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BIOSPHERE-ATMOSPHERE INTERACTIONS

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CHAPTER 6: BIOGEOCHEMICAL CYCLES OF AMAZON

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ACRONYMS AND ABBREVIATIONS

BNF: Biological nitrogen fixation
BVOC: biogenic volatile organic compounds
CCN: Cloud Condensation Nuclei
DOC: Dissolved Organic Carbon
ENSO: El Niño and the Southern Oscillation
GBP: Gross Biome Productivity
GPP: Gross Primary Productivity
IN: Ice Nuclei
LRT: marine aerosols and long-range transported
NMVOC: Non Methane Volatile Organic Compounds
NEE: Net Ecosystem Exchange of Carbon Dioxide
NPP: Net Primary Productivity
PBA: primary biological aerosols
POC: Particulate Organic Carbon
SAR: Synthetic Aperture Radar
SOA: Secondary Organic Aerosols
VOC: Volatile Organic Compounds
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• The Amazon forest is a major store of carbon and an ongoing sink of carbon that makes a modest contribution to slowing down the rate of carbon dioxide rise in the atmosphere. This carbon sink has been weakening over recent decades.

• Available estimates of inputs of carbon from plants growing in seasonally inundated habitats are of similar order to estimates of CO₂ degassed from these habitats. Hence, aquatic environments would seem to be approximately in balance evasion, and do not require substantial inputs from uplands.

• Methane emissions from the Amazon basin are estimated to represent 6-8% of global methane emissions, though large uncertainties in both sources and sinks remain.

• The Amazon region also contributes a large fraction of global N₂O emissions from natural ecosystems; biological N fixation converts is a major source of available nitrogen for the regional biosphere.

• The release of biogenic volatiles from the forest plays an important role in affecting cloud condensation and rain fall.
ABSTRACT

The Amazon basin hosts the Earth’s largest extent of tropical forest, and the world’s largest river system. These two features make it a major contributor to regional and global biogeochemical cycles, such as the carbon cycle and major nutrient cycles. This chapter summarizes understanding of the cycles in Amazon of three key biogeochemical elements (carbon, nitrogen and phosphorus), spanning both terrestrial and aquatic ecosystems. In recent decades the intact Amazon biome has been a major carbon sink, though this sink appears to be weakening over time. The chapter also examines the net emissions of two other key trace gases with substantial contributions to radiative warming (methane and dinitrogen oxide), and finally summarizes understanding of trace gas and aerosol emissions from Amazon and their impact on atmospheric pollution, cloud properties and water cycling.

Keywords: carbon, carbon dioxide, methane, nitrogen, phosphorus, aerosols, clouds, aquatic, terrestrial

GRAPHICAL ABSTRACT

1 general diagram of Amazon ecosystems is credited to National Geographic
6.1. INTRODUCTION

The Amazon basin accounts for around 16% of the entire metabolism of the terrestrial biosphere, and the Amazon basin is the largest drainage basin in the world, contributing around one-fifth the global freshwater discharge. These features make it a major contributor to regional and global biogeochemical cycles, including the cycles of carbon, nitrogen, phosphorus and other nutrients. The chapter highlights and summarizes some of the main aspects of the biogeochemistry of the Amazon region. The focus is on the relatively intact regions of Amazon, to understand baseline or natural biogeochemical processes. Deforested and other human-modified landscapes are discussed in Part II of the report. However, in part of the chapter where we draw up budgets for the whole region (of carbon or methane), we inevitably include anthropogenic emissions in order to have a complete picture. The chapter starts with first considering the carbon cycle of Amazon, its seasonal variability and the role of mechanisms in the intact Amazon forest as a carbon sink. The subsequent section describes the cycling of key nutrients in Amazon, especially nitrogen and phosphorus. Then we look at the contribution of the region to global budgets of other major greenhouse gases, methane and N₂O. Finally, we turn to emissions of other biogenic trace gases and aerosols, and their role in affecting cloud physics and dynamics and ozone chemistry.

When considering the literature on the biogeochemical cycles of Amazon region as a whole, it is important to define what is meant by Amazon. Different studies use different definitions. For example, forest carbon cycle studies tend to focus on the whole lowland forest biome, including areas outside of the Amazon watershed (e.g., the Guyanas) but excluding non-lowland forest biomes such as the planalto and the Andean montane regions. In contrast, hydrological studies tend to focus on the entire watershed. Here, we adopt the definitions of Eva et al. (2005) for these areas. The five regions of Amazon sensu lato (the whole Amazon-Tocantins watershed plus adjoining lowland forest regions) are Amazon basin lowland forests (5,569,174 km²), Guyana lowland forests (970,161 km²), Gurupi lowland forests (161,463 km²), the non-forest biome Amazon watershed in the planalto (864,951 km²) and the montane Andes in the Amazon watershed (555,564 km²). The narrowest definition (lowland forest biome within the Amazon basin) is also referred to as Amazon sensu stricto.

We first focus on forest biomass carbon dynamics: as much of the carbon in the Amazon is in aboveground biomass, the forest and its fate is linked to the global carbon cycle. However, water availability and nutrients can limit productivity and affect carbon cycling: we next discuss the water, nitrogen and phosphorus cycles. We then focus attention on two other important greenhouse
gases with significant sources in the Amazon: methane and nitrous oxide. Finally, forests are linked to climate not only through their ability to evaporate water, but through production of gases and aerosols that in turn influence radiation and cloud properties and precipitation. Our focus throughout is largely on largely intact ecosystems in Amazon, mainly forests and freshwaters, but under recent and current climate and atmospheric conditions. Hence these intact ecosystems are not equivalent to preindustrial Amazonian ecosystems. Degraded and extensively modified Amazonian ecosystems are discussed Part II in this report.

6.2. CARBON CYCLE IN THE AMAZON

6.2.1 The Amazon carbon cycle throughout the Cenozoic and Pleistocene

The South American broadleaf tropical forest biome probably began to approach its modern closed-canopy and angiosperm-dominated structure in the wake of the Chicxulub asteroid impact 66 million years ago, and the associated extinction of megafaunal dinosaurs (Carvalho et al. 2021) (see Chapter 1). In the warm and most climates of the Paleogene (66-23 M yr BP) there was “tropical” (or megathermal – not affected by frost) forest covering much of South America, connecting the proto-Amazon and Atlantic Forest biomes and extending much further south to Patagonia (Maslin et al. 2005). The suitable climate and high atmospheric CO$_2$ concentrations of this early “mega-Amazon” could have resulted in substantially higher productivity and overall biomass than the modern Neotropical biome. Over the last 50 million years CO$_2$ concentrations have broadly declined, and there has been an associated cooling and drying of the global and regional climate. The tropical forest biomes have retreated, the Atlantic Forest separated from the Amazonian biome (Maslin et al. 2005), and grasses spread from Africa in the Late Miocene (~10 Myr BP), resulting in the creation of new fire-dominated savanna biomes such as the cerrado, and the further retreat of the forest biome (Osborne et al. 2007). Carbon stocks and ecosystem productivity are likely to have declined along with these atmospheric changes.

Over the Pleistocene (2.6 Myr - 11.7 kyr BP), the establishment of large northern ice gaps greatly amplified climate instability. The presence of extensive polar ice caps enables the ice-albedo feedback to operate, where slight cooling/warming leads to further expansion/retreat of ice sheets, leading to increased/decreased reflection of solar radiation, and so to a positive feedback that amplifies small changes in Earth’s rotation and orbit into dramatic changes in climate. The last 1 million years have been dominated by a roughly 100,000 year cycle, 90% of which is largely a cool
climate with low atmospheric CO₂ (~180 ppm) and extreme climate variability, broken by short (~10,000 year period) of warmer and wetter conditions, higher CO₂ (~280 pm) and less climate variability (the Holocene being a prime example). The low CO₂ concentrations of glacial periods (180 ppm) may be close to the threshold of viability of photosynthesis, and would have greatly reduced ecosystem productivity.

There has been much speculation as to how Amazonian forests varied during these glacial-interglacial cycles. Haffer (1969) famously suggested that during glacial maxima the forest biome retreated into refugia separated by cerrado, and this process was a driver of Amazonian speciation. This scenario has not stood the test of time: the broad consensus seems to be that during glacial periods there was only modest retreat in forest extent at the boundaries. Paleoecological and speleotherm data suggest that the climate was undoubtedly drier, but the lower temperatures reduced evapotranspiration rates and enabled forest to persist (Mayle et al. 2004, Bush et al. 2017, Wang et al. 2017). However, substantial areas of forest may have been dry forests interweaved between moist rainforests. The variability of the climate may have enabled an occasional corridor of savanna corridor to open in eastern Amazon. Overall Amazonian carbon stocks are likely to have been only slightly reduced from present-day values, but productivity would have been substantially reduced and the rate of carbon cycling slower (Mayle et al. 2004).

In the latest interglacial period, the Holocene (11.7 kyr – present), rainforest productivity and carbon stocks initially increased with warmer, wetter and higher CO₂ conditions. However, over the Early–Mid-Holocene (ca. 8500–3600 yr BP), reduced precipitation and increased fire frequency affected much of the south of the region, resulting in forest retreat and savanna and dry forest expansion (Mayle et al. 2004). In the Late Holocene, the rain belt has expanded further south and the forest has gradually been expanding southwards, resulting in an overall increase in Amazon forest biomass to its peak values in the last thousand years (Mayle et al. 2004).
6.2.2. Carbon cycle processes in terrestrial Amazonian forests

Figure 1. Some of the key concepts in the terrestrial carbon cycle (the numbers indicated are for the entire terrestrial carbon cycle). Plants take up carbon dioxide through photosynthesis: this is the Gross Primary Productivity (GPP). Much of the carbon is used for plant metabolism and respiration, with the remainder being used to produce biomass including wood, leaves and fine roots. The short-lived tissue is rapidly shed and decomposed, releasing carbon dioxide back to the atmosphere as heterotrophic respiration. Carbon in woody tissue and soils tends to accumulate over time through ecological succession but is mostly released back to the atmosphere through tree mortality and decomposition. Overall, the processes of woody biomass creation and tree mortality have not been in balance in recent decades, leading to a net biomass carbon sink, equivalent to positive Net Biome Productivity (NBP).

Amazon forest carbon cycle

The net carbon balance of terrestrial Amazonian systems is the resultant of large fluxes of uptake and release. With their year-long growing season, tropical forests such as those of Amazon are amongst the most productive natural ecosystems on Earth. A range of studies across the basin have
described the carbon cycle processes of Amazonian forests. Figure 2 illustrates the carbon cycle of a typical central Amazonian forest near Manaus, Brazil, derived from (Malhi et al. 2009).

The input of carbon to the forest through photosynthesis is termed Gross Primary Productivity (GPP): typically about one-third of GPP is used for biomass production of primarily wood, fine roots, leaves and reproductive tissues (Net Primary Productivity or NPP), and two-thirds is used up by plant metabolism, resulting in the release of carbon dioxide by the vegetation (autotrophic respiration) (Malhi et al. 2009). Above-ground woody biomass growth, the most commonly measured aspect of carbon uptake by vegetation, only accounts for around 8-13% of the photosynthetic carbon uptake (Malhi et al. 2015). Canopy and fine root productivity account for similar amounts of carbon use but leaves and fine root tissues are short-lived and make up a small proportion of total biomass stocks. All biomass ends up as dead material, either through litterfall, herbivory or through mortality. This material is broken down and metabolised, primarily by fungi but also by bacteria and soil macrofauna such as termites, releasing the carbon dioxide back to the atmosphere as heterotrophic respiration. There are additional, smaller fluxes to and from the ecosystem: volatile organic compounds such as isoprenoids (isoprene, monoterpenes, sequiterpenes) and methane account for more than 0.5% of GPP (Kesselmeier et al. 2002), and outflow of dissolved organic carbon in stream water of less than 1% of GPP, though this fraction will vary by soil and vegetation and is not well sampled. The net carbon balance of a mature terra firme Amazonian forest could be expected to be zero from ecosystem first principles, as the uptake of carbon through photosynthesis is compensated by release of carbon through heterotrophic and autotrophic respiration. However, long term inventories suggest a net rate of increase of vegetation biomass of 0.6 Mg C ha\(^{-1}\) yr\(^{-1}\) (where Mg is 10\(^3\) grams) (see below), equivalent to about 2% of photosynthesis (Brienen et al. 2015).
Figure 2. The carbon cycle of a typical Amazonian forest (near Manaus, central Amazon).
Adapted from data in (Malhi et al. 2009). GPP = Gross Primary Productivity (predicted as sum of NPP and autotrophic respiration, and directly estimated from flux tower measurements (NEE + Reco); NEE - net carbon flux or net ecosystem exchange, Reco - combination of autotrophic and heterotrophic respiration, NPP - Net Primary Productivity, in total, and above ground (AG) and belowground (BG) components, and its components as (i) canopy production (leaves, flower, fruit, twigs); (ii) branch turnover; (iii) volatile organic carbon emissions (VOC); (iv) above-
ground woody tissue production (stem); (v) coarse root production; (vi) fine root production; R - Respiration, in total and autotrophic (aut) and heterotrophic (het) components, and its components as (vii) leaf respiration; (viii) wood tissue respiration; (ix) root respiration; (x) soil heterotrophic respiration; (xi) total soil respiration, either directly measured or predicted as sum of inputs assuming no net change in soil carbon stocks; D - detritus fluxes, as (xii) fine litterfall; (xiii) coarse woody debris production; (xiv) root detritus production; (xv) Fdoc - carbon export in the form of dissolved organic carbon. Units are Mg C/ha/year.

Variation of GPP and NPP across Amazon and their relation to climate, geology, and hydrology

The total GPP of Amazon is around 20 Pg C y\(^{-1}\) accounting for around 16% of global terrestrial GPP (Beer et al. 2010). There are relatively few direct measurements of NPP and GPP across Amazon. Broadly, the magnitude of GPP is determined more by seasonality in rainfall rather than soil nutrient status, with the highest values found in the wet forests of northwestern Amazon, and lower values found in regions with a long dry season, where photosynthesis rates in the dry season are reduced by either stomatal closure or by increasing deciduousness (Malhi et al. 2015). The highest productivities reported for the Amazon are in the aseasonal and relatively fertile forests near Iquitos in Peru (Malhi et al. 2015). Sandy soils, such as those found in the upper Rio Negro, support lower productivity. However, rates of NPP and woody biomass production do not follow the same regional pattern, and higher rates of woody growth tend to be found in western Amazon. This may be because the soils of western Amazon tend to have higher nutrient content (Malhi et al. 2004), reflecting their younger age and geological history or their poor soil structure (Quesada et al. 2012). There is a strong gradient in tree turnover across Amazon, with trees in western and southern Amazon tending to both grow faster and die younger, and trees in eastern Amazon and especially on the Guyana shield being slow-growing and long-lived (Quesada et al. 2012). This change in dynamics affects the patterns of biomass, with the highest biomass (and vegetative carbon stock) Amazon forests tending to be found in north-eastern Amazon (Johnson et al., 2016). Hence, in mature forests, rates of tree growth are negatively correlated with forest biomass, and tree mortality and turnover rates influence biomass more strongly than productivity and tree growth rates do. In montane systems in the Andes, the productivity of forests declines with elevation, halving by about 3000 m elevation (Malhi et al. 2018). Forest turnover rates show no trend with elevation, so forest biomass declines in proportion to declining productivity.
Both the magnitude and nature of soil carbon stocks are highly variable across Amazon. Soil types range from highly weathered ferralsols dominating in eastern parts of the Basin, through to a predominance of younger soils in the western basin and lower montane slopes, occasional patches of sandy soils, and carbon-rich organic soils dominating in wetland regions such as northern Peru, and in montane cloud forests (Quesada et al. 2020).

**Seasonal variation of carbon cycle**

Plant phenology—the timing of cyclic or recurrent biological events in plants such as leaf, stem or root growth, leaf senescence, or flowering—is a sensitive indicator of plant and forest function that links seasonal climate rhythms to seasonality of carbon cycle processes (Albert et al. 2019; Reich et al. 2004; Jones et al. 2014; Saleska et al. 2003). The seasonality of GPP fluxes emerges from the phenology of leaf growth and senescence (Wu et al. 2016; Lopes et al. 2016; Wagner et al. 2017), while seasonality of soil respiration is likely linked to climate seasonality and the phenology of both leaves and fine root dynamics (Keller et al. 2004; Raich 2017; Girardin et al. 2016). Seasonality of soil respiration is also buffered by deep soil CO₂ production, which lags surface soil CO₂ production due to slower drying down of deep soil horizons in the dry season (Davidson et al. 2004). Understanding how seasonal rhythms of biology, climate, and resources interact to regulate carbon fluxes is thus a key part of understanding and predicting forest drought response, resilience, and changes into the future.

GPP seasonality exhibits distinct patterns across the Amazon, including a notable contrast - readily seen from space, ground surveys, or eddy flux towers - between dry season increases in GPP ("greening") in intact rainforest regions of the central Amazon versus seasonal declines ("browning") in converted forests, southern forests, or savanna woodlands (Figure 3). There is debate over these patterns and the mechanisms driving them (including whether they might be remote sensing artefacts, Huete et al. 2006; Morton et al., 2014; Saleska et al., 2016), and how they might be modeled (Lee et al., 2005; Baker et al., 2008; Restrepo-Coupe et al., 2017), but recent work combining flux data, satellites, phenocams, and leaf-level data suggests they emerge from patterns of water availability (Guan et al. 2015) and root distribution (Ivanov et al., 2012; Brum et al. 2019), sunlight (Restrepo-Coupe et al., 2013), and plant phenological strategy (Wu et al., 2016; Wagner et al. 2017).
Figure 3. (Requested permission to reproduce the figure under evaluation) (upper left panel) Dry season gross primary productivity (GPP), photosynthetic flux, relative to maximum at each site (GPP GPP\textsubscript{max} \textsuperscript{-1}) dynamics versus number of days since dry-season onset, across different sites in Amazon (see legend to the right, with equatorial forests in green/blue solid lines, Southern forest orange line, pastures as dotted yellow lines, ecotone forest as dashed, and cerrado in solid brown). (upper right panel) GPP fractional change during the dry season, relative to its magnitude at start of the dry season (error bars indicate site-specific interannual variability) (modified from Restrepo-Coupe et al., (2013)). (lower panel) MODIS enhanced vegetation index (EVI) across an ecotone from Santarém forests to Cerrado near Cuiabá (modified from Ratana et al. 2012, 2006).

Seasonal variation in biosphere functioning couple carbon and water exchanges with the atmosphere and contributes to global scale seasonal variations in atmospheric CO\textsubscript{2} and H\textsubscript{2}O. Because leaf stomata link evapotranspiration to GPP, dry season maxima in GPP facilitate a corresponding dry-season maxima in forest ET (Shuttleworth, 1988, Hasler and Avissar 2007; see also Chapter 7). By moistening the dry-season atmospheric boundary layer, these fluxes hasten transition to the wet season ahead of the southward migration of the intertropical convergence zone (Wright et al. 2017, Fu and Li 2004).

The net carbon sink in intact Amazonian forests

Old-growth forests are in principle in long-term equilibrium, with woody biomass growth balanced by mortality, and photosynthesis equal to sum of autotrophic and heterotrophic respiration plus a minor amount exported to streams and rivers (Figure 2). Hence net carbon balance would be zero. In practice, an old-growth forest stand may not be in carbon neutrality because of (i) long term episodic disturbance and recovery; (ii) some large long-lived trees may continue to accumulate biomass for many centuries or even millennia; (iii) secular atmospheric change (rising CO\textsubscript{2} concentration, changes in temperature or rainfall) may lead to long-term trends in productivity and/or respiration. The RAINFOR network has monitored above-ground biomass changes in Amazon, and currently spans over 400 plots across the region. The network observations have suggested an increase in biomass of old growth forests over time, summing to 0.38 (0.28-0.49 95% C.I.) Pg C year\textsuperscript{-1} if extrapolated over the Amazon forest biome in the 2000s (Brienen et al. 2015) (Figure 4). This accumulation seems to stop in drought years (Phillips et al. 2009) and seems to be declining over time (Brienen et al. 2015). Increasing length of the dry season may lead to the intact forests of the Amazon becoming a carbon source in the near future (see chapter 19, working group 8). The widespread nature of the observed biomass accumulation (plus similar observations from
Africa and Borneo) suggests that a global driver such as increasing atmospheric CO$_2$ could be responsible for this net carbon sink (Hubau et al. 2020; Qie et al. 2019). An alternative possibility is recovery from past anthropogenic disturbance (with accessible sites more likely to have been disturbed in the past), although the timescales involved (> 100 years) and the observation of increasing growth rates over time, argue against this possibility.

**Figure 4.** (Requested permission to reproduce the figure under evaluation) *Long-term carbon dynamics of structurally intact old growth tropical forests in Amazon (from Brienen et al. 2015)*

Trends in net aboveground live biomass carbon (a), carbon gains to the system from wood production (b), and carbon losses from the system from tree mortality (c), measured in 321 forest inventory plots. Black lines show the overall mean change up to 2011 for 321 plots (or 274 units) weighted by plot size, and its bootstrapped confidence interval (shaded area). The red lines indicate the best model fit for the long-term trends since 1983 using general additive mixed models (GAMM), accounting explicitly for differences in dynamics between plots (red lines denote overall mean, broken lines denote s.e.m.).

### 6.2.3. Disturbances as modifiers of the Amazonian carbon cycle

The steady-state of the Amazonian carbon cycle can be disrupted abruptly, with long-lasting effects, by forest disturbances, both natural and anthropogenic. These, on one hand, can be associated with climate-driven intensification of seasonal cycles (Barichivich et al. 2018, Gouveia et al. 2019), which can be exacerbated by the interaction between deforestation and climate change (Zemp et al. 2017), increasing the frequency of flooding, wind storms and droughts. On the other hand, changes in the frequency and intensity of extreme climatic events, especially droughts, can favour human-induced forest disturbances related to human-ignited fires, which can lead to forest degradation. The combination of climatic and anthropogenic processes tends to reinforce each other (Cochrane, 2001; Cochrane & Laurance, 2002, 2008; Alencar, Solorzano & Nepstad, 2004; Aragão et al., 2007, 2008; Poulter et al., 2010, Zemp et al. 2017), exacerbating any single forcing impact.
Direct climate effect on the carbon cycle

Blowdowns are meteorological processes caused by downbursts associated with convective squall lines, resulting in large patches of tree mortality by uprooting or breakage of tree trunks (Espirito-Santo et al. 2014, Araujo et al. 2017). These events can cause significant gross losses of carbon from the aboveground live biomass, with large (≥5 ha, blowdowns only) and intermediate (0.1–5 ha, blowdowns plus other causes of death) events contributing to ~0.3% (~0.003 Pg C y$^{-1}$), and ~1.1% (~0.01 Pg C y$^{-1}$) of the loss. Most of the natural gross C loss, however, is concentrated in small (<0.1 ha) canopy disturbances accounting for ~98.6% (~1.28 Pg C y$^{-2}$) of total forest-dynamics related losses over the entire Amazon region (Figure 1; Espirito-Santo et al. 2014, where Pg is 10$^{15}$ grams). Despite the magnitude of impacts on C stocks, recovery of the disturbed patches of forests promotes net biomass accumulation that approximately balances the observed losses. Forests disturbed by blowdowns tend, however, to be more susceptible to the effects of other forest disturbances, such as droughts and fires. The impact of droughts may be larger in these forests as changes in plant community composition and structure, favoring the dominance of early successional stages species with fast growth rates (Nelson et al. 1994), which are characterized by low wood density, increases the susceptibility of this low wood-density dominated forests to drought-induced mortality (Phillips et al. 2009, 2010). The accumulation of dead wood from tree mortality can further destabilize the C cycle, by increasing forest vulnerability to fire, if these areas are near areas dominated by human-ignition sources. Both interannual climate variation (including drought and wet extremes) and fires impacts will be discussed below.

The frequency of interannual climate variations (e.g., recurring droughts or periods of excess wetness due to El Niño and the Southern Oscillation (ENSO) cycles, and associated occurrence of fires or blowdowns), structure Amazon forest functional composition and hence, carbon cycling. Forest carbon cycle responses to interannual droughts and temperature variations in different biogeographic regions provide insights into forest function, resilience and carbon cycling.

Drought-induced stress from water limitation in terra firme forests can reduce the overall capacity of the forest system to uptake atmospheric CO$_2$ and increase tree mortality in old growth Amazonian forests (Phillips et al., 2010; van der Molen et al., 2011), see Section 5 on Chapter 22. Drought can directly reduce the photosynthetic capacity of forests -- by promoting stomatal closure (Santos et al. 2018; Smith et al. 2020; Garcia et al., 2021) and/or inducing leaf shedding (Doughty et al. 2015; Anderson et al. 2010) -- and can contribute to excess mortality. Tree vulnerability to drought, however, widely varies across the functional diversity of tree species, with species having
more resilient hydraulic architecture (e.g. greater embolism resistance of their water-transporting xylem) less likely to succumb to drought (Rowland et al. 2015), a response consistent with developing ecohydrological theories of tree response to drought (Anderegg et al. 2018; Wu et al. 2020; Wang et al. 2020) that suggests forest vulnerability to drought is heterogeneous across the Amazon, depending on forest species compositions, functional traits, and local environments (Cosme et al. 2017; Oliveira et al. 2019; Esquivel-Muelbert et al. 2020; Barros et al. 2019; Aleixo et al. 2019; Castro et al. 2020).

Declines in photosynthetic uptake and/or increases in mortality are responsible for a reduction in aboveground (Nepstad et al., 2004; Phillips et al., 2009; da Costa et al., 2010) and belowground biomass production (Metcalfe et al., 2008). In addition to the reduction in carbon assimilation by vegetation, increased tree mortality has an additive effect on the reduced capacity of Amazonian forests to assimilate and store atmospheric carbon. Droughts tend to weaken or even reverse the net Amazonian forest sink (Gatti et al. 2014). The net carbon sink is quantified as Net Biome Productivity (NBP; Figure 1) and its reduction is the result of the additive effect of declines in photosynthesis during the drought and subsequent increases in heterotrophic respiration in the following wet season (Tian et al., 1998; Zeng et al., 2008) driven by widespread drought-induced tree mortality increasing the decomposing pool (Williamson et al., 2000; Phillips et al., 2009). Droughts, such as that of 2005, can, therefore, promote a biomass loss from tree mortality [approximately -1.1 (95% C.I. -2.04 to -0.49) Pg C], with an addition NPP reduction of -0.50 Pg C (Phillips et al., 2009). Assuming an exponential wood decomposition rate of 0.17 y⁻¹ (Chambers et al., 2000), it is expected that annual emissions from this pool of dead wood one year after the drought account for -0.18 (95% CI from -0.32 to -0.07) Pg C, steadily reducing over time (Aragão et al. 2014). While it did not experience excessive drought in 2005, the central Amazon also lost biomass carbon due to blowdowns associated with a single synoptic storm event (Chambers et al. 2014); thus, some biomass losses attributable to climate variability can be through processes other than mortality directly related to drought stress.

Hydrologic environments significantly structure drought response: seasonally inundated floodplain forests, in contrast to terra firme forests discussed above, are limited by hypoxia (low oxygen) and thus droughts, rather than increasing forest stress, relieve it and induce increases in growth and NPP (Schöngart and Wittmann 2011). However, these areas are vulnerable to altered hydroperiods, as indicated by increased mortality in floodplains influenced by dams that modulate discharge and inundation (Resende et al. 2020). Recent studies show that even in terra firme
forests, shallow water table regions with greater access to soil water show neutral or positive responses to drought, with decreased mortality and increases in recruitment and growth (Sousa et al. 2020; Esteban et al. 2020). Accounting for the difference between deep water table forests with limited water access, deep water table forests with large soil water storage capacity (Nepstad et al., 1994; Oliveira et al. 2005; Guan et al. 2015), and shallow water table forests with greater water access (one third of Amazonian terra firme forests) appears to reconcile earlier controversies over differences between remote sensing which showed vegetation green up (Saleska et al. 2007; Brando et al. 2010; Samanta et al., 2010; Janssen et al. 2021) and plot scale studies in deep water table regions which showed negative responses to drought. An important research priority is to increase understanding of the influence of both environmental and organismal functional heterogeneities to arrive at a more integrated understanding for forest responses to environmental perturbations such as drought (Longo et al. 2018; Levine et al. 2016).

Human-induced fire disturbances

Human-induced land use and cover change is the major factor determining fire occurrence in Amazonian forests as they are directly related to ignition sources. Human activities associated with droughts can exacerbate the occurrence of fires in Amazon and induce their spread into adjacent forest areas, altering the carbon cycle of these forests. Old-growth forests exposed to droughts which is associate to low rainfall, increases in temperature and vapor pressure deficit (VPD) inside the canopy (Ray et al. 2005) and decreases in relative humidity (Cardoso et al. 2003; Sismanoglu and Setzer 2005) and plant available water (PAW) (Nepstad et al. 2004), are more prone to the incursion of fires related to the deforestation process or the management of agricultural lands in Amazon. One of the most uncertain components of Amazonian forest fire impacts is the magnitude of short- and long-term carbon emissions and potential implications for CO₂ levels in the atmosphere and consequent global warming. Quantification of carbon emissions from understory forest fires is still lacking, preventing accurate estimates of the contribution of this component. Recently, van der Werf et al. (2010) estimated for the period between 1997 to 2009 that globally, fires were responsible for an annual mean carbon emission of 2.0 Pg C y⁻¹, with South America contributing 14.5%. Of this, about 8% appears to have been associated with forest fires, based on estimates from the Global Fire Emission Dataset (GFED) product for South America. According to Silva et al. (2020) forest fires contribute with cumulative gross emissions of carbon of ~126 Mg CO₂ ha⁻¹ for 30 years after a fire event and a mean annual efflux value of 4.2 Mg CO₂ ha⁻¹ y⁻¹. This same study showed that cumulative CO₂ uptake of burned forests offsets
only 35% (45.0 Mg CO$_2$ ha$^{-1}$) of the total gross emissions from forest fire within the same timeframe. Emissions from the decomposition of the dead organic matter account for ca. 58% (47.4 Mg CO$_2$ ha$^{-1}$) of total net emissions (Silva et al. 2020). The total contribution to the basin will depend on the burned area which can vary widely, between drought and non-drought years. In the Brazilian Amazon between 2008 and 2012 an average of 7,800 km$^2$ of old-growth forest were affected by fires, with a peak of 25,400 km$^2$ during the 2010 drought (Aragão et al. 2018). For the whole Amazon (geographical boundaries defined by Eva et al. 2005), data from MODIS product MCD64A1 collection 6 (Figure 5) demonstrate that 4.5% of Amazon has burned at least once in the last 12 years. It also suggests that, within this period, c.a. 60,000 km$^2$ of burned area occurred in areas already deforested and in areas mapped as primary forests in the year 2000 (Aragão et al. 2014). Forest fires, in its majority, result from the leakage of fires from deforested areas to adjacent forests (Aragão et al. 2016). Apart from at the driest fringes, most of the Amazon region is not naturally fire susceptible and its ecosystems are not resilient to fires.

Figure 5. Spatial distribution of the cumulative burned area in the Amazon basin from 2003 to
2020 based on the MODIS MCD64A1 c6 product.

6.2.4. Carbon cycle processes in aquatic Amazonian ecosystems

The uptake, release and transport of carbon by aquatic Amazonian ecosystems is a significant component of the regional carbon cycle. High rates of primary production by plants and algae in aquatic environments, considerable sedimentation in lakes and reservoirs, and large amounts of carbon dioxide and methane emitted from rivers, lakes and wetlands all lead to fluxes disproportionately large relative to the area of aquatic systems (Melack et al. 2009; Melack 2016). Remote sensing analyses of inundation and wetland habitats, inundation modeling, and extensive and intensive measurements in rivers, reservoirs, lakes and wetlands are now available, but considerable uncertainty and information gaps remain given the diverse aquatic habitats throughout the Amazon basin. Aquatic habitats range from headwater streams to lakes and floodplains fringing rivers. Junk et al. (2011) delineated major types of wetlands in the lowland Amazon based on climate, hydrology, water chemistry, and botany. Hess et al. (2015) used synthetic aperture radar (SAR) data at 100-m resolution to determine inundated area and areal extent of major aquatic habitats (open water, herbaceous plants and flooded forests) within the lowland basin (< 500 m asl). The amplitude, duration and frequency of inundation determine the temporal and spatial variations of these aquatic habitats and associated fluxes. Multi-year time series of inundation at 0.25° resolution and recently at 0.5 to 1 km resolution, derived from several satellite-borne sensors, are available (Hamilton et al. 2002; Prigent et al. 2020; Parrens et al. 2019). Hydrological models (e.g., Coe et al. 2007; Paiva et al. 2013) calculate river discharges well, while a paucity of digital elevation models on floodplains compromises inundation estimates.

Exchange of carbon dioxide and methane between surface water and overlying atmosphere depends on the concentration gradient between air and water and on physical processes at the interface, usually parameterized as a gas transfer velocity ($k$). Methane can also exit via bubbles and pass through tissues of rooted aquatic plants, both herbaceous and woody. Water to atmosphere fluxes of carbon dioxide from all aquatic environments in the catchments of the Amazon and Tocantins river systems, covering approximately 970,500 km$^2$, are estimated to be approximately 722 Tg C y$^{-1}$ (where Tg is $10^{12}$ grams) (Table 1).

Fluxes from hydroelectric reservoirs add 8.85 Tg C y$^{-1}$. Of the total, excluding hydroelectric reservoirs, fluxes from river channels represent about 19%, streams about 14%; floodable forests 36%, and other wetlands plus a small contribution from the open water of lakes and reservoirs
about 30%. While terrestrial sources of dissolved organic carbon (DOC) and particulate organic carbon (POC) contribute to these fluxes, the majority of the carbon evaded to the atmosphere is likely derived from organic matter in aquatic plants photosynthesizing with atmospheric CO₂ (Melack and Engle 2009). Hence, most of these water-to-atmosphere fluxes represent respiration of carbon fixed within aquatic habitats, not carbon transported from uplands. To estimate net fluxes from aquatic habitats, a portion of the aquatic NPP must be subtracted from the total fluxes listed in Table 1.

Floodplains and other wetlands are productive aquatic environments that export considerable amounts of carbon to rivers, accumulate sediments, and provide a portion of the organic carbon that leads to the evasion of CO₂ and CH₄ to the atmosphere. Melack et al. (2009) summarized estimates of net primary productivity (NPP) for the plants and algae on central Amazon floodplains. The total net production attributed to flooded forests (excluding wood increments), aquatic macrophytes, phytoplankton and periphyton for the 1.77 million km² characterized by Hess et al. (2003) is about 300 Tg C y⁻¹. Flooded forests account for 62% of the total, aquatic macrophytes account for 34% and the remaining 4% is associated with periphyton and phytoplankton. Approximately 10% of the total value equals the export of organic carbon by the Amazon River (Richey et al. 1990), methane emission is about 2.5% (Melack et al. 2004) and a similar percent is likely to be buried in sediments. The remaining portion is close to being sufficient to fuel the respiration that results in the degassing of 210 ± 60 Tg C y⁻¹ as carbon dioxide from the rivers and floodplains for this region (Richey et al. 2002).

Extrapolating the estimates of aquatic NPP to the whole Amazon basin is quite difficult. Primary production of these wetlands varies considerably between wetland types and regions from the most productive whitewater river floodplains with high amounts of fertile sediments to clearwater floodplains with intermediate fertility and the blackwater rivers with low fertility (Junk et al., 2011; Fonseca et al., 2019). Large uncertainties stem from the sparseness of measurements and uncertainties in habitat areas. Particularly large data gaps exist for the Llanos de Moxos (Bolivia), peatlands in the Pastaza Marañon foreland basin (Peru; Lähteenoja et al. 2012) and central-west Amazon (Lähteenoja et al. 2013), coastal freshwater wetlands (Castello et al. 2013), riparian zones along streams throughout the basin (Junk et al. 2011), small reservoirs associated with agriculture (Macedo et al. 2013) and habitats above 500 m. Improved estimates also require incorporation of seasonal and interannual variations in inundation and habitat areas.

Streams and small rivers likely receive almost all the CO₂ evaded from terrestrial-derived
respiration in soils and respiration of organic C from riparian and upland litter as summarized in Richey et al. (2009). Inorganic and organic carbon in large rivers is provided by a combination of terrestrial and aquatic carbon sources (with the proportion unknown), and much of this organic carbon is metabolized in the rivers (Mayorga et al. 2005; Ellis et al. 2012; Ward et al. 2013; 2016). Photo-oxidation of organic carbon appears to make small contributions to CO₂ in large rivers (Amaral et al. 2013; Remington et al. 2011).

Based on available estimates of NPP of seasonally inundated herbaceous habitats and litterfall in woody habitats, and the area of these habitats listed in Table 1, annual inputs of labile, organic carbon (~900 Tg C y⁻¹) are of similar order to estimates of CO₂ degassed from these habitats plus storage in sediments. Herbaceous plants are highly productive and most turnover and decompose rapidly, and litterfall from flooded forests tends to decompose readily also. Hence, NPP associated with the aquatic environments would seem to be sufficient to approximately balance evasion, and not require substantial inputs from uplands.

**Table 1. Annual carbon dioxide fluxes to the atmosphere from aquatic habitats in the Amazon basin including deltaic river channels, coastal freshwater habitats, and Tocantins basin. Basin areas are based on catchment boundaries for river systems, not presence of tropical forest vegetation. (These effluxes derive mostly from respiration of carbon produced within aquatic habitats; net fluxes require accounting for hard-to-quantify inputs from aquatic NPP.)**

<table>
<thead>
<tr>
<th>Aquatic habitats</th>
<th>Annual carbon dioxide fluxes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivers²</td>
<td>137 Tg C y⁻¹</td>
</tr>
<tr>
<td>Streams³</td>
<td>100 Tg C y⁻¹</td>
</tr>
<tr>
<td>Lakes⁴</td>
<td>25 Tg C y⁻¹</td>
</tr>
<tr>
<td>Flooded forests⁵</td>
<td>260 Tg C y⁻¹</td>
</tr>
<tr>
<td>Other wetlands⁶</td>
<td>200 Tg C y⁻¹</td>
</tr>
</tbody>
</table>

² Channel areas from Allen & Pavelsky (2018) plus L. Hess (personal communication) and Castello et al. (2013) for delta, and Sawakuchi et al. (2017) for Xingu and Tapajos mouthbays. Fluxes averaged from Richey et al. (1990), Rasera et al. (2008), Sawakuchi et al. (2017), Less et al. (2018) and Amaral et al. (2019).
³ Johnson et al. (2008) approximated evasion of CO₂ from headwater streams basin wide with a statistical approach that requires validation based on actual measurements in Andean, blackwater or savanna streams.
⁴ Open water area of lakes is the difference between total open water area (Hess et al. 2015) and river channel area (Allen & Pavelsky 2018) guided by lake areas estimated by Sippel et al. (1992). Area includes estimates of fringing floating plants. Fluxes averaged from Rudorff et al. (2011), Amaral (2017) and Amaral et al. (2019).
⁵ Floodable forests estimated by Hess et al. (2015), and seasonally weighted fluxes derived from Amaral et al. (2020).
⁶ Aquatic categories lumped as other wetlands (195000 km²) include interfluvial wetlands in Negro basin (21000 km²), savanna floodplains in Roraima (4000 km²), Moxos (35000 km²) and Bananal and others in Tocantins basin (35000 km²), Marajos Island and other freshwater coastal wetlands (50000 km²), and other wetlands scattered throughout the basin (50000 km²). Floodable areas from Hess et al. (2015), seasonal averages for Roraima, Moxos and Bananal and others in Tocantins basin from Hamilton et al. (2002) and Castello et al. (2013) plus L. Hess (personal communication). Fluxes for interfluvial wetlands in Negro basin (0.77 Gg C km⁻² y⁻¹; Belger et al. 2011), Roraima (3.5 Gg C km⁻² y⁻¹; Jati 2014), Pantanal (as surrogate for herbaceous areas in Moxos, Bananal and other wetlands in Tocantins basin; 1 Gg C km⁻² y⁻¹; Hamilton et al. 1995) and estimate for Marajos Island, other freshwater coastal wetlands, and other scattered inundated areas (1 Gg C km⁻² y⁻¹).
6.3. NUTRIENT CYCLING IN THE AMAZON BASIN

“Nutrient limitation lies at the heart of ecosystem ecology” (Townsend et al. 2011). Tropical forests are responsible for about a quarter of global terrestrial NPP, which, in turn, is modulated by the environmental availability of water, energy and nutrients. Nevertheless, multiple interactions among biogeochemical cycles, in multiple nutrients can affect the Amazon C cycle, the co-limitation by nitrogen and phosphorus is an important constraint to plant productivity in this system. In general, weathered tropical soils have a lower P availability, leading to higher N:P ratios in leaves from tropical forests when compared to high-latitude plants. In contrast, highlighting the diversity of the Amazon region, less weathered soils contain a low nitrogen: phosphorus ratio, potentially making them more limited by nitrogen than by phosphorus (Nardoto et al. 2013). Due to the dominance of more weathered soils in the region, model results suggest that taking into account phosphorus limitation may result in a reduction in the NPP response to the increase of CO₂ in the atmosphere (CO₂ fertilization) by up to 50%, in the Amazon (Fleischer et al., 2019).

6.3.1. Nitrogen

Nitrogen is abundant in Earth’s atmosphere in the form of the N₂ molecule, but this stable form is not directly available for biological processes. The conversion of N₂ into reactive forms (e.g., NH₃, NOₓ, among others) is essential for life as nitrogen is the foundation for proteins, enzymes, amino-acids, and essential nutrients for biological growth. Within natural ecosystems this conversion is performed by biological nitrogen fixation and, to a much smaller extent, by lightning. Another key process for life and biological functioning is the conversion of the organic nitrogen into mineral forms, which are preferably absorbed by plants (ammonium, NH₄⁺, and nitrate, NO₃⁻). This process, called nitrogen mineralization, is a vital part of soil fertility, and key in terrestrial tropical systems, considering the high intensity of organic

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7 The 159 hydroelectric reservoirs currently in the Amazon basin cover approximately 5350 km² (Almeida et al., 2019). Hydroelectric reservoirs in the Tocantins basin cover approximately 5380 km². Many are small and the few large ones account for most of the area. In Bolivia (50 km²), Ecuador (35 km²) and Peru (103 km²) almost all are above 1000 m asl. All in Brazil are in lowlands (~500 m asl; 10730 km²) with several in tropical forests and many others in tropical savannas and agricultural landscapes. Very few have adequate sampling to characterize CO₂ emissions. In contrast to methane, almost all evasion to the atmosphere occurs from the reservoir surface with little degassed at the turbines, though some CO₂ generated in the reservoir is emitted downstream (Kemenes et al., 2016). The estimation of emissions from Brazilian reservoirs was done in two parts: Average fluxes and areas (total 4615 km²) from Kemenes et al. (2011) plus slight additional downstream fluxes (Kemenes et al., 2016) for Balbina, Samuel, Curua-Una and Tucuruí were used to yield 5.7 Tg C y⁻¹. The average value for Amazon reservoirs of 510 g m⁻² y⁻¹, approximated from Barros et al. (2011) was applied to the remaining 6115 km² of Brazilian reservoirs to yield 3.1 Tg C y⁻¹. Estimating the emissions from the reservoirs in Bolivia, Ecuador the Peru is more difficult because no measurements exist and at higher elevations temperatures will be lower and the watersheds different from conditions in Brazil. Hence, half the rate applied to the southern Brazilian reservoirs is used to yield an emission of 0.5 Tg C y⁻¹. In total, emissions from hydroelectric reservoirs can be estimated to be approximately 8.85 Tg C y⁻¹ with considerable uncertainty and a definite need for many more measurements, especially because more dams are planned. The extent that this estimate represents net emissions, i.e., emissions additional to those associated with the undammed rivers are unknown, but reservoir emissions are likely to be much higher than those in natural rivers.
matter decomposition. Mineralization also leads to N immobilization, when N is incorporated in soil microbial biomass, and to denitrification, which is the reduction of nitrate (NO$_3^-$) or nitrite (NO$_2^-$) into the gases nitric oxide (NO), nitrous oxide (N$_2$O), or dinitrogen (N$_2$), with ensuing loss of nitrogen from the ecosystem. Inputs of nitrogen to the Amazon ecosystems are derived largely from biological nitrogen fixation by microorganisms, which is a process mediated by microorganisms in symbiotic association to specific families of plants and as free-living microorganisms. Other inputs derived from atmospheric deposition might also be relevant in specific areas of the region.

The abundance of the Fabaceae family in the Amazon forest could indicate the important input of nitrogen through the biological nitrogen fixation (BNF). Some calculations suggested N$_2$ fixation in order of 15 kg N ha$^{-1}$ y$^{-1}$, for ecosystems on Ultisols and Oxisols, and 25 kg N ha$^{-1}$ y$^{-1}$, in more fertile soils (Martinelli et al., 2012). However, Nardoto et al. (2012) suggested through $^{15}$N analysis a low incidence of N$_2$ fixation by the Fabaceae family, and the maximum symbiotic fixation rate at the level of 3 kg N ha$^{-1}$ y$^{-1}$ for the Amazon forest. Recent results by Reis et al. (2020) suggested BNF rates in the South American moist forests are in order of 10 ± 1 kg N ha$^{-1}$ y$^{-1}$, where 60% of this total originates from free-living N fixing organisms, and 40% from symbiotic association with legume family plants. These numbers highlight the importance of internal cycling for nitrogen in the Amazon, which is strongly depending on regular precipitation and soil water availability in the dry season and on the availability of other soil nutrients like phosphorus. Atmospheric wet and dry deposition of reactive nitrogen was estimated to be at the order of 4% of the BNF for the evergreen broadleaf forest in Amazon (Chen et al., 2010). In regions under higher anthropogenic pressure, the rate of reactive nitrogen deposition can be significant, as reported by Markewiks et al. (2004) for Paragominas, where the authors found the N input in precipitation at the order of 4 kg N ha$^{-1}$ y$^{-1}$.

Internal nitrogen recycling in soil, from undisturbed forests, is the main source of NO and N$_2$O (see sub-item 6.4.2) to the atmosphere in the Amazon. NO emissions were measured as 4.7 ng N m$^{-2}$ s$^{-1}$ in May 1999 (transition season) and about 4.0 ng N m$^{-2}$ s$^{-1}$ in September 1999 (dry season) in an Amazon rainforest site in Rondônia (Gut et al., 2002a). Davidson et al. (2008), on analysing emissions from a water-exclusion experiment in the Tapajós forest, in Santarém (PA), reported NO emissions from the control plot (area without any water exclusion) at rates of 0.9 kg N ha$^{-1}$, as a mean value over five years. However, these emissions do not directly reach the atmosphere above the forest. Major parts of NO are processed within the canopy by oxidation to NO$_2$ and taken up by plants. Thus, there is a "canopy reduction factor" for the NOx release into the atmosphere (Gut et al. 2002b). These ratios can be completely changed when polluted air from
biomass burning sources is advected, which leads to high NOx concentrations. Due to the precursor properties of NOx molecules, ozone (O\textsubscript{3}) concentrations also increase directly. NO\textsubscript{2} concentrations in a rainforest in Rondônia were about three times higher in September/October 1999 then during the wet season in April/May 1999 due to anthropogenic forest fires (Andreae et al., 2002). Enhanced NOx concentrations lead to higher OH concentrations. As OH is the major atmospheric oxidizer, this also strongly affects the oxidation capacity of the atmosphere. This could lead to changes in cloud formation and rainfall patterns if deforestation and urbanization won't decline (Liu et al., 2018).

Deforestation and forest regrowth strongly affect soil nutrient cycling and nitrogen dynamics (Figueiredo et al. 2019). Chronosequence studies have shown enhanced gross nitrogen mineralization in young regrowing forests followed by a decay which leads to only about half the gross nitrogen mineralization in older regrowth forests compared to the undisturbed forest (Figueiredo et al. 2019). Further discussion on secondary forest and land use after deforestation can be found in Chapter 19, Part II of Report.

### 6.3.2. Phosphorus

On old, heavily weathered soils found in much of Amazon, it is likely that phosphorus (P) is a more critical limiting macronutrient than nitrogen. Phosphorus plays an essential role in many biological processes such as in metabolism and as a building block of DNA, but in natural ecosystems can be very limited. This is primarily because soluble forms of P are only found at low concentrations (Markewitz et al. 2004; Johnson et al. 2001) and gaseous forms are almost non-existent (phosphine, PH\textsubscript{3}, being a very rare exception). The effect of low P availability is further exacerbated because many tropical soils can occlude soil P and render it unavailable to plants. The main inputs of P into the Amazonian ecosystems are from weathering, either from local soils or from Andean material transported in rivers and deposited in floodplains, and deposition in the form of dust (e.g., from the Sahara) or ash (from biomass burning). P in biogenic aerosols and from biomass burning represents recycling of P largely within the Amazon system, whereas P deposition from Saharan dust is the primary form of new atmospheric input of P.

The main loss term is export of sediment or organic material via the river system, or through harvesting. Within the basin, lateral movement of P, for example from floodplains rich in Andes-derived sediments) may be facilitated by animals (Doughty et al. 2013; Buendía et al. 2018); such animal-mediated lateral transfer may have been much stronger in the past prior to megafaunal
extinction and more recent defaunation.

Total atmospheric deposition of P is estimated to be 16–30 kg P km\(^{-2}\) yr\(^{-1}\) (Vitousek and Sanford 1986), of which Saharan dust inputs are estimated to be no more than 13%, and the bulk is from biogenic aerosols and biomass burning (Mahowald et al. 2005). Vitousek and Sanford (1986) estimated that the recycling of phosphorus through litterfall is 140–410 kg P km\(^{-2}\) yr\(^{-1}\), an order of magnitude greater than atmospheric inputs.

Local weathering inputs are estimated to average 2.5 kg P km\(^{-2}\) yr\(^{-1}\) (Doughty et al. 2013). However, weathering rates are very variable; the oxisols that dominate much of eastern Amazon have virtually no weatherable apatite left, so weathering inputs of P are practically zero. The Amazon basin experiences continental isostatic rebound, where the slow erosion rates are compensated by slow uplift and weathering of new material (Buendía et al. 2018). Multiplied up by the area of the Amazon basin (including the Guyanas), the total P inputs are ~2.8 Tg C yr\(^{-1}\).

Fluvial export of P, based on discharge at Óbidos, is 1.46 Tg P yr\(^{-1}\), about half of the inputs to the basin (Devol et al. 1991).

There are strong gradients in P availability across the basin, with the lowest availability on the old weathered oxisols of eastern Amazon, and higher concentrations on younger soils in western Amazon (Quesada et al. 2010). The high productivity of the Amazon forest despite this low P availability is facilitated by very tight recycling of P within the forest system, where around half of leaf P is either resorbed prior to leaf senescence, and most of the rest is rapidly captured by fungal hyphae soon after litter fall or plant death (Cuevas and Medina 1986; Markewitz et al. 2004).

### 6.4. OTHER MAJOR GREENHOUSE GASES

#### 6.4.1 Methane

*Terrestrial methane fluxes*

Methane is the second strong greenhouse gas due its importance regarding the anthropogenic radiative forcing contributing to Earth’s climate change, and with a warming potential relative to CO2 of 28 for a 100-year time horizon. In addition, methane is the primary anthropogenic volatile organic compound (VOC) in the global troposphere (Fiore et al. 2002), contributing to the tropospheric O\(_3\) formation by photochemical reactions (West et al. 2006), and in the stratosphere, methane reacts with chlorine atoms, which are a stratospheric ozone-depleter (Cicerone 1987).
Methane is produced by different processes (i.e., biogenic, thermogenic, or pyrogenic), of anthropogenic or natural origin and is consumed by a few sinks. The balance between the sources and sinks determines the methane budget. In terrestrial environments, anoxia in soil leads to the production of methane as a terminal step in the degradation of organic matter by anaerobic methanogenic archaea. Methanotrophs in terrestrial soils can consume methane under aerobic conditions. The balance between the two processes is regulated by climatic and edaphic factors, such as soil temperature, oxygen content, soil pH, water table and electron acceptors (Conrad 2009).

Well-drained soils of the upland forest in the Amazon are often a net CH$_4$ sink, estimated to be 1-3 Tg CH$_4$ yr$^{-1}$ (Davidson and Artaxo 2004; Dutaur and Verchot 2007). However, rainfall, poor drainage and soil properties can create localised anoxic microsites that can facilitate methane production causing forests to switch from sinks to small sources (Verchot et al. 2000). Oxygen availability in forest soils is known to influence methane production, with emissions of 0.5-2.3 mg of CH$_4$ m$^{-2}$ d$^{-1}$ observed in a montane forest in Puerto Rico (Teh et al. 2005). Anaerobic decay of waterlogged wood (Zeikus and Ward 1974) and deadwood (Covey et al. 2016) are also sources of methane. Methane can be produced by a variety of fungi and archaea within tree stems, a process identified by Zeikus and Ward (1974) and now recognised as common and perhaps present in living trees with no visual decay (Covey & Megenigal 2018).

Methane sources have been detected within forest canopies (Carmo et al. 2006). Tank bromeliads (Martinson et al. 2010) and termites (Martius et al. 1993) are known to produce methane and also harbor methanogens. Large, site specific emissions from termites (25.9 ± 11.2 mg CH$_4$ g termite$^{-1}$ yr$^{-1}$; Martius et al. 1993) and tank bromeliads (3.6 g CH$_4$ ha$^{-1}$ d$^{-1}$; Ecuadorian Andes, Martinson et al. 2010) have been reported. A recent study in an Amazon forest found high emissions from mounds of soil feeding termites ranging from 3.5-16.4 µg CH$_4$ m$^{-2}$ d$^{-1}$, suggesting the likely underestimation of the role of termites at an ecosystems scale (van Asperen et al. 2020). Epiphytic bryophytes on tree stems and branches can act as sources and sinks of methane, as indicated by two studies in non-Amazonian forests (Lenhart et al. 2015; Machacova et al. 2017). These methane sources within canopies are highly heterogeneous with limited measurements, hence, it is difficult to estimate their regional source strength.

Methane can be produced by a novel abiotic pathway from plant tissues, with an estimated global source strength of up to 1 Tg CH$_4$ yr$^{-1}$ (Bloom et al. 2010). Reactive oxygen species in plant tissues commonly produced in response to plant stress are known to drive these abiotic methane emissions.
Upland tree stem and leaf surfaces are postulated to offer additional terrestrial sinks (Covey and Megonigal 2018); however, direct observations are presently lacking.

Anthropogenic activities in terrestrial ecosystems can both emit or take up methane. Anthropogenic sources of methane are discussed in detail in Working Group 8. Briefly, land use changes such as logging or conversion of forests to agriculture reduce the capacity of the soil methane sink due to soil compaction (Bustamante et al. 2009). Forest fire is known to emit methane in the short term (Wilson et al. 2016), reduce the methane sink in some forests, reduce methane emissions from wetland trees in flooded forests initially, but later may result in enhanced emissions due to the increased availability of substrates for methanogenesis. Land conversion to animal farming with the introduction of ruminant livestock increase emissions due to enteric fermentation. Waste management and direct production during biomass burning increases methane emissions. Land conversion following river damming changes the flooding regime both upstream and downstream and are documented to increase methane emissions (see next section).

Freshwater methane fluxes

Methane emission to the atmosphere from aquatic environments (Table 2) reflects differences between CH\textsubscript{4} production by methanogens, mainly in anoxic sediments, and consumption by methanotrophs, as well as physical processes. These processes are influenced by environmental variables such as water temperature, dissolved oxygen, trophic status and substrate availability. CH\textsubscript{4} can reach the atmosphere by three pathways: via diffusive fluxes at the air-water interface, via bubbles that form in the sediment, rise through the water column and are emitted to the atmosphere (ebullition), and through the vascular systems of herbaceous and woody plants. Wetland adapted trees are known to transport and emit soil produced methane to the atmosphere via tree trunk and leaf surfaces (Pangala et al. 2017). Ebullitive fluxes depend on bubble formation and hydrostatic pressure over the sediment, while diffusive fluxes are dependent on concentration gradients and turbulence, which vary on multiple time and space scales. Factors such as wind speed, diel variation in thermal structure and physical processes such as convective and advective mixing are all known to influence gas distributions and transfer velocities, and consequently gas fluxes.

Table 3 summarizes methane fluxes from major aquatic environments in the Amazon basin. Fluxes of methane from all aquatic environments within the catchments of the Amazon and Tocantins river systems, covering 970000 km\textsuperscript{2}, are estimated to be approximately 51 Tg CH\textsubscript{4} y\textsuperscript{-1}. Given the varied approaches and associated uncertainties in these values, the procedure used for each category is
described briefly, including both the area of each category and the average annual flux per km², based on selected studies with the most comprehensive or representative data, if possible.

River channels areas (85500 km²) are based on Allen and Pavelsky (2018) plus L. Hess (personal communication) and Castello et al. (2013) for the delta, and Sawakuchi et al. (2017) for Xingu and Tapajos mouthbays. Average fluxes (8 Mg CH₄ km⁻² y⁻¹) are from Sawakuchi et al. (2014) and Barbosa et al. (2016). Stream channel area (50000 km²) is estimated from geomorphological features (Richey et al. 2002; Beighley and Gummadi 2001), and average fluxes (6.6 Mg CH₄ km⁻² y⁻¹) for tropical and subtropical streams are from Stanley et al. (2016). Open water area of lakes is the difference between total open water area (Hess et al. 2015) and river channel area (Allen & Pavelsky, 2018) guided by lake areas estimated by Sippel et al. (1992). Lake area includes estimates of areas with floating plants. Fluxes are averaged from Barbosa et al. (2020). Floodable forest area (615000 km²) is derived from Melack & Hess (2010) and Hess et al. (2015). Seasonally weighted fluxes from water surfaces under flooded forests (26.6 Mg CH₄ km⁻² y⁻¹) are derived from Barbosa et al. (2020) and Barbosa et al. (in review) for varzea and from Rosenqvist et al. (2002) for igapo. Wetland trees are the dominant source of methane from the flooded forests, estimated to be 21.2 ± 2.5 Tg CH₄ yr⁻¹; forested wetland soils are responsible for an additional 1.1 ± 0.7 Tg CH₄ yr⁻¹ (Pangala et al. 2017).

Aquatic categories lumped as other wetlands (195000 km²) include interfluvial wetlands in Negro basin (21000 km²), savanna floodplains in Roraima (4000 km²), Moxos (35000 km²) and Bananal and others in Tocantins basin (35000 km²), Marajos Island and other freshwater coastal wetlands (50000 km²), and other wetlands scattered throughout the basin (50000 km²). Floodable areas are based on Hess et al. (2015); seasonal averages for Roraima, Moxos and Bananal and others in Tocantins basin are from Hamilton et al. (2002) and Castello et al. (2013) plus L. Hess (personal communication). Fluxes are estimated as follows: interfluvial wetlands in Negro basin (28 Mg CH₄ km⁻² y⁻¹; Belger et al. 2011), Roraima (5.3 Mg CH₄ km⁻² y⁻¹; Jati 2014), Pantanal (as surrogate for herbaceous areas in Moxos and elsewhere; 80 Mg CH₄ km⁻² y⁻¹; Hamilton et al. 1995) and estimate for Marajos Island and other freshwater coastal wetlands (27 Mg C km⁻² y⁻¹).

Hydroelectric reservoirs (158) in the Amazon basin currently cover approximately 5350 km² (Almeida et al. 2019; see footnotes in Table 2). Hydroelectric reservoirs in the Tocantins basin cover approximately 5380 km². Very few have adequate sampling to characterize methane emission. One example is Balbina, where measurements over a year were made of diffusive and ebullitive fluxes from multiple stations within the reservoir, degassing at the turbines and downstream
(Kemenes et al., 2007). Another example is the multiyear study at Petit Saut (French Guiana), located in tropical forest, that included measurements in the reservoir and downstream (Abril et al., 2005). Both these studies indicate the importance of degassing of methane through the turbines and downstream. Additional measurements at Tucurui, Samuel and Curua-Una reservoirs indicated the significance of degassing at the turbines and downstream (Kemenes et al., 2016). Extrapolating all emissions based on reservoir areas combined with turbine and downstream emissions yields a total of 0.4 Tg CH$_4$ y$^{-1}$ for Balbina, Curua-Una, Samuel and Tucurui. To estimate emissions from the other Brazilian reservoirs, an overall average diffusive and ebullitive emission from the surfaces of ten reservoirs within southern portions of the basin (~29 g CH$_4$ m$^{-2}$y$^{-1}$, as summarized in Deemer et al. 2016) and the combined surface areas of all the additional Brazilian reservoirs yields 0.18 Tg CH$_4$ y$^{-1}$.

Estimating the emissions from the reservoirs in Bolivia, Ecuador and Peru is more difficult because no measurements exist and at higher elevations temperatures will be less and the watersheds different from conditions in Brazil. Hence, half the rate applied to the southern Brazilian reservoirs is used to yield an emission of ~0.002 Tg CH$_4$ y$^{-1}$. In total, methane emissions from hydroelectric reservoirs can be estimated to be approximately 0.58 Tg CH$_4$ y$^{-1}$ (Table 2) with considerable uncertainty and a definite need for many more measurements, including degassing through turbines and downstream, especially because more dams are planned. The extent that this estimate represents net emissions, i.e., emissions additional to those associated with the undammed rivers, are unknown, though upland forest soils are likely to be sinks for methane.

As noted in Section 6.2.2, large uncertainties stem from the sparseness of measurements of fluxes and uncertainties in habitat areas and their seasonal and interannual variations. Temporal differences in methane fluxes are owed to variations in inundation as a result of differences in river discharge, local runoff and rainfall, related ecological conditions and changes in areal coverage of different habitats. Multi-year time-series of measurements are not available to document possible trends or variations. Current hydrological models provide estimates of variations in inundation, but underestimate basin-wide conditions. Remote sensing products include inundated areas, though the longest time-series under-estimate areas in some habitats and have moderate spatial resolution, and high resolution products are temporally sparse. Distinguishing among the varied aquatic habitats relies on a combination of optical and microwave products which lack sufficient time-series.
Table 2. Annual methane fluxes to the atmosphere from aquatic habitats in the Amazon basin including deltaic river channels, coastal freshwater habitats and Tocantins basin plus hydroelectric reservoirs.

<table>
<thead>
<tr>
<th>Aquatic habitats</th>
<th>Annual methane fluxes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivers</td>
<td>0.7 Tg CH₄ y⁻¹</td>
</tr>
<tr>
<td>Streams</td>
<td>0.4 Tg CH₄ y⁻¹</td>
</tr>
<tr>
<td>Lakes</td>
<td>0.7 Tg CH₄ y⁻¹</td>
</tr>
<tr>
<td>Flooded forests:</td>
<td></td>
</tr>
<tr>
<td>Flux from water surface</td>
<td>16.4 Tg CH₄ y⁻¹</td>
</tr>
<tr>
<td>Flux from trees</td>
<td>21.2 Tg CH₄ y⁻¹</td>
</tr>
<tr>
<td>Flux from exposed soil</td>
<td>11.1 Tg CH₄ y⁻¹</td>
</tr>
<tr>
<td>Other wetlands</td>
<td>9.6 Tg CH₄ y⁻¹</td>
</tr>
<tr>
<td>Hydroelectric reservoirs</td>
<td>0.58 Tg CH₄ y⁻¹</td>
</tr>
</tbody>
</table>

Amazon methane budget

Both bottom up and top-down estimates with different spatial and temporal scales are available for the Amazon basin. Bergamaschi et al. (2009) used SCIAMACHY data to calculate total Amazon emissions of 47.5 to 53.0 Tg CH₄ yr⁻¹ in 2004 for an area of 8.6 × 10⁶ km². Based on an inversion model using in situ and remote sensing observations, Fraser et al. (2014) estimated an emission of 59.0 ± 3.1 Tg CH₄ yr⁻¹ from tropical South America (approximately ~9.7 × 10⁶ km²) in 2010. Tunnicliffe et al. (2020) using inverse modelling estimates derived from GOSAT satellite measurements combined with surface data, and the high-resolution regional atmospheric transport model NAME, reported mean emissions for the Brazilian Amazon wetlands substantially lower than other estimates (9.2 ± 1.8 Tg CH₄ yr⁻¹). Wilson et al. (2016) performed an inversion with TOMCAT model using aircraft vertical profile observations and estimated methane emissions of 36.5 to 41.1 Tg CH₄ y⁻¹ in 2010 and 31.6 to 38.8 Tg CH₄ y⁻¹ in 2011 (area of 5.8 x 10⁶ km²), with non-combustion emissions representing between 92 to 98% of total emissions. Pangala et al. (2017) provide a regional estimate of methane emissions of 42.7 ± 5.6 Tg CH₄ y⁻¹ (area of 6.77 x 10⁶ km²) based on regular vertical lower troposphere profiles covering the period 2010–2013, where 10% come from biomass burning. This estimate is similar to bottom-up estimates for the same area.
Estimates of total methane fluxes based on aircraft vertical profiles measurements for the northeastern Amazon (2.8°S, 54.9°W; considering an area of 0.6 x 10^6 km^2) are between 7.5 and 11.7 Tg CH_4 y^{-1} (Miller et al. 2007; Basso et al. 2016; Pangala et al. 2017), where natural sources, like wetlands, are likely important, with biomass burning representing almost 10% of total annual mean flux and anthropogenic emissions representing around 11% of the annual mean flux (Basso et al. 2016). This region has higher fluxes than other regions (Wilson et al. 2016; Pangala et al. 2017), which highlights a regional variability in methane emissions in the Amazon.

The overall methane budget includes multiple sources and sinks whose contributions are sensitive to feedback from drought conditions, and significant gaps remain in understanding how these droughts will affect methane budgets (Saito et al. 2016). During the 2010 drought methane emissions from biomass burning were around 5-6 times higher than 2011, varying from 0.5 to 7.0 Tg CH_4 y^{-1} depending on the climate condition (drought years), the Amazon region and the severity of the burn season (Wilson et al. 2016; Saito et al. 2016).

These top-down estimates of methane emissions indicate that the Amazon is an important source, extrapolating these estimates for the same area (for an Amazon area of 6.77 x 10^6 km^2) total methane emissions varying between 36.9 and 48.0 Tg CH_4 y^{-1} (Bergamaschi et al. 2009; Fraser et al. 2014; Wilson et al. 2016; Pangala et al. 2017). Suggesting a contribution from this region of 6-8% of global methane emissions, considering the global methane emission of 576 Tg CH_4 yr^{-1} (Saunois et al. 2020), highlighting a significant contribution from Amazon region to the global methane budget.

6.4.2. Nitrous oxide (N_2O)

Terrestrial biosphere N_2O processes

Nitrous oxide (N_2O) is, after carbon dioxide (CO_2) and methane (CH_4), the third most important long-lived greenhouse gas, and one of the main stratospheric ozone depleting substances. The majority of anthropogenic N_2O is produced by the agricultural sector, although natural systems emit nitrous oxide on the organic matter decomposition processes, particularly in the soil. Emissions of N_2O, predominantly from denitrification, are related to biological and physical-chemical characteristics of the soil. Soil microbial processes modulate organic matter mineralization and environmental conditions as soils water content, N availability, soils texture, pH, labile organic carbon content are important conditions for the transformation of organic matter in dissolved nutrients to the plants and soil biota. Rapid nutrient cycling related to higher temperatures, water availability and high N:P ratio result in tropical forests emitting high rates of N_2O to the
atmosphere. Tropical regions account to 71% of global natural ecosystem emissions (Yu and Zhuang 2019). Ciais et al. (2014) reported the global N$_2$O emissions from natural vegetation of 6.6 Tg N y$^{-1}$ (ranging from 3.3 to 9.0 Tg N y$^{-1}$, IPCC AR5). Recently, Tian et al. (2020) reported global emissions from natural soils (with strong contribution from the tropics) in the period from 2007-2016 on the order of 4.9 to 6.5 Tg N y$^{-1}$. Syakila and Kroeze (2011) simulated an increase of 8 times, of total anthropogenic N$_2$O emissions, from the beginning of the industrial revolution to 2006, from 1.1 Tg N y$^{-1}$, in 1850 to 8.3 Tg N y$^{-1}$ in 2006, with the emissions from global natural systems maintained at 10.5 Tg N y$^{-1}$, in the same period, global N$_2$O Model Intercomparison Project (NMIP) simulations (from 1860 onwards) indicate the highest N$_2$O global emissions derived from tropical areas, and tropical South America (particularly the Amazon region), accounting to 20% of global emissions (Tian et al. 2018). The models consider natural and human transformed land use (e.g., agriculture, pasture) in the simulations.

**Freshwater biosphere N$_2$O processes**

Most N$_2$O emissions from freshwater systems occur in wetlands. Guilhen et al. (2020) based on the wetlands along the Amazon, Madeira and Branco rivers, circa of 1.3 x 10$^6$ km$^2$, modelled the N$_2$O emissions derived from denitrification on the order of 1.8 kg ha$^{-1}$ y$^{-1}$, peaking in March. Total emissions from the denitrification process in the Amazon basin floodplains are estimated to be 1.03 Tg N- N$_2$O y$^{-1}$. Due to the abundance of nitrogen in the Amazon soils, in general, nitrate may not be limiting denitrification in the Amazon basin (Guilhen et al. 2020).

**The Amazon N$_2$O Budget**

Estimates for N$_2$O emissions in tropical forest soils ranged from 0.8 Tg N y$^{-1}$ (mean for 1991–2000) for South America (Felipe Pacheco and INMS, personal communication) to 2.40 Tg N y$^{-1}$ (Matson and Vitousek 1990) and 3.55 Tg N y$^{-1}$ (Breuer et al. 2000) for tropical humid forests globally. Melillo et al. (2001) and Davidson et al. (2001) calculated emissions from the Amazon tropical forest of 1.2 to 1.3 Tg N y$^{-1}$. Buscardo et al. (2016) estimated the highest N$_2$O emissions in the north-west portion of the basin and decreased with drier conditions towards the east and south, with an average estimate of 0.74 to 0.83 Tg N y$^{-1}$ for the entire Amazon basin, and the variation was due to the fraction attributed to soil respiration. Figueiredo et al. (2019) and Galford et al. (2010) suggest that the Amazon mature forest (including terra firme and periodically flooded forests) is responsible for circa of 6.5% of the global N$_2$O emissions from natural systems, and fluxes are estimated at the order of 0.5-2.5 kg N ha$^{-1}$ (Lent et al. 2015; Tian et al. 2020). In a comprehensive review conducted by Meurer et al. (2016) it was shown that the median annual flux rates from Amazonian forests were about 36% higher than the N$_2$O fluxes rates from the Atlantic
rainforest (2.42 and 0.88 kg N ha\(^{-1}\), respectively). Land use change significantly alters the emissions of N\(_2\)O. Due to increased soil N availability, when pasture replaces the forest, fluxes may double or triple, but then decrease in the following years after conversion, to less than half of the original emissions (Davidson et al. 2007). Biomass burning is currently responsible for about 0.7 Tg N yr\(^{-1}\) emission of N\(_2\)O (Davidson and Kanter 2014). In agricultural systems in the Amazon region, double cropping is an important management, and normally soy-maize or soy-cotton are the most common rotation. Soy fix nitrogen at rated of 200 kg ha\(^{-1}\), but N\(_2\)O emissions are fairly low, at levels of 0.1-0.2 kg ha\(^{-1}\) (Cruvinel et al. 2011) and the following crop with addition of mineral fertilizer, N\(_2\)O are at order of 0.2 to 0.8 kg ha\(^{-1}\), depending on the amount of fertilizer used (Jankowski et al. 2018). The regional N\(_2\)O emissions from natural ecosystems are presented in Figure 6.

**Figure 6.** N\(_2\)O emissions in the Amazon. Data produced by Felipe Pacheco, based on data and analysis from the International Nitrogen Management Assessment (INMS).
6.5. AEROSOLS AND TRACE GASES

6.5.1. Biogenic Non Methane Volatile Organic Compounds (NMVOCs)

The Amazonian ecosystem is regarded as the largest source of biogenic Non Methane Volatile Organic Compounds (NMVOCs), also known as biogenic volatile organic compounds (BVOCs) (Figure 7). Emissions of NMVOCs make a minor contribution to the carbon cycle (Figure 2, Kesselmeier et al. 2002). Biogenic NMVOCs are characterized by their high chemical reactivities and thus represent key players within the fields of oxidation processes in the atmosphere (Williams et al. 2016; Nölscher et al. 2016; Pfannerstill et al. 2018). They affect atmospheric chemistry and physics in major ways, by changing the oxidation capacity and particle production delivering so-called secondary organic aerosol (SOA) adding to the effect of primary biological particles in the atmosphere. Anthropogenic effects as well as climate and global change have severe effects on NMVOC emission rates (Peñuelas and Staudt 2010; Liu et al. 2016) and affect particle production, with consequences for water condensation, cloud production and finally the water cycle.

Figure 7. The NMVOC emissions of the Amazonian rainforest act as a water catching and water transporting organic system by chemical and physical processing of biogenic trace gases to secondary organic aerosol serving as condensation nuclei for water vapor.
Of significant importance is the heterogeneity of VOC emissions from vegetation and the dynamics of seasonal or developmental changes in Amazon (Yáñez-Serrano et al. 2015; Yáñez-Serrano et al. 2020). With increasing understanding of biogeochemical cycles and atmospheric reactivity, the large group of biogenic NMVOC received increasing interest as these compounds represent the dominant source of organic volatiles in the atmosphere, especially in forest dominated areas. Biogenic production and release of these NMVOCs are closely related to plant biodiversity and, consequently, the number of biogenic volatiles is enormous (Kesselmeier and Staudt 1999; Laothawornkitkul et al. 2009). In line with their large numbers, their roles are still a matter of discussion in view of ecology and chemistry. In particular, the complex composition of BVOCs, including oxygenated species, aromatic compounds, sulfurous compounds, and oxidation products and further unknown reactive compounds leaves questions to understand atmospheric reactivity (Kesselmeier and Staudt 1999; Nölscher et al. 2016; Pfannerstill et al. 2018; Yáñez-Serrano et al. 2018). These roles demonstrate the urgent needs for more NMVOC research in Amazon. Field locations such as the Amazonian Tall Tower Observatory (ATTO) can contribute to this research (Andreae et al. 2015). Complications are arising from deforestation activities changing the diversity of volatiles and thus the chemical reactivity. The loss of forested areas will affect not only the carbon cycle but also the NMVOC exchange between the surface and the atmosphere, particle production and, finally, the water cycle. Furthermore, the influence of fires on these processes are impressive, when comparing dry season related deforestation activities in tropical areas to wet season without fires, when considering the total particle numbers (Andreae 2019; Pöhlker et al. 2019). Though, the direct SOA contribution from fire emissions seems to be low, when analyzing Mediterranean fires (Bessagnet et al. 2008). Despite their roles, we still face significant gaps in understanding the emission regulation and fate of emitted NMVOC. Still major unknowns with potential impact are the emission capacity and quality of flooded areas and the role of root anoxia (Bracho-Nunez et al. 2012), and ecological interactions within the forest (Salazar et al. 2018). More process-based studies are needed to give us a better basis for further conclusions.

6.5.2. Physics and Chemistry of Aerosols and Cloud Condensation Nuclei (CCN)

Besides influencing water and nutrient cycles, aerosols affect radiation directly by light scattering and absorption as well as indirectly by cloud condensation and processing. Under natural conditions, the Amazon forest is one of the few continental regions where aerosol concentrations resemble those of the pre-industrial era, in the range of 300-500 particles per cm$^3$ and 9-12 μg.m$^{-3}$
(Andreae, 2007; Martin et al., 2010). Organic carbon dominates the composition of submicrometer aerosols in Amazon in the wet season, comprising about 70% of mass, followed by sulfate (10-15%) and equivalent black carbon (5-10%) (Andreae et al. 2015; Chen et al. 2015). Observations indicate that about 90% of submicron organic aerosol mass results from secondary production (Chen et al. 2009). Oxidation of BVOCs by O$_3$ and OH leads to the formation of semivolatile organic species, with sufficiently low vapor pressure to condense over pre-existent particles and produce secondary organic aerosols (SOA) (Graham et al. 2003; Pöhlker et al. 2012). Another pathway for the production of SOA from BVOC emissions consist of aqueous-phase oxidation and acid-catalyzed reactive uptake of isoprene oxidation products within cloud and fog droplets (Lim et al. 2010; Surratt et al. 2010). Characterization of submicrometer organic aerosols in a forest site in Amazon suggest comparable importance of aqueous and gas-phase pathways of SOA production (Chen et al. 2015).

Another mechanism of SOA production is new particle formation (NPF) in the diameter range <10 nm, followed by condensational growth to the accumulation mode (~100-300 nm). This process has been demonstrated to be a relevant source of particles in boreal forests (Dal Maso et al. 2005). However, the impact of NMVOC on particle production over Amazon is surprisingly different from what occurs in temperate and boreal forests (Andreae et al. 2018; Artaxo et al., under review). Long-term observations at Amazonian forest sites have shown that regional-scale NPF events are infrequent near the surface (3% of measurement days) (Rizzo et al. 2018). Instead, airborne measurements in Amazon reported high concentrations of nucleation and Aitken mode particles (diameter <~100 nm) in the upper troposphere. A conceptual model was developed to describe this important source of particles in Amazon (Figure 8). BVOC emitted at surface are transported upward inside convective clouds to the upper troposphere, where they experience ideal conditions for particle nucleation: high actinic flux, low temperatures, and small condensation sink. SOA are produced from BVOC oxidation in the upper troposphere and are eventually transported to the surface by convective downdrafts, increasing in size by condensation on its way down (Andreae et al. 2018; Wang et al. 2016).

In the Amazon forest, coarse mode aerosols (diameter > 2.5 μm) dominate the mass size spectra during the wet season, including primary biological aerosols (PBA), marine aerosols and long-range transported (LRT) African aerosols (Andreae et al. 2015; Martin et al. 2010; Moran-Zuloaga et al. 2018). Pollen, bacteria, spores and fragments of biological material are examples of PBA emitted in the Amazon forest (China et al. 2016; Huffman et al. 2012; Pöhlker et al. 2012). LRT of
aerosols from Africa is typically observed in Amazon between December and April, consisting of Saharan dust and biomass burning aerosols from the Sahel region (Baars et al. 2011; Pöhlker et al. 2019; Saturno et al. 2018). LRT episodes are relatively frequent in the wet season (5 to 10 events per year), usually lasting from 3 to 10 days (Moran-Zuloaga et al. 2018; Rizzolo et al. 2017). During LRT episodes, concentration enhancements on aerosol mass, equivalent black carbon, crustal elements (Al, Si, Ti, Fe) and potassium are observed, providing key nutrients to the Amazonian ecosystem (Martin et al. 2010; Moran-Zuloaga et al. 2018; Rizzolo et al. 2017; Saturno et al. 2018).

Aerosol particles constitute an essential ingredient for cloud formation and development, since they can act as cloud condensation nuclei (CCN), over which the water vapor condenses producing cloud droplets. Moreover, some particles, known as ice nuclei (IN), can initiate the formation of ice crystals inside clouds, providing faster growth to precipitable droplet sizes compared to CCN, and thus influencing precipitation (Andreae and Rosenfeld 2008). Measurements and modelling indicate that biogenic SOA act as CCN in the Amazon forest, while IN consist of coarse mode PBA and LRT mineral dust particles from Africa. In addition, coarse mode aerosols can act as giant CCN, generating large droplets and inducing rain in warm clouds (Pöhlker et al. 2016, 2018; Pöschl et al. 2010; Prenni et al. 2009). While aerosols provide nuclei for cloud formation, convective clouds may stimulate the formation of SOA particles through in-cloud processing of biogenic emissions (Figure 8), making an intrinsic connection between aerosol and cloud processes. An ensemble of observations demonstrates the biosphere-atmosphere integration in Amazon, joining biogenic emissions, clouds and precipitation, depicting the forest as a biogeochemical reactor. The biosphere emits BVOCs and aerosols, which are processed by photochemistry, providing nuclei for the formation of warm and cold clouds, which result in precipitation, sustaining the hydrological cycle and biological reproduction in the ecosystem, closing a virtuous cycle (Pöhlker et al., 2012; Pöschl et al., 2010).
Figure 8. Interactions between biogenic emissions, long range transport (LRT) of aerosols and clouds in Amazon. Biogenic volatile organic compounds (BVOCs) are oxidized near the surface, leading to the production of secondary organic aerosols (SOA). Primary biological aerosols (PBA), SOA and LRT aerosols activate into cloud condensation nuclei (CCN) and ice nuclei (IN), promoting the development of clouds and precipitation. BVOCs are transported by convective updrafts to the upper troposphere, where ideal conditions for particle nucleation are found. SOA are produced from BVOC oxidation in the upper troposphere and are eventually transported to the surface by convective downdrafts, constituting an important natural source of particles.

6.5.3. Ozone and Photochemistry

Ozone (O$_3$) is a highly reactive trace gas, with globally largely varying atmospheric concentrations. There is no significant direct source of tropospheric O$_3$, therefore its concentration strongly depends on precursors like NOx, CO and VOCs (Rummel et al. 2007, Yáñez-Serrano et al. 2015, Lu et al. 2019) and to a smaller part on the exchange between stratosphere and troposphere (Ancellet et al. 1994, Hu et al. 2010). Lifetime of O$_3$ depends on atmospheric chemistry which is controlled by temperature and radiation. The globally averaged lifetime of tropospheric O$_3$ is
approximately 23 days (Young et al. 2013), but due to surface deposition and chemical reactions it is much shorter in the boundary layer (Cooper et al. 2014) which can lead to strong gradients between a well-mixed boundary layer far from strong precursor emission sources and the free troposphere. Concentrations above the oceans or at remote undisturbed continental areas are significantly lower than those once in the surroundings of cities and burning biomass. Hence the remote Amazon rainforest has turned out to be an ideal place to study O$_3$ chemistry under nearly pristine conditions. This property has drastically changed due to increased biomass burning and deforestation, which leads to strongly enhanced NOx and O$_3$ concentrations over most parts of the Amazon basin especially during the drier season between July and October. The strongest sink of O$_3$ is dry deposition, which can occur through stomatal and nonstomatal uptake by leaves. Soil and water surfaces can additionally act as O$_3$ sinks (Clifton et al. 2020). Analyses of turbulence transport of tropospheric air into the forest combined with O$_3$ flux measurements can improve the evaluation of these processes. Mixing ratios of O$_3$ above 40 ppb which also occur in the remote Amazon due to biomass burning are known to cause damages on leaves (Pacifico et al. 2015) due to generation of reactive oxygen species that can induce cell death and lesions (Clifton et al. 2020). Hence even remote areas far away from biomass burning can get affected very negatively by the air pollution, transported over several hundreds of kilometers over the Amazon Basin.

6.6. CONCLUSIONS

Amazon is a key node and feature of the planetary biosphere: its biogeochemical cycles are major factors for the environment and climate and form the largest single-biome contribution to many key planetary biochemical processes. The geological and climatic variability across Amazon play an important role in shaping the features of the region’s biogeochemistry and ecosystem function. The exchange of trace gases, such as greenhouse gases and reactive gases, and secondary and primary particles contribute directly and/or indirectly to the greenhouse effect and affect atmospheric chemistry and physics. Emission (production) and deposition (uptake) processes affect the current concentration of greenhouse gases such as methane, carbon dioxide, ozone or nitrous oxide. Reactive trace gases affect the oxidative capacity of the atmosphere with significant influences on particle production and cloud condensation processes. Hence, climate is affected from local to regional and global aspects of atmospheric warming, chemical processing in the atmosphere and hydrology as well. Continued degradation of the Amazonian rainforest and passing of tipping points would result in a weakening and potential collapse of the biogeochemical network reaching
from the soil and forest up to the atmosphere. This would have severe consequences for Amazonian ecosystems and for the communities that rely on them.

6.7. RECOMMENDATIONS

- There is a need to better understand and create an early warning system for the stability of the Amazon carbon store and sink in the light of global environment change. Loss or reversal of the Amazon carbon sink would have global consequences for difficulty the challenge to limit peak warming to 1.5 °C or 2 °C.

- There is a need to better quantify and map the sources and sinks of methane and N₂O in the Amazon system.

- The potential role of the Amazon biome and its associated atmospheric chemistry in influencing cloud properties and regional and global climate needs to be better quantified and may be amongst the most significant contributions of Amazon to planetary function.

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CORE GLOSSARY

**Aerosol:** An aerosol is a suspension of fine solid particles or liquid droplets in air from anthropogenic and natural sources. Biogenic aerosols produced under natural conditions are dominant in the remote atmosphere, serving as surfaces for reactions, causing light scattering and enhancing water condensation. Primary biogenic aerosols (viruses, bacteria spores and plant debris) and secondary organic aerosols (SOA), produced by chemical processing of trace gases, are discriminated from volatile to semi-volatile and solid.

**Anoxic:** Oxygen-free conditions.

**Autotrophic respiration:** The metabolic activity of plants (autotrophs) resulting in a release of carbon dioxide.

**Carbon sink and source:** The property of an ecosystem to be a net absorber of carbon from the atmosphere (carbon sink) or net emitter (carbon source). The net carbon balance is the sum of many processes, such as photosynthesis, respiration and disturbance.

**Cloud condensation:** Atmospheric water molecules require a non-gaseous surface to change from the vapor to the liquid phase, a process which is called condensation. Small particles, typically 0.2 µm, serve as Cloud condensation nuclei (CCNs) on which water vapor condenses.

**Ebullition:** Release of gases, especially methane, from water to atmosphere by bubbling.

**Ecosystem respiration:** The rate of carbon release by an ecosystem, including respiration of plants (autotrophic respiration) and microbial decay and animal metabolism (heterotrophic respiration).

**Gas exchange velocity:** Parameter with units of m per s (or similar units) that characterizes the exchange of gases between the atmosphere and water bodies. It varies as a function of turbulent and other physical processes near the air-water interface.

**Gross primary productivity:** The rate of carbon uptake by an ecosystem through photosynthesis.

**Heterotrophic respiration:** The metabolic activity of heterotrophs (microbes, fungi and animals) resulting in release of carbon dioxide.

**Net primary productivity:** The rate of biomass production by an ecosystem, including in woody tissue, roots, leaves, flower, fruit, root exudates and volatile organic compounds. It is equivalent to gross primary
productivity minus autotrophic respiration.

**Net Ecosystem Exchange:** the net carbon balance of an ecosystem at local scale (hundreds to thousands of metres), equivalent to what might be measured by a carbon flux tower. The net flux to the atmosphere of all the processes consuming or releasing carbon dioxide.

**Squall lines:** A group of storms arranged in a line, often accompanied by high wind and heavy rain. Squall lines tend to pass quickly and are less prone to produce tornadoes than are supercells. They can be hundreds of kilometers long but are typically only 16 or 32 kilometers wide.

**Synthetic aperture radar:** An active remote sensing technique based on transmission and receipt of coherent microwave signals by an antenna. Allows detection of inundation and vegetation structure.

**Trace gases:** The most common gases in the atmosphere are nitrogen and oxygen with about 78.1% and 20.9%, respectively. All other gases are considered a trace gas. Some are quite stable, including the greenhouse gases carbon dioxide and methane. Biogenic volatile organic compounds are reactive trace gases.

**Volatile organic compounds:** Organic chemicals that have a high vapor pressure at room temperature. Numerous anthropogenic and biogenic sources and chemical species occur.