

*Full Length Research Paper*

# Hydrologic fluxes in the Volta River watershed : A paleo-terrestrial environment in West Africa

E. K. Hayford, J. Manu and D. Asiedu

Department of Geology, P.O.Box LG 58, University of Ghana, Legon, Accra

Accepted 6 April, 2010

The hydrologic cycle plays an important role in carbon cycling, due to the coupling of vapour release and CO<sub>2</sub> uptake during photosynthesis. This coupling, expressed as water use efficiency of transpiration ratio, can provide an inexpensive alternative for estimating the Net Primary Productivity (NPP) of terrestrial ecosystem. Stable isotopes of hydrogen and oxygen and long-term hydrologic and meteorological data together with stoichiometric relations of water and carbon are used to constrain water and carbon balances for the Volta River watershed. Soils annually respire 0.199 Pg C, and the balance of these fluxes or Net Ecosystem Productivity (NEP) is +0.029 Pg C Yr<sup>-1</sup>, implying an annual flux of CO<sub>2</sub> to the atmosphere. Annually, the Volta river watershed receives about 380 km<sup>3</sup> of rainfall. Approximately 50% of this volume of water is returned to the atmosphere through plant transpiration. Associated with annual transpiration flux is a carbon flux of 0.170 × 10<sup>15</sup> g C Yr<sup>-1</sup> or 428 g C m<sup>-2</sup> yr<sup>-1</sup> from the terrestrial ecosystem. Modeled estimates of heterotrophic soil respiration exceed slightly the NPP estimate, implying that carbon flux to and from the Volta river watershed is close to being in balance or the watershed is a small annual source of carbon dioxide to the atmosphere. In addition to terrestrial carbon flux, the balance of photosynthesis and respiration in Volta Lake is 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.

**Key words:** Hydrologic cycle, carbon cycling, Volta river basin, isotope mass balance relation, carbon sink.

## INTRODUCTION

Radio nuclides 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 β- particles and γ-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 (<sup>3</sup>H) which

occurs in the atmosphere and in the hydrosphere. <sup>3</sup>H like <sup>14</sup>C, is produced in the atmosphere by the interaction of <sup>14</sup>N with cosmic-ray neutrons according to the reaction of Craig (1961a). The <sup>3</sup>H 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 to 20 days (Gat, 1981). For our purpose however, 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 (<sup>1</sup>H and D), while oxygen has three stable isotopes (<sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O). These together have nine isotopic configurations (H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, H<sub>2</sub><sup>18</sup>O, HD<sup>16</sup>O, HD<sup>17</sup>O, HD<sup>18</sup>O, D<sub>2</sub><sup>16</sup>O, D<sub>2</sub><sup>17</sup>O, D<sub>2</sub><sup>18</sup>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<sub>2</sub><sup>16</sup>O has a significantly higher vapour pressure than D<sub>2</sub><sup>18</sup>O (Hoefs, 1980; Hayford et al., 2006). For this

\*Corresponding author. E-mail: [ebehayf@ug.edu.gh](mailto:ebehayf@ug.edu.gh). Tel: 0233(0)277606338.

reason, water vapour formed by evaporation of liquid water, is enriched in  $^{16}\text{O}$  and H while the remaining water is enriched in  $^{18}\text{O}$  and D (Faure, 1986; Hayford et al., 2006). These stable isotopic composition of hydrogen and oxygen are reported in terms of  $^{18}\text{O}/^{16}\text{O}$  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, 2001). Testing the method of plant transpiration to estimate the annual carbon flux in the Mississippi River watershed, Lee and Veizer (2003) obtained estimates of NPP that are similar to modeled estimates of heterotrophic soil respiration. Thus, Lee and 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. Despite these studies, the role of terrestrial ecosystem in atmospheric carbon budgets remains unclear. Existing balances for the global carbon cycle cannot account for the fate of 1/4 of the  $\text{CO}_2$  released by the burning of fossil fuels. Thus giving rise to the concept popularly known as the “missing sink” (Houghton et al., 1998) or the “residual terrestrial sink” (Prentice et al., 2001). Sequestration of this carbon, was frequently assumed to be the result of  $\text{CO}_2$  nitrogen “fertilization” of the terrestrial biomass, but latest studies show that fertilization effects are not enough to explain more than a small fraction of the proposed sink (Schimel, 2000; Caspersen et al., 2000; Oren et al., 2001; Sarmiento and Gruber, 2002). Forest ecosystems, from tropical to boreal, and particularly those of the northern hemisphere have been tentatively identified as the source of this “residual terrestrial sink” (Ciais et al., 1995; Rayner et al., 1999; Sarmiento and Wofsy, 1999; Prentice et al., 2001).

The contention, however is difficult to resolve due to uncertainties in photosynthesis and respiration fluxes ; parameters that can be divided only by expensive and technically demanding protocols (Sellers et al., 1997). In addition, land utilization practices, such as conversion of cultivated lands of forest, improved agricultural practices (Paul et al., 1997), or sedimentation in terrestrial reservoirs (Stallard, 1998) can account for some of this “missing” carbon. In this paper, hydrological and land-cover data together with stable isotope measurements  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are used to constrain the annual water and carbon fluxes of the Volta river watershed. The overall purpose of this study is to constrain terrestrial and aquatic carbon fluxes, in order to comment on the source-sink characteristics of the system.

### The geology of the study area

The basement of the Volta basin is formed predominantly by the Birimian rocks of Precambrian formations of

the West African craton (on the west) dating from approximately 2.6 Ga to 1.6 Ga and the post Birimian sedimentary cover (Voltaian) on the east. The older formation of the early Proterozoic are folded, metamorphosed and invaded by granitoids during the Eburnean event of 2.15Ga (Bessoles, 1977). The Volta river basin, located between latitude  $6^\circ\text{N}$  to  $14^\circ\text{N}$  in West Africa, encompasses approximately  $406,000\text{ km}^2$  and stretches from the Gulf of Guinea to the southern boundary of the Sahel region (Figure 1b). Politically, the watershed is shared by several countries but the majority of the watershed lies in Ghana (40.2%) and Burkina Faso (42.1%) with the remaining area in Côte d'Ivoire, Mali, Togo and Benin. Collectively, three sub-basins comprise about 84% of the total drainage area: the Black Volta River ( $156900\text{ km}^2$ ), the White Volta River ( $111800\text{ km}^2$ ), and the Oti River ( $78800\text{ km}^2$ ) (Dickson and Benneh, 1995; Andreini et al., 2000). Each of these major tributaries, plus several small rivers located in the Lower Volta drainage area, discharge into 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 this paper, that the carbon balance obtained in this study will help to substantiate or modify figures.

## MATERIALS AND METHOD

### Theoretical background

The hydrologic and carbon cycles of terrestrial ecosystems are coupled via the process of photosynthesis. The water use efficiency (WUE) factor (Nobel,1999) quantifies this photosynthetic coupling and states that in order to fix a single mole of carbon, a plant must release  $n \times 10^2$  moles of water through plant respiration. The loss of water by transpiration may therefore be a defining parameter of the ecosystem's capacity to sequester  $\text{CO}_2$ . For this study, the hydrologic cycle of drainage basins first needs to be defined. The simple water balance equation is expressed as,

$$\text{ET} = \text{P} - \text{Q} - \Delta\text{S} \quad (1)$$

Where, ET is evapotranspiration, P is precipitation, Q is discharge and  $\Delta\text{S}$  is the change in ground water storage. The water balance equation is further simplified by averaging water fluxes for multi-year time scales, in which case  $\Delta\text{S}$  approximates zero. ET is thus easily obtained, since P and Q can be measured directly. Then,

$$\text{ET} = \text{P} - \text{Q} = \text{Evaporation} + \text{Interception} + \text{Transpiration} \quad (2)$$

Interception, a component of total evaporation, is the proportion of

rainfall that is re-evaporated from plant surfaces before reaching the ground. In tropical and sub-tropical regions, rainfall interception is typically 20 to 30% of annual rainfall (Brooks et al., 1991). It is often the least-constrained term of a hydrologic budget but is essentially controlled by the type of vegetation cover (Sellers and Lockwood, 1981; Hetherington, 1987).

In this study, interception values from field studies (Hopkins, 1966) are combined with GLC 2000 vegetation cover to estimate rainfall interception. Unlike interception and transpiration, evaporation and sublimation (snow) involve hydrogen and oxygen isotope fractionation of water molecules (Mosler and Stichler, 1975), and water at the mouth of rivers with a notable evaporative component is enriched in the heavy isotopes, compared to precipitation within the basin. The  $\delta D$  and  $\delta^{18}O$  values of the discharging river water therefore reflect the overall impact of evaporation during residence time of the water basin. In general, if evaporation is a significant factor, then the isotope data of river water plot (on a local evaporation line in the  $\delta D - \delta^{18}O$  crossplots), will produce a slope less steep than that of the meteoric water line (MWL). Evaporation component in the evapotranspiration (ET) flux can thus be extracted by using isotope mass balance equations, such as those proposed by Gonfiantini (1986), Gat and Bower (1991), Gat and Matsui (1991).

According to Gonfiantini (1986):

$$x = \frac{E}{I} = (\delta_s - \delta_l) \left( \frac{1-h+\Delta\epsilon}{(\delta_s+1)} \right) \times \left( \Delta\epsilon + \frac{\epsilon}{\alpha} \right) + (h(\delta_l - \delta_s))$$

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 ( $I$ ).  $\delta_s$  is the weighted mean  $\delta^{18}O$  (or  $\delta D$ ) value at the mouth of the river.  $\delta_l$  is the mean isotopic composition of precipitation; for closed systems,  $\delta_l$  is given by the intersection between the regression line for  $\delta^{18}O$  and  $\delta D$  values of discharge (local evaporation line) and the local meteoric water line (LMWL) (Gat and Matsui, 1991).  $\delta_a$  is the mean  $\delta^{18}O$  (or  $\delta D$ ) value of the water vapour, calculated by assuming isotopic equilibrium with local precipitation ( $\delta_a = \delta_l - \epsilon^*$ ). The limiting isotopic enrichment ( $\epsilon^*$ ) under local hydro-meteorological conditions is given by (Table 1):

$$\delta^* = \frac{h\delta_a + \epsilon}{h - \epsilon}$$

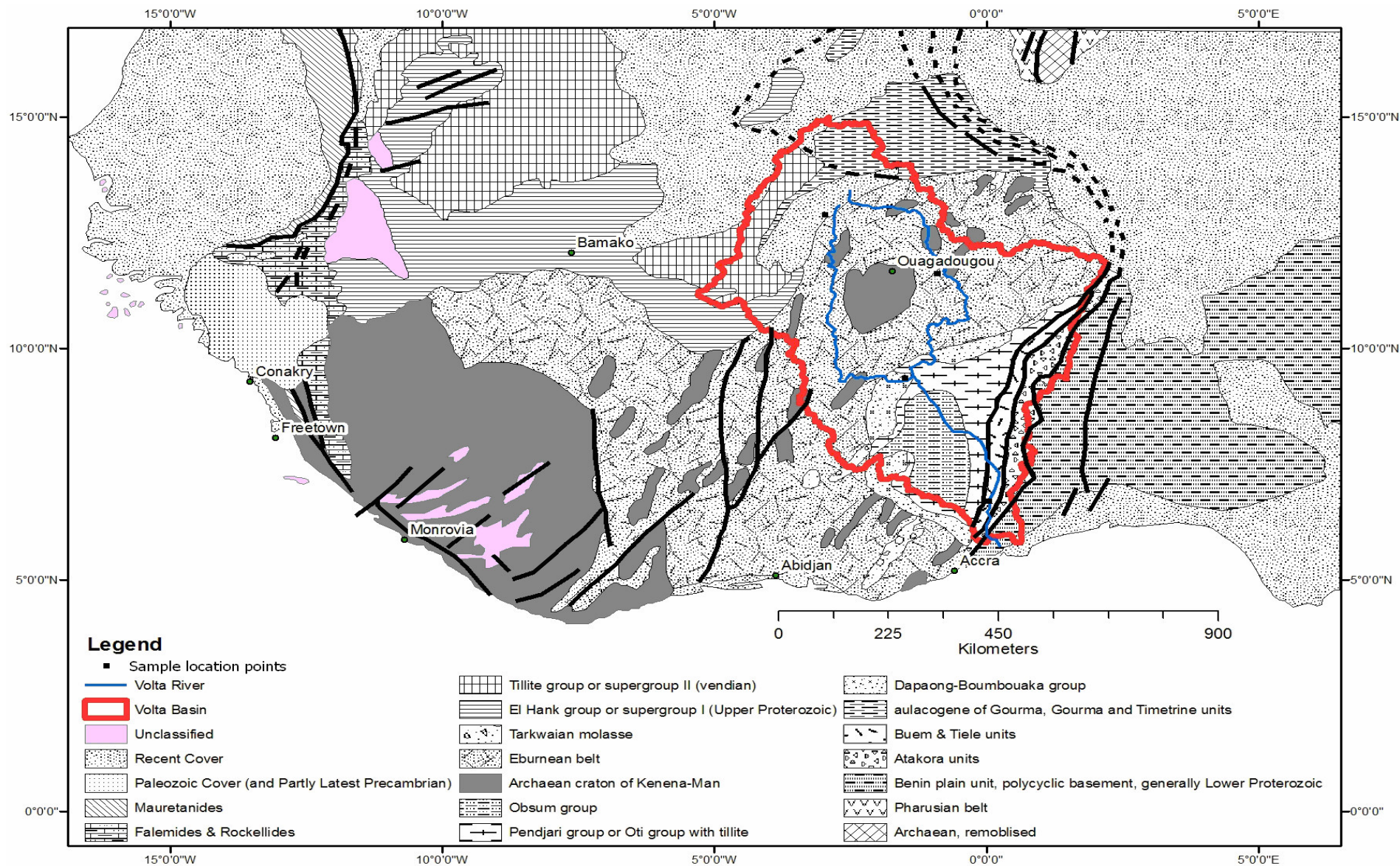
The mean relative humidity is represented by  $h$ ,  $\alpha$  is the equilibrium factor for oxygen ( $\ln \alpha = 1137T^{-2} - 0.4156T^{-1} - 0.00207$ ) and hydrogen isotopes ( $\ln \alpha = 24844T^{-2} - 76.248T^{-1} + 0.05261$ ) (Friedman and O'Neil, 1977).  $\Delta\epsilon$  is the kinetic enrichment factor for oxygen [ $14.2(1-h)$ ] and hydrogen isotopes [ $12.5(1-h)$ ] and  $\epsilon = \alpha - 1$ . Data from isotopic composition of water from Volta Lake, taken at 1 m (surface) and 18 m (bottom) were used for the calculation.  $\delta^{18}O$  and  $\delta D$  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. Oxygen and hydrogen isotope data are reported in ‰ relative to VSMOW, while carbon are reported in ‰ relative to VDPB. The percentage of oxygen saturation ( $\%O_{2sat}$ ) is calculated from the above measured values as well as equilibrium values relative to temperature and pressure given by Benson and Krause (1984). Using the method of Telmer and Veizer (2000, 2001), photosynthetic Net Primary Productivity (NPP) for terrestrial ecosystems was estimated. This is based on the fact that the water and carbon cycles are coupled during photosynthetic

activity. The measure of this coupling, the "Water Use Efficiency (WUE)" factor (Nobel, 1999), prescribes that a plant, in order to fix one mole of carbon, has to transpire  $n \times 10^2$  moles of water through plant transpiration. Knowing the hydrologic budget of a system and its transpiration component, it is indeed possible to calculate the carbon flux associated with the NPP.

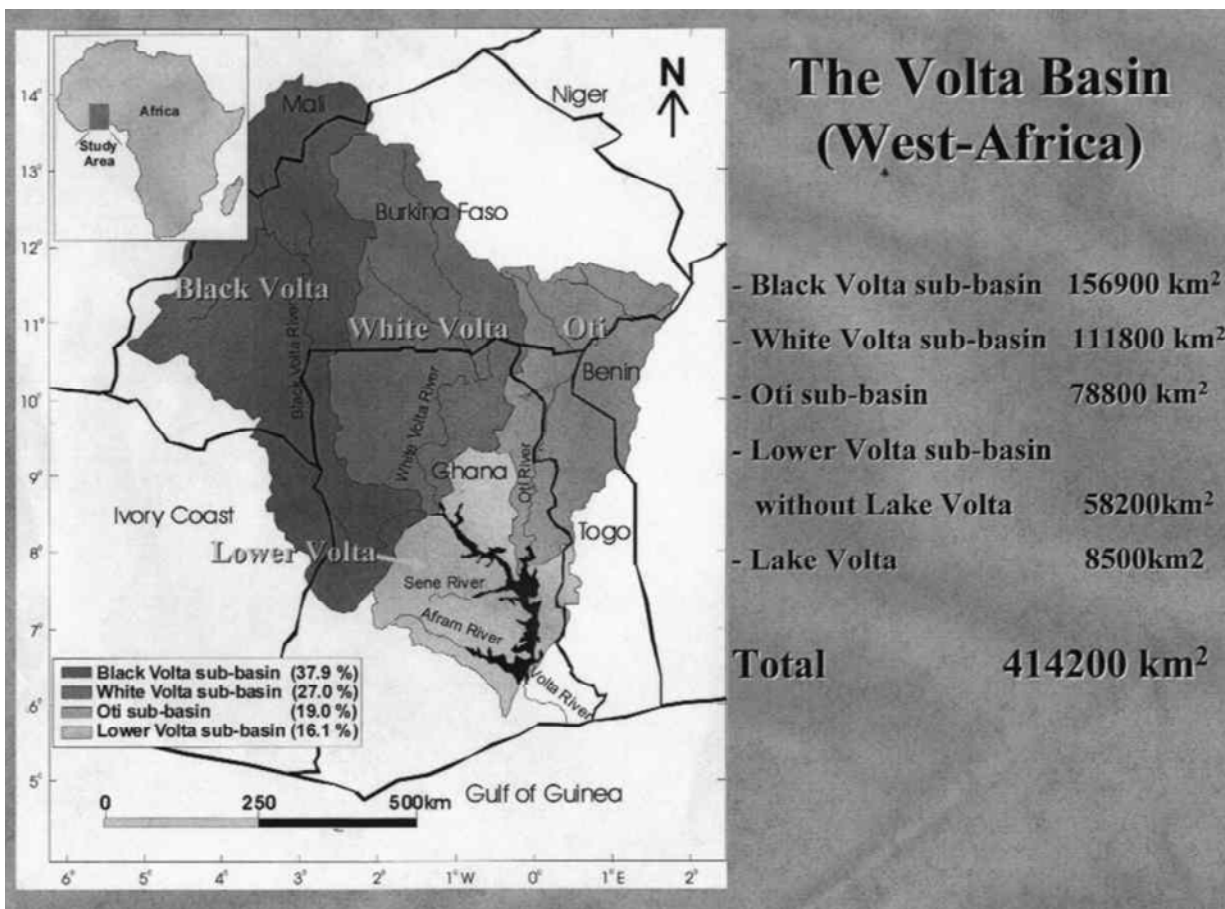
During this study, five sampling stations (Figure 1b) were established in the Volta River watersheds along a 1000 km transect running from the Gulf of Guinea to the northern portions of the watershed in Burkina Faso. Weekly rainfall samples were collected during summer 2003 for determination of  $\delta^{18}O$  and  $\delta D$  values from these locations. Given their distribution from north to south across the prevailing rainfall gradient, these samples are considered characteristics of rainfall figures throughout the watershed. These figures were to augment data from the Global Network for Isotopes in Precipitation (GNIP) stations, (that is Kano, Bamako, Borogo and Miamey) that are located in West Africa (IAEA/WMO, 2004). These stations generate a local Meteoric Water Line (LMWL) for West Africa. More 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 ( $\delta^{18}O_{H_2O}$ ,  $\delta D_{H_2O}$ ), dissolved oxygen ( $\delta^{18}O_{DO}$ ), and dissolved inorganic carbon ( $\delta^{13}C_{DIC}$ ). All stable isotope measurements were conducted at the G.G. Hatch Isotope Laboratory of the University of Ottawa, Canada. For D/H ratios, 0.3 mL of river was injected into an evacuated 6 mm Pyrex tube containing 100 mg of Zn and sealed. The water was subsequently oxidized with zinc at 500°C for 30 min to release  $H_2$  gas (Coleman et al., 1982). The  $H_2$  gas thus released was introduced into a VG 602D Mass Spectrometer through a tube cracker port. The reproducibility of hydrogen isotope analysis is less than  $\pm 2\%$ . For the  $^{18}O/^{16}O$  ratio of water, 1 mL of water sample was equilibrated with a small amount of  $CO_2$  gas at 25°C for 6 hours in a specially designed online equilibrator. After equilibration, the  $CO_2$  gas was extracted and purified cryogenically and introduced into a VG Isogas SIRA-12 triple collector mass spectrometer. Reproducibility of oxygen isotope analyses is less than  $\pm 0.1\%$ . Both hydrogen and oxygen isotope ratios are reported in  $\delta$  values relative to V-SMOW.

## RESULTS AND DISCUSSION

In discussing the hydrology of the Volta River watershed, it is important to note that the terrestrial and river portions of the annual water balance are differential factors. Secondly, the two inputs of water into the lake are (1) rainfall ( $7.9 \text{ km}^3$ ) and (2) river discharge ( $30.8 \text{ km}^3$ ), while the fluxes from the lake are i) evaporation ( $10.2 \text{ km}^3$ ) and ii) controlled outflow ( $28.4 \text{ km}^3$ ) from the Volta Lake to the Gulf of Guinea (Figure 2). The terrestrial portion of the drainage area is made up of the Black Volta River, White Volta River, Oti River watersheds (Figure 1) and the vegetative portion of the Lower Volta drainage area containing Volta Lake. Mean annual rainfall volume for the terrestrial portion of the Volta River watershed is about  $372 \text{ km}^3$ . Mean annual discharge from rivers to Volta Lake (Global Runoff Data Centre, Federal Institute of Hydrology, Koblenz, Germany) is estimated to be  $31 \text{ km}^3$ . This figure is made up of  $25 \text{ km}^3$  from the three largest tributaries (Black Volta River, White Volta River, Oti River watersheds) plus an additional  $6 \text{ km}^3$  from the small rivers of the Lower Volta drainage area (principally the Afram and Sene Rivers). The difference between



**Figure 1a:** The geology of West Africa showing the Volta River and the Volta River Basin covered predominantly by the Eburnean belt made up of the Birimian rocks and the pre Birimian sediments (the Obsum and Oti group of the Voltaian).



**Figure 1b:** The Volta Basin (West Africa) with a total area of 414200 km<sup>2</sup> showing the Black Volta sub-basin (156900 km<sup>2</sup>), the White Volta sub-basin (111800 km<sup>2</sup>), Oti sub-basin (78800 km<sup>2</sup>), Lower Volta sub-basin (58200 km<sup>2</sup>), Volta Lake (5800 km<sup>2</sup>).

Annual precipitation and discharge is the evapotranspiration flux (341 km<sup>3</sup>; Figure 2).

### Transpiration and terrestrial carbon fluxes

Using floral inventories and agricultural statistics, 85% of the grasses (Clayton, 1966) and 6% of the crops (UNEP/GEF, 2001) in the Volta watershed are estimated to utilize the C<sub>4</sub> photosynthetic pathway. Long-term water-use efficiency values from Jones (1992) are 1 mol of CO<sub>2</sub> per 500 to 1500 mol H<sub>2</sub>O for C<sub>3</sub> plants and 350 to 550 mol for C<sub>4</sub> plants. These values are similar to estimates from Molles (2002): 1 mol of CO<sub>2</sub> per 500 to 1200 mol H<sub>2</sub>O for C<sub>3</sub> plants and 1 mol of CO<sub>2</sub> per 350 to 450 moles H<sub>2</sub>O for C<sub>4</sub> plants. Thus, long-term WUE is considered to be in the range of 1 mol of CO<sub>2</sub> per 925 ± 506 moles H<sub>2</sub>O and 1 mol of CO<sub>2</sub> per 425 ± 96 mol H<sub>2</sub>O for C<sub>3</sub> and C<sub>4</sub> plants, respectively. The proportions of C<sub>3</sub> and C<sub>4</sub> plants in each respective sub-basin of the Volta River watershed and water-use efficiency (WUE) for each sub-basin are also listed in Table 1.

Annually, the terrestrial portion of the Volta watershed returns 190 km<sup>3</sup> (50% of total rainfall) to the atmosphere as a result of plant transpiration. Transpiration is the only component pertinent to the water balance with respect to carbon cycling. This is so, because the release of soil water by transpiration is proportional to photosynthetic carbon flux (Molles, 2002). Utilizing the coupling of transpiration and CO<sub>2</sub> flux during photosynthesis, annual transpiration is converted to NPP, yielding a first order estimate of annual photosynthetic carbon flux.

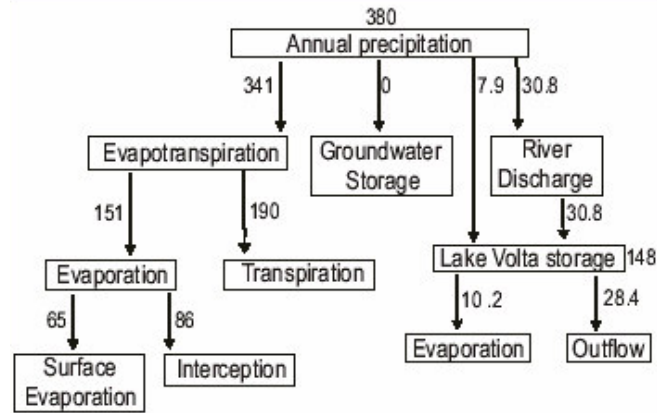
$$\text{NPP (mol C yr}^{-1}\text{)} = \text{Transpiration (mol H}_2\text{O yr}^{-1}\text{)} \div \text{WUE (mol H}_2\text{O per mol C)} \quad (2)$$

For the Volta River watershed, the carbon flux associated

with the plant transpiration is  $(10.5 \times 10^{15} \text{ mol H}_2\text{O}) \div (745 \text{ mol H}_2\text{O per mol CO}_2) = 1.4 \times 10^{13} \text{ mol CO}_2$  or  $0.170 \times 10^{15} \text{ g C yr}^{-1}$  or  $428 \text{ g C m}^{-2} \text{ yr}^{-1}$ .

Estimation of transpiration flux for the Lower Volta drainage area (given that accurate discharge data from the smaller rivers surrounding the lake is not available), was calculated with the mean water balance from the





**Figure 2.** Box diagram of annual water balance (in km<sup>3</sup>) for Volta River watershed.

**Table 1.** Variables used in the isotope mass balance equation

	White volta river	Black volta river	Oti river
$\delta_s$	-0.00262	-0.00245	-0.00209
$\delta_l$	-0.005	-0.005	-0.005
$\delta_a$	-0.01534	-0.01548	-0.01540
$\alpha$	1.010344	1.010483	1.010403
$\epsilon$	0.010344	0.010483	0.010403
$\Delta\epsilon$	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

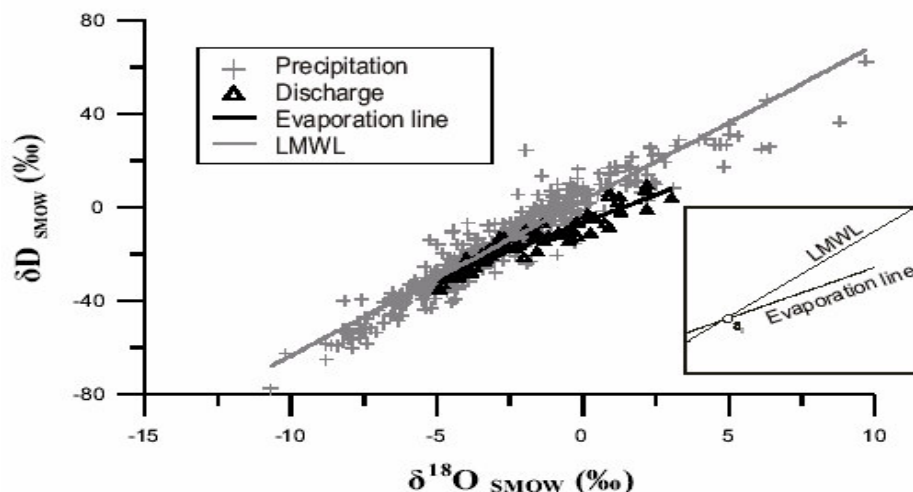
**Table 2.** Annual carbon flux estimates and net ecosystem productivity.

Sub-Basin	Transpiration (km <sup>3</sup> )	NPP <sup>†</sup> (10 <sup>15</sup> g C yr <sup>-1</sup> )	NPP (g C m <sup>-2</sup> yr <sup>-1</sup> )	Heterotrophic Soil Respiration (10 <sup>15</sup> g C yr <sup>-1</sup> )	Net Ecosystem Productivity (10 <sup>15</sup> g C yr <sup>-1</sup> )
Black Volta	75	0.069	437	0.077	+0.008
White Volta	58	0.052	461	0.053	+0.001
Oti River	34	0.031	389	0.040	+0.009
Lower Volta	23	0.020	400	0.029	+0.009
Total	190	0.170	428	0.199	+0.029

three larger watersheds. Transpiration flux is then converted to NPP with a water-use efficiency value calculated for vegetation in the Lower Volta drainage area. Annually, the Black Volta River, White Volta River and Oti River watersheds plus the vegetated region surrounding Volta Lake collectively sequester 0.170 x 10<sup>15</sup> g C yr<sup>-1</sup> from the atmosphere or 428 g C m<sup>-2</sup> yr<sup>-1</sup>. NPP for each of the three major watersheds varies from 389 to 461 g C m<sup>-2</sup> yr<sup>-1</sup> despite similar vegetation characteristics and climatic conditions (Table 2). The Oti River watershed experiences the lowest NPP but the highest proportions of discharge (17%) and evaporation

(31%) relative to annual water input. According to Andreini et al. (2000), despite draining only 23%, the Oti River watershed accounts for 44% of the discharge of the Volta River watershed.

Significant losses of annual rainfall due to higher discharge and evaporation result, reduces transpiration flux and diminishes the NPP. In contrast, transpiration in the White Volta River watershed accounts for 75% of the annual water input, and NPP is thus the highest amongst the three watersheds (461 g C m<sup>-2</sup> yr<sup>-1</sup>). NPP is an important component of the terrestrial carbon cycle, sequestering large amounts of carbon dioxide from the



**Figure 3.** Isotopic composition ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of rainfall (Local Meteoric Water Line) and river discharge (evaporation regression line).

atmosphere each year and strongly influencing intra-annual atmospheric  $\text{pCO}_2$  variability (Grace and Rayment, 2000; Schimel, 2001). However, soil respiration returns a considerable, if not greater, proportion of annual NPP to the atmosphere through the oxidation of soil organic matter during its degradation (Brown et al., 1982; Raich and Potter, 1995; Schlesinger and Andrew, 2000). In order to estimate the annual balance between NPP and respiration fluxes, Net Ecosystem Productivity (NEP) is considered a useful ecosystem parameter. In essence, NEP indicates whether a watershed acts as a net sink ( $\text{NPP} > \text{soil respiration}$ ) or a net source ( $\text{NPP} < \text{soil respiration}$ ) of carbon dioxide to the atmosphere (Thompson et al., 1996; Kirschbaum, 1995, 2000; Valentini, 2000; Buchmann and Schulz, 1999; Potter et al., 2003a, 2003b).

Although soil respiration flux cannot be estimated with the water balance approach, Raich and Potter (1995) propose total soil respiration values for a global latitude/longitude grid that are based on the relationship between carbon dioxide emission from soil, mean temperature, and precipitation. It is, however, necessary to divide the total soil respiration into autotrophic soil respiration (root respiration) and heterotrophic soil respiration (bacterial activity) (Hanson et al., 2000). According to Hanson et al. (2000), the percentages of mean autotrophic soil respiration to total soil respiration for non-forested and forested regions are 46 and 60% respectively. Considering the fact that 60% of the Volta watershed is non-forested, heterotrophic soil respiration ( $R_h$ ) for the Volta River watershed is calculated to be  $0.199 \times 10^{15} \text{ g C yr}^{-1}$ . Given the broad similarity of our NPP estimates and the modelled soil respiration fluxes from Raich and Potter (1995), NEP for the terrestrial portion of the Volta River watershed suggests that the system is close to being in balance ( $\text{NPP} \approx \text{heterotrophic soil respiration}$ ) or is a small annual source of carbon

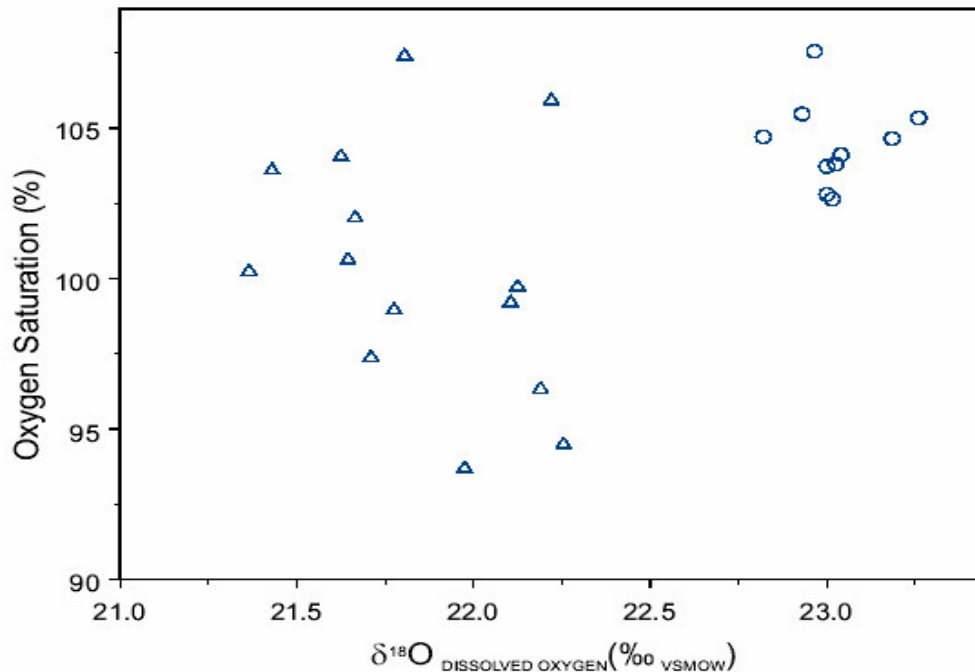
dioxide to the atmosphere ( $+0.029 \times 10^{15} \text{ g C yr}^{-1}$ ).

### Oxygen saturation and the isotopic composition of dissolved oxygen

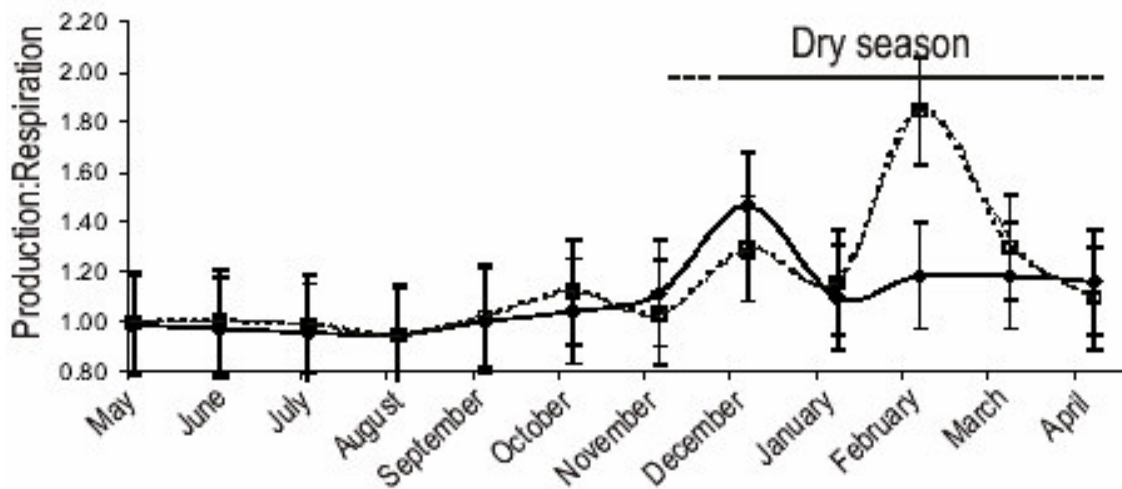
The Local Meteoric Water Line (LMWL) for West Africa, derived from both Global Network for Isotopes in Precipitation (GNIP) data and rainfall samples from this study (Figure 3), is defined by the equation  $\delta\text{D} = 6.6 \times \delta^{18}\text{O} + 2.0 \text{ ‰}$  ( $r^2 = 0.93$ ,  $n = 296$ ). The evaporation line for the entire Volta River watershed, calculated (Gonfiantini, 1986) from the collective river discharges of the Black Volta River, White Volta River, and Oti River, is  $\delta\text{D} = 5.2 \times \delta^{18}\text{O} - 4.6 \text{ ‰}$  ( $r^2 = 0.94$ ,  $n = 36$ ). Isotopic composition of mean annual precipitation ( $\delta_i$ ) is estimated from the intersection of the evaporation line and LMWL (Figure 3, Table 4). All variables used in the isotope mass balance equation to determine the proportion of evaporation are listed in 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 and Veizer, 2000, 2004). The isotopic signature of dissolved oxygen,  $\delta^{18}\text{O}_{\text{DO}}$ , 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  $\delta^{18}\text{O}_{\text{DO}}$  values less than 23.5‰ and will be over-saturated with respect to oxygen. In contrast, systems dominated by respiration are characterized by  $\delta^{18}\text{O}_{\text{DO}}$  greater than 23.5‰ and so have under-saturated oxygen concentrations.

Comparing  $\delta^{18}\text{O}_{\text{DO}}$  and  $\text{O}_2$  saturation (Figure 4), 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.



**Figure 4.** Relationship between oxygen saturation and  $\delta^{18}\text{O}_{\text{DO}}$  in Volta Lake. Triangles are samples taken during the rainy season and circles samples taken during the dry season.

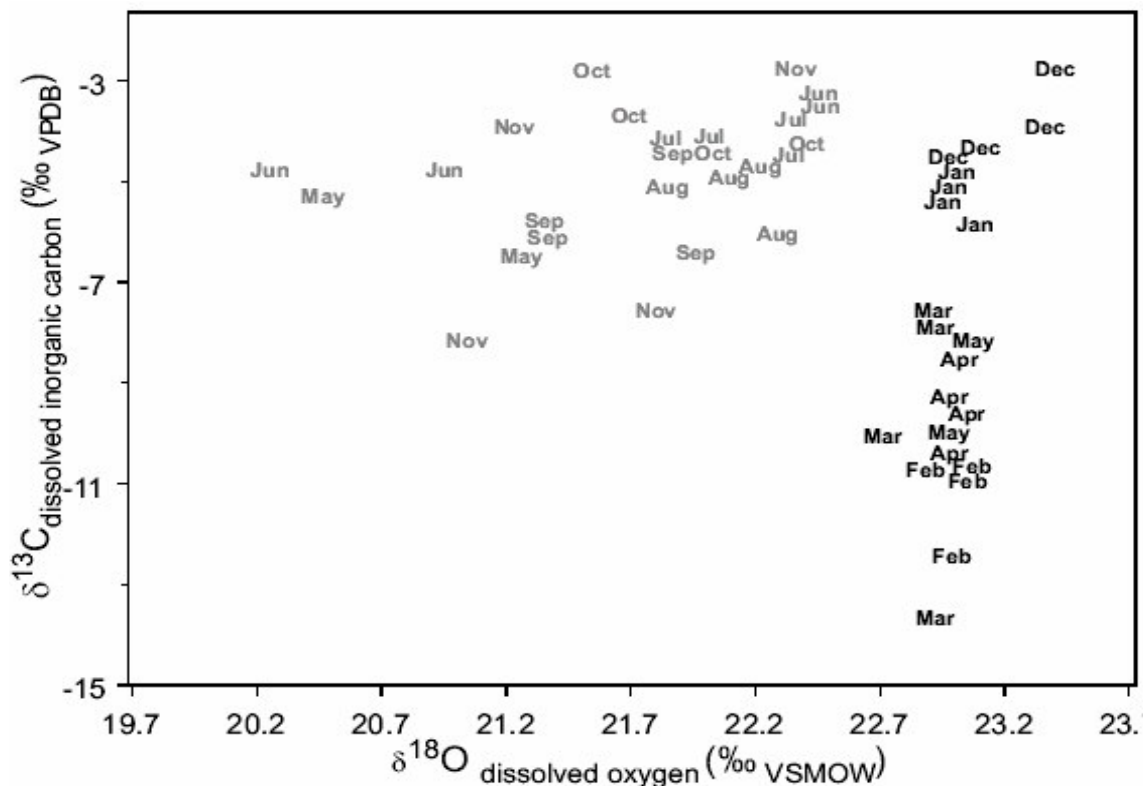


**Figure 5.** Production-to-respiration ratio in Volta Lake between April 2003 and March 2004, as calculated from the model described in Quay et al. (1995) that depends on  $\delta^{18}\text{O}_{\text{DO}}$ ,  $\delta^{18}\text{O}_{\text{w}}$  and oxygen saturation. Moving average of monthly measurements of surface waters are shown with a solid line and bottom waters with a dotted line. Error bars are  $\pm 1$  standard error.

During the dry season, the values cluster near atmospheric equilibrium, suggesting that oxygen content and isotopic composition are primarily controlled by atmospheric flux. Results from the balance between productivity (P) and respiration (R) in aquatic systems model for Volta Lake suggest that in the wet season, May to November, P: R is close to equilibrium in both surface

and bottom waters (Figure 5). Furthermore, productivity peaked in both surface and bottom water in December, and at depth in February. Mean annual P: R was  $1.09 \pm 0.15$  at the surface and  $1.15 \pm 0.25$  at 18 m, implying that photosynthesis exceeds respiration in the aquatic system and Volta Lake sequesters more carbon each year than is lost to the atmosphere. It is important to note, however,





**Figure 6.** Relationship between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DO}}$  in Volta Lake. Black dates indicate samples taken during the dry season while grey dates indicate samples from the rainy season.

that this estimate is for autochthonous production in the lake and does not account for allochthonous input of carbon from the watershed.

#### Carbon isotope compositions of water in the Volta basin

The isotopic signature of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) is indicative of photosynthetic production and respiration processes in the aquatic system. Photosynthesis preferentially consumes  $^{12}\text{C}$  in DIC, the lighter isotope of carbon, causing the residual DIC pool to become enriched in  $^{13}\text{C}$ . 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  $-9.5\text{‰}$  and its dissolution produces dissolved inorganic carbon with a composition of approximately  $-3\text{‰}$ , though this value varies with pH and temperature (Mook and Tan, 1991). The isotopic composition of allochthonous inputs into the lake is primarily dependent on the vegetation type and distribution in the watershed.

In general,  $\text{C}_3$  plants have  $\delta^{13}\text{C}$  values between  $-22$  to  $-35\text{‰}$  (mean:  $-26\text{‰}$ ) whereas  $\text{C}_4$  plants have  $\delta^{13}\text{C}$  values between  $-9$  to  $-16\text{‰}$  (mean:  $-13\text{‰}$ ) (Clark and Fritz, 1997). Estimates of the proportion of  $\text{C}_3$  to  $\text{C}_4$  plants in

the Volta River watershed,  $64\% \text{C}_3$  -  $36\% \text{C}_4$ , suggest that  $\delta^{13}\text{C}$  value of allochthonous organic matter should be about  $-21\text{‰}$ . Although only an approximation, the  $\delta^{13}\text{C}$  value of autochthonous organic matter is certainly more depleted and isotopically-distinct from carbon derived from direct exchange with the atmosphere (Table 4). For a qualitative assessment of respiration in Volta lake, this is considered sufficient. Mean  $\delta^{13}\text{C}_{\text{DIC}}$  at the lake's surface is  $-5.63\text{‰}$  and  $-6.82\text{‰}$  at  $18 \text{ m}$  depth. More enriched surface DIC (Table 3) is indicative of increased photosynthesis or less-respired carbon. During the latter part of the dry season  $\delta^{13}\text{C}_{\text{DIC}}$  is more depleted ( $-9.92\text{‰}$ ) on average compared to the remainder of the year, possibly due to increased respiration and/or allochthonous inputs during the dry season. Figure 6 illustrates the dependency of  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DO}}$  on seasonality. During the wet season,  $\delta^{13}\text{C}_{\text{DIC}}$  is more enriched and  $\delta^{18}\text{O}_{\text{DO}}$  is more depleted, possibly due to the influence of in situ production on both  $\text{O}_2$  and DIC. At the beginning of the dry season, both  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DO}}$  are closer to atmospheric composition suggesting that atmospheric flux controls the dissolved gases during this time of year. Later in the dry season,  $\delta^{18}\text{O}_{\text{DO}}$  remains near equilibrium while  $\delta^{13}\text{C}_{\text{DIC}}$  becomes more depleted, suggesting the input of allochthonous DIC. P:R is highest during this time, implying that allochthonous inputs of DIC may be

**Table 3.** Isotopic measurements of water samples from the Lake surface (1m) and from the Lake bottom (8m).

	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{18}\text{O}_{\text{DO}}$	$\delta^{18}\text{O}_{\text{DO}}$	% O <sub>2</sub> sat	% O <sub>2</sub> sat
Date	(surface)	(surface)	(bottom)	(bottom)	(surface)	(bottom)	(surface)	(bottom)	(surface)	(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		

overwhelming the isotopic signature of in-lake primary production. Monthly discharge data (Andreini et al., 2000; Opoku Ankomah et al., 1999) and DIC, calculated from alkalinity and pH, were used to calculate the amount of carbon transported from the rivers to the lake. Gyau-Boakye and Tumbulto (2000) proposed that only about 0.6% of discharge occurs during the dry

season. However as a result of higher pCO<sub>2</sub> in the rivers, nearly 10% of the allochthonous input of inorganic C to the Volta Lake occurs during the dry season. Annually, approximately  $0.004 \times 10^{15}$  g of inorganic carbon is input to the lake via river discharge. Estimates of primary productivity by Obeng-Asamoah (1977) suggest that volumetric production rates, range between 8.4 and 142.5

mg C m<sup>-3</sup> h<sup>-1</sup>, about 1000 g C m<sup>-2</sup> yr<sup>-1</sup>. Based on these literature values, Volta Lake sequesters approximately  $0.0085 \times 10^{15}$  g C yr<sup>-1</sup>. In summary, model results based on stable isotopic measurements (Quay et al. 1995) suggests that annual in-lake production significantly exceeds aquatic respiration. However, a more-detailed examination of the spatial and temporal variability

**Table 4.** Isotopic composition of river discharge, reported relative to VSMOW.

Location Date	White Volta river		Black Volta river		Oti river		Sene river		Afram river	
	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta\text{D}$
19-May-03	1.20	2.18	0.90	4.42	2.13	7.00				
31-May-03	1.24	4.09	0.88	5.84	2.21	9.30	-0.54	-12.6	-2.24	-10.03
14-Jun-03	-3.48	-20.29	-2.72	-13.36	-3.82	-28.57	-3.78	-25.12	-4.04	-27.24
28-Jun-03	-2.82	-16.41	-4.00	-25.64	-3.57	-22.53	-3.55	-19.34	-3.16	-17.58
12-Jul-03	-2.19	-17.00	-3.14	-20.76	-3.00	-19.31	-2.66	-9.93	-2.58	-12.74
26-Jul-03			-3.29	-22.26			-2.28	-13.22	-2.41	-12.76
09-Aug-03	-2.89	-13.39	-3.40	-23.23	-3.22	-18.12	-1.50	-10.28	-2.28	-10.3
23-Aug-03	-4.20	-27.43	-4.88	-35.28	-3.98	-21.96	-2.00	-8.44	-2.22	-9.59
06-Sep-03	-4.52	-30.81	-4.37	-28.51	-4.57	-30.32	-2.24	-9.68	-2.47	-12.58
20-Sep-03	-4.72	-30.73	-4.80	-33.23			-2.24	-14.22	-3.83	-22.39
04-Oct-03	-3.71	-25.86	-4.27	-30.50	-3.73	-23.31	-3.72	-21.44	-3.13	-17.08
18-Oct-03	-3.07	-17.21	-3.94	-25.21	-2.98	-18.69	-3.04	-10.94	-2.62	-12.98
01-Nov-03	-2.32	-17.30	-3.08	-17.94	-2.68	-17.26	-2.31	-11.93	-2.24	-11.81
15-Nov-03	-2.28	-17.99	-2.57	-17.20	-2.32	-17.94	-1.84	-6.21	-2.23	-10.7
29-Nov-03	-2.33	-17.09	-1.98	-10.30	-2.01	-21.61	-1.78	-8.9	-1.73	-8.02
13-Dec-03	-1.68	-13.13	-1.53	-13.54	-2.01	-21.82	-1.08	-7.9	-2.28	-15.24
27-Dec-03	-1.61	-10.24	-0.85	-11.51	-1.59	-19.33	0.06	-2.43	-2.26	-13.38
10-Jan-04	-1.20	-12.87	-0.60	-11.28	-1.37	-7.45	0.02	-5.16	-2.15	-14.32
24-Jan-04	-1.19	-12.73	-0.34	-10.46			0.00	-1.46	-2.12	-13.53
07-Feb-04	-1.34	-14.75	-0.18	-12.99	-0.76	-11.93	-1.77	1.59	-1.85	-10.32
21-Feb-04	-0.47	-14.70	0.24	-11.38	-0.19	-6.82	1.00	2.59	-1.65	-8.56
07-Mar-04			0.88	-8.78	0.39	-4.83	2.19	8.4		
21-Mar-04			2.21	-1.23	1.30	-2.47	1.48	6.47	-1.05	-4.46
04-Apr-04	-0.41	-13.35		-0.86	0.75	-7.34	2.37	6.58	-0.9	-3.18
18-Apr-04			3.04	3.44	-1.56		-0.68	7.02	-1.19	-3.72
02-May-04			0.14	-3.53	-0.26	-6.64	-0.60	1.92	-2.00	-7.02
10-May-04	-0.63	-11.43	0.26	-4.14	-0.24	-7.12	-2.41	-5.86	-2.48	-9.59

of dissolved organic and inorganic carbon inputs into Volta Lake is necessary to quantify the magnitude of the carbon flux to the atmosphere.

## Conclusion

The annual rainfall in the Volta river watershed has numerous components, some of which are readily-available from historical records; others however require alternative methods to be constrained. In this study, an isotopic mass balance is used to constrain annual evaporation flux, which in turn is used to determine the amount of water released to the atmosphere through plant respiration. Data show that, the Volta river watershed has a yearly estimated sequester of  $0.170 \times 10^{15}$  g C or  $428 \text{ g C m}^{-2} \text{ yr}^{-1}$  from the atmosphere.

Modelled estimates of heterotrophic soil respiration from Raich and Potter (1995) exceed NPP estimates from this study, implying that the Volta River watershed is a minor source of  $\text{CO}_2$  to the atmosphere. However, the error associated with the water-use efficiency values for  $\text{C}_3$  and

$\text{C}_4$  plants in this study is 55 and 23% respectively, implying that watershed NPP could be significantly higher if different water-use efficiency values were used. According to the calculations in this study, heterotrophic soil respiration for the Volta River watershed is estimated to be  $0.199 \times 10^{15}$  g C or  $501 \text{ g C m}^{-2} \text{ yr}^{-1}$ , showing a 15% difference compared to our NPP estimates. Using the existing water balance, the associated water-use efficiency needed to reach this rate of productivity is 625 moles  $\text{H}_2\text{O}$  per mole of carbon. This water-use efficiency corresponds to 60%  $\text{C}_4$  vegetation in the Volta River watershed. Intuitively, this situation seems improbable given the significance of croplands and woody vegetation in the watershed. The only ecosystems that may sustain such high water-use efficiency are  $\text{C}_4$ -dominated grasslands, which may occur in the Sahel region of West Africa. Most of the vegetation in the Volta River watershed, however, is woodland savanna and therefore a mixture of woody and grassy vegetation and unlikely to contain such high proportions of  $\text{C}_4$  vegetation.

Recognizing that NPP estimates from this study and the soil respiration estimate is global in scale, the 15%

discrepancy is relatively small given the dissimilarity of methods used for determination of each. Overall, the similarity of productivity and soil respiration fluxes suggests 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  $0.029 \times 10^{15} \text{ g C yr}^{-1}$ , implying a source of carbon to the atmosphere. Incorporating the additional  $0.026 \times 10^{15} \text{ g C}$  (estimated as 15% of annual NPP from Scholes and Walker, 1993) to be lost each year due to the burning of vegetation, the flux to the atmosphere could increase to  $0.052 \times 10^{15} \text{ g C yr}^{-1}$ .

## ACKNOWLEDGEMENTS

This research was supported financially by the National Sciences and Engineering Research Council of Canada (NSERC) and the Canadian Institute of Advanced Research.

## REFERENCES

- Andreini M, van de Giesen N, van Edig M, Fosu W, Andah W (2000). Volta Basin Water Balance. ZEF – Zentrum fuer Entwicklungsforschung, Bonn. Discussion Papers on Development Policy. p. 21.
- Benson BB, 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.
- Bessoles B (1977). Geologie de l'Afrigue, 1. Craton de l'Quest Africain. *Bur. De Rech. Geol. Min. Mem.* 88: 402-406.
- Brooks KN, Folliott PF, Gregersen HM, DeBano L.F (1991). Hydrology and the management of watersheds. Iowa State University Press, Ames, Iowa.
- Brown S, Lugo AE (1982). The Storage and Production of Organic Matter in Tropical Forests and Their Role in the Global Carbon Cycle. *Biotropica*, 14: 161-187.
- Buchmann N, Schulze ED (1999). Net CO<sub>2</sub> and H<sub>2</sub>O fluxes of terrestrial ecosystems. *Global Biogeochem. Cycles*, 13: 751-760.
- Caspersen JP, Pacala SW, Jenkins JC, Hurtt GG, Moorcraft PR, Birdsey RA (2000). Contributions of land-use history to carbon accumulation in U.S. forests. *Sci.*, 290 : 1148-1151.
- Ciais P, Tans PP, Trolier M, White JWC, Francey RJ (1995). A Large Northern Hemisphere Terrestrial CO<sub>2</sub> Sink Indicated by the <sup>13</sup>C/<sup>12</sup>C Ratio of Atmospheric CO<sub>2</sub>. *Sci.* 269: 1098-1101.
- Clark I, Fritz P (1997). Environmental Isotopes In Hydrogeology. CRC Press, Boca Raton, pp. 328-334.
- Clayton WD (1966). Gramineae (Poaceae). In: Hepper, F.N. (Ed.), Flora of West Tropical Africa, 2<sup>nd</sup> ed. 3. The Whitefriars Press Ltd., London, pp. 349-512.
- Coleman ML, Shepherd TJ, Durham JJ, Rouse JE, Moore GR (1982) Reduction of water with zinc for hydrogen isotope analysis. *Anal. Chem.*, 54 : 993-995.
- Craig H (1961a). Isotopic variations in meteoric waters. *Sci.* 133:17-20.
- Dickson B, Benneh G (1995). A New Geography of Ghana. Revised Edition. Longman Group UK Ltd, UK.
- Fan S, Gloor M, Mahlman J, Pacala S, Sarmiento J, Takahashi T, Tans P (1998). A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models. *Sciences*, 282: 442-446.
- Faure G (1986). Principles of Isotope Geology. Publ.: John Wiley and Sons, New York.
- Friedman I, O'Neil JR (1977). Compilation of stable isotope fractionation factors of geochemical interest, in Data of Geochemistry 6<sup>th</sup> ed., U.S. Geol. Surv. Prof. Pap, pp. 440-449
- Gat JR, Bowser C (1981). The heavy isotope enrichment of water in coupled evaporative systems. In: Taylor, HP, O'Neil JR, Kaplan IR. (Eds.), Stable Isotope Geochemistry: A tribute to Samuel Epstein. Geochemical Society Special Publication, 3, San Antonio, pp.159-168.
- Gat JR, Matsui E (1991). Atmospheric water balance in the Amazon basin: An isotopic evapotranspiration model. *J. Geophys. Res.*, 96: 13179-13188.
- Gonfiantini R (1986). Environmental isotopes in lake studies. In: Fritz P, Fontes JC. (Eds.), Handbook of environmental Isotope Geochemistry, 2. Elsevier Scientific Publishing Company, New York, pp. 113-168.
- Grace J, Rayment M (2000). Respiration in the balance. *Nature* 404: 819-820.
- Gyau-Boakye P, Tumbulto JW (2000). The Volta Lake and declining rainfall and streamflows in the Volta River Basin. *Environ. Dev. Sustainability*, 2: 1-10.
- Hanson PJ, Edwards NT, Garten CT, Andrews JA (2000). Separating root and soil microbial contributions to soil respiration: A review of methods and observations. *Biogeochem.* 48: 115-146.
- Hayford EK, Odamtten GT, Enu-Kwesi L (2006). Isotopic tracers for Net Primary Productivity for a terrestrial ecosystem : a case study of the Volta River Basin. *Ghana J. Sci.*, 46: 77-89.
- Hetherington ED (1987). The importance forests in the hydrological regime. In: Healy, M.C., Wallace, R.R. (Eds), Canadian Aquatic Resources, Ottawa: Department of Fisheries and Oceans, Ottawa, pp. 179-213.
- Hoefs Jr (1980). Stable Isotope Geochemistry, 2ne Edn. Springer Verlag, Heidelberg and New York. pp. 208-214.
- Hopkins B (1966). Vegetation of the Olokemeji Forest Reserve, Nigeria: IV. The Litter and Soil with Special reference to their seasonal change. *J. Ecol.*, 54: 687-703.
- Houghton RA (1998). The annual net flux of carbon to the atmosphere from changes in land use 1850-1990. *Tellus*, 51B: 298-313.
- IAEA/WMO (2004). Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: <http://isohis.iaea.org>
- Keough JR, Hagley CA, Ruzycki E, Sierszen M (1998).  $\delta^{13}\text{C}$  composition of primary producers and role of detritus in a freshwater coastal ecosystem. *Limnol. Oceanogr.* 43: 734-740.
- Kirschbaum MUF (1995). The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biol. Biochem.* 27: 753-760.
- Kirschbaum MUF (1995). Will changes in soil organic carbon act as a positive or negative feedback on global warming? *Biogeochemistry* 48: 21-51.
- 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, No.2, p. 10-15.
- Molles M (2002). Ecology: Concepts and Applications. McGraw-Hill, NY, NY.
- Mook WG, Tan FC (1991). Stable carbon isotopes in rivers and estuaries. In: Degens, E.T., Kempe, S., Richey, J.E., Biogeochemistry of Major World Rivers. Wiley and Sons, Toronto, pp. 245-264.
- Mosler H, Stichler W (1975). Deuterium and Oxygen- 18 contents as index of the properties of snow blankets, in snow mechanics, IAHS Publ., 114, 122-135.
- Nobel PS (1999). Physiochemical and Environmental Plant Physiology, 2<sup>nd</sup> ed., Academic Press, San Diego.
- Obeng-Asamoah EK (1977). A limnological study of the Afram arm of Volta Lake. *Hydrobiologia*, 55: 257-264.
- Opoku-Ankomah Y, Forson MA (1999). Atlantic sea surface temperature and rainfall variability in Ghana. *J. Climate*, 7: 551-558.
- Oren R, Ellsworth DS, Johnson KH, Phillips N, Ewers BE, Maier C, Schafer KVR, Mc Carthy H, Hendrey G, Mc Nulty SG, Katul GG (2001). Soil fertility limits: Carbon sequestration by forest ecosystems in a CO<sub>2</sub>-enriched Atmosphere. *Nature*, 411 : 469-472.
- Paul EA, Paustian K, Elliott ET, Cole CV (1997) Soil organic matter in temperate agro-ecosystem :Long-term experiments in North America, CRC Press, Boca Raton, FL.

- Pawellek F, Veizer J (2001). Carbon cycle in the Upper Danube and its tributaries. *Israel G. Earth Sci.*, 43, 187-194.
- Potter CS, 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.
- Potter C, Klooster S, Myneni R, Genovese V, Tan PN, Kumar V (2003)a. Continental-scale comparison of terrestrial carbon sink estimated from satellite data and ecosystem modelling 1982-1998. *Global Planet. Change*, 39 : 201-213.
- Potter C, Klooster S, Steinbach M, Tan P, Kumar V, Shekhar S, Nemani R, Myneni R (2003)b. Global teleconnections of climate to terrestrial carbon flux. *J. Geophys. Res.*, 108, (D17), JD002979.
- Prentice IC, Farquhar GD, Fasham MJR, Goulden ML, Heimann M, Jaramillo VJ, Kheshgi HS, Le Quéré C, Scholes RJ, Wallace DWR (2001). The carbon cycle and atmospheric CO<sub>2</sub>. In: In Houghton, JT, Ding Y, Griggs DJ, Noguer M, van der Linden PJ, Xiaosu D (Eds), *Climate Change (2001): The Scientific Basis*, Cambridge University Press, Cambridge, U.K., p. 944.
- Quay PD, Wilbur DO, Richey JE, Devol AH, Benner R, Forsberg BR (1995). The <sup>18</sup>O:<sup>16</sup>O of dissolved oxygen in rivers and lakes in the Amazon Basin: determining the ratio of respiration to photosynthesis rates in freshwaters. *Limn. Ocean.* 40: 718-729.
- Raich JW, Potter CS (1995). Global patterns of carbon dioxide emissions from soils. *Global Biogeochem. Cy.* 9: 23-36.
- Rayner PJ, Enting IG, Francey RJ, Langenfeld R (1999) Reconstructing the recent carbon cycle from atmospheric CO<sub>2</sub>, δ<sup>13</sup>C AND O<sub>2</sub>/N<sub>2</sub>. *Observations, Tellus*, 51B : 221- 232.
- Sarmiento JL, Gruber N (2002). Sinks for antropogenic Carbon, *Physics Today*, 55: 1-99.
- Sarmiento JL, Wofsy SC (1999). A U.S. Carbon circle science plan : A report of the carbon and climate working group, U.S. global change research program, Washington D.C.
- Schimel D, Melillo J, Handquin T, McGuire AD, Kicklighter D, Kittel T, Rosenbloom W, Running S, Thornton P, Ojima DO, Parton W, Kelly R, Sykes M, Neilson R, Rizzo (2000). Contribution of increasing CO<sub>2</sub> and climate to Carbon storage by ecosystem in the United States, *Science*, 287: 2004-2006.
- Schimel DS (2001). Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems. *Nat.* 414: 169-172
- Schlesinger WH, Andrew JA (2000). Soil respiration and the global carbon cycle. *Biogeochem.* 48: 7-20.
- Scholes RJ, Walker BH (1993). *An African Savanna: Synthesis of the Nylsvley Study*. Cambridge University Press, Cambridge.
- Sellers PJ, Lockwood A (1981). A numerical simulation of the effects of changing vegetation type on surface hydroclimatology. *Climate Change*, 3: 121-136.
- Sellers PJ, Hall FG, Kelly RD, Black A, Baldocchi D, Berry J (1979). Experiment overview, Scientific results, and future directions, *J. Geophys. Res.*, 102: 28731-28769.
- Stallard RF (1998). Terrestrial sedimentation and the carbon cycle, *Global Biochem. Cycles*, 12 : 231-257.
- 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 Biochem. Cycles*, 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 Biochem. Cycles*, 15: 1035-1040.
- Thompson MV, Randerson JT, Malmstroem CM, Field CB (1996). Change in net primary production and heterotrophic respiration: How much is necessary to sustain the terrestrial carbon sink? *Global Biogeochem. Cy.* 10: 711-726.
- United Nations Environment Program/Global Environment Facility (UNEP/GEF), (2001). *Volta River Basin Preliminary Transboundary Diagnostic Analysis. Final Report*.
- Valentini RG, Matteucci AJ, Dolman ED, Schultze C, Rebmann EJ, Moors A, Grainer P, Gross NO, Jenson K, Pilegaard A, Lindroth A, Grelle C, Bernhofer T, Grunwald M, Aubinet R, Ceulemans AS, Kowalski T, Vesala U, Rannic P, Berbigier D, Loustau J, Guomundsson H, Thorgeirsson A, Ibrom, K, Morgenstern R, Clement J, Moncrieff L, Montagnani S, Jarvis PG (2000). Respiration as the main determinant of carbon balance in European forests. *Nature*, 404: 861-865.
- Wang X, Veizer J (2000). Respiration-photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada. *Geochim. Cosmochim. Acta.* 64: 3775-3786.
- Wang XF, 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.