Analysis of Carbon Cycling Within a Malaysian Watershed

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Introduction and Objectives

Carbon cycling in Southeast Asian watersheds remains poorly understood, and has been addressed by only a handful of studies. With regards to the stable carbon isotope systematics of these areas, the paucity of information is even greater. Such studies can help clarify the nature of carbon inputs into these fluvial systems, in addition to constraining sources and sinks of carbon in the associated watershed [1]. This information can then shed light on the importance and role of tropical rivers within the global carbon cycle.

Results and Conclusion

Initial results indicate that the dissolved organic carbon (DOC) within Langat River is sourced predominantly from C3 type vegetation, with an average $\delta^{13}C$ value of -27.4 ± 3.1 ‰. DIC $\delta^{13}C$ averages about -12.7 ± 2.4 ‰, which suggests that weathering of mineral substrates by soil-derived carbonic acid plays a central role in riverine DIC. Further ^{13}C enrichment may occur *in situ*, due to CO_2 outgassing from the river surface. Measured concentrations of DIC and DOC showed greater variance, averaging 3.5 ± 2.1 ppm and 5.3 ± 3.5 ppm, respectively. These concentration data plot negatively and positively with $\delta^{13}C$, respectively. The negative correlation is consistent with the proposition that biologic activity plays an important role in DIC generation. The factors behind the DOC $\delta^{13}C$ relationships are less certain, but could be indicative of external inputs of more ^{13}C enriched carbon relative to C3 plants sources.

Using the pH and DIC data, averaged values of -18.5 +/- 2.8 ‰ and 2958 +/- 2475 ppm were calculated for $\delta^{13}C_{CO2(g)}$ and [pCO_2], respectively. Throughout the year, the Langat River is supersaturated with respect to CO_2 in the overlying air. Atmospheric CO_2 has therefore a minimal impact on the riverine carbon budget. Instead there is a net efflux of carbon from the river surface, in accord with the proposition based on carbon isotope data implying that the fluvial CO_2 is predominantly sourced from biologically-respired carbon [2].

A rough, low-end estimate of evasion flux of carbon from the river to the atmosphere is about 3.8 kg C m^{-2} yr^{-1}, comparable to the world-average value of 2.7 kg C m^{-2} yr^{-1} for tropical streams [3]. This suggest that a minimum of 8.5 kt C yr^{-1} is being outgassed, approaching the magnitude of the total carbon export of 20 kt C yr^{-1} to the sea, as estimated based on river flow and DIC/DOC concentration data. These results confirm previous studies that highlight the active role of rivers in global carbon cycling, beyond that of simple conduits of carbon transport from land to sea.

[1] Schulte *et al*. (2011) *Earth Sci. Rev.* **109**, 20-31. [2] Dubois *et al*. (2009) *Appl. Geochem.* **24,** 988-998. [3] Aufdenkampe *et al*. (2011) *Front. Ecol. Environ.* **9**, 53-60.

Experimental evidence that redox state influences amino acid stability under hydrothermal conditions

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The stability of amino acids under hydrothermal conditions is of great interest to geochemists and biochemists in understanding the metabolic cycles of the biosphere near deep-sea hydrothermal vents and potential mechanisms for the origin of life in such environments. Thermodynamic calculations suggest that amino acid stability is sensitive to both temperature and the redox state of the environment [1]. Previous experimental studies have shown that parameters such as temperature and catalytic reactor surfaces strongly affect the stability of amino acids under hydrothermal conditions [2]. However, despite the potential relevance, the redox state of amino acid systems has never been controlled experimentally. Here experiments were conducted to investigate the influence of redox conditions on the stability of glutamic acid under hydrothermal conditions in a flow-through cell with temperatures from 150 °C to 250°C at 136 bars. The redox state was controlled by equilibrating ~14 mmolal $H_{2(aq)}$ in solutions containing glutamic acid with varying pHs. Results indicate that under hydrothermal conditions glutamic acid is converted to the cyclic pyroglutamate, a redox neutral reaction, following first-order kinetics. Other reaction products including $CO_{2(aq)}$, NH_4^+, formate, and succinate are formed through redox controlled reactions. The concentrations of the reaction products are observed to be strongly dependent on the redox state of the system. This finding indicates that redox state defined by aqueous H_2 is an essential variable in determining the stability of biomolecules under hydrothermal conditions.

[1] Shock & Canovas (2010) *Geofluids* **Volume 10**, 161-192.
[2] Cox & Sewald (2007) *Geochim. Cosmochim. Acta.* **Volume71**, 797-820.