



Rising flux of nutrients (C, N, P and Si) in the lower Mekong River



Siyue Li^{a,b,*}, Richard T. Bush^a

^a Southern Cross GeoScience, Southern Cross University, NSW 2480, Australia

^b Key Laboratory of Reservoir Aquatic Environment, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China

ARTICLE INFO

Article history:

Received 5 January 2015

Received in revised form 14 July 2015

Accepted 3 October 2015

Available online 8 October 2015

This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Nicolas Gratiot, Associate Editor

Keywords:

Nutrient flux

Anthropogenic activities

Nutrient limitation

Nutrient stoichiometry

Global change

SUMMARY

Changing human land use is accelerating global element cycling and appreciably altering ecosystems in the riverine–estuarine systems. This is evident by dramatic shifts in the supply of nutrients (C, N, P, Si). However, very little is known about the magnitude and rates of these changes. We examine the Mekong, one of the world largest rivers, to assess on a whole-of-system scale, the spatial, monthly and inter-annual flux of nutrients and stoichiometric ratios using a huge data-set (1985–2011). Seasonal and spatial patterns are apparent and linked to hydrology. The estimated mean flux ($\times 10^9$ mol/y) of elements from the Mekong at Pakse are 414.5 for DIC, 4.1 for DIN (3.3 for NO_3^- -N and 0.8 for NH_4^+ -N), 10.2 for TN, 0.32 for DIP, 0.46 for TP and 62.8 for DSi, respectively, which are intermediate relative to other large rivers. However, compared to the river reach at Pakse, the total river fluxes are two-fold greater for C, N, P and DSi. Annual flux increases significantly for DIC, NO_3^- -N, DIN, TN and DSi, and is especially pronounced for all N and P species during the recent decade (1998 onward). Distinct shifts of nutrient stoichiometry, with far-reaching changes for phytoplankton productivity in the Mekong estuary are also evident, as the system shifts from potentially N limited to P limited. These notable changes to the exports and ratios of nutrient variables and anthropogenically-driven nutrient concerns are becoming a defining feature of the Mekong Plume to the South China Sea.

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1. Introduction

Agricultural fertilizer application and discharge of domestic and industrial sewage have increased at an alarming rate, more than doubling global riverine nutrient transports to the oceans in the past few decades. For example, riverine nitrate-N flux is estimated to have increased from 0.86×10^{12} mol/y in 1970 to 1.5×10^{12} mol/y in 1995, while dissolved inorganic phosphorus (DIP) is estimated to have increased from 25.8×10^9 mol/y to 83.9×10^9 mol/y (cf. Turner et al., 2003; Seitzinger et al., 2005, 2010). Such increases in biologically available forms of nitrogen (N) and phosphorus (P) are linked to eutrophication in both freshwater and coastal marine ecosystems and consequent declines of ecological function, reduction of vital water supplies, and increasing frequency of toxic algal blooms, hypoxia and incidents of massive fish kills (Turner et al., 2003; Conley et al., 2009). Projections of ever increasing N and P loads in the surface waters under the weight of human population expansion and industrialisation (cf. Seitzinger et al., 2010; Le et al., 2005, 2010; Luu et al., 2012),

is a sensitive issue amongst downstream communities and nations, who share common water resources.

In addition to the changes in amounts and forms (dissolved inorganic, organic, particulate) of riverine nutrients, the ratios have received much attention as a predictor of unnatural phytoplankton community composition and production rate, both globally and regionally (Redfield et al., 1963; Turner et al., 1998, 2003; Chai et al., 2009; Elser et al., 2009). The riverine exports of nutrients are a key influence on the receiving coastal marine systems (Justic et al., 1995; Seitzinger et al., 2002). Redfield et al. (1963) proposed a fixed element ratio (C:N:P:Si = 106:16:1:16) for sustained growth of aquatic organisms. Although universally known and widely applied to the study of aquatic environments, at the global-scale these nutrient ratios are known to deviate from the optimal stoichiometry of C:N:P:Si, for instance, DIN:DIP:DSi = 14:1:83 (Turner et al., 2003), DIN:DIP = 8–45 (Klausmeier et al., 2004), C:N:P = 88:14:1 (Seitzinger et al., 2005) and DIN:DIP:DSi = 30:1:114 (Seitzinger et al., 2010). These significant deviations from Redfield ratio indicate the growth-limiting deficiency of nutrient element for phytoplankton (Justic et al., 1995).

A number of detailed studies have linked riverine nutrient exports with anthropogenically driven changes on freshwater, coastal and marine ecosystems at global scales (cf. Meybeck, 1982;

* Corresponding author at: Southern Cross GeoScience, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia. Tel.: +61 2 66269235; fax: +61 2 6626 9499.

E-mail addresses: syli2006@163.com, siyue.li@scu.edu.au (S. Li).

Turner et al., 2003; Seitzinger et al., 2005, 2010), as well as at the river basin scale such as Yangtze (Liu et al., 2003; Duan et al., 2007, 2008; Muller et al., 2012), Mississippi (Turner and Rabalais, 1994; Turner et al., 2003; Lane et al., 2004; Raymond et al., 2008) and European rivers (Ludwig et al., 2009, 2010). Anthropogenic sources contribute widely to riverine fluxes of nutrients, such as nitrate and phosphate, which have demonstrated sharp increases in some systems. For example, N and P have increased by a factor of >5 in the Alboran of the Mediterranean (142.9×10^6 mol N/y in 1963 to 714.3×10^6 mol N/y in 1998, while 3.2×10^6 mol P/y in 1963 to 16.1×10^6 mol P/y in 1998) (Ludwig et al., 2009), and also in the Yangtze (the largest Asian monsoon river), up to five-fold vs 13-fold increase rates of the annual fluxes for DIN and DIP were reported (DIN flux increased 22.5×10^9 mol/y in 1963–1984 to 113.6×10^9 mol/y in 2009–2010, while the DIP budget varied between 96.8×10^6 mol/y and 1225.8×10^6 mol/y) (Muller et al., 2012 and references therein).

The Mekong River is one of the largest Asian rivers and like others in this region, is undergoing many stresses from rapid population growth, dam construction, and intensive agricultural expansion in particular, especially in the most recent two decades (MRC, 2003, 2010; Campbell, 2009; Grumbine and Xu, 2011). We hypothesize that such rapid development will be evident as a rising shift in nutrient flux notably for nitrate, phosphate and ammonium (anthropogenic pollution signature), and a decreasing shift in stoichiometric ratios of DSi:DIN and DSi:DIP. However, very little is known about the historical flux of nutrients from the Mekong to the oceans and/or, the stoichiometry of C:N:P:Si in the Anthropocene. Nevertheless, even from preliminary reports from just one hydrological monitoring station (Vientiane), exceptional increases in N and P concentrations are indicated (i.e., nitrate increased by a factor of 1.4 from 1996–1998 to 2003–2005, while TP and $\text{PO}_4\text{-P}$ increased by a factor of 2 in the similar period) (Lida et al., 2011, and reference therein). Eutrophication and algae blooms could become far more severe due to constantly elevated concentrations of N and P, and reservoir impoundments combined (Campbell, 2007; MRC, 2003, 2010). The implications for element cycles on local and global scales and river water quality for domestic and industrial use are potentially immense.

In order to address the aforementioned gaps in our understanding of the Mekong River system, a huge data-set was used to examine the multiple-scale concentrations, stoichiometric ratios and fluxes of nutrients in the Mekong River under anthropogenic effects. Here, we hypothesize the significant shifts of seasonal, spatial and inter-annual nutrient loads, and changing nutrient limitation of phytoplankton growth in the Mekong estuarine and adjacent sea areas. These results help to assess human intervention influences on water quality in the Mekong River, and inform new and much needed development of global riverine nutrient budget models.

2. Methods

2.1. Study area

This study focuses on the Mekong River ($8^{\circ}52' - 22^{\circ}53'\text{N}$, latitude; $98^{\circ}91' - 108^{\circ}99'\text{E}$, longitude), the 8th largest in terms of water discharge ($15,000 \text{ m}^3/\text{s}$ or $470 \text{ km}^3/\text{y}$). It carries substantial loads of dissolved and particulate materials to the South China Sea. For example, annually it transports 145 Mt/y of suspended sediment (Wang et al., 2011) and 123 Mt/y of solute to the ocean (Gaillardet et al., 1999). The headwaters arise from the high elevation (5200 m) Qinghai–Tibet Plateau (QHTP), converging to flow more than 4800 km southward through China, Myanmar, Thailand,

Laos, Cambodia and Vietnam (Kuenzer et al., 2013). Generally, the Mekong River basin is divided into two sub-basins: (i) the Upper Mekong Basin (UMB) covering an area of $195,000 \text{ km}^2$ in China, and; (ii) the Lower Mekong Basin (LMB) covering $600,000 \text{ km}^2$ downstream from China (Li et al., 2013, 2014). The UMB is largely mountainous with a low population density ($\sim 8 \text{ people/km}^2$ in 2000). By contrast, the LMB is predominantly lowlands and flood-plains and is highly populated ($\sim 80 \text{ people/km}^2$ at Pakse while $\sim 460 \text{ people/km}^2$ in the Delta in 2000) (MRC, 2003).

Climate of the Mekong basin spans cold temperate and tundra in the UMB to tropical monsoonal in the LMB with year-round temperature of $26 - 30^{\circ}\text{C}$ in the Delta region. Snowmelt is an important water source in the UMB, while the Lower Mekong is fed by runoff that is characterised by the pronounced wet and dry seasons of the monsoon. The annual hydrograph along the Mekong is strongly seasonal as a result of south-western monsoon climate with 85–90% of the annual rainfall occurring from May to October. This results in approximately 80% of the annual discharge occurring between June to November. River discharge generally begins to rise in May and peak in September, with the average peak flow at $26,380 \text{ m}^3/\text{s}$ over 1971–1998 at station Pakse (Fig. S1; Li et al., 2014). Flows recede from November to minimal rates of $1921 \text{ m}^3/\text{s}$ in March (Lu and Siew, 2006; Adamson et al., 2009; Li et al., 2013, 2014).

The farming systems involve extensive cultivation in upland areas and across the riparian zone on the riverine plain. In addition to agricultural activities, several cities (Vientiane and Phnom Penh) and small urbanisation with more dense inhabitants, are a source via rain runoff containing domestic and industrial sewages. The expansion of hydroelectric projects to meet the increasing demand for reliable power to underpin economic development, are a potential issue for water quality on the Mekong. For instance, five dams (Manwan in 1992, Dachaoshan in 2003, Jinhong in 2009, Xiaowan in 2010 and Gongguoqiao in 2011) are located in the upper Mekong mainstream in China. In addition, tens of large dams and reservoirs in the tributaries within Lao PDR, Vietnam and Cambodia have been planned, amongst them, 11 mainstream dams with 15 GW of power by Laos (Grumbine and Xu, 2011; Kuenzer et al., 2013). Prior research has reported that silicate and particulate nutrients can be trapped in large reservoirs by biological and non-biological mechanisms (cf. Turner et al., 2003).

The Mekong basin is experiencing dramatic land-surface disturbances, as a result of forest clearing, urbanisation, dam construction, expansion of irrigated rice farming with increasing use of fertilizers. The combined effect of anthropogenic activities could understandably alter the traditional hydrological conditions and nutrient characteristics in the basin and notably lead to increased concentrations of nitrate and phosphate (cf. MRC, 2010; Lida et al., 2011).

2.2. Data sources

The Mekong River Commission (MRC) has four member countries, Cambodia, Lao PDR, Thailand and Vietnam. The MRC monitors hydrological and water quality parameters including water discharge, nutrients, major dissolved ions and dissolved silica, as well as other accessory variables at about 50 hydrochemical stations along the Mekong River. For this study, we use primary data provided by the MRC (Metadata standard ISO 19115:2003/19139). The parameters were water flow, total suspended sediment (TSS), alkalinity, nutrients (nitrate-N ($\text{NO}_3\text{-N}$), nitrite-N ($\text{NO}_2\text{-N}$), ammonium-N ($\text{NH}_4\text{-N}$), total-N (TN), phosphate (DIP) and total phosphorus (TP)) and dissolved silica (DSi) measured in the LMB over the period 1985–2011. Most of the monitoring stations have

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