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ANALYSIS OF THE SEASONAL IMPACT ON ISOTOPIC BASELINES OF DISSOLVED INORGANIC CARBON (DIC) IN COASTAL WATERS SPERMONDE, SOUTH SULAWESI

ANALISIS PENGARUH MUSIM TERHADAP ISOTOP KARBON INORGANIK TERLARUT (DIC) DI PERAIRAN SPERMONDE, SULAWESI SELATAN

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ABSTRACT

Stable carbon isotopes have been commonly used as indicators for assessing environmental changes in aquatic ecosystems. They can be used to study the dynamics of organic matter as for understanding the overall functioning of the ecosystem, the connectivity of estuaries with terrestrial and marine coastal habitats. The objective of this study is determining the seasonal natural effects over isotopic ($^{13}C/^{12}C$) baselines in monitoring CO_2 storage in dissolved inorganic materials in Spermonde waters on the west coast of South Sulawesi to some outermost island. The results show that the stable carbon isotopic of DIC ($\delta^{13}C$-DIC) in the wet season varied between -5.36 ‰ and -7.74 ‰. These value are higher than on dry season (-4.34 ‰ to -6.82 ‰). Likewise, DIC concentration in the rainy season ranged between 9.5 mg C/L and 11.7 mg C/L, while in the dry season it varied from 8.5 mg C/L to 9.3 mg C/L. The $\delta^{13}C$-DIC and DIC concentrations decreased towards offshore, up to some of the outer islands. Increasing in the $\delta^{13}C$-DIC in Spermonde waters indicate that the DIC is most likely enriched by atmospheric $CO_{2(g)}$, which is outnumbered those of aquatic photosynthesis. This study shows that different levels and composition of $\delta^{13}C$-DIC stretch along different rivers are attributable to the varying landscapes and quality of organic matters.

Keywords: stable carbon isotope, dissolved inorganic carbon (DIC)

ABSTRAK

Isotop karbon stabil merupakan indikator untuk menilai perubahan lingkungan di ekosistem perairan. Uji ini dapat digunakan untuk mempelajari dinamika bahan organik serta memahami fungsi keseluruhan ekosistem, keterkaitan habitat muara-pesisir-laut. Tujuan dari penelitian ini adalah menentukan efek musim terhadap isotop ($^{13}C/^{12}C$) untuk memantau penyimpanan CO_2 dalam bahan anorganik terlarut di perairan Spermonde di pantai barat Sulawesi Selatan dan beberapa pulau terluar. Hasil penelitian menunjukkan bahwa isotop karbon stabil DIC ($\delta^{13}C$-DIC) pada musim hujan bervariasi antara -5,36 ‰ dan -7,74 ‰. Nilai ini lebih tinggi dibandingkan musim kemarau (-4,34 ‰ hingga -6,82 ‰). Demikian juga, konsentrasi DIC pada musim hujan berkisar antara 9,5 mg C/L dan 11,7 mg C/L, sedangkan pada musim kemarau bervariasi dari 8,5 mg C/L hingga 9,3 mg C/L. Konsentrasi $\delta^{13}C$-DIC dan DIC semakin berkurang ketika mengarah ke laut sampai dibeberapa pulau terluar. Meningkatnya $\delta^{13}C$-DIC di perairan Spermonde mengindikasikan bahwa DIC kemungkinan besar disuplai dari atmosfer $CO_{2\,(g)}$, yang jumlahnya lebih banyak daripada fotosintesis di air. Studi ini juga menunjukkan bahwa berbagai tingkat dan komposisi bentangan $\delta^{13}C$-DIC di sepanjang sungai yang berbeda disebabkan oleh perbedaan landskap dan kualitas bahan organik.

Kata kunci: *karbon isotop stabil, karbon anorganik terlarut (DIC)*

I. INTRODUCTION

River estuaries are generally considered to be the most sustainable-derived carbon to the atmosphere as CO_2. To date, CO_2 has received greater attention worldwide due to its involvement in the biogeochemical cycles of open coastal and marine areas. Biogeochemical cycles that occur in coastal ecosystems can affect the quality of the waters which causes biogeochemical functions and biological community structure of coastal waters to change (Borges, 2005; Borges *et al*., 2005; Carpenter and Brock, 2006; Chang, 2009; Robson, 2008).

Oceans have a very important role in reducing global warming or increasing atmospheric CO_2 concentrations. Organic materials in the ocean are transported by physical and biological processes (Karim, 2008; Brunet *et al*., 2009; Schlitzer, 2000) and are decomposed by non-photosynthetic organisms (heterotropic respiration) and eventually lifted and returned to the atmosphere (Atkins *et al*., 2013; Cai, 2011; Hancke *et al*., 2008). Some of these carbon deposits as $CaCO_3$ in the sediment and the rest is dissolved in sea water, then joins DIC (McCarthy, 2006; Mook, 1974). The stable carbon isotope composition of DIC [($^{13}C/^{12}C$) DIC] depends on the dissolution of minerals by CO_2 biogenic origin (DIC formation) and photosynthesis (DIC consumption) and carbon isotope exchange between atmospheric CO_2 and DIC (Brunet *et al*., 2009; Herzschuh *et al*., 2010; Hill and Middleton, 2006).

In measuring the isotope ratio of $^{13}C/^{12}C$, the GDP reference standard (Pee Dee Belemnite) is used in various types of natural matrices. If the positive value shows, the sample has a larger isotope composition than standard (more enriched), whereas if the negative value indicates that the sample isotope composition is smaller than the standard. Carbon sources in the estuary region have varying isotope ratios due to the mixing of dissolved organics from the land such as plankton, terrestrial plants, algae, and marine plants (Peterson and Fry, 1987; Mladenov *et al*., 2005; Bouillon, 2008; Cai, 2011).

Variations in stable carbon isotope ratios in coastal and marine waters become one particular (spatial) location character that affects the level of sources in the waters. The purpose in this study is determining spatial and seasonal natural effects over isotopic ($^{13}C/^{12}C$) baselines in monitoring CO_2 storage on the west coast of South Sulawesi to some of the outer islands in inorganic materials dissolved in Spermonde waters.

II. RESEARCH METHODS

2.1. Study Site

Seawater samples for Dissolved Inorganic Carbon (DIC) and $\delta^{13}C$-DIC were taken at ten stations. The study locations were in the estuary waters of the major rivers namely the Tallo and Pangkep coasts to some of the outermost islands (estuary of the Tallo river, Barrang Lompo island, Bone Tambung island, Langkai island and Kapoposang island) and Pangkep coast (Pangkep river mouth, Laiya island, the island of Sarappo Keke, the island of Kondong Bali and the island of Kapoposang) (Fig. 1).

2.2. Measurements and Analyses

Water quality is an important indicator in knowing the fertility level of waters and is also used as an indicator of water pollution. Measurement of water quality includes pH and water temperature data that is carried out for two times sea voyages, representing the dry season (June 2017) and the rainy season (Feb 2018). The partial pressure of CO_2 (pCO_2) of the water column was calculated using the OCMIP Model (Ocean Carbon Cycle Model Intercomparison Project) developed by Orr *et al.* (1999). The atmospheric pCO_2 is measured at the time of sampling using CO_2 meters.

Figure 1. Sampling site.

Table 1. The hydrographic condition of the sampling location.

Sampling Time	Sampling Location	Water T (°C)	pH	CO_2	G13C-DIC (‰ V-PDB)	DIC (mg C/L)
Dray Season (June 2017)	**Coastal**					
	Tallo Makassar Estuary	32.8	7.5	8	-6.82	8.9
	Sea					
	Barrang Lo,po Island	31.7	7.3	12	-6.71	9.1
	Bone Tambung Island	30.8	7.1	20	-6.17	8.7
	Langkai Island	30.5	7.6	20	-6.43	8.9
	Lanjukang Island	31.2	7.2	24	-5.23	8.5
	Coastal					
	Pangkep Estuary	31.0	7.1	12	-5.23	9.0
	Sea					
	Laiya Island	28.5	7.3	14	-4.72	8.9
	Sarappo Keke Island	29.7	7.2	20	-4.95	9.1
	Kondong Bali Island	30.8	7.0	16	-4.64	9.3
	Kapoposang Island	30.1	7.1	18	-4.34	8.7
Rainy Season (Feb 2018)	**Coastal**					
	Tallo Makassar Estuary	31.2	7.9	32	-7.74	10.8
	Sea					
	Barrang Lompo Island	30.6	7.6	20	-7.57	9.5
	Bone Tambung Island	31.0	7.8	24	-6.95	10.3

Sampling Time	Sampling Location	Water T (°C)	pH	CO_2	G13C-DIC (‰ V-PDB)	DIC (mg C/L)
	Langkai Island	29.8	7.5	18	-6.95	10.7
	Lanjukang Island	30.3	7.3	20	-6.74	9.8
	Coastal					
	Pangkep Estuary	31.1	8.0	20	-6.56	11.7
	Sea					
	Laiya Island	30.0	7.9	24	-6.49	10.5
	Sarappo Keke Island	30.7	7.6	18	-5.91	11.2
	Kondong Bali Island	31.5	7.7	20	-5.52	11.4
	Kapoposang Island	30.1	7.6	24	-5.36	10.0

To measure the value of δ^{13}C-DIC, the pre-weighed GF/F 0.7 µm using the vacuum pump (200 mmHg) and pre-weighed with at least 2 L of water collected per sample. Shortly after sampling, 0.02 ml of $HgCl_2$ was added, to stop biological activity (Dickson et al., 2007). Samples were kept in the dark and shipped on ice, immediately transported to the laboratory until the analysis. Preparation and isotope analysis δ^{13}C-DIC were done by taking 1 liter of sea water, to add $BaCl_2$ 10%, the reaction results are then left to form carbonate deposits. The deposits obtained are then filtered and dried in an oven at a temperature of 50-60 °C. The dried $BaCO_3$ deposits were then reacted with 100% H_3PO_4 in a tube under vacuum. The CO_2 gas released in the test tube is then captured using liquid N2 with a temperature of -195oC at the condition of the vacuumed tube, then the CO_2 gas obtained is analyzed the composition of the ^{13}C isotope ratio using EA-IRMS (elemental analyzer-isotope ratio mass spectrometry); and are expressed relative to the GDP standard (Craig, 1957). Analytical precision is ± 0.05 and measurements can be reproduced to ± 0.1 ‰.

Furthermore, DIC was measured using the titration method (Giggenbach and Goguel, 1989), with the principle of basing on pH changes after HCl and NaOH were added. DIC is obtained from the sum of HCO^{3-} and CO_3^{2-} in units of µmol/kg. DIC concentrations were obtained simultaneously with isotope values through linear regression from the standard internal DIC used in this study. The concentration of each sample is proportional to the area of chromatography obtained during isotope measurements.

III. RESULTS AND DISCUSSION

The average isotopic values, other chemical and environmental variables at the western coastal waters of South Sulawesi. Overall, from the two seasons of data collection, presented in Table 1. Coastal waters in the study locations including estuary waters with hydrographic conditions (water temperature and pH) in different seasons did not show significant differences. The water temperature in coastal and marine waters in both seasons is relatively the same, with an average value (± standard deviation) of 30.62±1.77 in the dry season, and 32.00±0.88 in the rainy season. Coastal water temperatures sometimes have higher temperatures; due to the effect of hotter land, while the temperature of the water from the estuary to the sea, has a lower temperature, this is likely due to the encouragement of sea water masses from offshore to the bay.

The results of pH measurements in coastal and marine waters showed the average (± standard deviation) pH values in the dry and rainy seasons were 7.29±0.28 and 7.32±0.36, respectively. The pH value is close to the normal pH; this is because it receives input from the land, namely household wastes, and acidic industries through the river. When approaching the lower pH values, the concentration of DIC in water rises, and the δ^{13}C-DIC decreases (less negative). Increase in sea surface temperature can reduce the solubility of CO_2 waters so that it can also cause a decrease in the pH value of the waters.

Furthermore, measurements of the isotope composition of dissolved inorganic carbon (δ^{13}C-DIC) are carried out, which are the main indicators of changes in the aquatic surface system. In determining season and location factors, we compare the results obtained from each sampling. The global average value of carbon isotope composition in DIC (δ^{13}C-DIC) at the west coast waters of South Sulawesi is using two data collection season's ranges from -4.34 ‰ to -7.74 ‰ while the DIC concentration ranged from 8.5 mg C/L to 11.7 mg C/L.

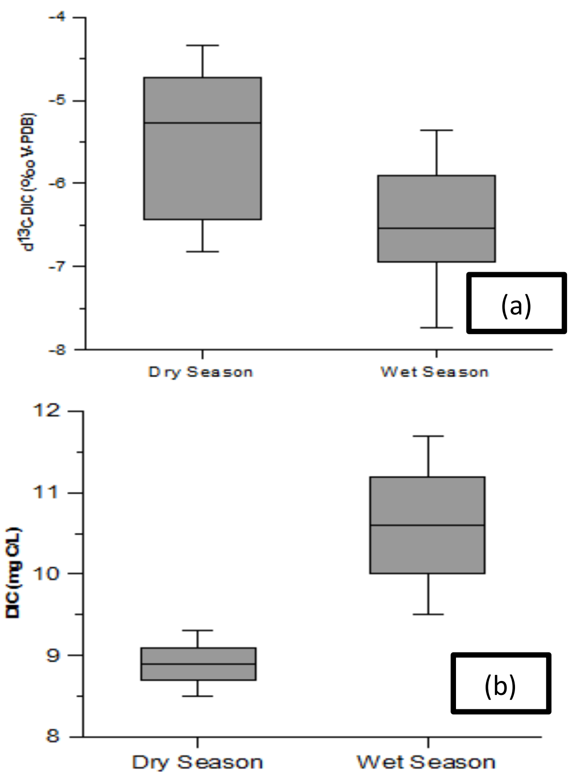

Figure 2. (a) δ^{13}C-DIC values and (b) concentration of DIC during the dry and wet season.

Isotope ratio values of δ^{13}C-DIC and DIC in coastal and marine waters vary between seasons and locations (Table 1). Isotope ratio value δ^{13}C-DIC and concentration of DIC concentration in the rainy season (March 2018) is higher than the dry season (June 2017). The isotope ratio value δ^{13}C-DIC with mean values (± standard deviation) ranging from -5.36 ‰ to -7.74 ‰ (-6.54 ‰ ±0.7) V-GDP in the wet season and around -4, 34 ‰ to -6.71 ‰ (-5.53 ‰ ±0.9) V-GDP in the dry season. While the DIC concentration with an average value (± standard deviation) ranged from 9.5 to 11.7 mg C/L (10.59 mg C/L±0.7) in the wet season, and in the dry season it was 8.5 to 9.3 mg C/L (8.91 mg C/L±0.2) (Figure 2).

The isotope ratio value of δ^{13}C-DIC starting from the estuary to some of the outer islands has a smaller value and a less negative tendency due to the period of sampling and the occurrence of extreme climate events lately. In the dry season, there is high evaporation of water and vegetative stress resulting in a value of δ^{13}C -DIC less negative as expected from respiration. Unlike the increase in photosynthesis in the aquatic system which will remove ^{12}C. As a result, the residual DIC will increase (enrich) the ^{13}C value (Table 1). Besides being caused by a dry season that produces less negative isotope values, this is also due to the dominance of biological processes and the gradual increase in the partial pressure of CO_2 in water (Barth and Veizer, 1999) as shown in Figure 3. The mean value for the calculated partial pCO_2 was 22.93 mgL^{-1}. There is no unreasonable statistical difference observed at the mean value of pCO_2, with different sampling times (p-value = 0.0957). These results indicate that pCO_2 is not affected by seasonal effects. However, the temporal pattern has a higher value in the rainy season (Figure 3).

Based on the pCO_2 value of the sea and the atmosphere, the nature of waters can be determined as a sink or source of CO_2. Water acts as a 'source' or releases CO_2 into the air/atmosphere if the pCO_2 value is higher than the atmospheric value (positive value) because there will be a flow of CO_2 from the water into the atmosphere. Instead, it acts as a sink of CO_2 from the atmosphere if the water pCO_2 value is lower than pCO_2 atm (negative value). The result shows that the changes to more positive values occur due to a variety of biological and physicochemical effects and generally have seasonal patterns that depend on climatic conditions and more specifically by temperature.

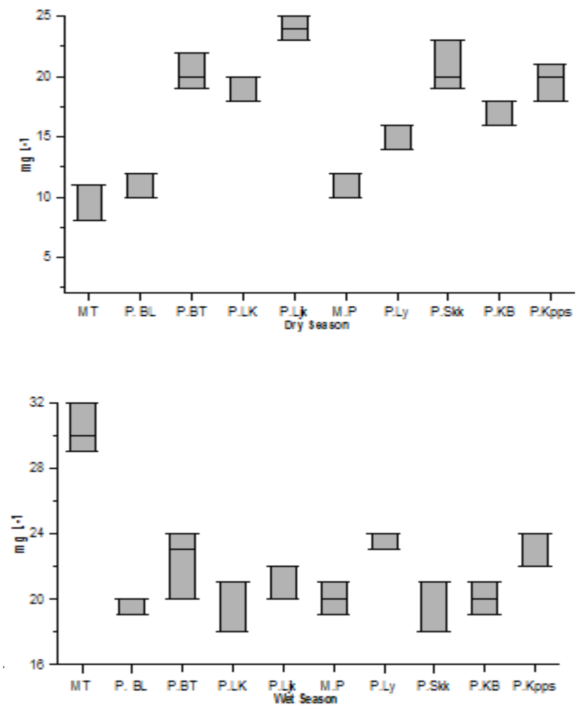

Figure 3. Spatial variations of $_{p}CO_2$ (mg L^{-}) during the dry and wet season.

Probably two substrates for photosynthesis have different isotope compositions, $CO_{2(aq)}$ being depleted ^{13}C by ~ 9 ‰ relative to bicarbonate at 25°C (Mook, 1974). Atmospheric input or DIC generated from carbonate dissolution will produce more enriched $\delta^{13}C$ signs (> -5‰) because the DIC produced by dissolving carbonates is composed of soil CO_2 ($\delta^{13}C$ depending on C3/C4 abundance) and carbonate ($\delta^{13}C$~0 Asumsi assuming ancient sea carbonate). Furthermore, based on location, the isotope ratio $\delta^{13}C$-DIC and DIC concentration in Tallo waters are higher than Pangkep waters, but the value of $\delta^{13}C$-DIC to the sea is smaller until some of the outer islands are based on horizontal lines from Tallo and Pangkep waters. The isotope ratio value of $\delta^{13}C$-DIC in Tallo waters to the outer islands ranges between -5.23 ‰ to -7.74 ‰ (-6.68 ‰±0.7) V-GDP whereas Pangkep waters ranged between -4.34 ‰ to -6.56 ‰ (-5.38 ‰±0.8) V-GDP. Furthermore, the DIC concentration in Tallo waters ranged from 8.5 to 10.8 mg C/L (9.52 mg C/L ±0.8), while in Pangkep waters ranged from 8.7 to 11.7 mg C/L (9.98 mg C/L ±1.1) (Figure 4).

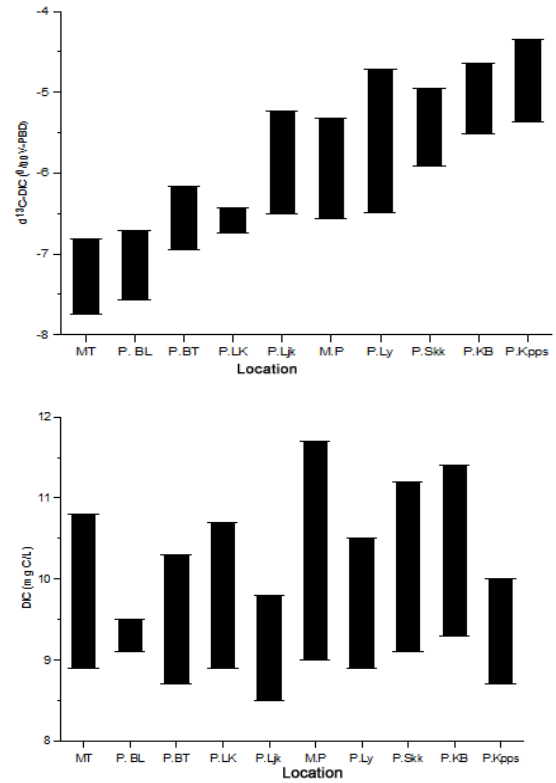

Figure 4. Spatial variations in the $\delta^{13}C$-DIC values and concentration of DIC.

DIC concentrations in rivers vary greatly depending on the geology of the catch and the degree of weathering (Brunet et al., 2009). DIC concentration values and water quality parameters are influenced by the situation and condition of the waters, both in the form of anthropogenic and weather factors. The influence of seasonal factors on the composition of $\delta^{13}CDIC$

values and DIC concentrations is very significant. There are significant differences in the composition of CD13CDIC values and the concentration of DIC between seasons (dry and rainy) and between locations (Makassar and Pangkep).

This shows that the role of the season in the composition distribution of δ^{13}C-DIC and DIC concentrations in the waters is quite large where the largest composition of δ^{13}C-DIC and DIC concentrations occur in the wet season. The high composition of δ13C-DIC during the rainy season or the season with high precipitation rates is also shown in several estuaries and coastal water systems in the world although the land character is different, such as on the Rhône River (1-3 mMC and δ^{13}C-DIC -5 to -10 ‰ V-GDP, and Northeast US Rivers (0.6 mMC and a value of δ^{13}C-DIC -10 ‰ V-GDP (Raymond and Bauer, 2011). Overall, the process causing a decrease in the value of δ^{13}C-DIC including respiration or oxidation photos of organic matter in a water column which has a lower dominance than processes that can increase δ^{13}C-DIC such as photosynthesis and carbon equilibrium between DIC and atmospheric CO_2. Released by the nearest source, the spatial-temporal character becomes information that is important enough to understand the hydrological and biogeochemical processes in a particular season.

IV. CONCLUSION

In the study area the main carbon sources are vegetative decomposition and to a lesser extent decomposition of carbonate and atmospheric CO_2. Different mechanisms acting together as long as the DIC isotope composition has been identified as carbonate decomposition, metabolic processes (respiration and photosynthesis), and degasification of CO_2 to the atmosphere. Dominance depends on the factor of the season when the measurement is done. The composition of δ^{13}C-DIC and DIC concentrations in Makassar coastal waters and Pangkep waters during the rainy season have more negative and less negative values in the dry season. On the other hand, that determines the effect of seasonal effects on isotope composition δ^{13}C-DIC and DIC concentration, due to high sample variability and extreme climatic factors that occur at baseline isotopes.

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REFERENCES

Atkins, M.L., I.R. Santos, S. Ruiz-Halpern, D.T. Maher. 2013. Carbon dioxide dynamics is driven by groundwater discharge in a coastal floodplain creek. *J. Hydrology*, 493:30-42.

Barth, J. and J. Veizer. 1999. Carbon cycle in St. Lawrence aquatic ecosystems at Cornwall (Ontario), Canada: seasonal and spatial variations. *Chemical Geology*, 159:107–128.

Borges, A.V. 2005. Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the coastal ocean? Estuaries 28:3–27.

Borges, A.V., B. Delille, and M. Frankignoulle. 2005. Budgeting sinks and sources of CO_2 in the coastal ocean: diversity of ecosystems counts. *Geophysical research letters*, 32 L14601.

Bouillon, S., R.M. Connolly, and S.Y. Lee. 2008. Organic matter exchange and cycling in mangrove ecosystems: Recent insights from stable isotope. *Studies J. Sea Research*, 59:44-58.

Brunet, F., D. Gaiero, J.L. Probst, P.J. Depetris, F.G. Lafaye, and P. Stille. 2005. $\delta^{13}C$ tracing of dissolved inorganic carbon sources in Patagonian rivers (Argentina). *Hydrology Process,* 19:3321-3344.

Brunet, F., K. Dubois, J. Veizer, G.R.N. Ndondo, J.R.N. Ngoupayou, J.L. Boeglin, and J.L. Probst. 2009. Terrestrial and fluvial carbon fluxes in a tropical watershed: Nyong basin, Cameroon. *Chemical Geology,* 265: 563–572.

Cai, W.J. 2011. Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration. *Annual Review of Marine Science,* 3:123-145.

Carpenter, S.R. and W.A. Brock. 2006. Rising variance: a leading indicator of ecological transition. *Ecology Letter,* 9:311–318.

Chang, C.C.Y., P.V. McCormick, S. Newman, and E.M. Elliott. 2009. Isotopic indicators of environmental change in a subtropical wetland. *Ecological Indicators*, 9:825–836.

Craig, H. 1957. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochimica Cosmochimica Acta,* 12:133-149.

Dickson, A.G., C.L. Sabine, J.R. Christian. 2007. Guide to best practice for ocean CO_2 measurements. PICES Special Publication. 191 p.

Doctor, D.H., C. Kendall, S.D. Sebestyen, J.B. Shanley, N. Ohte, E.W. Boyer. 2008. Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream. *Hydrological Processes*, 24:2410– 2423.

Eyre, B.D., A.J.P. Ferguson, A.P. Webb, D. Maher, J.M. Oakes. 2011. Metabolism of different benthic habitats and their contribution to the carbon budget of a shallow oligotrophic subtropical coastal system. *Biogeochemistry*, 103:87-110.

Hancke, T.B., L.M. Olsen, G. Johnsen, and R.N. Glud. 2008. Temperature effects on microalgal photosynthesis-light response measured by O_2 production, pulse-amplitude modulated fluore-scence, and ^{14}C assimilation. *J. of Phycology,* 44:501-514.

Herzschuh, U., S. Mischke, H.Meyer, B. Plessen, and C. Zhang. 2010. Using variations in the stable carbon isotope composition of macrophyte remains to quantify nutrient dynamics in lakes. *J. of Paleolimnology*, 43:739–750.

Hill, W.R. and R.G. Middleton. 2006. Changes in carbon stable isotope ratios during periphyton development. *Limnology Oceanography,* 51:2360–2369.

Karim, A., J. Veizer, and J. Barth. 2008. Net ecosystem production in the Great Lakes basin and its implications for the North American missing carbon sink: a hydrologic and stable isotope approach. *Global and Planetary Change*, 61:15–27.

Karim, A., K. Dubois, J. Veizer. 2011. Carbon and oxygen in the Laurentian Great Lakes: implications for CO_2 flux from terrestrial, aquatic systems to the atmosphere. *Chemical Geology,* 281:133–141.

Maher, D.T. and B.D. Eyre, 2012. Carbon budget for three autotrophic Australian estuaries: Implications for global estimates of the coastal air-water CO_2 flux. *Global Biogeochemical Cycle,* 26:1-18.

McCarthy, T.S. 2006. Groundwater in the wetlands of the Okavango Delta, Botswana, and its contribution to the structure and function of the ecosystem. *J. Hydrology,* 320:264–282.

Mladenov, N., D.M. McKnight, P. Wolski, and L. Ramberg. 2005. Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango Delta, Botswana. *Wetlands*, 25:622–638.

Mook, W.G., J.C. Bommerson, W.H. Staverman. 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth Planet. *Science Letter,* 22:169–176.

Peterson, B.J. and B. Fry. 1987. Stable isotopes in ecosystem studies. *Annual Review Ecology System*, 18:293-320.

Raymond, P.A. and J.E. Bauer. 2011. Use of ^{14}C and ^{13}C natural abundances for evaluating riverine, estuarine and coastal DOC and POC sources and cycling: a review and synthesis. *Organic Geochemistry,* 32:469-485.

Robson, B.J., D.P. Hamilton, I.T. Webster, and T. Chan. 2008. Ten steps applied to the development and evaluation of process-based biogeochemical models of estuaries. *Environment Modeling and Software*, 23:369-384.

Schlitzer, R. 2000. Applying the adjoint method for biogeochemical modeling: export of particulate organic matter in the world ocean. *Geophysical Monograph Series*, 114:107-124.

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