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Aqueous and Isotope Geochemisty of the Fly River, Papua New Guinea: Coupling of the Water and Carbon Cycles in Tropical Rainforest Biomes

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Aqueous and Isotope Geochemistry of the Fly River, Papua New Guinea: Coupling of the Water and Carbon Cycles in Tropical Rainforest Biomes

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Abstract

Terrestrial moisture fluxes associated with plant growth represent one of the largest movements of mass and energy in the Earth's outer spheres, yet the relative contributions of abiotic water vapor fluxes and those that are regulated solely by the physiology of plants remains contentious and poorly constrained. Herein, based on the interpretation of the stable isotopes of water as tracers of evaporation, a methodology for partitioning total evaporation (*ET*) into its constituent fluxes is developed. This methodology enabled the separation of evaporation from soils and water bodies (E_d), canopy evaporation (I_n), and plant transpiration (*T*) and was developed for the Fly River watershed (~76,000 km^2), situated in a rainforest-dominated region of central New Guinea and then subsequently applied to thirteen other watersheds in North America, South America, Africa, and Australia.

Estimates of the annual water balances for the selected watersheds suggest that *T* is the dominant water vapor flux in 'water-limited' regions, comprising approximately 67% of *ET* and 55% of *P*. Moreover, these regional estimates of *T* co-vary with *P* in a manner similar to that observed for independent estimates of net primary productivity (*NPP*), suggesting that similar to small-scale measurements of plant water-use, water vapor and carbon dioxide fluxes are inherently coupled and the flux of water vapor to the atmosphere during photosynthesis is several orders of magnitude larger than the corresponding sequestration of atmospheric carbon. Similar estimates of a partitioned terrestrial water vapor flux are scarce beyond this study and hence the results are informative, emphasizing the inter-dependency between solar radiation and terrestrial processes and the considerable uncertainty that is currently associated with these aspects of the Earth system. Although admittedly first-order in scale, the estimates offer a broadly conceptual perspective on the dynamics of energy exchange between terrestrial systems and the atmosphere, whereby the terrestrial carbon cycle is essentially driven by solar energy via the water cycle intermediary.

In order to constrain the sources of dissolved constituents in the Fly River watershed, additional data pertaining to the carbon isotope composition of dissolved carbon in river was collected. Monthly samples were collected for a period of two years and higher-resolution data was collected over a period of several weeks in 2007. These data suggested that the dissolution of carbonate minerals in the watershed were the predominant source of dissolved constituents and that constituents related to the dissolution of silicate minerals were negligible by comparison.

Resumé

Les flux terrestres d'humidité se sont associés à la croissance de plantes représentent un des plus grands mouvements de la masse et de l'énergie dans les sphères externes de la terre, pourtant les contributions relatives des flux abiotiques de vapeur d'eau et ceux qui sont réglées seulement par la physiologie des restes d'usines controversable et mal contraintes. Ci-dessus, basé sur l'interprétation des isotopes stables de l'eau comme traceurs d'évaporation, une méthodologie pour diviser l'évaporation totale (*ET*) dans ses flux constitutifs est développée. Cette méthodologie a permis la séparation de l'évaporation des sols et des corps de l'eau (E_d), de l'évaporation de verrière (I_n), et de la transpiration d'usine (*T*) et a été développée pour la fleuve de Fly (~76.000 km2), située dans une région forêt tropicale-dominée de la Nouvelle-Guinée centrale et plus tard puis appliquée à treize autres lignes de partage en Amérique du Nord, en Amérique du Sud, en Afrique, et en Australie.

Les évaluations des équilibres annuels de l'eau pour les lignes de partage choisies suggèrent que *T* soit le flux dominant de vapeur d'eau dans régions eau-limitées de `des', comportant approximativement 67% de *ET* et 55% du *P*. D'ailleurs, ces évaluations régionales de *T* co-changent avec *P* en quelque sorte semblable à cela observé pour des évaluations indépendantes de la productivité primaire nette (*NPP*), suggérant que semblable aux mesures de petite taille de l'usine eau-employer, vapeur d'eau et des flux d'anhydride carbonique sont en soi couplés et le flux de la vapeur d'eau à l'atmosphère pendant la photosynthèse est plusieurs ordres de grandeur plus importants que la séquestration correspondante du carbone atmosphérique. Les évaluations semblables d'un flux terrestre divisé de vapeur d'eau sont rares au delà de cette étude et par conséquent les résultats sont instructifs, soulignant l'interdépendance entre le rayonnement solaire et les processus terrestres et l'incertitude considérable qui est actuellement associée à ces aspects du système de la terre. Bien qu'évidemment de premier ordre dans la balance, les évaluations offrent une perspective largement conceptuelle sur la dynamique de l'échange d'énergie entre les systèmes terrestres et l'atmosphère, par lequel le cycle de carbone terrestre soit essentiellement conduit par énergie solaire par l'intermédiaire de l'intermédiaire de cycle de l'eau.

Afin de contraindre les sources des constituants dissous dans la ligne de partage de fleuve de mouche, des données additionnelles concernant la composition d'isotope carbonique du carbone dissous dans le fleuve ont été rassemblées. Des échantillons ont été rassemblés pour la période de deux ans et des données "higher-resolution" ont été rassemblées pendant plusieurs semaines en 2007. Ces données ont suggéré que la dissolution des minerais de carbonate dans la ligne de partage aient été la source prédominante des constituants dissous, y compris le calcium, le magnésium, et le bicarbonate, et que la dissolution des minerais de silicate était négligeable par comparaison.

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Chapter 1: Introduction

1.1 Overview of the Earth's climate system and the significance of water vapor

The principal source of energy that drives the dynamics of Earth's outer spheres, including its climate, is unquestionably the Sun, and it is the electromagnetic radiation that overwhelmingly dominates energy exchange between the Earth and its cosmic environment [*Kandel and Viollier*, 2005]. At a radiative balance of 235 W m^{-2} the Earth would have an average surface temperature of only –19 °C, resulting in a perpetually frozen planet [*Ruddiman*, 2001]. Fortunately, the planetary atmosphere traps sufficient long-wave energy re-radiated by the warm Earth's surface (natural greenhouse effect) to raise the surface temperature by about 33°C to a more hospitable average of 14 °C. This natural greenhouse effect is overwhelmingly due to water vapor, the principal greenhouse gas, and only to a lesser degree due to the other greenhouse gases (GHG), such as CO_2, CH_4, N_2O, and CFCs [*Stocker et al.*, 2001].

The addition of anthropogenic GHG since the advent of the Industrial Revolution is commonly perceived to have enhanced the global energy balance by about 1.5 W m^{-2}, with a compound anthropogenic greenhouse effect of approximately 2.4 W m^{-2} [*Ramaswamy et al.*, 2001]. However, satellite data for the last decade suggest that a decline in the cloud albedo alone could account for a 2 – 6 W m^{-2} enhancement of the short-wave solar energy input into the system [*Pallé et al.*, 2005]. The current scientific (and political) dispute boils down ultimately to the following: is the additional energy of approximately 2.4 W m^{-2} that is responsible for the centennial temperature rise of 0.6°C [*Houghton et al.*, 2001] due principally to GHG or is it due to some external factor, such as the Sun?

Presently, approximately 0.2°C of the centennial temperature rise is attributed to the observed increase in solar brightness, with the anthropogenic greenhouse effect (0.4°C) related to an increase of GHG in the atmosphere, principally CO_2 [*Mitchell et al.*, 2001]. The attribution of only one-third of the centennial temperature increase to solar forcing, despite a good correlation with solar indices [*Kristjánsson et al.*, 2002; *Valev*, 2006], is based on the empirical observation that, averaged over the 11-year solar cycle, variability in Total Solar Irradiance is only about 0.1% (less than 1.5 W m^{-2}) [*Lean*, 2005]. An amplifier related to solar dynamics would therefore be required to explain the entire magnitude of the trend. The impact of ultraviolet (UV) radiation on ozone and stratospheric dynamics [*Reid*, 2000] and/or galactic cosmic rays (GCR) [*Marsh and Svensmark*, 2003] were briefly considered to be such amplifiers, but dismissed because of the lack of understanding of physical processes, particularly cloud formation, that could point to a climate connection [*Ramaswamy et al.*, 2001]. Note that in regards to the Earth's radiative heat balance we are not dealing with mutually exclusive scenarios, as climate models would respond in a similar way to the addition of energy from any source and it is only the relative importance of these potential "drivers", at a variety of time scales, which is the contentious issue. Note also that compared to the sizes of the global energy fluxes, and their compound uncertainty (on the order of ± 6 W m^{-2}), the apparent centennial to annual trends are at the limit of detectability [*Kandel and Viollier*, 2005]. It is therefore not likely that the issue of principal climate driver(s) can be resolved by energy balance considerations. Instead, observations based on past climate trends, on a hierarchy of time/space scales, and their compatibility with the celestial versus GHG records may help to resolve their relative contributions.

A spate of recent empirical observations [*Veizer*, 2006, and references therein] demonstrates nevertheless that the "sun-climate connection is apparent in a plethora of high-

fidelity climate indicators" [*Lean*, 2005] and, as summarized in the Hadley Centre for Climate Prediction and Research review of [*Gray et al.*, 2005], the detection/attribution assessments of climate models "suggest that the solar influence on climate is greater than would be anticipated from radiative forcing estimates. This implies that either the radiative forcing is underestimated or there are some processes inadequately represented in those models." If so, climate modulation by indirect amplifying mechanisms, such as GCR, may play an important role. The most likely pathway for translation of the high-energy particle flux into a climate forcing variable involves the role of clouds [*Svensmark et al.*, 2006; *Vieira and da Silva*, 2006; *Perry*, 2007]. In order to quantify this process, a multi-year experimental program has recently been initiated by European Organization for Nuclear Research (CERN) [*Arnold et al.*, 2004; *Kanipe*, 2006].

Considering that solar radiation reflected by the atmosphere (and cloud albedo) accounts for approximately 77 W m^{-2}, and that total terrestrial evaporation and precipitation each account for 78 W m^{-2} (Figure 1a) [*Baede et al.*, 2001; *Stocker et al.*, 2001], even a minor change in cloudiness could potentially alter the planetary energy balance by more than the disputed 2.4 W m^{-2}, particularly if the highly-effective but contentious role of aerosols (terrestrial and/or GCR generated) is taken into account. Should the above be the case, the pattern of dominant energy flow in the planetary system could be viewed from the top-down (Figure 1b), instead of bottom-up, thus permitting celestial phenomena to act as the principal (yet not the sole) climate driver. In such a scenario, the relatively small carbon cycle would have to be seen as 'piggybacking' on the much larger water cycle, instead of driving it. That this may be the case is indicated by the observed coincidence of the South African hydrologic regime [*Alexander*, 2005] and the Southeast Asian monsoon patterns with the record of past solar variability [*Bhattacharyya and Narasimha*, 2005]. Causation between

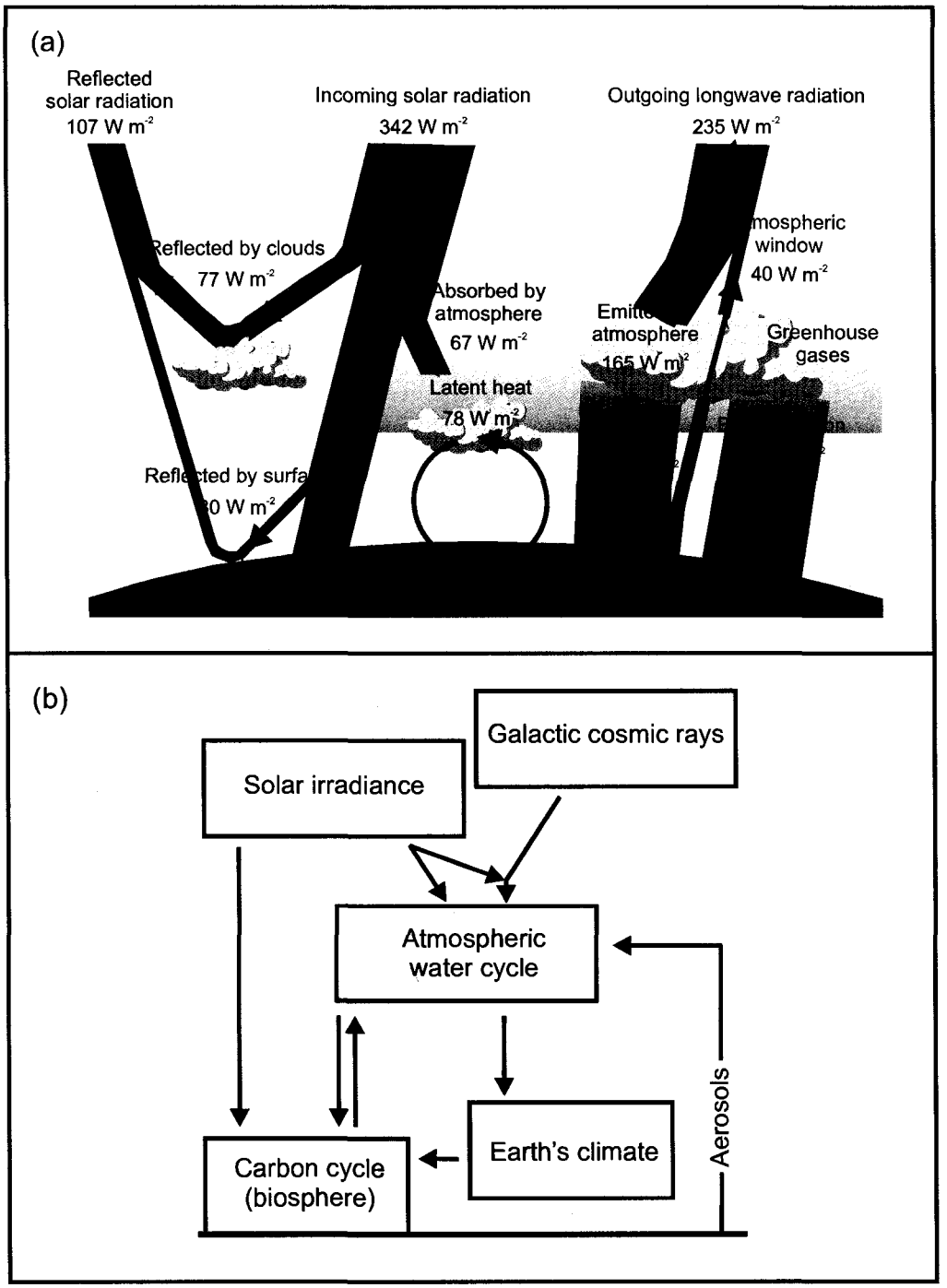


Figure 1. (a) A schematic illustration of the Earth's energy balance; note in particular the balance between terrestrial water vapor fluxes and the latent heat of condensation, both of which are approximately equivalent to the proportion of incoming solar radiation reflected by clouds. Energy balance components from [*Baede et al.*, 2001]; (b) a schematic diagram of the principal drivers of the Earth's climate system proposed as a test hypothesis for the coupling of the terrestrial water and carbon cycles. Galactic cosmic rays and aerosols are included, although their respective roles are more contentious than other aspects of the Earth's climate system. Figure from [*Ferguson and Veizer, in press*].

these terrestrial cycles and solar radiation can only be from the Sun to the Earth. This points to solar activity as the principal driver of the global water cycle, including moisture advection from the tropics to higher latitudes and of the coupled terrestrial water and carbon cycles. This is also likely the case on longer geological time-scales where the weathering of silicate rocks is perceived to be the dominant process that controls atmospheric CO_2 levels [*Berner*, 2003] and eventually, the Earth's climate. Yet, in reality, it is the water that is the agent of physical and chemical weathering and carbon cycling is a secondary by-product. Weathering would proceed without CO_2, albeit with some chemical reactions modified, but not without water, whatever the CO_2 levels. For almost any planetary process, over any time scale, the terrestrial water and carbon cycles are inherently coupled, with water being orders of magnitude more abundant [*Veizer*, 2005]. If this is so, what is the specific mechanism by which the terrestrial water and carbon cycles are coupled and how can this be evaluated?

1.2 Principal controls on the rate of primary productivity in terrestrial ecosystems

Globally, the distribution and vitality of the Earth's terrestrial ecosystems is determined principally by the intensity of radiation from the Sun, which supplies the energy required for plants to grow, and the availability of water, which limits the ability of plants to utilize this energy [*Nemani et al.*, 2002; *Law et al.*, 2002]. The inter-dependency of water and sunlight as factors affecting plant growth is intuitive, as photosynthesis proceeds more rapidly when and/or where water and sunlight are more abundant and vice versa. Spatially, this inter-dependency of water and sunlight is evident from the global patterns of net primary productivity (*NPP*) (Figure 2a), with rainforest ecosystems that are characterized by higher rates of plant growth occurring in regions of intense solar radiation and abundant rainfall and other ecosystems that function at a lower rate of photosynthetic activity developing in

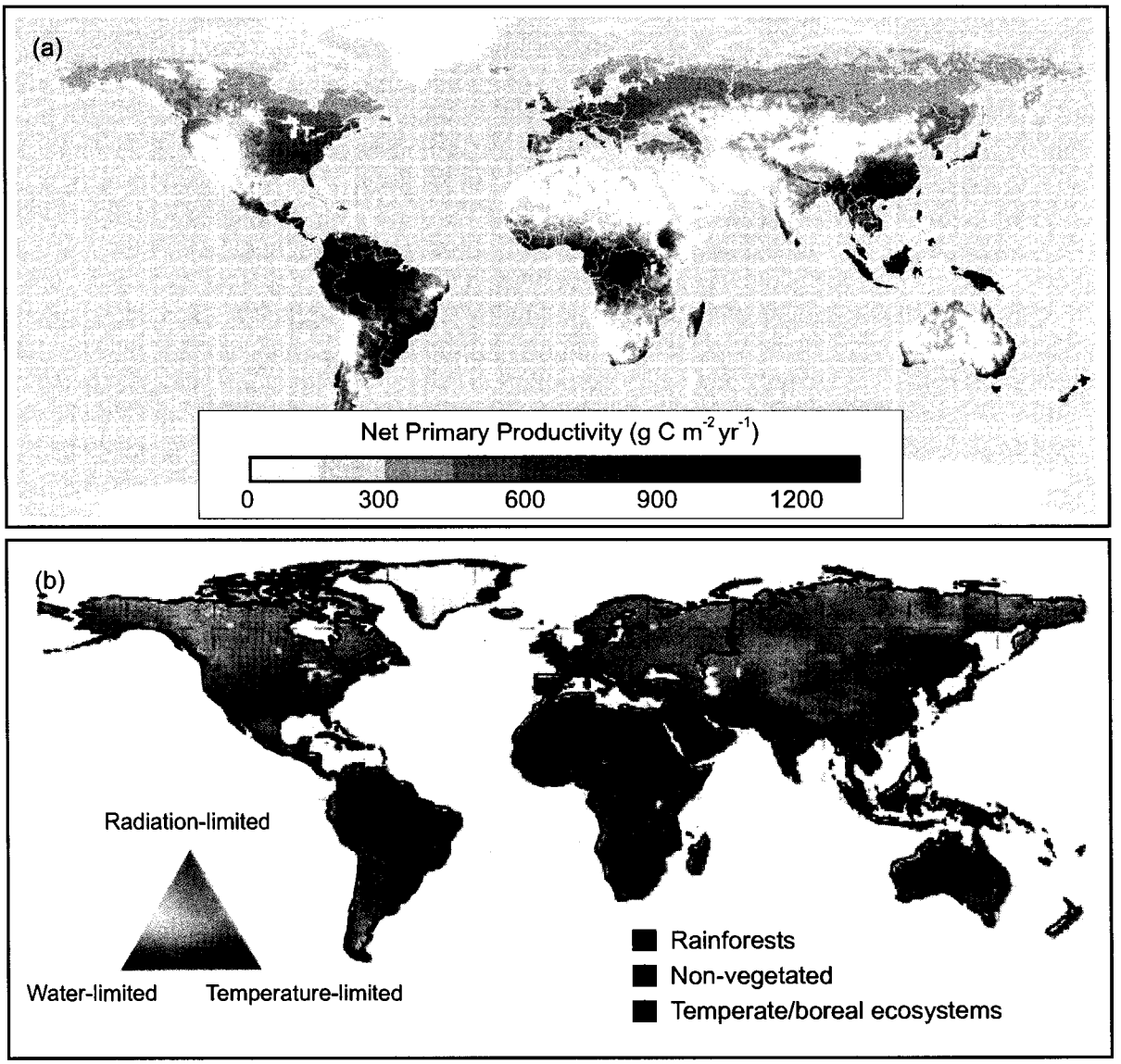


Figure 2. (a) Map of global annual net primary productivity (*NPP*) from the [*Atlas of the Biosphere*, 2002]; (b) the geographic distribution of potential climatic constraints to *NPP* derived from long-term climate statistics. Figure modified from [*Nemani et al.*, 2003]; water, temperature, and solar radiation limit the rate of plant growth over 40%, 33%, and 27% of the Earth's vegetated surface although these factors are often co-limiting. Temperate variability is, however, essentially implicit to the variability in solar radiation, suggesting that solar radiation limits *NPP* over approximately 60% of the Earth.

response to lesser amounts of precipitation or reduced intensity of solar radiation at higher latitudes. In Figure 2b, the essentially non-vegetated regions that are completely water-limited and the densely-vegetated rainforests that are radiation-limited represent end-members of a continuum, as *NPP* is generally co-limited by water availability, solar radiation, and temperature in many ecosystems [*Nemani et al.*, 2002]. The assertion that water and solar radiation represent the most fundamental limitations on plant growth is not intended to diminish the importance of other factors that affect *NPP* at smaller scales or over shorter time periods, although it should be explicitly recognized that at any scale, the primary purpose of plant photosynthesis is to convert light energy from the Sun to a storage form of chemical energy [*Nobel*, 2005]. Hence, incident solar radiation represents the ultimate 'driver' of plant photosynthesis in all terrestrial ecosystems, whereas the other factors that affect the rate of plant growth, such as nutrient and water availability, temperature, and the concentration of atmospheric carbon dioxide, are secondary factors that are either implicit to the variability of solar radiation (i.e. temperature) or represent factors that limit the ability of plants to utilize solar energy effectively (i.e. nutrient and water availability). Neither of these factors, however, supply energy to terrestrial systems and thus do not initiate nor sustain the process of plant photosynthesis.

Alleviating the influence of one of the limiting factors that restrain the rate of photosynthesis generally leads to an approximately proportional increase in the rate of *NPP* until an optimal rate is achieved that is characteristic of the ambient environmental and/or climatic conditions. This is evident at a variety of scales, including the occurrence of maximum rates of hourly photosynthesis at mid-day when solar radiation is most intense or in terms of seasonal variability, the occurrence of maximum rates of plant growth in temperature regions of the northern and southern hemispheres at the height of the growing

season when radiation is most intense and soil water exists solely in liquid form. Annually, the limitation of plant growth by water availability in temperate and sub-tropical regions is evident by the approximately linear relationship between *NPP* and annual water input by precipitation (*P*), a proxy for water availability (Figure 3). More quantitatively, with respect to the independent variable *P*, the linear regression models of *NPP* estimates from the Long Term Ecological Research (LTER) network [*Knapp and Smith*, 2001] and Global Primary Productivity Data Initiative (GPPDI) [*Zheng et al.*, 2001; *Zheng et al.*, 2003] can be described by the equations, $NPP = (0.45 \pm 0.11)\cdot(10^{-3})\cdot P$ g C m^{-2} yr^{-1} ($R^2 = 0.77$, $p < 0.0001$, $n = 11$) and $NPP = (0.49 \pm 0.05)\cdot(10^{-3})\cdot P$ g C m^{-2} yr^{-1} ($R^2 = 0.88$, $p < 0.0001$, $n = 12$), respectively. The nearly equivalent slopes of regression equations based on independent *NPP* data sets indicates that under conditions of water limitation, *NPP* can be predicted as approximately 0.05% of *P* in terms of mass (Note: *P* values are expressed in units of 10^3 g H_2O m^{-2} yr^{-1}, whereas *NPP* values are in units of g C m^{-2} yr^{-1}). Admittedly, most of the LTER sites are located in temperate regions of the northern hemisphere and inferences are thus biased to some extent. Nonetheless, the independent variable *P* explains 77% and 88% of the variability in the LTER and GPPDI data, respectively, suggesting that changes in water availability explain the majority of the variability in *NPP*.

In contrast to temperate and sub-tropical regions, *NPP* in equatorial regions does not generally increase in proportion to *P* beyond approximately 1500 mm (Figure 4). For example, *NPP* for the Luquillo Experimental Forest (955 g C m^{-2} yr^{-1}) [*Clark et al.*, 2001] corresponds to approximately 0.025% of *P* (3725 mm) by mass instead of 0.05% of *P* as predicted by the *NPP-P* relationship for 'water-limited' regions (Figure 3). Illustrated in Figure 4, *NPP* for the Luquillo Experimental Forest (LUQ) plots at or below a plateau of *NPP* values defined by gridded GPPDI data from [*Zheng et al.*, 2001]. The plateau of *NPP*

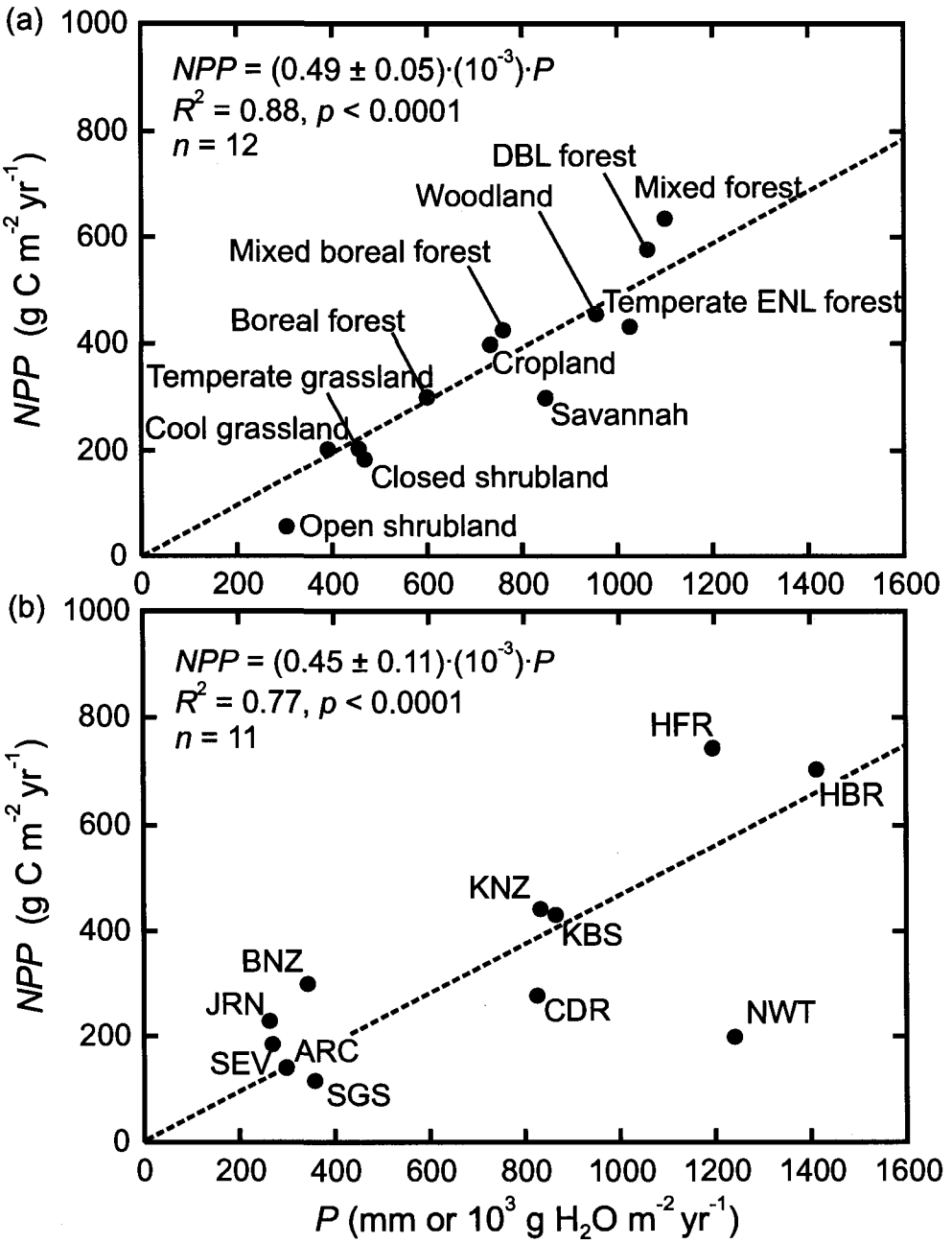


Figure 3. The relationship between mean annual precipitation (*P*) and: (a) global, biome-specific net primary productivity (*NPP*) data from the Global Primary Productivity Data Initiative (GPPDI) [*Zheng et al.*, 2003]. ENL - evergreen needleleaf, DBL - deciduous broadleaf; (b) *NPP* from Long Term Ecological Research (LTER) sites in North America [*Knapp and Smith*, 2001]. ARC - Arctic Tundra, BNZ - Bonanza, CDR - Cedar Creek, HFR - Harvard Forest, HBR - Hubbard Brook, JRN - Jornada, KBS - Kellogg, KNZ - Konza Prairie, NWT - Niwot Ridge, SEV - Sevilleta, SGS - Shortgrass Steppe.

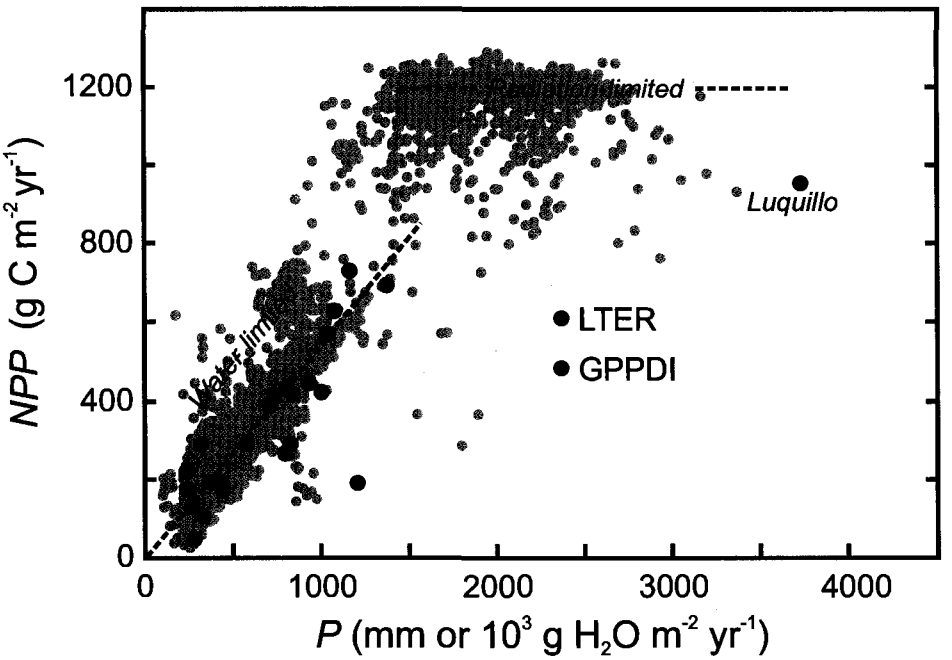


Figure 4. The relationship between mean annual above-ground *NPP* for the Long-Term Ecological Research (LTER) sites in North America [*Knapp and Smith*, 2001], Global Primary Productivity Data Initiative (GPPDI) [*Zheng et al.*, 2003] and mean annual precipitation (*P*). Gridded annual *NPP* data (*grey*) are from the GPPDI [*Zheng et al.*, 2001].

values illustrated in Figure 4 implies that water availability does not represent the limiting factor to plant growth in most tropical regions. Here, the intensity of solar radiation appears to be the likely limiting factor and the location of this plateau in terms of *P* represents the maximum rate of *NPP* for current solar conditions on Earth; this means that if the intensity of solar radiation in the tropics was more intense, the plateau would be located at a higher *P* value, whereas if solar irradiance was lower, the plateau would be located at a lower *P* value.

The limitation of *NPP* by solar radiation instead of water availability in tropical regions is further illustrated in Figure 5 by measurements of Leaf Area Index (*LAI*), precipitation, and solar radiation in forests of central Amazonia [*Myneni et al.*, 2007]. Note from Figure 5 that *LAI*, a proxy for the rate of plant growth, occurs during the dry season when solar radiation is most intense, not during the wet season. According to [*Myneni et al.*, 2007], higher leaf area occurs in the shorter dry season when solar radiation loads are high and lower leaf area occurs during the longer wet season when radiation loads decline significantly. The authors note that the increase in *LAI* precedes the increase in solar radiation, which they considered suggestive of anticipatory and opportunistic patterns of leaf flushing in moist tropical rainforests, yet for purposes of this study, the most relevant aspect of Figure 5 is that it supports the assertion that solar radiation, not water availability, controls the rate of plant growth in high-rainfall regions of the tropics [*Saleska et al.*, 2003; *Huete et al.*, 2006; *Saleska et al.*, 2007].

In the terrestrial ecosystems characterized by the GPPDI and LTER data described above and illustrated in Figures 3 and 4, *NPP* clearly co-varies with *P*. The relationship between *NPP* and *P* is not a particularly novel proposition, as the notion that primary productivity and water availability are inextricably coupled via the process of photosynthesis has been affirmed by a multitude of field measurements [*Bailey*, 1940; *Buchmann and Schulze*, 1999;

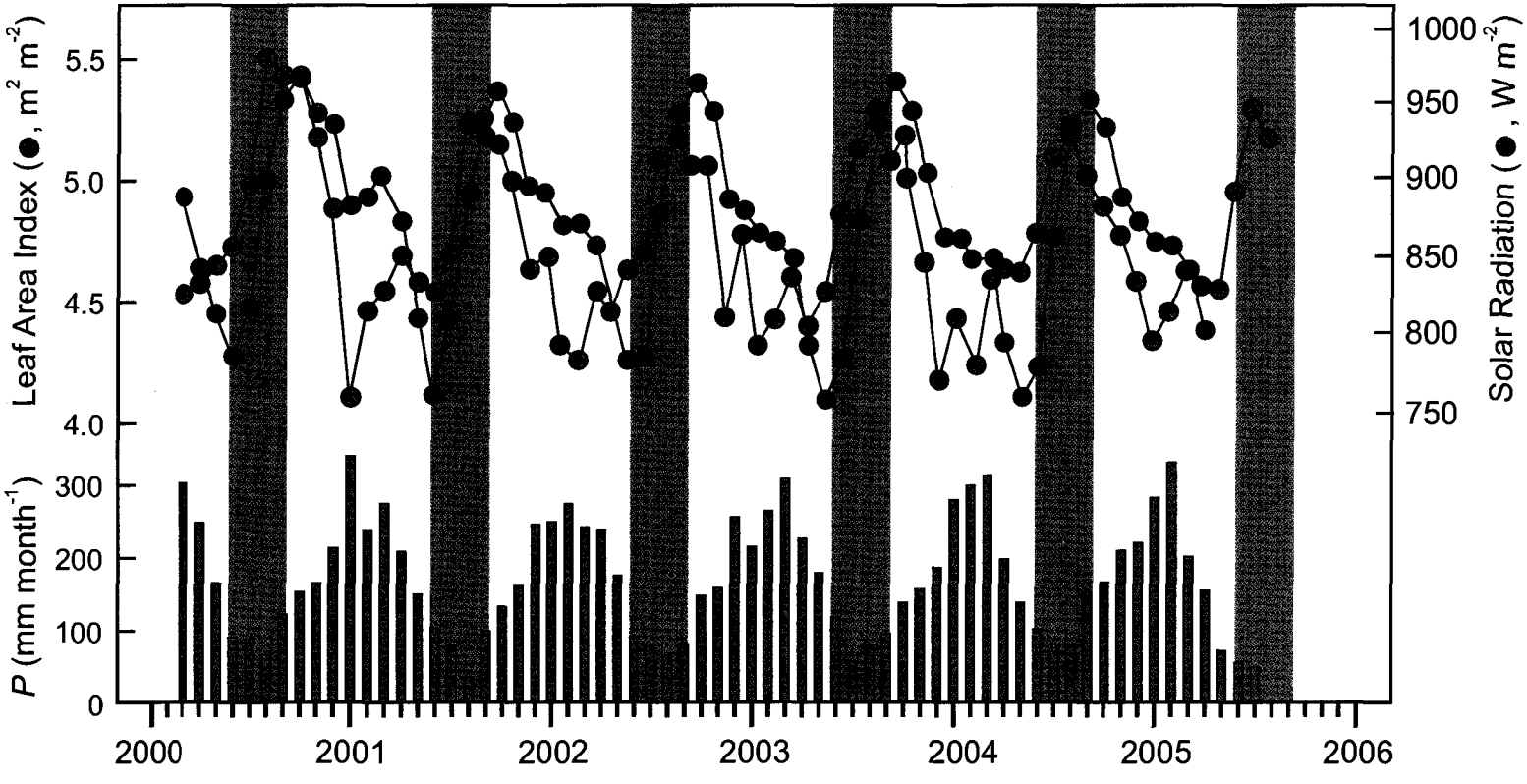


Figure 5. Measurements of monthly precipitation (*P*), Leaf Area Index (LAI), and solar radiation in rainforests of the central Amazon region. Figure modified from [*Myneni et al.,* 2007]. Maximum LAI, an indication of the rate of plant growth, occurs during the sunnier, drier season (*grey vertical bars*), implying that solar radiation is the principal control on the rate of primary productivity in regions where water availability is consistently high year-round.

Law et al., 2002], crop-yield calculations [*Briggs and Shantz*, 1914; *Sinclair et al.*, 1984; *Zoebl*, 2006], and leaf or plant scale measurements [*Farquhar et al.*, 1989; *Masle et al.*, 2005; *Nobel*, 2005]. The observation that plant growth is limited by water availability has spurned the development of numerous ratios that describe the amount of water utilized by a plant per unit of atmospheric carbon uptake via photosynthesis, including rain-use efficiency values [*Huxman et al.*, 2004], water-use efficiency values [*Jones*, 1992; *Molles*, 2002], and transpiration-use efficiency [*Farquhar et al.*, 1989; *Masle et al.*, 2005]. Each is based upon the principle that the amount of water available for plant transpiration represents the fundamental limitation to the rate of plant growth.

Plant transpiration represents the biologically-mediated transfer of soil water to the atmosphere via the vascular system of plants [*Nobel*, 2005]. In detail, the process of plant transpiration involves the exchange of water vapor and carbon dioxide between plants and the atmosphere via stomata, small openings on leaf surfaces which may open or close in order to regulate the diffusion of moisture from the leaf, and atmospheric carbon dioxide into the leaf, where the latter is converted to organic matter [*Farquhar et al.*, 1989; *Sellers et al.*, 1997; *Heldt*, 2005]. As the process of transpiration is considered a mechanism by which plants prevent desiccation when stomata are open and the inner leaf is exposed to the comparatively dry, terrestrial atmosphere, the exchange of water vapor and carbon dioxide occurs simultaneously via the same stomata [*Nobel*, 2005]. Moreover, as the concentration of water vapor in the air space of a leaf in equilibrium with cell water (31,000 parts per million at 25 °C) is two orders of magnitude higher than the concentration of CO_2 in the atmosphere (about 360 parts per million), a much larger amount of water vapor escapes to the atmosphere in relation to the influx of CO_2 via stomata [*Heldt*, 2005]. Hence, in order to replenish the water that escapes from the leaves in the form of water vapor, soil water must

be taken up continuously through the root system of a plant when leaf stomata are open. This causes a steady flow of water from the root system to the leaves during the process of photosynthesis. By necessity, plants must balance the carbon requirements for growth with the limits imposed by soil moisture availability, thereby maximizing their ability to sequester carbon dioxide from the atmosphere while minimizing water loss via plant transpiration.

Although the ratio of plant transpiration to photosynthetic carbon fixation varies depending on the photosynthetic pathway employed by a plant (C_3, C_4, or CAM) [*Werner and Martin*, 1999], the period (i.e. seconds, hours, growing season), and the scale (i.e. leaf, whole-plant, ecosystem) of observation, water vapor and carbon dioxide fluxes that occur during photosynthesis are, at any scale, inherently coupled and the flux of water vapor is several orders of magnitude larger than the associated carbon flux [*Nobel*, 2005; *Heldt*, 2005; *Masle et al.*, 2005]. Numerous models of the exchange of water, carbon, and heat between the atmosphere and terrestrial systems have utilized this predictable relationship in order to convert the water vapor flux via plant transpiration to photosynthetic carbon flux [*Choudhury et al.*, 1998; *Choudhury*, 2000; *Chen and Coughenour*, 2004; *Berry and Roderick*, 2004; *Kuchment et al.*, 2006], yet a lack of regional estimates of plant transpiration has essentially precluded the observation of this well-defined relationship at scales larger than individual plants. Fundamentally though, it should be acknowledged that although the limitation of *NPP* by water availability is often approximated by a comparison of *NPP* and *P*, this is mainly by necessity, as it is the proportion of *P* that becomes available for plant transpiration that is the fundamental restraint on the rate at which plant photosynthesis can proceed. A major focus of this study is to apportion *P* into fluxes that are biologically-mediated, such as plant transpiration, and those fluxes that are unrelated to biologically

activity in order to elucidate the relationship between terrestrial water and carbon fluxes via the terrestrial biosphere.

1.3 Study objectives - Partitioning evaporation and plant transpiration water fluxes from terrestrial systems

Globally, approximately 35% of mean annual precipitation to the continents is transferred to the oceans as river water [*Dai and Trenberth*, 2002], suggesting that the remainder (65%) is returned to the atmosphere via some form of evaporation, either as abiotic water vapor fluxes from soils and water bodies or biologically-mediated water vapor fluxes associated with plant growth (i.e. plant transpiration). Nonetheless, despite recognition that these fluxes of water vapor may have a discernible influence on atmospheric moisture content and the Earth's climate [*Nobre et al.*, 1991; *Foley et al.*, 2003; *Nobre et al.*, 2004; *Feddema et al.*, 2005], few quantitative estimates of the relative contributions of evaporation and plant transpiration to this annual terrestrial water vapor flux are available at a regional scale. This is mainly due to the difficulty associated with partitioning these fluxes based on empirical data. Both are types of evaporation, as each involves a thermodynamic phase transition from liquid water to water vapor, yet in this context, evaporation (E_d) represents the abiotic flux of moisture from land surfaces and water bodies, whereas plant transpiration (T) represents the biologically-mediated transfer of moisture from soils to the atmosphere via the vascular system of plants (Figure 6).

Collectively, E_d and T (plus canopy evaporation, I_n) constitute total evaporation or 'evapotranspiration' (ET) as defined by a conventional water budget equation for a closed hydrologic system,

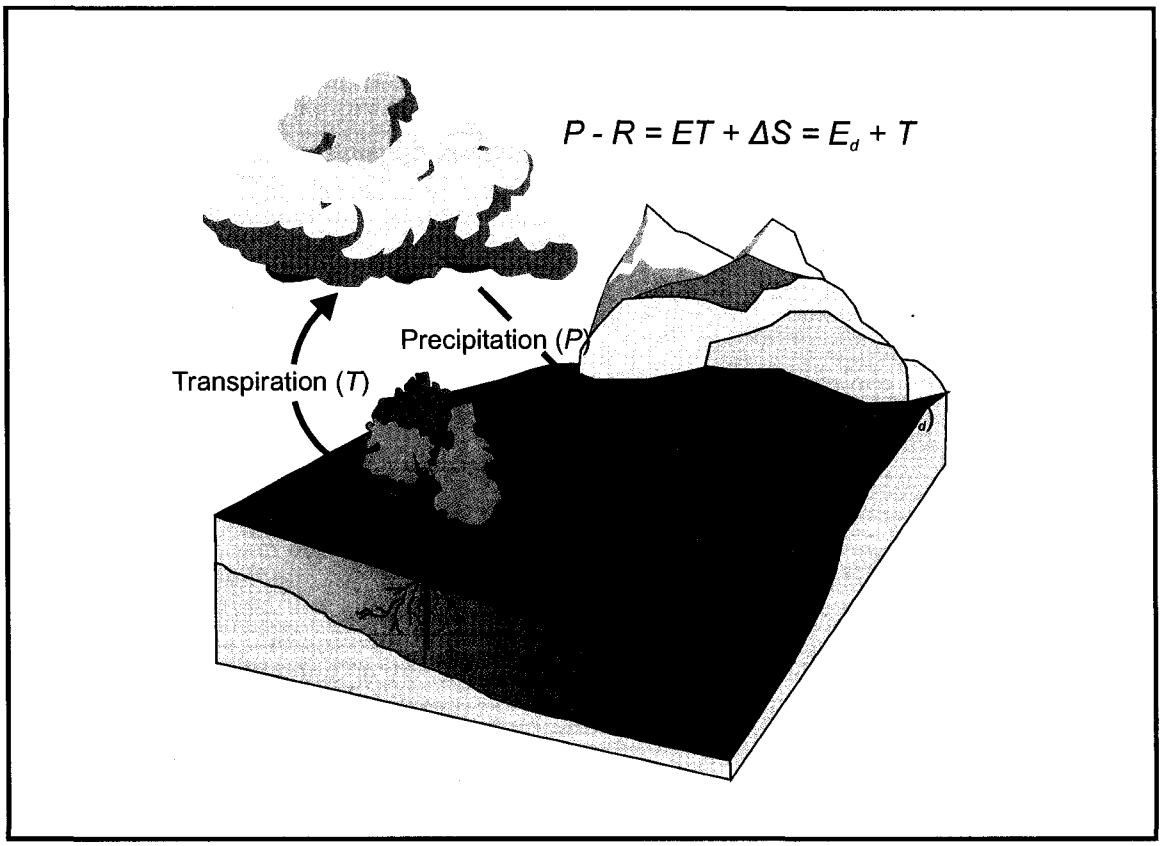


Figure 6. Schematic diagram of the annual water balance of a closed watershed, which can be described by the apportionment of annual water input by precipitation.

$$P = R + ET + \Delta S \quad (1)$$

where P and R represent area-standardized estimates of mean annual water input by precipitation and river outflow (i.e. runoff), respectively, and ΔS represents the inter-annual change in the proportion of P stored in a watershed. Based on measurements of P and R over an extended period of time (years to decades), ΔS can be assumed to be constant and the annual water input by P is balanced by outputs via ET and R. Consequently, $(P - R)$ represents an approximation of ET. Further apportionment of ET into its constituents fluxes is generally difficult without additional information and for this reason E_d is often assumed to be negligible in densely-vegetated regions [*Fleischbein et al.*, 2006], by necessity implying that the entirety of the terrestrial water vapor flux (less I_n) can be attributed to T. Conversely, in sparsely-vegetated regions [*Choudhury*, 2000] or those covered to a large extent by open water [*Machavaram and Krishnamurthy*, 1995], E_d is often considered more significant than T. Intuitively, it should be apparent that neither E_d nor T are likely to be completely negligible in most hydrologic systems, yet a quantitative description of their relative contributions to ET often requires the use of non-conventional hydrological techniques, principally the use of the stable isotopes of water as tracers of the hydrologic cycle [*Gibson et al.*, 1993; *Ferretti et al.*, 2003; *McGuffie and Henderson-Sellers*, 2004; *Fekete et al.*, 2006].

Previous studies of large watersheds in North America [*Telmer and Veizer*, 2000; *Lee and Veizer*, 2003; *Karim et al.*, 2007; *Ferguson et al., in press*] and Africa [*Brunet*, personal communication; *Freitag et al.*, 2007] have utilized the stable isotopes of water in order to partition ET into a fractionating water flux, E_d, and a non-fractionating water flux, $(T + I_n)$.

Despite the use of a conventional steady-state isotope mass balance equation by each of the previous studies, methodological inconsistencies have essentially precluded a quantitative comparison of the relative proportions of E_d and T between watersheds that encompass different types of vegetation or reside in disparate climatic regimes. Nonetheless, based primarily on the principle of plant water-use efficiency and the limited data that was available, [*Lee and Veizer*, 2003] proposed that regional estimates of *NPP* and T should define similar relationships with respect to water input by P, varying in proportion to P in 'water-limited' regions before reaching a threshold or plateau in tropical regions where solar radiation is the limiting factor to plant growth. Hence, the principal objective of this study was to develop a unified methodology for partitioning E_d and T in large watersheds located in North America, South America, Africa, Australia, and New Guinea and test the hypothesis that estimates of T and *NPP* behave similarly to water availability and that the flux of water vapor to the atmosphere exceeds the sequestration of atmospheric carbon by the biosphere by several orders of magnitude. The methodology is initially developed for the Fly River watershed of central New Guinea and is subsequently applied to thirteen other previously-studied watersheds in order to elucidate the behavior of T in varied hydrologic systems. Fundamentally, the methodology developed is intended to offer first-order estimates of E_d and T at a regional scale, instead of a detailed assessment of a single type of hydrologic system, yet an important component of the study is to develop a more quantitative, statistically-based approach to resolving the various components of the terrestrial water balance and identify the principle sources of uncertainty that will likely be encountered in future studies.

Chapter 2. Study Area

2.1 The location and a general description of New Guinea

Located north of Australia between the Coral Sea and the South Pacific Ocean, the island of New Guinea (874,900 km^2) is second only to Greenland in terms of area and is the largest island of the Indonesian Archipelago (Figure 7a). Politically, the island is split between the Indonesian province of Papua (east of 141°E) and the Independent State of Papua New Guinea (PNG) to the west of 141°E. The most prominent physiologic feature of the island is the Central Cordillera, a tectonically-active system of mountains which is oriented approximately parallel to the equator and extends to elevations close to 5,000 meters above sea-level. The Sudirman Range, for example, located in the Central Cordillera of western New Guinea, contains the highest point between the Himalayas and the Americas (Carstenz Pyramid or Puncak Jaya, 4,884 meters above sea-level) and several of the tallest peaks in this mountain range contain equatorial glaciers [*Allison and Peterson*, 1976].

Due to the location of New Guinea amidst the Inter-Tropical Convergence Zone, which marks the convergence of airstreams from the northern and southern hemispheres, and the orientation of the Central Cordillera perpendicular to inter-hemispheric moisture transport, the occurrence of orographic rainfall in the mountains of New Guinea is high. During the Austral winter (May to October), moisture is transported to New Guinea by tropical easterlies (i.e. trade winds) from the western Pacific Ocean, whereas during the Austral summer (December to March), moisture is transported from the northwest [*Barry*, 1978]. The reception of moisture from the northern and southern hemispheres at different times of the year generally causes rainfall to be persistently high year-round, particularly at higher

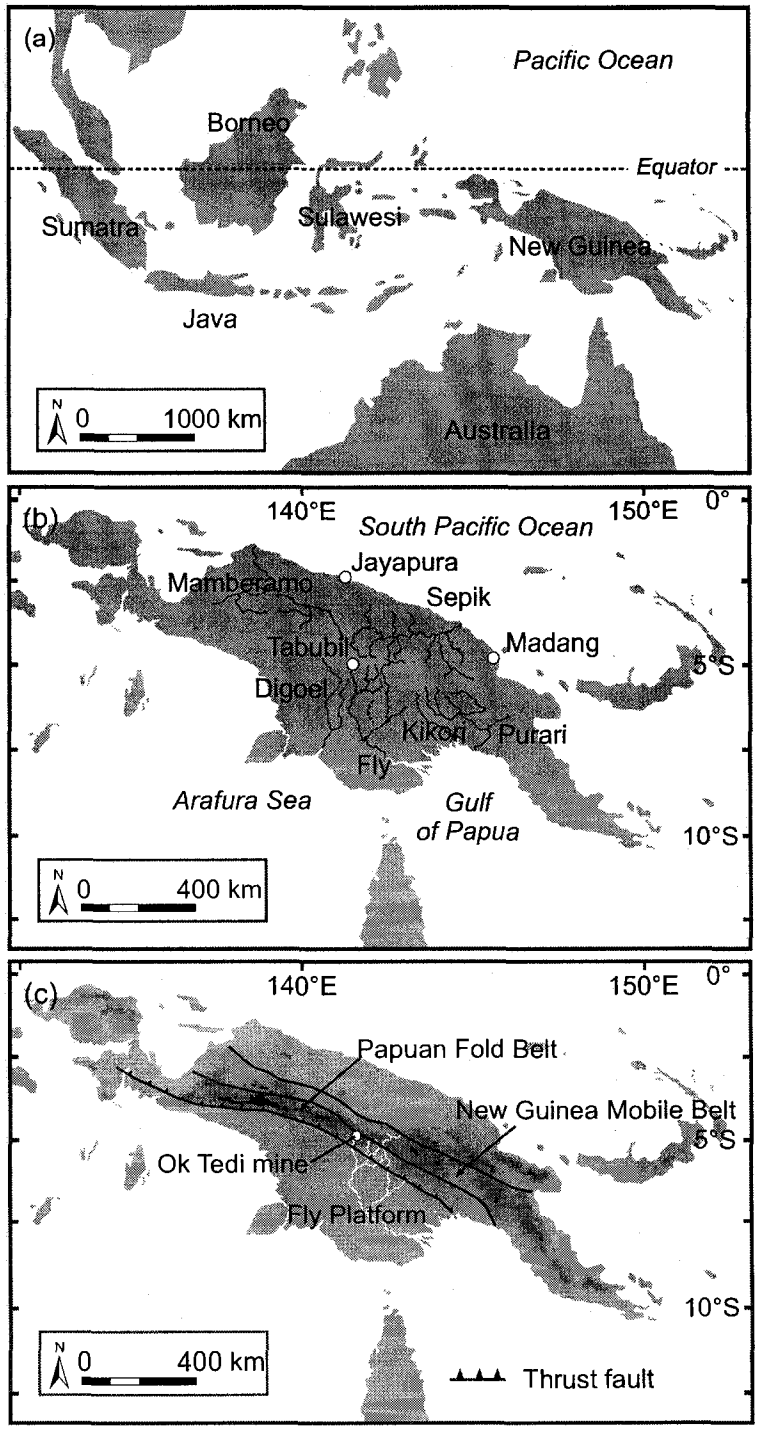


Figure 7. (a) The location of New Guinea, the largest and eastern-most island of the Indonesian Archipelago; (b) the major rivers of New Guinea. Also shown, the locations of Jayapura (Indonesia) and Madang (PNG), both Global Network for Isotopes in Precipitation (GNIP) stations, and Tabubil; (c) tectonic setting: the Papuan Fold Belt (thrust fault shown with teeth on the overriding plate), the New Guinea Mobile Belt, and the Fly Platform. The Fly River is located between the Central Cordillera region (shaded relief, see Figure 7 for legend) and the Gulf of Papua.

elevations, although reduced rainfall is often observed in lowland regions during the period of moisture transport by the trade-winds.

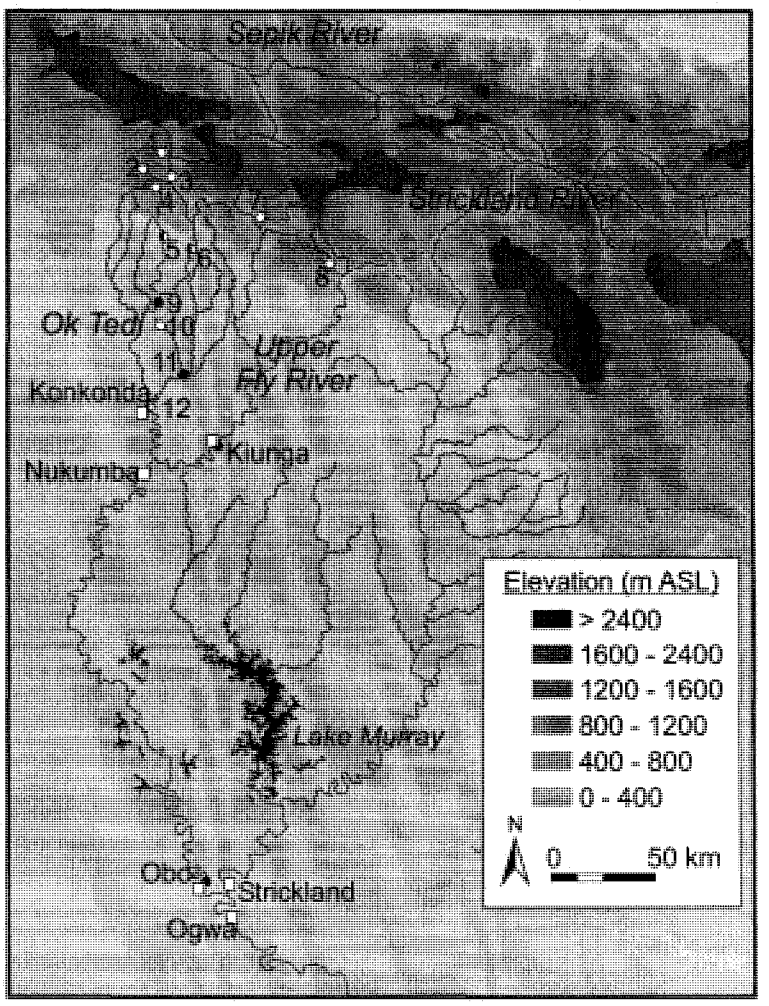
Related to high rainfall in the mountains, several relatively large river systems originate in the Central Cordillera region of New Guinea, including the Sepik River and Mamberamo River, which flow roughly northwards to the South Pacific Ocean, and the Digoel River, Kikori River, Purari River, and Fly River, which flow southwards to the Arafura Sea and Gulf of Papua (Figure 7b). River runoff values (i.e. discharge volume per unit area) for these many rivers of New Guinea are amongst the highest in the world and considering their relatively small area, they contribute a disproportionately large amount of freshwater and sediment to the oceans. According to [*Milliman et al.*, 1999], fluvial sediments leaving the large islands of the Indonesian Archipelago (Figure 7a) represent approximately 20 – 25% of annual sediment export to the oceans worldwide despite the islands accounting for only 2% of global land area. Although most rivers of New Guinea are currently un-gauged or were gauged only periodically in the past, [*Milliman et al.*, 1999] estimate that 1.9 billion tons of sediment or approximately 40% of the sediment export from the Indonesian Archipelago is derived from New Guinea alone. Moreover, [*Nittrouer et al.*, 1995] estimate that the island of New Guinea contributes approximately 2300 km^3 of freshwater to the ocean each year, roughly 20% and 35% of the collective discharge of rivers in South America (17.8×10^6 km^2) and North America (24.5×10^6 km^2), respectively (land areas from [*Dai and Trenberth*, 2002]).

2.2 The Fly River watershed, Papua New Guinea

In terms of annual river flow, the Fly River is the largest river of New Guinea (120 – 160 km^3) and 23rd largest in the world [*Perry et al.*, 1996]. Discharge from the Fly River occurs

into large, macro-tidal deltaic ecosystems fringed with mangrove and inter-tidal mudflats. Water from the Fly River mixes with water from the other rivers of the southern coast of New Guinea in a combined estuary with a 2 – 30 m-thick, low-salinity water mass that often extends 100 km offshore [*Brunskill*, 2004]. The turbid, mangrove-debris-laden water is driven landward by trade-winds during the Austral winter and seaward by winds related to the Asian monsoon. The Fly River delta front is abruptly truncated and most of the fine sediment from all of the rivers along the southern-coast accumulates in the northern apex of the arc of the Gulf of Papua, as clear-water coral reefs dominate in the Coral Sea to the south nearer Australia.

In terms of drainage area, the Fly River watershed encompasses approximately 76,000 km^2 between the Star Mountains region and the river delta in south-central New Guinea (Figure 7c). The principal tributaries of the Fly River are the Ok Tedi (Ok = *river* in local vernacular), the Upper Fly River, and the Strickland River (Figure 8). Topographically, the Fly River watershed can be broadly sub-divided into two sections: (a) a mountainous headland region where rivers are relatively narrow, turbulent, and fast-flowing and (b) a lowland region where relief is subdued and river courses meander strongly through a permanently inundated region surrounded by a floodplain of inter-connected lakes and swamps. The Ok Tedi and Upper Fly River both originate in the former, higher-relief portion of the watershed and collectively encompass approximately 10,400 km^2. The confluence of the Ok Tedi and Upper Fly River occurs at D'Albertis Junction and below this confluence the rivers collectively flow into the Middle Fly River region, which is defined as the section of river between D'Albertis Junction and Everill Junction (where the Middle Fly River merges with the Strickland River). Although considered a tributary, the Strickland River is



Rainfall stations
1. Falomian
2. Ok Mani
3. Tabubil
4. Kumkit
5. Lukwi
6. Haidawoagum
7. Olsobip
8. Biangabip
9. Ninegrum
10. KM59
11. Rumginae
12. Konkonda.

Streamflow gauges
Ok Tedi at Konkonda
Upper Fly River at Kiunga
Middle Fly River at Obo

LEGEND
○ Rainfall station
• Streamflow gauge
□ Monthly sampling site

Figure 8. A detailed map of the major tributaries of the Fly River (the Ok Tedi, the Upper Fly River, and the Strickland River) with GTOPO30 digital elevation data. Also shown, the northward-flowing Sepik River. In addition to the square symbol, the locations of the monthly sampling sites in the Fly River watershed are labeled by name.

larger in terms of drainage area (36,740 km^2) than the Middle Fly River (21,260 km^2) and contributes 60 – 70% of total outflow below their confluence.

2.2.1 Climate and hydrology

The Ok Tedi and Upper Fly River watersheds are located mainly in the high-relief region of the Fly River watershed, where elevation varies from 50 m ASL near D'Albertis Junction to 2500 m ASL in the upper reaches of the watersheds (Figure 8). Due to the elevation, most of the region is characterized by relatively cool temperatures (18 – 22 °C) compared to lower elevation regions of New Guinea. In terms of precipitation, the Star Mountains region lies within a comparatively small area of New Guinea known as the mid-altitude-fringe, high-rainfall zone. This climatic zone extends along the southern flank of the Central Cordillera and is characterized by monthly rainfall in excess of 400 mm [*Hyndman and Menzies*, 1990].

Mean annual rainfall accumulation at rainfall stations located in the Star Mountains region usually ranges from 6000 mm to 8000 mm, yet can exceed 10,000 mm at stations located at higher elevations (Figure 9). Seasonal variation in the amount of rainfall is generally low at rainfall stations located in the Star Mountains region (Figure 9a,b,c). The effect of seasonality is more pronounced in the Middle Fly River region, where annual accumulation is relatively high (~2500 – 5000 mm) yet substantially less than rainfall at stations located at higher elevations in the Star Mountains region [*McAlpine et al.*, 1983]. As less orographic precipitation occurs at lower elevations, represented by the rainfall pattern at Konkonda in Figure 9d, rainfall is more dependent on seasonal shifts in atmospheric circulation patterns, such as the onset of trade-wind activity in the Austral winter. In addition to seasonal effects, the amount of incident rainfall in the Fly River watershed is affected by phases of the El Niño Southern Oscillation (ENSO), with less rainfall during the El Niño phase and higher rainfall during the La Niña phase [*Brunskill*, 2004].

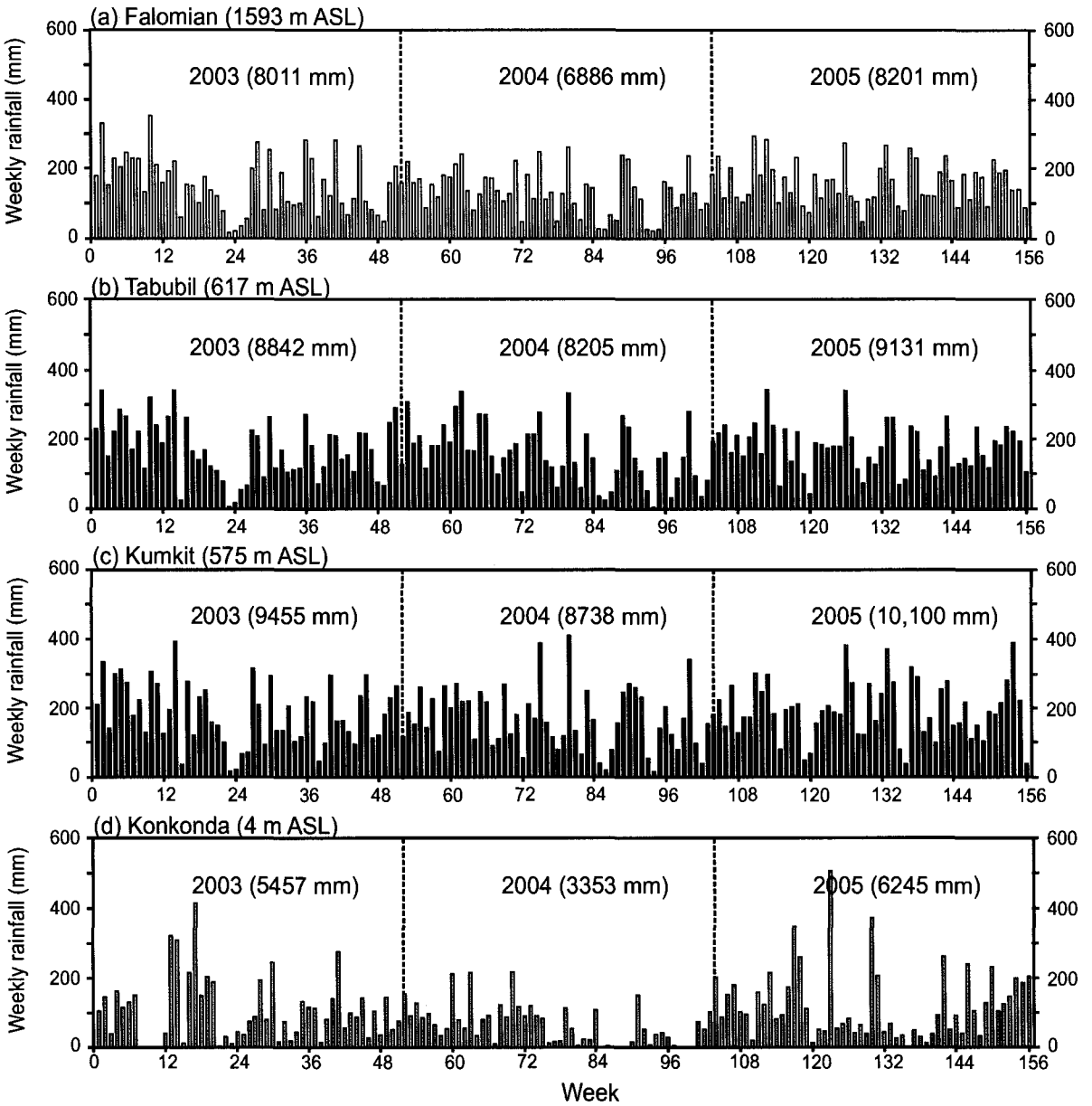


Figure 9. Weekly rainfall accumulation at Falomian, Tabubil, Kumkit, and Konkonda for 2003, 2004, and 2005. Annual rainfall accumulation amounts for each year are given in parentheses.

Particularly for the Ok Tedi and the Upper Fly River, incident rainfall in the Star Mountains and river flows downstream are closely related and most of the water and river-borne sediment in the Fly River drainage system is derived from the mountainous headwaters [*Bird et al*, 1994; *Brunskill*, 2004]. In general, river flow for the Ok Tedi responds predictably to rainfall in the region surrounding Tabubil, whereas the Upper Fly River is affected more directly by rainfall events occurring near Olsobip and Biangabip. The predictable response of river flows to rainfall events upstream within approximately 24 hours is illustrated in Figure 10a and 10b by daily rainfall data at Tabubil, Lukwi, and Konkonda and river runoff for the Ok Tedi at Konkonda and the Upper Fly River at Kiunga. The close correspondence between rainfall and river runoff is also shown in Figure 10c by incident rainfall at Lukwi and Kumkit and daily river runoff for the Ok Ma at Lukwi and by hourly rainfall and river flow in Figure 11 for a period of March 2007.

Periods of reduced river flow are generally observed during the period of reduced rainfall related to moisture transport by trade winds during the Austral winter (May – October) and peak flow conditions are observed during moisture transport from the northern hemisphere in the Austral summer (November – April) (Figure 9). River flow is also reduced during the El Niño phase of ENSO, often to the point of prohibiting ship movement on the Fly River due to low water levels [*Brunskill*, 2004]. In general though, a substantial proportion of the variability in rainfall and river flow that is observed on an intra-annual basis can be observed over a period of hours to days, as intense rainfall events can occur year-round and river flows often respond rapidly to these short-term events [*Veness, personal communication*].

2.2.2 Geological and tectonic setting

In terms of tectonic setting, the Star Mountains region is comprised in part of Proterozoic-Paleozoic basement rocks of the northern margin of the Australian continent that

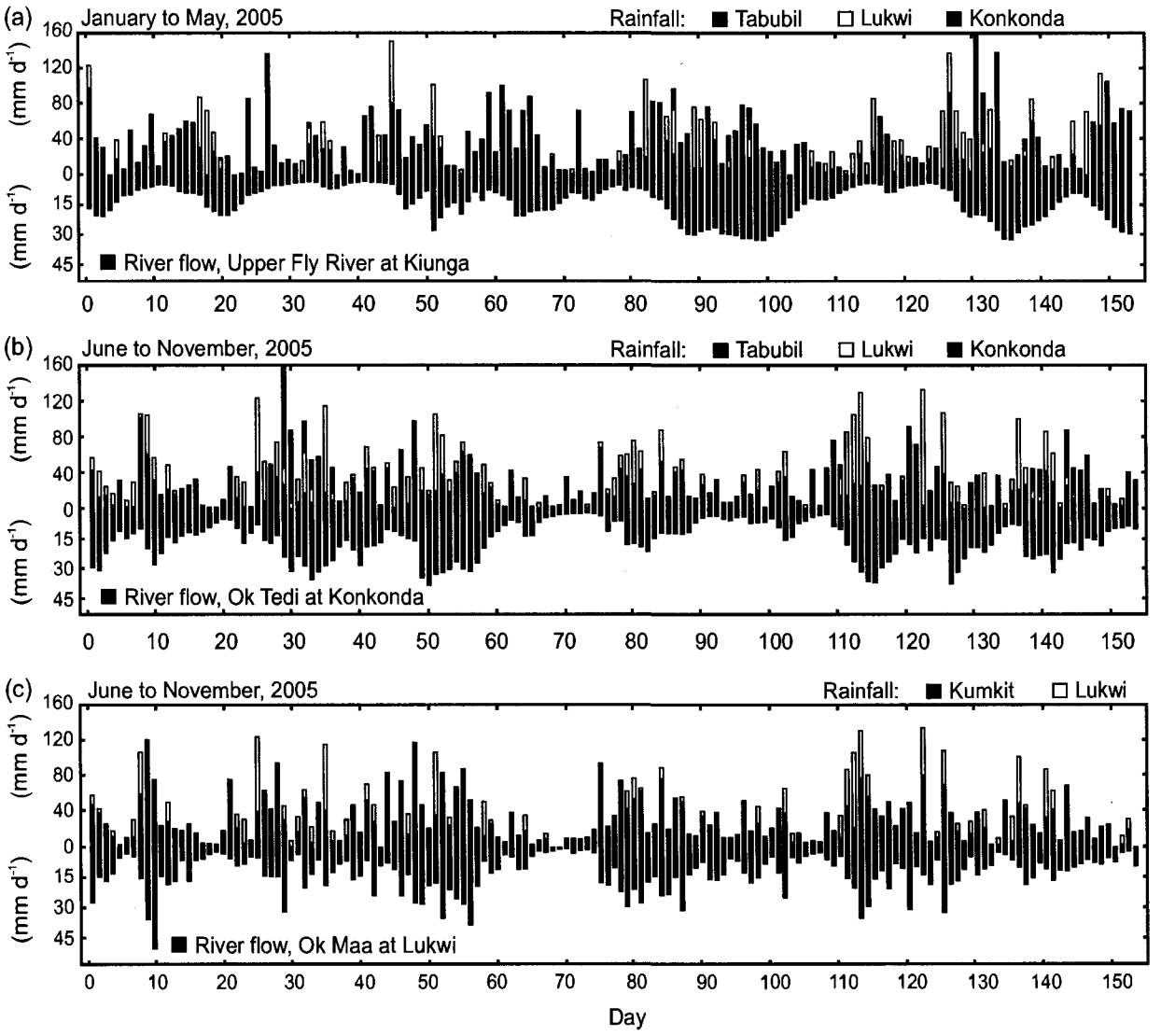


Figure 10. Daily rainfall and river runoff for (a) the Upper Fly River; (b) the Ok Tedi; (c) the Ok Maa. Rainfall exceeds runoff, implying some transfer of water vapor via evaporation and transpiration (i.e. *ET*).

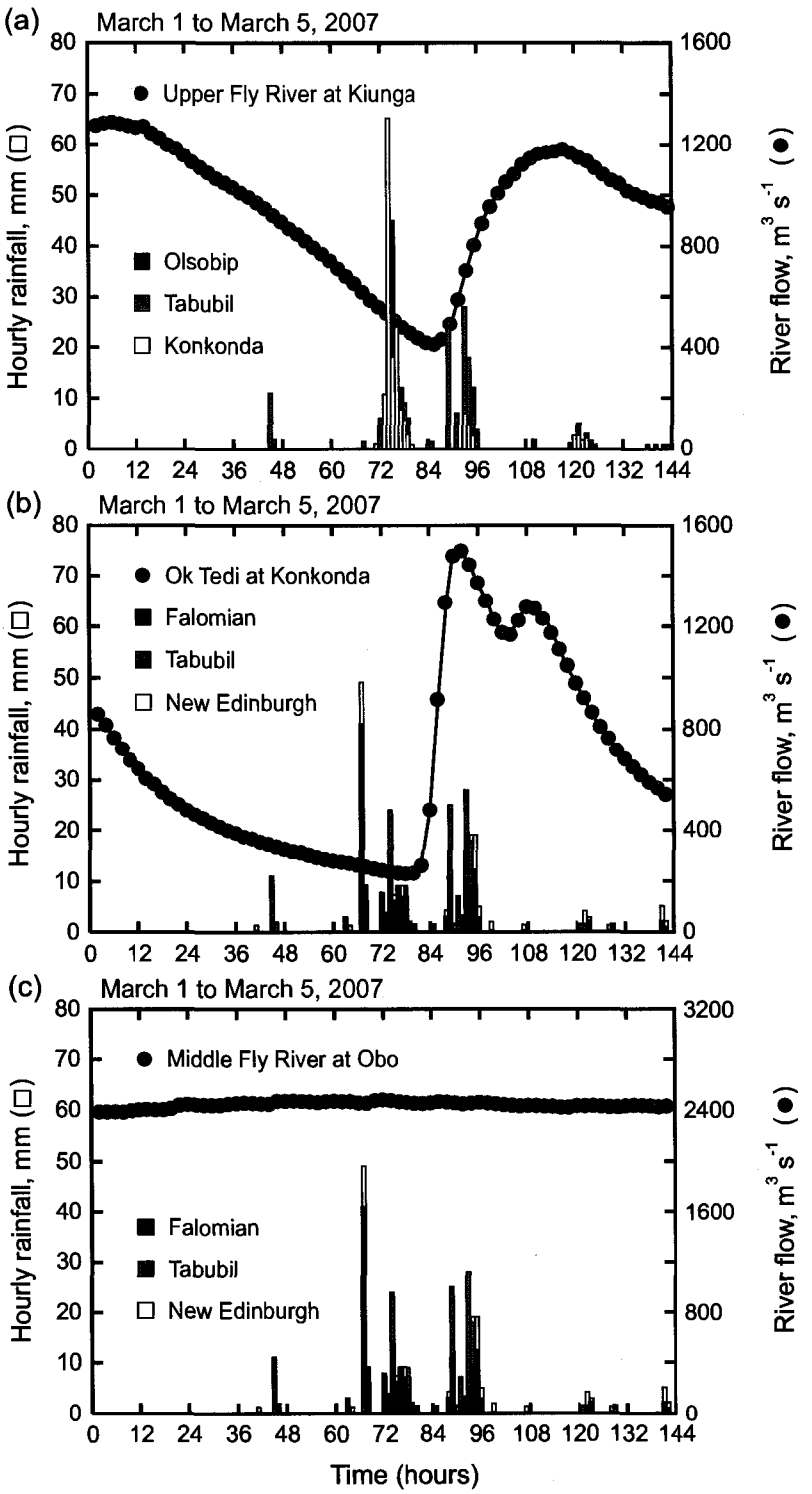


Figure 11. Hourly Rainfall at selected stations located in the Star Mountains and the response of river flow downstream in March 2007. (a) Upper Fly River at Kiunga; (b) the Ok Tedi at Konkonda; (c) the Middle Fly River at Obo.

are overlain by a fold-thrust belt of Mesozoic and Tertiary platform cover rocks [*Hendry et al.*, 2005]. More specifically, the headwaters of the Fly River and Strickland River are located within the Papuan Fold Belt, a system of north-westerly thrusting folds and faults [*Loffler*, 1977] that essentially defines the Central Cordillera region of southern/central New Guinea (Figure 7c). The dominant physiologic feature of the Star Mountains region is the Hindenburg Wall, a 300-m-tall cliff face located within the Victor Emmanuel Fold Belt. Recurring landslides and rock-falls are a prominent geomorphic process in the region and in addition to the many small landslides that occur every year, each comprised mainly of sediments, about one large rock-fall occurs from the Hindenburg Wall every decade [*Gilliseson*, 1983]. According to this author, approximately 2.5 – 3.5 million m^3 of slide material from a 1977 landslide was eventually transported down the Ok Tedi.

In terms of drainage lithology, the Fly River watershed is underlain by a mixture of carbonate rocks (70%) and silicate rocks (30%) [*Brunksill*, 2004], yet thick deposits of alluvial sediments related to the Fly Platform generally limit bedrock exposure to the upper-most reaches of the Ok Tedi and Upper Fly River and sections of the Upper Strickland River. In the headwaters region of the Ok Tedi and Upper Fly River, Miocene-Pleistocene igneous intrusive rocks within the Papuan Fold Belt host the major mineral-producing district surrounding Mount Fubilan. The mining operations of Ok Tedi Mining Limited focus on a large copper and gold porphyry deposit at Mount Fubilan that was initially discovered by first-pass helicopter-supported reconnaissance in 1968 [*Bamford*, 1972]. Conducted by BHP Billiton Inc., mining of the gold-rich cap began in 1984 and copper production began in 1986. As of December 31, 2004, the Ok Tedi mine has produced 166,328 tons of copper, 15,272 kilograms of gold, and 35,217 kilograms of silver [*OTML*, 2007].

Aside from localized porphyry deposits, the region surrounding Mount Fubilian is dominated by continental margin marine siltstones, mudstones and limestones that were deposited in an extensional framework from the Cretaceous to mid-Miocene [*Hendry et al.*, 2005]. Carbonate rocks are mainly associated with the Darai Limestone Megasequence, the deposition of which commenced during the Upper Oligocene in response to rifting in a back-arc setting. Regional subsidence associated with the back-arc extension led to the development of an extensive carbonate platform across the Gulf of Papua until carbonate sedimentation was terminated in the Upper Miocene by prograding clastic sediments from the uplifted northern parts of the Papuan Basin [*Morgan et al.*, 2005].

Overall, igneous rocks comprise less than 5% of drainage lithology and these rocks are generally limited to the region surrounding Mount Bosavi, a dormant volcano located near the eastern margin of the Strickland River watershed. Similarly, evaporite deposits in the watershed are negligible [*Brunskill*, 2004].

2.2.3 Description of vegetation and land-cover

Approximately 80% of New Guinea is covered by tropical rainforest, which represents a portion of the third largest tract of contiguous tropical rainforest next to Amazonia and central Africa (Figure 12). Vegetation in the Fly River watershed is primarily tropical lowland broadleaf forest (80%), of both alluvial and hill type, with water bodies (2%, mainly Lake Murray) and shifting mosaics of small-scale agriculture (i.e. garden plots) and natural vegetation (18%) comprising the remainder of vegetation [*Stibig et al.*, 2003]. In the portions of the watersheds south of Lake Murray, savanna-type ecosystems comprise the majority of this natural vegetation.

The most extensive habitat in the region is lowland broadleaf evergreen forest, which can be divided coarsely into alluvial and hill forest. Depending on the effects of local topography

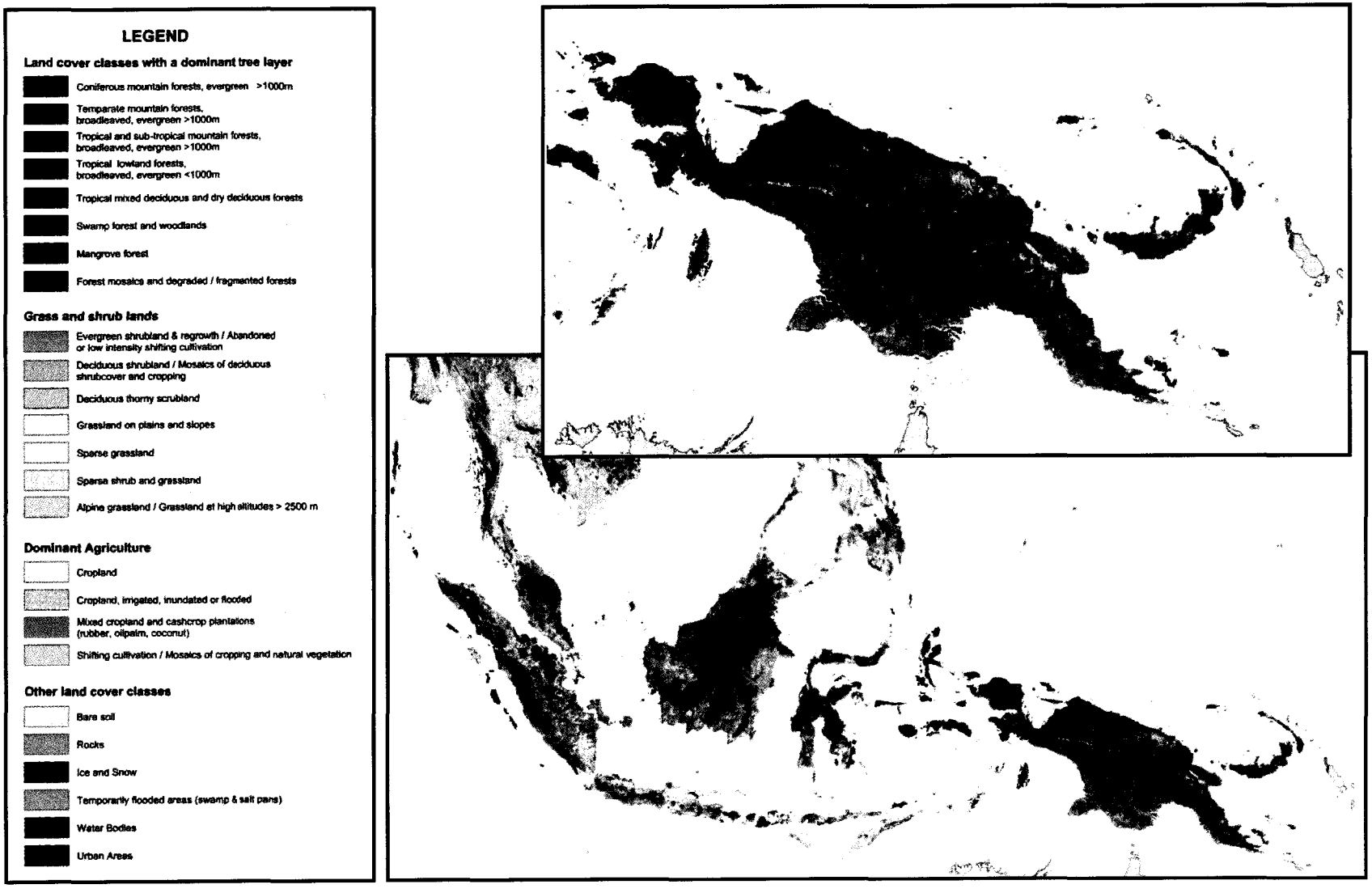


Figure 12. Distribution of vegetation in Southeast Asia. GLC2000 data from [*Stibig et al.*, 2003]. Inset map shows vegetation for the island of in New Guinea, wherein lowland and mountain tropical rainforests predominate.

and climate, the transition between alluvial (i.e. lowland) and hill/montane forest types usually occurs at 1000 meters above-sea-level (m ASL) in the Star Mountains [*Hyndman and Menzies*, 1990]. By this criterion and the GTOPO30 digital elevation model developed by the U.S. Geological Survey's Center for Earth Resources Observation and Science [*USGS/EROS*], 68% and 80% of the forest in the Ok Tedi and Upper Fly River watersheds, respectively, occurs at an elevation less than 1000 m ASL. Lowland alluvial forest has a canopy that is multi-tiered and irregular (60 – 80% closure) that usually reaches 25 – 30 m above the ground-surface, with many emergents reaching 40 – 50 m. The forest understory contains a shrub and herb layer with a variety of climbers, epiphytes, and ferns [*Petocz*, 1989]. According to [*Paijmans*, 1976], the mixed floristic composition of the canopy trees includes *Pometia pinnata, Octomeles sumatrana, Ficus* spp., *Alstonia scholaris,* and *Terminalia* spp. and additional important genera include *Pterocarpous, Artocarpus, Planchonella, Canarium, Elaeocarpus, Cryptocarya, Celtis, Dracontomelum, Dysoxylum, Syzygium, Vitex, Spondias,* and *Intsia.* In contrast to Malaysia and Borneo, dipterocarps are present but do not form extensive forests in New Guinea [*Nightingale*, 1992]. The canopy of the lowland hill forest is lower and more closed than the lowland alluvial forest and contains a denser herbaceous layer. Palms are fewer in number and the dominant canopy trees include species of *Pometia, Canarium, Anisoptera, Cryptocarya, Terminalia, Syzygium, Ficus, Celtis, Dysoxylum, and Buchanania. Koompassia, Dillenia, Eucalyptopsis, Vatica,* and *Hopea* are locally abundant [*Paijmans*, 1976; *Hyndman and Menzies*, 1990].

Rainforest ecosystems throughout most of the Fly River and Strickland River watersheds are considered primary and mainly undisturbed, yet some small-scale timber extraction does occur and forests immediately adjacent to the Ok Tedi and Middle Fly River have been damaged by the accumulation of sediments related to OTML mining activities. As part of

their operations near Mount Fubilan, OTML discharges mine tailings directly into the Ok Tedi. These mine-derived sediments are subsequently entrained and carried downriver where they are deposited in the floodplain region of the Ok Tedi and Middle Fly River region. Damage related to mine-derived sediments, commonly referred to as 'dieback' in reference to the recession of trees away from the river banks due to mine-derived sediment flux from the river, has occurred mainly above the confluence of Ok Tedi and Upper Fly River and in the Middle Fly River region and as of June 30, 2006, covered an area of 1,602 km^2 [*Marshall*, 2006].

Mining activities do not occur in the Upper Fly River watershed and thus unlike the Ok Tedi and Middle Fly River, this watershed is unaffected by mine-derived sediments. The Porgera Mine, owned by Placer Dome Limited, operates in the upper-most headwaters of the Strickland River in the Highlands Region of PNG. The extent of damage to the Strickland River watershed related to this operation is not well-characterized, as the majority of this watershed is largely inaccessible except by helicopter and unlike the Fly River watershed, no detailed studies have been conducted.

Chapter 3.

Sample Collection and Analytical Procedures

3.1 Sample collection procedures

Sample collection was conducted during two periods, a 30-month period from October 6, 2003, to April 4, 2006, and a twelve-day period from February 23 to March 6, 2007. Sample collection procedures for each period are described separately in sections 3.1.1 and 3.1.2.

3.1.1 October 2003 to April 2006

Samples of rainwater were collected approximately 5 – 10 times per month at the meteorological station at Tabubil (680 m ASL, Figure 8) according to the International Atomic Energy Agency (IAEA)/World Meteorological Organization (WMO) technical procedure [*IAEA/WMO*, 2004]. As per this procedure, samples were collected with a 1-L Nalgene™ bottle affixed to pole in an area unobstructed by vegetation and a small amount of paraffin mineral oil was added to the sample collection bottle in order to prevent evaporation during the period of rainfall accumulation. Samples were not filtered and were stored in 30-mL Nalgene™ bottles.

Samples of river water were collected approximately each month at six sites located near the mouths or after the confluences of the major tributaries (Figure 8). Sites are located at Kiunga (mouth of the Upper Fly River), Konkonda (mouth of the Ok Tedi), Nukumba (below the confluence of the Ok Tedi and Upper Fly River), Obo (Middle Fly River before the confluence of the Fly River and Strickland River), Str01 (mouth of the Strickland River), and Ogwa (below the confluence of the Fly River and Strickland River). Hourly river flow

data for the Upper Fly River at Kiunga, the Ok Tedi at Konkonda, and the Middle Fly River at Obo were available from gauges maintained and operated by the OTML Environment Department. Sample collection for river water was suspended from July to December of 2004 due to a period of reduced rainfall. During this period, low water levels in the Middle Fly River prevented the movement of copper-bearing freighters downriver and the monthly OTML sampling program was consequently suspended. Sample collection for rainfall continued during this period.

The monthly sampling procedure for river water consisted of 'landing' a helicopter via pontoons on the river surface at the monthly sampling sites and subsequently collecting three samples from 1 – 2 meters below the water surface (one sample was collected from near each river bank and one sample was collected from middle of the river). These samples were merged together as a composite sample of river water. Samples were filtered through a 25 mm diameter, 0.45 μm MFS disposable membrane into two 40-mL borosilicate vials. Particular care was taken to ensure that no air bubbles were trapped beneath the cap. Samples were preserved with $HgCl_2$ to prevent microbial activity and refrigerated at 4°C before shipment to the University of Ottawa.

3.1.2 February 23 to March 5, 2007

Sample collection was conducted aboard the OTML-commissioned research vessel *Tahua Chief*. Samples of river water from the Middle Fly River at Obo were collected every two hours for a period of 72 hours beginning at 1900h on February 23 and ending at to 1900h February 26. Samples of water from the Upper Fly River at Kiunga were collected every two hours for a period of 96 hours beginning at 0600h on March 1 and ending at 1200h on March 5. Water samples were collected from the side of the ship with a 1-L Nalgene™

bottle affixed to a PVC pipe that was extended approximately 3 – 4 meters below the water surface. During the process of sample collection, measurements of pH, water temperature, dissolved oxygen, and specific conductivity were collected with a Hydrolab^{TM} water quality multi-probe. Due to instrument malfunction, these field measurements of water quality parameters were not collected from 0100h to 1900h on February 26.

In the ship's clean laboratory, water samples were filtered through a 25-mm diameter, 0.45-μm MFS disposable membrane into two 40-mL borosilicate vials for stable isotope analyses and two 30-mL low-density polyethylene (LDPE) Nalgene^{TM} bottles for determination of major ion concentrations. For the 40-mL vials, particular care was taken to ensure that there were no air bubbles trapped inside the vials (i.e. no head-space). Also, in addition to the stock rubber cap, the borosilicate vials were fitted with an additional Teflon cap manufactured by Chromatographic Specialties Inc. (Brockville, ON, Canada) in order to ensure that there was no exchange of air between the water sample and the atmosphere during storage. Samples were refrigerated at 4°C while aboard the *Tahua Chief* and at the University of Ottawa.

Additional samples of river water and rainfall were collected at various locations while aboard the *Tahua Chief*. These samples were collected and processed in an identical manner to those collected from the Middle Fly River at Obo and the Upper Fly River at Kiunga. Six samples of river water were collected from the Ok Tedi at Konkonda, the Middle Fly River at Nukumba, the Strickland River at Str01, and the Fly River at Ogwa (see Figure 8 for the locations of the monthly sampling sites). Samples of rainwater were collected near Obo and Kiunga. When possible, rainwater was collected throughout the entire rainfall event in order to yield a time-integrated sample.

Samples of groundwater/soil water were collected from three springs within the town of Kiunga (these springs are identified as Kiunga Airport, Ongas, and Ninegrum Corner). The artesian spring near the airport in Kiunga was located within a small pool at the base of a hill-slope; water could be seen bubbling gently from beneath the surface amidst white, sand-like sediments that were noticeably different in colour and texture from the sediment within the pool. Samples of the sediment and water directly from the spring were collected. The springs at Ongas and Ninegrum Corner are located in forested regions within the town of Kiunga and are sources of drinking water for the local community. At Ninegrum Corner, water trickles from a small PVC pipe, whereas at Ongas, the spring is artesian and results in a small pool approximately 20 – 25 m^2 in area. Groundwater samples were also collected in the area surrounding Tabubil and the mine-site at Mount Falomian (samples were collected from a point of groundwater discharge from the pit wall of the mine).

3.2 Analytical methods

3.2.1 Major ions

The concentrations of major anions (Cl^-, NO_3^-, SO_4^{2-}) in water samples were analyzed by Ion Chromatography (Dionex DX-100) and the concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES) in the Geochemistry Laboratory at the University of Ottawa. The analytical precision for both cations and anions is ±5%.

3.2.2 Carbon isotope composition of dissolved organic and inorganic carbon

Water samples collected from October 2003 to April 2006 were analyzed for carbon isotope content within four to sixteen weeks of initial collection in PNG. The duration of

time between collection and analysis was determined mainly by the process of shipping samples from PNG to the University of Ottawa. Some samples, such as those collected from June 2005 to August 2005 were stored un-refrigerated for several months due to delays involved with shipping. Samples collected from February 23 to March 5 of 2007 were analyzed within two to four weeks of initial collection.

The concentrations and the ^{13}C content of dissolved inorganic carbon (*DIC*) and dissolved organic carbon (*DOC*) were determined with a total inorganic carbon–total organic carbon analyzer interfaced to a Finnigan Mat DeltaPlus isotope ratio mass spectrometer (IRMS) for analysis by continuous flow at the G.G. Hatch Isotope Laboratory, University of Ottawa [*St-Jean*, 2003]. *DIC* and *DOC* concentration are expressed in mg C L^{-1}. ^{13}C content is expressed by convention as δ values, representing deviation in parts per thousand (‰) from the standard Vienna Pee Dee Belemnite (VPDB), such that $\delta^{13}C = [R_{sample}/R_{standard}) - 1] \times 1000$ with R representing $^{13}C/^{12}C$. Isotope data was normalized using three internal standards and the 2σ analytical precision for $\delta\,^{13}C$ values was ±0.2‰.

DIC is a mixture of three dissolved carbonic species, carbonic acid (H_2CO_3), which includes $CO_{2(aq)}$, bicarbonate ions (HCO_3^-), and carbonate ions (CO_3^{2-}). Hereafter in this section, the concentration of total *DIC* will be referred to as C_T. For a given sample, the number of moles of C_T was determined by dividing the mass of carbon (i.e. g C L^{-1}) by the molecular weight of carbon (12.011 g mol^{-1}). According to [*Clark and Fritz*, 1997], the thermodynamic reaction constants (K_T) that are used to partition C_T into constituent carbonic species vary with temperature (T in equations below). These temperature-dependent K_T values were calculated according to the following equations taken from [*Drever*, 1997],

$$pK_{CO2} = -7 \cdot 10^{-5} \cdot T^2 + 0.016 \cdot T + 1.11 \quad (2)$$

$$pK_1 = 1.1 \cdot 10^{-4} \cdot T^2 - 0.012 \cdot T + 6.58 \quad (3)$$

$$pK_2 = 9 \cdot 10^{-5} \cdot T^2 - 0.0137 \cdot T + 10.62 \quad (4)$$

$$pK_{CaCO3} = 6 \cdot 10^{-5} \cdot T^2 + 0.0025 \cdot T + 8.38 \quad (5)$$

where T represents water temperature expressed in kelvins, K.

In order to determine the proportions of C_T comprised by each constituent carbonic species, the following expressions were used,

$$[H_2CO_3] = \frac{[H^+]}{K_1}[HCO_3^-] \quad (6)$$

$$[CO_3^{2-}] = \frac{[K_2]}{[H^+]}[HCO_3^-] \quad (7)$$

wherein $[H^+]$, $[CO_3^{2-}]$, and $[HCO_3^-]$ represent the concentrations of hydrogen ions, carbonate ions, and bicarbonate ions, respectively, and K_1 and K_2 represent the first and second dissociation constants of carbonic acid, respectively. In turn, C_T can be expressed as,

$$C_T = \left(\frac{[H^+]}{K_1} + 1 + \frac{[K_2]}{[H^+]} \right) [HCO_3^-] \quad (8)$$

By substitution and re-arrangement, the distribution of dissolved carbonic species can be specified as fractions of C_T,

$$[HCO_3^-] = \left(\frac{[H^+]K_1}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right) \cdot C_T \quad (9)$$

$$[H_2CO_3] = \left(\frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right) \cdot C_T \quad (10)$$

$$[CO_3^{2-}] = \left(\frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right) \cdot C_T \quad (11)$$

The $\delta^{13}C$ value of C_T can be expressed by the activities/concentration of $[H_2CO_3]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ and the $\delta^{13}C$ value of each carbonic species,

$$C_T \cdot \delta^{13}C_{DIC} = [H_2CO_3] \cdot \delta^{13}C_{H_2CO_3} + [HCO_3^-] \cdot \delta^{13}C_{HCO_3^-} + [CO_3^{2-}] \cdot \delta^{13}C_{CO_3^{2-}} \quad (12)$$

In order to facilitate the comparison of carbon isotope content and account for changing pH conditions, $\delta^{13}C$ values for individual carbonic species (primarily HCO_3^-) are reported instead of $\delta^{13}C$ values of C_T. This precludes ambiguity related to the isotope fractionation

that occurs during the processes of calcite dissolution (i.e. $CaCO_3 \rightarrow HCO_3^-{}_{(aq)}$) and the hydration of carbon dioxide ($CO_{2(g)} \rightarrow HCO_3^-{}_{(aq)}$) and the influence of varying proportions of dissolved carbonic species. The fractionation factors (α) for carbonic species at varying water temperatures were determined with the following equations,

$$10^3 \ln\alpha^{13}C_{CO2(aq)\text{-}CO2(g)} = -0.373 \cdot 10^3 \cdot T^{-1} + 0.19 \quad (13)$$

$$10^3 \ln\alpha^{13}C_{HCO3\text{-}CO2(g)} = 9.552 \cdot 10^3 \cdot T^{-1} - 24.10 \quad (14)$$

$$10^3 \ln\alpha^{13}C_{CO3(aq)\text{-}CO2(g)} = 0.87 \cdot 10^6 \cdot T^{-2} - 3.4 \quad (15)$$

$$10^3 \ln\alpha^{13}C_{CO2(g)\text{-}CaCO3} = -2.9880 \cdot 10^6 \cdot T^{-2} + 7.6663 \cdot 10^3 \cdot T^{-1} - 2.4612 \quad (16)$$

Equations (13), (14), (15), and (16) were taken from [*Vogel et al.*, 1970], [*Mook et al.*, 1974], [*Deines et al.*, 1974], and [*Bottinga*, 1968], respectively, and were compiled in [*Clark and Fritz*, 1997]. The $\delta^{13}C$ values of specific carbonic species were calculated with the following expressions,

$$\delta^{13}C_{HCO_3^-} = \delta^{13}C_{DIC} + \left(\frac{[H_2CO_3]}{C_T}\right)\alpha^{13}C_{H_2CO_3-HCO_3^-} - \left(\frac{[CO_3^{2-}]}{C_T}\right)\alpha^{13}C_{CO_3^{2-}-HCO_3^-} \quad (17)$$

$$\delta^{13}C_{H_2CO_3} = \delta^{13}C_{DIC} + \left(\frac{[HCO_3^-]}{C_T}\right)\alpha^{13}C_{HCO_3^--H_2CO_3} - \left(\frac{[CO_3^{2-}]}{C_T}\right)\alpha^{13}C_{CO_3^{2-}-H_2CO_3} \quad (18)$$

$$\delta^{13}C_{CO_3^{2-}} = \delta^{13}C_{DIC} + \left(\frac{[H_2CO_3]}{C_T}\right)\alpha^{13}C_{H_2CO_3-CO_3^{2-}} - \left(\frac{[HCO_3^-]}{C_T}\right)\alpha^{13}C_{HCO_3^--CO_3^{2-}} \quad (19)$$

3.2.3 Oxygen and hydrogen isotope content of water

Water samples collected from October 2003 to April 2006 were analyzed for oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) isotope content within six months of initial collection in PNG. As samples were sealed and refrigerated during storage, immediate analysis for water isotopes was not deemed necessary. Samples collected from February 23 to March 5, 2007, were analyzed within two to four weeks of collection.

The $^{18}O/^{16}O$ ratios of water samples were measured by the standard CO_2-H_2O equilibration technique [*Epstein and Mayeda*, 1953] and the $^{2}H/^{1}H$ ratio of water samples was determined using the zinc reduction technique [*Coleman et al.*, 1982]. Analyses were completed in the G.G. Hatch Isotope Laboratory at the University of Ottawa. Oxygen-18 and deuterium content are expressed by convention as δ values, representing deviation in parts per thousand (‰) from Vienna-Standard Mean Ocean Water (VSMOW), such that $\delta^{2}H$ or $\delta^{18}O = [R_{sample}/R_{standard}) - 1] \times 1000$ with R representing either $^{18}O/^{16}O$ or $^{2}H/^{1}H$.

Normalization of $\delta^{2}H$ or $\delta^{18}O$ measurements was achieved using internal standards and IAEA reference materials, including VSMOW, Greenland Ice Sheet Precipitation (GISP), and Standard Light Antarctic Precipitation (SLAP), following the guidelines of [*Coplen*, 1996], such that $\delta^{18}O$ and $\delta^{2}H$ values of SLAP are –55.5‰ and –428‰, respectively. The 2σ precision of isotope analyses was ±0.1‰ for $\delta^{18}O$ and ±2‰ for $\delta^{2}H$.

Chapter 4.

Isotope and Geochemical Data

4.1 pH, water temperature, and the concentrations of major ions in rainwater, river water, and groundwater

4.1.1 February 2004 to April 2006

The concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (HCO_3^{-}, SO_4^{2-}) elements in river water collected from February 2004 to April 2006 are provided in Appendix 1 with measurements of pH. These data are from the Ok Tedi Mining Limited (OTML) database and the concentrations of HCO_3^{-} for these samples represent carbonate alkalinity. Measurements of water temperature, chloride (Cl^{-}) and nitrate (NO_3^{-}) were not available from this database. Mean pH values and the mean concentrations of dissolved ions are summarized in Table 1, wherein concentrations are expressed in units of micro-moles per litre (μmol L^{-1} or μM) and the sums of positive (Σ^{+}) and negative (Σ^{-}) charges related to cations and anions, respectively, are expressed in micro-equivalents per litre (μeq L^{-1}).

In most samples collected from the monthly sites, Σ^{+} and Σ^{-} were close to equivalent, indicating that despite the absence of Cl^{-} and NO_3^{-} concentrations, the sum of positive charges associated with the major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) was balanced by the negative charges associated with HCO_3^{-} and SO_4^{2-}. The correspondence between Σ^{+} and Σ^{-} values indicates that the concentrations of Cl^{-} and NO_3^{-} are probably low compared to HCO_3^{-} and SO_4^{2-}. No predictable changes in the concentrations of cations over the sampling period could be resolved from the monthly data. Spatially, river water was generally more dilute in the headwaters region, as mean Σ^{+} and Σ^{-} values for the Middle Fly River at Obo, the

Table 1. Summary of mean values for pH and the concentration of major ions in river water samples collected at the monthly sampling sites from October 2003 to April 2006 (95% confidence intervals are given for each mean value). Data taken from OTML's Water Quality Database.

		Values expressed in μM								μeq L^{-1}	
Location	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	HCO_3^{-}	SO_4^{2-}	NO_3^{-}	Σ^{+}	Σ^{-}
Kiunga	7.9 ± 0.1	502 ± 46	36 ± 2	9 ± 2	40 ± 7	-	946 ± 92	75 ± 23	-	1129 ± 100	1104 ± 104
Konkonda	8.2 ± 0.1	494 ± 43	53 ± 6	25 ± 3	77 ± 10	-	1050 ± 104	147 ± 27	-	1192 ± 105	1326 ± 122
Nukumba	8.0 ± 0.1	516 ± 32	42 ± 2	16 ± 2	48 ± 6	-	1042 ± 78	97 ± 20	-	1180 ± 66	1214 ± 96
Obo	7.9 ± 0.1	592 ± 30	41 ± 2	18 ± 2	46 ± 4	-	1062 ± 136	117 ± 25	-	1324 ± 61	1297 ± 161
Str01	8.0 ± 0.1	592 ± 41	86 ± 10	17 ± 5	95 ± 9	-	1206 ± 155	152 ± 40	-	1469 ± 97	1443 ± 241
Ogwa	7.9 ± 0.1	615 ± 41	76 ± 4	16 ± 2	75 ± 7	-	1278 ± 106	130 ± 19	-	1473 ± 89	1462 ± 175

Table 2. Summary of pH, water temperature, and the concentrations of major ions in samples of rainfall, soilwater, and river water collected from February 23 to March 6, 2007 (95% confidence intervals are given for each mean value).

			Values expressed in μM								μeq L^{-1}	
Location	T, °C	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	HCO_3^{-}	SO_4^{2-}	NO_3^{-}	Σ^{+}	Σ^{-}
Rainfall[a]												
Kiunga	22.6	8.2	8	3	5	29	0	126	0	0	56	126
Kiunga	24.4	6.8	7	2	4	22	16	90	0	0	44	106
Obo	24.1	6.8	3	1	6	14	45	95	0	0	28	140
Obo	25.0	7.7	2	1	1	7	27	70	0	0	14	97
River water												
Ok Menga	21.4±0.2	7.1±0.2	842±13	100±3	6±1	37±3	0±0	-	25±6	7±1	1970	-
Kiunga	25.6±0.2	6.6±0.1	357±28	32±2	8±0	35±2	0±0	818	12±1	0±0	822	842
Konkonda	28.3±0.1	7.2±0.1	505±11	59±1	31±1	111±4	38±3	1036	124±1	0±0	1269	1284
Nukumba	25.5±0.0	7.3±0.0	491±9	42±1	16±0	50±1	13±2	-	55±1	0±0	1133	-
Obo	28.1±0.2	7.1±0.1	586±21	46±2	19±1	59±3	14±1	1139	76±6	0±0	1343	1291
Str01	25.5±0.0	7.3±0.0	555±3	95±1	17±2	115±2	17±2	1256	103±2	0±0	1433	1256*
Ogwa	26.2±0.0	7.2±0.0	563±6	80±1	17±1	89±1	14±2	1236	88±1	0±0	1391	1236*
Groundwater												
Kiunga[b]	27.2±0.4	4.5	4	6	5	18	18	31	-	32	43	81*
Falomian[c]	18.8±0.1	3.4	7328	2038	440	838	183	0	34838	26	10644	-

[a] Actual measurements for rainfall, not mean values

[b] Soil water from locations within the town of Kiunga

[c] Groundwater from the mine-site (95% confidence interval not shown)

* Values calculated without incorporating the charge associated with SO_4^{2-}

Strickland River at Str01, and the Fly River at Ogwa were higher than values for the Ok Tedi at Konkonda, the Upper Fly River at Kiunga, and the Middle Fly River at Nukumba. pH values for each of the monthly sites were usually slightly alkaline, with mean values ranging from 7.9 (Upper Fly River at Kiunga) to 8.2 (Ok Tedi at Konkonda).

For each of the monthly sampling sites, Ca^{2+} was the dominant cation, comprising approximately 80 – 90% of all cations on a molar basis. The concentrations of the other cations in river generally decreased as follows: $Mg^{2+} > Na^{+} > K^{+}$ (each of these cations comprised less than 10% of total cations on a molar basis). HCO_3^- was the dominant anion in river water, representing approximately 90% of total anions on a molar basis. SO_4^{2-} comprised the remainder of the total anions.

4.1.2 February 23 to March 5, 2007

The concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-) in river water collected from February 23 to March 6, 2007, are provided in Appendix 2 with measurements of pH and water temperature, wherein the concentrations of dissolved ions are expressed in units of micro-moles per litre (μmol L^{-1} or μM) and the charge balances for cations (Σ^{+}) and anions (Σ^{-}) are expressed in micro-equivalents per litre (μeq L^{-1}). Unlike HCO_3^- data for the monthly samples collected from February 2004 to April 2006, the concentrations of HCO_3^- for samples collected in 2007 were based on the concentration of HCO_3^- from the G.G. Hatch Laboratory (see section 3.2.2).

pH values for river water samples collected from the Middle Fly River at Obo during this period were slightly alkaline and were characterized by a mean pH value of 7.7 (Table 2). In samples collected from the Upper Fly River at Kiunga, pH values were close to neutral and slightly more acidic than those collected from the Middle Fly River at Obo, ranging from 6.5

to 7.8 with a mean pH of 7.1. In general, mean pH values for the water samples collected from the monthly sampling sites from February 23 to March 5, 2007, were lower than corresponding mean pH values for samples collected from February 2004 to April 2006. Samples of rainwater were more acidic than river water, characterized by pH values of 6.8 to 8.2. Samples of groundwater collected near the town of Kiunga were characterized by pH values of 4.3 to 4.7, considerably more acidic than samples of river water and rainwater. Even more acidic were the groundwater samples collected from the mine-pit wall at Falomian, where the mean pH value was 3.4 (Table 2).

In most samples of river water collected from the Middle Fly River at Obo (February 23 to February 26, 2007) and the Upper Fly River at Kiunga (March 1 to March 5, 2007), Σ^{+} and Σ^{-} were close to equivalent (Table 2). The concentration of HCO_3^- in samples collected from the Ok Menga and the Middle Fly River at Nukumba were not available and hence Σ^{-} values were not calculated for these samples. Σ^{-} for samples of rainwater exceeded Σ^{+} substantially; SO_4^{2-} and NO_3^- were negligible in these samples. A similar imbalance was observed for groundwater samples collected near the town of Kiunga.

For the samples of river water collected from February 23 to March 5, 2007, Ca^{2+} was the dominant cation, comprising approximately 80 – 90% of all cations on a molar basis. The concentrations of the other cations in river generally decreased as follows: $Mg^{2+} > Na^{+} > K^{+}$ (each of these cations comprised less than 10% of total cations on a molar basis). HCO_3^- was the dominant anion in river water, representing approximately 90% of total anions on a molar basis, and the other anions decreased as follows: $SO_4^{2-} > Cl^- > NO_3^-$. The concentration of Na^{+} in river water often exceeded Cl^- by approximately 2 – 4 times. In samples of rainwater, the concentrations of cations and anions were low compared to river water and groundwater.

Ca^{2+} concentrations, for example, were less than 10 μM. Also, unlike samples of rainwater and groundwater, Na^{+} was the dominant cation in rainwater.

In samples of groundwater collected from the mine-site at Falomian, concentrations of major cations were an order of magnitude larger than corresponding concentrations in river water. Ca^{2+} and Mg^{2+} were the predominant cations in these samples and SO_4^{2-} was the dominant anion in these samples (HCO_3^{-} in these samples was negligible as H_2CO_3 was the dominant carbonic species, Table 3). Σ^{+} exceeds Σ^{-} substantially for these samples. Obtaining accurate measurements of the concentrations of dissolved ions in these samples was problematic, as these samples were collected from the mine pit-wall and represent deep groundwater that circulates through deposits of sulphide minerals (i.e. acid rock drainage, *ARD*).

During the period of sample collection from February 23 to February 26, 2007, samples of river water were collected every two hours in order to constrain the potential response of water quality parameters to changes in the rate of river flow. In Figure 11, the hourly rates of river flow for the Ok Tedi at Konkonda, the Upper Fly River at Kiunga, and the Middle Fly River at Obo (March 1 to March 5, 2007) are illustrated in order to provide some perspective on the rates of river flow at these locations and how river flow responds to incident rainfall. From this figure, the rate of river flow for the Ok Tedi at Konkonda and the Upper Fly River at Kiunga respond more rapidly to incident rainfall in the Star Mountains region, whereas river flow for the Middle Fly River at Obo is essentially constant during the period of interest.

During the period of sample collection from the Middle Fly River at Obo, the rate of river flow increased by about 5% from 2100 $m^3\ s^{-1}$ to 2300 $m^3\ s^{-1}$. This pattern of increasing

Table 3. Summary of pH, water temperature, and the concentrations of major ions in samples of rainfall, soilwater, and river water .

Location	T, °C	pH	Dissolved inorganic carbon (DIC) DIC, mg C L^{-1}	HCO_3^-, μM	$\delta^{13}C$ HCO_3^-, ‰	H_2CO_3, μM	$\delta^{13}C$ H_2CO_3, ‰	Water $\delta^{18}O$, ‰	δ^2H, ‰
Rainfall[a]									
Kiunga	22.6	8.2	1.5	122	-8.3	6	-16.2	-12.4	-79.1
Kiunga	24.4	6.8	1.5	57	-2.1	64	-11.6	-14.8	-92.7
Obo	24.1	6.8	1.5	61	-3.4	68	-10.2	-1.8	-14.0
Obo	25.0	7.7	0.9	64	1.0	9	-7.0	-5.7	-20.4
River water (February 23 to March 6, 2007)									
Ok Menga	21.4±0.2	7.6±0.2	-	-	-	-	-	-11.3±0.0	-78±1
Kiunga	25.6±0.2	7.1±0.1	11.8±1	440±91	-12.4±0.1	351±43	-19.5±0.3	-10.3±0.1	-72±1
Konkonda	28.3±0.1	7.7±0.1	13.0±2	959±135	-11.2±0.1	119±13	-18.7±0.2	-8.9±0.0	-61±0
Obo	28.1±0.2	7.6±0.1	14.5±1	1027±43	-11.1±0.2	176±25	-18.6±0.2	-8.5±0.2	-60±1
Str01	25.5±0.0	7.8±0.0	15.7±3	1169±223	-11.7±0.1	136±24	-19.4±0.1	-11.1±0.1	-70±5
Ogwa	26.2±0.0	7.7±0.0	15.5±2	1135±132	-11.4±0.1	157±18	-18.2±0.2	-10.1±0.1	-73±1
River water (February 2004 to April 2006)									
Kiunga	-	8.2±0.1	10.9±2.6	878±214	-8.4±3.2	26±6	-15.8±3.2	–7.6±0.5	–52±5
Konkonda	-	7.9±0.1	10.7±3.2	870±260	-9.9±3.0	12±4	-17.4±3.0	–8.4±0.7	–56±4
Nukumba	-	8.0±0.1	12.0±3.5	926±282	-9.5±3.0	21±8	-17.0±3.0	–8.4±0.6	–59±5
Obo	-	7.9±0.1	13.0±2.3	1061±267	-8.6±2.8	31±8	-15.7±2.8	–8.3±0.6	–57±4
Str01	-	8.0±0.1	13.0±3.0	992±248	-8.0±2.7	20±5	-15.3±2.7	–9.4±0.6	–67±4
Ogwa	-	7.9±0.1	13.4±2.6	1081±194	-8.3±2.6	29±8	-15.7±2.6	–9.0±0.5	–64±4
Soilwater/groundwater									
Falomian[b]	18.8±0.1	4.5	2.1	0	-	171	-3.7±0.3	-10.5±0.0	-72±2
Kiunga[c]	27.2±0.4	3.4	22.1	10	-	1831	-17.5±2.0	-9.1±0.1	-65±1

95% confidence intervals are given for mean values

[a] Actual data shown, not mean values

[b] Groundwater from the mine-site

[c] Soil water from locations within the town of Kiunga

river flow is illustrated identically in Figures 13, 14, and 15. During the period of sample collection from the Middle Fly River at Obo, the concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) in river water co-varied, with concentration maxima observed at approximately 60h. The concentration maxima did not correspond to any discernible change in the rate of river flow.

During the period of sample collection from the Upper Fly River at Kiunga, the rate of river flow was more variable and the observed change in river flow was more substantial compared to the Middle Fly River at Obo. For the Upper Fly River at Kiunga, the rate of river flow decreased from an initial rate of 1400 m^3 s^{-1} to a minimum of 400 m^3 s^{-1} at hour 84 (i.e. 84h) before increasingly abruptly to 1200 m^3 s^{-1} at 120h. This pattern is illustrated identically in Figures 16, 17, and 18. From Figure 10, it is evident that the increase in the rate of river flow was caused by rainfall events that occurred approximately 20 – 24 hours prior. Similar to the concentrations of major cations in samples collected from the Middle River at Obo, concentrations in river water from the Upper Fly River at Kiunga co-varied. However, unlike samples collected from the Middle Fly River at Obo, the observed maxima in concentrations corresponded to the increase in river flow. This response was particularly evident by the abrupt increase in Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} concentrations immediately after river flow began to increase at 84h. After the peaks in concentration, the concentrations of Ca^{2+}, Mg^{2+}, and Na^{+} declined until the end of the period of sample collection at 108h, whereas the concentration of Na^{+} declined initially with the other cations yet began to increase once again near the end of the period of sample collection.

4.2 $\delta^{13}C$ values of dissolved organic carbon and dissolved inorganic carbon

The concentrations and $\delta^{13}C$ values of total dissolved inorganic carbon (*DIC*) and dissolved organic carbon (*DOC*) in water samples collected from February 2004 to April

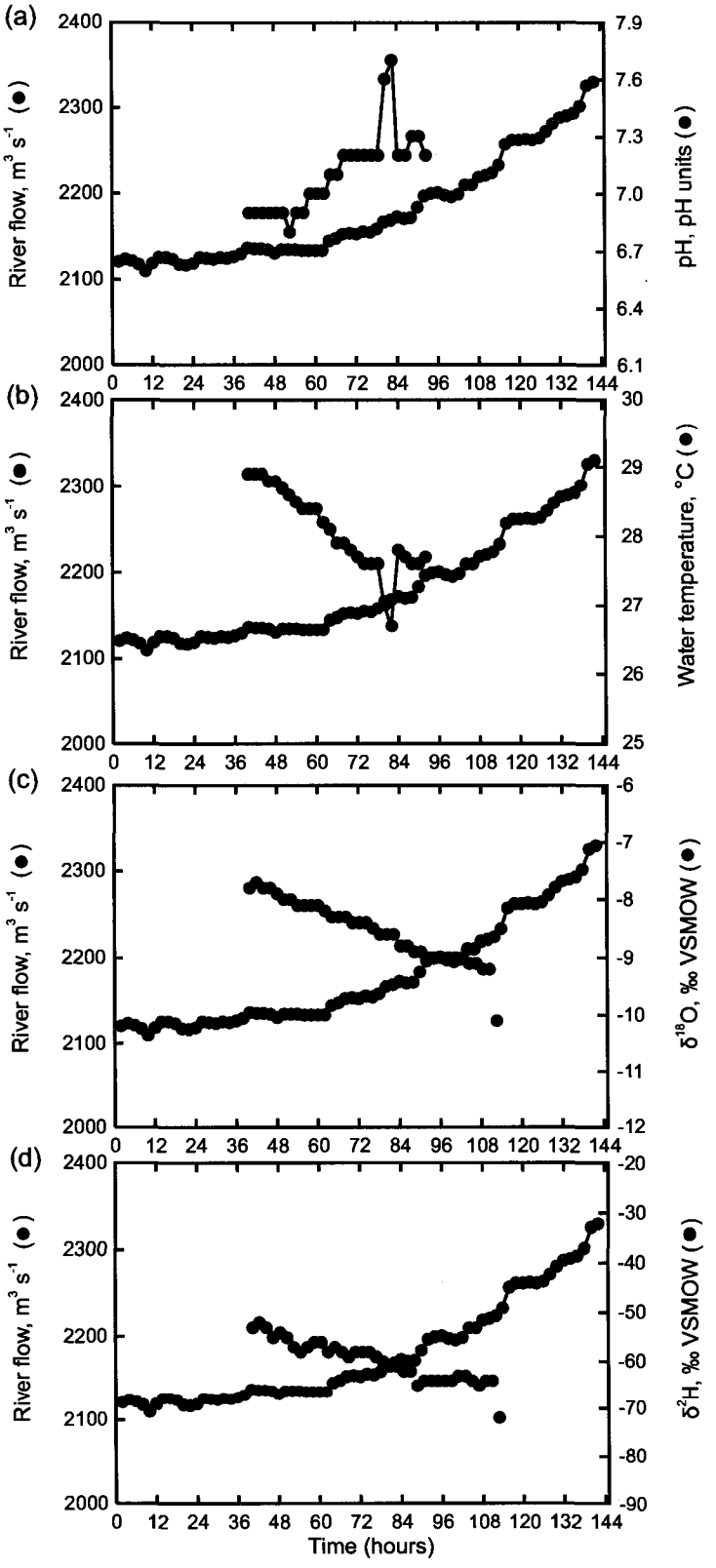


Figure 13. For the Middle Fly River at Obo, the response of (a) pH; (b) water temperature; (c) $\delta^{18}O$ of water and (d) $\delta^{2}H$ of water to changes in river flow.

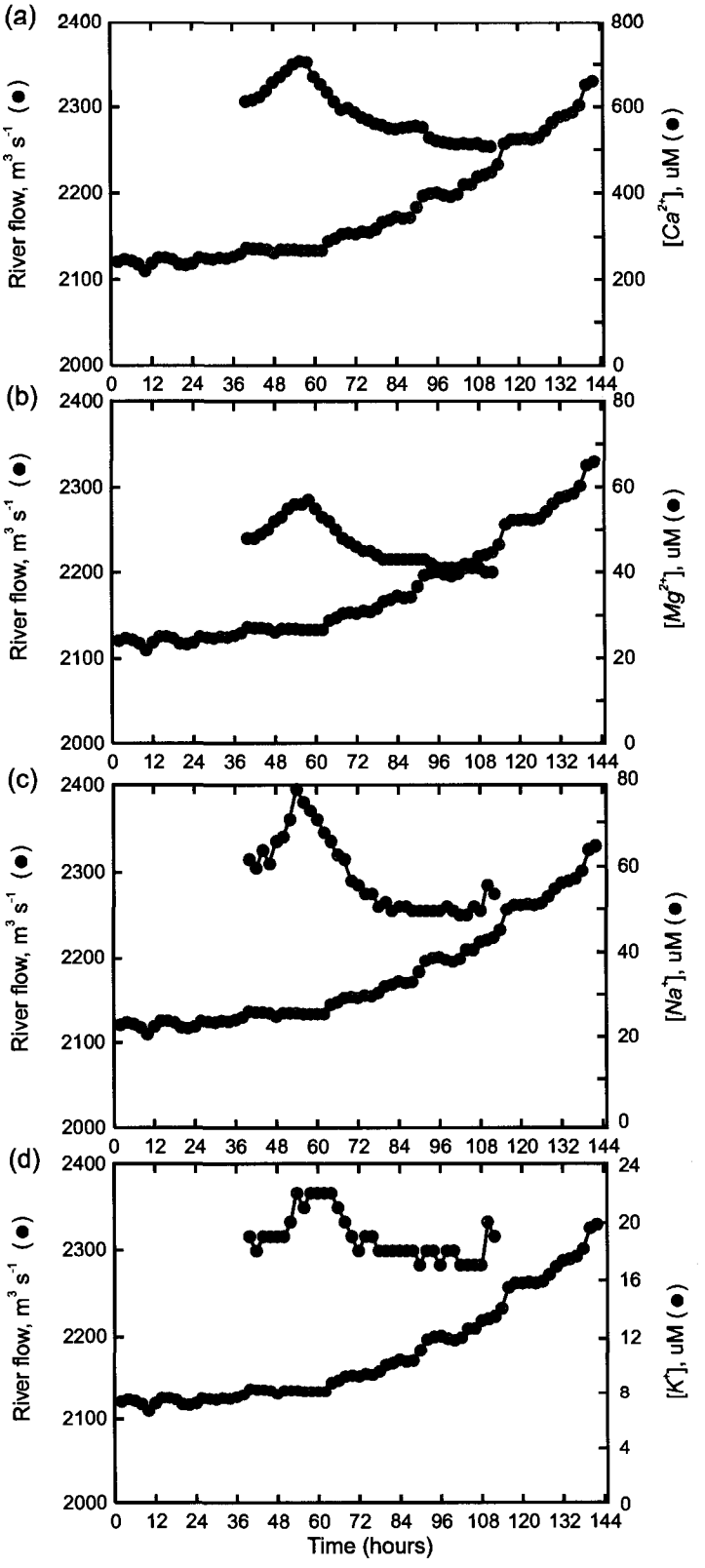


Figure 14. For the Middle Fly River at Obo, the response of (a) Ca^{2+}; (b) Mg^{2+}; (c) Na^{+} and (d) K^{+} to changes in river flow.

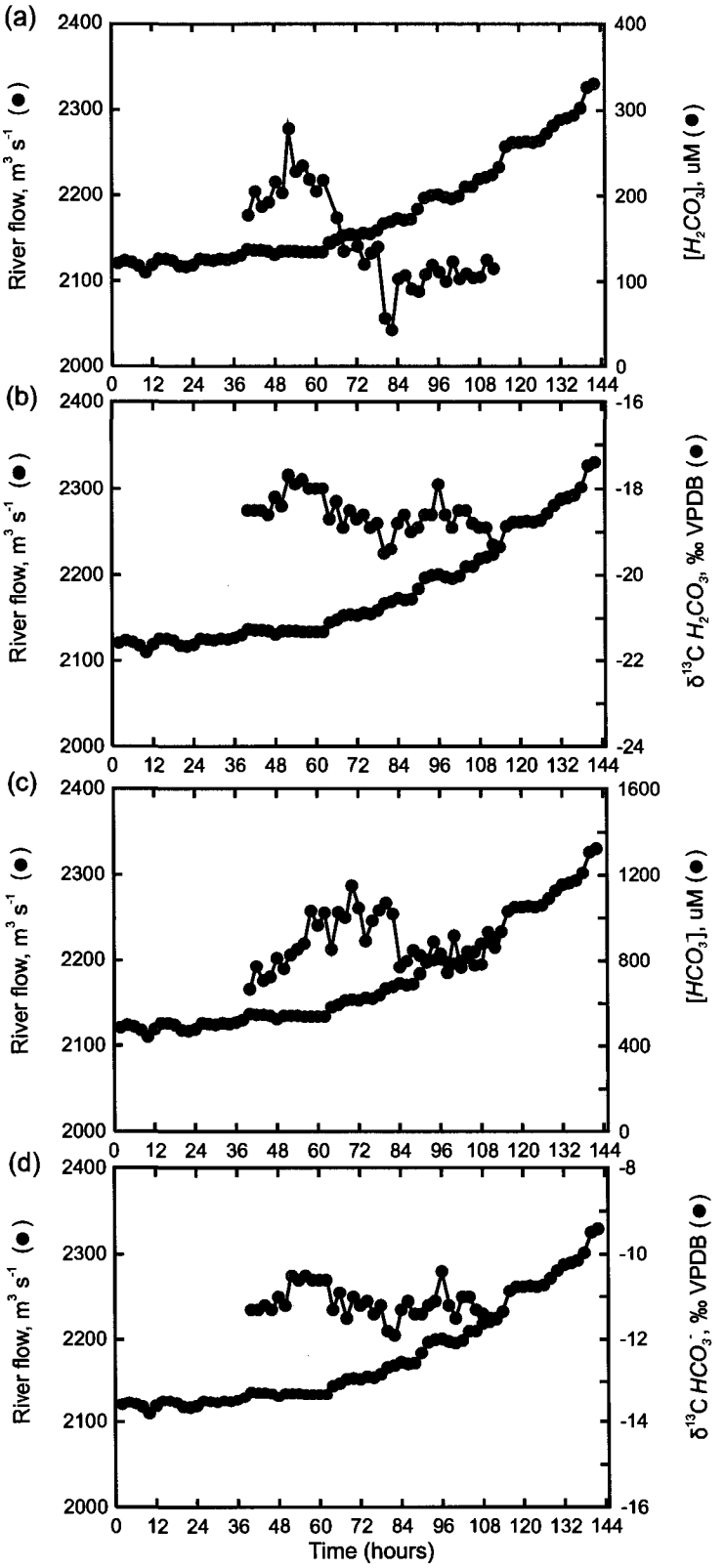


Figure 15. For the Middle Fly River at Obo, the response of (a) H_2CO_3; (b) $\delta^{13}C$ of H_2CO_3; (c) HCO_3^- and (d) $\delta^{13}C$ of HCO_3^- to changes in river flow.

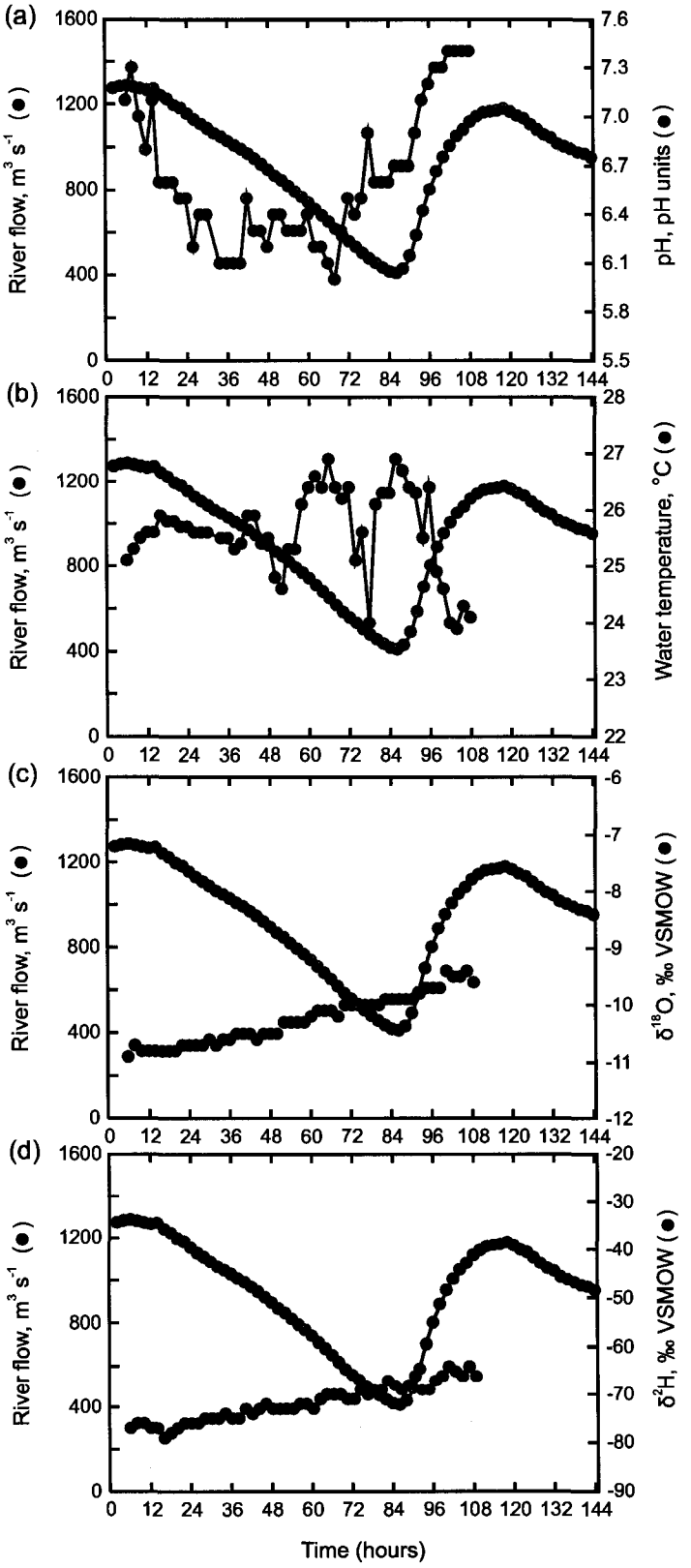


Figure 16. For the Upper Fly River at Kiunga, the response of (a) pH; (b) water temperature; (c) $\delta^{18}O$ of water and (d) $\delta^{2}H$ of water to changes in river flow.

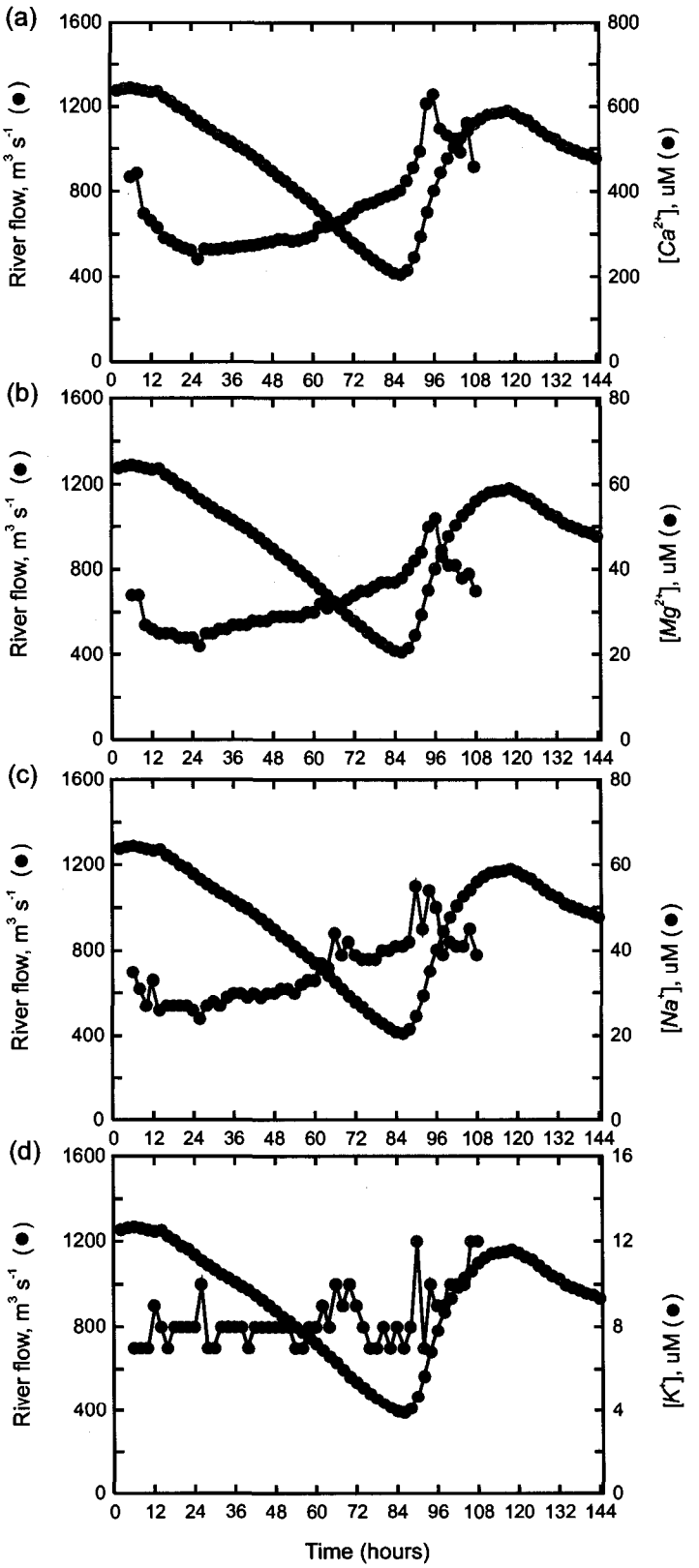


Figure 17. For the Upper Fly River at Kiunga, the response of (a) Ca^{2+}; (b) Mg^{2+}; (c) Na^{+} and (d) K^{+} to changes in river flow.

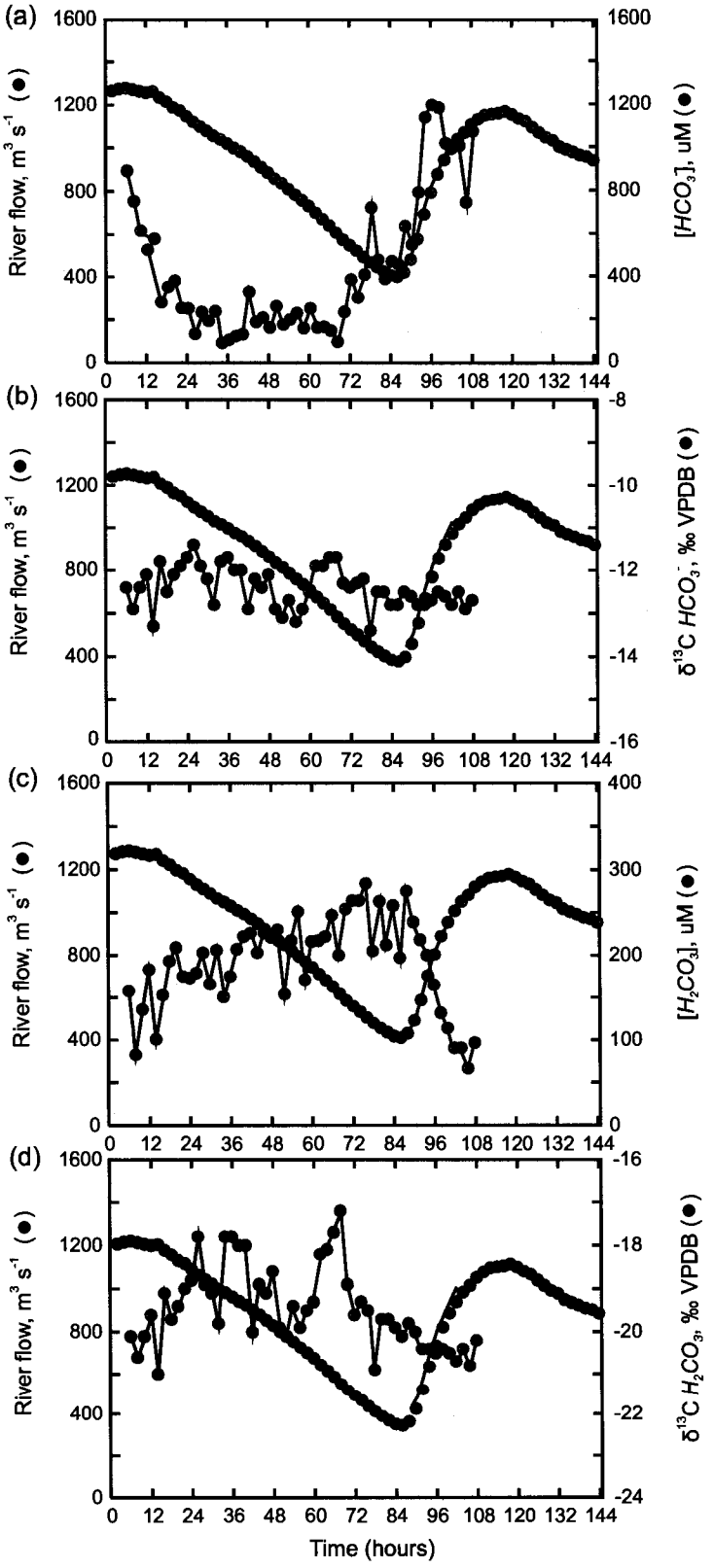


Figure 18. For the Upper Fly River at Kiunga, the response of (a) H_2CO_3 (b) $\delta^{13}C$ of H_2CO_3 (c) HCO_3 and (d) $\delta^{13}C$ of HCO_3^- to changes in river flow

2006 are provided in Appendix 3. pH values and calculated K_T values used to partition *DIC* (or C_T) into constituent carbonic species (see section 3.2.2) are provided in Appendix 4 for samples collected from February 2004 to April 2006 and in Appendix 5 for samples collected from February 23 to March 6, 2007. Note that measurements of water temperature were not available from the OTML database. Hence, for samples collected from February 2004 to April 2006, a constant water temperature of 301.15 K was used for the calculation of K_T values for the Ok Tedi at Konkonda, the Upper Fly River at Kiunga, and the Middle Fly River at Nukumba, whereas a constant water temperature of 303.15 K was used for the calculation of K_T values for the Middle Fly River at Obo, the Strickland River at Str01, and the Fly River at Ogwa. The data required to resolve the $\delta^{13}C$ values of *DIC* into $\delta^{13}C$ values of HCO_3^- and H_2CO_3 are provided in Appendices 6 and 7, the former being for samples collected from February 2004 to April 2006 and the latter for samples collected from February 23 to March 6, 2007.

As pH values were generally less than 8.5, the concentrations of CO_3^{2-} ions in water samples collected from the Fly River watershed were negligible. HCO_3^- was generally the most abundant carbonic species in river water, comprising 60 – 90% of C_T. In samples of groundwater and some river water samples that had relatively low pH values, H_2CO_3 represented a larger proportion of C_T. As HCO_3^- was the principal carbonic acid species and HCO_3^- is considered to be in isotope equilibrium with H_2CO_3, the subsequent discussion is generally limited to the description of $\delta^{13}C$ values of HCO_3^-, the principal carbonic species in the tributaries of the Fly River.

4.2.1 February 2004 to April 2006

Mean $\delta^{13}C$ values of HCO_3^- in water samples collected from February 2004 to April 2006 ranged from -8.0‰ (Strickland River at Str01) to -9.9‰ (Upper Fly River at Kiunga) (Table

3). The range of $\delta^{13}C$ values of HCO_3^- for individual samples collected during this period was considerable and evident from the large 95% confidence intervals associated with the mean values. More specifically, $\delta^{13}C$ values of HCO_3^- for samples of river water collected from June 2005 to August 2005 were approximately -20‰ (Appendix 6) and thus much lighter than the calculated mean values, whereas $\delta^{13}C$ values of HCO_3^- for other samples were sometimes positive (i.e. 2 – 3‰) and hence much heavier than mean values for the different stations. The concentrations of HCO_3^- for the samples collected from June 2005 to August 2005 were generally high, sometimes exceeding 2000 µM, whereas the concentrations of HCO_3^- for the samples with positive $\delta^{13}C$ values of HCO_3^- were close to the mean concentration or lower. The concentrations of HCO_3^- yielded by analyses in the G.G. Hatch Isotope Laboratory did not correspond well with Σ^+ values provided in section 4.1.1 (recall that the Σ^+ and Σ^- values in that section were calculated from the OTML database and thus the concentration of HCO_3^- was based on measurements of carbonate alkalinity, not data from the University of Ottawa). As water samples must be neutral in charge, this disparity between Σ^+ values and the concentration of HCO_3^- suggests some form of error, which will be discussed further in Chapter 6.

Mean concentrations of DOC were between 1.6 µg L^{-1} (Ok Tedi at Konkonda) and 3.1 µg L^{-1} (Fly River at Ogwa). Mean $\delta^{13}C$ values of DOC in river water ranged from –27.9‰ (Strickland River at Str01) to –28.9‰ (Ok Tedi at Konkonda). $\delta^{13}C$ values of DOC (Appendix 3) were essentially constant and there were no spatial or temporal variations in the data.

4.2.2 February 23 to March 5, 2007

Mean $\delta^{13}C$ values of HCO_3^- in water samples collected from February 23 to March 5, 2007, ranged from -11.1‰ (Middle Fly River at Obo) to -12.4‰ (Upper Fly River at Kiunga) (Table 3, Appendix 8). Unlike monthly samples collected from February 2004 to April 2006, the $\delta^{13}C$ values of HCO_3^- for individual samples collected in 2007 were consistently close to the mean values and did not show the level of variability observed for the monthly data collected from October 2003 to April 2006 (from Table 3, note the differences in 95% confidence intervals for $\delta^{13}C$ values between the two data sets).

During the period of sample collection from February 23 to February 26, 2007, river flow for the Middle Fly River at Obo increased by about 5% compared to the initial rate of flow. $\delta^{13}C$ values of HCO_3^- (and H_2CO_3) did not respond noticeably to the change in river flow (Figure 15). During the period of sample collection from the Upper Fly River at Kiunga, the change in river flow was more substantial compared to the Middle Fly River at Obo, as the rate of river flow decreased from an initial rate of 1400 $m^3\ s^{-1}$ to a minimum of 400 $m^3\ s^{-1}$ at hour 84 (i.e. 84h) before increasingly abruptly to 1200 $m^3\ s^{-1}$ at 120h. The $\delta^{13}C$ values of HCO_3^- were fairly consistent and did not respond appreciably to the change in river flow (Figure 18).

4.3 $\delta^{18}O$ and δ^2H values of water

4.3.1 Rainfall

$\delta^{18}O$ and δ^2H values of rainfall collected at Tabubil from October 2003 to April 2006 are provided in Appendix 9 and variability over the period of 2004 to 2005 is illustrated in Figure 19. Over this period, the mean $\delta^{18}O$ and δ^2H values were –8.3‰ and –56‰, respectively (Table 4). Mean $\delta^{18}O$ and δ^2H values for 2004, 2005, and 2006 are also summarized in Table 4 with minimum and maximum values for each year.

Table 4. Summary of $\delta^{18}O$ and $\delta^{2}H$ values of rainfall at Tabubil, Star Mountains region, Papua New Guinea.

Year	Mean		Minima			Maxima			n
	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰	$\Delta^{18}O$, ‰	$\delta^{2}H$, ‰	Date	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰	Date	
2004	–8.3 ± 1.1	–56 ± 9	–17.5	–124	31/12	–1.4	6	23/08	82
2005	–9.3 ± 1.3	–63 ± 11	–19.9	–149	04/11	–1.8	–3	02/09	58
2006[a]	–12.2 ± 1.3	–92 ± 7	–19.1	–153	11/04	–6.0	–49	14/03	21

[a] January to April

Mean values ± 2 standard errors (i.e. 95% confidence intervals).

In 2004, rainfall samples collected from January to the end of March were characterized by $\delta^{18}O$ and $\delta^{2}H$ that were generally lighter than the annual mean values for 2004 ($\delta^{18}O$ values ranged from –7.9‰ to –16.8‰ and $\delta^{2}H$ values from –48‰ to –127‰). In April, $\delta^{18}O$ and $\delta^{2}H$ values were usually heavier than the annual mean values for 2004. $\delta^{18}O$ and $\delta^{2}H$ values of rainfall during the month of May were lighter than the annual mean values and were similar to values for January to March. This period of isotopically-depleted rainfall prevailed until June, when $\delta^{18}O$ and $\delta^{2}H$ values of rainfall abruptly shifted to values that were heavier than the annual mean values. This abrupt shift in $\delta^{18}O$ and $\delta^{2}H$ values was evident from a 7.0‰ difference between the $\delta^{18}O$ value of rainfall on June 3 (–11.6‰) and June 5 (–4.6‰). $\delta^{18}O$ and $\delta^{2}H$ values of rainfall in 2004 were heaviest in August, within approximately 2‰ and 6‰ of VSMOW, respectively. From June to early November, $\delta^{18}O$ and $\delta^{2}H$ values of rainfall remained heavier than annual mean values (Figure 19a). In late November, $\delta^{18}O$ and $\delta^{2}H$ values of rainfall were lighter than the annual mean values, reaching minima in December and January when $\delta^{18}O$ values were generally lighter than –10‰ and –70‰, respectively.

In 2005, the intra-annual variation in $\delta^{18}O$ and $\delta^{2}H$ values of rainfall was similar to the pattern observed in 2004. $\delta^{18}O$ and $\delta^{2}H$ values of rainfall were relatively light from January to early February. From late February to mid March, $\delta^{18}O$ and $\delta^{2}H$ values of rainfall became relatively heavy before shifting back to lighter values near the end of March. The transition

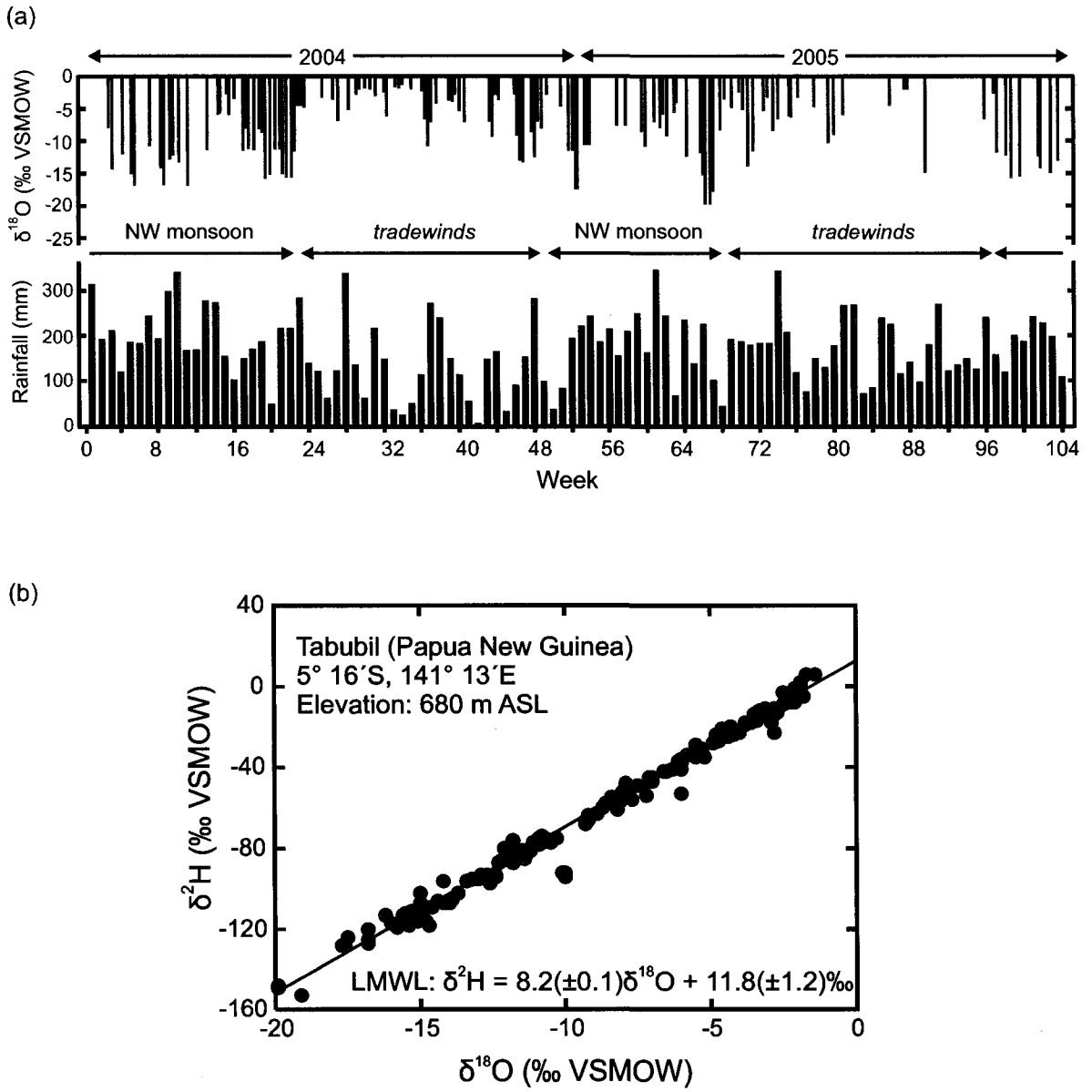


Figure 19. (a) Intra-annual variation in the amount and $\delta^{18}O$ value of rainfall at Tabubil for 2004 and 2005; (b) $\delta^{18}O$ and $\delta^{2}H$ values of rainfall and the corresponding local meteoric water line (LMWL) for Tabubil. The 95% confidence intervals for the slope and $\delta^{2}H$ intercept are given in parentheses and elevation is given in meters above sea level (m ASL).

was evident from an approximately 8‰ and 72‰ isotope separation between $\delta^{18}O$ and $\delta^{2}H$ values of rainfall on March 16 (–4‰ and –22‰) and March 24 (–12.4‰ and –94‰). $\delta^{18}O$ and $\delta^{2}H$ values of rainfall that were lighter than the annual mean values for 2005 persisted until mid-April when values shifted towards VSMOW. These heavier $\delta^{18}O$ and $\delta^{2}H$ values of rainfall prevailed from until November when values became lighter than the annual mean values for the remainder of 2005 and from January to April, 2006, when sample collection ended.

Utilizing $\delta^{2}H$ as the independent variable, $\delta^{18}O$ and $\delta^{2}H$ values of rainfall collected from November 11, 2003, to April 4, 2006, defined a regression line (or local meteoric water line, LMWL) of the equation $\delta^{2}H = 8.2(\pm0.1)\cdot\delta^{18}O + 11.8\ (\pm1.2)‰$ ($R^2 = 0.99$, $p < 0.0001$, $n = 163$) (Figure 19b). 95% confidence intervals for the slope and $\delta^{2}H$-intercept values are given in parentheses. In 2004, $\delta^{18}O$ and $\delta^{2}H$ values of rainfall collected from January 16 to December 31 defined a regression line of the equation $\delta^{2}H = 8.2(\pm0.1)\cdot\delta^{18}O + 12.3(\pm1.2)‰$ ($R^2 = 0.99$, $p < 0.0001$, $n = 82$). In 2005, $\delta^{18}O$ and $\delta^{2}H$ values of rainfall collected from January 1 to December 26 defined a regression line of the equation $\delta^{2}H = 8.1(\pm0.1)\cdot\delta^{18}O + 11.9(\pm1.2)‰$ ($R^2 = 0.99, p < 0.0001, n = 58$).

4.3.2 River water and groundwater

$\delta^{18}O$ and $\delta^{2}H$ values of river water collected at monthly sampling sites from October 2003 to April 2006 are given in Appendix 3. A statistical summary of the values for river water samples is presented in Table 5, including arithmetic mean $\delta^{18}O$ and $\delta^{2}H$ values for each monthly sampling site. $\delta^{18}O$ and $\delta^{2}H$ values of river water for each site are illustrated graphically in Figure 20 with the LMWL defined by $\delta^{18}O$ and $\delta^{2}H$ values of rainfall at

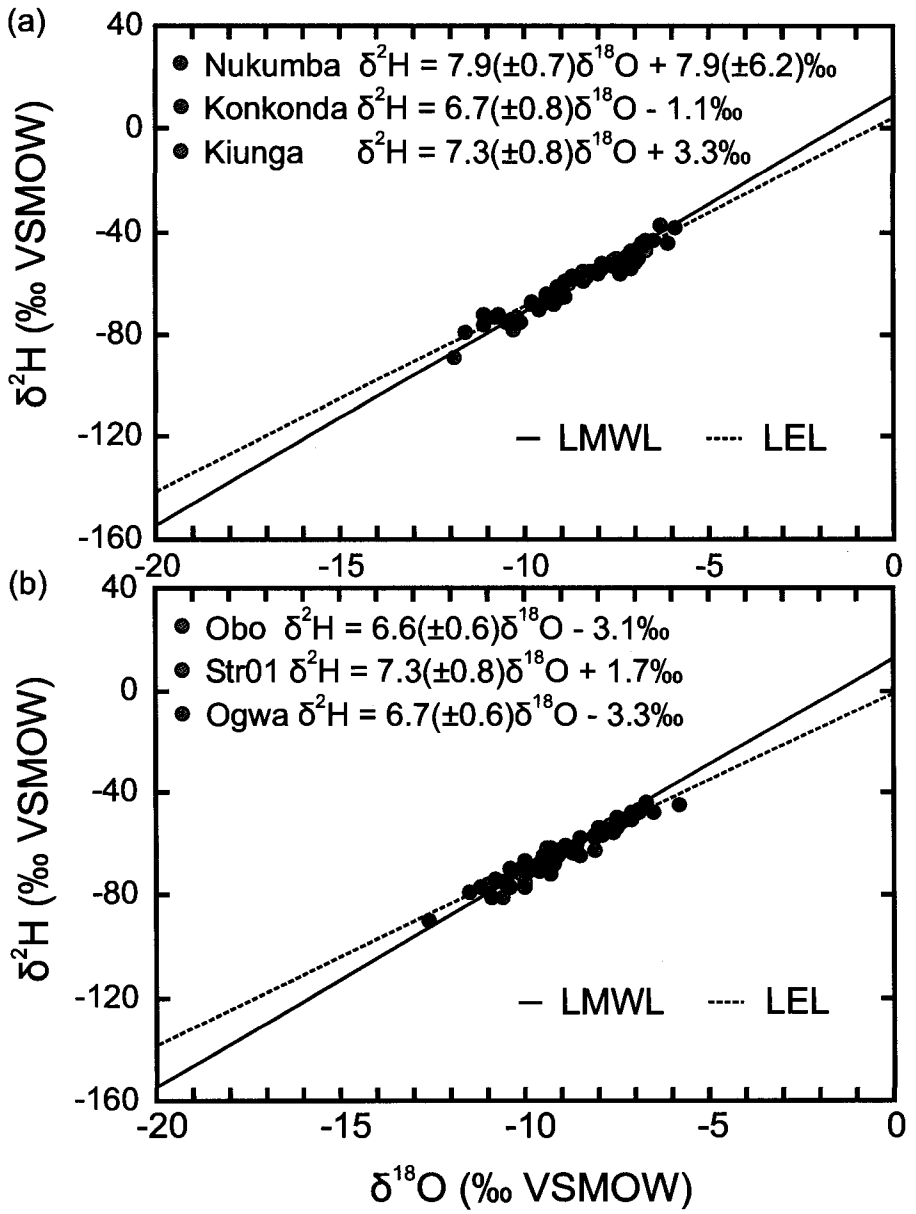


Figure 20. $\delta^{18}O$ and δ^2H values of river water samples collected from (a) the Upper Fly River at Kiunga, the Ok Tedi at Konkonda, and the Middle Fly River at Nukumba and (b) the Middle Fly River at Obo, the Strickland River at Str01, and the Fly River at Ogwa. The LEL defined by the $\delta^{18}O$ and δ^2H values for each river are provided with 95% confidence intervals in parentheses and the LMWL defined by $\delta^{18}O$ and δ^2H values of rainfall at Tabubil is shown for comparison.

Tabubil. Also included in Figure 20 are the equations for each regression line (or local evaporation line, LEL).

Table 5. Summary of $\delta^{18}O$ and $\delta^{2}H$ values of river water collected at monthly sampling sites from October 2003 to April 2006

Location	Mean		Minima			Maxima			
	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰	Date	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰	Date	*n*
Konkonda	−8.2±0.5	−57±4	−11.1	−73	04/04/2006	−5.9	−38	04/08/2005	24
Kiunga	−8.3±0.5	−58±5	−11.6	−79	04/04/2006	−6.1	−37	07/11/2003	21
Nukumba	−8.4±0.7	−59±5	−11.9	−89	04/04/2006	−6.7	−43	21/07/2005	23
Obo	−8.2±0.6	−58±5	−10.8	−70	04/04/2006	−5.8	−45	20/09/2005	24
Str01	−9.4±0.6	−67±4	−12.6	−90	04/04/2006	−7.1	−49	27/06/2004	23
Ogwa	−8.8±0.4	−64±4	−11.5	−81	04/04/2006	−5.9	−38	06/10/2003	26

Mean values ± 2 standard errors (i.e. 95% confidence intervals)

$\delta^{18}O$ and $\delta^{2}H$ values of river water at most of the monthly sampling sites defined LEL that were characterized by similar, yet slightly shallower slopes compared to that of the LMWL. The slopes of each LEL were statistically significant at the 0.0001 level and ranged from 6.6 ± 0.6 (Middle Fly River at Obo) to 7.9 ± 0.7 (Middle Fly River at Nukumba). The 95% confidence limits for the slopes of LEL for the Upper Fly River at Kiunga (7.3 ± 0.8), the Middle Fly River at Nukumba (7.9 ± 0.7), and the Strickland River at Str01 (7.3 ± 0.8) overlapped with the 95% confidence limit for the LMWL. The 95% confidence limits for the slopes of the other LEL did not overlap with that of the LMWL. Only $\delta^{18}O$ and $\delta^{2}H$ values of river water for samples collected from the Middle Fly River at Nukumba defined a LEL with a statistically-significant $\delta^{2}H$ intercept at the 0.05 level; the equation for this LEL was $\delta^{2}H = 7.9(\pm0.7)\cdot\delta^{18}O + 7.9(\pm6.2)‰$ ($R^2 = 0.99$, $p < 0.0001$, $n = 23$). The slope and $\delta^{2}H$-intercept for this LEL were thus not statistically different from the slope and $\delta^{2}H$-intercept of the LMWL.

$\delta^{18}O$ and $\delta^{2}H$ values of river water collected from February 23 to March 5, 2007, are appended in Appendix 8. $\delta^{18}O$ values for samples collected from the Middle Fly River at Obo ranged from -7.8‰ to -10.1‰ and $\delta^{2}H$ values ranged from -53‰ to -77‰ (Figure 21a).

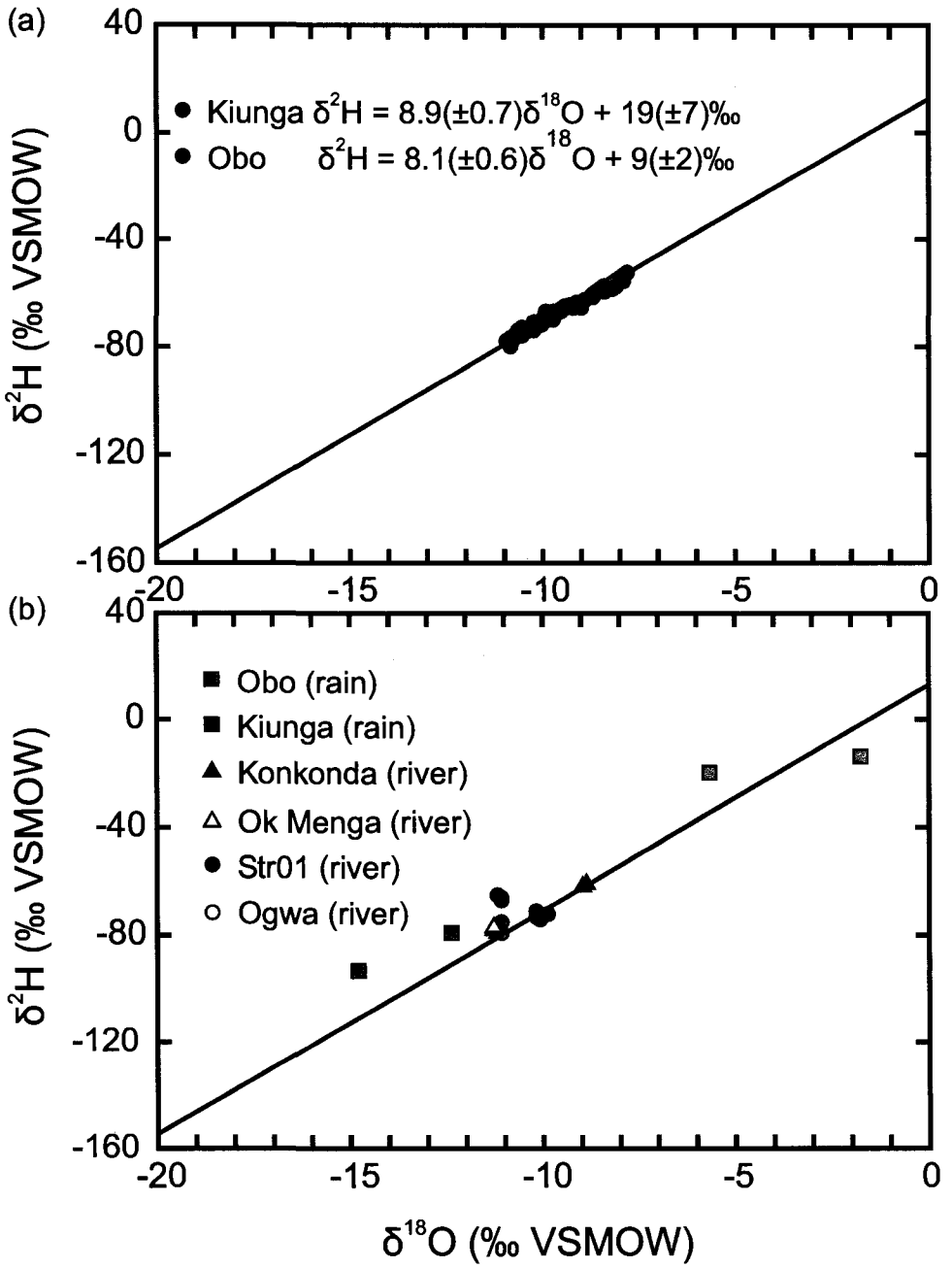


Figure 21. (a) $\delta^{18}O$ and δ^2H values of river water samples collected from February 23 to March 5, 2007, from the Middle Fly River at Obo and the Upper Fly River at Kiunga; (b) $\delta^{18}O$ and δ^2H values of river water and rainfall samples collected from February 23 to March 5, 2007. The LMWL defined by $\delta^{18}O$ and δ^2H values of rainfall at Tabubil is shown for purposes of comparison.

$\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the Middle Fly River at Obo defined a regression line of the equation $\delta^{2}H = 8.1(\pm0.6)\cdot\delta^{18}O + 9(\pm2)‰$ ($R^2 = 0.96$, $p < 0.0001$, $n = 37$). $\delta^{18}O$ values for samples collected from the Upper Fly River at Kiunga ranged from -9.4‰ to -10.6‰ and $\delta^{2}H$ values ranged from -64‰ to -74‰. $\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the Upper Fly River at Kiunga defined a regression line of the equation $\delta^{2}H = 8.9(\pm0.7)\cdot\delta^{18}O + 19(\pm7)‰$ ($R^2 = 0.93$, $p < 0.0001$, $n = 52$). The regression lines defined by $\delta^{18}O$ and $\delta^{2}H$ values for samples collected from the Middle Fly River at Obo and the Upper Fly River at Kiunga from February 23 to March 5, 2007, were similar to the LMWL for the Star Mountains region and were not as shallow as the regression lines defined by the monthly samples.

During the period of sample collection from February 23 to February 26, 2007, river flow for the Middle Fly River at Obo increased by about 5% compared to the initial rate of flow. During this period, $\delta^{18}O$ and $\delta^{2}H$ values of river water decreased by 3‰ and 20‰, respectively (Figure 13). During the period of sample collection from the Upper Fly River at Kiunga, the change in river flow was more substantial compared to the Middle Fly River at Obo, as the rate of river flow decreased from an initial rate of 1400 $m^3 s^{-1}$ to a minimum of 400 $m^3 s^{-1}$ at hour 84 (i.e. 84h) before increasingly abruptly to 1200 $m^3 s^{-1}$ at 120h. From 0h to 84h, $\delta^{18}O$ and $\delta^{2}H$ values of river water increased by approximately 1.0‰ and 10‰, respectively, yet $\delta^{18}O$ and $\delta^{2}H$ values did not respond noticeably to the abrupt increase in river flow (Figure 16).

Chapter 5.

Partitioning Evaporation and Plant Transpiration Water Fluxes

5.1 Methodology

The mass-dependent isotope fractionation that accompanies the phase transitions of water (i.e. evaporation, sublimation, and condensation) causes the predictable apportionment of the heavier, rarer isotopes of water (oxygen-18, ^{18}O; deuterium, ^{2}H) within the principal isotopologues of the water molecule ($^{1}H_2{}^{16}O$, $^{1}H^{2}H^{16}O$, $^{1}H_2{}^{18}O$). Consequently, the naturally-occurring stable isotopes of water ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) in global precipitation exhibit systematic spatial and temporal variations and collectively define a regression line that is commonly referred to as the global meteoric water line (GMWL, Figure 22a) [*Craig*, 1961; *Dansgaard*, 1964; *Rozanski et al.*, 1993]. At a regional scale, mass-dependent isotope fractionation leads to the existence of two linear trends on a conventional $\delta^{18}O$-$\delta^{2}H$ diagram, one trend defined by waters which retain their original isotope composition derived from precipitation and a second trend defined by waters which, to some extent, have undergone heavy-isotope enrichment due to evaporation (i.e. surface waters) (Figure 22b) [*Froehlich et al.*, 2002; *Gibson et al.*, 2005]. The former trend defines a local meteoric water line (LMWL) with a slope and $\delta^{2}H$-intercept value governed by the prevailing meteorological conditions of the moisture source area, rainout and the trajectory of the air mass, and second-order kinetic effects such as those associated with snow formation and evaporation from raindrops [*Clark and Fritz*, 1997; *Araguás-Araguás et al.*, 1998]. The second linear trend, commonly referred to as a local evaporation line (LEL), is defined by $\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the point of outflow from a watershed.

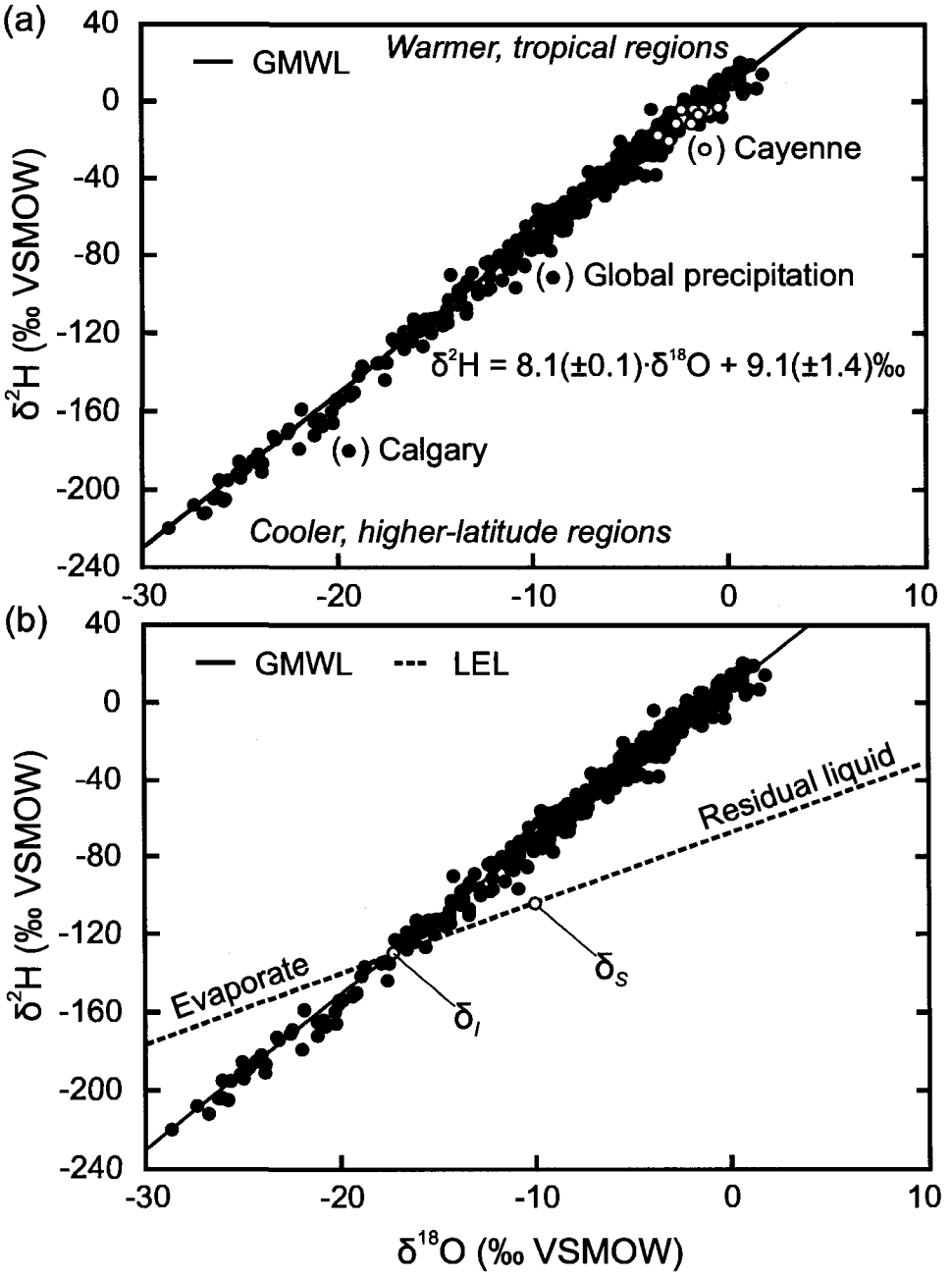


Figure 22. (a) The global meteoric water line (GMWL) illustrates the predictable behaviour of ^{18}O and ^{2}H in precipitation due to mass-dependent isotope fractionation. In this figure, the GMWL is based on monthly $\delta^{18}O$ and $\delta^{2}H$ values of precipitation from the various GNIP stations used for the description of watersheds in North America, Africa, and Australia to be discussed later in the text (Chapter 7). $\delta^{18}O$ and $\delta^{2}H$ values of precipitation for Cayenne (French Guyana) and Calgary (Canada) are shown to illustrate differences in the isotope composition of precipitation in the tropics versus higher latitudes (see section 5.2); (b) a conceptual representation of the relationship between a local evaporation line (LEL) defined by $\delta^{18}O$ and $\delta^{2}H$ values of river water and the GMWL from (a).

Analogous to the isotope composition of precipitation at a specified location, which is determined by the initial isotope composition of water evaporated at the moisture source and the path of moisture transport to the location of eventual condensation [*Jouzel*, 2006], river water at a given location within a watershed is primarily determined by the initial isotope composition of water input and the cumulative influence of evaporation upstream, as mass-dependent isotope fractionation causes an evaporating moisture flux to become preferentially depleted in ^{18}O and ^{2}H and leaves the residual liquid in the watershed enriched in these heavier isotopes [*Gibson and Edwards*, 2002]. Although direct sampling of evaporate is not feasible, the $\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the point of outflow can be interpreted as a proxy for the residual liquid and the variability of these values is circumscribed by the LEL. In watersheds where direct evaporation from soils and water bodies is volumetrically significant relative to annual water input, $\delta^{18}O$ and $\delta^{2}H$ values of river water define a LEL with a shallower slope than the LMWL, such that the offset between $\delta^{18}O$ and $\delta^{2}H$ values of individual samples from the LMWL increases in approximate proportion to the cumulative fraction of water transferred to the atmosphere by evaporation in upstream areas.

According to [*Gibson and Edwards*, 2002], the intersection of the LEL and LMWL provides an amount-weighted estimate of the $\delta^{18}O$ and $\delta^{2}H$ values of water entering a hydrologic system and thus is unaffected by heavy-isotope enrichment due to E_d within the watershed. Inferences regarding the influence of evaporation within a hydrologic system are usually based upon the relationship between the LMWL and LEL, as these linear features are considered more representative of prevailing hydrologic conditions than individual $\delta^{18}O$ and $\delta^{2}H$ values. Fundamentally, studies that purport to separate fractionating and non-fractionating water vapor fluxes also rely upon the assumptions that evaporation is

incomplete (i.e. a residual, ^{18}O-^{2}H-enriched liquid remains), the isotope composition of soil water is relatively unaffected by the process of water uptake by plants [*Moreira et al.*, 1997; *Twining et al.*, 2006], and that a relatively small number of $\delta^{18}O$ and $\delta^{2}H$ values are representative of processes occurring over large areas [*Gibson et al.*, 1993; *Gibson et al.*, 2005; *Fekete et al.*, 2006]. If these assumptions are deemed valid and only direct evaporation from soils and water bodies affects the isotope composition of water during its movement through a watershed, the proportion of fractionating water vapor fluxes to water input can be resolved by examining the isotope separation between $\delta^{18}O$ and $\delta^{2}H$ values of water input (i.e. precipitation) and output (i.e. river outflow) from a particular geographical region [*Gonfiantini*, 1986; *Gibson et al.*, 1993; *Lee and Veizer*, 2003]. Rivers are often the focus of these studies because their watersheds usually define a closed hydrologic system and the isotope composition of river water reflects, to an extent, the influence of evaporative water vapor fluxes in regions that contribute to river flow.

Based on the magnitude of the isotope separation between water input by precipitation (δ_I) and river outflow (δ_S), a variety of isotope mass-balance equations are proposed to quantify the ratio of evaporation to water input under steady-state [*Gonfiantini*, 1986; *Gat and Bowser*, 1991; *Gibson et al.*, 1993] and non-steady-state hydrologic conditions [*Gibson*, 2002]. Modified from [*Gibson*, 2002], the water and stable isotope mass balance of a well-mixed hydrologic system, such as a lake or a watershed, assuming constant density of water, may be written respectively as,

$$\frac{dV}{dt} = I - R - E_v \tag{20}$$

$$V\frac{d\delta_L}{dt}+\delta_L\frac{dV}{dt}=I\delta_I-R\delta_R-E\delta_E \tag{21}$$

where V is the volume of water in the system, t is time, dV is the change in volume over the interval dt, I is the input of water, R is the outflow where $R = R_s + R_G$ (R_s is the surface outflow and R_G is the groundwater outflow), E_v is evaporation, and δ_L, δ_I, δ_R, and δ_E are the isotope compositions of water in the system, water input, outflow, and evaporative flux, respectively. For purposes of this study, precipitation is considered the principal input of water to the system and hence δ_I represents the mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation. Further, the isotope composition of water output is $\delta_R = (\delta_S R_S + \delta_G R_G)/R$ where δ_S and δ_G are identical and considered approximately equal to δ_L to maintain the isotope mass balance. Estimates of δ_R are possible through flow-weighted sampling of water at the river mouth, yet δ_E cannot be measured directly. Based on a linear resistance model described by [*Craig and Gordon*, 1965] and modified by [*Gibson*, 2002], δ_E can be estimated by,

$$\delta_E=\frac{\left(\delta_L-h\delta_A-\varepsilon\right)}{\left(1-h+\varepsilon_K/1000\right)} \tag{22}$$

where h is the ambient humidity normalized to saturation vapor pressure, δ_A is the isotope composition of ambient moisture, and $\varepsilon = \varepsilon^* + \varepsilon_K$ is the total isotope fractionation comprised of the equilibrium component (ε^*), considered a function of temperature, and the kinetic component (ε_K), which is controlled by the turbulent/diffusion mass transfer mechanisms and humidity.

Under constant atmospheric and hydrologic conditions (i.e. hydrologic steady-state, such that $dV/dt = 0$ in equation 20), air-water isotope exchange will proceed and surface waters will enrich (or deplete) to an isotope steady-state reflective of the isotope and hydrologic characteristics of the system [*Gibson*, 2002]. Assuming well-mixed conditions, substitution of equation (22) into equation (21) yields:

$$V\frac{d\delta_L}{dt} + \delta_L\frac{dV}{dt} = I\delta_I - R\delta_L - \frac{E_v}{1-h+\varepsilon_K/1000}\left(\delta_L - h\delta_A - \varepsilon\right) \tag{23}$$

In situations where volumetric changes are negligible and the volume of water in the hydrologic system can be considered constant (i.e. $P = R + ET$ from equation 1 or $dV/dt = 0$ from equation 20), it is possible to describe isotope changes in surface water over time t by assuming $dV/dt = 0$ in equation (23), which yields a steady-state isotope mass balance equation that enables quantification of the proportion of evaporation (E_v) with respect to water input (I). As multi-year precipitation and river flow data were used to define ET and inter-annual changes in water volume were considered to be insignificant, the assumption of hydrologic steady-state was considered valid and the steady-state isotope mass balance equation proposed by [*Gonfiantini*, 1986] was utilized to estimate the rate of E_v relative to the annual water input I,

$$\frac{E_v}{I} = \frac{\left(\delta_S - \delta_I\right)\left(1-h+\Delta\varepsilon\right)}{\left(\delta_S+1\right)\left(\Delta\varepsilon+\varepsilon/\alpha\right)+h\left(\delta_A-\delta_S\right)} \tag{24}$$

where h is the ambient humidity normalized to saturation vapor pressure, α is the equilibrium fractionation factor for oxygen ($\ln\alpha = 1137T^{-2} - 0.4156T^{-1} - 0.00207$) and hydrogen ($\ln\alpha = 24844T^{-2} - 76.248T^{-1} + 0.05261$) isotopes during evaporation [*Friedman and O'Neil*, 1977], $\Delta\varepsilon$ is the kinetic enrichment factor for oxygen [14.2(1-h)] and hydrogen isotopes [12.5(1-h)], $\varepsilon = \alpha - 1$, and, δ_I, δ_A and δ_S are the mean $\delta^{18}O$ (or δ^2H) values of precipitation, ambient moisture, and outflow, respectively.

Fundamentally, E_v/I values represent the amount of evaporative water loss from a watershed required to produce the observed isotope separation between initial water input (δ_I) and output (δ_S) at the ambient climatic conditions (i.e. temperature and relative humidity). In this study, precipitation was considered the main source of annual water input and the $\delta^{18}O$ and δ^2H values that define the point of intersection between the LEL and LMWL were interpreted as the mean annual isotope composition of precipitation for a given watershed. This intersection must be only be considered an approximation, as it is implicitly assumed that the individual $\delta^{18}O$ and δ^2H values that define a LMWL are spatially representative of incident precipitation within a watershed and that the period of data collection was temporally representative of the prevailing hydrologic conditions. Moreover, the use of a LMWL in order to approximate water input to the soil zone also assumed that incident precipitation and throughfall are indistinguishable in terms of isotope composition. In order to account for these uncertainties, a range of $\delta^{18}O$ and δ^2H values that are defined by the intersections of the 95% confidence intervals of the LEL with the LMWL were utilized in order to approximate the potential uncertainty associated with spatial and temporal variability within a watershed and the potential influence of canopy evaporation on water input to the soil zone. Consequently, it is assumed that most of the variability associated with these processes would lie within the 95% confidence interval of δ_I, which enables

information on the proportion of variance described by the LEL for each watershed to be incorporated. For example, a LEL with a smaller 95% confidence interval will define a narrower range of $\delta^{18}O$ and $\delta^{2}H$ values compared to a LEL that is less constrained; this offers the opportunity for refinement as additional data become available.

δ_S was approximated as the flow-weighted mean $\delta^{18}O$ (or $\delta^{2}H$) value of river water at the point of outflow from the watershed (i.e. the river mouth). The 95% confidence interval for a given δ_S value were used to approximate the error associated with the isotope composition of outflow. The 95% confidence intervals for δ_I and δ_S are both used to approximate the error associated with the E_v/I value from equation (24). Mean annual values for temperature and humidity from [*New et al.*, 2000] were substituted into equation (24) and were used to calculate the isotope fractionation factors for this equation. In order to approximate the isotope composition of atmospheric moisture, isotope equilibrium between atmospheric moisture and mean annual precipitation is assumed such that $\delta_A = \delta_I - \varepsilon^*$ [*Gat and Matsui*, 1991; *Gammons et al.*, 2006].

5.2 Isotope constraints on inter-hemispheric moisture transport and sources of rainfall in the headwaters of the Fly River

Based on monthly mean $\delta^{2}H$ and $\delta^{18}O$ values of precipitation available from the Global Network for Isotopes in Precipitation (GNIP) network [*IAEA/WMO*, 2004], the equation for the global meteoric water line (GMWL) is $\delta^{2}H = 8.1(\pm0.1)\cdot\delta^{18}O + 9.1(\pm1.4)$ ‰ ($R^2 = 0.99$, $p < 0.0001$, $n = 299$). $\delta^{2}H$ and $\delta^{18}O$ values of precipitation from cooler, higher-latitude regions often plot near the bottom-left of the GMWL, whereas $\delta^{2}H$ and $\delta^{18}O$ values of precipitation from warmer, low-latitude regions usually plot near the top-right of the GMWL (Figure 22a). As a substantial proportion of global atmospheric moisture is derived from evaporation from

tropical oceans, precipitation that occurs at low-latitudes is often relatively enriched in ^{18}O and ^{2}H and resembles the isotope composition of ocean water (i.e. VSMOW, 0‰). Moisture transported pole-ward by atmospheric circulation patterns (i.e. Hadley cells) is subjected to repeated condensation events related to cooler temperatures. As ^{18}O and ^{2}H have a higher affinity for the denser, liquid phase of water (i.e. condensate) compared to the gaseous phase of atmospheric vapor, these repeated condensation events cause the progressive depletion of residual atmospheric moisture reservoir in ^{18}O and ^{2}H. This temperature-dependent process of heavy-isotope depletion leads to progressively lighter $\delta^{2}H$ and $\delta^{18}O$ values of precipitation at higher latitudes [*Clark and Fritz*, 1997]. As rain-out is related to any process that causes condensation to occur (i.e. a decrease in air temperature), a similar pattern of progressively lighter $\delta^{2}H$ and $\delta^{18}O$ values of precipitation is usually observed with increased distance from coastal regions towards the interior of continents (i.e. the 'continental effect') and in regions where a change in elevation causes orographic precipitation to occur.

In detail, the GMWL consists of a series or imbricate stack of local meteoric water lines (LMWLs), the slopes and $\delta^{2}H$-intercepts of which are determined by intra-annual variation in the $\delta^{2}H$ and $\delta^{18}O$ values of precipitation within a particular region. At higher latitudes, such as those of North America, Europe, and northern Asia, $\delta^{2}H$ and $\delta^{18}O$ values of precipitation vary according to changes in the source of moisture but also seasonal changes in air temperature and the form of precipitation (i.e. whether precipitation occurs as rain or snow) [*Clark and Fritz*, 1997]. Consequently, $\delta^{2}H$ and $\delta^{18}O$ values of precipitation are usually lighter during cooler months of the year, plotting near the bottom-left of a LMWL, and heavier during the warmer months, plotting near the top-right of LMWL. In terms of the GMWL, this temperature-dependent isotope separation is analogous to the differences observed between $\delta^{2}H$ and $\delta^{18}O$ values of precipitation from different latitudes. In equatorial

regions, where temperature is generally consistent year-round and precipitation usually occurs only as rain, δ^2H and $\delta^{18}O$ values of precipitation often vary mainly according to fluctuations in the source of atmospheric moisture, the pathway of moisture transport from source to the point of condensation, and the amount of incident rainfall (i.e. the 'amount' effect) [*Araguás–Araguás et al.*, 1998].

$\delta^{18}O$ and δ^2H values of rainfall collected at Tabubil from October 2003 to February 2006 defined a LMWL of the equation $\delta^2H = 8.2(\pm0.1)\cdot\delta^{18}O + 11.8(\pm1.2)$ ‰ ($R^2 = 0.99$, $p < 0.0001$, $n = 163$) (Figure 23). In 2004 and 2005, $\delta^{18}O$ and δ^2H values of rainfall collected during the Austral winter were similar to the isotope composition of VSMOW (i.e. $\delta^{18}O$ and δ^2H plotted near top-right of Figure 23). These heavier $\delta^{18}O$ and δ^2H values reflect the relative proximity of New Guinea to the moisture source during the Austral winter, as atmospheric moisture during this period is transported by trade-winds from the western Pacific Ocean over the lowland regions of southern New Guinea before reaching Tabubil in the Star Mountains. $\delta^{18}O$ and δ^2H values of rainfall collected at Tabubil during this period of moisture transport via trade winds defined a LMWL of the equation $\delta^2H = 7.9(\pm0.2)\cdot\delta^{18}O + 8.0(\pm3.1)$ ‰ ($R^2 = 0.99$, $p < 0.0001$, $n = 58$).

In contrast to samples collected during the Austral winter, rainfall collected during the Austral summer was relatively depleted in ^{18}O and ^{2}H by comparison and $\delta^{18}O$ and δ^2H values plotted further from VSMOW near the bottom-left of Figure 23. These lighter values reflect the higher contribution of moisture from the northern hemisphere related to the Indonesian-Australian northwest monsoon. Atmospheric moisture transported from the northern hemisphere encounters the Central Cordillera on the northern side of New Guinea and subsequent condensation of moisture as orographic rainfall causes the depletion of atmospheric moisture in ^{18}O and ^{2}H (i.e. Rayleigh distillation). Consequently, atmospheric

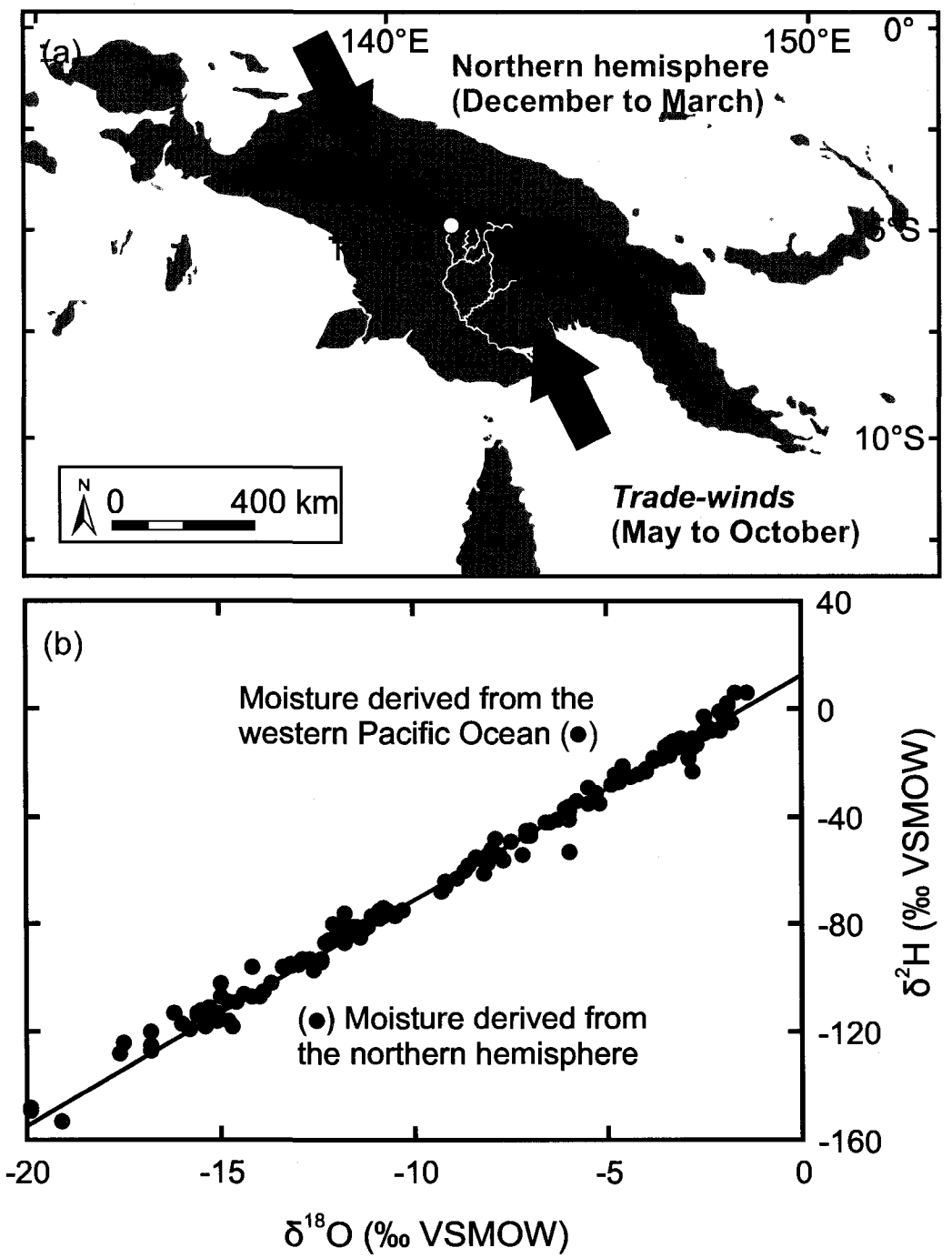


Figure 23. (a) Map of New Guinea showing the direction of moisture transport during the Austral summer (December to March), when moisture is transported from the northern hemisphere, and the Austral winter (May to October), when moisture is transported to New Guinea by trade-winds from the western Pacific Ocean; (b) $\delta^{18}O$ and $\delta^{2}H$ values of rainfall samples collected at Tabubil during the study period. $\delta^{18}O$ and $\delta^{2}H$ values of rainfall collected during the period of trade-wind activity (*red circles*) are generally heavier than $\delta^{18}O$ and $\delta^{2}H$ values of rainfall collected during the period of moisture transport from the northern hemisphere (*blue circles*) (see section 5.2).

moisture reaching the leeward side of the Central Range during the Austral summer is located near the distal portion of the 'rain-out' trajectory and $\delta^{18}O$ and $\delta^{2}H$ values of rainfall are lighter during this period compared to rainfall collected during the Austral winter (Figure 18 and Figure 23). $\delta^{18}O$ and $\delta^{2}H$ values of rainfall collected at Tabubil during this period of moisture transport from the northern hemisphere defined a LMWL of the equation $\delta^{2}H = 8.4(\pm0.3)\cdot\delta^{18}O + 13.7(\pm2.2)$ ‰ ($R^2 = 0.99, p < 0.0001, n = 80$).

$\delta^{18}O$ and $\delta^{2}H$ values of precipitation at several stations from the Global Network for Isotopes in Precipitation (GNIP, *IAEA/WMO*, 2004] in New Guinea were available for comparison with data collected from the Star Mountains, although both stations are located at lower elevations near the coast. Madang is located along the eastern coast of New Guinea in PNG and Jayapura is located along the northern coast of the island in the Indonesian province of Papua (Figure 7b). $\delta^{18}O$ and $\delta^{2}H$ values of precipitation at Madang and Jayapura are graphically illustrated in Figure 24 and the equations of the LMWL are summarized in Table 6. The slope and intercept of the LMWL for the Star Mountains region was more

Table 6. Summary of mean $\delta^{18}O$ and $\delta^{2}H$ values of precipitation and local meteoric water lines (LMWLs) for sites relevant to the Star Mountains region, western Papua New Guinea

Location	Lat.	Lon.	Mean $\delta^{18}O$, ‰	Mean $\delta^{2}H$, ‰	LMWL or GMWL, ‰	*n*
Madang	5°13′S	145°48′E	−7.2 ± 0.5	−46 ± 4	$\delta^{2}H = 7.6(\pm0.3)\cdot\delta^{18}O + 8.2(\pm2.2)$	102
Jayapura	2°32′S	140°43′E	−5.1 ± 0.3	−34 ± 2	$\delta^{2}H = 6.6(\pm0.2)\cdot\delta^{18}O - 0.0(\pm1.3)$	274
Tabubil	5°16′S	141°13′E	−9.2 ± 0.8	−63 ± 6	$\delta^{2}H = 8.2(\pm0.1)\cdot\delta^{18}O + 11.8(\pm1.2)$	161
Global	-	-	−7.8 ± 0.2	−52 ± 2	$\delta^{2}H = 8.0(\pm0.0)\cdot\delta^{18}O + 9.1(\pm0.3)$	3257

Mean values ± 2 standard errors (i.e. 95% confidence intervals)

similar to the GMWL than the LMWL for Jayapura and Madang, although each LMWL compared reasonably well given the differences in elevation and location within New Guinea.

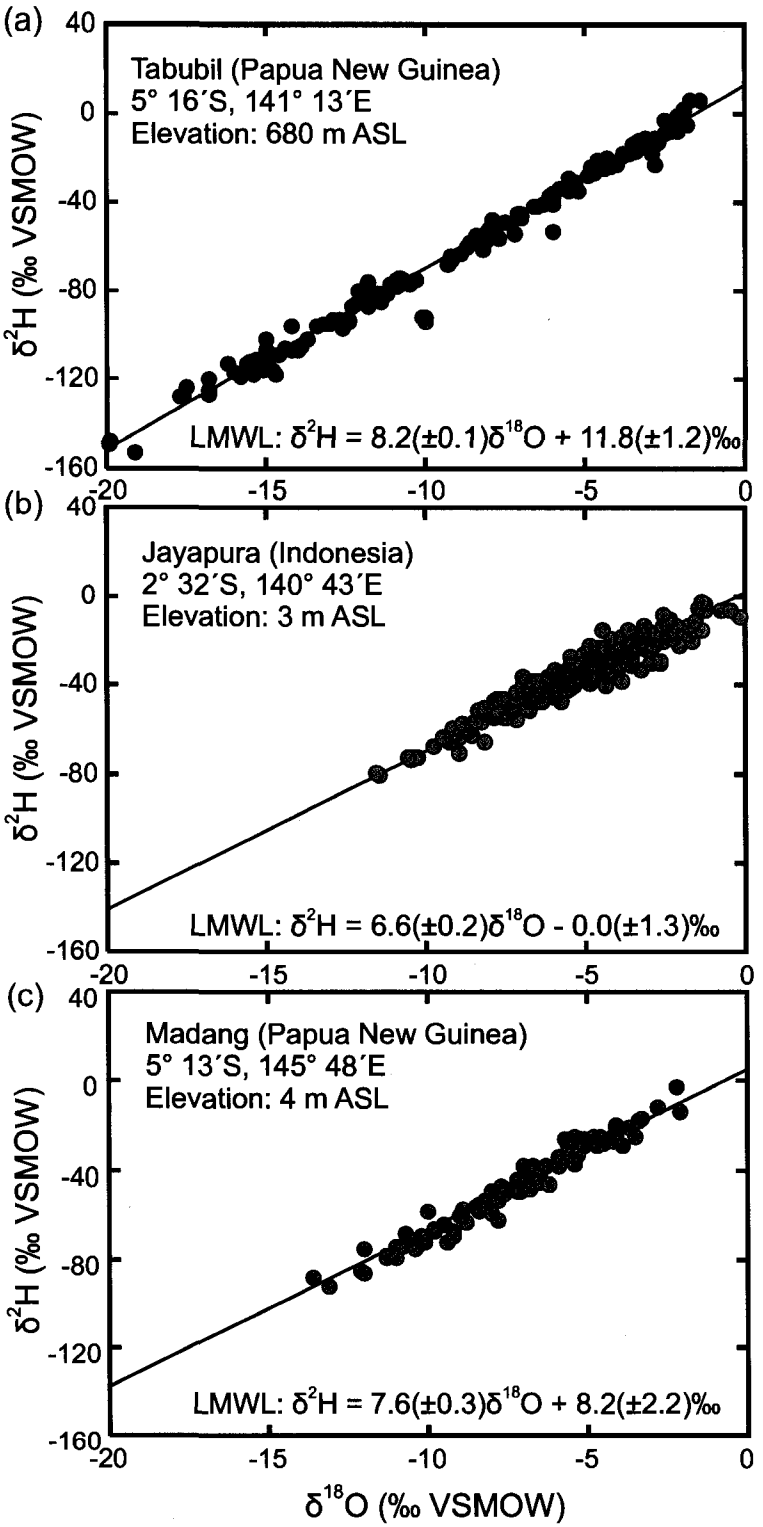


Figure 24. $\delta^{18}O$ and $\delta^{2}H$ values of rainfall and the corresponding local meteoric water line (LMWL) for (a) Tabubil, located in the Star Mountains region of central New Guinea; (b) Jayapura, located along the northern coast of New Guinea; (c) Madang, located on the eastern coast of New Guinea. The 95% confidence intervals for the slope and $\delta^{2}H$ intercept are given in parentheses and elevation is given in meters above sea level (m ASL).

5.3 Resolving the influence of evaporation on the isotope composition of outflow via river water

$\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the tributaries of the Fly River usually defined a LEL with a similar, albeit slightly shallower, slope than the LMWL defined by $\delta^{18}O$ and $\delta^{2}H$ values of rainfall at Tabubil (Figure 20). A similar situation is observed in other regions principally covered by tropical rainforest in South America [*Negrel and Lachassagne*, 2000; *Lachniet and Patterson*, 2002; *Martinelli et al.*, 2004; *Goller et al.*, 2005], and Insular Southeast Asia [*Stephens and Rose*, 2005] and Africa [*Brunet, personal communication*].

In part, the similarity of the LEL for the Upper Fly River and Ok Tedi with the LMWL for the Star Mountains reflects the sensitivity of river flow downstream to water inputs by rainfall and short residence time of waters in the areas that contributes to river flow. This sensitivity is probably due to the intensity of rainfall in the headwaters of the Upper Fly River and Ok Tedi, which causes large volumes of water to infiltrate into the soil zone over a short period of time. In turn, river flow in the Middle Fly River region is influenced strongly by river flow from the Upper Fly River and Ok Tedi.

The similarity of LEL for tributaries of the Fly River and the LMWL for the Star Mountains suggests, at least qualitatively, that the volume of water 'lost' via E_d may be much less than the non-fractionating water vapor fluxes (i.e. $T + I_n$). Nonetheless, if the volume of water transferred to the atmosphere via evaporation were volumetrically significant with respect to water input, the isotope composition of soil water, and therefore river water, may be altered to the extent that it may be distinguishable from the isotope composition of initial water input. More quantitatively, by incorporating information on temperature, humidity, and related isotope fractionation factors for oxygen and hydrogen isotopes, an isotope mass

balance equation can be used to estimate the amount of evaporation required to generate the observed isotope separation between initial rainfall (δ_I) and eventual outflow via river water (δ_S). Input parameters substituted into equation (24) and calculated E_v/I values for each of the tributaries are summarized in Table 7.

Table 7. Input parameters for the steady-state isotope mass balance equation and calculated E_v/I values

Location	Input parameters							Output
	T_a K	h %	δ_I ‰	δ_S ‰	ε^* ‰	$\Delta\varepsilon_k$ ‰	δ_A ‰	E_v/I %
Konkonda	298.5	83	−8.6 ± 1.0	−17.9 ± 1.0	9.3	2.4	−7.6 ± 0.5	5.8 ± 1
Kiunga	298.9	83	−9.4 ± 1.0	−18.7 ± 1.0	9.3	2.4	−8.4 ± 0.7	5.8 ± 1
Nukumba	298.7	83	–	–	9.3	2.4	−8.4 ± 0.6	–
Obo	299.0	77	−9.3 ± 0.8	−18.6 ± 0.8	9.3	3.3	−8.3 ± 0.6	5.2 ± 1
Strickland	297.4	81	−11.2 ± 1.2	−20.6 ± 1.2	9.4	2.7	−9.4 ± 0.6	12.2 ± 2
Ogwa	298.0	80	−10.1 ± 0.9	−19.5 ± 0.9	9.4	2.6	−9.0 ± 0.5	6.4 ± 1

Input parameters shown are for oxygen isotopes (see text for abbreviations)
Mean values ± 2 standard errors (i.e. 95% confidence intervals)
E_v – evaporation, I – annual water input

δ_S values for the Ok Tedi at Konkonda and the Upper Fly River at Kiunga were approximately 1‰ heavier than δ_I (Table 7), which implied, to some extent, that waters have been enriched in ^{18}O and ^{2}H due to isotope fractionation during evaporation. The isotope separation between δ_I and δ_S values for the Ok Tedi and Upper Fly River watersheds corresponded to E_v/I values of 5.8% for both watersheds, a correspondence which seems plausible given the similarity in climate and the resemblance of rainfall and runoff patterns in these watersheds. The E_v/I value for the Fly River at Obo was similar (5.2%), suggesting either that the influence of evaporation was not appreciably higher downstream or alternatively, that the LMWL for the Star Mountains may be less representative of the isotope composition of rainfall occurring at lower elevations. Similar qualifications regarding the applicability of the LMWL are also relevant to the Strickland River watershed, as a substantial proportion of water input to this watershed is expected to be derived from regions

which may not be characterized by the LMWL for the Star Mountains. It is plausible that differences in the isotope composition of rainfall exist between rainfall occurring at different elevations and locations in the study area, although it is probable that $\delta^{18}O$ and $\delta^{2}H$ values for this rainfall would plot within the 95% confidence interval for the LMWL for the Star Mountains due to similar patterns of regional moisture transport.

Although uncertainty regarding the applicability of the LMWL to the Strickland River watershed is recognized, it may be significant to note that the sampling station at the mouth of the Strickland River is located below point of inflow from Lake Murray, the largest lake in PNG (at least 430 km^2 depending on the season). Evaporation in the expansive, lowland region of inter-connected lakes and swamps surrounding Lake Murray may be substantial and the influence of inflow from Lake Murray may affect the E_v/I value calculated from samples of the Strickland River. The implication is that the higher E_v/I value reflects input of evaporatively-enriched water from Lake Murray, not higher evaporation in the Strickland River watershed as a whole. The E_v/I value for the Fly River at Ogwa, which represents total outflow from the hydrologic system, was 6.4%, slightly higher than the value for the Fly River at Obo and approximately half that of the Strickland River watershed. As detailed flow data were not available for the Strickland River, the contribution by each river cannot be resolved, yet historical flow data suggests the Strickland River contributes approximately 60% of total flow at Ogwa and hence an alternative explanation may be the similarity between E_v/I estimates at Obo and Ogwa reflects the incomplete mixing of river water below the confluence of the Fly River and Strickland River.

With respect to E_v/I values, it is important to consider that although the slopes of LEL for each tributary were statistically significant at the 0.0001 level, only $\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the Middle Fly River at Nukumba, located below the confluence

of the Ok Tedi and Upper Fly River, defined a LEL with a statistically-significant intercept value at the 0.05 level (Figure 20a). As the LEL for the Middle Fly River at Nukumba was not statistically different from the LMWL, δ_I and δ_S could be interpreted as equivalent on a statistical basis, implying that non-fractionating water vapor fluxes were the principal component of the annual terrestrial water vapor flux and fluxes which fractionate the stable isotopes of water, such as direct evaporation from soils and water bodies, were negligible. Considering the isotope separation between δ_I and δ_S values for the Ok Tedi and Upper Fly River were similar to the Middle Fly River at Nukumba, this implication also applies to these watersheds. Nonetheless, relatively low E_v/I values (i.e. 5 – 10%) do not necessarily exclude the possibility that the intensity of evaporation cannot be significantly higher than this annual estimate in certain regions or at different times of the year. For example, in regions where drainage conditions are poor, such as the lowland regions of the Fly River watershed, it is probable that only a proportion of the gross watershed area actually contributes to river flow and the accurate definition of this area is problematic. In a spatial context, this means that the intensity of evaporation could be much higher within the watershed but that these fluxes were undetected due to the limited hydrologic connectivity between internal drainage areas, and that temporally, seasonal variations in the intensity of evaporation are subsumed into an annual estimate under assumed conditions of hydrologic and isotope steady-state.

5.4 Annual water balances of the Ok Tedi and Upper Fly River watersheds

Recall from equation (1) that P and R are considered to be the fundamental framework of the annual water balance for a watershed and ET can be estimated by the difference. As (P – R) represents an approximation of the total flux of water vapor from a closed hydrologic system to the atmosphere, we propose to apportion (P – R) for the Ok Tedi and Upper Fly River watersheds by incorporating literature estimates of net water input (i.e. $P - I_n$) and by

utilizing E_v/I values yielded by equation (24) in order to partition the E_d and T components of the annual water balance. Due to uncertainty regarding the storage component of the annual water balance and the inadequate distribution of rainfall stations at lower elevations, we did not attempt to close the annual water balance of either the Strickland River watershed or the Middle Fly River watershed.

5.4.1 Annual terrestrial water vapor flux, ET

River flows for the Ok Tedi and Upper Fly River were closely related to the intensity of rainfall in regions upstream, exemplified in Figure 10 by daily rainfall accumulation at Tabubil (680 m ASL), Lukwi (302 m ASL), and Konkonda (4 m ASL) and river flow at Konkonda and Kiunga. Due to their proximity, rainfall patterns for stations surrounding Tabubil were often similar and peaks in daily rainfall accumulation often occurred concurrently at stations such as Falomian, Tabubil, and Ok Mani. For this reason, sustained periods of high rainfall in this region generally corresponded to periods of higher river flow downstream and vice versa, as the similarity of rainfall patterns at different stations indicated that a relatively large area was affected by a particular rainfall event.

The predictable response of river flow for the Ok Tedi and Upper Fly River to rainfall events upstream suggested that rainfall patterns at the different rainfall stations closely approximated water input to the proportion of gross watershed area that contribute most significantly to river flow. Moreover, the rapid response of river flow to rainfall events offers some perspective on the sensitivity of these rivers to changes in water input by rainfall and implies, to an extent, that changes in water storage are probably close to negligible during periods of consistently high daily rainfall [*Bruno et al.*, 2006]. Based on soil tension measurements in the Amazon, [*De Moraes et al.*, 2006] assumed that changes in water storage were negligible for the first meter of the soil zone and in further consideration of

estimates by [*Bruno et al.*, 2006] that approximately 56% of water uptake by plants occurred at depths of 0 – 2 meters, it was assumed that changes in the proportion of P stored in the soil zone were negligible ($\Delta S = 0$) and that ($P - R$) represents an approximation of (ET).

Although some uncertainty may be related to the area of contributing drainage and hence the rate of river discharge per unit area (i.e. runoff), the amount of rainfall at individual stations appears to exceed runoff, implying that a proportion of annual rainfall is either stored in the watersheds or has been transferred to the atmosphere via ($E_d + I_n + T$). In smaller tributaries of the Ok Tedi, such as the Ok Maa (100 km^2), this was particularly evident by comparison of runoff at the river mouth with daily rainfall at Kumkit, located in the headwaters, and Lukwi, located near the river mouth (Figure 10c). In 2005, annual rainfall at Kumkit and Lukwi was 10,100 mm and 10,501 mm, respectively, yet annual runoff at the river mouth was 7080 mm, implying that 3000 – 3400 mm of annual water input was not unaccounted for by outflow. Consider further that 1 mm yr^{-1} corresponds to 10^3 g H_2O m^{-2} yr^{-1} and the magnitude of this water flux becomes more apparent, particularly at a regional scale.

Using a kriging interpolation technique [*Buytaert et al.*, 2006] and monthly rainfall at each of the twelve rainfall stations, monthly estimates of P were calculated for the Ok Tedi and Upper Fly River watersheds. Despite differences in the magnitudes of P and R, ($P - R$) for both watersheds in 2004 were within ~10 – 20% of ($P - R$) for 2005 and annual estimates for 2004 and 2005 were essentially equivalent (Table 8).

Table 8. Annual water input by rainfall and outflow via river runoff for the Ok Tedi and Upper Fly River watersheds, 2004 and 2005

	Values in mm or 10^3 g H_2O m^{-2} yr^{-1}		
	P	R	$P - R$
Ok Tedi watershed			
2004	5981 ± 804	3302 ± 884	2679 ± 1049
2005	8136 ± 720	5869 ± 885	2267 ± 905
Upper Fly River watershed			
2004	5508 ± 768	2836 ± 520	2672 ± 837
2005	7584 ± 624	5226 ± 832	2358 ± 846

Mean values ± 2 standard errors (i.e. 95% confidence intervals)

Hence, changes in water input appear to affect the proportions of the water balance, yet P and R co-vary such that $(P - R)$ remains relatively constant (Figure 25). Based on the monthly sampling frequency and the suspension of sample collection for a period of six months in 2004, it was not considered appropriate to apply identical E_v/I estimates to both years; instead, an annual estimate of $(P - R)$ based on the entire period of sample collection was proposed (Table 9).

Table 9. Components of the annual water balance for the Ok Tedi and Upper Fly River watersheds, 2004 – 2005

	Values in mm or 10^3 g H_2O m^{-2} yr^{-1}				
Watershed	P	R	I_w	E	T
Ok Tedi	7056 ± 696	4583 ± 816	1129 ± 226	344 ± 59	1000 ± 1098
Upper Fly	6540 ± 648	4032 ± 696	961 ± 209	324 ± 56	1223 ± 975

Mean values ± 2 standard errors (i.e. 95% confidence intervals)

Estimates of $(P - R)$ indicate that 35 – 40% of P was transferred to the atmosphere as water vapor via ET, yet the potential uncertainty related to fluctuations in the extent of contributing drainage area due to variable patterns of rainfall and limited hydrologic connectivity within the watersheds cannot be discounted. An alternative explanation for the magnitude of $(P - R)$ may be that the actual area of contributing drainage is smaller than estimates defined in this study and that the magnitude of $(P - R)$ is proportionally smaller in relation to this reduction in area. The contributing drainage area for each watershed was

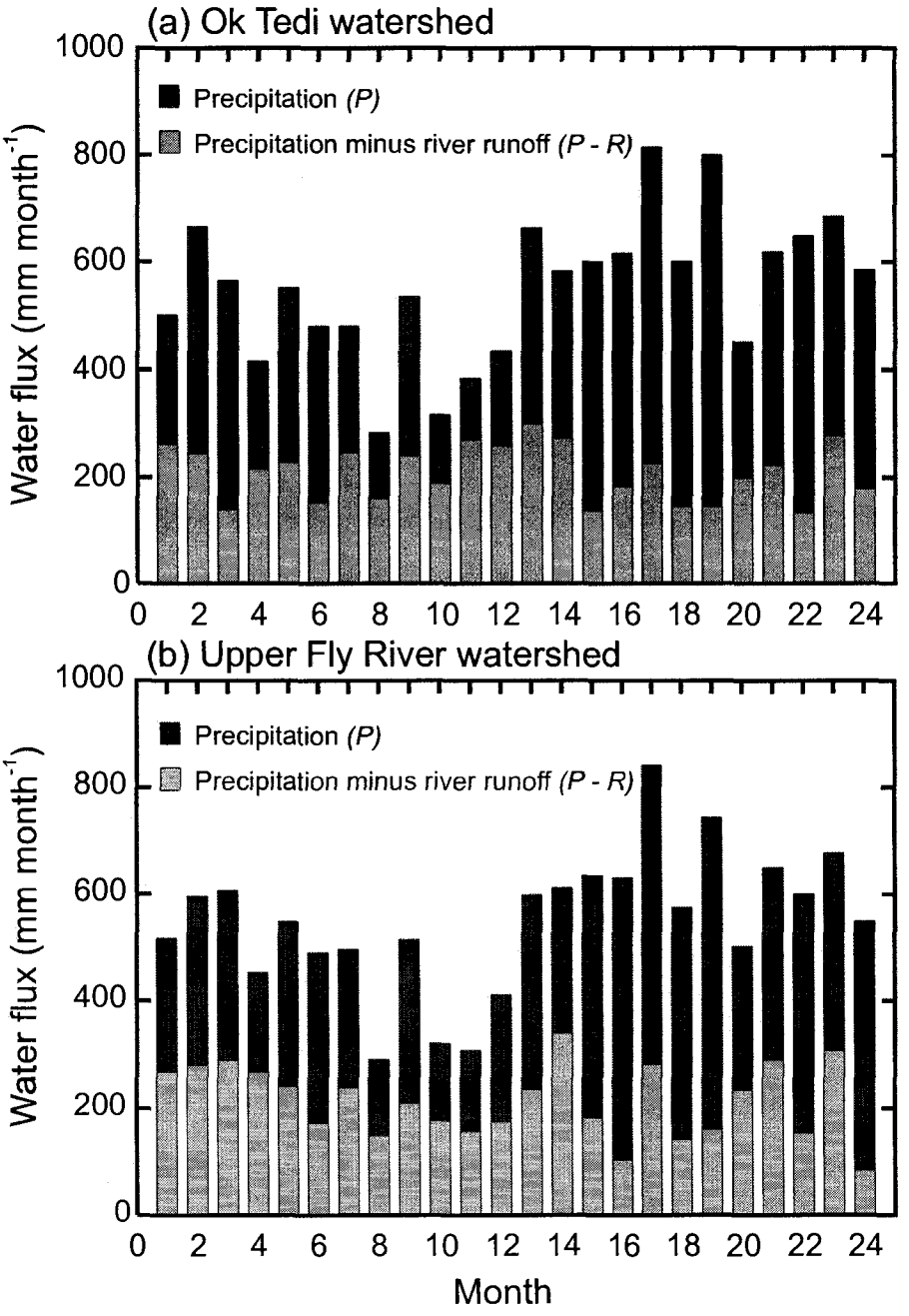


Figure 25. Mean monthly rainfall (P) estimates for the Ok Tedi and Upper Fly River watersheds and river runoff (R) for the Ok Tedi at Konkonda and the Upper Fly River at Kiunga, 2004 - 2005. (P - R) is a proxy for ET, the proportion of water input by P that is transferred to the atmosphere via evaporation from soils and water bodies and plant transpiration; changes in water input appear to affect the proportions of the water balance, yet P and R co-vary such that (P - R) remains relatively constant.

defined by topography and the distribution of rainfall stations, although subdued topography complicates the definition of the proportion of gross watershed area that contributes to river flow. Hence, without additional information, the contributing area of drainage for each watershed was considered to be close to equivalent at 5,200 km^2 and this area was used to standardize mean monthly river flow volume for the Ok Tedi and Upper Fly River. As no data are available regarding hydrologic connectivity in the region, further discussion of the error associated with the extent of contributing drainage area would be entirely speculative and beyond the scope of this study, yet it is critical to recognize that the actual contributing drainage areas are probably not identical.

5.4.2 Rainfall interception, I_n

Rainfall interception (I_n), defined as the proportion of gross rainfall that is caught or intercepted by plant surfaces and subsequently evaporated or sublimated before it can infiltrate into soil waters, may account for a substantial proportion of annual rainfall in densely-vegetated regions and varies depending on the intensity, duration, and form of precipitation, the growth stage and structure of vegetation, and ambient environmental conditions, such as temperature and humidity [*Fleischbein et al.*, 2006; *Holwerda et al.*, 2006]. Although I_n represents a type of evaporation, often referred to as canopy evaporation, [*Goller et al.*, 2005] report that $\delta^{18}O$ and $\delta^{2}H$ values of throughfall in a tropical rainforest in Ecuador were essentially equivalent to the isotope composition of rainfall before interaction with the canopy, which suggests that canopy evaporation does not significantly affect the isotope composition of water which enters the soil zone. Similar results are reported for tropical rainforests in Costa Rica [*Rhodes et al.*, 2006] and Southeast Asia [*Liu et al.*, 2007]. In each of these studies, the regression lines defined by $\delta^{18}O$ and $\delta^{2}H$ values of throughfall were not statistically different from the LMWL, suggesting that although some water loss via

canopy evaporation may occur, the amount of water is likely small compared to P and the proportion of annual rainfall evaporated from plant surfaces cannot be considered a water input and thus I_n must be accounted for in order to estimate E_d and T.

Measurements of I_n for rainforests of New Guinea were not available. As climate and canopy structure are broadly similar amongst rainforests [*Leigh*, 1999], estimates of I_n from other regions were incorporated as an approximation of this process in tropical rainforests of New Guinea, acknowledging that considerable uncertainty is associated with this aspect of the annual water balance. According to [*Kumagai et al.*, 2004], studying the annual water balance of a lowland tropical rainforest of northern Borneo, I_n accounted for ~15% (432 mm) of annual gross rainfall (2884 mm). By comparison, [*Asdak et al.*, 1998] reported ~11% (251 mm) of P (2199 mm) in a pristine, closed-canopy rainforest of central Borneo, with error estimates of ±10%. Given the apparent similarities of I_n for lowland rainforests of Borneo, a value of 11±4% to be justified, as the reported error from [*Asdak et al.*, 1998] was doubled in order to approximate a 95% confidence interval and encompass I_n from [*Kumagai et al.*, 2004]. For the proportion of rainforests which occurs above 1000 m ASL, an annual I_n estimate of 40±11% reported by [*Fleischbein et al.*, 2006] for a montane rainforest in Ecuador was used although this estimate was significantly lower than estimates by [*Holwerda et al.*, 2006] for a tropical montane forest of Puerto Rico; I_n values from the forests of Ecuador were selected because they have mean values derived from four years of throughfall measurements and were presented in the context of annual water balances for several small watersheds in the Andes.

In a rainfed, inter-cropped system of cassava, maize, and rice in West Java (Indonesia), [*van Dijk and Bruijnzeel*, 2001] estimated that I_n accounted for 18% (284 mm) of P (1577 mm) and although vegetation was not identical in New Guinea, this I_n value (±6%) for the

mosaics of small-scale agriculture and natural vegetation (20% and 9% of land-cover in the Ok Tedi and Upper Fly River watersheds, respectively). In order to estimate area-weighted I_n/P, the literature values described above were assigned to each constituent GLC2000 land-cover class in the watersheds. For the Ok Tedi and Upper Fly River watersheds, compound estimates of annual I_n were 1129 ± 226 mm and 961 ± 209 mm, respectively (Table 9).

5.4.3 Direct evaporation from soils and water bodies, E_d, and plant transpiration, T

The E_v/I values from equation (24) enabled the separation of ET from equation (1) into fractionating water vapor fluxes (i.e. direct evaporation from water bodies and soils, E_d) and non-fractionating water vapor fluxes (i.e. canopy evaporation, I_n, plus plant transpiration, T). E_d was then calculated as the product of the E_v/I value from equation (24) and $(P - I_n)$, which represents the net water input to the soil zone. T was considered the residual amount of water required to balance equation (1) and the error assigned to T was the propagated errors of P, R, I_n, and E_d calculated by a sum of squares.

Estimates of E_d for the Ok Tedi and Upper Fly River watersheds were 344 ± 59 mm and 324 ± 56 mm, respectively, calculated as the product of net water input $(P - I_n)$ and the E_v/I values from equation (24). Using the proportions of net water input ascribed to E_d and R, T was considered the residual flux required to balance the annual water input by P for the Ok Tedi and Upper Fly River watersheds, 1000 ± 1098 mm and 1223 ± 975 mm, respectively (Table 9). As the magnitudes of P and R are much larger than ET, errors assigned to T are comparatively large, 80% for the Upper Fly River watershed and 110% for the Ok Tedi watershed, yet these errors are intended to approximate 95% confidence intervals (Note: if the uncertainty associated with P and R is not considered, the error is reduced to 25 – 30%).

5.5 Summary and sources of uncertainty regarding the terrestrial water balance of the Fly River watershed

In this section, the annual water balances of the Ok Tedi and Upper Fly River watersheds were constrained in order to resolve the relative contributions of E_d and T to ET. T was identified as a major component of ET, comprising 40 – 50% of ET, whereas E_d appeared to be secondary in terms of volumetric significance, comprising 15% of ET. Estimates of E_d, and hence T, were based strictly upon observations of the isotope separation between annual water input by rainfall and eventual outflow via rivers, and as such, many processes that occur at smaller scales during water transport through the hydrologic system are subsumed into annual, watershed-scale estimates. This simplification does not diminish the relevance or importance of these aspects of the terrestrial water cycle, but merely reflects the scope of this study and the lack of hydrologic data available for many remote, tropical regions. Moreover, the sources of uncertainty encountered in this study, including the extent of hydrologic connectivity within large watersheds, the importance of sub-surface flow paths in dictating the response of river flow to rainfall, and the spatial representation of regional P by extrapolation of point measurements, are applicable to most studies of regional hydrology and the assessment of these offer some perspective on the necessity for additional, more detailed studies of not only tropical watersheds but those located at northern latitudes.

The more frequent collection of water samples over a multi-year period would be particularly useful given the short-term variability of precipitation and river flow within the Fly River watershed and the availability of this higher resolution data may afford the opportunity to resolve seasonal variability in the intensities of E_d and T. Some perspective on this short-term variability is offered by samples collected in the spring of 2007 (see Chapter 6), yet the brevity of this period of sample collection only provides a snap-shot of hydrologic

conditions in the region and the data are not useful for the separation of isotope fractionating and non-fractionating water vapor fluxes.

A substantial source of uncertainty regarding the net water input to the soil zone was the estimate of rainfall interception (I_n) for rainforests of central New Guinea, as the use of I_n estimates from other regions where P is comparatively low only offers an approximation of a process that directly affects the magnitudes of E_d and T. For example, a 5% increase in the I_n/P ratio corresponds to a 325 – 350 mm reduction in T, which offers some perspective on the considerable uncertainty associated with this aspect of the water balance, yet further discussion of the applicability of different I_n values to forests of New Guinea is speculative given the lack of available measurements. As most studies of the interaction between precipitation and vegetation have focused on a specific type of vegetation, not a region comprised of a variety of vegetation types, scaling these estimates to an entire watershed was a substantial source of uncertainty which was only exasperated by the application of estimates from one region to another. Moreover, without additional information, there was no viable method to ascertain whether these estimates were appropriate, as comparisons of watershed-scale I_n to the literature values they are based on was not perceived to be particularly informative. Consequently, this aspect of the study probably represents the most substantial source of uncertainty related to apportioning ET, as estimates of I_n also affected E_d, as E_d was calculated as the product of the an E_v/I value from equation (24) and $(P - I_n)$.

In addition to magnitude of I_n, some literature data suggest that the process of canopy evaporation may result in the incorporation of partially-evaporated waters into the soil zone, which would cause net water input to be more enriched in ^{18}O and ^{2}H than the δ_I value yielded by the intersection of the LEL and LMWL. As data collected from tropical rainforests in Ecuador indicate that $\delta^{18}O$ and $\delta^{2}H$ values of individual samples of throughfall

typically plot along the LMWL [*Goller et al.*, 2005], it seems reasonable to assume that the effect of partial evaporation on net water input to the soil zone would likely lie within the 95% confidence intervals ascribed to δ_I values for the Ok Tedi and Upper Fly River watershed and thus this uncertainty would be incorporated into the E_v/I values for the watersheds. In principle, the influence of partial evaporation on water balance estimates from the Fly River watershed would tend to reduce the isotope separation between δ_I and δ_S values, thereby decreasing the E_v/I, and increasing the proportion of ET attributed to non-fractionating water fluxes, thus supporting the assertion that fractionating water vapor fluxes are a negligible component of ET in tropical rainforests.

Chapter 6.

Isotope Constraints on the Sources of Dissolved Constituents in the Fly River watershed

6.1 Background information and objectives

As part of its operation in the Star Mountains region of New Guinea, Ok Tedi Mining Limited (OTML) has collected a large amount of geochemical data from the major tributaries of the Fly River. The main focus of this sampling campaign is to characterize the influence of mine-derived sediments on the quality of freshwater systems adjacent to the river and to evaluate the potential role that contaminants may play in affecting the health of local communities within the Fly River watershed [*OTML*, 2007]. Consequently, most of the geochemical data pertains to the concentrations of major elements, dissolved metals, and suspended sediments in river water. Beyond the collection of monthly samples from the major tributaries, numerous studies have been conducted within the watershed over the last twenty years in conjunction with OTML personnel, including research involving members of the Tropical River Ocean Processes in Coastal Settings (TROPICS) project [*Brunskill*, 2004] and the National Science Foundation (NSF)-funded MARGINS program (Source to Sink – Papua New Guinea) [*NSF-MARGINS Program*, 2004].

Several studies have focused on the flux of dissolved constituents [*Martin et al.*, 2000] and suspended sediments [*Harris et al.*, 1993; *Brunskill et al.*, 1995; *Brunskill*, 2004] to the Gulf of Papua, although few of these studies have incorporated information on spatial and/or temporal variability of the stable isotope composition of river water or forms of dissolved carbon therein. Hence, in order to complement the geochemical data acquired by OTML for

major tributaries of the Fly River, samples of river water were collected from the OTML monthly sampling sites in order to test the hypothesis that information on the stable isotope composition of river water (δ^2H, $\delta^{18}O$) and dissolved carbon ($\delta^{13}C$) could provide some constraint on the sources of dissolved constituents to surface waters in the watershed and eventually, provide some perspective on the sources of dissolved constituents to the Gulf of Papua. In addition to the monthly samples of river water collected over a period of approximately two years, samples were also collected at a higher sampling frequency over a period of approximately one month in 2007 in order to characterize the response of dissolved constituents to short-term changes in rainfall and river flow.

6.2 Carbon isotope constraints on the sources of dissolved carbon in the Fly River watershed

Rock weathering, anthropogenic activities, and precipitation are each considered sources of dissolved species to river water, although the relative importance of each depends on a variety of climatic, geologic, and environmental factors [*Meybeck*, 2003]. In large river systems, precipitation does not usually supply a significant proportion of major ions to river water, as the concentrations of most ions in precipitation are generally low and hence overwhelmed by those ions related to terrestrial processes, such as mineral dissolution [*Galy and France-Lanord*, 1999; *Gaillardet et al.*, 1999]. In this study, the negligible contribution of major ions by precipitation was verified by samples of rainwater collected near the towns of Kiunga and Obo, wherein the concentrations of dissolved ions were several orders of magnitude smaller than corresponding concentrations in river water (Table 2). Due to the remote location and extremely low population density of central New Guinea, air-borne anthropogenic sources were not considered a substantial contributor of major ions to

freshwater systems, although effluents related to mining activities in the headwaters region of Ok Tedi were identified as a potential source of dissolved species to river water as OTML discharges mine tailing directly into the Ok Tedi as part of its operations near Mt Fubilan [*OTML,* 2007]. Reports commissioned by OMTL [*Marshall*, 2006] have verified that mining operations have a substantial impact on rivers in the watershed, particularly in terms of suspended sediments, yet mining activities were considered unlikely to have an appreciable impact on the concentrations of major cations, such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} or HCO_3^- in most of the tributaries. For example, recall that mining activities do not occur in the Upper Fly River at Kiunga, yet from Table 1, there are no statistically-discernible differences between the mean concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, or K^{+} for the Upper Fly River at Kiunga and the Ok Tedi at Konkonda even though the mine is located in the headwaters of the Ok Tedi.

Considering the negligible inputs of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} by precipitation and human activities, carbonate and silicate minerals were identified as the primary sources of these cations and HCO_3^- to river water. The dissolution of silicate and carbonate minerals releases a predictable assemblage of aqueous species depending on mineralogy, and the relevant dissolution reactions can be generalized as,

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow 2Na^+ + Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 4H_4SiO_4 \quad (25)$$

$$(Na,K)AlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow Na^+ + K^+ + Al_2SiO_5(OH)_4 + 2HCO_3^- + H_4SiO_4 \quad (26)$$

$$(Ca,Mg)CO_3 + H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \quad (27)$$

where $NaAlSi_3O_8$ is the mineral *albite*, $(Na,K)AlSi_3O_8$ is a mixture of *albite* and *orthoclase*, $CaCO_3$ is calcite, $(Ca,Mg)CO_3$ is *dolomite*, and the main source of acidity is considered carbonic acid (H_2CO_3). Note: These equations are presented for purposes of the general discussion of mineral dissolution, yet are not interpreted as representative of conditions specifically in the Fly River watershed.

Due to uptake of silica by plants and its incorporation into secondary clay minerals, such as kaolinite ($Al_2Si_2O_5(OH)_4$) in equation (25), silica in river water does not necessarily reflect the dissolution of silicate minerals [*Viers et al.*, 2000]. [*Millot et al.*, 2003], amongst numerous others, assert that Na^+ and K^+ are the most reliable indicators of silicate weathering, as Na^+ is mainly derived from cyclic salts, the dissolution of halite, and silicate weathering, whereas the dominant source of K^+ is from silicate weathering alone. Several corrections are proposed to correct the concentrations of Na^+ and K^+ in river water for atmospheric inputs, such as the chemistry of precipitation [*Qin et al.*, 2005], or the ratio of cations in seawater [*Gaillardet et al.*, 1999]. Although neither silicate nor carbonate minerals were probable sources of chloride (Cl^-), the Cl^- correction proposed by [*Dalai et al.*, 2002] was considered a reasonable index for the dissolution of cyclic salts and sedimentary halite ($NaCl$). Accordingly, the silicate components of Na^+ and K^+ can be approximated as $Na_s = Na_r - Cl_r$ and $K_s = K_r$, where the subscript r refers to the measured concentration (in μmol per litre or μmol L^{-1}) in river water and s refers to the proportions of Na^+ and K^+ derived from silicate minerals [*Dalai et al.*, 2002]. However, note from Table 1 that the mean concentrations of Na^+ and K^+ in samples of river water were generally an order of magnitude less than Ca^{2+}. Consequently, although Na^+ often exceeds Cl^-, implying some contribution by silicate mineral dissolution, the predominance of Ca^{2+} suggests that the dissolution of

carbonate minerals is much more significant in the Fly River watershed. Consequently, it is not considered justifiable to attempt even a semi-quantitative discussion of the relative contribution of silicate mineral dissolution based on the concentrations of major cations and the focus of subsequent discussion will be the interpretation of $\delta^{13}C$ values of dissolved carbonic species, principally HCO_3^-, which was interpreted as a proxy for the contribution by different sources of HCO_3^-, some of which are related to the dissolution of carbonate and silicate minerals.

By stoichiometry, the dissolution of one mole of $CaCO_3$ according to equation (27) involves the generation of two moles of HCO_3^- ions; one mole of carbon from the mineral structure of $CaCO_3$ and one mole from H_2CO_3. Consequently, HCO_3^- derived from the dissolution of $CaCO_3$ by acidity related to H_2CO_3 is predicted to be a 1:1 mixture of HCO_3^- derived from these two sources of carbon, $CaCO_3$ and $H_2CO_3^-$, and the $\delta^{13}C$ value of HCO_3^- in river water will thus depend primarily on the $\delta^{13}C$ values of carbon within $CaCO_3$ and H_2CO_3.

Previous studies have affirmed that the dissolution of CO_2 derived from the oxidation of soil organic matter or root respiration is the main source of CO_2 to soil waters, as the diffusion of atmospheric CO_2 into soil waters is usually precluded by its high pCO_2, resulting in a unidirectional flux of CO_2 to the atmosphere [*Amiotte-Suchet et al.*, 1999]. [*Bird et al.*, 1994] reported $\delta^{13}C$ values for forest soil organic matter in the Fly River watershed that ranged from -26.2‰ to -29.7‰. The mean $\delta^{13}C$ value for *DOC* in river water collected from the major tributaries of the Fly River from October 2003 to April 2006 was -28.4‰, indicative of the prevalence of C_3 vegetation in the watershed and similar to $\delta^{13}C$ values reported by [*Bird et al.*, 1994] for soil organic carbon. Using a $\delta^{13}C$ of -28.4‰ as

representative of respired soil CO_2 in the Fly River watershed and incorporating the isotope fractionation associated with hydration of gaseous CO_2, the $\delta^{13}C$ value of HCO_3^- derived from the oxidation of soil organic matter (at 30°C) was estimated to be -20.8‰. If the addition isotope fractionation (4.4‰) associated with CO_2 diffusion in the soil zone proposed by [*Cerling et al.*, 1991] is incorporated, the estimated $\delta^{13}C$ value of HCO_3^- derived from the oxidation of soil organic matter would be -16.4‰. Assuming a $\delta^{13}C$ value of 0‰ for marine calcite, the $\delta^{13}C$ value of HCO_3^- derived from the dissolution of carbonate minerals was estimated to be approximately –2.2‰.

Assuming a 1:1 mixture of HCO_3^- from $CaCO_3$ and H_2CO_3 derived principally from the oxidation of soil OC, the predicted $\delta^{13}C$ value of HCO_3^- generated during carbonate mineral dissolution was estimated to be –11.5‰. The dissolution of carbonate minerals by acidity that is unrelated to a source of carbon and therefore does not contribute HCO_3^- directly, such as sulfuric acid (H_2SO_4), generates HCO_3^- with a $\delta^{13}C$ value of –2.2‰, identical to the end-member value of $CaCO_3$. As silicate minerals are not a source of carbon and their dissolution by H_2SO_4 does not generate HCO_3^-, the $\delta^{13}C$ value of HCO_3^-generated by silicate mineral dissolution is derived solely from H_2SO_4, yielding HCO_3^- with a $\delta^{13}C$ value of –20.8‰. The contribution of the soil HCO_3^- end-member to HCO_3^- in river water can therefore be interpreted as a proxy for the inputs by silicate mineral dissolution, although the dissolution of soil CO_2 unrelated to mineral dissolution must also be considered.

Mean $\delta^{13}C$ values of HCO_3^- in water samples collected from February 23 to March 5, 2007, ranged from -11.1 ± 0.2‰ (Middle Fly River at Obo) to -12.4 ± 0.1‰ (Upper Fly River at Kiunga) (Table 3). These mean $\delta^{13}C$ values of HCO_3^- were essentially equivalent to the predicted $\delta^{13}C$ value of HCO_3^- generated by the dissolution of $CaCO_3$ by H_2CO_3 (–

11.5‰). Moreover, mean $\delta^{13}C$ values of H_2CO_3 for these samples ranged from -18.6 ± 0.2‰ (Middle Fly River at Obo) to -19.5 ± 0.3‰ (Upper Fly River at Kiunga), which are also close to the predicted $\delta^{13}C$ value of the H_2CO_3 end-member defined by $\delta^{13}C$ values for soil OC from [*Bird et al.*, 1994] and *DOC* from this study.

Mean $\delta^{13}C$ values of HCO_3^- in water samples collected from February 2004 to April 2006 were 2‰ to 3‰ heavier than mean values for samples collected from February 23 to March 5, 2007 (Table 3), but the range of $\delta^{13}C$ values of HCO_3^- within this dataset is a source of concern regarding the reliability of these values. Although mean $\delta^{13}C$ values of HCO_3^- for these monthly samples seems reasonable if the additional isotope fractionation (4.4‰) associated with CO_2 diffusion in the soil zone were incorporated [*Cerling et al.*, 1991], a more likely explanation is that these samples degraded during storage, yet the exact process by which sample degradation occurred is speculative. Given the brief period of storage for samples collected from February 23 to March 6, 2007, $\delta^{13}C$ values of HCO_3^- for these samples seem more reliable. Based on the information available, a quantitative assessment of the preferred period of storage for samples intended for carbon isotope analysis cannot be offered although measurement within 3 – 4 weeks of collection seems prudent, as is the use of additional Teflon cap (see section 3.1.2) in order to ensure that there is no exchange of air between the water sample and the atmosphere during storage.

End-member mixing models are often proposed to explain seasonal variability in river chemistry as a mixture of groundwater and soil water, the premise being that older waters tend to accumulate dissolved constituents, such as major cations and HCO_3^- due to the prolonged exposure of minerals to dissolution [*Rademacher et al.*, 2001]. The influence of groundwater on river chemistry during periods of baseflow has been emphasized in

numerous studies [*Anderson et al.*, 1997; *Johnson et al.*, 2000) and the mixing between groundwater and surface runoff end-members has recently been invoked by [*Tipper et al.*, 2006] in order to explain seasonal variations in the chemistry of several rivers of the Himalaya. The authors assert that river water during the monsoon period more closely resembles that of recent and comparatively dilute precipitation due to the apparent brevity of exposure of surface waters to processes of mineral dissolution. In contrast, [*Markewitz et al.*, 2001] reported higher concentrations of cations and HCO_3^- during periods of enhanced river flow in an Amazonian river, which the authors ascribed to the 'flushing' of shallow surface soil layers rather than the input of weathering products from deeper soils carried by groundwater flow. Similarly, [*Smolders et al.*, 2004] reported a similar 'flushing' of dissolved constituents during periods of increased river flow in the Bolivian Andes. Although the mechanism by which large amounts of water that have resided in a hydrologic system for extended periods of time can be rapidly displaced is contentious, testing the hypothesis that rainfall events occurring upstream in the headwaters of the Fly River may result in an appreciable response in the chemistry of river water downstream was an impetus behind sample collection from the Upper Fly River at Kiunga and the Middle Fly River at Obo in 2007.

In response to changes in the rate of river flow, $\delta^{13}C$ values of HCO_3^- in water samples collected from the Middle Fly River at Obo and the Upper Fly River at Kiunga from February 2004 to April 2006 showed little response. $\delta^{18}O$ and $\delta^{2}H$ values of water were similar unresponsive to changes in river flow, although numerous studies have proposed to use these types of isotope data to resolve the contributions of pre-event and event waters to river flow. Although limited data were available, the data collected in this study do not support the hypothesis that $\delta^{18}O$ and $\delta^{2}H$ values of water or $\delta^{13}C$ values of HCO_3^- can be

utilized to definitively resolve these contributions at the scales considered in this study. Instead, these data seemingly behave as passive tracers of water movement. Speculatively, using these data as tracers of water movement and sources of dissolved constituents could be more efficacious under conditions where sub-surface waters are allowed to accumulate for a longer period of time, thereby enabling development of a more distinct isotope composition compared to event water (i.e. rainfall). In this instance, the contribution of pre-event waters during periods of increased river flow could be more easily resolved, yet in the Fly River watershed wherein rainfall is consistently high and the residence time of waters in the hydrologic system is presumably quite short, resolving the contribution of pre-event waters based on stable isotope data would probably remain problematic.

In contrast to the isotope data, in samples collected from the Upper Fly River at Kiunga, peaks in the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} that occurred immediately after the increase in river flow could be interpreted as indicative of soil-water flushing (Figure 15). However, in comparison to rainwater, the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} in samples of shallow soil-water collected near Kiunga were similarly dilute, which contradicts the assertion that the displacement of shallow soil-waters into rivers is the cause of higher concentrations after an increase in river flow. Instead, an increase in the concentrations of these cations would more likely to be attributed to the displacement of deeper sub-surface waters, such as those collected from the pit wall of the mine-site tens of meters below the pre-mine ground-surface, wherein the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} were very high compared to rainwater and shallow soil-waters (these samples were representative of deep groundwater and likely reflect acid rock drainage or ARD).

Note that the $\delta^{13}C$ values of HCO_3^- for river water collected from February 23 to March 5, 2007, were essentially equivalent to the predicted value for a 1:1 mixture of HCO_3^- derived from $CaCO_3$ and H_2CO_3. Hence, the conclusion that is most supported by the available data is that HCO_3^- in river water is derived almost entirely from the dissolution of carbonate minerals by acidity related to the oxidation of soil organic matter. The consistency of $\delta^{13}C$ values of HCO_3^- in river water, together with the fact that these values never approach the $\delta^{13}C$ value of the soil HCO_3^- end-member at -20.8‰, suggests that the dissolution of silicate minerals is essentially negligible compared to carbonate mineral dissolution. This implies that carbon from H_2CO_3 is rarely contributed to river water without an equivalent amount of carbon derived from $CaCO_3$ and that acidity related to other sources of carbon, such as H_2SO_4, is not a significant aspect of mineral dissolution at a regional scale. The predominance of Ca^{2+} in river water, which is almost equivalent to HCO_3^- on a charge equivalency basis (i.e. $\mu eq\ L^{-1}$), also supports this conclusion and was not unexpected given the susceptibility of carbonate minerals to dissolution [*Barth et al.*, 2003] and the predominance of carbonate minerals in the Fly River watershed [*Brunskill*, 2004]. The principal source(s) of the other cations, such as Mg^{2+}, Na^+, and K^+, is less certain although the dissolution of cyclic salts (*NaCl*) and silicate minerals are the most probable. Separating the relative contributions of these sources, however, is problematic given the low concentrations of these cations in river water compared to Ca^{2+} and the inherent uncertainty related to the types of corrections involved.

6.3 The controls on the chemical flux of dissolved constituents to the Gulf of Papua

Considering their relatively small drainage areas, high-standing islands of the Indonesian Archipelago contribute a disproportionately large amount of freshwater and sediments to the

oceans each year [*Milliman et al.*, 1999]. The flux of dissolved constituents via rivers is commonly perceived to be an expression of a complex inter-dependency of climatic and tectonic factors which may affect the intensity of silicate and carbonate mineral dissolution in a drainage area [*Gaillardet et al.*, 1999]. The importance ascribed to climatic and tectonic factors varies, as separating the influence of these factors is often complicated by differences in regional climate, landscape development, and the chemical composition and reactivity of various rock types within a drainage area. Moreover, although increased rates of chemical flux are typically interpreted as causally-related to enhanced rates of mineral dissolution in a drainage area [*West et al.*, 2005], the fundamental question arises, is the rate of flux of dissolved constituents via rivers a proxy for the process of mineral dissolution or is this flux primarily dependent on drainage lithology and the rate of river runoff itself?

Rates of chemical flux via river water are typically calculated as the product of river flow per unit area (i.e. river runoff) and the concentration of a given cation in river water [*Gaillardet et al.*, 1999; *West et al.*, 2006]. From Figure 26, wherein weekly river flow data and the concentrations of major cations and HCO_3^- are shown for the Middle Fly River at Obo, it is evident that river flow at this location varies on an intra-annual basis. In general, reduced flow conditions are observed during the period of moisture transport via trade winds, as the amount of rainfall at lower elevations is often reduced during this period. The most relevant aspect of Figure 26 is that the concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, and HCO_3^- are generally consistent from month to month and do not vary significantly in response to changes in river flow. Several months of monthly data are missing from this database, yet the relative constancy of dissolved constituents in river water is supported by data collected from the Middle Fly River at Obo from February 23 to February 26, 2007 (Table 2).

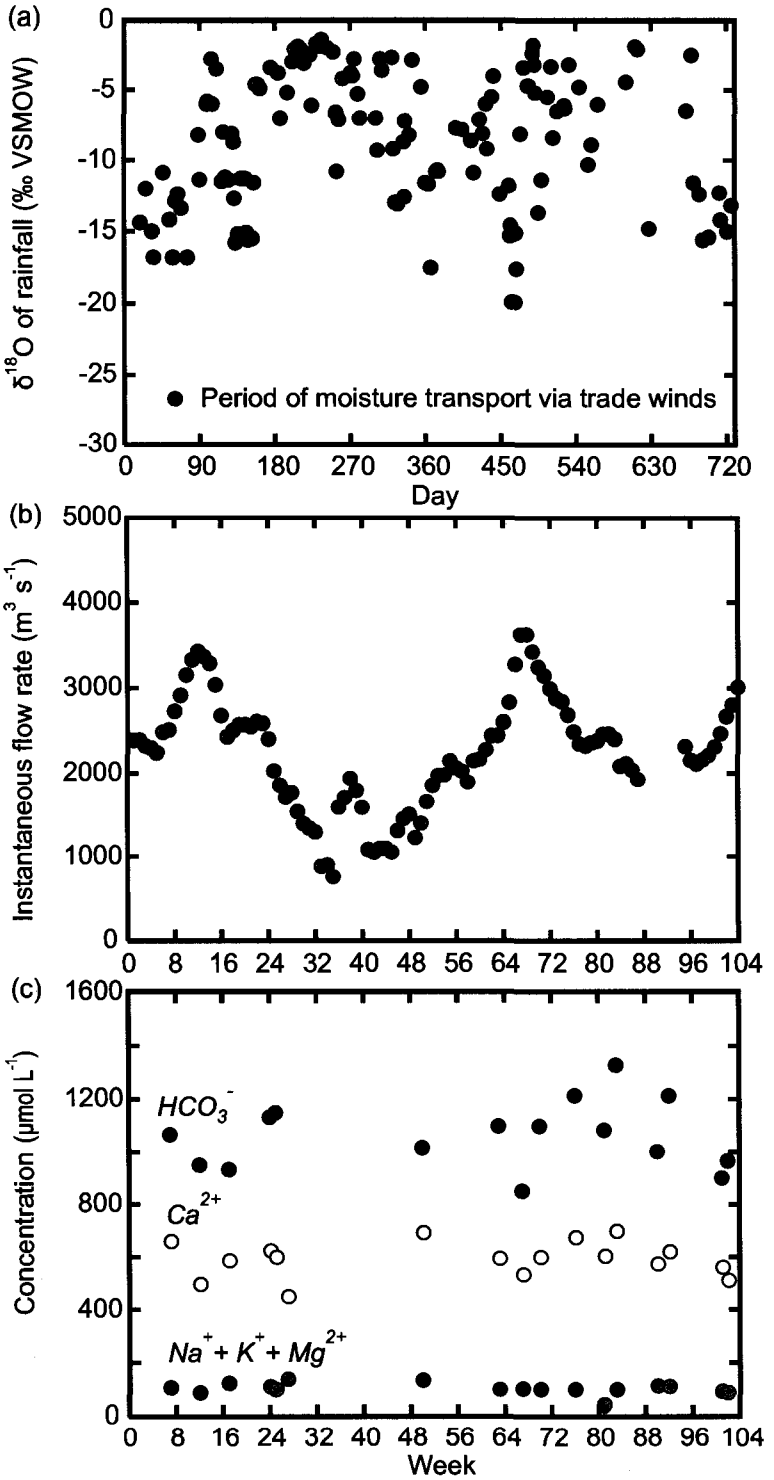


Figure 26. (a) $\delta^{18}O$ and $\delta^{2}H$ values of rainfall at Tabubil, defining periods of moisture transport from the northern and southern hemispheres; (b) weekly river flow for the Middle Fly River at Obo; (c) concentrations of major cations and anions in monthly river water samples collected from the Middle Fly River at Obo. From a comparison of (a) and (b), reduced flow conditions coincide with the period of moisture transport via trade winds (inferred from heavier $\delta^{18}O$ and $\delta^{2}H$ values of rainfall). Despite the intra-annual variability in river flow, the concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and HCO_3^{-} are relatively consistent.

The most important aspect of temporal changes in both river flow and the concentrations of dissolved constituents in the Middle Fly River at Obo is that these changes are less than an order of magnitude. For the other tributaries, such as the Ok Tedi at Konkonda and the Upper Fly River at Kiunga, changes in river flow were more substantial yet similar to the Middle Fly River at Obo; changes in concentration were much smaller in magnitude than the concurrent changes in river flow. Consequently, the rate of chemical flux for each tributary of the Fly River was dependent almost exclusively on the rate of river flow, not the concentration of dissolved ions in river. For these reasons, the calculation of mean annual rates of chemical flux for the tributaries of the Fly River was justified.

Based on the rate of mean annual river flows for the study period (October 2003 to April 2006) and the concentrations of major ions in monthly samples of river water (Table 1), mean annual rates of flux were calculated for each tributary of the Fly River. Rates of chemical flux are summarized in Table 10, wherein area-standardized fluxes are expressed on a molar basis in units of 10^3 mol km^{-2} yr^{-1} and in terms of mass, in units of 10^3 kg km^{-2} yr^{-1}. These fluxes are solely based upon the concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and HCO_3^{-} in river water, as the separation of the contributions by different mineral types was not feasible based on the data available (see section 6.2). From Table 10, the flux of Ca^{2+} far exceeds the collective flux of Mg^{2+}, Na^{+}, and K^{+}. Often, after minor corrections for the input of cyclic salts, it is the fluxes of Na^{+} and K^{+} via river water that are interpreted as proxies for silicate mineral dissolution. Compared to 'silicate cation denudation rates' compiled for various global river systems by [*West et al.*, 2005], the flux of (Na^{+} + K^{+}) from the Fly River at Ogwa (6000 kg km^{-2} yr^{-1}), which essentially represents total flux to the Gulf of Papua, would rank relatively high yet is less than half that of the flux attributed to the Ok Tedi at Konkonda (14,000 kg km^{-2} yr^{-1}) (no chloride correction was imposed so these fluxes

Table 10. Fluxes of dissolved constituents from the tributaries of the Fly River, 2004 – 2005.

		Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}		HCO_3^-	
Location	R, mm	10^3 kg km^{-2}	10^3 mol km^{-2}	10^3 kg km^{-2}	10^3 mol km^{-2}	10^3 kg km^{-2}	10^3 mol km^{-2}	10^3 kg km^{-2}	10^3 mol km^{-2}	10^3 kg km^{-2}	10^3 mol km^{-2}
Kiunga	4611	93	2315	4	101	4	106	2	40	266	6639
Konkonda	5248	104	2592	7	169	9	232	5	128	336	8387
Nukumba	5046	104	2604	5	128	5	136	3	79	321	8003
Obo	3734	89	2210	4	93	4	99	3	66	242	6036
Str01	1811	43	1072	4	94	4	99	1	30	133	3325
Ogwa	2516	62	1547	5	116	4	108	2	39	196	4894

represent maxima). Clearly, the higher flux of ($Na^+ + K^+$) attributed to the Ok Tedi at Konkonda is due to a higher rate of river runoff compared to the Fly River at Ogwa, as Na^+ and K^+ concentrations are comparable for both rivers, as are the concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- (Table 1). Consequently, the interpretation of these fluxes as a proxy for the rate of mineral dissolution is dubious and unlikely to provide information on the types of minerals being dissolved or the rate at which this occurs in the drainage area.

Chapter 7.

Coupling of the Terrestrial Water and Carbon Cycles

7.1 Partitioning isotope fractionating and non-fractionating water vapor fluxes from large watersheds located in North America, South America, Africa, and Australia

In this chapter, E_d and T are partitioned in thirteen additional watersheds based on the methodology developed in Chapter 5. Most of the selected watersheds are located in temperate and sub-tropical regions that receive less than 1500 mm of mean annual precipitation (P) and hence the main purpose of this section is to compare estimates of E_d and T from watersheds located in 'water-limited' regions to those of rainforest biomes of New Guinea. This comparison enables the evaluation of the hypothesis outlined in section 1.3, that the terrestrial carbon cycle is 'piggybacking' on the much larger terrestrial water cycle and that estimates of T and NPP should respond similarly to water inputs via P.

7.1.1 Watershed locations

Thirteen watersheds were selected from the literature (Figure 27, Table 11). In North America, the selected rivers included the North and South Saskatchewan Rivers (the principal tributaries of the Nelson River which flows into Hudson Bay) [*Ferguson et al.*, 2007], the Mississippi River [*Lee and Veizer*, 2003], the Ottawa River (a tributary of the St. Lawrence River) [*Telmer and Veizer*, 2000], and the St. Lawrence River [*Barth and Veizer*, 2004; *Karim et al.*, 2007]. In South America, the Piracicaba River watershed is located in the state of São Paolo in southern Brazil and flows into a tributary of the Paraná River [*Martinelli et al.*, 2004]. In West Africa, the Black Volta River, the White Volta River, and the Oti River are the principal tributaries of the Volta River, which flows into Lake Volta in

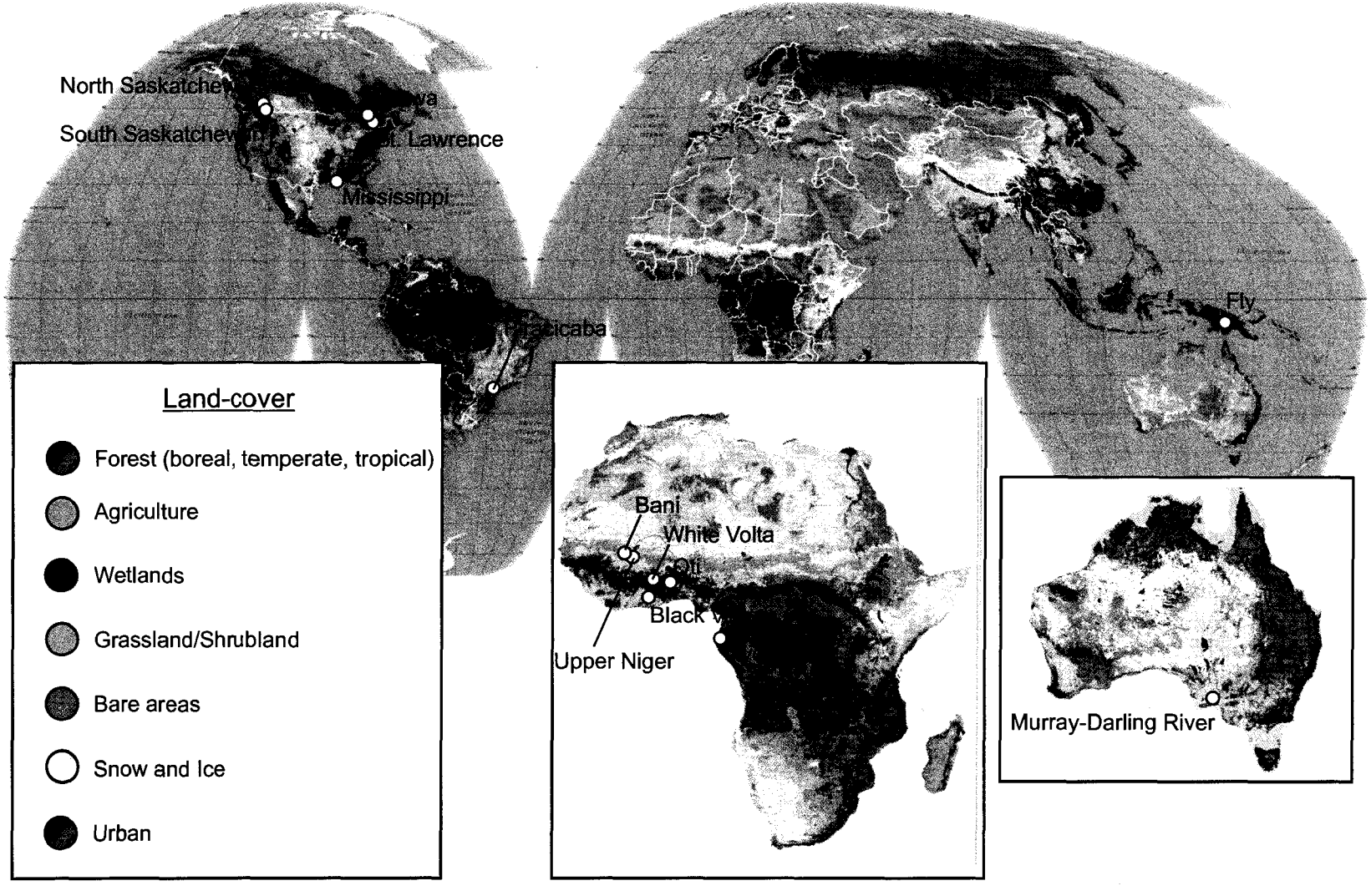


Figure 27. The locations of the selected watersheds in North America, South America, Africa, Australia, and New Guinea. The locations of the streamflow gauges used for definition of R in Chapter 7 are overlain upon a map of global land-cover [*GLC2000*, 2003]. Refer to Table 11 for the distribution of vegetation within each watershed; themes for the global land-cover map are provided in the legend.

southern Ghana before eventual outflow occurs into the Atlantic Ocean [*Freitag et al.*, 2007], and the Upper Niger River and the Bani River are headwater tributaries of the Niger River. The Nyong River (Cameroon) [*Brunet, personal communication*] flows into the Atlantic Ocean. The Murray-Darling River is the largest watershed in Australia and flows into the Southern Ocean [*Simpson and Herczeg*, 1991].

7.1.2 Precipitation and rainfall interception, P - I_n

Using ArcGIS™ software and monthly precipitation data from a 10′ gridded terrestrial climatology for the period 1961 – 1990 [*New et al.*, 2000], area-weighted estimates of *P* for the thirteen watersheds were defined by the grid points completely contained by the boundaries of each watershed. Vegetation within each of the thirteen watersheds was classified based on the Global Land Cover (GLC) 2000 datasets for North America [*Latifovic et al.*, 2002], Africa [*Mayaux et al.*, 2004], Southeast Asia [*Stibig et al.*, 2003] and South America [*Eva et al.*, 2003] (Table 11). This classification was used to estimate I_n and thus the

Table 11. Vegetation classifications and areas for watersheds in North America, South America, Africa, Australia, and New Guinea

Watershed	Area, 10^3 km^2	Principal types of vegetation[a], %	/Total, %
North America			
North Saskatchewan	131.0	Cropland, 33.6; grassland, 27.9; temperate forest, 26.3	87.8
South Saskatchewan	141.0	Cropland, 45.3; temperate forest, 30.4; grassland, 16.0	91.7
Ottawa	146.0	Temperate forest, 84.2; cropland, 5.9, water bodies, 5.2	95.3
St. Lawrence	764.6	Water bodies, 35.8; temperate forest, 32.9; cropland, 20.5	89.2
Mississippi	2964.0	Grassland/shrubland, 38.1; cropland, 33.2; temperate forest, 26.4	97.7
Africa			
Bani	101.6	Cropland, 45.5; shrubland, 54.5	100
Upper Niger	137.0	Cropland, 37.7; shrubland, 33.9; woodland, 19.3	90.9
Black Volta	134.0	Grassland, 44.0; cropland, 21.3; deciduous forest, 18.0	83.3
White Volta	93.0	Grassland, 40.0; cropland, 23.6; deciduous forest, 18.8	82.4
Oti	58.7	Grassland, 42.5; shrubland, 21.4; deciduous forest, 22.3	86.2
Nyong	26.4	Tropical rainforest, 80.1; shrubland, 11.1; forest/crop mosaic, 4.0	95.2
South America			
Piracicaba	10.9	Cropland, 37.7; forest, 33.6; savanna/shrubland, 18.5; urban, 8.3	91.3
Australia/Oceania			
Ok Tedi	5.2	Tropical rainforest, 80.3; forest/crop mosaic, 19.7	100
Upper Fly	5.2	Tropical rainforest, 90.9; forest/crop mosaic, 9.0	100
Murray-Darling	991.0	Shrublands, 53.1; croplands, 26.8; forest/woodlands, 13.8	93.7

[a] Land-cover distribution generalized from GLC2000 data (see Appendix 10).

net water input to each watershed, which was approximated as $P - I_n$. In order to calculate an area-weighted estimate of I_n for each watershed, the corresponding GLC2000 land-cover class for each grid point from [*New et al.* 2000] was determined using ArcGIS™ software and literature I_n values were assigned to each point (see Appendix 10 for the I_n values assigned to each vegetation class). An area-weighted estimate of I_n for each watershed was calculated as the sum of I_n values for each data point completely contained by the watershed boundaries.

7.1.3 Outflow via river water, R

Estimates of R were based upon historical records of river flow that were acquired from the on-line Global River Discharge Database of the Center for Sustainability and the Global Environment, University of Wisconsin at Madison [*SAGE*, 2007]. Using annual volumetric flow data and gross watershed areas from this database, R was calculated as the mean rate of annual runoff for each watershed and the 95% confidence intervals were reported as estimates of uncertainty. In actuality, the proportion of gross watershed area that contributes to annual river flow on an annual basis probably fluctuates due to intermittent or restricted hydrologic connectivity within a watershed and this would affect the definition of R, but for consistency, gross watershed areas were utilized throughout this study by necessity. In most of the previously-studied watersheds, R comprised only a small proportion of P (Figure 28), which suggests that more water is transferred to the atmosphere each year as water vapor than is transferred to the oceans via river outflow from these watersheds. A quantitative description of the magnitude of this excess is limited by considerations of the extent of internal hydrologic connectivity, the extrapolation of point measurements of precipitation to larger areas, and the validity of assumptions regarding of hydrologic steady-state, yet despite

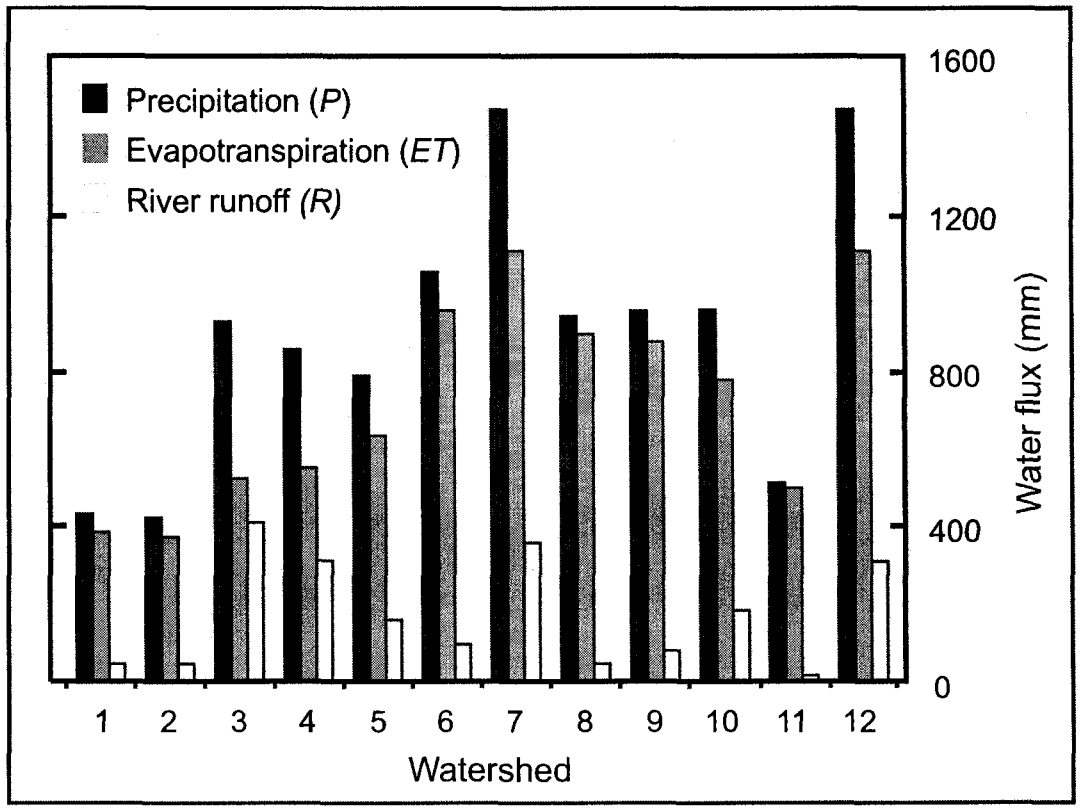


Figure 28. The conventional annual water balances for watersheds in North America, South America, Africa, and Australia *ET* is generally exceeds *R*, implying that more water may be transferred to atmosphere each year as water vapor than is transferred to the oceans via rivers. 1. North Saskatchewan River, 2. South Saskatchewan River, 3. Ottawa River, 4. St. Lawrence River, 5. Mississippi River, 6. Bani River, 7. Upper Niger River, 8. Black Volta River, 9. White Volta River, 10. Oti River, 11. Murray-Darling River, 12. Piracicaba River.

the inherent sources of uncertainty, it can be reasonably inferred from equation (1) that the difference between P and R can be considered an approximation of ET and from Figure 28, that ET generally exceeds R in magnitude.

7.1.4 Direct evaporation, E_d, and plant transpiration, T

As described in section 5.1, resolving the relative contributions by isotope fractionating and non-fractionating water vapor fluxes involves interpretation of the isotope separation between annual water input via precipitation and outflow via river water. This begins with a comparison of the LMWL and LEL for a particular watershed. In watersheds where direct evaporation from soils and water bodies is volumetrically significant relative to annual water input, $\delta^{18}O$ and $\delta^{2}H$ values of river water generally define a LEL with a shallower slope than the LMWL, such that the offset between $\delta^{18}O$ and $\delta^{2}H$ values of individual samples from the LMWL increases in approximate proportion to the cumulative fraction of water transferred to the atmosphere by evaporation in upstream areas. This concept is graphically illustrated in Figure 29 by the LMWL and LEL for the North and South Saskatchewan River watersheds [*Ferguson et al.*, 2007] and in Figure 30 by the LMWL and LEL for the Volta River watershed of West Africa [*Freitag et al.*, 2007]. More quantitatively, the equations for the LMWL and LEL for each watershed plus those of New Guinea are summarized in Table 12 (a more detailed description of data sources is included in Appendices 11 and 12). Note from Table 12 that most of the watersheds are characterized by LEL with a shallower slope than the corresponding LMWL for that watershed.

The intersection of the LMWL and LEL was used to approximate annual water input by precipitation (δ_I) and δ_S was considered the volume-weighted mean isotope composition of outflow via river water (see section 5.1). δ_I and δ_S values and the other input parameters for equation (24) are summarized in Table 13 with E_v/I values for each of the watersheds.

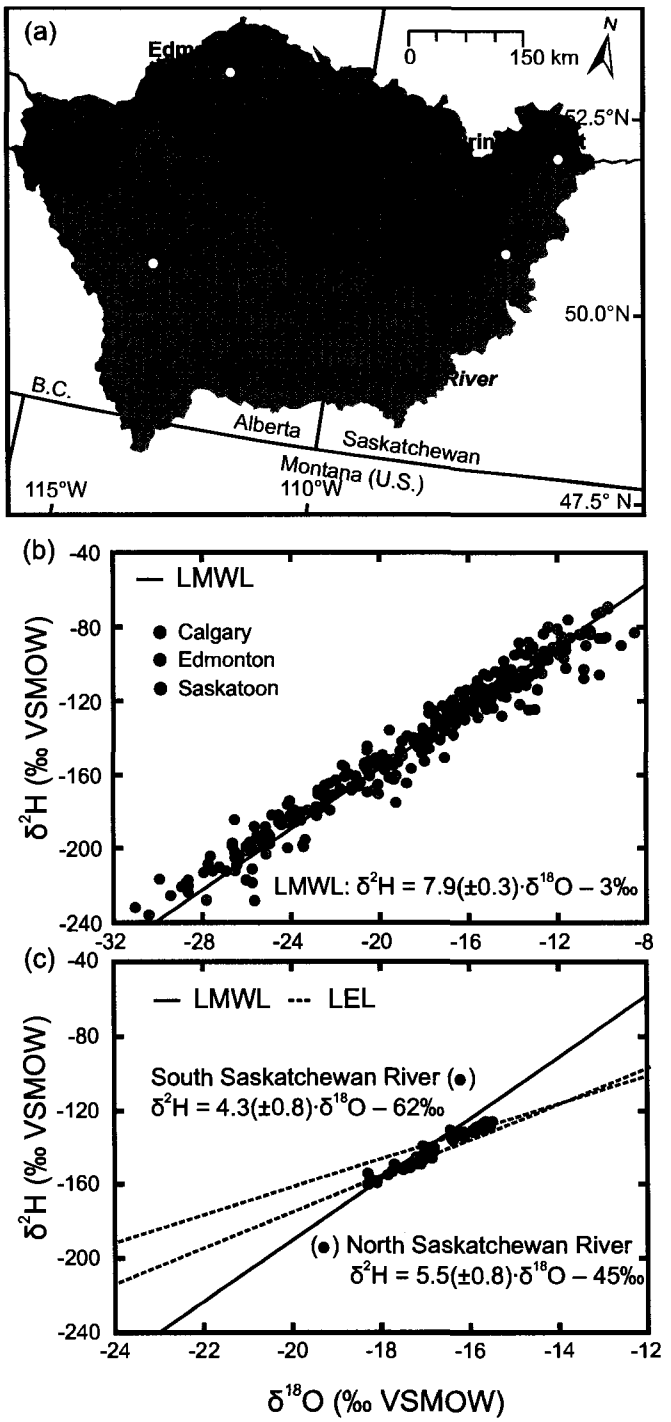


Figure 29. (a) The locations of sampling stations in the North and South Saskatchewan River watershed; (b) the LMWL for the North and South Saskatchewan River watersheds is defined by $\delta^{18}O$ and $\delta^{2}H$ values of precipitation at Edmonton, located in the North Saskatchewan River watershed, and Calgary and Saskatoon, each located in the South Saskatchewan River watershed; (c) LEL defined by $\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the North Saskatchewan River at Prince Albert and the South Saskatchewan River at Saskatoon (95% confidence intervals are given in parentheses).

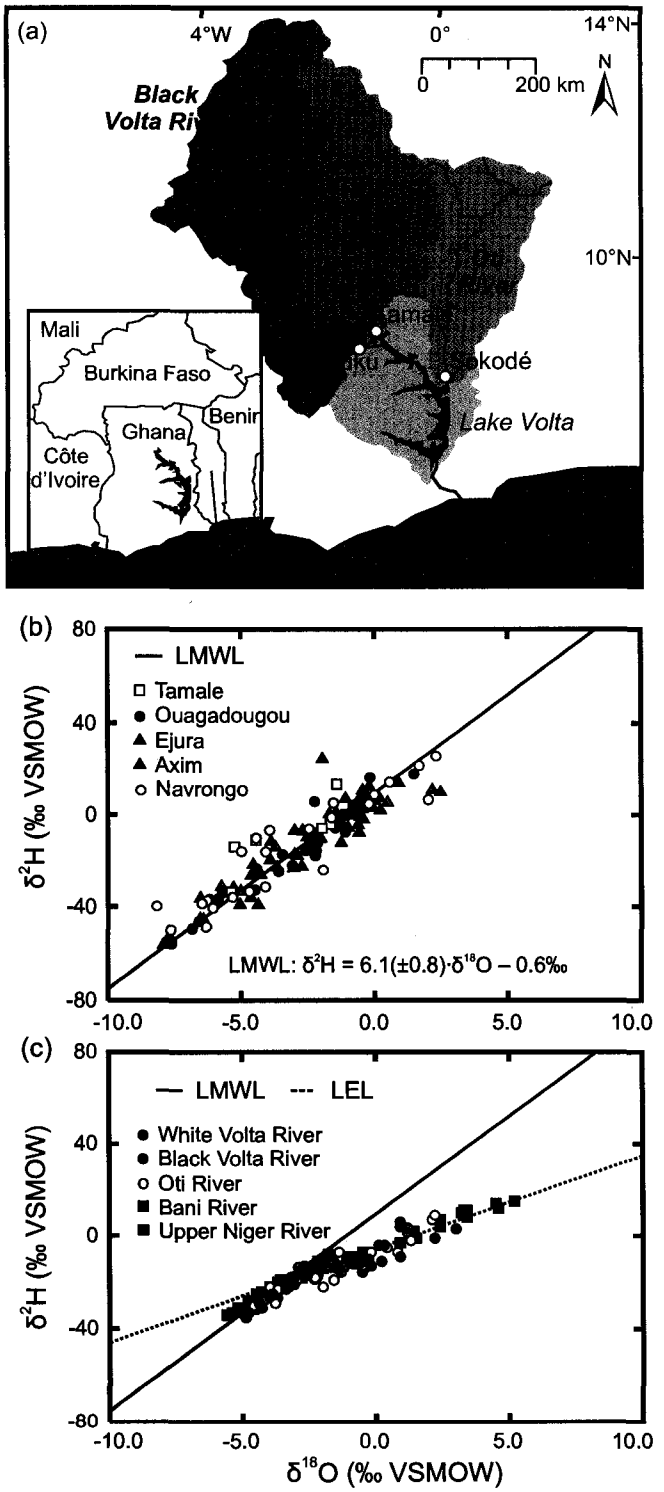


Figure 30. (a) The location of the Volta River watershed in West Africa; (b) $\delta^{18}O$ and $\delta^{2}H$ values of rainfall at stations located in West Africa; (c) $\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the major tributaries of the Volta River and the Bani River and Upper Niger River (both tributaries of the Niger River).

Table 12. Local evaporation lines (*LEL*) and local meteoric water lines (*LMWL*) for watersheds in North America, South America, Africa, Australia, and New Guinea

Watershed	Water input by precipitation	Outflow at the river mouth		
	LMWL[a]	LEL[b]	Location	n^c
North America				
North Saskatchewan	$\delta^2H = 7.9\pm0.1\cdot\delta^{18}O + 3.4$	$\delta^2H = 5.5\pm0.8\cdot\delta^{18}O - 45.1$	Prince Albert	35
South Saskatchewan	$\delta^2H = 7.9\pm0.1\cdot\delta^{18}O + 3.4$	$\delta^2H = 4.3\pm0.8\cdot\delta^{18}O - 61.5$	Saskatoon	35
Ottawa	$\delta^2H = 7.5\pm0.2\cdot\delta^{18}O + 6.1$	$\delta^2H = 6.1\pm0.5\cdot\delta^{18}O - 15.5$	Carillon	15
St. Lawrence	$\delta^2H = 7.5\pm0.2\cdot\delta^{18}O + 4.5$	$\delta^2H = 6.9\pm0.6\cdot\delta^{18}O - 2.8$	Cornwall	25
Mississippi	$\delta^2H = 7.5\pm1.6\cdot\delta^{18}O - 0.4$	$\delta^2H = 6.0\pm1.8\cdot\delta^{18}O - 3.0$	Melville	13
Africa				
Bani	$\delta^2H = 6.2\pm0.6\cdot\delta^{18}O - 0.4$	$\delta^2H = 4.3\pm0.3\cdot\delta^{18}O - 6.2$	Douna	27
Upper Niger	$\delta^2H = 6.2\pm0.6\cdot\delta^{18}O - 0.4$	$\delta^2H = 4.8\pm0.2\cdot\delta^{18}O - 4.1$	Banankoro	29
Black Volta	$\delta^2H = 6.1\pm0.8\cdot\delta^{18}O - 0.6$	$\delta^2H = 4.7\pm0.7\cdot\delta^{18}O - 7.1$	Bamboi	26
White Volta	$\delta^2H = 6.1\pm0.8\cdot\delta^{18}O - 0.6$	$\delta^2H = 4.8\pm0.9\cdot\delta^{18}O - 6.0$	Nawuni	22
Oti	$\delta^2H = 6.1\pm0.8\cdot\delta^{18}O - 0.6$	$\delta^2H = 4.9\pm0.7\cdot\delta^{18}O - 6.3$	Sabari	23
Nyong	$\delta^2H = 8.1\pm0.2\cdot\delta^{18}O + 10.9$	$\delta^2H = 7.7\pm1.1\cdot\delta^{18}O + 7.7$	Dehane	31
South America				
Piracicaba	$\delta^2H = 9.1\pm1.3\cdot\delta^{18}O + 16.7$	$\delta^2H = 6.3\pm0.6\cdot\delta^{18}O - 0.9$	Artemis	34
Australia/Oceania				
Ok Tedi	$\delta^2H = 8.2\pm0.1\cdot\delta^{18}O + 11.8$	$\delta^2H = 6.7\pm0.8\cdot\delta^{18}O - 1.1$	Konkonda	26
Upper Fly	$\delta^2H = 8.2\pm0.1\cdot\delta^{18}O + 11.8$	$\delta^2H = 7.3\pm0.8\cdot\delta^{18}O + 3.3$	Kiunga	22
Murray-Darling	$\delta^2H = 8.1\pm0.7\cdot\delta^{18}O + 12.7$	$\delta^2H = 5.1\pm0.5\cdot\delta^{18}O - 9.0$	Rufus Junction	21

[a] Defined by $\delta^{18}O$ and δ^2H values of regional precipitation
[b] Defined by $\delta^{18}O$ and δ^2H values of river water
[c] Refers to number of data points used for LEL

Table 13. Summary of input parameters for $\delta^{18}O$ and E_v/I values for previously-studied watersheds in North America, South America, Africa, Australia, and New Guinea

Watershed	T, K	h, %	δ_I, ‰	δ_A, ‰	ε, ‰	$\Delta\varepsilon$, ‰	δ_S, ‰	E_v/I, %
North America								
North Saskatchewan	274.9	70	−20.4 ± 3.0	−20.4	11.5	4.3	−18.7 ± 0.3	8.5 ± 1
South Saskatchewan	276.3	66	−18.2 ± 3.3	−29.6	11.4	4.8	−15.9 ± 0.2	11.7 ± 2
Ottawa	276.7	75	−13.0 ± 2.2	−24.3	11.3	3.6	−10.9 ± 0.3	11.8 ± 2
St. Lawrence	278.6	75	−11.6 ± 1.0	−22.8	11.1	3.6	−7.4 ± 0.6	34.3 ± 4
Mississippi	283.2	66	−5.1 ± 1.1	−17.9	10.7	4.8	−6.1 ± 0.4	5.0 ± 2
Africa								
Bani	299.8	58	−3.0 ± 0.3	−12.2	9.2	6.0	−1.3 ± 1.2	8.3 ± 8
Upper Niger	299.8	58	−3.2 ± 0.3	−12.4	9.2	6.0	−2.2 ± 0.5	4.7 ± 2
Black Volta	301.3	57	−4.3 ± 0.8	−13.4	9.1	6.0	−1.6 ± 0.9	14.1 ± 5
White Volta	301.5	56	−5.1 ± 1.1	−14.2	9.1	6.2	−2.0 ± 0.7	16.2 ± 7
Oti	300.9	61	−4.4 ± 0.8	−13.6	9.1	5.5	−1.6 ± 0.8	15.2 ± 9
Nyong[a]	298.9	80	-	-	9.3	2.8	−2.6 ± 0.2	-
South America								
Piracicaba	293.1	77	−6.2 ± 1.1	−16.0	9.8	3.3	−5.8 ± 0.2	2.1 ± 0
Australia/Oceania								
Ok Tedi	298.5	83	−8.6 ± 1.0	−17.9	9.3	2.4	−7.6 ± 0.5	5.8 ± 1
Upper Fly	298.9	83	−9.4 ± 1.0	−18.7	9.3	2.4	−8.4 ± 0.7	5.8 ± 1
Murray-Darling	293.2	47	−7.2 ± 0.9	−17.0	9.8	7.5	−3.0 ± 0.7	21.6 ± 6

[a] E_v/I value undefined for Nyong River watershed

Table 14. Summary of water balance components for previously-studied watersheds in North America, South America, Africa, Australia, and New Guinea

Watershed	Annual values expressed in mm or 10^3 g H_2O m^{-2} yr^{-1}				
	P	R	I_n	E_d	T
North America					
North Saskatchewan	461 ± 21	59 ± 27	137 ± 13	28 ± 3	248 ± 37
South Saskatchewan	430 ± 23	59 ± 23	111 ± 19	37 ± 8	229 ± 39
Ottawa	948 ± 20	418 ± 112	177 ± 55	91 ± 18	277 ± 128
St. Lawrence	859 ± 9	312 ± 10	140 ± 24	247 ± 30	276 ± 41
Mississippi	796 ± 12	177 ± 19	212 ± 31	29 ± 11	384 ± 40
Africa					
Bani	1068 ± 23	100 ± 26	192 ± 82	82 ± 73	694 ± 115
Upper Niger	1545 ± 70	488 ± 28	268 ± 106	60 ± 29	729 ± 133
Black Volta	955 ± 17	60 ± 12	166 ± 72	111 ± 39	618 ± 85
White Volta	969 ± 19	85 ± 17	107 ± 46	140 ± 58	641 ± 78
Oti	970 ± 19	189 ± 38	110 ± 41	131 ± 78	540 ± 98
Nyong	1835 ± 76	527 ± 42	178 ± 161	0 ± 0	1130 ± 183
South America					
Piracicaba	1468 ± 169	355 ± 56	202 ± 89	27 ± 6	979 ± 199
Australia/Oceania					
Ok Tedi	7056 ± 696	4583 ± 816	1129 ± 226	344 ± 59	1000 ± 1098
Upper Fly	6540 ± 648	4032 ± 696	961 ± 209	324 ± 56	1223 ± 975
Murray-Darling	506 ± 13	8 ± 3	84 ± 40	91 ± 26	325 ± 50

P – precipitation; R – river runoff; I_n – interception; E_d – evaporation; T – plant transpiration

Components of the annual water balances for the watersheds are summarized in Table 14, including estimates of P, R, I_n, E_d, and T. These are area-standardized estimates expressed in mm, where 1 mm is equivalent to 10^3 g H_2O m^{-2} yr^{-1}. Note that T was standardized to the vegetated proportion of each watershed (Table 11), whereas the other water balance components were standardized to total watershed area. For this reason, $(R + I_n + T + E_d)$ exceeds P for some watersheds.

T values for the 'water-limited' watersheds of North America and Africa ranged from 229 ± 39 mm (North Saskatchewan River watershed) to 729 ± 133 mm (Upper Niger River watershed) (Figure 31a). In Australia, T for the Murray-Darling River watershed (325 ± 50 mm) was relatively low and similar to values for the watersheds of North America, whereas the highest T value for the previously-studied watersheds (979 ± 199 mm) was calculated for the Piracicaba River watershed of South America. A linear regression model for T with

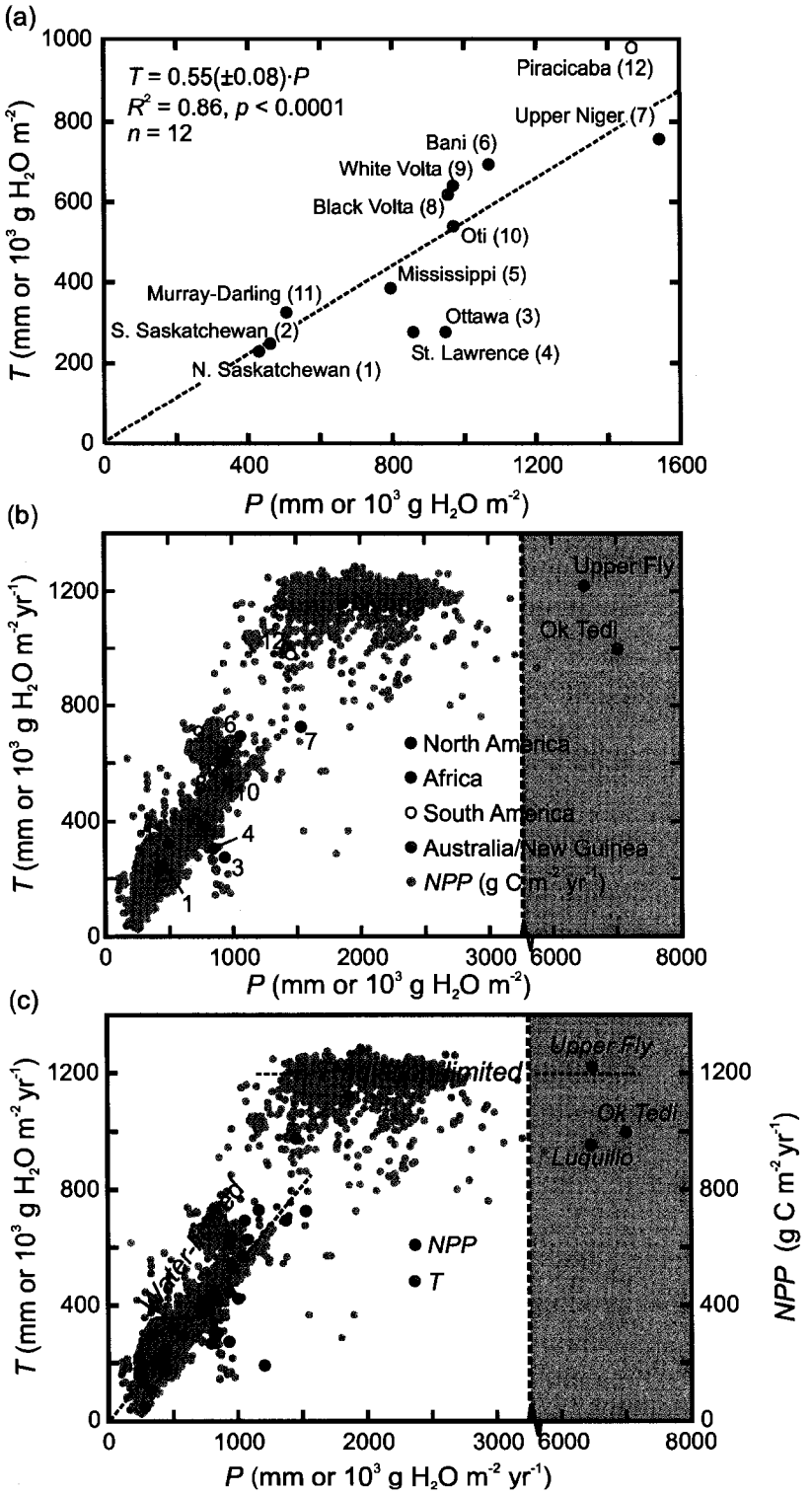


Figure 31. (a) The relationship between mean annual precipitation (P) and plant transpiration (T) for watersheds that receive less than 1500 mm of P; (b) the relationship between P and T for watersheds in North America, South America, Africa, Australia, and New Guinea (shaded region represents $P > 5500$ mm). Uncertainty for T as in Table 14. GPPDI *NPP* data shown as grey circles. 1. North Saskatchewan River, 2. South Saskatchewan River, 3. Ottawa River, 4. St. Lawrence River, 5. Mississippi River, 6. Bani River, 7. Upper Niger River, 8. Black Volta River, 9. White Volta River, 10. Oti River, 11. Murray-Darling River, 12. Piracicaba River (c) a comparison of T estimates with LTER and GPPDI *NPP* data.

respect to *ET* for the 'water-limited' watersheds can be described by the equation $T = (0.67 \pm 0.04) \cdot ET$ mm. This relationship indicates that in most water-limited regions, *T* represents the major conduit (67%) for moisture transfer from the continents to the atmosphere and that the other forms of evaporation represent a comparatively small proportion of *ET* by comparison.

In watersheds that receive less than 1500 mm of *P* (Table 14), the relationship between *T* and *P* can be described by the regression equation $T = (0.55 \pm 0.08) \cdot P$ g H_2O m^{-2} yr^{-1} ($R^2 = 0.86$, $p < 0.0001$, $n = 12$) (Figure 31a) (Note: the Upper Niger River watershed was included in the regression model as *P* for this watershed was 1535 ± 70 mm). This regression model indicates that under conditions of water limitation, *T* can be predicted as 55% of *P*, implying that approximately half of *P* is returned to the atmosphere via *T* each year. The similarity of *P-T* and *P-NPP* relationships (Figure 31c) suggests that water availability represents the fundamental restraint on the rate of plant growth in most temperate and sub-tropical ecosystems, as higher *P* corresponds to higher *T* and *NPP*. Moreover, the similar behavior of *T* (in 10^3 g H_2O m^{-2} yr^{-1}) and *NPP* (in g C m^{-2} yr^{-1}) in response to changes in *P* (in 10^3 g H_2O m^{-2} yr^{-1}) supports the assertion that the fluxes of carbon and water are inherently coupled via process of photosynthesis and that the water flux exceeds the carbon flux by several orders of magnitude in terms of mass. Although not intended as a quantitative assessment of the exact ratio between *T* and *NPP*, *T* and *NPP* can be predicted as approximately 55% and 0.05% of *P*, respectively. This disparity between *T* and *NPP* (approximately 1000 to 1) conforms to observations at leaf or plant scales despite *T* values representing water efflux from the multitude of vegetation types within a particular watershed.

In regions covered primarily by tropical rainforest, the availability of water and the intensity of solar radiation promote more rapid rates of photosynthesis and *NPP* values reach a plateau beyond which additional water input by *P* does not translate to higher rates of *NPP*

(Figure 31c). In their study of vegetation in Australia, [*Berry and Roderick*, 2004] estimate that T may reach a similar physiologic threshold between 800 – 1000 mm in high-rainfall regions of northern Australia. Estimates of T for the Ok Tedi and Upper Fly River watersheds appear to confirm the existence of this plateau as estimates of P for these watersheds were high (7056 mm and 6540 mm, respectively), yet T comprised only 10 – 15% of water input by P (1000 ± 1098 mm and 1223 ± 975 mm, respectively). Despite the uncertainty associated with estimates of T for the Ok Tedi and Upper Fly River watersheds, which precludes a quantitative comparison, a plateau of T values broadly affirms the proposal by [*Leigh*, 1999] that T values are relatively constant in tropical rainforests where water availability does not represent a rate-limiting factor. Instead of water, the intensity of incident solar radiation is the probable control on *NPP* and T [*Saleska et al.*, 2003; *Huete et al.*, 2006; *Mynenei et al.*, 2007; *Saleska et al.*, 2007]. It seems therefore reasonable to infer that both T and *NPP* are generally limited by water availability in most temperate and sub-tropical regions (P < 1500 mm), whereas in tropical regions, the intensity of incident solar radiation represents the limiting factor and the plateau is potentially due to the fact that the system is operating near a saturation point with respect to incident solar energy flux.

7.2 Sources of uncertainty related to component of the annual water balances

7.2.1 Spatial and temporal heterogeneity of the isotope composition of river water and precipitation and uncertainty related to the extent of internal hydrologic connectivity

Estimates of P were determined as the sums of the individual data points from [*New et al.*, 2000] that were completely contained by the gross boundaries of the selected watersheds. As such, the entire watershed was considered to receive at least some amount of precipitation that contributed to the overall P value for the watershed. However, only a proportion of gross watershed area typically contributes to annual river flow at the mouth [*Eash*, 1994], which

would seemingly lead to a discrepancy between the gross watershed area that was used to calculate mean annual precipitation and the net contributing area that determines the volume of annual river flow. For this reason, [*Ferguson et al.*, 2007] incorporated information on areas of non-contributing drainage within the North and South Saskatchewan River watersheds into their study of the annual water balances of these watersheds, which enabled P to be calculated specifically for the area that contributes to annual river flow. This enabled a more accurate description of the annual water balances of these watersheds, yet aside from the North and South Saskatchewan River, information on internal hydrologic connectivity was not available for any of the watersheds selected in this study. Gross watershed areas were therefore used by necessity to calculate P and R. However, since gross watershed areas were used to standardize P and R, both values are affected proportionally by differences in the assumed watershed area and hence although the magnitudes of P and R could be affected by changes in the area of contributing drainage, their relative proportions and relationship to each other are unaffected.

In terms of the representation of watershed-scale processes by samples of river water collected from the mouth, it is implicitly assumed that variability in the isotope composition of these samples are indicative of hydrologic processes that occur throughout the watershed. However, given the potential discrepancy between sampling locations for precipitation and the area that contributes to annual river flow, there exists the possibility that river flow may be biased towards areas that area not properly characterized in terms of the isotope composition of precipitation. With respect to the variability of the isotope composition of precipitation within a watershed, few options exist beyond calculating the LMWL based on available GNIP data or samples of precipitation collected by individual researchers. Logistically, samples are often collected from sites of convenience and as such, they may not

be comprehensive in terms of spatial coverage. To an extent, this critique applies to almost every watershed included in this study, but is particularly relevant to the more remote watersheds of Africa and New Guinea and to large watersheds, such as the Mississippi River watershed. In an attempt to circumscribe the internal variability in the isotope composition of precipitation within a watershed, 95% confidence intervals were assigned to each individual LMWL and the corresponding δ_I values calculated from the intersection of the LEL and LMWL. This calculation of uncertainty was used primarily because it could be applied consistently to each watershed and offers the ability to refine estimates of uncertainty in the future as additional data become available. Despite the acknowledgement that spatial variability of the isotope composition of precipitation within a watershed may exist, further discussion is entirely speculative without additional data and hence no further discussion is offered.

A further assumption regarding the representation of watershed-scale processes by samples of the outflow from a watershed is the assumption that $\delta^{18}O$ and $\delta^{2}H$ values of individual samples of river water are not merely a reflection of evaporation that occurs directly from the river surface itself. The validity of this assumption is difficult to evaluate with the data that are currently available, yet in terms of scale, the assumption that river water reflects regional hydrologic processes seems plausible as watershed areas are often several orders of magnitude larger than the area covered by the river surface itself and it is unlikely that a river is completely isolated from the surrounding drainage areas. Nonetheless, the disproportionately large contribution by certain areas within a watershed [*Ocampo et al.*, 2006] or the overprinting of watershed-scale processes by evaporation from the river [*Simpson and Herczeg*, 1991] represent sources of uncertainty that affect this study and are likely to be problematic for future hydrologic studies of comparable scale. Nonetheless, as

few data are available concerning the definition of non-contributing drainage areas in well-studied watersheds, the expectation that this process could be resolved based on the data currently available is unrealistic. Some small-scale studies suggest that the stable isotopes of water could offer information on the extent of internal hydrologic connectivity within a watershed and the contribution of specific water sources to soil water and surface waters [*Twining et al.*, 2006] yet these types of studies typically require a comprehensive, spatially-representative database of the isotope composition of groundwater, precipitation, and surfaces waters and a sampling frequency that corresponds with the temporal pattern of hydrologic variability. Consequently, inferences regarding the proportion of gross watershed area that contributes to river flow are beyond the capability of monthly sampling campaigns, although this source of uncertainty should be acknowledged and considered in planning future studies. More explicitly, it should be acknowledged that the repeated collection of monthly samples over a multi-year period is unlikely to enable a more quantitative description of internal hydrologic connectivity within a large watershed and this source of uncertainty may hinder future studies that focus on the hydrology of large watersheds.

7.2.2 Canopy evaporation and the infiltration of partially-evaporated waters

In section 7.1.4, LMWL were used to approximate the isotope composition of water input by precipitation to each watershed, yet in actuality, water input to the soil zone occurs after precipitation has interacted with the variety of vegetation types that comprise land-cover within the watershed. The magnitude of water that is re-evaporated before entering the soil zone was approximated by necessity via with data compiled from the literature for different vegetation types, yet the process of canopy evaporation itself was assumed to be a non-fractionating process. This means that the isotope composition of throughfall or stemflow (i.e. water that has interacted with vegetation) was considered indistinguishable

from that of incident precipitation. By definition, any water that enters the soil zone via stemflow or throughfall cannot be classified as part of I_n, as I_n refers exclusively to the proportion of incident precipitation that re-evaporates from the surfaces of plants before entering the soil zone. Nonetheless, some literature data suggests that the incorporation of partially-evaporated, ^{18}O-^{2}H-enriched water that remains on plant surfaces after a precipitation event could affect the isotope composition of net water input to the soil zone [*Twining et al.*, 2006]. The validity of assuming a negligible effect by I_n may vary depending on the type of vegetation and prevailing climatic conditions, yet aside from the model proposed by [*Gat*, 1996], there is no predictable association between vegetation type, climate, and rainfall intensity that would enable an appropriate correction to be applied to each watershed in this study. Moreover, data for numerous types of vegetation, including tropical rainforests [*Goller et al.*, 2005] and temperate forests [*Mora and Jahren*, 2001], suggests that the influence of partial evaporation on throughfall and stemflow is relatively minor and that $\delta^{18}O$ and $\delta^{2}H$ values of individual throughfall/stemflow samples typically plot along the LMWL. Based on the available data, it therefore seems reasonable to assume that the effect of partial evaporation on net water input to the soil zone would likely lie within the 95% confidence intervals ascribed to δ_I values for the various watersheds, which from Table 13, vary from 0.3‰ to 3.3‰. As the 95% confidence intervals for δ_I was incorporated into the E_v/I values from equation (24), the uncertainty associated with the effect of partial evaporation would be characterized by the uncertainty assigned to E_v/I values themselves. Moreover, the influence of partial evaporation would tend to reduce the isotope separation between δ_I and δ_S values, thereby decreasing the E_v/I, and increasing the proportion of ET attributed to non-fractionating water fluxes.

Chapter 8.

Summary and Conclusions

8.1 Isotope constraints on the sources of dissolved constituents

Samples of river water were collected from the major tributaries of the Fly River in order to test the hypothesis that the stable isotope composition of river water (δ^2H, $\delta^{18}O$) and dissolved carbon therein ($\delta^{13}C$) could provide some constraint on the sources of dissolved constituents. Based on the interpretation of carbon isotope data, HCO_3^-, the principal anion in river water, appears to be derived almost exclusively from the dissolution of carbonate minerals by acidity related to the oxidation of soil organic matter, whereas the dissolution of silicate minerals appears to be close to negligible by comparison. This implies that carbon derived from soil CO_2 is rarely contributed to river water without an equivalent amount of carbon derived from $CaCO_3$. The predominance of Ca^{2+} in river water, which is almost equivalent to HCO_3^- on a charge equivalency basis, supports this interpretation of the stable isotope data.

The principal source(s) of the other major cations, such as Mg^{2+}, Na^+, and K^+, is less certain, although the dissolution of cyclic salts and silicate minerals were identified as potential sources. However, separating the relative contributions of these sources was problematic given their low concentrations compared to Ca^{2+} and the substantial uncertainty that is inherent to the types of corrections required. In conclusion, although carbon isotope data offered some perspective on the different sources of dissolved constituents to the Fly River, these data supported the well-established conception that the susceptibility of carbonate minerals to dissolution causes these minerals to dominate the dissolved chemistry

of aqueous systems located in areas where carbonate minerals are present. With respect to oxygen and hydrogen isotopes, these data offered some perspective on the sources of moisture to New Guinea and the influence of evaporation over a period of several years, yet the higher-resolution data collected over a period of several days offered little indication that these data could be used to evaluate the contribution of pre-event soil waters to river flow at the scales considered in this study. The collection of a more comprehensive set of data may enable such an evaluation in the future, yet without the collection of samples at a frequency that corresponds to the variability of river flow, it is unlikely that these types of data will offer more information than can be deduced from conventional geochemical indices.

8.2 Terrestrial water and carbon cycling

Based on conventional annual water balances and the interpretation of the distribution of the stable isotopes of water ($\delta^{18}O$, $\delta^{2}H$) in rainfall and river water, a methodology for partitioning E_d and T was developed for a rainforest-dominated region of central New Guinea. This methodology was subsequently applied to thirteen other watersheds located in North America, South America, Africa, and Australia, which enabled an evaluation of the hypothesis that the terrestrial water and carbon cycles are inherently coupled via the terrestrial biosphere.

Linear regression models based on T and NPP suggest that approximately 55% of annual water input by P in 'water-limited' regions is returned to the atmosphere via T, where NPP corresponds to approximately 0.05% of P in terms of mass. In contrast to 'water-limited' regions, estimates of T (and NPP) for tropical regions that are not limited by water availability appear to remain relatively constant, defining a plateau at which plants may

function near a physiologic threshold defined by current solar conditions. As few estimates of *T* from tropical watersheds are currently available beyond this study, it is difficult to further ascertain the relationship between *T* and solar radiation although *NPP* and *T* generally define a similar pattern in response to variable *P* and a disparity between water vapor and carbon fluxes via the terrestrial biosphere was evident. Specifically, estimates of *T* for the watersheds of New Guinea suggest that for each square meter of vegetation, approximately one million grams of water are transferred to the atmosphere each year (i.e. for *T*, 1 mm = 10^3 g H_2O m^{-2} yr^{-1}). By comparison, *NPP* estimates for tropical rainforest biomes generally range from 800 to 3000 g C m^{-2} yr^{-1}, which in terms of mass, corresponds to a carbon flux from the atmosphere to the terrestrial biosphere that is several orders of magnitude smaller than *T*.

With respect to biosphere-atmosphere exchange processes, watershed-scale estimates of *T* offer a relatively unique perspective on terrestrial water cycling because they represent the efflux of water from a multitude of vegetation types. Similar estimates of a partitioned terrestrial water vapor flux are scarce beyond this study and hence the results are informative, emphasizing the inter-dependency between solar radiation and terrestrial processes and the considerable uncertainty that is currently associated with these aspects of the Earth system.

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Appendix 1. pH measurements and concentrations of major ions in samples of river water collected at monthly sites, February 2004 to April 2006

Location	Date	Year	pH	Ca^{2+}, µM	Mg^{2+}, µM	Na^{+}, µM	K^{+}, µM	SO_4^{2-}, µM	HCO_3^{-}, µM	Σ^{+}, µeq L^{-1}	Σ^{-}, µeq L^{-1}
Konkonda	17/02	2004	8.4	439	37	74	23	103	-	1049	-
Konkonda	23/03	2004	8.0	666	70	96	28	198	-	1596	-
Konkonda	30/04	2004	8.0	509	49	83	36	153	-	1235	-
Konkonda	15/06	2004	8.1	599	62	96	38	172	-	1456	-
Konkonda	25/06	2004	8.1	609	66	126	28	187	-	1504	-
Konkonda	09/07	2004	8.3	324	49	65	28	138	-	839	-
Konkonda	13/12	2004	8.0	467	41	70	23	146	689	1109	981
Konkonda	18/03	2005	8.2	-	-	-	-	-	-	-	-
Konkonda	30/04	2005	8.3	409	48	60	17	147	852	991	1146
Konkonda	10/05	2005	8.3	474	41	43	15	94	1098	1088	1286
Konkonda	19/05	2005	8.2	-	-	-	-	-	-	-	-
Konkonda	21/06	2005	8.2	499	41	87	26	145	1053	1193	1343
Konkonda	21/07	2005	8.5	518	52	82	24	77	770	1246	924
Konkonda	02/08	2005	8.1	599	82	87	26	181	1279	1475	1641
Konkonda	04/08	2005	8.2	-	-	-	-	-	-	-	-
Konkonda	20/09	2005	8.4	357	33	43	18	67	1475	841	1609
Konkonda	06/10	2005	8.3	429	37	52	18	43	1131	1002	1217
Konkonda	02/12	2005	8.1	516	49	78	23	113	984	1231	1210
Konkonda	16/12	2005	8.2	427	45	78	23	265	1054	1045	1584
Konkonda	31/01	2006	8.1	496	70	100	26	229	1230	1258	1688
Konkonda	15/02	2006	8.2	492	45	65	20	150	984	1159	1284
Konkonda	04/04	2006	8.2	-	-	-	-	-	-	-	-
Kiunga	17/02	2004	8.1	-	-	-	-	-	-	-	-
Kiunga	23/03	2004	7.9	492	37	48	10	84	934	1116	1102
Kiunga	30/04	2004	7.8	576	45	35	5	47	1066	1282	1160
Kiunga	15/06	2004	8.0	389	37	30	10	100	607	892	807
Kiunga	25/06	2004	7.9	654	41	43	26	47	1213	1459	1307
Kiunga	09/07	2004	8.0	676	41	87	8	29	1246	1529	1304
Kiunga	18/03	2005	7.9	349	41	26	8	86	869	814	1041

Kiunga	10/05	2005	7.7	491	40	38	8	81	1000	1108	1162
Kiunga	19/05	2005	7.5	-	-	-	-	-	-	-	-
Kiunga	21/06	2005	7.9	449	29	30	3	100	754	989	954
Kiunga	21/07	2005	7.8	499	41	43	8	21	885	1131	927
Kiunga	02/08	2005	7.9	504	37	40	7	99	820	1129	1018
Kiunga	04/08	2005	7.9	-	-	-	-	-	-	-	-
Kiunga	20/09	2005	7.6	624	41	43	8	67	1197	1381	1331
Kiunga	06/10	2005	7.8	434	29	26	8	39	754	960	832
Kiunga	02/12	2005	7.7	419	33	26	8	45	885	938	975
Kiunga	16/12	2005	7.8	539	41	39	8	75	951	1207	1101
Kiunga	31/01	2006	8.0	509	45	48	8	205	1131	1164	1541
Kiunga	15/02	2006	8.1	536	45	52	8	-	1066	1222	-
Kiunga	04/04	2006	7.9	387	33	30	8	-	705	878	-
Nukumba	17/02	2004	8.3	521	37	65	20	93	902	1201	1088
Nukumba	23/03	2004	7.7	497	41	43	15	92	1033	1134	1217
Nukumba	30/04	2004	8.0	447	41	48	18	104	738	1042	946
Nukumba	15/06	2004	7.8	599	41	43	26	87	1098	1349	1272
Nukumba	25/06	2004	8.0	599	41	87	18	92	1082	1385	1266
Nukumba	09/07	2004	8.1	399	53	52	20	84	1066	976	1234
Nukumba	13/12	2005	8.0	492	41	52	15	84	852	1133	1020
Nukumba	18/03	2005	8.0	-	-	-	-	-	-	-	-
Nukumba	30/04	2005	8.0	572	53	45	13	91	1180	1308	1362
Nukumba	10/05	2005	8.2	449	37	39	8	67	918	1019	1052
Nukumba	19/05	2005	8.0	-	-	-	-	-	-	-	-
Nukumba	21/06	2005	8.2	574	41	43	15	86	1180	1288	1352
Nukumba	21/07	2005	8.3	554	45	48	14	89	1033	1260	1211
Nukumba	02/08	2005	7.8	649	41	43	15	88	1164	1438	1340
Nukumba	04/08	2005	8.0	-	-	-	-	-	-	-	-
Nukumba	20/09	2005	8.1	449	37	48	15	98	1213	1035	1409
Nukumba	06/10	2005	8.1	506	37	39	15	55	1377	1140	1487
Nukumba	02/12	2006	7.5	482	37	39	13	97	803	1090	997
Nukumba	16/12	2006	8.0	526	45	61	18	246	1098	1221	1590
Nukumba	31/01	2006	7.9	506	41	52	13	-	984	1159	984
Nukumba	15/02	2006	8.2	479	37	39	13	-	902	1084	902

Nukumba	04/04	2006	8.0	-	-	-	-	-	-	-	-
Obo	17/02	2004	8.0	659	41	48	18	101	1066	1466	1268
Obo	23/03	2004	7.3	497	37	35	15	77	951	1118	1105
Obo	30/04	2004	7.7	586	45	57	20	83	934	1339	1100
Obo	15/06	2004	8	624	41	43	26	90	1131	1399	1311
Obo	25/06	2004	7.8	599	41	43	15	82	1148	1338	1312
Obo	09/07	2004	7.9	449	53	65	20	115	-	1089	-
Obo	13/12	2004	8.0	691	49	61	23	167	1016	1564	1350
Obo	18/03	2005	7.9	594	34	43	21	138	1098	1320	1374
Obo	30/04	2005	7.9	532	44	33	24	112	852	1209	1076
Obo	10/05	2005	7.5	599	41	43	15	108	1098	1338	1314
Obo	19/05	2005	7.9	-	-	-	-	-	-	-	-
Obo	21/06	2005	8.3	674	41	43	15	86	1213	1488	1385
Obo	21/07	2005	7.9	604	-	42	-	107	1082	1250	1296
Obo	27/07	2005	8.0	-	-	-	-	-	-	-	-
Obo	02/08	2005	7.9	699	41	43	15	66	1328	1538	1460
Obo	20/09	2005	7.7	574	41	57	15	84	1000	1302	1168
Obo	02/10	2005	8.1	621	45	48	18	61	1213	1398	1335
Obo	02/12	2005	8.0	561	37	43	13	109	902	1252	1120
Obo	16/12	2005	7.8	511	33	39	15	269	967	1142	1505
Obo	31/01	2006	7.5	579	37	43	15	194	1033	1290	1421
Obo	15/02	2006	8.2	559	37	43	15	119	984	1250	1222
Obo	04/04	2006	7.9	-	-	-	-	-	-	-	-
Str01	17/02	2004	8.1	614	91	117	18	130	1066	1545	1326
Str01	23/03	2004	8.0	571	82	91	13	121	1115	1410	1357
Str01	30/04	2004	8.0	721	103	109	18	147	1016	1775	1310
Str01	15/06	2004	8.1	541	37	91	54	110	1000	1301	1220
Str01	25/06	2004	8.1	506	86	104	13	101	869	1301	1071
Str01	09/07	2004	8.1	474	95	70	13	90	-	1221	-
Str01	13/12	2004	8.0	479	76	91	15	126	852	1216	1104
Str01	18/03	2005	8.0	-	-	-	-	-	-	-	-
Str01	30/04	2005	7.8	673	44	73	16	100	1213	1523	1413
Str01	10/05	2005	8.0	649	82	87	10	94	1344	1559	1532
Str01	19/05	2005	8.0	-	-	-	-	-	-	-	-

Str01	21/06	2005	8.2	524	82	87	13	85	852	1312	1022
Str01	21/07	2005	8.1	576	82	84	18	146	1115	1418	1407
Str01	27/07	2005	8.1	699	123	130	18	166	1623	1792	1955
Str01	20/09	2005	7.6	689	119	135	15	192	1639	1766	2023
Str01	02/10	2005	8.1	626	95	96	15	108	1852	1553	2068
Str01	02/12	2005	8.0	671	103	104	13	198	1180	1665	1576
Str01	16/12	2005	7.9	566	95	96	15	439	-	1433	878
Str01	31/01	2006	8.1	646	86	96	15	197	1557	1575	1951
Str01	15/02	2006	8.2	459	74	70	13	169	869	1149	1207
Str01	04/04	2006	8.0	-	-	-	-	-	-	-	-
Ogwa	17/02	2004	8.0	656	74	96	18	121	1098	1574	1340
Ogwa	23/03	2004	7.7	591	70	70	18	119	1148	1410	1386
Ogwa	30/04	2004	7.8	596	70	78	18	116	984	1428	1216
Ogwa	15/06	2004	8.0	599	82	87	26	115	1131	1475	1361
Ogwa	25/06	2004	8.0	549	82	87	13	86	1295	1362	1467
Ogwa	09/07	2004	8.0	374	70	70	15	125	1033	973	1283
Ogwa	18/03	2005	7.1	-	-	-	-	-	-	-	-
Ogwa	30/04	2005	7.9	-	-	-	-	-	-	-	-
Ogwa	10/05	2005	7.9	674	81	61	23	138	1213	1594	1489
Ogwa	19/05	2005	7.9	773	82	87	15	124	1557	1812	1805
Ogwa	21/06	2005	8.2	599	82	43	13	99	1213	1418	1411
Ogwa	21/07	2005	8.0	645	74	65	16	140	-	1519	280
Ogwa	27/07	2005	7.9	-	-	-	-	-	-	-	-
Ogwa	02/08	2005	8.1	699	82	87	18	125	1590	1667	1840
Ogwa	20/09	2005	7.7	641	86	96	15	109	1377	1565	1595
Ogwa	06/10	2005	8.0	681	91	96	15	65	1803	1655	1933
Ogwa	02/12	2005	8.0	654	78	78	13	150	1443	1555	1743
Ogwa	16/12	2005	7.9	541	70	74	15	241	1131	1311	1613
Ogwa	31/01	2006	7.8	681	70	70	15	202	1279	1587	1683
Ogwa	15/02	2006	8.3	-	-	-	-	-	-	-	-
Ogwa	04/04	2006	7.9	-	-	-	-	-	-	-	-

Appendix 2. Concentrations of major cations and anions in water samples collected from February 23 to March 6, 2007

					Values expressed in µM								Values expressed in µeq L^{-1}		
Location	Date	Time	T, °C	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	HCO_3^{-}	SO_4^{2-}	NO_3^{-}	Σ^{+}	Σ^{-}	$\Sigma^{+}-\Sigma^{-}$
River water															
Obo	23/02	1900	28.9	7.4	613	48	19	63	17	989	71	0	1404	1148	256
Obo	23/02	2100	28.9	7.4	616	48	18	61	15	1145	71	0	1407	1302	105
Obo	23/02	2300	28.9	7.4	623	49	19	65	19	1046	70	0	1428	1205	223
Obo	24/02	0100	28.8	7.4	638	50	19	62	18	1071	79	0	1457	1247	210
Obo	24/02	0300	28.8	7.4	658	52	19	67	19	1202	88	0	1506	1397	109
Obo	24/02	0500	28.7	7.4	670	53	19	68	18	1130	99	0	1533	1346	187
Obo	24/02	0700	28.6	7.3	685	55	20	72	22	1338	111	0	1572	1582	-10
Obo	24/02	0900	28.5	7.4	701	56	22	79	23	1266	117	0	1615	1523	92
Obo	24/02	1100	28.4	7.4	708	56	21	76	0	1306	115	0	1625	1536	89
Obo	24/02	1300	28.4	7.5	706	57	22	74	19	1424	113	0	1622	1669	-47
Obo	24/02	1500	28.4	7.5	671	55	22	72	18	1330	104	0	1546	1556	-10
Obo	24/02	1700	28.2	7.5	654	53	22	69	16	1414	96	0	1505	1622	-117
Obo	24/02	1900	28.1	7.6	634	52	22	67	14	1109	84	0	1461	1291	170
Obo	24/02	2100	27.9	7.6	612	50	21	64	13	1334	76	0	1409	1499	-90
Obo	24/02	2300	27.9	7.7	593	48	20	63	11	1239	69	0	1365	1388	-23
Obo	25/02	0100	27.8	7.7	597	47	19	58	12	1422	63	0	1365	1560	-195
Obo	25/02	0300	27.7	7.7	587	46	18	57	12	1295	60	0	1341	1427	-86
Obo	25/02	0500	27.6	7.7	576	45	19	55	13	1104	58	0	1316	1233	83
Obo	25/02	0700	27.6	7.7	569	45	19	55	12	1221	58	0	1302	1349	-47
Obo	25/02	0900	27.6	7.7	560	44	18	52	12	1281	58	0	1278	1409	-131
Obo	25/02	1100	27.0	8.1	557	43	18	53	14	1168	58	0	1271	1298	-27
Obo	25/02	1300	26.7	8.2	550	43	18	51	12	1092	59	0	1255	1222	33
Obo	25/02	1500	27.8	7.7	548	43	18	52	15	953	63	0	1252	1094	158
Obo	25/02	1700	27.7	7.7	551	43	18	52	13	985	62	0	1258	1122	136
Obo	25/02	1900	27.6	7.8	553	43	18	51	14	1007	67	0	1261	1155	106
Obo	25/02	2100	27.6	7.8	555	43	17	51	14	979	72	0	1264	1137	127
Obo	25/02	2300	27.7	7.7	552	43	18	51	13	995	72	0	1259	1152	107
Obo	26/02	0100	-	-	528	42	18	51	13	1097	70	0	1209	1250	-41
Obo	26/02	0300	-	-	521	41	17	51	12	1028	67	0	1192	1174	18
Obo	26/02	0500	-	-	518	41	18	52	12	920	65	0	1188	1062	126
Obo	26/02	0700	-	-	515	41	18	51	13	1131	65	0	1181	1274	-93
Obo	26/02	0900	-	-	513	41	17	50	13	949	63	0	1175	1088	87
Obo	26/02	1100	-	-	515	41	17	50	14	1008	68	0	1179	1158	21

Obo	26/02	1300	-	-	513	41	17	52	15	961	68	0	1177	1112	65
Obo	26/02	1500	-	-	515	41	17	51	14	966	69	0	1180	1118	62
Obo	26/02	1700	-	-	508	40	20	57	20	1153	67	0	1173	1307	-134
Obo	26/02	1900	-	-	507	40	19	55	15	1088	63	0	1168	1229	-61
Kiunga	01/03	0600	25.1	7.6	434	34	7	35	0	1167	14	0	978	1195	-217
Kiunga	01/03	0800	25.3	7.8	443	34	7	31	0	893	13	0	992	919	73
Kiunga	01/03	1000	25.5	7.5	348	27	7	27	0	853	9	0	784	871	-87
Kiunga	01/03	1200	25.6	7.3	332	26	9	33	0	858	9	0	758	876	-118
Kiunga	01/03	1400	25.6	7.6	315	25	8	26	0	753	9	0	714	771	-57
Kiunga	01/03	1600	25.9	7.1	291	25	7	27	0	567	8	0	666	583	83
Kiunga	01/03	1800	25.8	7.1	285	25	8	27	0	714	8	0	655	730	-75
Kiunga	01/03	2000	25.8	7.1	274	24	8	27	0	775	8	0	631	791	-160
Kiunga	01/03	2200	25.7	7.0	267	24	8	27	0	592	9	0	617	610	7
Kiunga	02/03	0000	25.7	7.0	262	24	8	26	0	586	9	0	606	604	2
Kiunga	02/03	0200	25.6	6.7	241	22	10	24	0	511	8	0	560	527	33
Kiunga	02/03	0400	25.6	6.9	265	25	7	27	0	636	8	0	614	652	-38
Kiunga	02/03	0600	25.6	6.9	263	25	7	28	0	522	8	0	611	538	73
Kiunga	02/03	0800	-	-	264	26	8	27	0	646	8	0	615	662	-47
Kiunga	02/03	1000	25.5	6.6	267	26	8	29	0	419	8	0	623	435	188
Kiunga	02/03	1200	25.5	6.6	266	27	8	30	0	488	9	0	624	506	118
Kiunga	02/03	1400	25.3	6.6	270	27	8	30	0	575	9	0	632	593	39
Kiunga	02/03	1600	25.4	6.6	271	27	7	29	0	618	9	0	632	636	-4
Kiunga	02/03	1800	25.9	7.0	273	28	8	30	0	765	9	0	640	783	-143
Kiunga	02/03	2000	25.9	6.8	277	28	8	29	0	603	9	0	647	621	26
Kiunga	02/03	2200	25.4	6.8	281	28	8	30	0	672	9	0	656	690	-34
Kiunga	03/03	0000	25.5	6.7	283	29	8	30	0	631	10	0	662	651	11
Kiunga	03/03	0200	24.8	6.9	288	29	8	31	0	719	10	0	673	739	-66
Kiunga	03/03	0400	24.6	6.9	288	29	8	31	0	481	9	0	673	499	174
Kiunga	03/03	0600	25.3	6.8	284	29	7	30	0	643	10	0	663	663	0
Kiunga	03/03	0800	25.3	6.8	286	29	7	32	0	744	10	0	669	764	-95
Kiunga	03/03	1000	26.1	6.8	290	30	8	33	0	508	9	0	681	526	155
Kiunga	03/03	1200	26.4	6.9	295	30	8	33	0	680	11	0	691	702	-11
Kiunga	03/03	1400	26.6	6.7	316	32	9	37	0	621	11	0	742	643	99
Kiunga	03/03	1600	26.4	6.7	317	31	8	36	0	634	12	0	740	658	82
Kiunga	03/03	1800	26.9	6.6	320	32	10	44	14	687	11	0	758	723	35
Kiunga	03/03	2000	26.4	6.5	329	32	9	39	10	548	12	0	770	582	188
Kiunga	03/03	2200	26.2	6.8	337	33	10	42	13	755	12	0	792	792	0

Kiunga	04/03	0000	26.4	7.0	348	34	9	39	0	897	12	0	812	921	-109
Kiunga	04/03	0200	25.1	6.9	363	35	8	38	0	828	13	0	842	854	-12
Kiunga	04/03	0400	25.6	7.0	369	35	7	38	0	960	12	0	853	984	-131
Kiunga	04/03	0600	24.0	7.4	373	36	7	38	0	1089	13	0	863	1115	-252
Kiunga	04/03	0800	26.1	7.1	382	37	8	40	0	976	13	0	886	1002	-116
Kiunga	04/03	1000	26.3	7.1	388	37	7	40	0	790	13	0	897	816	81
Kiunga	04/03	1200	26.3	7.1	393	37	8	41	0	960	14	0	909	988	-79
Kiunga	04/03	1400	26.9	7.2	402	38	7	41	0	820	14	0	928	848	80
Kiunga	04/03	1600	26.7	7.2	425	40	8	42	0	1145	15	0	980	1175	-195
Kiunga	04/03	1800	26.4	7.2	456	42	12	55	16	992	15	0	1063	1038	25
Kiunga	04/03	2000	26.3	7.4	494	44	7	45	0	1183	18	0	1128	1219	-91
Kiunga	04/03	2200	25.5	7.6	607	50	10	54	0	1488	22	0	1378	1532	-154
Kiunga	04/03	0000	26.4	7.7	629	52	9	50	0	1482	23	0	1421	1528	-107
Kiunga	05/03	0200	24.9	7.8	548	43	9	39	0	1410	19	0	1230	1448	-218
Kiunga	05/03	0400	24.6	7.8	533	41	10	42	0	1214	20	0	1200	1254	-54
Kiunga	05/03	0600	24.0	7.9	525	41	10	41	0	1162	17	0	1183	1196	-13
Kiunga	05/03	0800	23.9	7.9	492	38	10	41	0	1161	20	0	1111	1201	-90
Kiunga	05/03	1000	24.3	7.9	561	39	12	45	0	858	21	0	1257	900	357
Kiunga	05/03	1200	24.1	7.9	458	35	12	39	0	1237	20	0	1037	1277	-240
Konkonda	00/03	1520	28.3	7.7	510	59	30	107	34	1017	125	0	1275	1301	-26
Konkonda	00/03	1520	28.3	7.7	511	59	30	107	35	997	125	0	1277	1282	-5
Konkonda	00/03	1520	28.5	7.7	513	59	31	109	38	1106	124	0	1284	1392	-108
Konkonda	00/03	1520	28.5	7.7	512	59	32	112	40	799	123	0	1286	1085	201
Konkonda	00/03	1520	28.2	7.8	491	58	32	115	39	1153	124	0	1245	1440	-195
Konkonda	00/03	1520	28.2	7.8	490	58	32	116	40	1143	123	0	1244	1429	-185
Nukumba	01/03	0400	25.5	7.7	487	42	16	51	14	-	56	0	1125	-	-
Nukumba	01/03	0400	25.5	7.8	483	42	16	52	12	-	55	0	1118	-	-
Nukumba	01/03	0400	25.5	7.8	482	42	16	50	0	-	56	0	1114	-	-
Nukumba	01/03	0430	25.5	7.8	501	43	16	50	13	-	55	0	1154	-	-
Nukumba	01/03	0430	25.5	7.8	500	43	16	50	12	-	55	0	1152	-	-
Nukumba	01/03	0430	25.5	7.8	492	42	16	49	12	-	54	0	1133	-	-
Ogwa	25/02	1040	26.3	7.7	569	80	16	88	14	1474	89	0	1402	1666	-264
Ogwa	25/02	1050	26.2	7.7	558	79	16	88	15	1232	88	0	1378	1423	-45
Ogwa	25/02	1100	26.2	7.7	568	80	17	90	15	1056	87	0	1403	1245	158
Ogwa	25/02	1105	26.2	7.7	565	80	17	89	14	1167	87	0	1396	1355	41
Ogwa	25/02	1125	26.2	7.7	565	80	17	88	11	1253	87	0	1395	1438	-43
Ogwa	25/02	1130	26.2	7.7	555	78	16	88	15	1231	88	0	1370	1422	-52

Strickland	25/02	1235	25.4	7.7	558	95	18	115	18	1144	102	0	1439	1366	73
Strickland	25/02	1240	25.4	7.8	555	95	17	115	18	1466	105	0	1432	1694	-262
Strickland	25/02	1315	25.4	7.8	557	96	15	112	15	1171	104	0	1433	1394	39
Strickland	25/02	1320	25.5	7.8	556	96	16	117	18	1051	100	0	1437	1269	168
Strickland	25/02	1340	25.6	7.8	552	95	21	118	16	1448	103	0	1433	1670	-237
Strickland	25/02	1345	25.5	7.8	552	95	17	114	18	-	101	0	1425	-	-
Ok Menga	06/03	1500	21.2	7.3	867	107	8	41	0	-	37	7	1997	-	-
Ok Menga	06/03	1500	21.3	7.5	837	99	6	39	0	-	22	7	1917	-	-
Ok Menga	06/03	1500	21.6	7.5	837	99	6	37	0	-	22	6	1915	-	-
Ok Menga	06/03	1505	21.5	7.7	837	99	5	35	0	-	26	7	1912	-	-
Ok Menga	06/03	1505	21.5	7.7	836	99	5	35	0	-	23	6	1910	-	-
Ok Menga	06/03	1505	21.3	7.7	838	99	5	36	0	-	22	6	1915	-	-
Soilwater															
Airport	03/03	1625	26.8	4.7	7	6	8	13	11	50	0	12	47	61	-14
Airport	03/03	1640	26.8	4.7	4	5	8	14	12	54	0	11	40	66	-26
Ongas	03/03	1700	27.1	4.3	3	8	5	18	18	16	0	52	45	34	11
Ongas	03/03	1705	27.1	4.3	4	8	4	19	20	17	0	52	47	37	10
Ningerum	03/03	1720	27.6	4.6	2	5	2	23	20	25	0	33	39	45	-6
Ningerum	03/03	1725	27.5	4.5	2	5	1	22	22	21	0	32	37	43	-6
Groundwater															
Falomian	06/03	1230	18.8	3.4	7306	2056	450	859	293	0	36866	51	20033	-	-
Falomian	06/03	1230	18.8	3.4	7305	2046	447	850	201	0	32745	34	19999	-	-
Falomian	06/03	1230	18.9	3.4	7319	2092	467	891	156	0	33777	11	20180	-	-
Falomian	06/03	1235	18.7	3.4	7342	2010	423	805	209	0	34529	26	19932	-	-
Falomian	06/03	1235	18.7	3.4	7337	2030	437	832	126	0	35263	20	20003	-	-
Falomian	06/03	1235	18.7	3.4	7359	1995	415	788	114	0	35850	11	19911	-	-
Rainfall															
Obo	24/02	1530	25.0	6.8	2	1	1	7	0	95	0	0	14	95	-81
Obo	25/02	1850	24.1	7.7	3	1	6	14	16	70	0	0	28	86	-58
Kiunga	01/03	2210	22.6	8.2	8	3	5	29	45	126	0	0	56	171	-115
Kiunga	04/03	1025	24.4	6.8	7	2	4	22	27	90	0	0	44	117	-73

Appendix 3. Concentrations and $\delta^{13}C$ values of dissolved organic and inorganic carbon and $\delta^{18}O$ and $\delta^{2}H$ values of water for monthly river water samples collected from October 2003 to April 2006

Location	Date	Year	DOC, ppm C	$\delta^{13}C$ DOC, ‰	DIC, ppm C	$\delta^{13}C$ DIC, ‰	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰
Konkonda	06/10	2003	-	-	-	-	-7.1	-47
Konkonda	07/11	2003	-	-	-	-	-7.3	-
Konkonda	17/02	2004	1.9	-31.2	9.6	1.9	-9.4	-64
Konkonda	23/03	2004	2.1	-34.0	9.3	2.1	-10.8	-73
Konkonda	30/04	2004	1.6	-29.1	10.7	-10.2	-8.9	-59
Konkonda	15/06	2004	1.0	-29.0	7.7	-7.0	-8.3	-56
Konkonda	25/06	2004	0.7	-28.2	10.7	-8.5	-8.3	-57
Konkonda	09/07	2004	1.0	-29.4	12.2	-12.8	-7.3	-50
Konkonda	13/12	2004	2.3	-28.9	7.2	-7.9	-6.7	-44
Konkonda	18/03	2005	-	-	-	-	-7.5	-50
Konkonda	30/04	2005	1.4	-28.7	1.7	1.7	-9.1	-61
Konkonda	10/05	2005	1.6	-29.1	5.9	-5.6	-8.2	-55
Konkonda	19/05	2005	1.5	-28.4	7.3	-6.7	-8.5	-58
Konkonda	21/06	2005	0.6	0.0	11.8	-20.3	-7.6	-51
Konkonda	21/07	2005	1.2	-28.2	27.0	-19.6	-6.5	-43
Konkonda	02/08	2005	0.7	-26.8	29.3	-19.2	-7.6	-53
Konkonda	04/08	2005	2.0	-28.4	21.7	-21.0	-5.9	-38
Konkonda	20/09	2005	2.2	-28.5	3.7	-5.6	-7.1	-54
Konkonda	06/10	2005	1.6	-27.8	5.9	-5.9	-7.4	-56
Konkonda	02/12	2005	1.6	-28.0	10.7	-8.9	-9.1	-66
Konkonda	16/12	2005	4.4	-30.4	7.9	-7.4	-8.9	-65
Konkonda	31/01	2006	1.2	-27.4	9.4	-4.5	-9.8	-68
Konkonda	15/02	2006	1.8	-28.2	6.3	-4.2	-8.4	-59
Konkonda	04/04	2006	1.7	-28.0	8.4	-7.8	-11.1	-72
Kiunga	06/10	2003	-	-	-	-	-6.1	-44
Kiunga	07/11	2003	-	-	-	-	-6.3	-37
Kiunga	17/02	2004	2.6	-31.3	12.5	2.6	-9.8	-67
Kiunga	23/03	2004	1.7	-28.7	8.4	1.7	-10.7	-72
Kiunga	30/04	2004	2.9	-29.4	7.8	-12.4	-8.3	-56
Kiunga	15/06	2004	1.4	-28.8	10.0	-9.0	-8.3	-56
Kiunga	25/06	2004	1.3	-28.5	12.7	-10.5	-8.0	-56
Kiunga	09/07	2004	2.2	-29.8	10.1	-12.5	-6.8	-44
Kiunga	18/03	2005	2.6	-28.3	5.0	-6.4	-7.3	-50
Kiunga	10/05	2005	2.7	-29.6	6.7	-8.5	-7.9	-52
Kiunga	19/05	2005	2.4	-29.5	5.5	-10.3	-8.7	-57
Kiunga	21/06	2005	1.7	-28.8	25.2	-20.8	-7.0	-47
Kiunga	21/07	2005	1.7	-28.1	14.5	-18.9	-6.5	-43
Kiunga	02/08	2005	1.1	-26.6	18.0	-18.2	-7.1	-49
Kiunga	04/08	2005	2.8	-29.0	23.3	-20.9	-	-
Kiunga	20/09	2005	2.2	-27.7	9.3	-6.0	-6.9	-50
Kiunga	06/10	2005	2.3	-28.7	5.6	-7.5	-7.1	-54
Kiunga	02/12	2005	2.3	-28.6	9.87	-9.9	-	-
Kiunga	16/12	2005	1.8	-27.9	11.7	-11.0	-	-
Kiunga	31/01	2006	1.8	-28.3	7.6	-5.5	-	-
Kiunga	15/02	2006	2.5	-29.2	5.4	-7.3	-	-
Kiunga	04/04	2006	2.3	-28.7	8.9	-10.7	-	-
Nukumba	6/10	2003	-	-	-	-	-7.0	-47
Nukumba	7/11	2003	-	-	-	-	-6.7	-47
Nukumba	17/02	2004	2.2	-31.3	11.3	2.2	-9.4	-66
Nukumba	23/03	2004	3.4	-29.4	6.9	3.4	-11.1	-76

Nukumba	30/04	2004	2.5	-28.9	10.4	-13.0	-8.5	-58
Nukumba	15/06	2004	1.8	-29.1	9.0	-9.3	-8.7	-57
Nukumba	25/06	2004	0.9	-28.4	7.8	-9.8	-7.9	-54
Nukumba	09/07	2004	1.6	-29.6	13.1	-11.8	-7.6	-52
Nukumba	13/12	2005	3.0	-25.4	12.2	-12.3	-6.9	-46
Nukumba	18/03	2005	2.3	-28.2	-	-	-7.5	-51
Nukumba	30/04	2005	2.0	-28.4	5.5	-1.8	-10.5	-75
Nukumba	10/05	2005	5.6	-31.3	7.1	-7.3	-7.6	-51
Nukumba	19/05	2005	2.3	-28.7	5.7	-8.3	-8.8	-60
Nukumba	21/06	2005	1.5	-28.5	26.3	-20.3	-7.2	-49
Nukumba	21/07	2005	4.3	-30.8	25.5	-20.1	-6.7	-43
Nukumba	02/08	2005	1.4	-28.4	32.2	-18.7	-7.0	-47
Nukumba	04/08	2005	1.3	-26.4	20.5	-19.4	-	-
Nukumba	20/09	2005	2.2	-28.3	4.7	-4.5	-7.0	-52
Nukumba	06/10	2005	1.7	-27.9	6.9	-6.1	-7.1	-54
Nukumba	02/12	2006	2.8	-28.6	10.6	-11.8	-10.3	-78
Nukumba	16/12	2006	2.3	-27.8	11.1	-9.5	-9.5	-68
Nukumba	31/01	2006	2.6	-29.0	9.2	-7.9	-10.2	-75
Nukumba	15/02	2006	2.4	-29.0	7.6	-7.2	-8.4	-55
Nukumba	04/04	2006	2.2	-28.7	8.0	-8.1	-11.9	-89
Obo	06/10	2003	-	-	-	-	-6.4	-
Obo	07/11	2003	-	-	-	-	-6.9	-47
Obo	17/02	2004	2.7	-28.2	14.8	2.7	-9.1	-63
Obo	23/03	2004	3.4	-28.3	6.8	3.4	-10.8	-74
Obo	30/04	2004	2.4	-28.7	13.4	-11.2	-8.6	-61
Obo	15/06	2004	1.6	-28.6	9.8	-8.3	-8.5	-58
Obo	25/06	2004	2.1	-29.0	10.2	-10.4	-7.7	-55
Obo	09/07	2004	1.9	-29.0	11.6	-11.4	-7.1	-51
Obo	13/12	2004	2.8	-30.7	8.3	-4.4	-7.1	-48
Obo	18/03	2005	3.7	-28.2	8.8	-6.1	-6.9	-48
Obo	30/04	2005	4.5	-27.8	4.7	-1.0	-9.9	-71
Obo	10/05	2005	3.3	-28.5	10.1	-7.4	-8.9	-62
Obo	19/05	2005	3.0	-28.3	10.7	-8.0	-8.9	-62
Obo	21/06	2005	1.8	-27.7	29.7	-19.1	-7.4	-52
Obo	21/07	2005	1.7	-27.2	22.3	-16.9	-7.3	-51
Obo	27/07	2005	2.0	-28.1	26.5	-20.3	-6.7	-45
Obo	02/08	2005	1.8	-26.9	31.4	-18.4	-6.7	-44
Obo	20/09	2005	2.2	-28.0	9.4	-6.0	-5.8	-45
Obo	06/10	2005	2.0	-27.3	9.8	-6.5	-6.5	-48
Obo	02/12	2005	2.4	-28.2	7.5	-8.7	-9.4	-62
Obo	16/12	2005	3.1	-27.5	9.7	-8.8	-9.2	-68
Obo	31/01	2006	2.9	-28.5	12.0	-8.5	-10.1	-
Obo	15/02	2006	2.9	-28.4	10.6	-7.9	-9.3	-72
Obo	04/04	2006	2.3	-28.9	11.7	-10.2	-10.4	-70
Str01	06/10	2003	-	-	-	-	-9.5	-68
Str01	07/11	2003	-	-	-	-	-7.8	-55
Str01	17/02	2004	1.0	-33.5	14.6	1.0	-10.0	-67
Str01	23/03	2004	2.3	-28.0	8.7	2.3	-11.5	-79
Str01	30/04	2004	2.1	-28.5	15.7	-11.8	-9.7	-69
Str01	15/06	2004	2.0	-28.3	7.8	-7.7	-9.2	-65
Str01	25/06	2004	1.8	-28.9	6.2	-9.5	-8.7	-64
Str01	09/07	2004	1.8	-28.7	13.6	-13.4	-8.1	-57
Str01	13/12	2004	3.0	-26.5	9.7	-11.1	-7.1	-49
Str01	18/03	2005	4.1	-26.6	-	-	-7.5	-50
Str01	30/04	2005	3.0	-27.4	7.2	-1.5	-10.9	-81
Str01	10/05	2005	2.3	-27.8	9.1	-5.7	-8.9	-61

Str01	19/05	2005	2.5	-27.9	10.1	-5.8	-10.1	-70
Str01	21/06	2005	2.5	-28.1	24.1	-21.0	-8.6	-61
Str01	21/07	2005	2.2	-26.4	14.5	-11.4	-8.6	-61
Str01	27/07	2005	1.7	-27.6	33.4	-17.8	-8.9	-62
Str01	20/09	2005	1.7	-26.5	12.9	-5.1	-9.6	-71
Str01	06/10	2005	1.9	-27.4	12.1	-6.5	-8.5	-65
Str01	02/12	2005	2.5	-26.6	12.9	-7.3	-10.5	-76
Str01	16/12	2005	2.6	-26.9	11.1	-8.0	-10.4	-77
Str01	31/01	2006	2.6	-27.3	9.5	-4.3	-11.2	-77
Str01	15/02	2006	2.7	-28.4	9.9	-9.0	-9.3	-62
Str01	04/04	2006	2.4	-28.0	13.5	-8.7	-12.6	-90
Ogwa	06/10	2003	-	-	-	-	-7.1	-50
Ogwa	07/11	2003	-	-	-	-	-7.3	-
Ogwa	17/02	2004	2.3	-27.8	15.8	2.3	-9.6	-68
Ogwa	23/03	2004	2.8	-28.4	10.0	2.8	-11.0	-76
Ogwa	30/04	2004	2.2	-28.6	11.3	-9.5	-9.1	-65
Ogwa	15/06	2004	1.9	-28.3	9.5	-7.8	-8.9	-63
Ogwa	25/06	2004	2.1	-29.0	9.0	-9.6	-8.1	-58
Ogwa	09/07	2004	2.3	-28.8	15.5	-13.3	-7.6	-56
Ogwa	27/06	2004	3.1	-29.9	-	-	-7.2	-51
Ogwa	18/03	2005	3.2	-29.9	7.4	-6.2	-8.0	-54
Ogwa	30/04	2005	4.2	-27.7	5.7	-1.5	-10.1	-72
Ogwa	10/05	2005	2.7	-28.1	10.6	-5.5	-9.3	-65
Ogwa	19/05	2005	2.9	-28.0	13.3	-7.9	-9.4	-67
Ogwa	21/06	2005	1.91	-28.0	14.6	-19.5	-7.9	-56
Ogwa	21/07	2005	14.5	-26.7	15.7	-12.1	-7.9	-57
Ogwa	27/07	2005	2.1	-27.2	23.6	-16.4	-7.7	-53
Ogwa	02/08	2005	1.6	-27.4	28.3	-18.6	-8.0	-57
Ogwa	20/09	2005	2.0	-26.8	11.0	-5.2	-7.5	-54
Ogwa	06/10	2005	1.8	-27.0	13.8	-7.6	-8.1	-63
Ogwa	02/12	2005	2.8	-28.0	16.2	-10.4	-10.6	-81
Ogwa	16/12	2005	3.1	-27.1	10.9	-7.4	-10	-77
Ogwa	31/01	2006	2.9	-28.0	15.5	-8.5	-10.5	-75
Ogwa	15/02	2006	2.9	-28.0	9.3	-6.0	-9.5	-65
Ogwa	04/04	2006	2.5	-28.2	14.5	-9.5	-11.5	-79

Appendix 4. Speciation of dissolved inorganic carbon (DIC) in monthly river water samples collected from February 2004 to April 2006

Location	Date	Year	pH	T, K	DIC, mgC/L	DIC, umol/L	pK CO_2	pK_1	pK_2	pK $CaCO_3$	H_2CO_3, %	HCO_3^-, %	H_2CO_3, µmol/L	HCO_3^-, µmol/L
Konkonda	17/02	2004	8.4	301.15	9.6	799	1.50	6.33	10.31	8.50	1	98	7	783
Konkonda	23/03	2004	8.0	301.15	9.3	774	1.50	6.33	10.31	8.50	2	97	16	754
Konkonda	30/04	2004	8.0	301.15	10.7	891	1.50	6.33	10.31	8.50	2	97	19	868
Konkonda	15/06	2004	8.1	301.15	7.7	641	1.50	6.33	10.31	8.50	2	98	11	627
Konkonda	25/06	2004	8.1	301.15	10.7	891	1.50	6.33	10.31	8.50	2	98	15	871
Konkonda	09/07	2004	8.3	301.15	12.2	1016	1.50	6.33	10.31	8.50	1	98	11	995
Konkonda	13/12	2004	8.0	301.15	7.2	599	1.50	6.33	10.31	8.50	2	97	12	584
Konkonda	18/03	2005	8.2	301.15	-	-	1.50	6.33	10.31	8.50	1	98	-	-
Konkonda	30/04	2005	8.3	301.15	1.7	142	1.50	6.33	10.31	8.50	1	98	1	139
Konkonda	10/05	2005	8.3	301.15	5.9	491	1.50	6.33	10.31	8.50	1	98	5	481
Konkonda	19/05	2005	8.2	301.15	7.3	608	1.50	6.33	10.31	8.50	1	98	8	595
Konkonda	21/06	2005	8.2	301.15	11.8	982	1.50	6.33	10.31	8.50	1	98	13	962
Konkonda	21/07	2005	8.5	301.15	27	2248	1.50	6.33	10.31	8.50	1	98	15	2199
Konkonda	02/08	2005	8.1	301.15	29.3	2439	1.50	6.33	10.31	8.50	2	98	41	2384
Konkonda	02/08	2005	8.2	301.15	21.7	1807	1.50	6.33	10.31	8.50	1	98	24	1769
Konkonda	20/09	2005	8.4	301.15	3.7	308	1.50	6.33	10.31	8.50	1	98	3	302
Konkonda	06/10	2005	8.3	301.15	5.9	491	1.50	6.33	10.31	8.50	1	98	5	481
Konkonda	02/12	2005	8.1	301.15	10.7	891	1.50	6.33	10.31	8.50	2	98	15	871
Konkonda	16/12	2005	8.2	301.15	7.9	658	1.50	6.33	10.31	8.50	1	98	9	644
Konkonda	31/01	2006	8.1	301.15	9.4	783	1.50	6.33	10.31	8.50	2	98	13	765
Konkonda	15/02	2006	8.2	301.15	6.3	525	1.50	6.33	10.31	8.50	1	98	7	514
Konkonda	04/04	2006	8.2	301.15	8.4	699	1.50	6.33	10.31	8.50	1	98	9	685
Kiunga	17/02	2004	8.1	301.15	12.5	1041	1.50	6.33	10.31	8.50	2	98	17	1017
Kiunga	23/03	2004	7.9	301.15	8.4	699	1.50	6.33	10.31	8.50	3	97	18	678
Kiunga	30/04	2004	7.8	301.15	7.8	649	1.50	6.33	10.31	8.50	3	96	21	626
Kiunga	15/06	2004	8.0	301.15	10	833	1.50	6.33	10.31	8.50	2	97	17	811
Kiunga	25/06	2004	7.9	301.15	12.7	1057	1.50	6.33	10.31	8.50	3	97	28	1026
Kiunga	09/07	2004	8.0	301.15	10.1	841	1.50	6.33	10.31	8.50	2	97	18	819
Kiunga	18/03	2005	7.9	301.15	5.0	416	1.50	6.33	10.31	8.50	3	97	11	404

Kiunga	10/05	2005	7.7	301.15	6.7	558	1.50	6.33	10.31	8.50	4	96	23	534
Kiunga	19/05	2005	7.5	301.15	5.5	458	1.50	6.33	10.31	8.50	6	94	29	428
Kiunga	21/06	2005	7.9	301.15	25.2	2098	1.50	6.33	10.31	8.50	3	97	55	2035
Kiunga	21/07	2005	7.8	301.15	14.5	1207	1.50	6.33	10.31	8.50	3	96	39	1164
Kiunga	02/08	2005	7.9	301.15	18	1499	1.50	6.33	10.31	8.50	3	97	39	1454
Kiunga	04/08	2005	7.9	301.15	23.3	1940	1.50	6.33	10.31	8.50	3	97	51	1882
Kiunga	20/09	2005	7.6	301.15	9.3	774	1.50	6.33	10.31	8.50	5	95	39	733
Kiunga	06/10	2005	7.8	301.15	5.6	466	1.50	6.33	10.31	8.50	3	96	15	450
Kiunga	02/12	2005	7.7	301.15	9.87	822	1.50	6.33	10.31	8.50	4	96	34	786
Kiunga	16/12	2005	7.8	301.15	11.7	974	1.50	6.33	10.31	8.50	3	96	32	939
Kiunga	31/01	2006	8.0	301.15	7.6	633	1.50	6.33	10.31	8.50	2	97	13	617
Kiunga	15/02	2006	8.1	301.15	5.4	450	1.50	6.33	10.31	8.50	2	98	7	439
Kiunga	04/04	2006	7.9	301.15	8.9	741	1.50	6.33	10.31	8.50	3	97	19	719
Nukumba	17/02	2004	8.3	301.15	11.3	941	1.50	6.33	10.31	8.50	1	98	10	922
Nukumba	23/03	2004	7.7	301.15	6.9	574	1.50	6.33	10.31	8.50	4	96	23	550
Nukumba	30/04	2004	8.0	301.15	10.4	866	1.50	6.33	10.31	8.50	2	97	18	844
Nukumba	15/06	2004	7.8	301.15	9.0	749	1.50	6.33	10.31	8.50	3	96	24	723
Nukumba	25/06	2004	8.0	301.15	7.8	649	1.50	6.33	10.31	8.50	2	97	14	633
Nukumba	09/07	2004	8.1	301.15	13.1	1091	1.50	6.33	10.31	8.50	2	98	18	1066
Nukumba	13/12	2005	8.0	301.15	12.2	1016	1.50	6.33	10.31	8.50	2	97	21	990
Nukumba	18/03	2005	8.0	301.15	-	-	1.50	6.33	10.31	8.50	2	97	-	-
Nukumba	30/04	2005	8.0	301.15	5.5	458	1.50	6.33	10.31	8.50	2	97	10	446
Nukumba	10/05	2005	8.2	301.15	7.1	591	1.50	6.33	10.31	8.50	1	98	8	579
Nukumba	19/05	2005	8.0	301.15	5.7	475	1.50	6.33	10.31	8.50	2	97	10	462
Nukumba	21/06	2005	8.2	301.15	26.3	2190	1.50	6.33	10.31	8.50	1	98	29	2144
Nukumba	21/07	2005	8.3	301.15	25.5	2123	1.50	6.33	10.31	8.50	1	98	22	2080
Nukumba	02/08	2005	7.8	301.15	32.2	2681	1.50	6.33	10.31	8.50	3	96	88	2585
Nukumba	04/08	2005	8.0	301.15	20.5	1707	1.50	6.33	10.31	8.50	2	97	36	1663
Nukumba	20/09	2005	8.1	301.15	4.7	391	1.50	6.33	10.31	8.50	2	98	6	382
Nukumba	06/10	2005	8.1	301.15	6.9	574	1.50	6.33	10.31	8.50	2	98	10	561
Nukumba	02/12	2006	7.5	301.15	10.6	883	1.50	6.33	10.31	8.50	6	94	56	825
Nukumba	16/12	2006	8.0	301.15	11.1	924	1.50	6.33	10.31	8.50	2	97	19	900
Nukumba	31/01	2006	7.9	301.15	9.2	766	1.50	6.33	10.31	8.50	3	97	20	743

Nukumba	15/02	2006	8.2	301.15	7.6	633	1.50	6.33	10.31	8.50	1	98	8	620
Nukumba	04/04	2006		301.15	8.0	666	1.50	6.33	10.31	8.50	2	97	14	649
Obo	17/02	2004	8.0	303.15	14.8	1232	1.53	6.32	10.29	8.51	2	97	25	1201
Obo	23/03	2004	7.3	303.15	6.8	566	1.53	6.32	10.29	8.51	9	90	54	512
Obo	30/04	2004	7.7	303.15	13.4	1116	1.53	6.32	10.29	8.51	4	96	44	1068
Obo	15/06	2004	8.0	303.15	9.8	816	1.53	6.32	10.29	8.51	2	97	17	795
Obo	25/06	2004	7.8	303.15	10.2	849	1.53	6.32	10.29	8.51	3	96	27	819
Obo	09/07	2004	7.9	303.15	11.6	966	1.53	6.32	10.29	8.51	3	97	25	937
Obo	13/12	2004	8.0	303.15	8.3	691	1.53	6.32	10.29	8.51	2	97	14	674
Obo	18/03	2005	7.9	303.15	8.8	733	1.53	6.32	10.29	8.51	3	97	19	711
Obo	30/04	2005	7.9	303.15	4.7	391	1.53	6.32	10.29	8.51	3	97	10	380
Obo	10/05	2005	7.5	303.15	10.1	841	1.53	6.32	10.29	8.51	6	94	52	788
Obo	19/05	2005	7.9	303.15	10.7	891	1.53	6.32	10.29	8.51	3	97	23	865
Obo	21/06	2005	8.3	303.15	29.7	2473	1.53	6.32	10.29	8.51	1	98	25	2423
Obo	21/07	2005	7.9	303.15	22.3	1857	1.53	6.32	10.29	8.51	3	97	47	1802
Obo	27/07	2005	8.0	303.15	26.5	2206	1.53	6.32	10.29	8.51	2	97	45	2150
Obo	02/08	2005	7.9	303.15	31.4	2614	1.53	6.32	10.29	8.51	3	97	67	2537
Obo	20/09	2005	7.7	303.15	9.4	783	1.53	6.32	10.29	8.51	4	96	31	750
Obo	02/10	2005	8.1	303.15	9.8	816	1.53	6.32	10.29	8.51	2	98	13	798
Obo	02/12	2005	8.0	303.15	7.5	624	1.53	6.32	10.29	8.51	2	97	13	609
Obo	16/12	2005	7.8	303.15	9.7	808	1.53	6.32	10.29	8.51	3	96	26	779
Obo	31/01	2006	7.5	303.15	12	999	1.53	6.32	10.29	8.51	6	94	62	936
Obo	15/02	2006	8.2	303.15	10.6	883	1.53	6.32	10.29	8.51	1	98	11	864
Obo	04/04	2006	7.9	303.15	11.7	974	1.53	6.32	10.29	8.51	3	97	25	945
Str01	17/02	2004	8.1	303.15	14.6	1216	1.53	6.32	10.29	8.51	2	98	20	1188
Str01	23/03	2004	8.0	303.15	8.7	724	1.53	6.32	10.29	8.51	2	97	15	706
Str01	30/04	2004	8.0	303.15	15.7	1307	1.53	6.32	10.29	8.51	2	97	27	1274
Str01	15/06	2004	8.1	303.15	7.8	649	1.53	6.32	10.29	8.51	2	98	11	635
Str01	25/06	2004	8.1	303.15	6.2	516	1.53	6.32	10.29	8.51	2	98	8	505
Str01	09/07	2004	8.1	303.15	13.6	1132	1.53	6.32	10.29	8.51	2	98	18	1107
Str01	13/12	2004	8.0	303.15	9.7	808	1.53	6.32	10.29	8.51	2	97	16	787
Str01	18/03	2005	8.0	303.15	-	-	1.53	6.32	10.29	8.51	2	97	-	-
Str01	30/04	2005	7.8	303.15	7.2	599	1.53	6.32	10.29	8.51	3	96	19	578

Str01	10/05	2005	8.0	303.15	9.1	758	1.53	6.32	10.29	8.51	2	97	15	738
Str01	19/05	2005	8.0	303.15	10.1	841	1.53	6.32	10.29	8.51	2	97	17	820
Str01	21/06	2005	8.2	303.15	24.1	2006	1.53	6.32	10.29	8.51	1	98	26	1965
Str01	21/07	2005	8.1	303.15	14.5	1207	1.53	6.32	10.29	8.51	2	98	20	1180
Str01	27/07	2005	8.1	303.15	33.4	2781	1.53	6.32	10.29	8.51	2	98	45	2718
Str01	20/09	2005	7.6	303.15	12.9	1074	1.53	6.32	10.29	8.51	5	95	53	1019
Str01	02/10	2005	8.1	303.15	12.1	1007	1.53	6.32	10.29	8.51	2	98	16	985
Str01	02/12	2005	8.0	303.15	12.9	1074	1.53	6.32	10.29	8.51	2	97	22	1047
Str01	16/12	2005	7.9	303.15	11.1	924	1.53	6.32	10.29	8.51	3	97	24	897
Str01	31/01	2006	8.1	303.15	9.5	791	1.53	6.32	10.29	8.51	2	98	13	773
Str01	15/02	2006	8.2	303.15	9.9	824	1.53	6.32	10.29	8.51	1	98	11	807
Str01	04/04	2006	8.0	303.15	13.5	1124	1.53	6.32	10.29	8.51	2	97	23	1096
Ogwa	17/02	2004	8.0	303.15	15.8	1315	1.53	6.32	10.29	8.51	2	97	27	1282
Ogwa	23/03	2004	7.7	303.15	10.0	833	1.53	6.32	10.29	8.51	4	96	33	797
Ogwa	30/04	2004	7.8	303.15	11.3	941	1.53	6.32	10.29	8.51	3	96	30	908
Ogwa	15/06	2004	8.0	303.15	9.5	791	1.53	6.32	10.29	8.51	2	97	16	771
Ogwa	25/06	2004	8.0	303.15	9.0	749	1.53	6.32	10.29	8.51	2	97	15	730
Ogwa	09/07	2004	8.0	303.15	15.5	1290	1.53	6.32	10.29	8.51	2	97	26	1258
Ogwa	18/03	2005	7.1	303.15	7.4	616	1.53	6.32	10.29	8.51	14	86	87	528
Ogwa	30/04	2005	7.9	303.15	5.7	475	1.53	6.32	10.29	8.51	3	97	12	461
Ogwa	10/05	2005	7.9	303.15	10.6	883	1.53	6.32	10.29	8.51	3	97	22	857
Ogwa	19/05	2005	7.9	303.15	13.3	1107	1.53	6.32	10.29	8.51	3	97	28	1075
Ogwa	21/06	2005	8.2	303.15	14.6	1216	1.53	6.32	10.29	8.51	1	98	16	1190
Ogwa	21/07	2005	8.0	303.15	15.7	1307	1.53	6.32	10.29	8.51	2	97	27	1274
Ogwa	27/07	2005	7.9	303.15	23.6	1965	1.53	6.32	10.29	8.51	3	97	50	1907
Ogwa	02/08	2005	8.1	303.15	28.3	2356	1.53	6.32	10.29	8.51	2	98	38	2303
Ogwa	20/09	2005	7.7	303.15	11.0	916	1.53	6.32	10.29	8.51	4	96	36	877
Ogwa	06/10	2005	8.0	303.15	13.8	1149	1.53	6.32	10.29	8.51	2	97	23	1120
Ogwa	02/12	2005	8.0	303.15	16.2	1349	1.53	6.32	10.29	8.51	2	97	27	1315
Ogwa	16/12	2005	7.9	303.15	10.9	908	1.53	6.32	10.29	8.51	3	97	23	881
Ogwa	31/01	2006	7.8	303.15	15.5	1290	1.53	6.32	10.29	8.51	3	96	41	1245
Ogwa	15/02	2006	8.3	303.15	9.3	774	1.53	6.32	10.29	8.51	1	98	8	759
Ogwa	04/04	2006	7.9	303.15	14.5	1207	1.53	6.32	10.29	8.51	3	97	31	1172

Appendix 5. Speciation of dissolved inorganic carbon (DIC) in water samples collected from February 23 to March 6, 2007

Location	Date	Time	pH	*T*, K	*DIC*, mg C/L	*DIC*, µmol/L	pK CO_2	pK_1	pK_2	pK $CaCO_3$	H_2CO_3, %	HCO_3^-, %	H_2CO_3, µmol/L	HCO_3^-, µmol/L
Obo-1	23/02	1900	7.4	302.05	12.9	1073	1.51	6.33	10.30	8.50	8	92	83	989
Obo-2	23/02	2100	7.4	302.05	14.9	1243	1.51	6.33	10.30	8.50	8	92	96	1145
Obo-3	23/02	2300	7.4	302.05	13.6	1136	1.51	6.33	10.30	8.50	8	92	88	1046
Obo-4	24/02	0100	7.4	301.95	14.0	1163	1.51	6.33	10.30	8.50	8	92	90	1071
Obo-5	24/02	0300	7.4	301.95	15.7	1305	1.51	6.33	10.30	8.50	8	92	101	1202
Obo-6	24/02	0500	7.4	301.85	14.7	1226	1.51	6.33	10.30	8.50	8	92	95	1130
Obo-7	24/02	0700	7.3	301.75	17.8	1482	1.51	6.33	10.30	8.50	10	90	142	1338
Obo-8	24/02	0900	7.4	301.65	16.5	1375	1.51	6.33	10.30	8.50	8	92	107	1266
Obo-9	24/02	1100	7.4	301.55	17.0	1418	1.51	6.33	10.30	8.50	8	92	111	1306
Obo-10	24/02	1300	7.5	301.55	18.3	1522	1.51	6.33	10.30	8.50	6	94	96	1424
Obo-11	24/02	1500	7.5	301.55	17.1	1422	1.51	6.33	10.30	8.50	6	94	90	1330
Obo-12	24/02	1700	7.5	301.35	18.2	1512	1.51	6.33	10.31	8.50	6	94	95	1414
Obo-13	24/02	1900	7.6	301.25	14.1	1171	1.50	6.33	10.31	8.50	5	95	60	1109
Obo-14	24/02	2100	7.6	301.05	16.9	1409	1.50	6.33	10.31	8.50	5	95	72	1334
Obo-15	24/02	2300	7.7	301.05	15.6	1295	1.50	6.33	10.31	8.50	4	96	53	1239
Obo-16	25/02	0100	7.7	300.95	17.9	1486	1.50	6.33	10.31	8.50	4	96	61	1422
Obo-17	25/02	0300	7.7	300.85	16.3	1354	1.50	6.33	10.31	8.50	4	96	56	1295
Obo-18	25/02	0500	7.7	300.75	13.9	1154	1.50	6.33	10.31	8.49	4	96	47	1104
Obo-19	25/02	0700	7.7	300.75	15.3	1276	1.50	6.33	10.31	8.49	4	96	52	1221
Obo-20	25/02	0900	7.7	300.75	16.1	1340	1.50	6.33	10.31	8.49	4	96	55	1281
Obo-21	25/02	1100	8.1	300.15	14.4	1196	1.49	6.34	10.32	8.49	2	98	20	1168
Obo-22	25/02	1300	8.2	299.85	13.4	1116	1.49	6.34	10.32	8.49	1	98	15	1092
Obo-23	25/02	1500	7.7	300.95	12.0	996	1.50	6.33	10.31	8.50	4	96	41	953
Obo-24	25/02	1700	7.7	300.85	12.4	1030	1.50	6.33	10.31	8.50	4	96	42	985
Obo-25	25/02	1900	7.8	300.75	12.6	1045	1.50	6.33	10.31	8.49	3	96	34	1007
Obo-26	25/02	2100	7.8	300.75	12.2	1016	1.50	6.33	10.31	8.49	3	96	33	979
Obo-27	25/02	2300	7.7	300.85	12.5	1040	1.50	6.33	10.31	8.50	4	96	43	995
Obo-28	26/02	0100	7.7	301.15	13.8	1146	1.50	6.33	10.31	8.50	4	96	47	1097
Obo-29	26/02	0300	7.7	301.15	12.9	1075	1.50	6.33	10.31	8.50	4	96	44	1028

Obo-30	26/02	0500	7.7	301.15	11.6	962	1.50	6.33	10.31	8.50	4	96	39	920
Obo-31	26/02	0700	7.7	301.15	14.2	1182	1.50	6.33	10.31	8.50	4	96	48	1131
Obo-32	26/02	0900	7.7	301.15	11.9	992	1.50	6.33	10.31	8.50	4	96	40	949
Obo-33	26/02	1100	7.7	301.15	12.7	1054	1.50	6.33	10.31	8.50	4	96	43	1008
Obo-34	26/02	1300	7.7	301.15	12.1	1005	1.50	6.33	10.31	8.50	4	96	41	961
Obo-35	26/02	1500	7.7	301.15	12.1	1010	1.50	6.33	10.31	8.50	4	96	41	966
Obo-36	26/02	1700	7.7	301.15	14.5	1205	1.50	6.33	10.31	8.50	4	96	49	1153
Obo-37	26/02	1900	8.2	301.15	13.4	1111	1.50	6.33	10.31	8.50	1	98	15	1088
Kiunga-1	01/03	0600	7.6	298.25	14.8	1235	1.47	6.35	10.33	8.48	5	95	65	1167
Kiunga-2	01/03	0800	7.8	298.45	11.1	927	1.47	6.35	10.33	8.48	3	96	31	893
Kiunga-3	01/03	1000	7.5	298.65	11.0	914	1.47	6.35	10.33	8.48	7	93	60	853
Kiunga-4	01/03	1200	7.3	298.75	11.5	954	1.47	6.34	10.33	8.48	10	90	95	858
Kiunga-5	01/03	1400	7.6	298.75	9.6	796	1.47	6.34	10.33	8.48	5	95	42	753
Kiunga-6	01/03	1600	7.1	299.05	8.0	667	1.48	6.34	10.33	8.48	15	85	99	567
Kiunga-7	01/03	1800	7.1	298.95	10.1	840	1.48	6.34	10.33	8.48	15	85	125	714
Kiunga-8	01/03	2000	7.1	298.95	11.0	912	1.48	6.34	10.33	8.48	15	85	136	775
Kiunga-9	01/03	2200	7.0	298.85	8.7	723	1.47	6.34	10.33	8.48	18	82	131	592
Kiunga-10	02/03	0000	7.0	298.85	8.6	716	1.47	6.34	10.33	8.48	18	82	130	586
Kiunga-11	02/03	0200	6.7	298.75	8.8	736	1.47	6.34	10.33	8.48	31	69	225	511
Kiunga-12	02/03	0400	6.9	298.75	9.8	813	1.47	6.34	10.33	8.48	22	78	177	636
Kiunga-13	02/03	0600	6.9	298.75	8.0	668	1.47	6.34	10.33	8.48	22	78	145	522
Kiunga-14	02/03	0800	6.9	298.75	9.9	827	1.47	6.34	10.33	8.48	22	78	180	646
Kiunga-15	02/03	1000	6.6	298.65	7.8	652	1.47	6.35	10.33	8.48	36	64	233	419
Kiunga-16	02/03	1200	6.6	298.65	9.1	759	1.47	6.35	10.33	8.48	36	64	271	488
Kiunga-17	02/03	1400	6.6	298.45	10.8	897	1.47	6.35	10.33	8.48	36	64	321	575
Kiunga-18	02/03	1600	6.6	298.55	11.6	962	1.47	6.35	10.33	8.48	36	64	344	618
Kiunga-19	02/03	1800	7.0	299.05	11.2	933	1.48	6.34	10.33	8.48	18	82	168	765
Kiunga-20	02/03	2000	6.8	299.05	9.8	813	1.48	6.34	10.33	8.48	26	74	210	603
Kiunga-21	02/03	2200	6.8	298.55	10.9	908	1.47	6.35	10.33	8.48	26	74	236	672
Kiunga-22	03/03	0000	6.7	298.65	10.9	910	1.47	6.35	10.33	8.48	31	69	279	631
Kiunga-23	03/03	0200	6.9	297.95	11.1	922	1.46	6.35	10.34	8.48	22	78	203	719
Kiunga-24	03/03	0400	6.9	297.75	7.4	617	1.46	6.35	10.34	8.48	22	78	136	481

Kiunga-25	03/03	0600	6.8	298.45	10.5	870	1.47	6.35	10.33	8.48	26	74	227	643
Kiunga-26	03/03	0800	6.8	298.45	12.1	1006	1.47	6.35	10.33	8.48	26	74	262	744
Kiunga-27	03/03	1000	6.8	299.25	8.2	685	1.48	6.34	10.32	8.49	26	74	177	508
Kiunga-28	03/03	1200	6.9	299.55	10.4	868	1.48	6.34	10.32	8.49	22	78	187	680
Kiunga-29	03/03	1400	6.7	299.75	10.7	892	1.49	6.34	10.32	8.49	30	70	270	621
Kiunga-30	03/03	1600	6.7	299.55	10.9	911	1.48	6.34	10.32	8.49	30	70	277	634
Kiunga-31	03/03	1800	6.6	300.05	12.8	1062	1.49	6.34	10.32	8.49	35	65	375	687
Kiunga-32	03/03	2000	6.5	299.55	11.1	927	1.48	6.34	10.32	8.49	41	59	379	548
Kiunga-33	03/03	2200	6.8	299.35	12.2	1017	1.48	6.34	10.32	8.49	26	74	262	755
Kiunga-34	04/03	0000	7.0	299.55	13.1	1094	1.48	6.34	10.32	8.49	18	82	196	897
Kiunga-35	04/03	0200	6.9	298.25	12.7	1061	1.47	6.35	10.33	8.48	22	78	232	828
Kiunga-36	04/03	0400	7.0	298.75	14.1	1173	1.47	6.34	10.33	8.48	18	82	212	960
Kiunga-37	04/03	0600	7.4	297.15	14.3	1188	1.45	6.36	10.34	8.47	8	92	98	1089
Kiunga-38	04/03	0800	7.1	299.25	13.8	1147	1.48	6.34	10.32	8.49	15	85	170	976
Kiunga-39	04/03	1000	7.1	299.45	11.1	927	1.48	6.34	10.32	8.49	15	85	137	790
Kiunga-40	04/03	1200	7.1	299.45	13.5	1127	1.48	6.34	10.32	8.49	15	85	167	960
Kiunga-41	04/03	1400	7.2	300.05	11.2	933	1.49	6.34	10.32	8.49	12	88	112	820
Kiunga-42	04/03	1600	7.2	299.85	15.7	1303	1.49	6.34	10.32	8.49	12	88	157	1145
Kiunga-43	04/03	1800	7.2	299.55	13.6	1130	1.48	6.34	10.32	8.49	12	88	137	992
Kiunga-44	04/03	2000	7.4	299.45	15.5	1287	1.48	6.34	10.32	8.49	8	92	103	1183
Kiunga-45	04/03	2200	7.6	298.65	18.9	1574	1.47	6.35	10.33	8.48	5	95	83	1488
Kiunga-46	04/03	0000	7.7	299.55	18.6	1550	1.48	6.34	10.32	8.49	4	96	65	1482
Kiunga-47	05/03	0200	7.8	298.05	17.6	1464	1.46	6.35	10.33	8.48	3	96	50	1410
Kiunga-48	05/03	0400	7.8	297.75	15.1	1261	1.46	6.35	10.34	8.48	3	96	43	1214
Kiunga-49	05/03	0600	7.9	297.15	14.4	1200	1.45	6.36	10.34	8.47	3	97	33	1162
Kiunga-50	05/03	0800	7.9	297.05	14.4	1198	1.45	6.36	10.34	8.47	3	97	33	1161
Kiunga-51	05/03	1000	7.9	297.45	10.6	885	1.46	6.35	10.34	8.48	3	97	24	858
Kiunga-52	05/03	1200	7.9	297.25	15.3	1276	1.45	6.35	10.34	8.48	3	97	35	1237
Konkonda-1	00/03	1520	7.7	301.45	12.8	1062	1.51	6.33	10.30	8.50	4	96	43	1017
Konkonda-2	00/03	1520	7.7	301.45	12.5	1042	1.51	6.33	10.30	8.50	4	96	42	997
Konkonda-3	00/03	1520	7.7	301.65	13.9	1156	1.51	6.33	10.30	8.50	4	96	47	1106
Konkonda-4	00/03	1520	7.7	301.65	10.0	835	1.51	6.33	10.30	8.50	4	96	34	799

Konkonda-5	00/03	1520	7.8	301.35	14.4	1196	1.51	6.33	10.31	8.50	3	96	39	1153
Konkonda-6	00/03	1520	7.8	301.35	14.2	1186	1.51	6.33	10.31	8.50	3	96	39	1143
Str-1	25/02	1235	7.7	298.55	14.4	1197	1.47	6.35	10.33	8.48	4	96	51	1144
Str-2	25/02	1240	7.8	298.55	18.3	1522	1.47	6.35	10.33	8.48	3	96	52	1466
Str-3	25/02	1315	7.8	298.55	14.6	1216	1.47	6.35	10.33	8.48	3	96	41	1171
Str-4	25/02	1320	7.8	298.65	13.1	1091	1.47	6.35	10.33	8.48	3	96	37	1051
Str-5	25/02	1340	7.8	298.75	18.1	1503	1.47	6.34	10.33	8.48	3	96	51	1448
Ogwa-1	25/02	1040	7.7	299.45	18.5	1542	1.48	6.34	10.32	8.49	4	96	64	1474
Ogwa-2	25/02	1050	7.7	299.35	15.5	1289	1.48	6.34	10.32	8.49	4	96	54	1232
Ogwa-3	25/02	1100	7.7	299.35	13.3	1105	1.48	6.34	10.32	8.49	4	96	46	1056
Ogwa-4	25/02	1105	7.7	299.35	14.7	1221	1.48	6.34	10.32	8.49	4	96	51	1167
Ogwa-5	25/02	1125	7.7	299.35	15.8	1311	1.48	6.34	10.32	8.49	4	96	55	1253
Ogwa-6	25/02	1130	7.7	299.35	15.5	1288	1.48	6.34	10.32	8.49	4	96	54	1231
Falomian-1	06/03	1230	3.4	291.95	2.3	191	1.39	6.39	10.39	8.45	100	0	191	0
Falomian-2	06/03	1230	3.4	291.95	2.4	201	1.39	6.39	10.39	8.45	100	0	200	0
Falomian-3	06/03	1230	3.4	292.05	1.8	147	1.39	6.39	10.39	8.45	100	0	147	0
Falomian-4	06/03	1235	3.4	291.85	2.2	180	1.38	6.39	10.40	8.45	100	0	180	0
Falomian-5	06/03	1235	3.4	291.85	1.8	152	1.38	6.39	10.40	8.45	100	0	152	0
Falomian-6	06/03	1235	3.4	291.85	1.9	154	1.38	6.39	10.40	8.45	100	0	154	0
Kiunga airport-1	03/03	1625	4.7	299.95	26.6	2213	1.49	6.34	10.32	8.49	98	2	2163	50
Kiunga airport-2	03/03	1640	4.7	299.95	28.7	2389	1.49	6.34	10.32	8.49	98	2	2336	54
Ongas-1	03/03	1700	4.3	300.25	20.9	1739	1.49	6.34	10.31	8.49	99	1	1723	16
Ongas-2	03/03	1705	4.3	300.25	22.0	1828	1.49	6.34	10.31	8.49	99	1	1812	17
Ninegrum-1	03/03	1720	4.6	300.75	16.7	1393	1.50	6.33	10.31	8.49	98	2	1368	25
Ninegrum-2	03/03	1725	4.5	300.65	17.8	1481	1.50	6.33	10.31	8.49	99	1	1460	21
Obo_rain-1	24/02	1530	6.8	298.15	1.5	128	1.47	6.35	10.33	8.48	26	74	34	95
Obo_rain-2	25/02	1850	7.7	297.25	0.9	73	1.45	6.35	10.34	8.48	4	95	3	70
Kiunga_rain-1	01/03	2210	8.2	295.75	1.5	128	1.44	6.36	10.36	8.47	1	98	2	126
Kiunga_rain-2	04/03	1025	6.8	297.55	1.5	122	1.46	6.35	10.34	8.48	26	74	32	90

Appendix 6. $\delta^{13}C$ values of bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3) in monthly river water samples collected from February 2004 to April 2006

Location	Date	Year	pH	T, K	H_2CO_3, µmol/L	HCO_3^-, µmol/L	$\delta^{13}C$ DIC, ‰	$\alpha CO_{2(aq)} - CO_{2(g)}$, ‰	$\alpha HCO_{3\,(aq)}^- - CO_{2(g)}$, ‰	$\alpha CO_{3\,(aq)}^{2-} - CO_{2(g)}$, ‰	$\alpha CaCO_3 - CO_{2(g)}$, ‰	$\delta^{13}C$ H_2CO_3, ‰	$\delta^{13}C$ HCO_3^-, ‰
Konkonda	17/02	2004	8.4	301.15	7	783	1.9	-1.05	7.62	6.19	-9.95	-5.5	2.0
Konkonda	23/03	2004	8.0	301.15	16	754	2.1	-1.05	7.62	6.19	-9.95	-5.3	2.3
Konkonda	30/04	2004	8.0	301.15	19	868	-10.2	-1.05	7.62	6.19	-9.95	-17.6	-10.1
Konkonda	15/06	2004	8.1	301.15	11	627	-7.0	-1.05	7.62	6.19	-9.95	-14.4	-6.9
Konkonda	25/06	2004	8.1	301.15	15	871	-8.5	-1.05	7.62	6.19	-9.95	-15.9	-8.4
Konkonda	09/07	2004	8.3	301.15	11	995	-12.8	-1.05	7.62	6.19	-9.95	-20.2	-12.8
Konkonda	13/12	2004	8.0	301.15	12	584	-7.9	-1.05	7.62	6.19	-9.95	-15.3	-7.8
Konkonda	18/03	2005	8.2	301.15	-	-	-	-1.05	7.62	6.19	-9.95	-	-
Konkonda	30/04	2005	8.3	301.15	1	139	1.7	-1.05	7.62	6.19	-9.95	-5.7	1.8
Konkonda	10/05	2005	8.3	301.15	5	481	-5.6	-1.05	7.62	6.19	-9.95	-13.0	-5.6
Konkonda	19/05	2005	8.2	301.15	8	595	-6.7	-1.05	7.62	6.19	-9.95	-14.1	-6.7
Konkonda	21/06	2005	8.2	301.15	13	962	-20.3	-1.05	7.62	6.19	-9.95	-27.7	-20.4
Konkonda	21/07	2005	8.5	301.15	15	2199	-19.6	-1.05	7.62	6.19	-9.95	-27.0	-19.9
Konkonda	02/08	2005	8.1	301.15	41	2384	-19.2	-1.05	7.62	6.19	-9.95	-26.6	-19.2
Konkonda	02/08	2005	8.2	301.15	24	1769	-21	-1.05	7.62	6.19	-9.95	-28.4	-21.1
Konkonda	20/09	2005	8.4	301.15	3	302	-5.6	-1.05	7.62	6.19	-9.95	-13.0	-5.6
Konkonda	06/10	2005	8.3	301.15	5	481	-5.9	-1.05	7.62	6.19	-9.95	-13.3	-5.9
Konkonda	02/12	2005	8.1	301.15	15	871	-8.9	-1.05	7.62	6.19	-9.95	-16.3	-8.8
Konkonda	16/12	2005	8.2	301.15	9	644	-7.4	-1.05	7.62	6.19	-9.95	-14.8	-7.4
Konkonda	31/01	2006	8.1	301.15	13	765	-4.5	-1.05	7.62	6.19	-9.95	-11.9	-4.4
Konkonda	15/02	2006	8.2	301.15	7	514	-4.2	-1.05	7.62	6.19	-9.95	-11.6	-4.1
Konkonda	04/04	2006	8.2	301.15	9	685	-7.8	-1.05	7.62	6.19	-9.95	-15.2	-7.8
Kiunga	17/02	2004	8.1	301.15	17	1017	2.6	-1.05	7.62	6.19	-9.95	-4.8	2.7
Kiunga	23/03	2004	7.9	301.15	18	678	1.7	-1.05	7.62	6.19	-9.95	-5.7	1.9
Kiunga	30/04	2004	7.8	301.15	21	626	-12.4	-1.05	7.62	6.19	-9.95	-19.7	-12.2
Kiunga	15/06	2004	8.0	301.15	17	811	-9	-1.05	7.62	6.19	-9.95	-16.4	-8.9
Kiunga	25/06	2004	7.9	301.15	28	1026	-10.5	-1.05	7.62	6.19	-9.95	-17.9	-10.3
Kiunga	09/07	2004	8.0	301.15	18	819	-12.5	-1.05	7.62	6.19	-9.95	-19.9	-12.4
Kiunga	18/03	2005	7.9	301.15	11	404	-6.4	-1.05	7.62	6.19	-9.95	-13.8	-6.2
Kiunga	10/05	2005	7.7	301.15	23	534	-8.5	-1.05	7.62	6.19	-9.95	-15.7	-8.2

Kiunga	19/05	2005	7.5	301.15	29	428	-10.3	-1.05	7.62	6.19	-9.95	-17.4	-9.8
Kiunga	21/06	2005	7.9	301.15	55	2035	-20.8	-1.05	7.62	6.19	-9.95	-28.2	-20.7
Kiunga	21/07	2005	7.8	301.15	39	1164	-18.9	-1.05	7.62	6.19	-9.95	-26.2	-18.7
Kiunga	02/08	2005	7.9	301.15	39	1454	-18.2	-1.05	7.62	6.19	-9.95	-25.6	-18.1
Kiunga	04/08	2005	7.9	301.15	51	1882	-20.9	-1.05	7.62	6.19	-9.95	-28.3	-20.8
Kiunga	20/09	2005	7.6	301.15	39	733	-6	-1.05	7.62	6.19	-9.95	-13.2	-5.6
Kiunga	06/10	2005	7.8	301.15	15	450	-7.5	-1.05	7.62	6.19	-9.95	-14.8	-7.3
Kiunga	02/12	2005	7.7	301.15	34	786	-9.9	-1.05	7.62	6.19	-9.95	-17.1	-9.6
Kiunga	16/12	2005	7.8	301.15	32	939	-11	-1.05	7.62	6.19	-9.95	-18.3	-10.8
Kiunga	31/01	2006	8.0	301.15	13	617	-5.5	-1.05	7.62	6.19	-9.95	-12.9	-5.4
Kiunga	15/02	2006	8.1	301.15	7	439	-7.3	-1.05	7.62	6.19	-9.95	-14.7	-7.2
Kiunga	04/04	2006	7.9	301.15	19	719	-10.7	-1.05	7.62	6.19	-9.95	-18.1	-10.5
Nukumba	17/02	2004	8.3	301.15	10	922	2.2	-1.05	7.62	6.19	-9.95	-5.2	2.3
Nukumba	23/03	2004	7.7	301.15	23	550	3.4	-1.05	7.62	6.19	-9.95	-3.8	3.7
Nukumba	30/04	2004	8.0	301.15	18	844	-13	-1.05	7.62	6.19	-9.95	-20.4	-12.9
Nukumba	15/06	2004	7.8	301.15	24	723	-9.3	-1.05	7.62	6.19	-9.95	-16.6	-9.1
Nukumba	25/06	2004	8.0	301.15	14	633	-9.8	-1.05	7.62	6.19	-9.95	-17.2	-9.7
Nukumba	09/07	2004	8.1	301.15	18	1066	-11.8	-1.05	7.62	6.19	-9.95	-19.2	-11.7
Nukumba	13/12	2005	8.0	301.15	21	990	-12.3	-1.05	7.62	6.19	-9.95	-19.7	-12.2
Nukumba	18/03	2005	8.0	301.15	-	-	-	-1.05	7.62	6.19	-9.95	-	-
Nukumba	30/04	2005	8.0	301.15	10	446	-1.8	-1.05	7.62	6.19	-9.95	-9.2	-1.7
Nukumba	10/05	2005	8.2	301.15	8	579	-7.3	-1.05	7.62	6.19	-9.95	-14.7	-7.3
Nukumba	19/05	2005	8.0	301.15	10	462	-8.3	-1.05	7.62	6.19	-9.95	-15.7	-8.2
Nukumba	21/06	2005	8.2	301.15	29	2144	-20.3	-1.05	7.62	6.19	-9.95	-27.7	-20.4
Nukumba	21/07	2005	8.3	301.15	22	2080	-20.1	-1.05	7.62	6.19	-9.95	-27.5	-20.2
Nukumba	02/08	2005	7.8	301.15	88	2585	-18.7	-1.05	7.62	6.19	-9.95	-26.0	-18.5
Nukumba	04/08	2005	8.0	301.15	36	1663	-19.4	-1.05	7.62	6.19	-9.95	-26.8	-19.3
Nukumba	20/09	2005	8.1	301.15	6	382	-4.5	-1.05	7.62	6.19	-9.95	-11.9	-4.4
Nukumba	06/10	2005	8.1	301.15	10	561	-6.1	-1.05	7.62	6.19	-9.95	-13.5	-6.0
Nukumba	02/12	2006	7.5	301.15	56	825	-11.8	-1.05	7.62	6.19	-9.95	-18.9	-11.3
Nukumba	16/12	2006	8.0	301.15	19	900	-9.5	-1.05	7.62	6.19	-9.95	-16.9	-9.4
Nukumba	31/01	2006	7.9	301.15	20	743	-7.9	-1.05	7.62	6.19	-9.95	-15.3	-7.7
Nukumba	15/02	2006	8.2	301.15	8	620	-7.2	-1.05	7.62	6.19	-9.95	-14.6	-7.2
Nukumba	04/04	2006	8.0	301.15	14	649	-8.1	-1.04	7.41	6.07	-9.69	-15.3	-8.0

Obo	17/02	2004	8.0	303.15	25	1201	2.7	-1.04	7.41	6.07	-9.69	-4.5	2.9
Obo	23/03	2004	7.3	303.15	54	512	3.4	-1.04	7.41	6.07	-9.69	-3.2	4.1
Obo	30/04	2004	7.7	303.15	44	1068	-11.2	-1.04	7.41	6.07	-9.69	-18.3	-10.9
Obo	15/06	2004	8.0	303.15	17	795	-8.3	-1.04	7.41	6.07	-9.69	-15.5	-8.2
Obo	25/06	2004	7.8	303.15	27	819	-10.4	-1.04	7.41	6.07	-9.69	-17.5	-10.2
Obo	09/07	2004	7.9	303.15	25	937	-11.4	-1.04	7.41	6.07	-9.69	-18.6	-11.3
Obo	13/12	2004	8.0	303.15	14	674	-4.4	-1.04	7.41	6.07	-9.69	-11.6	-4.3
Obo	18/03	2005	7.9	303.15	19	711	-6.1	-1.04	7.41	6.07	-9.69	-13.3	-5.9
Obo	30/04	2005	7.9	303.15	10	380	-1.0	-1.04	7.41	6.07	-9.69	-8.2	-0.8
Obo	10/05	2005	7.5	303.15	52	788	-7.4	-1.04	7.41	6.07	-9.69	-14.3	-7.0
Obo	19/05	2005	7.9	303.15	23	865	-8.0	-1.04	7.41	6.07	-9.69	-15.2	-7.8
Obo	21/06	2005	8.3	303.15	25	2423	-19.1	-1.04	7.41	6.07	-9.69	-26.3	-19.2
Obo	21/07	2005	7.9	303.15	47	1802	-16.9	-1.04	7.41	6.07	-9.69	-24.1	-16.8
Obo	27/07	2005	8.0	303.15	45	2150	-20.3	-1.04	7.41	6.07	-9.69	-27.5	-20.3
Obo	02/08	2005	7.9	303.15	67	2537	-18.4	-1.04	7.41	6.07	-9.69	-25.6	-18.3
Obo	20/09	2005	7.7	303.15	31	750	-6.0	-1.04	7.41	6.07	-9.69	-13.1	-5.7
Obo	02/10	2005	8.1	303.15	13	798	-6.5	-1.04	7.41	6.07	-9.69	-13.7	-6.4
Obo	02/12	2005	8.0	303.15	13	609	-8.7	-1.04	7.41	6.07	-9.69	-15.9	-8.6
Obo	16/12	2005	7.8	303.15	26	779	-8.8	-1.04	7.41	6.07	-9.69	-15.9	-8.6
Obo	31/01	2006	7.5	303.15	62	936	-8.5	-1.04	7.41	6.07	-9.69	-15.4	-8.1
Obo	15/02	2006	8.2	303.15	11	864	-7.9	-1.04	7.41	6.07	-9.69	-15.1	-7.9
Obo	04/04	2006	7.9	303.15	25	945	-10.2	-1.04	7.41	6.07	-9.69	-17.4	-10.1
Str01	17/02	2004	8.1	303.15	20	1188	1.0	-1.04	7.41	6.07	-9.69	-6.2	1.1
Str01	23/03	2004	8.0	303.15	15	706	2.3	-1.04	7.41	6.07	-9.69	-4.9	2.5
Str01	30/04	2004	8.0	303.15	27	1274	-11.8	-1.04	7.41	6.07	-9.69	-19.0	-11.7
Str01	15/06	2004	8.1	303.15	11	635	-7.7	-1.04	7.41	6.07	-9.69	-14.9	-7.6
Str01	25/06	2004	8.1	303.15	8	505	-9.5	-1.04	7.41	6.07	-9.69	-16.7	-9.4
Str01	09/07	2004	8.1	303.15	18	1107	-13.4	-1.04	7.41	6.07	-9.69	-20.6	-13.4
Str01	13/12	2004	8.0	303.15	16	787	-11.1	-1.04	7.41	6.07	-9.69	-18.3	-11.0
Str01	18/03	2005	8.0	303.15	-	-	-	-1.04	7.41	6.07	-9.69	-	-
Str01	30/04	2005	7.8	303.15	19	578	-1.5	-1.04	7.41	6.07	-9.69	-8.6	-1.3
Str01	10/05	2005	8.0	303.15	15	738	-5.7	-1.04	7.41	6.07	-9.69	-12.9	-5.6
Str01	19/05	2005	8.0	303.15	17	820	-5.8	-1.04	7.41	6.07	-9.69	-13.0	-5.7
Str01	21/06	2005	8.2	303.15	26	1965	-21	-1.04	7.41	6.07	-9.69	-28.2	-21.1

Str01	21/07	2005	8.1	303.15	20	1180	-11.4	-1.04	7.41	6.07	-9.69	-18.6	-11.4
Str01	27/07	2005	8.1	303.15	45	2718	-17.8	-1.04	7.41	6.07	-9.69	-25.0	-17.8
Str01	20/09	2005	7.6	303.15	53	1019	-5.1	-1.04	7.41	6.07	-9.69	-12.1	-4.7
Str01	02/10	2005	8.1	303.15	16	985	-6.5	-1.04	7.41	6.07	-9.69	-13.7	-6.4
Str01	02/12	2005	8.0	303.15	22	1047	-7.3	-1.04	7.41	6.07	-9.69	-14.5	-7.2
Str01	16/12	2005	7.9	303.15	24	897	-8	-1.04	7.41	6.07	-9.69	-15.2	-7.8
Str01	31/01	2006	8.1	303.15	13	773	-4.3	-1.04	7.41	6.07	-9.69	-11.5	-4.2
Str01	15/02	2006	8.2	303.15	11	807	-9	-1.04	7.41	6.07	-9.69	-16.2	-9.0
Str01	04/04	2006	8.0	303.15	23	1096	-8.7	-1.04	7.41	6.07	-9.69	-15.9	-8.6
Ogwa	17/02	2004	8.0	303.15	27	1282	2.3	-1.04	7.41	6.07	-9.69	-4.9	2.5
Ogwa	23/03	2004	7.7	303.15	33	797	2.8	-1.04	7.41	6.07	-9.69	-4.3	3.1
Ogwa	30/04	2004	7.8	303.15	30	908	-9.5	-1.04	7.41	6.07	-9.69	-16.6	-9.3
Ogwa	15/06	2004	8.0	303.15	16	771	-7.8	-1.04	7.41	6.07	-9.69	-15.0	-7.7
Ogwa	25/06	2004	8.0	303.15	15	730	-9.6	-1.04	7.41	6.07	-9.69	-16.8	-9.5
Ogwa	09/07	2004	8.0	303.15	26	1258	-13.3	-1.04	7.41	6.07	-9.69	-20.5	-13.2
Ogwa	18/03	2005	7.1	303.15	87	528	-6.2	-1.04	7.41	6.07	-9.69	-12.4	-5.2
Ogwa	30/04	2005	7.9	303.15	12	461	-1.5	-1.04	7.41	6.07	-9.69	-8.7	-1.3
Ogwa	10/05	2005	7.9	303.15	22	857	-5.5	-1.04	7.41	6.07	-9.69	-12.7	-5.3
Ogwa	19/05	2005	7.9	303.15	28	1075	-7.9	-1.04	7.41	6.07	-9.69	-15.1	-7.7
Ogwa	21/06	2005	8.2	303.15	16	1190	-19.5	-1.04	7.41	6.07	-9.69	-26.7	-19.6
Ogwa	21/07	2005	8.0	303.15	27	1274	-12.1	-1.04	7.41	6.07	-9.69	-19.3	-12.0
Ogwa	27/07	2005	7.9	303.15	50	1907	-16.4	-1.04	7.41	6.07	-9.69	-23.6	-16.3
Ogwa	02/08	2005	8.1	303.15	38	2303	-18.6	-1.04	7.41	6.07	-9.69	-25.8	-18.6
Ogwa	20/09	2005	7.7	303.15	36	877	-5.2	-1.04	7.41	6.07	-9.69	-12.3	-4.9
Ogwa	06/10	2005	8.0	303.15	23	1120	-7.6	-1.04	7.41	6.07	-9.69	-14.8	-7.5
Ogwa	02/12	2005	8.0	303.15	27	1315	-10.4	-1.04	7.41	6.07	-9.69	-17.6	-10.3
Ogwa	16/12	2005	7.9	303.15	23	881	-7.4	-1.04	7.41	6.07	-9.69	-14.6	-7.2
Ogwa	31/01	2006	7.8	303.15	41	1245	-8.5	-1.04	7.41	6.07	-9.69	-15.6	-8.3
Ogwa	15/02	2006	8.3	303.15	8	759	-6	-1.04	7.41	6.07	-9.69	-13.2	-6.0
Ogwa	04/04	2006	7.9	303.15	31	1172	-9.5	-1.18	10.87	8.26	-14.44	-20.0	-9.3

Appendix 7. $\delta^{13}C$ values of bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3) in water samples collected from February 23 to March 6, 2007

Location	Date	Time	pH	T, K	$\delta^{13}C$ DIC, ‰	H_2CO_3, µmol/L	HCO_3^-, µmol/L	$\alpha CO_{2(aq)} - CO_{2(g)}$, ‰	$\alpha HCO_3^-{}_{(aq)} - CO_{2(g)}$, ‰	$\alpha CO_3^{2-}{}_{(aq)} - CO_{2(g)}$, ‰	$\alpha CaCO_3 - CO_{2(g)}$, ‰	$\delta^{13}C$ H_2CO_3, ‰	$\delta^{13}C$ HCO_3^-, ‰
Obo-1	23/02	1900	7.4	302.05	-12.8	83	989	-1.04	7.52	6.14	-9.83	-19.7	-12.2
Obo-2	23/02	2100	7.4	302.05	-12.8	96	1145	-1.04	7.52	6.14	-9.83	-19.6	-12.2
Obo-3	23/02	2300	7.4	302.05	-12.8	88	1046	-1.05	7.53	6.14	-9.84	-19.6	-12.2
Obo-4	24/02	0100	7.4	301.95	-12.9	90	1071	-1.05	7.53	6.14	-9.84	-19.7	-12.3
Obo-5	24/02	0300	7.4	301.95	-12.5	101	1202	-1.05	7.54	6.15	-9.86	-19.4	-11.9
Obo-6	24/02	0500	7.4	301.85	-12.7	95	1130	-1.05	7.56	6.15	-9.87	-19.6	-12.1
Obo-7	24/02	0700	7.3	301.75	-12.3	142	1338	-1.05	7.57	6.16	-9.88	-19.0	-11.6
Obo-8	24/02	0900	7.4	301.65	-12.1	107	1266	-1.05	7.58	6.17	-9.90	-19.0	-11.6
Obo-9	24/02	1100	7.4	301.55	-12.0	111	1306	-1.05	7.58	6.17	-9.90	-18.9	-11.5
Obo-10	24/02	1300	7.5	301.55	-11.9	96	1424	-1.05	7.58	6.17	-9.90	-18.9	-11.5
Obo-11	24/02	1500	7.5	301.55	-11.9	90	1330	-1.05	7.60	6.18	-9.92	-19.0	-11.5
Obo-12	24/02	1700	7.5	301.35	-11.9	95	1414	-1.05	7.61	6.19	-9.94	-18.9	-11.4
Obo-13	24/02	1900	7.6	301.25	-12.4	60	1109	-1.05	7.63	6.20	-9.96	-19.5	-12.0
Obo-14	24/02	2100	7.6	301.05	-12.0	72	1334	-1.05	7.63	6.20	-9.96	-19.2	-11.6
Obo-15	24/02	2300	7.7	301.05	-12.3	53	1239	-1.05	7.64	6.21	-9.98	-19.6	-12.1
Obo-16	25/02	0100	7.7	300.95	-11.9	61	1422	-1.05	7.65	6.21	-9.99	-19.2	-11.6
Obo-17	25/02	0300	7.7	300.85	-12.1	56	1295	-1.05	7.66	6.22	-10.01	-19.4	-11.8
Obo-18	25/02	0500	7.7	300.75	-12.0	47	1104	-1.05	7.66	6.22	-10.01	-19.3	-11.7
Obo-19	25/02	0700	7.7	300.75	-12.3	52	1221	-1.05	7.66	6.22	-10.01	-19.5	-12.0
Obo-20	25/02	0900	7.7	300.75	-12.1	55	1281	-1.05	7.72	6.26	-10.09	-19.5	-11.9
Obo-21	25/02	1100	8.1	300.15	-12.2	20	1168	-1.05	7.76	6.28	-10.13	-19.7	-12.1
Obo-22	25/02	1300	8.2	299.85	-12.1	15	1092	-1.05	7.64	6.21	-9.98	-19.6	-12.1
Obo-23	25/02	1500	7.7	300.95	-12.2	41	953	-1.05	7.65	6.21	-9.99	-19.5	-11.9
Obo-24	25/02	1700	7.7	300.85	-12.0	42	985	-1.05	7.66	6.22	-10.01	-19.3	-11.7
Obo-25	25/02	1900	7.8	300.75	-12.2	34	1007	-1.05	7.66	6.22	-10.01	-19.5	-11.9
Obo-26	25/02	2100	7.8	300.75	-12.1	33	979	-1.05	7.65	6.21	-9.99	-19.5	-11.9
Obo-27	25/02	2300	7.7	300.85	-12.0	43	995	-1.05	7.62	6.19	-9.95	-19.3	-11.8
Obo-28	26/02	0100	7.7	301.15	-12.0	47	1097	-1.05	7.62	6.19	-9.95	-19.2	-11.7

Obo-29	26/02	0300	7.7	301.15	-11.3	44	1028	-1.05	7.62	6.19	-9.95	-18.5	-11.0
Obo-30	26/02	0500	7.7	301.15	-12.1	39	920	-1.05	7.62	6.19	-9.95	-19.3	-11.8
Obo-31	26/02	0700	7.7	301.15	-12.3	48	1131	-1.05	7.62	6.19	-9.95	-19.6	-12.1
Obo-32	26/02	0900	7.7	301.15	-11.9	40	949	-1.05	7.62	6.19	-9.95	-19.2	-11.6
Obo-33	26/02	1100	7.7	301.15	-11.9	43	1008	-1.05	7.62	6.19	-9.95	-19.2	-11.6
Obo-34	26/02	1300	7.7	301.15	-12.2	41	961	-1.05	7.62	6.19	-9.95	-19.4	-11.9
Obo-35	26/02	1500	7.7	301.15	-12.3	41	966	-1.05	7.62	6.19	-9.95	-19.5	-12.0
Obo-36	26/02	1700	7.7	301.15	-12.3	49	1153	-1.05	7.62	6.19	-9.95	-19.6	-12.1
Obo-37	26/02	1900	8.2	301.15	-12.5	15	1088	-1.06	7.93	6.38	-10.35	-20.2	-12.4
Kiunga-1	01/03	0600	7.6	298.25	-13.6	65	1167	-1.06	7.91	6.37	-10.32	-21.0	-13.2
Kiunga-2	01/03	0800	7.8	298.45	-13.6	31	893	-1.06	7.88	6.35	-10.29	-21.2	-13.4
Kiunga-3	01/03	1000	7.5	298.65	-13.8	60	853	-1.06	7.87	6.35	-10.28	-21.1	-13.3
Kiunga-4	01/03	1200	7.3	298.75	-14.0	95	858	-1.06	7.87	6.35	-10.28	-21.0	-13.2
Kiunga-5	01/03	1400	7.6	298.75	-14.5	42	753	-1.06	7.84	6.33	-10.24	-21.8	-14.1
Kiunga-6	01/03	1600	7.1	299.05	-14.4	99	567	-1.06	7.85	6.33	-10.25	-20.9	-13.2
Kiunga-7	01/03	1800	7.1	298.95	-15.0	125	714	-1.06	7.85	6.33	-10.25	-21.6	-13.9
Kiunga-8	01/03	2000	7.1	298.95	-14.7	136	775	-1.06	7.86	6.34	-10.26	-21.3	-13.6
Kiunga-9	01/03	2200	7.0	298.85	-14.8	131	592	-1.06	7.86	6.34	-10.26	-21.1	-13.5
Kiunga-10	02/03	0000	7.0	298.85	-14.6	130	586	-1.06	7.87	6.35	-10.28	-20.9	-13.2
Kiunga-11	02/03	0200	6.7	298.75	-15.1	225	511	-1.06	7.87	6.35	-10.28	-20.3	-12.9
Kiunga-12	02/03	0400	6.9	298.75	-15.2	177	636	-1.06	7.87	6.35	-10.28	-21.1	-13.5
Kiunga-13	02/03	0600	6.9	298.75	-15.4	145	522	-1.06	7.87	6.35	-10.28	-21.3	-13.8
Kiunga-14	02/03	0800	6.9	298.75	-16.1	180	646	-1.06	7.88	6.35	-10.29	-22.0	-14.5
Kiunga-15	02/03	1000	6.6	298.65	-15.6	233	419	-1.06	7.88	6.35	-10.29	-20.3	-13.0
Kiunga-16	02/03	1200	6.6	298.65	-15.6	271	488	-1.06	7.91	6.37	-10.32	-20.3	-13.0
Kiunga-17	02/03	1400	6.6	298.45	-15.8	321	575	-1.06	7.89	6.36	-10.31	-20.5	-13.2
Kiunga-18	02/03	1600	6.6	298.55	-15.8	344	618	-1.06	7.84	6.33	-10.24	-20.5	-13.2
Kiunga-19	02/03	1800	7.0	299.05	-15.8	168	765	-1.06	7.84	6.33	-10.24	-22.0	-14.4
Kiunga-20	02/03	2000	6.8	299.05	-15.8	210	603	-1.06	7.89	6.36	-10.31	-21.3	-13.8
Kiunga-21	02/03	2200	6.8	298.55	-15.9	236	672	-1.06	7.88	6.35	-10.29	-21.5	-14.0
Kiunga-22	03/03	0000	6.7	298.65	-15.9	279	631	-1.06	7.96	6.40	-10.39	-21.1	-13.6
Kiunga-23	03/03	0200	6.9	297.95	-16.2	203	719	-1.06	7.98	6.41	-10.42	-22.2	-14.5

Kiunga-24	03/03	0400	6.9	297.75	-16.4	136	481	-1.06	7.91	6.37	-10.32	-22.4	-14.8
Kiunga-25	03/03	0600	6.8	298.45	-16.2	227	643	-1.06	7.91	6.37	-10.32	-21.8	-14.3
Kiunga-26	03/03	0800	6.8	298.45	-16.7	262	744	-1.06	7.82	6.32	-10.21	-22.2	-14.8
Kiunga-27	03/03	1000	6.8	299.25	-16.3	177	508	-1.06	7.79	6.30	-10.17	-21.8	-14.4
Kiunga-28	03/03	1200	6.9	299.55	-15.6	187	680	-1.05	7.77	6.28	-10.14	-21.5	-14.0
Kiunga-29	03/03	1400	6.7	299.75	-15.6	270	621	-1.06	7.79	6.30	-10.17	-20.7	-13.3
Kiunga-30	03/03	1600	6.7	299.55	-15.5	277	634	-1.05	7.73	6.26	-10.10	-20.6	-13.3
Kiunga-31	03/03	1800	6.6	300.05	-15.5	375	687	-1.06	7.79	6.30	-10.17	-20.2	-13.0
Kiunga-32	03/03	2000	6.5	299.55	-15.4	379	548	-1.06	7.81	6.31	-10.20	-19.6	-12.5
Kiunga-33	03/03	2200	6.8	299.35	-15.8	262	755	-1.06	7.79	6.30	-10.17	-21.3	-13.8
Kiunga-34	04/03	0000	7.0	299.55	-15.4	196	897	-1.06	7.93	6.38	-10.35	-21.7	-14.0
Kiunga-35	04/03	0200	6.9	298.25	-15.6	232	828	-1.06	7.87	6.35	-10.28	-21.5	-13.9
Kiunga-36	04/03	0400	7.0	298.75	-15.2	212	960	-1.07	8.05	6.45	-10.50	-21.6	-13.8
Kiunga-37	04/03	0600	7.4	297.15	-15.1	98	1089	-1.06	7.82	6.32	-10.21	-22.2	-14.5
Kiunga-38	04/03	0800	7.1	299.25	-15.1	170	976	-1.06	7.80	6.30	-10.18	-21.6	-14.0
Kiunga-39	04/03	1000	7.1	299.45	-15.1	137	790	-1.06	7.80	6.30	-10.18	-21.6	-14.0
Kiunga-40	04/03	1200	7.1	299.45	-15.3	167	960	-1.05	7.73	6.26	-10.10	-21.7	-14.2
Kiunga-41	04/03	1400	7.2	300.05	-15.0	112	820	-1.05	7.76	6.28	-10.13	-21.6	-14.1
Kiunga-42	04/03	1600	7.2	299.85	-14.7	157	1145	-1.06	7.79	6.30	-10.17	-21.4	-13.8
Kiunga-43	04/03	1800	7.2	299.55	-14.9	137	992	-1.06	7.80	6.30	-10.18	-21.6	-14.0
Kiunga-44	04/03	2000	7.4	299.45	-14.4	103	1183	-1.06	7.88	6.35	-10.29	-21.6	-13.8
Kiunga-45	04/03	2200	7.6	298.65	-13.9	83	1488	-1.06	7.79	6.30	-10.17	-21.2	-13.5
Kiunga-46	04/03	0000	7.7	299.55	-13.6	65	1482	-1.06	7.95	6.39	-10.38	-21.2	-13.3
Kiunga-47	05/03	0200	7.8	298.05	-13.3	50	1410	-1.06	7.98	6.41	-10.42	-20.9	-13.1
Kiunga-48	05/03	0400	7.8	297.75	-13.4	43	1214	-1.07	8.05	6.45	-10.50	-21.1	-13.2
Kiunga-49	05/03	0600	7.9	297.15	-13.4	33	1162	-1.07	8.06	6.46	-10.52	-21.2	-13.2
Kiunga-50	05/03	0800	7.9	297.05	-13.2	33	1161	-1.06	8.01	6.43	-10.46	-20.9	-13.0
Kiunga-51	05/03	1000	7.9	297.45	-13.5	24	858	-1.06	8.03	6.45	-10.49	-21.3	-13.3
Kiunga-52	05/03	1200	7.9	297.25	-13.3	35	1237	-1.05	7.59	6.17	-9.91	-20.6	-13.1
Konkonda-1	00/03	1520	7.7	301.45	-11.8	43	1017	-1.05	7.59	6.17	-9.91	-19.0	-11.5
Konkonda-2	00/03	1520	7.7	301.45	-12.1	42	997	-1.05	7.57	6.16	-9.88	-19.3	-11.8
Konkonda-3	00/03	1520	7.7	301.65	-12.0	47	1106	-1.05	7.57	6.16	-9.88	-19.2	-11.8

Konkonda-4	00/03	1520	7.7	301.65	-12.1	34	799	-1.05	7.60	6.18	-9.92	-19.3	-11.8
Konkonda-5	00/03	1520	7.8	301.35	-12.0	39	1153	-1.05	7.60	6.18	-9.92	-19.3	-11.8
Konkonda-6	00/03	1520	7.8	301.35	-12.1	39	1143	-1.06	7.89	6.36	-10.31	-19.6	-11.8
Str-1	25/02	1235	7.7	298.55	-12.6	51	1144	-1.06	7.89	6.36	-10.31	-20.1	-12.3
Str-2	25/02	1240	7.8	298.55	-12.5	52	1466	-1.06	7.89	6.36	-10.31	-20.0	-12.2
Str-3	25/02	1315	7.8	298.55	-12.4	41	1171	-1.06	7.88	6.35	-10.29	-20.0	-12.2
Str-4	25/02	1320	7.8	298.65	-12.5	37	1051	-1.06	7.87	6.35	-10.28	-20.1	-12.3
Str-5	25/02	1340	7.8	298.75	-12.5	51	1448	-1.06	7.80	6.30	-10.18	-20.0	-12.3
Ogwa-1	25/02	1040	7.7	299.45	-11.6	64	1474	-1.06	7.81	6.31	-10.20	-19.0	-11.3
Ogwa-2	25/02	1050	7.7	299.35	-11.3	54	1232	-1.06	7.81	6.31	-10.20	-18.8	-11.0
Ogwa-3	25/02	1100	7.7	299.35	-11.5	46	1056	-1.06	7.81	6.31	-10.20	-18.9	-11.2
Ogwa-4	25/02	1105	7.7	299.35	-11.3	51	1167	-1.06	7.81	6.31	-10.20	-18.7	-11.0
Ogwa-5	25/02	1125	7.7	299.35	-11.4	55	1253	-1.06	7.81	6.31	-10.20	-18.8	-11.1
Ogwa-6	25/02	1130	7.7	299.35	-11.2	54	1231	-1.09	8.62	6.81	-11.26	-19.4	-10.9
Falomian-1	06/03	1230	3.4	291.95	-4.5	191	0	-1.09	8.62	6.81	-11.26	-3.5	ND
Falomian-2	06/03	1230	3.4	291.95	-4.4	200	0	-1.09	8.61	6.80	-11.24	-3.3	ND
Falomian-3	06/03	1230	3.4	292.05	-5.1	147	0	-1.09	8.63	6.81	-11.27	-4.0	ND
Falomian-4	06/03	1235	3.4	291.85	-4.7	180	0	-1.09	8.63	6.81	-11.27	-3.6	ND
Falomian-5	06/03	1235	3.4	291.85	-5.2	152	0	-1.09	8.63	6.81	-11.27	-4.1	ND
Falomian-6	06/03	1235	3.4	291.85	-4.9	154	0	-1.05	7.75	6.27	-10.11	-3.9	ND
Kiunga airport-1	03/03	1625	4.7	299.95	-16.4	2163	50	-1.05	7.75	6.27	-10.11	-15.6	ND
Kiunga airport-2	03/03	1640	4.7	299.95	-16.8	2336	54	-1.05	7.71	6.25	-10.07	-15.9	ND
Ongas-1	03/03	1700	4.3	300.25	-20.2	1723	16	-1.05	7.71	6.25	-10.07	-19.2	ND
Ongas-2	03/03	1705	4.3	300.25		1812	17	-1.05	7.66	6.22	-10.01	1.0	ND
Ninegrum-1	03/03	1720	4.6	300.75	-19.8	1368	25	-1.05	7.67	6.22	-10.02	-18.9	ND
Ninegrum-2	03/03	1725	4.5	300.65	-19.5	1460	21	-1.06	7.94	6.39	-10.36	-18.5	ND
Obo_rain-1	24/02	1530	6.8	298.15	-7.0	34	95	-1.06	8.03	6.45	-10.49	-12.6	-5.0
Obo_rain-2	25/02	1850	7.7	297.25		3	70	-1.07	8.20	6.55	-10.70	-7.8	0.4
Kiunga_rain-1	01/03	2210	8.2	295.75	-8.6	2	126	-1.06	8.00	6.43	-10.45	-16.4	-8.5
Kiunga_rain-2	04/03	1025	6.8	297.55	-7.1	32	90	-1.18	10.87	8.26	-14.44	-14.8	-4.4

Appendix 8. δ^2H and $\delta^{18}O$ values of water and $\delta^{13}C$ values of bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3) in water samples collected from February 23 to March 6, 2007

Location	Date	Time	pH	T, K	DIC, mg C L^{-1}	HCO_3^-, µM	H_2CO_3, µM	$\delta^{13}C$ HCO_3^-, ‰	$\delta^{13}C$ H_2CO_3, ‰	$\delta^{18}O$, ‰	δ^2H, ‰	Flow, m^3 s^{-1}
Obo-1	23/02	1900	7.4	302.05	12.9	847	225	-11.3	-18.5	-7.8	-53	2137
Obo-2	23/02	2100	7.4	302.05	14.9	981	261	-11.3	-18.5	-7.7	-52	2136
Obo-3	23/02	2300	7.4	302.05	13.6	897	239	-11.2	-18.5	-7.8	-53	2136
Obo-4	24/02	0100	7.4	301.95	14.0	918	245	-11.3	-18.6	-7.8	-55	2135
Obo-5	24/02	0300	7.4	301.95	15.7	1030	274	-11.0	-18.2	-7.9	-54	2131
Obo-6	24/02	0500	7.4	301.85	14.7	968	258	-11.2	-18.4	-8.0	-55	2135
Obo-7	24/02	0700	7.3	301.75	17.8	1109	373	-10.5	-17.7	-8.0	-57	2135
Obo-8	24/02	0900	7.4	301.65	16.5	1084	290	-10.6	-17.9	-8.1	-58	2135
Obo-9	24/02	1100	7.4	301.55	17.0	1118	299	-10.5	-17.8	-8.1	-57	2134
Obo-10	24/02	1300	7.5	301.55	18.3	1254	267	-10.6	-18.0	-8.1	-56	2134
Obo-11	24/02	1500	7.5	301.55	17.1	1172	249	-10.6	-18.0	-8.1	-56	2134
Obo-12	24/02	1700	7.5	301.35	18.2	1246	266	-10.6	-18.0	-8.2	-58	2134
Obo-13	24/02	1900	7.6	301.25	14.1	1000	170	-11.3	-18.7	-8.3	-57	2145
Obo-14	24/02	2100	7.6	301.05	16.9	1203	205	-10.9	-18.3	-8.3	-58	2148
Obo-15	24/02	2300	7.7	301.05	15.6	1140	154	-11.5	-18.9	-8.3	-59	2153
Obo-16	25/02	0100	7.7	300.95	17.9	1308	177	-11.0	-18.5	-8.4	-58	2154
Obo-17	25/02	0300	7.7	300.85	16.3	1191	161	-11.2	-18.7	-8.4	-58	2153
Obo-18	25/02	0500	7.7	300.75	13.9	1015	138	-11.1	-18.6	-8.4	-58	2156
Obo-19	25/02	0700	7.7	300.75	15.3	1123	152	-11.4	-18.9	-8.5	-59	2155
Obo-20	25/02	0900	7.7	300.75	16.1	1179	160	-11.2	-18.8	-8.6	-60	2159
Obo-21	25/02	1100	8.1	300.15	14.4	1132	62	-11.8	-19.5	-8.6	-61	2167
Obo-22	25/02	1300	8.2	299.85	13.4	1067	46	-11.9	-19.4	-8.6	-61	2169
Obo-23	25/02	1500	7.7	300.95	12.0	876	119	-11.3	-18.8	-8.8	-62	2173
Obo-24	25/02	1700	7.7	300.85	12.4	906	123	-11.1	-18.6	-8.8	-62	2171
Obo-25	25/02	1900	7.8	300.75	12.6	942	102	-11.4	-19.0	-8.9	-65	2172
Obo-26	25/02	2100	7.8	300.75	12.2	916	99	-11.4	-18.9	-8.9	-64	2184
Obo-27	25/02	2300	7.7	300.85	12.5	915	124	-11.2	-18.6	-9.0	-64	2197
Obo-28	26/02	0100	7.7	301.15	13.8	1009	136	-11.1	-18.6	-9.0	-64	2200

Obo-29	26/02	0300	7.7	301.15	12.9	946	128	-10.4	-17.9	-9.0	-64	2201
Obo-30	26/02	0500	7.7	301.15	11.6	847	114	-11.2	-18.6	-9.0	-64	2198
Obo-31	26/02	0700	7.7	301.15	14.2	1041	140	-11.5	-18.9	-9.0	-63	2196
Obo-32	26/02	0900	7.7	301.15	11.9	873	118	-11.0	-18.5	-9.0	-63	2199
Obo-33	26/02	1100	7.7	301.15	12.7	928	125	-11.0	-18.5	-9.1	-64	2210
Obo-34	26/02	1300	7.7	301.15	12.1	885	119	-11.3	-18.8	-9.1	-65	2210
Obo-35	26/02	1500	7.7	301.15	12.1	889	120	-11.4	-18.9	-9.2	-64	2219
Obo-36	26/02	1700	7.7	301.15	14.5	1061	143	-11.5	-18.9	-9.2	-64	2221
Obo-37	26/02	1900	8.2	301.15	13.4	979	132	-11.5	-19.3	-10.1	-72	2224
Kiunga-1	01/03	0600	7.6	298.25	14.8	1048	186	-12.4	-20.1	-10.9	-77	1288
Kiunga-2	01/03	0800	7.8	298.45	11.1	833	93	-12.9	-20.6	-10.7	-76	1282
Kiunga-3	01/03	1000	7.5	298.65	11.0	748	166	-12.4	-20.1	-10.8	-76	1274
Kiunga-4	01/03	1200	7.3	298.75	11.5	706	248	-12.1	-19.6	-10.8	-77	1267
Kiunga-5	01/03	1400	7.6	298.75	9.6	677	119	-13.3	-21.0	-10.8	-77	1272
Kiunga-6	01/03	1600	7.1	299.05	8.0	429	238	-11.8	-19.1	-10.8	-79	1244
Kiunga-7	01/03	1800	7.1	298.95	10.1	540	299	-12.5	-19.7	-10.8	-78	1225
Kiunga-8	01/03	2000	7.1	298.95	11.0	587	325	-12.1	-19.4	-10.8	-77	1198
Kiunga-9	01/03	2200	7	298.85	8.7	425	297	-11.9	-19.0	-10.7	-76	1184
Kiunga-10	02/03	0000	7	298.85	8.6	421	294	-11.7	-18.8	-10.7	-76	1157
Kiunga-11	02/03	0200	6.7	298.75	8.8	307	429	-11.4	-17.8	-10.7	-76	1131
Kiunga-12	02/03	0400	6.9	298.75	9.8	432	381	-11.9	-18.9	-10.7	-75	1110
Kiunga-13	02/03	0600	6.9	298.75	8.0	355	313	-12.2	-19.1	-10.6	-75	1089
Kiunga-14	02/03	0800	6.9	298.75	9.9	440	387	-12.8	-19.8	-10.7	-75	1066
Kiunga-15	02/03	1000	6.6	298.65	7.8	236	416	-11.8	-17.8	-10.6	-74	1050
Kiunga-16	02/03	1200	6.6	298.65	9.1	275	484	-11.7	-17.8	-10.6	-75	1031
Kiunga-17	02/03	1400	6.6	298.45	10.8	324	572	-12.0	-18.0	-10.5	-75	1010
Kiunga-18	02/03	1600	6.6	298.55	11.6	348	614	-12.0	-18.0	-10.5	-73	993
Kiunga-19	02/03	1800	7	299.05	11.2	550	383	-12.9	-20.0	-10.5	-74	971
Kiunga-20	02/03	2000	6.8	299.05	9.8	387	427	-12.2	-18.9	-10.6	-73	948
Kiunga-21	02/03	2200	6.8	298.55	10.9	430	478	-12.4	-19.1	-10.5	-72	922
Kiunga-22	03/03	0000	6.7	298.65	10.9	379	531	-12.1	-18.6	-10.5	-73	897
Kiunga-23	03/03	0200	6.9	297.95	11.1	487	434	-12.9	-19.9	-10.5	-73	869

Kiunga-24	03/03	0400	6.9	297.75	7.4	326	291	-13.1	-20.1	-10.3	-73	848
Kiunga-25	03/03	0600	6.8	298.45	10.5	412	458	-12.7	-19.4	-10.3	-73	820
Kiunga-26	03/03	0800	6.8	298.45	12.1	476	530	-13.2	-19.9	-10.3	-72	794
Kiunga-27	03/03	1000	6.8	299.25	8.2	326	359	-12.9	-19.5	-10.3	-72	769
Kiunga-28	03/03	1200	6.9	299.55	10.4	464	404	-12.5	-19.3	-10.2	-73	742
Kiunga-29	03/03	1400	6.7	299.75	10.7	375	516	-11.9	-18.2	-10.1	-71	711
Kiunga-30	03/03	1600	6.7	299.55	10.9	383	528	-11.9	-18.1	-10.1	-70	681
Kiunga-31	03/03	1800	6.6	300.05	12.8	390	672	-11.7	-17.7	-10.1	-70	652
Kiunga-32	03/03	2000	6.5	299.55	11.1	291	636	-11.7	-17.2	-10.2	-70	618
Kiunga-33	03/03	2200	6.8	299.35	12.2	485	533	-12.3	-18.9	-10.0	-71	585
Kiunga-34	04/03	0000	7	299.55	13.1	647	447	-12.4	-19.6	-10.0	-71	559
Kiunga-35	04/03	0200	6.9	298.25	12.7	562	499	-12.3	-19.3	-10.0	-69	534
Kiunga-36	04/03	0400	7	298.75	14.1	690	483	-12.2	-19.5	-10.0	-70	505
Kiunga-37	04/03	0600	7.4	297.15	14.3	924	264	-13.4	-20.9	-10.0	-69	479
Kiunga-38	04/03	0800	7.1	299.25	13.8	739	408	-12.5	-19.7	-10.0	-69	457
Kiunga-39	04/03	1000	7.1	299.45	11.1	598	329	-12.5	-19.7	-9.9	-67	436
Kiunga-40	04/03	1200	7.1	299.45	13.5	727	400	-12.8	-19.9	-9.9	-68	418
Kiunga-41	04/03	1400	7.2	300.05	11.2	651	282	-12.8	-20.1	-9.9	-69	411
Kiunga-42	04/03	1600	7.2	299.85	15.7	908	395	-12.5	-19.8	-9.9	-68	431
Kiunga-43	04/03	1800	7.2	299.55	13.6	786	343	-12.6	-20.0	-9.9	-66	492
Kiunga-44	04/03	2000	7.4	299.45	15.5	1009	278	-12.8	-20.4	-9.8	-69	588
Kiunga-45	04/03	2200	7.6	298.65	18.9	1337	235	-12.8	-20.4	-9.7	-69	703
Kiunga-46	04/03	0000	7.7	299.55	18.6	1361	188	-12.7	-20.5	-9.7	-67	803
Kiunga-47	05/03	0200	7.8	298.05	17.6	1315	147	-12.5	-20.4	-9.7	-66	889
Kiunga-48	05/03	0400	7.8	297.75	15.1	1132	127	-12.6	-20.5	-9.4	-64	955
Kiunga-49	05/03	0600	7.9	297.15	14.4	1099	99	-12.8	-20.7	-9.5	-65	1007
Kiunga-50	05/03	0800	7.9	297.05	14.4	1098	99	-12.5	-20.4	-9.5	-66	1052
Kiunga-51	05/03	1000	7.9	297.45	10.6	811	73	-12.9	-20.8	-9.4	-64	1082
Kiunga-52	05/03	1200	7.9	297.25	15.3	1170	105	-12.7	-20.2	-9.6	-66	1120
Konkonda-1	01/03	1520	7.7	301.45	12.8	936	126	-10.9	-18.4	-9.0	-62	-
Konkonda-2	01/03	1520	7.7	301.45	12.5	917	123	-11.2	-18.6	-8.9	-61	-
Konkonda-3	01/03	1520	7.7	301.65	13.9	1018	137	-11.2	-18.6	-8.9	-61	-

Konkonda-4	01/03	1520	7.7	301.65	10.0	736	99	-11.2	-18.6	-8.9	-61	-
Konkonda-5	01/03	1520	7.8	301.35	14.4	1079	115	-11.3	-18.7	-8.9	-61	-
Konkonda-6	01/03	1520	7.8	301.35	14.2	1070	114	-11.3	-19.1	-8.9	-61	-
Str-1	25/02	1235	7.7	298.55	14.4	1050	147	-11.7	-19.4	-11.2	-65	-
Str-2	25/02	1240	7.8	298.55	18.3	1368	152	-11.7	-19.4	-11.1	-66	-
Str-3	25/02	1315	7.8	298.55	14.6	1093	122	-11.7	-19.4	-11.2	-65	-
Str-4	25/02	1320	7.8	298.65	13.1	981	109	-11.8	-19.5	-11.1	-67	-
Str-5	25/02	1340	7.8	298.75	18.1	1352	150	-11.7	-19.4	-11.1	-75	-
Ogwa-1	25/02	1040	7.7	299.45	18.5	1354	187	-10.6	-18.3	-10.1	-74	-
Ogwa-2	25/02	1050	7.7	299.35	15.5	1131	157	-10.4	-18.1	-10.2	-73	-
Ogwa-3	25/02	1100	7.7	299.35	13.3	970	134	-10.6	-18.2	-9.9	-72	-
Ogwa-4	25/02	1105	7.7	299.35	14.7	1071	148	-10.4	-18.0	-10.1	-72	-
Ogwa-5	25/02	1125	7.7	299.35	15.8	1151	159	-10.4	-18.1	-10.2	-73	-
Ogwa-6	25/02	1130	7.7	299.35	15.5	1131	156	-10.2	-18.6	-10.2	-71	-
Ok Menga	06/03	1700	-	294.36	-	-	-	-	-	-11.3	-78	-
Ok Menga	06/03	1700	-	294.40	-	-	-	-	-	-11.3	-78	-
Ok Menga	06/03	1700	-	294.71	-	-	-	-	-	-11.2	-79	-
Ok Menga	06/03	1700	-	294.69	-	-	-	-	-	-11.3	-77	-
Ok Menga	06/03	1700	-	294.63	-	-	-	-	-	-11.3	-77	-
Ok Menga	06/03	1700	-	294.48	-	-	-	-	-	-11.2	-78	-
Falomian-1	06/03	1230	3.4	291.95	2.3	0	191	ND	-3.4	-10.5	-71	-
Falomian-2	06/03	1230	3.4	291.95	2.4	0	201	ND	-3.3	-10.5	-71	-
Falomian-3	06/03	1230	3.4	292.05	1.8	0	147	ND	-4.0	-10.5	-70	-
Falomian-4	06/03	1235	3.4	291.85	2.2	0	180	ND	-3.6	-10.5	-73	-
Falomian-5	06/03	1235	3.4	291.85	1.8	0	152	ND	-4.1	-10.6	-75	-
Falomian-6	06/03	1235	3.4	291.85	1.9	0	154	ND	-3.9	-10.5	-73	-
Kiunga airport-1	03/03	1625	4.7	299.95	26.6	16	2197	ND	-15.4	-9.1	-67	-
Kiunga airport-2	03/03	1640	4.7	299.95	28.7	17	2372	ND	-15.8	-9.1	-65	-
Ongas-1	03/03	1700	4.3	300.25	20.9	5	1734	ND	-19.2	-9.2	-65	-
Ongas-2	03/03	1705	4.3	300.25	22.0	5	1823	ND	-	-9.3	-65	-
Ninegrum-1	03/03	1720	4.6	300.75	16.7	8	1385	ND	-18.8	-9.0	-64	-
Ninegrum-2	03/03	1725	4.5	300.65	17.8	7	1474	ND	-18.4	-9.0	-63	-

Obo_rain-1	24/02	1530	6.8	298.15	1.5	61	68	-3.4	-10.2	-12.4	-79	-
Obo_rain-2	25/02	1850	7.7	297.25	0.9	64	9	1.0	-7.0	-14.8	-93	-
Kiunga_rain-1	01/03	2210	8.2	295.75	1.5	122	6	-8.3	-16.2	-1.8	-14	-
Kiunga_rain-2	04/03	1025	6.8	297.55	1.5	57	64	-2.1	-11.6	-5.7	-20	-

ND – not defined

Appendix 9. $\delta^{18}O$ and $\delta^{2}H$ values of rainfall collected at Tabubil from November 2003 to April 2006

Location	Date	Year	Julian day	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰
Tabubil	03/11	2003	33	-4.3	-20
Tabubil	01/12	2003	61	-17.7	-128
Tabubil	16/01	2004	107	-7.9	-48
Tabubil	19/01	2004	110	-14.4	-106
Tabubil	26/01	2004	117	-12	-84
Tabubil	02/02	2004	124	-15	-107
Tabubil	04/02	2004	126	-16.8	-120
Tabubil	16/02	2004	138	-10.9	-75
Tabubil	23/02	2004	145	-14.2	-107
Tabubil	27/02	2004	149	-16.8	-125
Tabubil	01/03	2004	152	-12.9	-93
Tabubil	04/03	2004	155	-12.4	-93
Tabubil	08/03	2004	159	-13.4	-96
Tabubil	15/03	2004	166	-16.8	-127
Tabubil	29/03	2004	180	-8.2	-56
Tabubil	30/03	2004	181	-11.4	-84
Tabubil	07/04	2004	189	-6.0	-36
Tabubil	08/04	2004	190	-5.8	-34
Tabubil	13/04	2004	195	-2.8	-14
Tabubil	14/04	2004	196	-6.0	-37
Tabubil	19/04	2004	201	-3.5	-14
Tabubil	26/04	2004	208	-11.5	-81
Tabubil	28/04	2004	210	-8.0	-52
Tabubil	30/04	2004	212	-11.2	-81
Tabubil	04/05	2004	216	-11.4	-85
Tabubil	08/05	2004	220	-8.1	-57
Tabubil	10/05	2004	222	-8.7	-60
Tabubil	11/05	2004	223	-12.7	-93
Tabubil	12/05	2004	224	-15.8	-119
Tabubil	15/05	2004	227	-15.2	-113
Tabubil	19/05	2004	231	-11.3	-81
Tabubil	24/05	2004	236	-11.3	-82
Tabubil	25/05	2004	237	-15.1	-116
Tabubil	27/05	2004	239	-15.6	-114
Tabubil	01/06	2004	244	-15.5	-112
Tabubil	03/06	2004	246	-11.6	-81
Tabubil	05/06	2004	248	-4.6	-23
Tabubil	07/06	2004	250	-4.6	-21
Tabubil	10/06	2004	253	-4.9	-28
Tabubil	23/06	2004	266	-3.4	-13
Tabubil	02/07	2004	275	-3.8	-19
Tabubil	05/07	2004	278	-7.0	-47
Tabubil	13/07	2004	286	-5.2	-35
Tabubil	19/07	2004	292	-3.0	-14
Tabubil	22/07	2004	295	-2.1	0
Tabubil	26/07	2004	299	-1.9	1
Tabubil	29/07	2004	302	-2.1	-1
Tabubil	02/08	2004	306	-3.1	-11
Tabubil	09/08	2004	313	-2.5	-9
Tabubil	11/08	2004	315	-6.1	-37
Tabubil	17/08	2004	321	-1.7	6
Tabubil	20/08	2004	324	-1.9	2

Tabubil	23/08	2004	327	-1.4	6
Tabubil	30/08	2004	334	-2.0	-3
Tabubil	06/09	2004	341	-2.3	-8
Tabubil	09/09	2004	344	-6.6	-42
Tabubil	10/09	2004	345	-10.8	-76
Tabubil	13/09	2004	348	-7.1	-47
Tabubil	17/09	2004	352	-4.2	-24
Tabubil	20/09	2004	355	-	-41
Tabubil	27/09	2004	362	-3.8	-18
Tabubil	29/09	2004	364	-4.0	-23
Tabubil	01/10	2004	366	-2.8	-11
Tabubil	05/10	2004	370	-5.3	-31
Tabubil	08/10	2004	373	-7.0	-45
Tabubil	27/10	2004	392	-7.0	-46
Tabubil	29/10	2004	394	-9.3	-68
Tabubil	01/11	2004	397	-2.8	-23
Tabubil	03/11	2004	399	-3.6	-18
Tabubil	15/11	2004	411	-2.7	-13
Tabubil	17/11	2004	413	-9.2	-64
Tabubil	19/11	2004	415	-13.0	-95
Tabubil	22/11	2004	418	-13.1	-95
Tabubil	29/11	2004	425	-8.7	-60
Tabubil	30/11	2004	426	-12.6	-97
Tabubil	01/12	2004	427	-7.2	-54
Tabubil	06/12	2004	432	-8.2	-61
Tabubil	09/12	2004	435	-2.9	-18
Tabubil	20/12	2004	446	-4.8	-24
Tabubil	25/12	2004	451	-11.6	-83
Tabubil	29/12	2004	455	-11.7	-83
Tabubil	31/12	2004	457	-17.5	-124
Tabubil	01/01	2005	458	-17.5	-124
Tabubil	07/01	2005	464	-10.8	-75
Tabubil	08/01	2005	465	-10.8	-74
Tabubil	09/01	2005	466	-10.7	-75
Tabubil	10/01	2005	467	-10.8	-77
Tabubil	31/01	2005	488	-7.7	-56
Tabubil	07/02	2005	495	-7.8	-54
Tabubil	18/02	2005	506	-8.6	-58
Tabubil	21/02	2005	509	-10.9	-78
Tabubil	28/02	2005	516	-7.1	-45
Tabubil	04/03	2005	520	-8.1	-54
Tabubil	07/03	2005	523	-6.0	-38
Tabubil	09/03	2005	525	-9.2	-66
Tabubil	14/03	2005	530	-5.5	-35
Tabubil	16/03	2005	532	-4.0	-22
Tabubil	24/03	2005	540	-12.4	-94
Tabubil	04/04	2005	551	-11.8	-87
Tabubil	05/4	2005	552	-15.3	-111
Tabubil	06/4	2005	553	-14.6	-109
Tabubil	07/4	2005	554	-19.9	-148
Tabubil	11/4	2005	558	-19.9	-149
Tabubil	12/4	2005	559	-15.1	-113
Tabubil	13/04	2005	560	-17.6	-128
Tabubil	18/04	2005	565	-8.1	-56
Tabubil	21/04	2005	568	-3.4	-17
Tabubil	26/04	2005	573	-4.7	-27

Tabubil	27/04	2005	574	-4.7	-27
Tabubil	02/05	2005	579	-2.4	-7
Tabubil	03/05	2005	580	-1.8	-5
Tabubil	04/05	2005	581	-3.2	-12
Tabubil	05/05	2005	582	-5.2	-35
Tabubil	09/05	2005	586	-13.7	-102
Tabubil	13/05	2005	590	-11.4	-83
Tabubil	20/05	2005	597	-5.5	-29
Tabubil	24/05	2005	601	-3.3	-12
Tabubil	27/05	2005	604	-8.4	-55
Tabubil	01/06	2005	609	-6.5	-42
Tabubil	09/06	2005	617	-6.1	-4
Tabubil	10/06	2005	618	-6.3	-41
Tabubil	15/06	2005	623	-3.2	-14
Tabubil	27/06	2005	635	-4.8	-27
Tabubil	08/07	2005	646	-10.3	-75
Tabubil	12/07	2005	650	-8.9	-63
Tabubil	19/07	2005	657	-6.0	-41
Tabubil	22/08	2005	691	-4.4	-25
Tabubil	02/09	2005	702	-1.9	-3
Tabubil	05/09	2005	705	-2.1	-8
Tabubil	19/09	2005	719	-14.8	-109
Tabubil	02/11	2005	763	-6.5	-42
Tabubil	08/11	2005	769	-2.5	-3
Tabubil	11/11	2005	772	-11.6	-84
Tabubil	18/11	2005	779	-12.4	-94
Tabubil	22/11	2005	783	-15.6	-113
Tabubil	29/11	2005	790	-15.4	-114
Tabubil	29/11	2005	790	-15.4	-118
Tabubil	12/12	2005	803	-12.3	-87
Tabubil	13/12	2005	804	-14.2	-96
Tabubil	21/12	2005	812	-15.0	-102
Tabubil	26/12	2005	817	-13.2	-95
Tabubil	02/01	2006	824	-11.8	-76
Tabubil	04/01	2006	826	-16.0	-117
Tabubil	09/01	2006	831	-12.1	-80
Tabubil	11/01	2006	833	-12.2	-86
Tabubil	17/01	2006	839	-13.9	-105
Tabubil	20/01	2006	842	-16.2	-113
Tabubil	30/01	2006	852	-14.0	-107
Tabubil	03/02	2006	856	-11.1	-77
Tabubil	13/02	2006	866	-7.5	-49
Tabubil	10/03	2006	891	-10.5	-76
Tabubil	10/03	2006	891	-10.5	-77
Tabubil	12/03	2006	893	-10.5	-77
Tabubil	13/03	2006	894	-10.5	-77
Tabubil	14/03	2006	895	-6.0	-53
Tabubil	20/03	2006	901	-10.0	-94
Tabubil	26/03	2006	907	-10.0	-92
Tabubil	06/04	2006	918	-10.1	-92
Tabubil	07/04	2006	919	-14.8	-116
Tabubil	10/04	2006	922	-14.7	-118
Tabubil	10/04	2006	922	-14.7	-118
Tabubil	11/04	2006	923	-19.1	-153

Appendix 10. Interception (I_n) values used for previously-studied watersheds in North America, Africa, and Australia

Vegetation type	Reference	I_n/P_g, %
GLC2000 - North America	[*Latifovic et al.*, 2002]	
Temperate broadleaf deciduous forest	[*Bryant et al.*, 2005]	17.4 ± 6.0
Temperate needleleaf evergreen forest	[*Bryant et al.*, 2005]	22.3 ± 7.0
Temperate mixed broadleaf/needleleaf forest	[*Bryant et al.*, 2005]	18.6 ± 7.0
Temperate broadleaf/needleleaf shrubland	[*Bryant et al.*, 2005]	18.9 ± 6.0
Temperate grassland	[*Couturier and Ripley*, 1973]	21.0 ± 11.0
Cropland	[*Cook et al.*, 2006]	10.6 ± 5.0
Temperate needleleaf evergreen forest (lichen understorey)	[*Pypker et al.*, [2005]	24.0 ± 8.0
GLC2000 - Africa	[*Mayaux et al.*, 2004]	
Evergreen lowland forest (1,2,5,6)	[*Hutjes et al.*, 1990]	9.0 ± 10.0
Montane forest (<1000 m)	[*Holwerda et al.*, 2006]	27.0 ± 9.0
Montane forest (>1000 m)	[*Veneklaas and Van Ek*, 1990]	15.3 ± 5.8
Mosaic: forest/croplands, forest/savannah (7, 8)	[*Jackson*, 2000]	10.0 ± 3.4
Closed deciduous forest and woodland (9, 10)	[*Samba et al.*, 2001]	15.5 ± 6.5
Deciduous shrubland (11)	[*Bryant et al.*, 2005]	18.9 ± 5.6
Grassland (12,13,14,15,16)	[*Thurow et al.*, 1987]	18.1 ± 7.3
Croplands (17,18,19)	[*Van Dijk and Bruijzneel*, 2001]	18.0 ± 10.0
Tree crops (20)	[*Jackson*, 2000]	11.8 ± 4.0
GLC2000 - Southeast Asia	[*Stibig et al.*, 2003]	
Closed multi-layered forest	[*Asdak et al.*, 1998]	15.0 ± 5.0
Closed forest (Eucalyptus)	[*Greenwood et al.*, 1985]	24.0 ± 17.8
Open forest (Eucalyptus)	[*Greenwood et al.*, 1985]	24.0 ± 17.8
Open woodlands	[*Greenwood et al.*, 1985]	24.0 ± 17.8
Closed shrublands	[*Navar and Bryan*, 1990]	18.9 ± 6.0
Open Shrublands	[*Navar and Bryan*, 1990]	18.9 ± 6.0
Grasslands with sparse shrubs	[*Edraki et al.*, 2004]	8.0 ± 4.0
Swamp grasslands	[*Edraki et al.*, 2004]	8.0 ± 4.0
Croplands	[*van Dijk and Bruijnzeel*, 2001]	18.0 ± 10
GLC2000 - South America	[*Eva et al.*, 2003]	
Evergreen lowland forest (10,11,30,31,33)	[*Lloyd and Marques-Filho*, 1988]	8.9 ± 4.4
Closed deciduous forest (20)	[*Huber and Iroume*, 2001]	34.7 ± 3.2
Intensive agriculture	[*Van Dijk and Bruijzneel*, 2001]	18.0 ± 10.0
Mosaic agriculture (51,52)	[*Jackson*, 2000]	10.0 ± 3.4
Forest plantations	[*Jackson*, 2000]	11.8 ± 4.0
Grass and shrub savannah (60 – 75)	[*Thurow et al.*, 1987]	18.1 ± 10.0
Montane forest (<1000 m)	[*Holwerda et al.*, 2006]	27.0 ± 9.0
Montane forest (>1000 m)	[*Veneklaas and Van Ek*, 1990]	15.3 ± 5.8

I_n – rainfall interception, P_g – gross precipitation

Appendix 11. Sources of $\delta^{18}O$ and $\delta^{2}H$ values of rainfall and river water for previously-studied watersheds of North America, Africa, and Australia

A11.1 North and South Americas

In North America, the selected rivers included the North and South Saskatchewan Rivers (the principal tributaries of the Nelson River which flows into Hudson Bay), the Mississippi River, the Ottawa River (a tributary of the St. Lawrence River), and the St. Lawrence River.

$\delta^{18}O$ and $\delta^{2}H$ values of river water collected near the mouths of the North Saskatchewan River at Prince Albert and South Saskatchewan River near Saskatoon (Figure 29) were available from [*Ferguson et al.*, 2007]. The LMWL for these watersheds are based upon $\delta^{18}O$ and $\delta^{2}H$ values of precipitation at Calgary (51.02°N, 114.02°W) and Edmonton (53.57°N, 113.52°W) both of which are part of the Global Network for Isotopes in Precipitation (GNIP) network [*IAEA/WMO*, 2004] and additional isotope data for precipitation at Saskatoon were available from [*Ferguson et al.*, 2007] (Figure 29).

For the St. Lawrence River, $\delta^{18}O$ and $\delta^{2}H$ values of river water collected near Cornwall (51.02°N, 114.02°W) is from [*Barth and Veizer*, 2004] and represents outflow from the Great Lakes region of North America. The isotope composition of precipitation in this region was characterized by data from GNIP stations located at Ottawa (45.32°N, 75.67°W), Atikokan (48.75°N, 91.62°W), Simcoe (42.85°N, 80.27°W), and Chicago (41.78°N, 87.75°W).

For the Ottawa River, $\delta^{18}O$ and $\delta^{2}H$ values for river water were from Carillon, a station located near the river mouth [*Telmer and Veizer*, 2000; *Myre and Hillaire-Marcel*, 2004], and the LMWL was based on $\delta^{18}O$ and $\delta^{2}H$ values for precipitation from the GNIP station at Ottawa.

$\delta^{18}O$ and $\delta^{2}H$ values of river water collected near the mouth of the Mississippi River (at Melville) was taken from [*Lee and Veizer*, 2003] and $\delta^{18}O$ and $\delta^{2}H$ values of precipitation for the Mississippi River watershed were from GNIP stations located at Coshocton (40.36°N, 81.80°W), Chicago (41.78°N, 87.75°W), Calgary (51.02°N, 114.02°W), Hatteras (35.27° N, 75.55°W), and Denver (39.77° N, 104.88°W).

In South America, the Piracicaba River watershed is located in the state of São Paolo in southern Brazil and flows into a tributary of the Paraná River. $\delta^{18}O$ and $\delta^{2}H$ values of river

water collected near the river mouth at Artemis (22.67°S, 47.77°W) was available from *Martinelli et al.* [2004] and the GNIR database [http://isohis.iaea.org/]. For precipitation, $\delta^{18}O$ and $\delta^{2}H$ values from the GNIP station located near Rio de Janeiro (22.90°S, 43.17°W) was used.

A11.2 West Africa

In West Africa, the Black Volta River, the White Volta River, and the Oti River are the principal tributaries of the Volta River, which flows into Lake Volta in southern Ghana before eventual outflow occurs into the Atlantic Ocean (Figure 30). The Upper Niger River and the Bani River are headwater tributaries of the Niger River. The Nyong River (Cameroon) flows into the Atlantic Ocean. $\delta^{18}O$ and $\delta^{2}H$ values of river water collected near the mouths of the Black Volta River, White Volta River, and Oti River are from Bamboi, Nawuni, and Sabari, respectively [*Freitag et al.,* 2007] (Figure 30). $\delta^{18}O$ and $\delta^{2}H$ values of river water collected from the Upper Niger River at Banankoro and the Bani River at Douna were available from the GNIR database. Douna is located immediately before the confluence of the Bani River and Upper Niger River whereas the station at Banankoro is located ~230 km upstream of this confluence.

In the Nyong River watershed, located between the Niger River and Congo River watersheds in Cameroon, $\delta^{18}O$ and $\delta^{2}H$ values of river water collected near the river mouth at Dehane were available from [*Brunet, personal communication*]. $\delta^{18}O$ and $\delta^{2}H$ values of precipitation in West Africa was from the GNIP stations at Kano (12.05°N, 8.52°E), Bamako (12.32°N, 7.57°W), and Niamey (13.52°N, 2.08°E), five stations within the Volta River watershed [*Freitag et al.*, 2007], and five stations located within the Nyong River watershed [*Brunet, personal communication*].

A11.3 Australia

In Australia, outflow from the Murray-Darling River watershed was characterized by $\delta^{18}O$ and $\delta^{2}H$ values for samples collected from several stations located below Rufus Junction [*Simpson and Herczeg*, 1991]. $\delta^{18}O$ and $\delta^{2}H$ values of precipitation was characterized by data from GNIP stations located near Brisbane (27.43°S, 153.07°E), Adelaide (34.92°S, 138.57°E) and Melbourne (37.82°S, 144.97°E).

Appendix 12. $\delta^{18}O$ and $\delta^{2}H$ values of river water for previously-studied watersheds of North America, Africa, and Australia

Watershed	Site	Date	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰
North Saskatchewan River	Prince Albert	18-Sep-00	-18.2	-145
North Saskatchewan River	Prince Albert	22-Sep-00	-18.0	-143
North Saskatchewan River	Prince Albert	27-Sep-00	-17.9	-144
North Saskatchewan River	Prince Albert	19-Oct-00	-18.4	-145
North Saskatchewan River	Prince Albert	2-Nov-00	-19.0	-152
North Saskatchewan River	Prince Albert	24-Nov-00	-19.7	-155
North Saskatchewan River	Prince Albert	6-Dec-00	-20.2	-159
North Saskatchewan River	Prince Albert	21-Dec-00	-20.6	-154
North Saskatchewan River	Prince Albert	4-Jan-01	-19.4	-149
North Saskatchewan River	Prince Albert	17-Jan-01	-20.5	-157
North Saskatchewan River	Prince Albert	6-Feb-01	-20.5	-158
North Saskatchewan River	Prince Albert	2-Mar-01	-20.6	-160
North Saskatchewan River	Prince Albert	20-Mar-01	-20.3	-158
North Saskatchewan River	Prince Albert	11-Apr-01	-19.5	-153
North Saskatchewan River	Prince Albert	22-Apr-01	-19.2	-151
North Saskatchewan River	Prince Albert	8-May-01	-18.7	-149
North Saskatchewan River	Prince Albert	11-May-01	-18.7	-151
North Saskatchewan River	Prince Albert	16-May-01	-18.6	-148
North Saskatchewan River	Prince Albert	22-May-01	-18.5	-149
North Saskatchewan River	Prince Albert	25-May-01	-18.3	-148
North Saskatchewan River	Prince Albert	1-Jun-01	-17.7	-146
North Saskatchewan River	Prince Albert	7-Jun-01	-18.1	-147
North Saskatchewan River	Prince Albert	15-Jun-01	-18.3	-147
North Saskatchewan River	Prince Albert	21-Jun-01	-18.4	-149
North Saskatchewan River	Prince Albert	27-Jun-01	-18.2	-149
North Saskatchewan River	Prince Albert	12-Jul-01	-18.4	-146
North Saskatchewan River	Prince Albert	17-Jul-01	-17.6	-142
North Saskatchewan River	Prince Albert	24-Jul-01	-17.7	-144
North Saskatchewan River	Prince Albert	2-Aug-01	-18.0	-143
North Saskatchewan River	Prince Albert	9-Aug-01	-18.0	-142
North Saskatchewan River	Prince Albert	10-Aug-01	-18.1	-139
North Saskatchewan River	Prince Albert	16-Aug-01	-17.8	-140
North Saskatchewan River	Prince Albert	22-Aug-01	-17.6	-140
North Saskatchewan River	Prince Albert	30-Aug-01	-18.0	-144
South Saskatchewan River	Saskatoon	18-Sep-00	-16.2	-131
South Saskatchewan River	Saskatoon	22-Sep-00	-16.3	-132
South Saskatchewan River	Saskatoon	27-Sep-00	-16.3	-131
South Saskatchewan River	Saskatoon	19-Oct-00	-16.7	-135
South Saskatchewan River	Saskatoon	2-Nov-00	-16.5	-133
South Saskatchewan River	Saskatoon	24-Nov-00	-16.7	-135
South Saskatchewan River	Saskatoon	6-Dec-00	-16.8	-134
South Saskatchewan River	Saskatoon	21-Dec-00	-16.8	-130
South Saskatchewan River	Saskatoon	4-Jan-01	-16.8	-133
South Saskatchewan River	Saskatoon	11-Jan-01	-16.6	-133
South Saskatchewan River	Saskatoon	17-Jan-01	-16.5	-132
South Saskatchewan River	Saskatoon	6-Feb-01	-16.7	-135
South Saskatchewan River	Saskatoon	2-Mar-01	-16.7	-136

South Saskatchewan River	Saskatoon	20-Mar-01	-16.5	-133
South Saskatchewan River	Saskatoon	11-Apr-01	-16.2	-134
South Saskatchewan River	Saskatoon	22-Apr-01	-15.6	-128
South Saskatchewan River	Saskatoon	8-May-01	-15.7	-129
South Saskatchewan River	Saskatoon	11-May-01	-15.8	-130
South Saskatchewan River	Saskatoon	16-May-01	-15.5	-129
South Saskatchewan River	Saskatoon	22-May-01	-15.7	-131
South Saskatchewan River	Saskatoon	25-May-01	-15.8	-131
South Saskatchewan River	Saskatoon	1-Jun-01	-15.7	-130
South Saskatchewan River	Saskatoon	7-Jun-01	-15.5	-129
South Saskatchewan River	Saskatoon	15-Jun-01	-15.4	-127
South Saskatchewan River	Saskatoon	21-Jun-01	-15.8	-130
South Saskatchewan River	Saskatoon	27-Jun-01	-15.7	-130
South Saskatchewan River	Saskatoon	12-Jul-01	-14.9	-125
South Saskatchewan River	Saskatoon	17-Jul-01	-15.0	-126
South Saskatchewan River	Saskatoon	24-Jul-01	-15.0	-128
South Saskatchewan River	Saskatoon	2-Aug-01	-15.3	-126
South Saskatchewan River	Saskatoon	9-Aug-01	-15.3	-127
South Saskatchewan River	Saskatoon	10-Aug-01	-15.2	-125
South Saskatchewan River	Saskatoon	16-Aug-01	-15.2	-128
South Saskatchewan River	Saskatoon	22-Aug-01	-15.3	-128
South Saskatchewan River	Saskatoon	30-Aug-01	-15.3	-130
Ottawa River	Carillon	17-Apr-93	-11.8	-87
Ottawa River	Carillon	17-May-93	-11.4	-84
Ottawa River	Carillon	17-Jun-93	-11.2	-84
Ottawa River	Carillon	3-Aug-93	-10.5	-80
Ottawa River	Carillon	31-Aug-93	-10.4	-79
Ottawa River	Carillon	24-Sep-93	-10.0	-77
Ottawa River	Carillon	8-Oct-93	-10.0	-78
Ottawa River	Carillon	2-Nov-93	-10.3	-77
Ottawa River	Carillon	5-Dec-93	-10.6	-80
Ottawa River	Carillon	6-Jan-94	-11.3	-86
Ottawa River	Carillon	7-Feb-94	-11.0	-84
Ottawa River	Carillon	6-Mar-94	-10.8	-84
Ottawa River	Carillon	14-Apr-94	-11.8	-89
Ottawa River	Carillon	22-Apr-94	-11.4	-86
Ottawa River	Carillon	11-May-94	-11.0	-82
St Lawrence River	Cornwall	1-May-95	-6.8	-47
St Lawrence River	Cornwall	1-Jun-95	-6.9	-46
St Lawrence River	Cornwall	1-Jul-95	-6.6	-51
St Lawrence River	Cornwall	1-Aug-95	-6.6	-46
St Lawrence River	Cornwall	1-Sep-95	-6.5	-48
St Lawrence River	Cornwall	1-Oct-95	-6.6	-50
St Lawrence River	Cornwall	1-Nov-95	-6.8	-51
St Lawrence River	Cornwall	1-Dec-95	-6.9	-51
St Lawrence River	Cornwall	1-Apr-96	-8.4	-61
St Lawrence River	Cornwall	1-May-96	-7.7	-54
St Lawrence River	Cornwall	1-Jun-96	-7.4	-49
St Lawrence River	Cornwall	26-Oct-84	-6.6	-51
St Lawrence River	Cornwall	28-Jan-85	-6.7	-51

St Lawrence River	Cornwall	25-Mar-85	-7.0	-52
St Lawrence River	Cornwall	24-Jun-85	-7.1	-52
St Lawrence River	Cornwall	29-Jul-85	-6.8	-50
St Lawrence River	Cornwall	26-Aug-85	-6.6	-52
St Lawrence River	Cornwall	28-Oct-85	-6.6	-51
St Lawrence River	Cornwall	29-Jan-86	-7.0	-52
St Lawrence River	Cornwall	26-Mar-86	-7.5	-55
St Lawrence River	Cornwall	27-May-86	-7.3	-53
St Lawrence River	Cornwall	25-Jun-86	-7.1	-53
St Lawrence River	Cornwall	28-Aug-86	-6.7	-51
St Lawrence River	Cornwall	28-Oct-86	-6.7	-51
St Lawrence River	Cornwall	9-Feb-87	-6.8	-52
St Lawrence River	Cornwall	3-Jun-87	-7.1	-54
St Lawrence River	Cornwall	14-Aug-87	-6.7	-52
White Volta River	Tamale	19-May-03	1.2	2
White Volta River	Tamale	31-May-03	1.2	4
White Volta River	Tamale	14-Jun-03	-3.5	-20
White Volta River	Tamale	28-Jun-03	-2.8	-16
White Volta River	Tamale	12-Jul-03	-2.2	-17
White Volta River	Tamale	9-Aug-03	-2.9	-13
White Volta River	Tamale	23-Aug-03	-4.2	-27
White Volta River	Tamale	6-Sep-03	-4.5	-31
White Volta River	Tamale	20-Sep-03	-4.7	-31
White Volta River	Tamale	4-Oct-03	-3.7	-26
White Volta River	Tamale	18-Oct-03	-3.1	-17
White Volta River	Tamale	1-Nov-03	-2.3	-17
White Volta River	Tamale	15-Nov-03	-2.3	-18
White Volta River	Tamale	29-Nov-03	-2.3	-17
White Volta River	Tamale	13-Dec-03	-1.7	-13
White Volta River	Tamale	27-Dec-03	-1.6	-10
White Volta River	Tamale	10-Jan-04	-1.2	-13
White Volta River	Tamale	24-Jan-04	-1.2	-13
White Volta River	Tamale	7-Feb-04	-1.3	-15
White Volta River	Tamale	21-Feb-04	-0.5	-15
White Volta River	Tamale	4-Apr-04	-0.4	-13
White Volta River	Tamale	10-May-04	-0.6	-11
Black Volta River	Bondouku	19-May-03	0.9	4
Black Volta River	Bondouku	31-May-03	0.9	6
Black Volta River	Bondouku	14-Jun-03	-2.7	-13
Black Volta River	Bondouku	28-Jun-03	-4.0	-26
Black Volta River	Bondouku	12-Jul-03	-3.1	-21
Black Volta River	Bondouku	26-Jul-03	-3.3	-22
Black Volta River	Bondouku	9-Aug-03	-3.4	-23
Black Volta River	Bondouku	23-Aug-03	-4.9	-35
Black Volta River	Bondouku	6-Sep-03	-4.4	-29
Black Volta River	Bondouku	20-Sep-03	-4.8	-33
Black Volta River	Bondouku	4-Oct-03	-4.3	-31
Black Volta River	Bondouku	18-Oct-03	-3.9	-25
Black Volta River	Bondouku	1-Nov-03	-3.1	-18
Black Volta River	Bondouku	15-Nov-03	-2.6	-17

Black Volta River	Bondouku	29-Nov-03	-2.0	-10
Black Volta River	Bondouku	13-Dec-03	-1.5	-14
Black Volta River	Bondouku	27-Dec-03	-0.9	-12
Black Volta River	Bondouku	10-Jan-04	-0.6	-11
Black Volta River	Bondouku	24-Jan-04	-0.3	-10
Black Volta River	Bondouku	7-Feb-04	-0.2	-13
Black Volta River	Bondouku	21-Feb-04	0.2	-11
Black Volta River	Bondouku	7-Mar-04	0.9	-9
Black Volta River	Bondouku	21-Mar-04	2.2	-1
Black Volta River	Bondouku	18-Apr-04	3.0	3
Black Volta River	Bondouku	2-May-04	0.1	-4
Black Volta River	Bondouku	10-May-04	0.3	-4
Oti River	Sokode	19-May-03	2.1	7
Oti River	Sokode	31-May-03	2.2	9
Oti River	Sokode	14-Jun-03	-3.8	-29
Oti River	Sokode	28-Jun-03	-3.6	-23
Oti River	Sokode	12-Jul-03	-3.0	-19
Oti River	Sokode	9-Aug-03	-3.2	-18
Oti River	Sokode	23-Aug-03	-4.0	-22
Oti River	Sokode	6-Sep-03	-4.6	-30
Oti River	Sokode	4-Oct-03	-3.7	-23
Oti River	Sokode	18-Oct-03	-3.0	-19
Oti River	Sokode	1-Nov-03	-2.7	-17
Oti River	Sokode	15-Nov-03	-2.3	-18
Oti River	Sokode	29-Nov-03	-2.0	-22
Oti River	Sokode	13-Dec-03	-2.0	-22
Oti River	Sokode	27-Dec-03	-1.6	-19
Oti River	Sokode	10-Jan-04	-1.4	-7
Oti River	Sokode	7-Feb-04	-0.8	-12
Oti River	Sokode	21-Feb-04	-0.2	-7
Oti River	Sokode	7-Mar-04	0.4	-5
Oti River	Sokode	21-Mar-04	1.3	-2
Oti River	Sokode	4-Apr-04	0.8	-7
Oti River	Sokode	2-May-04	-0.3	-7
Oti River	Sokode	10-May-04	-0.2	-7
Mississippi River	Melville	10-May-00	-6.6	-42
Mississippi River	Melville	23-May-00	-6.1	-40
Mississippi River	Melville	6-Jun-00	-5.0	-33
Mississippi River	Melville	23-Jun-00	-6.0	-40
Mississippi River	Melville	8-Jul-00	-5.6	-36
Mississippi River	Melville	25-Aug-00	-5.2	-36
Mississippi River	Melville	21-Sep-00	-5.6	-38
Mississippi River	Melville	28-Nov-00	-5.9	-39
Mississippi River	Melville	14-Dec-00	-6.8	-44
Mississippi River	Melville	24-Jan-01	-6.7	-41
Mississippi River	Melville	27-Feb-01	-6.5	-39
Mississippi River	Melville	14-Mar-01	-6.3	-37
Mississippi River	Melville	2-Apr-01	-7.5	-52
Bani River	Douna	19-Jul-90	-2.2	-11
Bani River	Douna	29-Jul-90	-4.8	-30

Bani River	Douna	8-Aug-90	-5.6	-34
Bani River	Douna	18-Aug-90	-5.2	-33
Bani River	Douna	28-Aug-90	-4.3	-26
Bani River	Douna	7-Sep-90	-3.9	-22
Bani River	Douna	18-Sep-90	-3.8	-22
Bani River	Douna	28-Sep-90	-3.6	-19
Bani River	Douna	8-Oct-90	-3.3	-19
Bani River	Douna	18-Oct-90	-3.1	-19
Bani River	Douna	28-Oct-90	-2.8	-17
Bani River	Douna	7-Nov-90	-2.5	-14
Bani River	Douna	17-Nov-90	-2.2	-15
Bani River	Douna	27-Nov-90	-2.0	-14
Bani River	Douna	9-Dec-90	-1.7	-13
Bani River	Douna	23-Dec-90	-1.1	-11
Bani River	Douna	6-Jan-91	-0.9	-9
Bani River	Douna	20-Jan-91	-0.4	-9
Bani River	Douna	17-Feb-91	0.9	-3
Bani River	Douna	3-Mar-91	1.5	-1
Bani River	Douna	13-Mar-91	2.4	4
Bani River	Douna	27-Mar-91	3.4	8
Bani River	Douna	10-Apr-91	4.6	12
Bani River	Douna	18-Apr-91	4.5	14
Bani River	Douna	24-May-91	5.2	15
Bani River	Douna	29-Jun-91	-1.3	-13
Bani River	Douna	22-Jul-91	-3.1	-18
Upper Niger River	Banankoro	7-Jul-90	-1.8	-8
Upper Niger River	Banankoro	17-Jul-90	-3.4	-20
Upper Niger River	Banankoro	27-Jul-90	-5.2	-32
Upper Niger River	Banankoro	7-Aug-90	-5.4	-33
Upper Niger River	Banankoro	18-Aug-90	-5.2	-31
Upper Niger River	Banankoro	28-Aug-90	-4.8	-29
Upper Niger River	Banankoro	7-Sep-90	-4.8	-28
Upper Niger River	Banankoro	18-Sep-90	-4.6	-28
Upper Niger River	Banankoro	28-Sep-90	-4.3	-24
Upper Niger River	Banankoro	8-Oct-90	-4.0	-22
Upper Niger River	Banankoro	18-Oct-90	-3.7	-20
Upper Niger River	Banankoro	28-Oct-90	-3.4	-19
Upper Niger River	Banankoro	8-Nov-90	-3.3	-19
Upper Niger River	Banankoro	19-Nov-90	-3.3	-20
Upper Niger River	Banankoro	29-Nov-90	-3.1	-19
Upper Niger River	Banankoro	9-Dec-90	-2.8	-16
Upper Niger River	Banankoro	23-Dec-90	-2.7	-17
Upper Niger River	Banankoro	6-Jan-91	-2.6	-17
Upper Niger River	Banankoro	20-Jan-91	-2.0	-12
Upper Niger River	Banankoro	3-Feb-91	-1.1	-9
Upper Niger River	Banankoro	17-Feb-91	-0.5	-7
Upper Niger River	Banankoro	3-Mar-91	0.7	0
Upper Niger River	Banankoro	17-Mar-91	1.4	2
Upper Niger River	Banankoro	31-Mar-91	2.4	7
Upper Niger River	Banankoro	14-Apr-91	3.4	11

Upper Niger River	Banankoro	17-Apr-91	3.3	11
Upper Niger River	Banankoro	23-May-91	3.2	10
Upper Niger River	Banankoro	27-Jun-91	-2.8	-18
Upper Niger River	Banankoro	2-Aug-91	-4.5	-25
Murray Darling River	Morgan	1-Jan-89	-2.7	-19
Murray Darling River	Morgan	1-Apr-89	-1.7	-16
Murray Darling River	Morgan	1-Jun-89	-4.7	-34
Murray Darling River	Waikerie	1-Jan-89	-2.0	-19
Murray Darling River	Waikerie	1-Apr-89	-1.5	-18
Murray Darling River	Waikerie	1-Jun-89	-4.8	-34
Murray Darling River	Murray Bridge	1-Jan-89	-1.7	-17
Murray Darling River	Murray Bridge	1-Apr-89	-1.3	-14
Murray Darling River	Murray Bridge	1-Jun-89	-5.1	-35
Murray Darling River	Lock 5	1-Jan-89	-2.5	-21
Murray Darling River	Lock 5	1-Apr-89	-1.7	-17
Murray Darling River	Lock 5	1-Jun-89	-5.4	-35
Murray Darling River	Lock 3	1-Jan-89	-2.0	-19
Murray Darling River	Lock 3	1-Apr-89	-1.4	-19
Murray Darling River	Lock 3	1-Jun-89	-5.2	-34
Murray Darling River	Rufus Junction	1-Jan-89	-3.8	-28
Murray Darling River	Rufus Junction	1-Apr-89	-1.9	-21
Murray Darling River	Rufus Junction	1-Jun-89	-4.4	-34
Murray Darling River	Taliem Bend	1-Jan-89	-1.0	-15
Murray Darling River	Taliem Bend	1-Apr-89	-1.8	-17
Murray Darling River	Taliem Bend	1-Jun-89	-5.3	-36