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ISOTOPIC TRACERS FOR NET PRIMARY PRODUCTIVITY FOR A TERRESTRIAL ECOSYSTEM: A CASE STUDY OF THE VOLTA RIVER BASIN

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Abstract

The coupling effect of vapour release and CO_2 uptake during photosynthesis plays an important role in the carbon and hydrologic cycles. The water use efficiency (WUE) for transpiration was used in calculating the net primary productivity (NPP) for terrestrial ecosystem. Three parameters were used in calculating the water and carbon balance of the River Volta watershed. These are 1) stable isotopes of hydrogen and oxygen, 2) long-term data on precipitation and evapotranspiration, and 3) stoichiometric relations of water and carbon. Results indicate that soils in the watershed annually respire 0.199 Pg C, and that the NPP is +0.029 Pg C yr^{-1}. This implies an annual change in CO_2 to the atmosphere within the watershed. Annually, River Volta watershed receives about 380 km^3 of rainfall; approximately 50 per cent of which is returned to the atmosphere through plant transpiration. Associated with annual transpiration flux is a carbon flux of 0.170×10^{15} g C yr^{-1} or 428 g C m^{-2} yr^{-1} from the terrestrial ecosystem. Modeled estimates of heterotrophic soil respiration exceeds slightly the estimated NPP values, implying that carbon flux to and from the Volta river watershed is close to being in balance. In other words, the watershed releases annually more carbon dioxide to the atmosphere than it takes. Apart from the terrestrial carbon flux, the balance of photosynthesis and respiration in the Volta lake was also examined. The lake was found to release carbon dioxide to the atmosphere although the magnitude of the flux is smaller than that of the terrestrial ecosystem.

Résumé

HAYFORD E. K., ODAMTTEN G. T. & ENU-KWESI L.: *Traceurs isotopiques pour la productivité de base nette pour un écosystème terrestre: Une étude de cas du Bassin de Fleuve Volta.* L'effet de couplage du dégagement de vapeur et d'absorption de CO_2 pendant la photosynthèse, joue un rôle important dans les cycles du carbone et du hydrologie. D'après ce couplage, Efficacité d'Utilisation d'Eau (EUE) pour la transpiration était la méthode employée pour le calcul de la productivité de base nette (PBN) pour l'écosystème terrestre. Dans cette méthode, trois paramètres étaient employés pour de calcul de l'équilibre d'eau et du carbone de la ligne de partage des eaux de Fleuve Volta. Ce sont : 1) les isotopes stables de l'hydrogène et l'oxygène. 2) les données sur une longue période de précipitation et d'évapotranspiration et 3) les rapports stæchiométriques d'eau et du carbone. Les résultats indiquent que les sols dans la ligne de partage des eaux respirent annuellement 0.199 Pg C, et que la productivité de base nette (PBN) est + 0.029 Pg C yr^{-1}. Ceci imploque un changement annuel en CO_2 à l'atmosphère dans les limites de la ligne de partage des eaux. Annuellement, la ligne de partage des eaux de Fluve Volta reçoit à peu près 380 km^3 de pluviosité; approximativement 50 % duquel est renvoyé à l'atmosphère par la transpiration végétale. Associé avec le flux de transpiration est le flux du carbone de 0.170 x 10^{15} g C yr^{-1} ou 428g Cm^{-2} yr^{-1} de l'écosystème terrestre. Les estimations modèles de respiration hétérotrophe du sol dépassent un peu nos valeurs d'estimation de PBN, impliquant que le flux du carbone à destination ou en provenance de la ligne de partage des eaux de Fleuve Volta est près d'être équilibre. Autrement dit, la ligne de partage des eaux dégage annuellement plus de dioxyde de carbone à l'atmosphère qu'elle reçoit. En dehors de flux du carbone terrestre, l'équilibre de photosynthèse et de respiration dans le Lac de Volta était également étudié. On a constaté que le lac dégage dioxyde de carbone à l'atmosphère bien que l'ampleur du flux soit plus petit que celui de l'écosystème terrestre.

Introduction

Many radionuclides are produced in the atmosphere of the Earth by nuclear reactions caused by cosmic rays. These cosmic rays are composed primarily of highly energized nucleons. These highly energized nucleons emit protons, alpha particles (and/or b- particles and g-particles) which enter the nucleus of a target atom to form a product nucleus of a higher atomic number (Faure, 1986). Such spallation reaction occur in the atmosphere of the Earth when protons and secondary neutrons from cosmic-rays interact with atoms of oxygen nitrogen and argon. The resulting cosmogenic radionuclides either remain in the atmosphere for substantial periods of time or are rapidly removed from it by precipitation. Several of the cosmogenic radionuclides have sufficiently long half-lives, thus, making them useful for the study of hydrologic processes. One such cosmogenic isotope is tritium (^3H) which occurs in the atmosphere and in the hydrosphere, and like ^{14}C is produced in the atmosphere by the interaction of ^{14}N with cosmic-ray neutrons according to the reaction of Craig (1961a). The ^3H serves as a tracer for the study of atmospheric, hydrologic and oceanographic processes (Gat, 1981). The resident time of tritiated water in the lower stratosphere is between 1 and 10 years. Once it has reached the lower troposphere, the tritiated water rains out in 5-20 days (Gat,1981).

Stable isotopes are used to constrain terrestrial and aquatic carbon fluxes in the Volta river watershed. On the chart of the nuclides, hydrogen has two stable isotopes (^1H and D), while oxygen has three stable isotopes (^{16}O, ^{17}O, and ^{18}O). These together have nine isotopic configurations ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, $HD^{18}O$, $D_2{}^{16}O$, $D_2{}^{17}O$, $D_2{}^{18}O$) whose atomic masses are approximately given by their mass numbers. The vapour pressure of the different isotopic molecules of water are inversely proportional to their masses. Therefore, $H_2{}^{16}O$ has a significantly higher vapour pressure than $D_2{}^{18}O$ (Hoefs, 1980). For this reason, water vapour formed by evaporation of liquid water is enriched in ^{16}O and H while the remaining water is enriched in ^{18}O and D (Faure, 1986). These stable isotopic composition of hydrogen and oxygen are reported in terms of $^{18}O/^{16}O$ and D/H ratios and related to a standard called SMOW (Standard Mean Ocean Water) proposed by Craig (1961a). Using this application on the Danube river, the second largest river in Europe, precipitation was found to be more depleted in light isotopes with increase in latitude and altitude (Pawelleck *et al.*, 2001). Testing the method of plant transpiration, to estimate the annual carbon flux in the Mississippi river watershed, Lee & Veizer (2003) obtained estimates of NPP that are similar to modeled estimates of heterotrophic soil respiration. Thus, Lee & Veizer (2003) concluded that, the Mississippi river watershed is not likely to contain a significant proportion of the residual carbon sink postulated to exist in the northern hemisphere.

It is now well known that the existing balance for the global carbon circle cannot account for about ¼ of the carbon dioxide released by the burning of fossil fuels, giving rise to the concept popularly known as the “missing sink” (Houghton *et al.*, 1998) or the “residual terrestrial sink” (Prentice *et al.*, 2001). It was frequently assumed that CO_2 and nitrogen “fertilization” of the terrestrial biomass resulted in sequestration of this carbon. Recent studies show that fertilization effects are too small to explain more than a small fraction of the proposed sink (Sarmiento & Gruber, 2002). Thus, despite many studies (Potter & Klooster, 1999), the role of terrestrial ecosystems in the atmospheric carbon budgets remains unclear. As a result of this uncertainty in the assessment of the global carbon budget, the distribution and magnitude of potential terrestrial carbon sink are important questions yet to be properly addressed. In order to fix one mole of carbon, a plant has to transpire $n \times 10^2$ moles of water (where n is an integer). Knowing the hydrologic budget of a system, essentially its transpiration component, it is possible to calculate the carbon flux associated with the NPP of Telmer & Vizer (2001).

The Volta river watershed, located between latitude 6° N to 14º N in West Africa, encompasses approximately 406,000 km^2 and stretches from the Gulf of Guinea to the southern boundary of the Sahel region (Fig. 1). Politically, the watershed is shared by several countries but the majority of the watershed lies in Burkina Faso (42.1%) and Ghana (40.2%) with the remaining area in Côte d'Ivoire, Mali, Togo and Benin. Collectively, three sub-basins, namely the Black Volta river (156900 km^2), the White Volta river (111800 km^2), and the Oti river (78800 km^2) constitute about 84% of the total drainage area (Dickson & Benneh, 1995; Andreini *et al*., 2000). Each of these major tributaries and several small rivers, located in the Lower Volta drainage area, discharge into the Volta Lake with the three largest rivers accounting for ~80% of total discharge.

The Volta river basin is well suited to the present study. This is because the area is well characterized in terms of its hydrologic and meteorological conditions and the relevant data can easily be obtained from many sources. Besides, the basin encompasses distinct hydrologic and climatic sub-regions permitting examination of relationship between carbon circling and various environmental parameters. Presently, Africa is one of the less frequently studied area for carbon cycling and so registers a deficit in data collection. It is, therefore, the hope of the authors of this paper that the carbon balance obtained in the study will help substantiate or modify figures. Hydrological and land-cover data, together with stable isotope

Fig. 1. (a) Location of Volta river watershed in West Africa, (b) Distribution of GLC2000 land-cover classes in the Volta watershed. (Modified from Mayaux *et al*., 2004).

measurements of $\delta^{18}O$ and δD, are used to constrain terrestrial and aquatic carbon fluxes in the Volta river watershed.

Experimental

In general, the hydrologic budget of a watershed is defined by the∆expression:

$$P = Q + ET + \Delta S \qquad (1)$$

where P is water input by precipitation, Q is annual river discharge, ET is evapotranspiration, and S is the change in groundwater storage. Precipitation and discharge components of the equation are determined from historical records of rainfall and runoff. Furthermore, on decadal ti∆me-scales, the change in groundwater storage (S) is considered negligible. The remaining component of the annual water balance is evapotranspiration (ET), which includes surface evaporation (E), plant transpiration (T), and rainfall interception (I). Interception, the proportion of precipitation that is caught by vegetation and evaporated to the atmosphere before reaching the ground, can be estimated with empirically determined interception values for different plant types and their distribution in the watershed (Sellers & Lockwood, 1981; Hetherington, 1987). Subsequently, evaporation and plant transpiration remain the only undefined terms in the annual water balance expression. Separating evaporation and transpiration is important because transpiration is the only water flux associated with carbon sequestration.

Transpiration and interception are both non-fractionating processes and do not alter the isotopic composition ($\delta^{18}O$-δD) of surface water as it moves through the hydrologic system. However, owing to isotopic fractionation during evaporation, river discharge (surface water leaving the hydrologic system) is enriched in the heavier isotopes, ^{18}O and D, relative to precipitation (water entering the hydrologic system). If evaporation is a significant component of the annual water balance, a plot of the isotopic composition ($\delta^{18}O$-δD) of river discharge defines a regression line with a shallower slope than that of regional precipitation. The difference in slopes is proportional to the degree of evaporation in the watershed. Numerous isotope mass balance equations are proposed to quantify the proportion of annual evaporation relative to total rainfall (Gonfiantini, 1986; Gat & Bowser, 1991; Gat & Matsui, 1991; Gibson *et al.*, 1993). Once evaporation flux is defined, the remaining moisture flux can be attributed solely to plant transpiration. Utilizing the coupling of transpiration and carbon dioxide flux during photosynthesis, annual transpiration is converted to NPP, yielding a *first order* estimate of annual photosynthetic carbon flux, where net primary productivity is equal to transpiration (T) divided by water use efficiency (WUE).

$$\text{NPP (mol C yr}^{-1}\text{)} = \text{T (mol H}_2\text{O yr}^{-1}\text{)} \div \text{WUE (mol H}_2\text{O per mol C)} \qquad (2)$$

The apparent relationship between WUE and NPP deserves a more detailed consideration. In plants, water loss and CO_2 uptake are related. Consequently, the regulating factor for WUE and the productivity of the plant can be either the atmospheric CO_2 concentration or water availability. From a global perspective, it is to compare the amount of photosynthetically available water to the amount of atmospheric CO_2 With the current CO_2 concentration of 360 p.p.m., the atmosphere contains 63.6×10^{15} moles of CO_2 (Schlesinger,1997). The quantity of photosynthetically available water in the soils (i.e. root zone) is about 3228 to 3600×10^{15} moles (Webb *et al.*, 1993; Berner & Berner, 1996). Taking the higher estimate as an example, the calculated mole ratio between soil H_2O and atmospheric CO_2 is, thus, 58 :1, significantly less than even the short term WUE of C3 (500:1) or C4 (250:1) plants. Considering the rapid turnover rate of soil water (residence time of 1.2 years) compared to atmospheric CO_2 (residence time of 5 years), the ratio between effective amount of soil water and atmospheric CO_2 becomes 250:1, still lower than the WUE of the dominant C3 plants.

The mathematical expression for photosynthesis and respiration using the relationshipbetween WUE and NPP has been expressed by many authors including Gonfiantini (1986), Rabinowitch (1951), Chartier (1970) and Charles-Edward & Ludwig (1974). The model of leaf photosynthesis including photorespiration by Charles-Edward & Ludwig (1974) combines diffusion from the atmosphere through the intercellular air spaces to the sites of photosynthesis in the mesophyll tissue. The mathematical relationship derived from the model describes a hyperbola for the dependence of the net exchange rate on CO_2 and oxygen with 12 parameters. Simplified to three parameter equation, gives the following:

$$P_n = P_g - R_l - R_d \qquad (3)$$

where Pg is the gross photosynthetic rate, R_l is the component of respiration that depends on the light flux density (photorespiration) and R_d is a component of respiration. In this work, the equation of Gonfiantini (1986), which establishes a clear relationship between evaporation and weighted mean $\delta^{18}O$ (or δD) values, was used.

According to Gonfiantini (1986),

$$x = \frac{E}{I} = (\delta_s - \delta_a)\left(\frac{(1-h+\Delta\varepsilon)}{(\delta_s+1)}\right) \times \left(\Delta\varepsilon + \frac{\varepsilon}{\alpha}\right) + (h(\delta_a - \delta_s)) \qquad (4)$$

where x is the proportion of evaporation (E) with respect to total water input (I). It is important to note that interception flux (the proportion of annual rainfall re-evaporated from plant surfaces before reaching the ground-surface) is subtracted from total annual rainfall to calculate total water input (I). δ_S is the weighted mean $\delta^{18}O$ (or δD) value at the mouth of the river. δ_I is the mean isotopic composition of precipitation; for closed systems, δ_I is given by the intersection between the regression line for $\delta^{18}O$ and δD values of discharge (local evaporation line) and the local meteoric water line (LMWL) (Gat & Matsui, 1991). δ_a (Table 1) is the mean $\delta^{18}O$ (or dD) value of the water vapour, calculated by assuming isotopic equilibrium with local precipitation ($\delta_a = \delta_I - \varepsilon^*$). The limiting isotopic enrichment (ε^*) under local hydro-meteorological conditions is given by:

$$\delta^* = \frac{h\delta_a + \varepsilon}{h - \varepsilon} \qquad (5)$$

The mean relative humidity is represented by *h*, α is the equilibrium factor for oxygen ($\ln\alpha = 1137T^{-2} - 0.4156T^{-1} - 0.00207$) and hydrogen isotopes ($\ln\alpha = 24844T^{-2} - 76.2\Delta48T^{-1} + 0.05261$) (Friedman & O'Neil, 1977). ε is the kinetic enrichment factor for oxygen [14.2(1-h)] and hydrogen isotopes [12.5(1-h)] and $\varepsilon = \alpha - 1$ (Table 1).

Stable isotopes can be used to estimate the proportion of photosynthesis to respiration (P:R) of aquatic ecosystems, including rivers and lakes (Quay *et al*., 1995; Wang & Veizer, 2000, 2004).

TABLE 1

Variables used in the isotope mass balance equation

	White Volta river	*Black Volta river*	*Oti river*
d_S	-0.00262	-0.00245	-0.00209
d_I	-0.005	-0.005	-0.005
d_a	-0.01534	-0.01548	-0.01540
a	1.010344	1.010483	1.010403
e	0.010344	0.010483	0.010403
Δ e	0.003124	0.002414	0.002414
T (°K)	301.6	300.0	300.9
Humidity (%)	78	83	83
Evaporation*(%)	15.6	22.6	30.7

The isotopic signature of dissolved oxygen ($\delta^{18}O_{DO}$) in an aquatic ecosystem is the result of three processes: (i) exchange with the atmosphere, (ii) photosynthesis, and (iii) respiration. Aquatic systems dominated by photosynthesis are characterized by $\delta^{18}O_{DO}$ values less than 23.5‰, and will be over saturated with respect to oxygen. In contrast, systems dominated by respiration are characterized by $d^{18}O_{DO}$ values greater than 23.5‰, and under saturated oxygen concentrations. If atmospheric exchange dominates, oxygen saturation will be close to 100 per cent and $\delta^{18}O_{DO}$ will be approximately 23.5‰.

Carbon isotope composition of water in the Volta river watershed

The isotopic signature of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) is a reflection of photosynthetic production and respiration processes in the aquatic system. Photosynthesis preferentially consumes ^{12}C (the lighter isotope of carbon), causing the residual dissolved inorganic carbon (DIC) to become enriched in ^{13}C. In contrast, respiration converts isotopically-light organic carbon into inorganic carbon, resulting in a depleted DIC pool (Keough *et al.*, 1998). Atmospheric carbon dioxide has an isotopic composition of about –9.5‰, which when dissolved produces inorganic carbon with a composition of approximately –3‰ in the solution. This value, however, varies with *p*H and temperature (Mook & Tan, 1991).

Sources and sinks

The words source and sink were originally used by plant scientists in connection to plant growth problems. In this paper, the concept of source and sink is used relative to the carbon budget. The existing global carbon cycle involves the release of CO_2 into the atmosphere by the burning of fossil fuel and the use of the CO_2 by plant bodies. Generally, the source is the area of saturation and the sink, the area of deplation. Peng *et al*. (1979) estimated the rate of gaseous exchange between the atmosphere and lakes by measuring the disequilibrium between ^{226}Ra and ^{222}Rn due to the evasion of ^{222}Rn into the atmosphere. The mean rate of gross exchange of CO_2 between the atmosphere and lakes (at an atmospheric CO_2 concentration of 300 p.p.m.v. was found to be 18±5 moles $m^{-2}yr^{-1}$). This implies a mean residence time for CO_2 in the atmosphere before transfer into the lake to be 8.5±2 years. This gas exchange across air and water interface varies depending on wind and wave. Globally, about 4.4×10^{14} mole of carbon is released annually from burning of fossil fuels (Rotty, 1983). About 2.3×10^{14} mol of this carbon accumulates as CO_2 in the atmosphere, enhancing the much discussed greenhouse effect.

Rivers linking the terrestrial system and the ocean transport yearly about $2.5 – 5.0 \times 10^{13}$ mol carbon particulate and dissolved forms (Meybeck, 1987). Studies of dissolved inorganic carbon (DIC) in some major rivers such as the Amazon and Rhein showed that Pco_2 in these rivers is about 10-15 times greater than expected for equilibrium with the atmosphere (Kempe, 1982). According to Bolin *et al*. (1986), the carbon exchange between gas phase and solution has a factor $\xi = \{\Delta Pco_2/Pco_2\}/\Delta(DIC)/(DIC)$, where ξ is a Revelle factor, ΔPco_2 the finite change in partial pressure, Pco_2 the partial pressure and Δ(DIC) the finite dissolved inorganic carbon. In this paper, however, stable isotope measurements of $\delta^{18}O$ and δD are utilized to constrain the annual water and carbon fluxes using the WUE factor and the estimated NPP as indicated in equation (2).

Case study: Volta river basin

Five sampling stations were established along the Volta river watershed on a 1000 km transect running from the Gulf of Guinea to the northern portions of the watershed in Burkina Faso. The locations were selected from north to south to represent the prevailing rainfall gradient throughout the watershed. Weekly rainfall samples were collected during the rainy season of 2003 for the determination of isotopic composition of H_2O. This was to compliment data collected from the global network for isotopes in precipitation (GNIP) stations that generates a local meteoric water line (LMWL) for West Africa. Using the method proposed by Telmer & Vizer (2000, 2001) estimates of photosynthetic net primary productivity (NPP) for terrestrial ecosystems were obtained. This is based on the coupled effect of water and carbon during photosynthetic activity. To measure this coupling, the "water use efficiency (WUE) factor from Nobel (1999) was used.

Samples from the Volta lake were also taken at the Akosombo dam from the lake surface (1m) and from the bottom (18 m) for the measurement of the isotopic composition of water ($\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{18}O_{DO}$, $\delta^{13}C_{DIC}$) using the method described by Lee & Veizer (2003) for determining isotopic mass balance. For the determination of isotopic composition of water, samples were taken from Volta lake at 1 m (surface) and 18 m (bottom). $\delta^{18}O$ and δD are the isotopic signatures of water, $\delta^{13}C_{DIC}$ is the isotopic signature of dissolved inorganic carbon, and $\delta^{18}O_{DO}$ is the isotopic signature of dissolved oxygen. All isotope measurements were done at the G. G. Hatch Isotope Laboratory, University of Ottawa. For procedures, precisions and instrumentation details see Lee & Veizer (2003) and Barth *et al.* (2004). Oxygen and hydrogen isotope data are reported in ‰ relative to VSMOW (Vienna Standard Mean Ocean Water), while that of carbon is reported in ‰ relative to PDB (Belemnites of the Peedee Formation) standards. O_{2sat} is the percentage of oxygen saturation, calculated from measured values and temperature and pressure dependent equilibrium values given by Benson & Krause (1984).

Results and discussion

The LMWL for West Africa, derived from both GNIP data and rainfall samples from this study, is defined by the equation $\delta D = 6.6 \times \delta^{18}O + 2.0$ ‰ ($r^2 = 0.93$, $n = 296$) (Fig. 5). The evaporation line for the entire Volta river watershed, calculated from the collective river discharges of the Black Volta River, White Volta river, and Oti river, is $\delta D = 5.2 \times \delta^{18}O - 4.6$‰ ($r^2 = 0.94$, $n = 36$). Isotopic composition of mean annual precipitation (δ_I) is estimated from the intersection of the evaporation line and LMWL (Fig. 4). The results of the isotope mass balance equation are presented in Table 2. The proportion of total water input (rainfall minus interception) evaporated from each watershed varies from 15.6 per cent (White Volta river watershed) to 30.7 per cent (Oti river watershed). In the entire Volta river watershed, 17 per cent (65 km^3) of annual rainfall is lost due to land-based evaporation.

In Table 2, $\delta^{18}O_{DO}$ ranged from 21.63 to 23.26‰ at the surface and between 21.37 and 23.19‰ at 18 m. The average value of $\delta^{18}O_{DO}$ is depleted compared to atmospheric oxygen (22.32‰ at the surface and 22.36‰ at the bottom). This implies that the lake was on average, over saturated with saturation range from 93.70 to 107.43 per cent at the lake's surface, and between 94.51 and 107.56 per cent at 18 m (Table 2). Comparing $\delta^{18}O_{DO}$ and O_{2sat} (Fig. 2), a negative correlation between the variables during the wet season is observed, suggesting that respiration and production control the net value of oxygen during this period. During the dry season, the values cluster near atmospheric equilibrium, suggesting that the oxygen content and isotopic composition are primarily controlled by atmospheric flux.

The isotopic composition of allochthonous inputs into the lake primarily depends on the type of vegetation and its distribution in the watershed. Located in the Sudan and Guinea-Congolian zones, most of the natural vegetation in the Volta river watershed is woodland savanna. This woodland savanna is characterized by woody and herbaceous plants, with tall grasses forming the ground cover beneath a continuous canopy of deciduous trees (Mistry, 2000). These are put into C_3 plants (plants less resistant to high temperature,

TABLE 2

Isotopic measurements of water samples from the lake surface (1 m) and from the lake bottom(8m)

Date	$\delta^{18}O$ (surface)	δD (surface)	$\delta^{18}O$ (bottom)	δD (bottom)	$\delta^{13}C_{DIC}$ (surface)	$\delta^{13}C_{DIC}$ (bottom)	$\delta^{18}O_{DO}$ (surface)	$\delta^{18}O_{DO}$ (bottom)	$\%O_2$ sat (surface)	$\%O_2$ sat (bottom)
14 May 03	-0.3	-6.31	-0.31	-4.51	-8.09	-9.93	23.08	22.98	98.97	99.76
31 May 03	0.07	0.1	-0.02	-2.8	-5.25	-6.43	20.47	21.27		
12 Jun 03	-0.06	0.93	0.06	1.3	-4.73	-4.72	20.96	20.26	97.40	100.26
27 Jun 03	-0.14	-1.35	-0.19	0.91	-3.18	-3.46	22.46	22.47		
14 Jul 03	-0.3	-2.39	-0.08	-0.92	-3.59	-4.31	22.36	22.34	96.35	99.23
25 Jul 03	0.06	-0.95	0.28	0.15	-4.05	-4.19	22.02	21.87		
08 Aug 03	0.61	-0.74	0.39	-0.75	-5.06	-4.64	21.85	22.22	93.71	94.51
26 Aug 03	0.36	-1.98	0.14	-0.67	-4.69	-6	22.1	22.29		
08 Sep 03	0.26	2.86	0.31	-2.17	-5.93	-5.86	21.37	21.36	100.65	102.04
22 Sep 03	0.32	-1.46	0.25	-2.42	-4.2	-6.34	21.92	21.97		
06 Oct 03	0.35	0.44	0.46	-1.72	-3.65	-4.34	21.7	22.03	104.08	105.94
20 Oct 03	0.51	0.77	0.62	1.77	-2.74	-4.21	21.55	22.41		
14 Nov 03	0.76	-3.51	0.56	4.03	-2.72	-7.5	22.37	21.81	107.43	103.63
28 Nov 03	0.6	-0.78	0.44	-0.11	-3.86	-8.09	21.24	21.05		
12 Dec 03	0.01	0.12	-0.03	-3.03	-2.72	-3.86	23.41	23.37	105.33	104.65
29 Dec 03	-0.06	-2.7	-0.09	-3.3	-4.28	-4.44	23.11	23		
12 Jan 04	-0.12	0.12	-0.07	-1.41	-4.76	-5.36	23.01	22.96	102.79	103.80
23 Jan 04	-0.15	-0.95	-0.14	2.36	-4.96	-5.79	22.99	23.09		
09 Feb 04	-0.03	-1.08	-0.04	-0.18	-10.58	-10.63	23.02	22.93	104.11	107.55
23 Feb 04	-0.04	-3.26	-0.13	-0.87	-10.89	-12.4	23.06	23		
05 Mar 04	-0.11	-1.75	-0.15	-0.28	-7.49	-7.86	22.92	22.93	104.71	105.47
22 Mar 04	-0.07	0.15	-0.27	-0.29	-10	-13.6	22.72	22.93		
02 Apr 04	-0.15	-3.69	-0.23	-2.88	-9.23	-10.35	22.98	22.98	103.72	102.63
30 Apr 04	-0.26	-4.56	-0.23	-4.04	-8.47	-9.35	23.02	23.05		

drought, high salinity and low humidity), and C_4 plants (plants resistant to high temperature, drought, high salinity and low humidity). In general, C_3 plants have $\delta^{13}C$ values between -22 to-35‰ (mean -26‰) whereas C_4 plants have $\delta^{13}C$ values between -9 to -16‰ (mean -13‰) (Clark & Fritz, 1997). Estimates of the proportion of C_3 to C_4 plants in the Volta river watershed, 64 per cent C_3-36 per cent C_4, suggest that $\delta^{13}C$ value of allochthonous organic matter should be about -21‰. Although these figures are an approximation, the $\delta^{13}C$ value of autochthonous organic matter is certainly more depleted and isotopically-distinct compared to carbon derived from direct exchange with the atmosphere. For a qualitative assessment of respiration in Volta lake, this is considered sufficient.

Mean $\delta^{13}C_{DIC}$ at the lake's surface is -5.63‰ and -6.82‰ at 18 m depth. More enriched surface dissolved inorganic carbon is indicative of increased photosynthesis and less-respired carbon. During the latter part of the dry season, $\delta^{13}C_{DIC}$ is more depleted (-9.92‰) on average compared to the remainder of the year, possibly due to increased respiration and/or allochthonous inputs during the dry season. Fig. 3 illustrates the dependency of $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ on seasonality. During the wet season, $\delta^{13}C_{DIC}$ is more enriched and $\delta^{18}O_{DO}$ is more depleted, possibly due to the influence of *in situ* production on both O_2 and DIC. At the beginning of the dry season, both $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ are closer to atmospheric

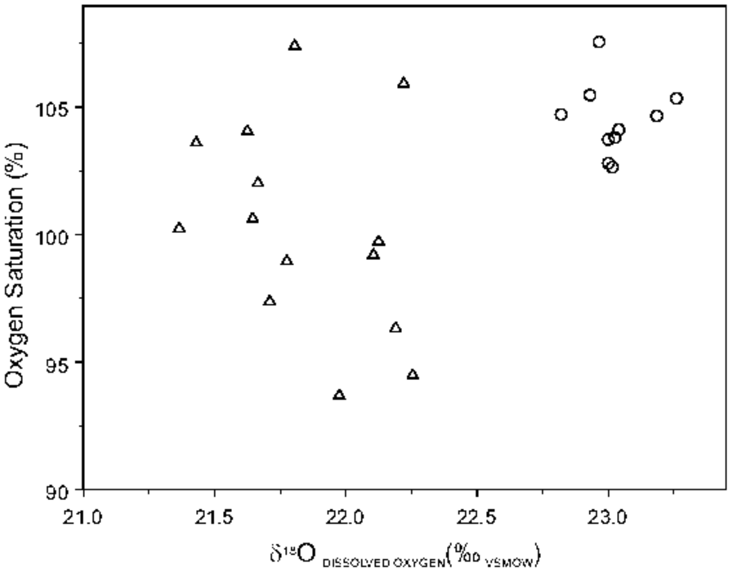

Fig. 2. Relationship between oxygen saturation and $\delta^{18}O_{DO}$ in Volta lake. Triangles are samples taken during the rainy season and circles samples taken during the dry season.

composition suggesting that atmospheric flux controls the dissolved gases during this time of the year. Later in the dry season, $\delta^{18}O_{DO}$ remains near equilibrium while $\delta^{13}C_{DIC}$ becomes more deple-ted, suggesting increased input of allochthonous dissol-ved inorganic carbon. During this time, productivity: respi-ration (P:R) is highest, implying that allochthonous inputs of DIC may be exceeding the isotopic signature of primary production in the lake (Fig. 4).

Quay *et al.* (1995) proposed a model to determine the balance between productivity (P) and respiration (R) in aquatic systems. This model

Fig. 3. Relationship between $\delta^{13}C_{DIC}$ and $\delta^{18}O_{DO}$ in Volta lake. Black dates indicate samples taken during the dry season while grey dates indicate samples from the rainy season.

Fig. 4. Production-to-respiration ratio in Volta lake between April 2003 and March 2004, as calculated from the model described in Quay *et al.* (1995) that depends on $\delta^{18}O_{DO}$, $\delta^{18}O_{w}$ and oxygen saturation. Moving average of monthly measurements of surface waters are shown with a solid line and bottom waters with a dotted line. Error bars are ±1 standard error.

Fig. 5. Isotopic composition ($\delta^{18}O$ and δD) of rainfall (Local meteoric water line) and river discharge (evaporation regression line)

is based on the degree of oxygen saturation, the isotopic composition of dissolved oxygen and the isotopic composition of water. Results from this model for Volta lake suggest that in the wet season (May- November), P:R is close to equilibrium in both surface and bottom waters (Fig. 4). There was peak production in both surface and bottom water in December, and at depth in February. Mean annual P: R was 1.09 ± 0.15 at the surface and 1.15 ± 0.25 at 18 m, implying that photosynthesis exceeds respiration in the aquatic system and that the Volta lake sequestrates more carbon each year than is lost to the atmosphere. It is important to note, however, that this esti-mate is for autochthonous production in the lake and does not account for allochthonous input of carbon from the watershed.

The results show that the Volta river watershed sequestrates 0.17×10^{15} g C or 428 g C $m^{-2} yr^{-1}$ from the atmosphere. For comparison, Whittaker & Likens (1973) estimate that mean annual NPP for savannas, including tropical grasslands, is 405 (90 – 900) g C $m^{-2} yr^{-1}$. Olson *et al.* (1983) estimate that mean annual NPP for various types of tropical and temperate savanna vegetation, including tropical dry forest and semi-arid woodlands, is 437 g C $m^{-2} yr^{-1}$. Recent mean annual NPP proposed by Scholes & Hall (1996) is 547 (198 – 1860) g C $m^{-2} yr^{-1}$ for savannas, drought-deciduous woodlands, and *Eucalyptus* and *Acacia* woodlands. In general, the similarity of these various estimates of NPP suggests that the water balance approach to estimating annual photosynthetic carbon flux is viable and offers, for the first time, some information on the long-term flux of carbon from a relatively large portion of West Africa.

Modelled estimates of heterotrophic soil respiration from Raich & Potter (1995) exceed NPP estimates from this study, implying that the Volta river watershed is a small source of carbon dioxide to the atmosphere. However, the error associated with the water-use efficiency values for C_3 and C_4 plants in this study is 55 and 23 per cent, respectively, implying that watershed NPP could be significantly higher if different water-use efficiency values were used. According to Raich & Potter (1995), heterotrophic soil respiration for the Volta river watershed is estimated to be 1.99 × 10^{16} g C or 501 g C m^{-2} yr^{-1}. This value is 15 per cent different from the estimated NPP. Using the existing water balance, the associated water-use efficiency needed to reach the equivalent rate of primary productivity is 625 moles H_2O per mole of carbon compared to the 745 moles H_2O per mole of carbon used in this study. This water-use efficiency corresponds to 60 per cent C_4 vegetation in the Volta river watershed. This proportion of C_4 vegetation seems improbable, given the significance of C_3 croplands and woody vegetation in the watershed.

The only ecosystems that may sustain such high water-use efficiency are C_4-dominated grasslands, which may occur in the Sahel region of West Africa. Most of the vegetation in the Volta river watershed, however, is considered woodland savanna and, therefore, a mixture of woody and grassy vegetation and is unlikely to contain such high proportions of C_4 vegetation. Recognizing that NPP estimates from this study are considered *first order* and the soil respiration estimate is global in scale, the 15 per cent discrepancy is relatively small given the dissimilarity of methods used for the determination of each. Overall, the similarity of productivity and soil respiration fluxes suggest that carbon fluxes to and from the Volta river watershed are close to being in balance, or that respiration slightly exceeds terrestrial productivity. For the Volta river watershed, the difference between NPP and heterotrophic soil respiration is 2.9 × 10^{15} g C yr^{-1}, implying a source of carbon to the atmosphere. Incorporating the additional 0.026 × 10^{15} g C (estimated as 15% of annual NPP; Scholes & Walker, 1993) to be lost each year due to the burning of vegetation, the flux to the atmosphere could increase to 5.2 × 10^{15} g C yr^{-1}.

Conclusion

Differences in terrestrial NPP between the Black Volta river, White Volta river, and Oti river watersheds appear to be related solely to the annual water cycle. This is so because atmospheric carbon dioxide concentration, temperature, and vegetation characteristics are similar for all three watersheds. Importantly, NPP estimates for the Volta river watershed highlight the strong coupling of water and carbon cycles in terrestrial ecosystems. This invariably demonstrates the value of watershed-scale estimates in constraining the terrestrial carbon cycle. Model results based on stable isotopic measurements (Quay *et al*., 1995) suggest that annual in-lake production significantly exceeds aquatic respiration.

Even though the results obtained may be of interest to the Volta River Authority (VRA) in addressing the yearly fluctuating water level in the lake, a more-detailed examination of the spatial and temporal variability of dissolved organic and inorganic carbon inputs into Volta lake is necessary to quantify the magnitude of the carbon flux and loss of water to the atmosphere.

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References

ANDREINI, M., VAN DE GIESEN, N., VAN EDIG, M., FOSU,

W. & Andah, W. (2000) Volta Basin Water Balance. *Discussion Papers on Development Policy 21*. ZEF – Zentrum fuer Entwicklungsforschung, Bonn.

Barth J. A. C., Tait, A. & Bolshaw, M. (2004) Automated analyses of $^{18}O/^{16}O$ ratios in dissolved oxygen from 12 ml samples. *Limnol. Oceano. Methods* **2**, 35-41.

Berner, E. K. & Berner, B. A. (1996) Global Environment, Cycles, Water, Air and Geochemical tydes. Prentice Halt Inc., New York.

Benson, B. B. & Krause, D. (1984) The concentration and isotope fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnol. Oceanogr* **29,** 620-632.

Bolin, B., Doos, B. R., Jager, J. & Warrick, R. A. (1986) *The greenhouse effect, climate change and ecology.* John Willy and Sons, New York.

Charles-Edwards, D. A. & Ludwig, L. J. (1974) A model for leaf photodynthesis by C3 plant species. *Ann. Bot*. **38**, 921-930.

Clark, I. & Fritz, P. (1997) *Environmental Isotopes in Hydrogeology.* CRC Press, Boca Raton 328 pp.

Craig, H. (1961a) Standard of reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* **133**, 1833-1934.

Faure, G. (1986) *Principles of Isotope Geology.* John, Wiley and Sons. New York

Friedman, I. & O'Neil, J. R. (1977) *Compilation of stable isotope fractionation factors of geochemical interest in data of Geochemistry,* 6th edn. U.S. Geol. Surv. Prof. Pap, 440-KK 49 pp.

Gat, J. R. (1981) The isotopes of hydrogen and oxygen in precipitation. In *Handbook of Environmental Isotope Chemistry*, vol. 1A (P. Fritz and J. Ch. Fontes, ed.), pp 21-47. Elsevier, Amsterdam.

Gat, J. R. & Bowser, C. (1991) The heavy isotope enrichment of water in coupled evaporative systems. In *Stable Isotope Geochemistry: A tribute to Samuel Epstein.* (H. P. Taylor, J. R. O'Neil , I. R. Kaplan ed.), pp. 159-164. Geochemical Society Special Publication 3, San Antonio.

Gat, J. R. & Matsui, E. (1991) Atmospheric water balance in the Amazon basin: An isotopic evapotranspiration model. *J. Geophys. Res.* **96**, 13179-13188.

Gibson, J. J., Edwards, T. W. D., Bursey, G. G. & Prowse, T. D. (1993) Estimating evaporation using stable isotopes: quantitative results and sensitivity analysis for two catchments in northern Canada. *Nordic Hydrol.* **24**, 79-94.

Gonfiantini, R. (1986) Environmental isotopes in lake studies. In *Handbook of environmental Isotope Geochemistry*, Vol. 2. (P. Fritz J. C. Fontes and ed.), pp. 113-168. Elsevier Scientific Publishing Company, New York.

Hetherington, E. D. (1987) The importance of forests in the hydrological regime. In *Canadian Aquatic Resources, Ottawa.* (M. C. Healy R. R. and Wallace ed), pp. 179-213. Department of Fisheries and Oceans, Ottawa.

Hoefs, Jr. (1980) *Stable Isotope Geochemistry*, 2nd edn. Springer – Verlag, Heidelberg and New York. 208 pp.

Houghton, R. A., Davidson, E. A. & Woodwell, G. M. (1998) Missing sinks, feedbacks, and understanding the roll of terrestrial ecosystem in the global carbon balance. *Global Biogeochem Cy.*, **12**, 25-34.

Keough, J. R., Hagley, C. A., Ruzycki, E. & Sierszen, M. (1998) $\delta^{13}C$ composition of primary producers and role of detritus in a freshwater coastal ecosystem. *Limnol. Oceanogr.* **43**, 734-740.

Lee, D. & Veizer, J. (2003) Water and carbon cycles in the Mississippi River Basin: Potential implications for the Northern Hemisphere –Residual Terrestrial Sink. *Global Biogeochem. Cy*. **17**(2).

Mook W. G. & Tan, F. C. (1991) Stable carbon isotopes in rivers and estuaries. In *Biogeochemistry of major world rivers*. (E. T. Degens, S. Kempe and J. E. Richey, ed.), pp. 245-264. Wiley and Sons, Toronto.

Nobel, P. S. (1999) *Physiochemical and environmental plant physiology*, 2nd edn. Academic Press, San Diego.

Olson, J. S., Watts, J. A. & Allison, L. J. (1983) *Carbon in live vegetation of major world ecosystems.* ORNL-5862. Oak Ridge National Laboratory, Environmental Science Division. Oak Ridge, TN.

Pawelleck, F., Frauenstein, F. & Veizer, J. (2001) Hydrochemistry and isotope chemistry of the upper Danube River. *Geochemica et Chosmochemica Acta* **66** (21), 3839-3854.

Potter, C. S. & Klooster, S. (1999) Detecting a terrestrial biosphere sink for carbon dioxide: Inter-annual ecosystem modeling for the mid-1980's *Climate Change* **42**, 489-503.

Prentice, I. C., Farquhar, G. D., Fasham, M. J. R., Goulden, M. L., Heimann, M., Jaramillo, V. J.,

KHESHGI, H. S., LE QUÉRÉ, C., SCHOLES, R. J. & WALLACE, D. W. R. (2001) The carbon cycle and atmospheric carbon dioxide. In *Climate Change 2001: The Scientific Basis.* (J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden and D. Xiaosu, ed), pp 183-237. Cambridge University Press, Cambridge, U.K.

QUAY, P. D., WILBUR, D. O., RICHEY, J. E., DEVOL, A. H. BENNER, R. & FORSBERG, B. R. (1995) The ^{18}O:^{16}O of dissolved oxygen in rivers and lakes in the Amazon Basin: Determining the ratio of respiration to photosynthesis rates in freshwaters. *Limn. and Ocean.* **40**, 718-729.

RABINOWITCH, E. L. (1951) *Photosynthesis and related processes.* Interscience, New York.

RAICH, J. W. & POTTER, C. S. (1995) Global patterns of carbon dioxide emissions from soils. *Global Biogeochem. Cy.* **9**, 23-36.

ROTTY, R. M. (1983) Distribution and changes in industrial carbon dioxide production *J. Geophys. Res.* **88**, 130-1308.

SCHILESINGER, W. H. (1997) Biogeochemistry: and analysis of global change. Academic Press, San Diego.

SARMIENTO, J. L. & WOFSY, S. C. (1999) A U.S. Carbon cycle science plan. *A Report of the carbon and climate working group, U. S. Global change research program,* Washington D. C.

SELLERS, P. J. & LOCKWOOD, A. (1981) A numerical simulation of the effects of changing vegetation type on surface hydroclimatology. *Climate Change* **3**, 121-136.

SCHOLES, R. J. & HALL, D. O. (1996) The carbon budget of tropical savannas, woodlands and grasslands. In *Global change: effects of coniferous forests and grasslands,* (A. I. Breymeyer, D. O. Hall, J. M. Melillo and G. I. Agren, ed.), pp. 69-100. John Wiley and Sons Ltd., Chichester, UK.

SCHOLES, R. J. & WALKER, B. H. (1993) *An African Savanna: Synthesis of the Nylsvley Study.* Cambridge University Press, Cambridge, UK. 318 pp.

TELMER, K. & VEIZER, J. (2000) Isotopic constraints on the transpiration, evaporation, energy and NPP budgets of a large boreal watershed: Ottawa river basin, Canada *Global Biogeochem Cy*. **14,** 149-165.

TELMER, K. & VEIZER, J. (2001) Correction to isotopic constraints on the transpiration, evaporation, energy and gross primary production budgets of a large boreal watershed: Ottawa river basin, Canada. *Global Biogeochem Cy.* **15**, 1035.

WANG, X. & VEIZER, J. (2000) Respiration-photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada. *Geochim. Cosmochim. Acta* **64**, 3775-3786.

WEBB, R. S., ROSENZWEIG, C. E. & LEVINE, E. R. (1993) Specifying land surface characteristics in general circulation models: Soil profile data set and derived water-holding capacities. *Global Biogeochemical Cy.* **7**, 97-108.

WANG, X. F. & VEIZER, J. (2004) Erratum to Xuefeng Wang and Jan Veizer (2000) Respiration-photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada. *Geochim. Cosmochim. Acta* **64**(22), 3775-3786; **68**: 933-934.

WHITTAKER, R. & LIKENS, G. (1973). Carbon in the biota. In *Carbon and the Biosphere* (G. Woodwell and E. Pecan, ed.) CONF 720510, National Technical Information Service, Washington, D.C.

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