IRELAND**

LAURA HAYNES, Pomona College

Research Advisor: Dr. Robert Gaines

**PHOSPHATE AND TRACE METAL RECORDS FROM AN IRISH MARL LAKE: TRACING
ANTHROPOGENIC INFLUENCE OVER SHORT AND LONG TIME SCALES**

ALYSSA DONOVAN, Amherst College

Research Advisor: Anna Martini

PHOSPHATE AND TRACE METAL RECORDS FROM AN IRISH MARL LAKE: TRACING ANTHROPOGENIC INFLUENCE OVER SHORT AND LONG TIME SCALES

ALYSSA DONOVAN, Amherst College

Research Advisor: Anna Martini

INTRODUCTION

Lake sediments act as historical archives for input from global, regional, and local sources, whether atmospheric or fluvial in nature (Edwards, 2001), and, as such, are excellent recorders of environmental change. The geochemical consequences of modern and historical agriculture and metallurgy can remain entrained in these lake sediments for long periods of time: the Great Famine is recorded in phosphorus profiles (Donohue, 2010), and there are myriad studies documenting lead and copper concentrations from Roman and Grecian mining (Hong et al., 1994; Hong et al., 1996; Schettler and Romer, 2006). Today, phosphorus levels are of great interest due to the increasing prevalence of cultural eutrophication in the water bodies of Europe and America. Likewise, though identifying evidence of ancient mining remains of scientific and historical interest, trace metals such as mercury and lead are of a public concern due to their inherent human toxicity. This project focuses on the record of anthropogenic influence resulting from agriculture and industry on the Irish marl lake Lough Carra.

SITE DESCRIPTION

Lough Carra is a polymictic marl lake in County Mayo, Ireland. At 15.6km² in size, it is the largest marl lake in the country. Its average depth is only 1.8m, but reaches 20m in a few areas (less than 6% of the lakebed is deeper than 6m). Lough Carra is divided into three distinct geochemical basins: the north Castleburke basin, the middle Castlecarra basin, and the southern Twin Islands basin. The lake is underlain by Carboniferous limestones, and catchment soils include

brown earths (68%), podzolics (25%), and basin peats (7%) (Hobbs et al., 2005). The catchment (114km²) lacks any urban population centers. Land use is primarily agricultural; both the eastern and western shores includes grassland used for cattle, sheep, and pig grazing (Donohue, 2010, Hobbs et al., 2005, Styles, 2006).

PREVIOUS WORK

PHOSPHORUS AND EUTROPHICATION

Previous water quality studies have been performed in Lough Carra. Hobbs et al. (2005) analyzed total phosphorus (TP) concentrations and Fe:P ratios in all three basins. All locations displayed a trend of increasing Fe:P ratios with depth: 5.6-64 at the water-sediment boundary, to ~15 at 80cm. The lower values at the top of the sediment column are indicative of the reduced ability of Lough Carra's sediments to bind additional phosphorus at sorption sites on Fe-hydroxides (Hobbs et al., 2005). In addition to modern eutrophication, Donohue (2010) revealed a transformation in the trophic state of Lough Carra over a 2-10 year period following the Great Irish Famine of 1845-1850: a sharp drop of TP concentrations coincided with a monotonic decline in %OM, $\delta^{15}\text{N}$, and population density, and a transformation in diatom assemblage (Donohue, 2010).

METALS

There have been no previous studies of trace metal concentrations in Lough Carra. The closest analogy is the study done by Schettler and Romer (2005),

who found records of atmospheric lead deposition by Roman mining in the brackish karst lake of An Loch Mór in the Aran Islands, Western Ireland.

METHODS

FIELD SAMPLING

Three short (<1m) gravity cores (LC 15, LC 16, LC 19) and one long (8m) Usinger core (LC 20) were taken around the Twin Islands and Castlecarras basins. The short cores were returned to the field laboratory, extruded, and every other centimeter bagged. The long core was split in half, photographed, described, and a sampled at 5cm intervals for trace metal analysis.

LABORATORY ANALYSIS

At Amherst College, sediment was dried at 60°C and then homogenized in an agate mortar and pestle. Chemical analysis proceeded as follows:

Mercury: sediment aliquots were run on the Hydra-C Cold Vapor Atomic Absorption Spectrum mercury analyzer.

Trace Metals: 2mg of sample was added to 10mL of 2% trace metal grade acetic acid and shaken on a shaker table for 16 hours. The supernatant was then filtered through a 20µm nylon filter, and analyzed on an ICP-OES for major and minor cations.

Total Phosphorus: 0.1g of sample was combusted in a furnace at 550°C for two hours. The remaining sediment was mixed with 25mL of 1N HCl in a beaker and placed in a boiling water bath for 30 minutes. The sample was then diluted to 50mL and left to cool for one hour. 2mL of sample was mixed with 1mL of a mixed reagent following the EPA ascorbic acid method, and then analyzed in a UV/VIS spectrophotometer for absorption at 885nm (EPA, 1993).

RESULTS

SHORT CORES (LC15, LC16, LC19)

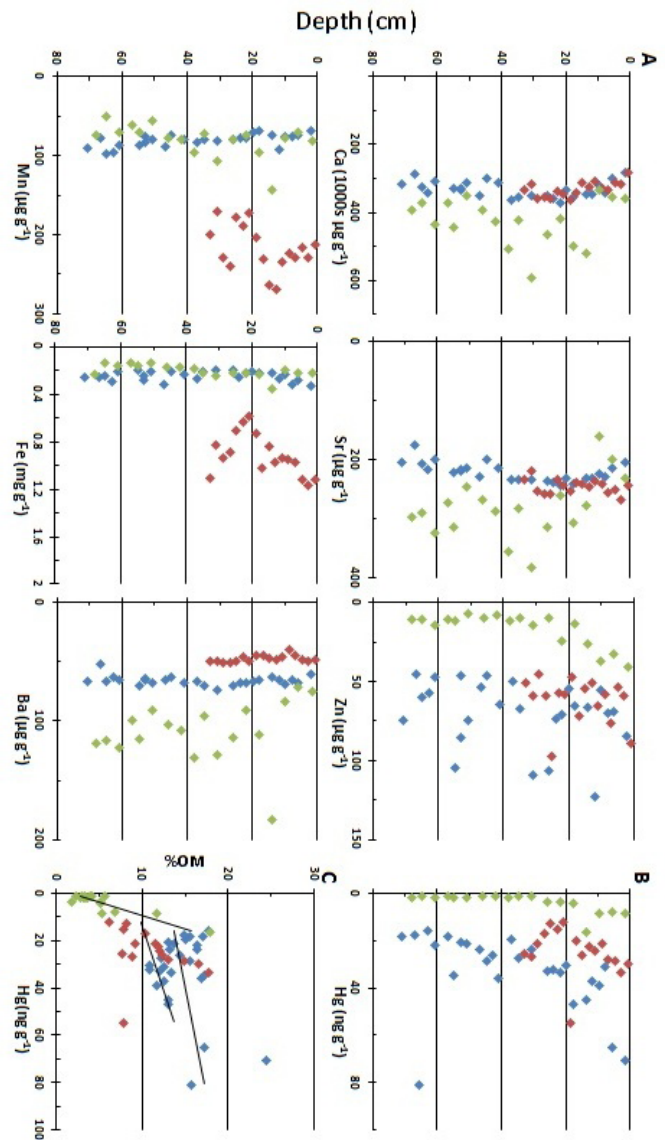


Figure 1. (A) Metal concentrations (ppm) versus depth for LC 15 (blue), LC 16 (green), and LC 19 (red). (B) Mercury concentrations (ppb) versus depth for LC 15, LC 16, and LC 19. (C) %OM vs. Mercury for LC 15, LC 16, and LC 19.

The short marl cores ranged in wt% CaCO₃ from 74% to 87%. The short cores displayed similar concentrations and profiles for most metals relative to one another (Fig. 1A). Mn and Fe provided the most unique results: the concentrations of these elements in LC19 are much higher (200-300ppm vs 100ppm for Mn, 600-1200ppm vs. 200ppm for Fe) than in LC15 and LC16, and the profiles show steep peaks at depth.

Mercury ranged from 15.7-80.6ppb in LC15, 12.3-54.5ppb in LC19, and 1.1-16.1ppb in LC16. Overall, Hg concentration decreased with depth (Fig. 1B). LC15 and LC16 values decrease monotonically down the core. LC19 values reach a minimum concentration at 20cm and increases from there with depth.

had an average value of 2.23, and ranged from 0.73 to 5.1. LC19 values averaged 6.82, and ranged from 3.06 to 14.07. The Fe:P ratios decrease rapidly from bottom to top. LC15 increases sharply to a maximum at 12cm and a minimum at 20cm, and then increases slowly to the bottom of the core.

LONG CORE (LC20)

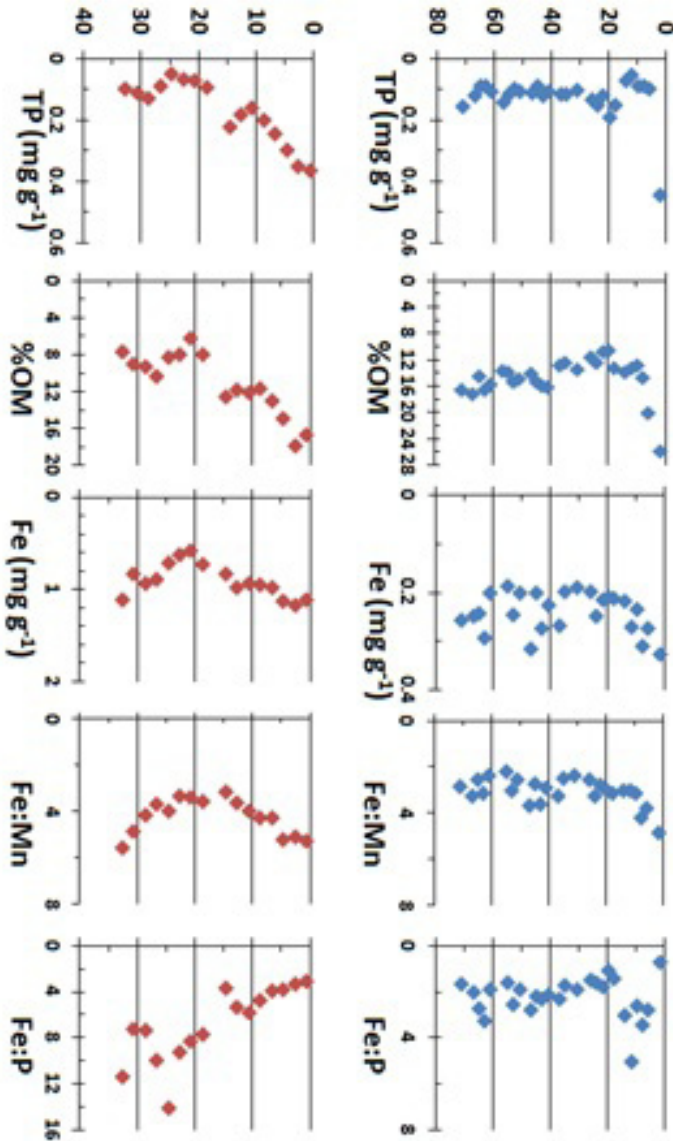


Figure 2. TP, %OM, Fe, Fe:Mn, and Fe:P versus depth for LC 15 (blue) and LC19 (red).

Total Phosphorus (TP) was determined for LC15 and LC19 (Fig. 2). Concentrations were similar (~400ppm) for the top 5 centimeters, dropping to an average of ~120ppm for the rest of the cores. Likewise, the depth profiles correlate well between cores. The Fe:P values, however, were distinctly different. LC15

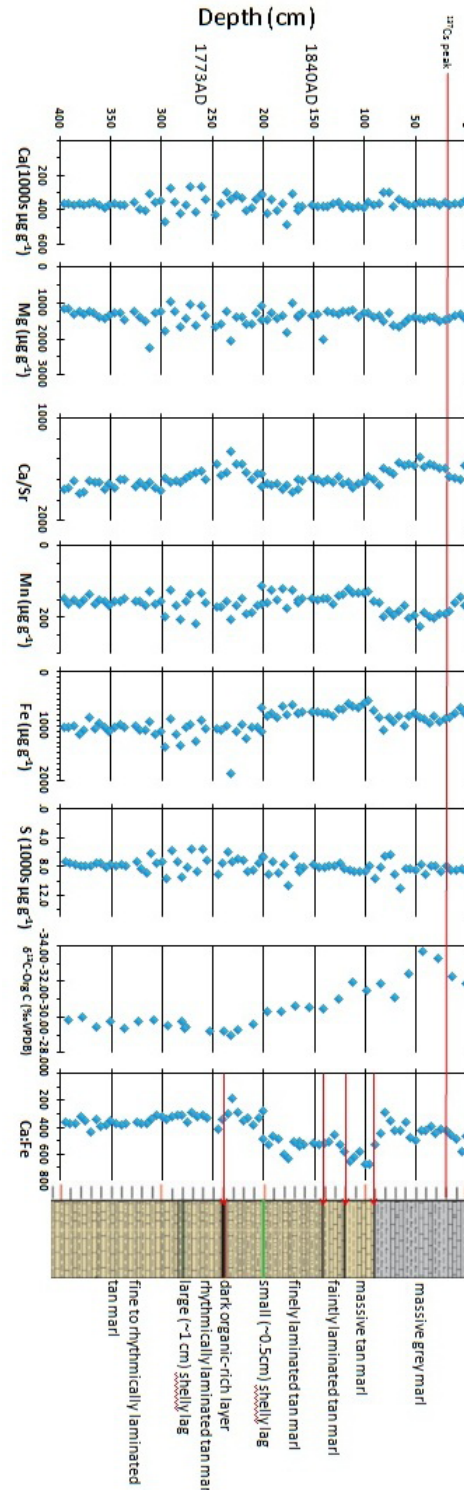


Figure 3. Stratigraphic column, metal concentrations (ppm), δ¹³C-Org versus depth for LC 20.

Concentrations for all metals (excepting Zn) are well-constrained for the top 150 and bottom 300-400 centimeters of the core, whereas 150-300cm shows widely scattered concentrations (Fig. 3). Ca/Sr increases slightly downcore. Ca/Fe varies greatly with depth; its peaks correlate with changes in sediment lithology. Overall, both Mn and Fe increase slightly down-core. However, the first 100cm of depth for both metals shows great variability, including a whole-core maximum that occurs at approximately 50cm.

DISCUSSION

METAL CONCENTRATIONS IN SHORT CORES

Wt % Calcium and %OM overlap in LC 15 and LC 19, deep-water short cores. Water column carbonate production and delivery of OM in these sites thus seem to be behaviorally similar irrespective of basin location. LC 16, the shallow (~1m overlying water) core, has higher Ca concentrations and lower %OM. It is likely that carbonate supersaturation is more readily maintained in these warm, shallow waters and increased CaCO_3 input has “diluted” the %OM.

However, with respect to Mn and Fe concentrations, LC15 and LC16 overlap and LC19 differs by ~100ppm for Mn and ~500ppm for Fe (Fig. 1A). Mn and Fe are mobile metals heavily influenced by variations in redox conditions. Mn becomes mobile at O_2 concentrations below 2mg/l and Fe becomes mobile at even lower concentrations (Kruopiene, 2007). As such, Mn concentrations should be lower than Fe concentrations in strongly reducing environments due to greater mobility (Hobbs et al., 2005). An inverse correlation between Fe:Mn and Fe concentrations, then, suggests a reducing environment. Fe:Mn vs. Fe concentrations for LC15, LC19, and LC20 all display a positive correlation (Fig. 4), so Mn and Fe concentration variability between cores is suggestive of source variance rather than redox conditions (Hobbs et al., 2005).

Zn and Hg form similar patterns (Fig. 1A,1B). This similarity may be in part due to their affinity for adsorbing onto organic matter; the lower concentrations at LC 16 are thus simply due to the high CaCO_3 precipitation rate and accordingly lower %OM. If Hg input is held constant, a strong linear

correlation should develop when compared to organic matter concentrations (Ravichandran, 2003). In Figure 1C no such correlation emerges for the deepwater cores, suggesting available Hg is greatly varied, as expected from atmospheric anthropogenic inputs over the Industrial Age. A strong correlation appears to exist in LC16, but is primarily due to 2 high %OM samples. Due to high sedimentation rates at Lough Carra, both LC15 and LC19 do not seem to reach to pre-industrial revolution values for atmospheric Hg (USGS).

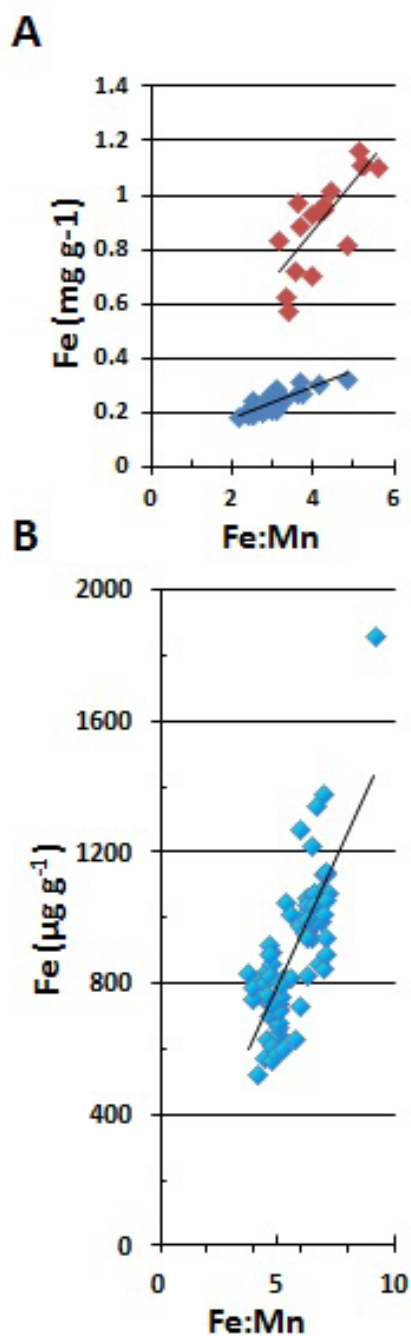


Figure 4. Fe:Mn versus Fe (ppm) for (A) LC 15 (blue) and LC 19 (red) and (B) LC 20.

PHOSPHORUS IN SHORT CORES

Fe:P values for LC15 are much lower than Hobbs reported for his basin studies (Hobbs et al., 2005). The values for LC19 are higher than those of LC15, likely due to greater TP input from the nearby river (Fig. 2). Overall, the trend of decreasing Fe:P values towards the surface reflects a decreasing amount of free sorption sites on the surface of Fe/Mn oxyhydroxides in the sediment and thus a decreasing ability for the sediment to bind additional phosphorus (Hobbs et al., 2005). At a Fe:P value less than 2, phosphorus retention on Fe/Mn oxyhydroxides is completely inhibited (Gunnars et al., 2002). The low values of Fe:P for LC15 (~0-4) thus suggest a lack of retention ability at the sediment-water interface, and the possibility of re-mobilization of phosphorus into the water column.

Sedimentation rates estimated by O'Reilly (2011) suggest an age of ~1750 AD for the base of LC15. Though this extends to before the Industrial Revolution and the Great Famine, we were unable to locate the onset of either in the short cores, in either $\delta^{13}\text{C}$ -Org or TP for the Famine, and Hg for the Industrial Revolution. It is likely, then, that the sedimentation rates for our basins are higher than those suggested by O'Reilly.

LONG CORE METAL CONCENTRATIONS AND $\delta^{13}\text{C}$ -ORG

The Ca/Sr ratios in LC 20 increase with depth, suggesting overall calcite re-crystallization in the core. The minimum peak occurs at around 230cm and is in line with the dark organic-rich layer (Fig. 3). Lithographic correlation also exists with Ca:Fe ratios: peaks in the Ca:Fe profile align with transitions between sedimentary units, possibly due to changes in sedimentation rate and/or sediment type.

$\delta^{13}\text{C}$ -Org trends to greater ^{12}C enrichment as you move up-core into younger sediments (Fig. 3). The $\delta^{13}\text{C}$ -Org profile may result from the Suess effect, which describes atmospheric $^{12}\text{CO}_2$ enrichment as a consequence of burning fossil fuels (Suess, 1955). This enriched CO_2 is then incorporated into photosynthetic organisms.

Donohue (2010) noted in his study that the human population in the Lough Carra catchment dropped 40% between 1841-1861 and that the population loss was reflected in decreased nutrient fluxes to the lake. Unlike the short cores, LC 20 is long enough to extend back to this time period. Our sedimentation rates were estimated by a combination of bulk density calculations and ^{14}C dating of shells and plant matter. The period of scatter in LC 20 (150-300cm) correlates with the period of highest sedimentation rate (1.83 cm/yr), estimated at around 1840-1773AD. Curiously, the onset and end of the scatter period matches population trends. The Irish population had been increasing steeply since around 1750 (Daultrey et al., 1981) and 1750 and reached a peak at 8 million people right before the Famine hit. Afterwards, population declined rapidly, dropping to ~6 million by 1860. Though we lack pre-famine census data or population estimates for County Mayo, the post-famine population trend is similar to that of the country as a whole.

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