

# Assessing fluvial organic carbon flux and its response to short climate variability and damming on a large-scale tropical Asian river basin

Clément Fabre, Xi Wei, Sabine Sauvage, Thi Phuong Quynh Le, Sylvain Ouillon, Didier Orange, Marine Herrmann, José-Miguel Sánchez-Pérez

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- 1 Assessing Fluvial Organic Carbon Flux and its Response to Short
- 2 Climate Variability and Damming on A Large-scale Tropical Asian River
- 3 Basin
- 4 Clément Fabre<sup>a,1</sup>, Xi Wei<sup>a,1</sup>, Sabine Sauvage<sup>a\*</sup>, Thi Phuong Quynh Le<sup>b</sup>, Sylvain
- 5 Ouillon<sup>c,d</sup>, Didier Orange<sup>e</sup>, Marine Herrmann<sup>c,d</sup>, José-Miguel Sánchez-Pérez<sup>a</sup>
- 6 a Laboratoire Ecologie Fonctionnelle et Environnement, Université de Toulouse,
- 7 CNRS, INPT, UPS, Avenue de l'Agrobiopole, 31326 Auzeville-Tolosane, France.
- 8 b Institute of Natural Product Chemistry (INPC), Vietnam Academy of Science and
- 9 Technology (VAST), 100000 Hanoi, Vietnam.
- 10 ° LEGOS, Université de Toulouse, IRD, CNES, CNRS, UPS, 31400 Toulouse, France.
- 11 d USTH, Vietnam Academy of Science and Technology (VAST), 100000 Hanoi,
- 12 Vietnam.
- 13 <sup>e</sup> HydroSciences Montpellier, Université de Montpellier, CNRS, IMT, IRD, 34095
- 14 Montpellier, France
- 15 These co-authors contributed equally to this work as first authors
- \* Corresponding author: Sabine Sauvage: sabine.sauvage@univ-tlse3.fr

## 17 **Abstract**:

- 18 Fluvial organic carbon (OC) transfer is an essential resource for downstream
- ecosystems. Multiple factors affect its transfer process, e.g., climate or anthropogenic

activities. Quantifying OC fluxes with fine spatiotemporal resolution is challenging in anthropised catchments. This study aims to quantify daily OC dynamics and to assess the impacts of short climate variability and damming on OC spatiotemporal transfer processes in a large tropical Asian river basin (the Red River) for an extended period (2003-2013) by combining empirical equations with modelling outputs. Firstly, empirical equations for calculating dissolved (DOC) and particulate OC (POC) concentrations were calibrated based on in-situ sampling data. Then, simulated daily discharge (Q) and suspended sediment concentrations were used to quantify daily OC fluxes. Results show that the parameters of the DOC and POC equations well represent the subbasins characteristics, underlining the effects of soil OC content, mean annual Q and Chlorophyll a. DOC and POC exports reached 222 and 406 kt yr<sup>-1</sup> at the basin outlet, accounting for 0.38% of the total OC (TOC) exported by Asian rivers to the ocean. However, the specific yields of DOC (1.62 t km<sup>-2</sup> yr<sup>-1</sup>) and POC (2.96 t km<sup>-2</sup> yr<sup>-1</sup>) of the Red River basin were ~1.5 times those of other Asian basins. By comparing a reference scenario (without dams) to current conditions, we estimated 12% and 88% decreases in DOC and POC fluxes between 2008-2013 and 2003-2007, mainly due to damming. This study shows that climate variability may not impact OC dynamics in rivers as it explained less than 2% of the variations. However, dam management, especially recent ones operating since 2008, deeply influences OC variations as the POC/TOC ratio decreased from 86% to 47%. Damming significantly decreased POC exports due to sediment retention, altering the equilibrium of OC cycling downstream, which may impact the food chain.

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**Keywords:** organic carbon, short climate variability, dam, modelling, Red River.

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## 1. Introduction

Rivers are a key connection between terrestrial and marine ecosystems and play an essential role in the global transport of suspended sediment (SS) and associated elements, such as metals, contaminants and nutrients. Fluvial organic carbon (OC) is an essential component in the biogeochemical processes (Bianchi, 2011). It can be classified into two forms: dissolved (DOC) and particulate organic carbon (POC), and is mainly derived from the following three pools: (1) an autochthonous pool derived from in-situ biological production, such as phytoplankton, metabolite of animals and plants in rivers; (2) an allochthonous pool derived from terrestrial organic matter, coming from soil leaching and erosion; (3) an anthropogenic pool derived from agricultural, industrial and domestic release (Hope et al., 1994; Rizinjirabake et al., 2018). Fluvial OC is also regarded as an indicator of water quality (Wen et al., 2019). Metal ions and pesticides can be adsorbed onto OC and carried to the oceans (Boithias et al., 2014; Garneau, 2014). Hence, measuring, quantifying and studying the fate of fluvial OC allows for comprehensively evaluating the degree of organic contamination in water bodies.

Tropical humid ecosystems are hot spots of terrestrial carbon storage, and tropical

rivers strongly contribute to global fluvial carbon flux (Carvalhais et al., 2014; Huang et al., 2012; Zhang et al., 2019). Ludwig et al. (1996) indicated that about 45% of the OC exported to the oceans originated from tropical wet areas. Based on previous global-scale OC fluxes estimations, the Asian rivers contributed to 36%~67% of the DOC exports (Carlson and Hansell, 2015; Chaplot and Mutema, 2021; Dai et al., 2012; Fabre et al., 2020; Huang et al., 2012; Li et al., 2017; M. Li et al., 2019; Ludwig et al., 1996) and ~50% of the POC exports (Beusen et al., 2005; Huang et al., 2012; Li et al., 2017; Ludwig et al., 1996), with a substantial part coming from anthropogenic sources (Wen et al., 2021). Previous studies also pointed out that the rivers in mainland Asia have the highest specific export rates in terms of DOC and POC (Huang et al., 2012; M. Li et al., 2019; Luo et al., 2022). The Asian monsoon region is identified as a unique and important area to research global carbon dynamics and climate feedback (Fang et al., 2010; Shi et al., 2019; Zhang et al., 2019). Hence, quantifying OC fluxes through tropical Asian rivers is essential further to assess the balance between continental and oceanic fluxes. However, most OC flux estimations were calculated monthly or annually, and hardly any study estimated OC fluxes on a daily time scale. Sampling and modelling are usually performed at fortnightly or monthly intervals, which might induce underestimation when there is a storm or intense rainfall during the intervals since most OC export happens during flood events (Zhang et al., 2019). Hope et al. (1994) indicated that fluvial carbon flux was likely underestimated when studied only based

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on seasonal data. For most rivers, the OC concentration varies with discharge and season (Coynel et al., 2005). Discharge (Q) is the primary factor controlling the output of OC (Hope et al., 1994), and suspended sediment concentration (SSC) is also the main determinant of POC flux (Boithias et al., 2014; Huang et al., 2012; Ludwig et al., 1996). Q and SSC fluctuate depending on the seasons but also due to intensive daily rainfall and storms, inducing substantial variability of OC concentration and fluxes at the seasonal and daily scales. Therefore, it is essential to develop methods to quantify OC fluxes and their variability from interannual to daily scales to understand OC transport dynamics better and highlight the emergence of hot spots within a catchment. Long-term global changes at the basin scale, such as climate variability and increased damming, have altered carbon biogeochemical cycles (Hope et al., 1994; Hu et al., 2015; Y. Li et al., 2019; Seitzinger et al., 2010). East and Southeast Asia are the major regions influenced by the Asian monsoon and have been considered one of the most critical and sensitive regions in the global climate system (Fang et al., 2010). At the continental scale, the greatest number of large reservoirs and the most significant summed reservoir capacities are located in Asia (Vörösmarty et al., 1997). Future hydropower development is primarily concentrated in developing countries and emerging economies of Southeast Asia (Zarfl et al., 2015). Therefore, understanding the answers of fluvial OC biogeochemical and dynamical processes to those global changes is essential to assess the impact of global changes further. Maavara et al.

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(2017) showed that current and future OC burial in dams occurs in Asia.

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In the same way, Liu et al. (2020) showed that reservoir impoundment led to 105 106 increasing DOC flux and decreasing POC flux in Asia. Nevertheless, catchment-scales studies are needed to understand local consequences of dam 107 108 implementation. For example, reservoirs impact the POC dynamics in the Yangtze 109 and the Yellow catchments (Liu et al., 2019; Wu et al., 2020; Zeng et al., 2020). 110 The Red River basin is a tropical basin shared among China, Laos and Vietnam, 111 affected by human activities such as intensive agriculture and damming. Previous 112 studies, based on both in-situ sampling data and modelling, have investigated the 113 impacts of human activities on hydrology and SS (Dang et al., 2010; Le et al., 2007; 114 Le et al., 2020; Lu et al., 2015; Vinh et al., 2014; Wang et al., 2011; Wei et al., 2019; 115 2021). These studies especially found strong retention of SS caused by dams. 116 Studies about nutrients associated with Q and SS, such as organic carbon, have also 117 been conducted. Most of these studies analysed the concentrations and fluxes of 118 nutrients based on the sampling data (Dang et al., 2013; Le et al., 2018, 2017a, 2010, 2005); few used numerical modelling (Le et al., 2017b; Nguyen et al., 2018). In-situ 119 120 sampling is a direct and accurate way to quantify fluvial carbon at the local or regional 121 scale. From sampling data, Le et al. (2017a) estimated that the average export of total OC (TOC) during 2008-2010 was 270 kt yr<sup>-1</sup> at Hanoi, of which 142 kt yr<sup>-1</sup> was DOC, 122 and 128 kt yr<sup>-1</sup> was POC; Dang et al. (2013) quantified the annual POC flux of 243 kt 123 yr<sup>-1</sup> at Son Tay during 2006-2009 (see Figure 1 for sampling locations). However, 124

in-situ field sampling at large spatial and temporal scales is expensive and often impracticable. Combined with available in-situ data, a numerical modelling approach allows for overcoming these shortages. Le et al. (2017b) and Nguyen et al. (2018) used a modelling approach to identify a seasonal OC variation and estimated a TOC export of 324 kt yr<sup>-1</sup> at Son Tay during 2013-2014. However, as explained above, simulations at a seasonal scale do not represent the whole range of OC flux variability and might induce underestimations (Hope et al., 1994). Therefore, assessing and calculating OC flux at a daily time step would be more precise using daily Q, SSC and OC concentrations.

This work aims to understand the DOC and POC transport dynamics and quantify DOC and POC fluxes and variabilities based on a daily time step through the Red

to assess the influence of short climate variability and damming on DOC and POC transport and fluxes; (3) to propose a new approach to evaluate DOC and POC at different points in the basin with accessible environmental parameters.

River basin. The specific objectives of this paper are: (1) to quantify DOC and POC

fluxes through the basin during a long-term period (2003-2013) on a daily time step; (2)

#### 2. Materials and Methods

# 2.1. Study area

The Red River basin covers a total area of approximately 159,000 km<sup>2</sup>. Our study area focuses on the continental drainage catchment at Son Tay, which is also the

- apex of the delta, resulting in a surface of 137,200 km<sup>2</sup> (Figure 1).
- 147 The Red River is comprised of three main tributaries: the upper part of the main river
- 148 before the confluence (the Thao River), which is the current main sediment load
- 149 contributor (~80%) to Son Tay (Le et al., 2007; Vinh et al., 2014; Wei et al., 2021); the
- Da River, on the right river bank; the Lo River, on the left riverbank (Figure 1).
- 151 The elevation in the basin ranges from 20m to 3000m. Most areas are mainly
- mountainous, with slopes mainly above 6%. The upper part of the Red River basin is
- 153 formed by tectonically active mountains vulnerable to high erosion with intensive
- rainfall (Bai et al., 2015; Barton et al., 2004; He et al., 2007; Wei et al., 2021).
- Land use is presented in Figure 2. Forest and agriculture account cover most of the
- Red River basin. Land use change during 2000-2010 was insignificant, as only less
- than 4% of the bare land in the Red River basin was converted to agricultural land (Le
- 158 et al., 2018).
- 159 Concerning the hydrological cycle, the whole Red River basin is influenced by the
- 160 monsoon system, from the humid subtropical monsoon in the upstream basin to the
- 161 humid tropical monsoon in the downstream part, and associated with strong
- seasonality. The mean annual rainfall is 1590 mm in the Red River basin, and over
- 163 85-90% of the yearly precipitation falls during the southwest monsoon season (May to
- October; Le et al., 2007; Li et al., 2016). The rainfall is unevenly distributed (Li et al.,
- 165 2008; Luu et al., 2010; Xie, 2002). Runoff shows high inter-seasonal variations, with a
- 166 flood season occurring between May and October, with over 80% of the total annual

runoff. The discharge at Son Tay is about 3,000 m<sup>3</sup> s<sup>-1</sup>, with floods exceeding 20,000

168 m<sup>3</sup> s<sup>-1</sup> (Vietnam Ministry of Natural Resources and Environment; MONRE). The

annual water volumes within the catchment are 20.7, 28.2, 51.9, and 99.0 km<sup>3</sup> yr<sup>-1</sup> at

Yen Bai, Vu Quang, Hoa Binh and Son Tay stations, respectively.

171 Concerning suspended matter, sediment fluxes were strongly affected by the

172 construction of dams (Le et al., 2007; Lu et al., 2015; Vinh et al., 2014; Wei et al.,

2021). This basin has six important dams with large storage capacities (Figure 1). The

two dams on the Thao River started operating in 2008 and 2011. The two dams on the

Lo River were impounded in 1972 and 2008. Two larger dams on the Da River started

to operate in 1989 and 2011. More details about these dams can be found in Wei et al.

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## 2.2. Data sources

- 179 Daily Q and SSC data were obtained from the Vietnam Ministry of Natural Resources
- and Environment at Yen Bai, Vu Quang, Hoa Binh and Son Tay stations from 2003 to
- 181 2013 (see Figure 1).
- Modelling inputs such as topography (digital elevation model), land use, soil map,
- 183 rainfall and temperature were used to simulate daily Q and SSC using the Soil and
- Water Assessment Tool (SWAT; Neitsch et al., 2009), as detailed in the previous work
- of Wei et al. (2019). Land use and soil map are presented in Figure 2.
- POC and DOC data come from Dang (2011) and Le et al. (2017a). Dang (2011)
- 187 provided POC and DOC concentrations at Yen Bai, Vu Quang, Hoa Binh and Son Tay

during 2008-2009, with sampling frequency generally monthly or bimonthly. POC was
determined using a LECO CS 125 analyser, and DOC was measured with a TOC
5000 Shimadzu. Analytical accuracy was evaluated between 3 and 5 % (Dang et al.
(2010).

Le et al. (2017a) sampled DOC and POC one to three times per month from 2003-2004, 2008-2010, and 2012-2013 at Yen Bai, Vu Quang, Hoa Binh and Son Tay. Due to the sampling difficulties, data are missing for some years or months. In the same way, POC was measured with a LECO CS 125 analyser, while DOC was determined with an ANATOC II TOC analyser. Detailed information about these sampling and laboratory measurements can be found in Dang (2011) and Le et al. (2017a).

## 2.3. Organic carbon calculation

200 2.3.1. DOC equation

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- The equation for calculating the DOC concentration [DOC] from daily Q was taken from the work of Fabre et al. (2019):
- $[DOC] = \frac{\alpha * Q}{\beta + Q}$  (1)
- where [DOC] is in mg L<sup>-1</sup>, Q in mm d<sup>-1</sup>; the parameter  $\alpha$  (mg L<sup>-1</sup>) represents a potential of maximum [DOC] at the outlet of each sub-basin, and the parameter  $\beta$  (mm d<sup>-1</sup>) is the Q when [DOC] is half of  $\alpha$ .
- 207 2.3.2. POC equation
- The equation for calculating the POC concentration was proposed by Boithias et al.

209 (2014), who generalised the relation between the POC and suspended sediment 210 concentration (SSC) as follows:

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$$\begin{cases} \%POC = \frac{9.40}{SSC - a} + b \text{ (if SSC} > a) \\ \%POC = \%POC_{max} \text{ (if SSC} \le a) \end{cases}$$
 (2)

where %POC is the percentage of POC in the suspended sediment, %POC<sub>max</sub> is the maximum value over the basin, SSC is in mg L<sup>-1</sup>, and parameters a and b are linked to environmental variables related to each sub-basin (see details in section 3.1.4). The parameter a (in mg L<sup>-1</sup>) is the vertical asymptote corresponding to a low SSC with organic matter rich in OC, such as phytoplankton and residuals. The parameter b (in %) is the horizontal asymptote representing the suspended matters with low OC concentration, nearly equals to soil organic carbon content (Boithias et al., 2014; Fabre et al., 2019). When SSC is smaller than a, %POC equals its maximum value, %POC<sub>max</sub>.

#### 2.4. Modelling strategy

2.4.1. Parameters calibration for DOC and POC

The four parameters  $(\alpha, \beta, a, b)$  in Equations 1 and 2 were manually calibrated based on the discrete OC sampling data and the observed daily Q and SSC at each station. It allowed determining values of specific parameters associated with each sub-basin, which are representatives of the characteristics of these sub-basins. The values of each parameter were calibrated separately in order to obtain simulated values as close as possible to the observed values. The maximum value of %POC was set by considering covering 99.9% of the dataset.

#### 2.4.2. Scenarios setting

The SWAT is a physically-based model used to simulate the quality and quantity of Q, SSC and nutrients over the river basin and to predict the environmental impacts of human activities and short climate variability (Neitsch et al., 2009). The version of SWAT we used in this study (SWAT 2012) cannot compute the DOC and POC concentrations. Wei et al. (2019) applied the SWAT model on the Red River, obtaining simulated daily Q and SSC from 2000 to 2013 in good agreement with in-situ measurements (scenario of current conditions, with dams). A reference scenario (without dams) was also implemented to assess separately the impacts of short climate variability and dams on Q and SSC, respectively. Current conditions and reference scenario settings are presented in Figure 3. More detailed information on simulated Q and SSC can be found in Wei et al. (2019).

This study aims to apply the simulated daily Q and SSC of the current conditions and the reference scenario (without dams) to calculate the simulated DOC and POC fluxes under those conditions (Figure 3).

# 2.5. Model evaluation and validation for DOC and POC

The simulated OC fluxes of current conditions from modelling would be validated by comparing them to the results from the Load Estimator (LOADEST) regression model, which U.S. Geological Survey developed for estimating constituent loads in rivers (Runkel et al., 2004) and had been applied to many studies (Huntington and Aiken, 2013; McClelland et al., 2007; Sickman et al., 2007; Tamm et al., 2008). Daily water releases and OC concentrations are available in both high and low flow periods, which

makes the LOADEST approach consistent. LOADEST model will provide a more consistent dataset of data based on observed values, which will allow calculating monthly observed fluxes. LOADEST model is calibrated through regression analysis based on discrete OC sampling data and observed daily Q. The best regression model (Approximate Maximum Likelihood Estimator) is used with LOADEST to estimate daily DOC and POC fluxes, respectively. The mean annual DOC and POC fluxes from other studies in the same basin (Dang, 2011; Le et al., 2017a) were also used as references for validating the simulations from this study.

The coefficient of determination (R²) and the Nash–Sutcliffe efficiency (NSE) were used as statistical tests to evaluate the quality of our calculation by comparing the results from LOADEST with ours (Moriasi et al., 2007; Nash and Sutcliffe, 1970). R² values greater than 0.3 or 0.4 are considered satisfactory for monthly nitrogen or sediment loads, respectively (Moriasi et al., 2015). NSE values greater than 0.35 and 0.45 are generally considered satisfactory for monthly nitrogen or sediment loads, respectively (Moriasi et al., 2015). We assumed we could use these thresholds for organic carbon studies.

## 3. Results

## 3.1. DOC and POC concentrations

3.1.1. DOC equation application

The value of parameters  $\alpha$  and  $\beta$  in Equation 1 obtained for each station and the number of sampling DOC used for inferring the parameters are listed in Table 1. The

values of parameter  $\alpha$  vary from 4.5 to 5.5; parameter  $\beta$  ranges from 0.7 to 2.5, geographically increasing from the upstream to the downstream.

## 3.1.2. DOC concentrations temporal variations

The daily variations of observed and simulated DOC concentrations at four stations from 2003 to 2013 are presented in Figure 4. The observed DOC concentrations were measured over some short periods and did not show apparent seasonal variations. The simulated DOC concentrations are in the range of the observations (values of the range are presented in the following sub-section), with most sampling points captured by our simulations. Generally, simulated DOC concentration varies following Q variations, increasing from May to July, staying high during the highest floods in August and September, and decreasing from October to April.

Simulated mean annual DOC concentrations increase in the following order: Yen Bai  $(1.39 \text{ mg L}^{-1}) < \text{Vu Quang } (1.50 \text{ mg L}^{-1}) < \text{Hoa Binh } (1.60 \text{ mg L}^{-1}) < \text{Son Tay } (1.81 \text{ mg L}^{-1}).$ 

## 3.1.3. DOC concentration ranges and spatial variations

Simulated DOC concentrations at four stations varied slightly (Figure 5a). At Yen Bai station, DOC concentration ranges from 0.01 to 4.13 mg L<sup>-1</sup> with an average of 1.25 mg L<sup>-1</sup> (observations from 0.20 to 5.90 mg L<sup>-1</sup>); at Vu Quang, DOC was in the range of 0.03 to 4.01 mg L<sup>-1</sup> with an average of 1.50 mg L<sup>-1</sup> (observations from 0.33 to 5.70 mg L<sup>-1</sup>); at Hoa Binh, DOC concentration varied from 0.05 to 4.05 mg L<sup>-1</sup> with an average of 1.60 mg L<sup>-1</sup> (observations from 0.12 to 5.65 mg L<sup>-1</sup>); at Son Tay, DOC shifted from

294 0.05 to 4.11 mg  $L^{-1}$  with an average of 1.81 mg  $L^{-1}$  (observations from 0.36 to 6.00 mg  $L^{-1}$ ).

## 3.1.4. POC equation application

Figure 6 shows the percentage of POC in suspended sediment (%POC) against the suspended sediment concentration (SSC) computed from available measurements in 2003-2013. %POC shows a significant negative relationship with SSC, following well Equation 2.

We obtained different values for the parameters *a*, *b*, and %POC<sub>max</sub> for the four stations (Table 1). The parameter *a* varies broadly, with a maximum value of 40.0 mg L<sup>-1</sup> at Yen Bai and a minimum of 5.0 mg L<sup>-1</sup> at Hoa Binh. Parameter *b* varies from 1.0 to 1.7%, with a maximum at Hoa Binh and a minimum at Yen Bai. %POC<sub>max</sub> varies strongly, with a minimum of 10 mg L<sup>-1</sup> at Yen Bai and a maximum of 40 mg L<sup>-1</sup> at Hoa Binh.

## 3.1.5. POC concentrations temporal variations

Figure 7 illustrates the daily variations of simulated and observed POC concentrations at four stations from 2003 to 2013. POC concentrations showed great seasonal and inter-annual variations. POC peak flows occurred from May to October. Seasonal variations strongly weakened during more recent years (2008-2013), and the POC peak flows decreased. For Yen Bai, Vu Quang, Hoa Binh and Son Tay stations, the standard deviation is 10.11, 2.75, 0.84, and 3.55 mg L<sup>-1</sup>, respectively, over 2003-2007, and 3.76, 0.83, 0.53, and 0.96 mg L<sup>-1</sup>, over 2008-2013; and the maximum POC

concentration is 82.77, 18.86, 7.91, 22.72 mg L<sup>-1</sup> during 2003-2007 and 30.12, 9.50,
 12.31, and 6.52 mg L<sup>-1</sup> respectively during 2008-2013.

Simulations are in the same range as discrete samplings (values of the range are presented in the following sub-section) and produce acceptable results. Comparing the simulated POC concentrations to the observations, simulated POC peaks can be underestimated for some years. Simulated POC base values are generally in good agreement with in-situ observations.

## 3.1.6. POC concentration ranges and spatial variations

Figure 5b presents the simulated POC concentration ranges at the four stations. From the simulations, POC concentrations vary from 0.85 to 82.77 mg L<sup>-1</sup> with an average of 8.35 mg L<sup>-1</sup> at Yen Bai (observations from 0.14 to 67.20 mg L<sup>-1</sup>), from 0.40 to 18.86 mg L<sup>-1</sup> with an average of 2.30 mg L<sup>-1</sup> at Vu Quang (observations from 0.20 to 5.17 mg L<sup>-1</sup>), from 0.36 to 12.31 mg L<sup>-1</sup> with an average of 0.96 mg L<sup>-1</sup> at Hoa Binh (observations from 0.18 to 3.27 mg L<sup>-1</sup>) and from 0.43 to 22.72 mg L<sup>-1</sup> with an average of 3.03 mg L<sup>-1</sup> at Son Tay (observations from 0.20 to 23.78 mg L<sup>-1</sup>). Our simulations have larger ranges compared to observations because our simulations period covers the years before dam implementation when the POC concentrations were high. The POC low concentrations at these four stations do not differ much, but significant differences occur at POC peak fluxes.

## 3.2. Fluxes of DOC and POC

3.2.1. DOC flux variations

Daily variations of DOC fluxes at four stations are presented in Figure 8a. Simulated

DOC fluxes fit well with the observations during low flow periods. Daily simulations represent the DOC flux fluctuations realistically during flood seasons.

As described in section 2.5, the LOADEST model results are used as references to validate our simulations. Figure 8b shows the DOC fluxes from LOADEST and our simulations at a monthly scale. Compared to the results from LOADEST, the simulated base DOC flux is lower, and the peak DOC flux is higher for some years; the R<sup>2</sup> at these four stations varies from 0.65 to 0.74, and the NSE is in the range of 0.02-0.56, which indicates that our simulations of DOC fluxes at monthly scale are acceptable to good. At Son Tay outlet, 85% of the total export of DOC happened in the southwest monsoon seasons (from May to October).

Annual DOC simulated fluxes variations are presented in Figure 9. The mean annual DOC flux during the study period at Yen Bai, Vu Quang, Hoa Binh and Son Tay stations are 44, 53, 88 and 222 kt yr<sup>-1</sup>, respectively. The maximum annual DOC flux occurred in 2008, the maximum flood year during the study period. The minimum annual DOC flux occurred in 2010, the drier year during the study period.

# 3.2.2. POC flux variations

Figure 10a illustrates the daily variations of POC fluxes at four stations. As for daily DOC fluxes, simulated POC fluxes are in the range of the observations.

The observed data were sampled after 2007, and some dams (the Nansha, Madushan, Tuyen Quang and Son La dams) were under construction during the 2003-2007 period and have been operating since 2008. The POC conditions before

and after 2008 were hence different because of the impacts of dam constructions on suspended sediment. The POC sampling concentrations before 2008 are few and limited. Here we thus only compared the POC fluxes from LOADEST and our simulation over the 2008-2013 period. Our simulation results during 2003-2007 were plotted to provide insight into POC fluxes during this period (Figure 10b). Generally, the results from LOADEST and our simulation fit well on both POC peak and base fluxes: R<sup>2</sup> is between 0.50-0.59, while NSE varies from 0.34 to 0.56, indicating a satisfactory performance. At Son Tay, 88% of the total POC fluxes are exported to the delta from the southwest monsoon season. Figure 11 shows the simulated annual POC flux variations for the four stations between 2003-2013. The mean annual POC fluxes of Yen Bai, Vu Quang, Hoa Binh and Son Tay stations are 318, 83, 55 and 406 kt yr<sup>-1</sup>, respectively. The Thao River exported the highest POC loads among the three tributaries, followed by the Lo River. Contrary to what was obtained for the DOC export, the Da River exported the smallest POC flux. The POC flux was the highest at the confluence (Son Tay station). The maximum annual POC flux generally occurred in 2007, while the minimum annual POC flux occurred in 2011. 3.2.3. Spatial variations of new dams impacts on DOC and POC dynamics The effects of dams implementation on each main tributary were assessed by

comparing values obtained during the period 2003-2007 and the period 2008-2013.

Table 2 shows the effects of the new dams on OC dynamics. New dams induce a

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spatially homogeneous decrease between 64 and 71% for POC while it shows slight variations (between -9% and +5%) for DOC.

Concerning the contribution of the main tributaries to the outlet, the implementation of the new dams seems not to impact the balance of the contributions by the tributaries. For POC, the Thao River is responsible of 70% of the export followed by the Lo River with about 20% and by the Da River with 10%. For DOC, the main contributor is the Da River with 46% of the exports, followed by the Lo River with 30% and by the Thao River with 24% of the exports.

#### 3.2.4. TOC flux variations

Annual simulated TOC fluxes showed significant inter-annual variations (Figure 12). The mean annual TOC fluxes for the study period were 350, 136, 143 and 628 kt yr<sup>-1</sup> at Yen Bai, Vu Quang, Hoa Binh and Son Tay stations, respectively. Comparing the TOC export among the three tributaries, TOC fluxes exported by the Lo and Da rivers were of the same order, and the Thao River exported around 2.5 times higher TOC than the Lo and Da rivers. The highest TOC fluxes were generated in 2007 and the lowest in 2010.

# 3.3. TOC fluxes variations under the reference scenario

Figure 13a presents simulated monthly TOC flux variations under the reference scenario and current conditions at Son Tay station. The differences between the reference scenario and current conditions for monthly DOC fluxes are slight (p=0.5), while they are significant for monthly POC fluxes (p<0.001). The differences in the

dynamic processes between the reference scenario and current conditions occur during the flood seasons and are much more significant for POC than DOC: the average monthly fluxes during June and August under the reference scenario and current conditions for DOC are 42.0 and 40.3 kt month<sup>-1</sup>. They are 271.5 and 72.4 kt month<sup>-1</sup> for POC.

The annual fluxes of POC under the reference scenario and current conditions also differ considerably compared to the DOC fluxes (Figure 13b). When comparing the period after new dams (2008-2013) to the previous period (2003-2007), the annual DOC flux was reduced by 12%: a 1% increase due to Q change induced by short climate variability and a 13% decrease due to dam constructions. The annual POC flux decreased by 87%, of which 2% was due to Q variation caused by short climate variability and 85% due to damming. POC variations resulted in the variations of POC percentage in TOC (POC/TOC) at Son Tay station (Figure 14).

The POC/TOC ratio under the reference scenario is higher (from 81 to 89% with an averaged value of 85%, standard deviation=1.7%) than that under current conditions (from 33 to 90% with an averaged value of 58%, standard deviation=13.6%); moreover, the POC/TOC ratio under reference scenario shows a weaker seasonal variability than under current conditions (Figure 14a).

The ratio POC/TOC under current conditions decreased after 2007, and its seasonal variability also changed afterwards (Figure 14a). During 2003-2007, the maximum POC/TOC generally occurred in September and October, whereas the minimum

- POC/TOC showed up during February and March. During 2008-2013, the maximum POC/TOC showed up generally in February and March and the minimum in December, January or June.
- There is a clear negative POC/TOC ratio shift in 2008 under current conditions (Figure 14). The mean annual POC/TOC ratio under the reference scenario stayed the same (86%) during 2003-2007 and 2008-2013, while under current conditions, it decreased from 74% during 2003-2007 to 47% during 2008-2013.

# 4. Discussion

#### 4.1. Parameter analysis

4.1.1. Parameters of DOC

The parameter  $\alpha$  is the potential maximum fluvial DOC concentration at each station, and it can be related to its sources. Previous studies indicated that DOC increased with increasing soil carbon content (Manninen et al., 2018). The soil organic matter, through soil erosion and leaching, was the main source of fluvial DOC (Dang, 2011; Le et al., 2017a; Lloret et al., 2016). Figure 15a presents the soil organic carbon content through the Red River basin. The average soil organic carbon contents (% soil weight) of the drainage area of Yen Bai, Vu Quang, Hoa Binh and Son Tay are 1.60%, 1.79%, 1.92% and 1.77%, respectively. Figure 15b shows that the relationship between the parameter  $\alpha$  and the average soil organic carbon content of the drainage area of each station is significant, indicating a positive correlation. The increasing order of mean annual DOC concentration during 2003-2013 at the outlet of each river

is consistent with the increasing order of the average soil organic carbon content: Yen Bai < Son Tay< Vu Quang < Hoa Binh.

The parameter  $\beta$  corresponds to the discharge Q when the DOC concentration is half of  $\alpha$ , so it is linked to  $\alpha$ . Besides,  $\beta$  increases in the following order: Yen Bai < Vu Quang < Hoa Binh < Son Tay (Table 1), and the annual mean Q for these four stations (Yen Bai:  $608 \text{ m}^3 \text{ s}^{-1}$ , Vu Quang:  $848 \text{ m}^3 \text{ s}^{-1}$ , Hoa Binh:  $1529 \text{ m}^3 \text{ s}^{-1}$ , Son Tay:  $3052 \text{ m}^3 \text{ s}^{-1}$ ) increase in the same order. We assume that within the same basin, the parameter  $\beta$  can be positively correlated with Q. However, this needs further study and confirmation from other basins worldwide.

Equation 1 was also applied at the outlet of the Yenisei River basin, located in the Arctic region with a watershed surface of 2,540,000 km<sup>2</sup>. The parameters  $\alpha$  and  $\beta$  were 15.0 and 1.29, respectively (Fabre et al., 2019). The  $\alpha$  at the outlet of the Yenisei River basin is higher than at the Red River outlet due to the high soil OC contents in the Yenisei basin. It agrees with the relationship between the parameter  $\alpha$  and the soil organic carbon content (% soil weight; Figure 15).

#### 4.1.2. Parameters of POC

The maximum %POC decreases in the following order (Table 1): Hoa Binh (40) >= Son Tay and Vu Quang (15) > Yen Bai (10). The SSC at Hoa Binh station was the lowest (annual mean during 2003-2013 is 34 mg  $L^{-1}$ ) compared to other stations (annual mean SSC for Yen Bai, Vu Quang, and Son Tay is 631, 99 and 137 mg  $L^{-1}$ , respectively) due to the retention by the dams, especially by the Hoa Binh dam (Dang

et al., 2010; Wei et al., 2019). Besides, algae and phytoplankton in the reservoir can contribute to high particulate organic carbon. Therefore, these two factors induce a high maximum %POC at Hoa Binh station. On the contrary, at Yen Bai station, the SSC is the highest with low autochthonous organic production compared to other stations (Dang et al., 2010; Dang, 2011; Nguyen et al., 2018). Therefore, the maximum %POC is small.

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The parameter a is a basin-specific constant that includes anthropogenic impacts and corresponds to low SSC values and to matter rich in OC, such as phytoplankton and residuals. Comparing the minimum SSC values of the three tributaries, the Thao River presents the highest concentration (15.2 mg L<sup>-1</sup>). In contrast, at Hoa Binh station on the Da River, the lowest concentration (0.6 mg L<sup>-1</sup>) is observed, which explains the corresponding values of a - high at Yen Bai (40, Table 1) and low at Hoa Binh (5). Besides, thanks to the Nansha and Madushan dams constructions, local villagers have entered into extensive fish farming (Rousseau, 2014), while fish feed and faeces are rich in organic matter (Beristain, 2005). Moreover, near the Nansha dam, a sugarcane processing plant often releases chemicals and wastes into the Red River (Rousseau, 2014). These factors make the water quality downstream of the Madushan dam very bad (Rousseau, 2014), which contributes to explaining the high parameter a value at Yen Bai. In addition, the concentrations of Chl-a of these three tributaries from large to small was in the following order: Yen Bai (1.9 µg L<sup>-1</sup>) > Vu Quang (1.3  $\mu$ g L<sup>-1</sup>) > Hoa Binh (1.1  $\mu$ g L<sup>-1</sup>; no data for Son Tay in Le et al., 2017a),

484 which is in the same order as the values of parameter a (Figure 15d). Therefore, the 485 parameter a accurately expresses the characteristics of each tributary in this study. 486 As described in subsection 2.3.2, parameter b is the horizontal asymptote representing the suspended matters with low OC concentration near soil content. 487 488 From Figure 15e, we can see that parameter b shows a positive and significant 489 correlation with the average soil organic carbon content of the drainage area of each 490 station. Hence, the values of the parameter b well represent the characteristics of 491 each sub-basin. The parameters a and b were set to 5 mg L<sup>-1</sup> and 2.1%, respectively, in an agricultural 492 basin in southeast France (Boithias et al., 2014); and to 0.95 mg L<sup>-1</sup> and 3.9%, 493 respectively in an Arctic basin (Fabre et al., 2019). The minimum SSC observed in the 494 study river of Boithias et al. (2014) is 5 mg L<sup>-1</sup>, while it is around 1 mg L<sup>-1</sup> of Fabre et al. 495 (2019); hence, they set the parameter a to 5 mg L<sup>-1</sup> and 0.95 mg L<sup>-1</sup>. In our study, the 496 parameter a is higher than the minimum SSC observed at each station, which 497 498 indicates the contributions from phytoplankton and residuals in the Red River that 499 were not observed in the study rivers of Boithias et al. (2014) and Fabre et al. (2019). 500 In the study area of Boithias et al. (2014), the topsoil organic matter content is about 501 2%, which is higher than our basin (1.6-1.9%). In the study case of Fabre et al. (2019), 502 the permafrost stores abundant soil OC, leading to a high parameter b. Therefore, the 503 parameter *b* from their study is higher than ours (from 1.0% to 1.7%). From the above, 504 the parameters a and b obtained from Boithias et al. (2014), Fabre et al. (2019), and this study seem to represent the specific characteristics of various local basins.

4.1.3. Application: a new method to evaluate the DOC and POC concentrations Our results also enable us to propose a new method to evaluate the DOC and POC concentrations at any point within the Red River basin. If one knows the values of average soil organic carbon content of the drainage area, mean annual discharge and the Chl-a concentration in the river, using the relationships in Figure 15 allows to determine  $\alpha$ ,  $\beta$ , a and b; Equation 1 and 2 can then be used to evaluate the DOC and POC concentrations.

# 4.2. Comparison of the OC contents with other studies

4.2.1. Comparison with other studies for the Red River

We first compared our simulations with results from other studies based on in-situ sampling in the Red River basin (Table 3). To make things comparable, we performed our comparison over the 2008-2009 period.

Our simulated results are slightly lower (about -17%) for the mean annual DOC concentration compared to the other two studies (Dang, 2011; Le et al., 2017a). In both studies, discrete samplings were just taken once or twice per month, and at dry seasons the frequency was even lower, while our results were calculated based on a daily time step simulation. Those different temporal scales can induce differences in mean annual DOC concentration estimations. The mean yearly DOC flux of 2008-2009 at Vu Quang and Hoa Binh stations estimated by Dang (2011) is around 60% higher than that of Le et al. (2017a). Note that the LOADEST results are close to the ones of Le et al. (2017a; Table 3) as a large proportion of sampling data used by

the LOADEST comes from their dataset. Comparing our results to the LOADEST, the DOC fluxes are 17-28% higher at the three tributaries and 3% higher at the outlet Son Tay station. Hope et al. (1994) indicated that low-frequency sampling led to underestimating the fluvial carbon flux due to the under-representation of storm flow conditions. Finally, our study produces an estimation of 222 kt yr<sup>-1</sup> of DOC flux at Son Tay (Table 3) over 2003-2013, which accounts for 0.26% of the total DOC export by Asian rivers to the seas, estimated to 85.45 Mt yr<sup>-1</sup> by Li et al. (2019). Significant differences in mean annual POC concentration during 2008-2009 can be found between Dang (2011) and Le et al. (2017a): POC concentrations from Le et al. (2017a) are only 31% of that from Dang (2011); our results are between theirs (Table 3). POC concentrations are strongly linked to SSC, which can vary significantly from sampling location and time. Le et al. (2017a) estimated that the POC fluxes are about 59% of the values Dang (2011) estimated, especially at Yen Bai station, where the SSC is very high. Comparing our results to the LOADEST, our estimations are 10-31% lower on the three tributaries and 34% lower at Son Tay. Since POC fluxes transported by the Asian rivers are 76.90 Mt yr<sup>-1</sup> (Li et al., 2017), the export of POC at Son Tay (406 kt yr<sup>-1</sup> over 2003-2013 in our study) accounts for 0.37% of the total POC export by the Asian rivers. The estimated TOC flux during 2003-2013 at Son Tay equals 628 kt yr<sup>-1</sup>. Regardless of the time, the mean annual TOC at Son Tay was estimated from 324 to 506 kt yr<sup>-1</sup> (Dang, 2011; Nguyen et al., 2018), and our simulation is higher than theirs (94%

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higher than Nguyen et al. (2018) and 24% higher than Dang (2011), again due to the difference of calculation time step: our simulations at a daily time step consider all flood events. Finally, our results suggested that the Red River exported 628 kt yr<sup>-1</sup> of TOC over 2003-2013, i.e. contributed approximately 0.38% of TOC exported by the Asian rivers (164 Mt yr<sup>-1</sup>, Li et al., 2017).

#### 4.2.2. Comparison with other rivers

Compared with other Asian and tropical rivers, the exports of DOC and POC through the Red River are not that large, especially for POC (Table 3). However, when comparing specific yields, the Red River basin yields high DOC and POC values. It is in agreement with some previous studies, indicating that the rivers in mainland Asia, especially those originating from the Himalayan plateau, have the highest specific POC and DOC export rates worldwide (Aucour et al., 2006; Galy et al., 2007; Huang et al., 2012; M. Li et al., 2019).

The DOC flux of the Red River is 58% and 10% higher than that of the Pearl and Mekong Rivers, respectively, which are geographically close to the Red River (Table 3). In the same way, the DOC exports of the Red River are 14%, 171% and 370% higher than that of the Yangtze, Godavari and Yellow Rivers. Compared to other large rivers, the specific fluxes are in the same range as that of the Amazon and Congo rivers, the two largest basins in the world.

However, the DOC yield of the Red River basin (1618 kg km<sup>-2</sup> yr<sup>-1</sup>) is about twice that of the Pearl and Yangtze basins and around half that of the Mekong and Congo

basins (Table 3). Though the DOC flux of the Red River is smaller than those of the Pearl and Yangtze Rivers, its specific DOC yield is higher than theirs. The high DOC yield of the Red River basin comes from high leaching from soil and rocks. Previous studies pointed out that the DOC in the Red River is mainly allochthonous during rainy seasons, e.g. soil leaching, and anthropogenic during dry seasons (industrial and domestic wastewater; Dang, 2011; Le et al., 2017a). Infiltration is a key factor in the hydrological pattern of this basin (Bui et al., 2014), accelerating leaching processes. Soil erosion is high within the Red River basin, ranging from 1.6 to 174 t ha<sup>-1</sup> yr<sup>-1</sup> (Mai et al., 2013; Nguyen et al., 2012; Podwojewski et al., 2008; Tuan et al., 2014). Though the POC flux of the Red River is relatively low compared to other Asian rivers (from -1% for the Yellow River to -76% for the Mekong River, Table 3), its specific yield (2959 kg km<sup>-2</sup> yr<sup>-1</sup>) is high compared to the Mekong (41%) and the Pearl River (+148%) basins which are two basins close by. Le et al. (2017a) emphasised that the main source of the POC was soil leaching and erosion, not phytoplankton. The soil erosion in this basin is high. Besides, POC is related to SSC, and the SSC in the Thao River is very high, with annual mean concentrations of 631 mg L<sup>-1</sup> at Yen Bai and 137 mg L<sup>-1</sup> at

# 4.3. Controls and influences on OC fluxes

Son Tay from 2003 to 2013.

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Figure 9, Figure 11 and Figure 12 show the annual evolution of simulated DOC, POC and TOC fluxes at four stations. The interannual variability of DOC flux is significant but not massive (standard deviations equal to 14, 11, 26, and 55 kt yr<sup>-1</sup> for Yen Bai, Vu

Quang, Hoa Binh and Son Tay, respectively). The DOC flux was the highest in 2008 (Figure 9), which is the flood year and was relatively low during 2010-2013 (averagely 33, 49, 61 and 176 kt yr<sup>-1</sup> for Yen Bai, Vu Quang, Hoa Binh and Son Tay, respectively) which are the drought years. Comparing DOC fluxes under the reference scenario and current conditions allows quantifying the impacts of Q variations associated with short climate variability and dam constructions (Figure 13). Under the reference scenario, due to the Q variation associated with short climate variability, the DOC flux during 2008-2013 only increased by 1% compared to 2003-2007, and the flood year 2008 was the main contributor. Under current conditions, dams induced a 13% reduction of DOC flux, allowing peak flow regulation during flood seasons. Previous studies also revealed that short climate variability and dam constructions within the Red River basin impacted Q. However, they showed that Q was more influenced by short climate variability than dams (Wei et al., 2019). They found that the annual mean Q was reduced by 13% from 2000-2007 to 2008-2013 at the outlet, with 9% due to short climate variability and 4% due to the dams. A distinct decrease in POC flux can be noticed after 2007 at all four stations (Figure 11) when some new dams started to operate. At the outlet (Son Tay), the POC flux in 2008 was only 45% of that in 2007, even though 2008 was a flood year, and the average POC fluxes decreased by 88% in 2008-2013 compared to 2003-2007. These

dams have trapped the suspended sediment and changed the grain size distribution

of downstream sediment (Wei et al., 2019), consequently affecting the POC transfer.

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Indeed, SSC decreased drastically by 67% in 2008 (Wei et al., 2019). Similarly to DOC fluxes, POC fluxes under the reference scenario varied little (2%) between 2003-2007 and 2008-2013. Dams caused an 85% decrease in POC flux. Our study reveals that dams induced severe sequestration of POC fluxes in the Red River basin due to suspended sediment retention. This sediment retention due to damming (up to 90%) was already assessed in Wei et al. (2021). Reducing water and nutrient fluxes might influence aquatic ecosystems and water and nutrient availability for human activities in the dams and further downstream (Trinh et al., 2015). Dams in this basin have different degrees of influence on DOC and POC fluxes. Our conclusions are in agreement with other studies in other basins, showing that: the water-sediment regulation of dams had no significant influence on DOC fluxes (Xia et al., 2016a) but a substantial impact on the POC fluxes (Li et al., 2015; Xia et al., 2016b). Due to the drop in POC flux, the TOC flux decreased by 31% at the outlet in 2008 compared to the previous year (Figure 12). At Son Tay, the POC flux accounted for 74% of the TOC flux during 2003-2007, while it only accounted for 47% during 2008-2013, with the main part of organic carbon in the dissolved phase (Table 4). Previous studies indicated that the Asian rivers draining erosion-prone mountainous terrain deliver more POC than DOC, particularly during the rainy seasons (Ludwig et al., 1996; Park et al., 2018). However, with the construction and operation of new dams, the composition ratio of TOC changed from POC-dominating to DOC-dominating (Table

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4). Besides, the dynamic variations of POC/TOC were also modified by dam regulation (Figure 14a). Before new dam constructions, the POC/TOC ratio was low around March and high in the flood season. However, after the impoundment of new dams, the dams fulfilled flood-control functions during June and July, retaining water and SS. Therefore, the POC/TOC ratio also decreased during the flood season. Moreover, dams discharge water for irrigation around March, releasing SS, which induces high POC/TOC. A fundamental change in POC/TOC was observed in 2008. Two new dams (Nansha on the Thao River and Tuyen Quang on the Lo River) started operation in 2008, and two new dams (Madushan on the Thao River and Son La on the Da River) were impounded in 2011. Compared to the other two tributaries, the POC/TOC ratio at Yen Bai on the Thao River did not decrease that sharply (Table 4). The Madushan and Nansha dams are around 230 km upstream of Yen Bai station. Therefore, the terrestrial inputs and the river bed degradation can regulate the suspended sediment and POC over this distance. At Hoa Binh station, before the new Son La dam became operational, the POC/TOC percentage was already low because of the Hoa Binh dam, which was impounded in 1989. Therefore, the most significant impact on the POC/TOC ratio at Son Tay is due to the change of the POC/TOC from the Lo River, i.e. Tuyen Quang dam contributes most to the decrease of POC/TOC at Son Tay. Dam impoundments impact the hydrological cycle and nutrient cycling, which could

unbalance more aquatic ecosystems. Other factors related to human influence on

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aquatic ecosystems, such as increased nutrient inputs, should be evaluated to understand their impacts on OC dynamics. In the same way, modelling the full carbon cycling may help identify interactions between organic and inorganic carbon within the catchment (Tian et al., 2015; Nakayama, 2022). Quantifying the effects of human pressures on freshwater ecosystems and the interactions between organic and inorganic carbon may refine our estimates of OC exports.

#### 4.4. Errors and uncertainties in the estimation

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Parameters in Equations 1 and 2 were calibrated based on discrete sampling data. However, sampling cannot be carried out when discharge is very high. Therefore, sampling DOC and POC concentrations at high discharge were lacking. More intensive sampling during flood season would help to obtain more precise parameters. Some DOC sampling data can be scattered during low discharge periods due to the uncertainty source, such as industrial and urban discharge. Along the Red River, the inhabitants are mainly farmers and villagers who might discharge the waste into the river. Moreover, %POC can vary greatly even on the same day due to the instantaneous suspended sediment concentration. Hence, the data from Le et al. (2017a) and Dang (2011) can differ even under a similar SSC concentration. Errors in estimating OC concentration and flux can also come from the simulated Q and SSC. Figure 16 presents the deviations between observed and simulated Q and SSC, focusing on dates where DOC and POC sampling were conducted. It shows that the POC and DOC equation parameters are determined based on a dataset not representative of the different hydrological conditions, especially at Son Tay station. It leads to biases, as explained in the previous paragraph.

Simulated Q and SSC errors are within acceptable limits (Wei et al., 2019). Nevertheless, even acceptable simulated Q and SSC may lead to high biases, especially at a daily time step where offsets in water or sediment transport may lead to a bad representation of the peaks. Moreover, LOADEST was used to validate our simulation, which can produce high biases when calculating long-term loading (Hirsch, 2014; Stenback et al., 2011).

As mentioned in section 3.1.5, POC parameters calibration was based on the data sampled since 2008 when new dams started operating. Therefore, the POC concentration and flux before 2008 were an insight to estimate the potential retention of POC in the reservoirs roughly. According to Wei et al. (2019), the dynamic transfer processes of SS before and after new dam constructions were different. Therefore, POC dynamic transfer processes and fluxes would be different before and after the new dam construction. Hence, the parameter *b* related to POC (Equation 2) should be different before 2008.

## 4.5. Perspectives

In this study, we used the original version of SWAT and used simulated discharge and suspended sediment fluxes combined with empirical equations to estimate organic carbon loads in the Red River. We showed that a simple approach with easy-to-obtain variables is limited in representing daily fluctuations of DOC and POC concentrations

in a watershed presenting multiple anthropogenic pressures, even if monthly variations are well represented. Nevertheless, some catchment-scales models can simulate carbon cycling within the watershed, including DOC and POC transport, which may lead to a better representation of daily variations in DOC and POC concentrations. ORCHIDEE MICT-LEAK can capture DOC dynamics and be applied in large Arctic rivers (Bowring et al., 2019; 2020). In the same way, INCA-C, a revised version of the INCA model, can simulate DOC fluxes in catchments (Futter et al., 2007).

Concerning SWAT, the CENTURY model (Parton et al., 1994) was recently implemented in SWAT, refining the simulation of soil organic matter dynamics (Yang et al., 2016; Zhang et al., 2013; Zhang, 2018). This new version of SWAT is called SWAT-C. SWAT-C was further developed by implementing modules simulating POC and DOC loading and transport processes (Du et al., 2020, 2023; Qi et al., 2019, 2020). Applying SWAT-C on the Red River may refine the results presented in this paper.

Moreover, a better understanding of the processes influencing OC in soils and rivers and its interactions with other nutrients and a better quantification of the human influence on OC transport from soils to rivers will help capture OC dynamics at the outlet of watersheds under anthropogenic pressures. As an example, deeper analysis on the isotopy or the stoichiometry balance of the DOC and POC within the basin may help in understanding the origins of the OC transported in the Red River catchment.

The main contributors for POC and DOC are the Thao River and the Da River, respectively. This difference in contribution may be explained by various factors such as a diversity in aquatic ecosystems functioning, land use, dam management, or soil type that may impact the characteristics of the organic carbon exported from the tributary to the main outlet, and further its interaction with other biogeochemical cycles in the delta and the sea (Luu et al., 2010).

## 5. Conclusions

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Based on a hydrological model already set up, calibrated and validated over the Red River basin and on DOC and POC samplings, this paper estimates DOC and POC exports for ten years (2003-2013) in the large tropical Red River basin based on a model of OC dynamics. Intra-annual and inter-annual variations are difficult to assess from discrete in-situ samplings and only possible at the hydrometric stations. Based on the daily simulated OC concentration, discharge, and suspended sediment from a modelling study, daily OC fluxes were simulated considering all short-term events at hydrometric stations and anywhere within the basin. It allows an understanding of the spatiotemporal variations of OC in this basin. Discharge and suspended sediment are crucial factors for fluvial OC fluxes. However, the OC fluxes and specific yield have been altered by short climate variability and intensive human activities in this basin. Especially, dam impoundments clearly trapped POC, reducing TOC export and a different OC composition ratio, impacting the food chain downstream.

This study reveals that during 2003-2013, at the outlet of the Red River basin, the exports of DOC and POC were 222 and 406 kt yr<sup>-1</sup> respectively, accounting for 0.38% of the total OC export by Asian rivers. However, the specific yields of DOC (1618 kg km² yr¹) and POC (2959 kg km² yr¹) of the Red River basin were high (more than double) compared to other Asian basins such as the Yellow, Yangtze, and Pearl. By comparing the scenario of reference scenario (without dams) to current conditions, we found a 12% and an 88% decrease in DOC and POC fluxes, respectively, mainly due to dams regulations (less than 2% of variations were explained by short climate variability). The percentage of POC in TOC decreased from 86% to 74% until 2007 and 47% with new dams. Dam constructions altered the TOC yield and its constituent ratio.

The corresponding parameters of the DOC and POC equations well represented the characteristics of each sub-basin, showing the effect of soil OC and Chlorophyll a.

Further research may better represent daily variations of DOC and POC concentrations and the interactions with other elements to better understand the anthropogenic influence on OC dynamics.

Finally, this study shows that climate variability may not impact OC dynamics as much as damming. The latter significantly decreased POC exports due to sediment retention, altering the equilibrium of OC cycling downstream, which may impact the food chain. If this statement is valid for the other Asian Rivers, the quality of OC inputs to the oceans may be drastically altered.

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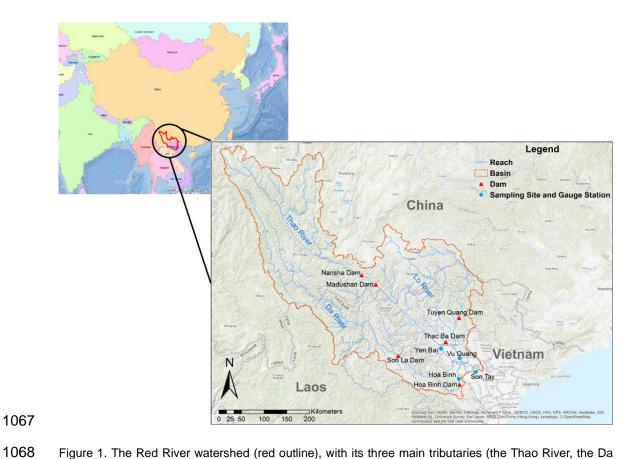


Figure 1. The Red River watershed (red outline), with its three main tributaries (the Thao River, the Da River and the Lo River): sampling sites and gauge stations (blue points); large dams locations (red triangles).

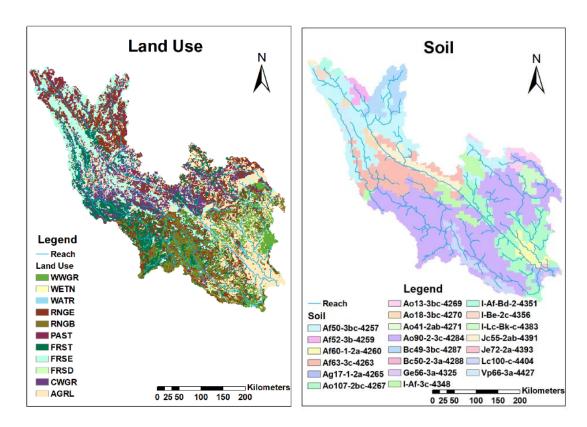


Figure 2. Land use and soil map of the Red River basin (Wei et al., 2019).

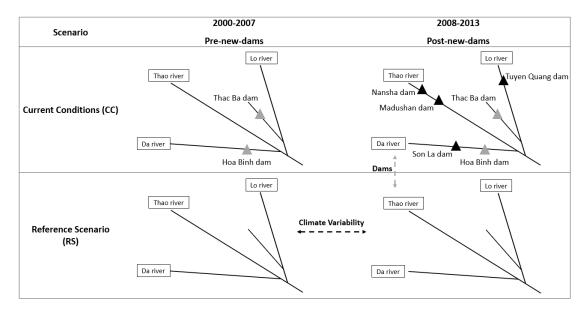


Figure 3. The setting for Current Conditions and Reference Scenario: grey triangles are the old dams impounded before the study period, and black triangles are the new dams impounded since 2008. By comparing current conditions to the reference scenario during 2008-2013, the impacts of these dams can be quantified; by comparing the period 2008-2013 to 2003-2007 under the reference scenario, the impacts of short climate variability can be quantified.

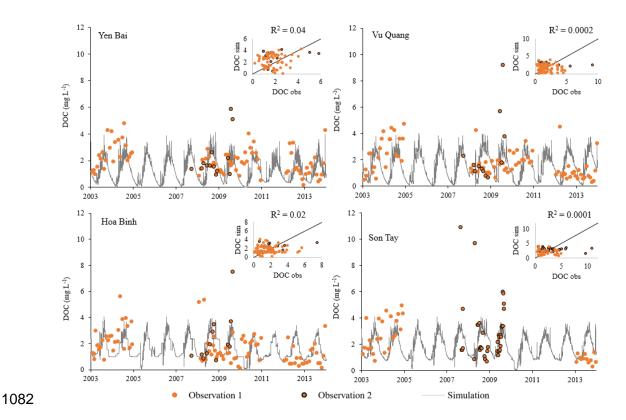


Figure 4. Daily variations of dissolved organic carbon (DOC) concentration (mg L<sup>-1</sup>) at four stations from 2003 to 2013. Observation 1 (orange dots) shows the DOC measured by Le et al. (2017a); observation 2 (orange and black dots) indicates the DOC measured by Dang (2006); calculations from Equation 1 based on the simulated discharge (Q, m³ s<sup>-1</sup>) from Wei et al. (2019) with the values of the parameters given in Table 1 are the solid grey line.

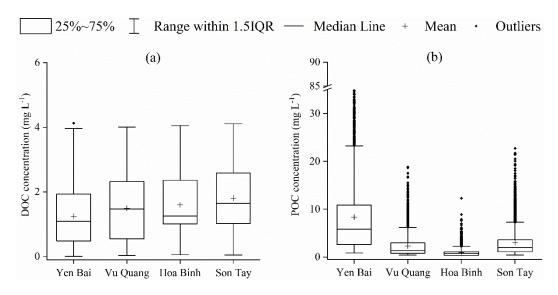


Figure 5. Box plot of daily simulated dissolved organic carbon (DOC) and daily particulate organic carbon (POC) concentration (mg L<sup>-1</sup>) at four stations during 2003-2013 in the Red River basin. IQR represents the interquartile range.

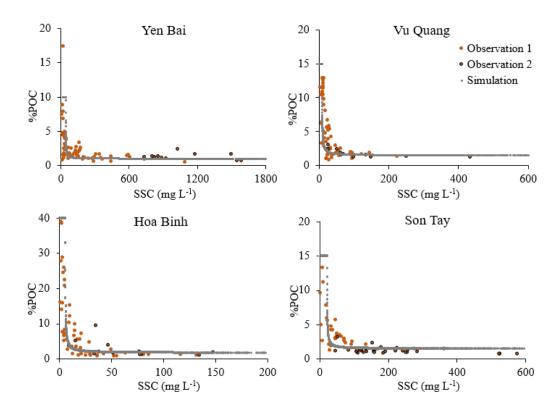


Figure 6. Relationship between the percentage of POC concentration (%POC) in the suspended sediment concentration (SSC, mg L<sup>-1</sup>) and observed SSC (mg L<sup>-1</sup>). Observation 1 (black dot) corresponds to the measurements from Le et al. (2017a); observation 2 (black and brown dots) corresponds to the measurements from Dang (2006); brown dots were the calculations from Equation 2 based on the observed SSC data collected from the Vietnam Ministry of Natural Resources and Environment (MONRE). %POC<sub>max</sub>, the maximum limit of %POC, was set as 10%, 15%, 40% and 15% for Yen Bai, Vu Quang, Hoa Binh and Son Tay, respectively.

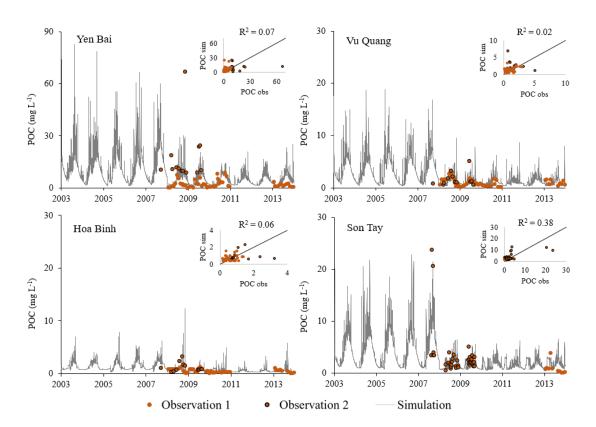


Figure 7. Daily variation of particulate organic carbon (POC) concentration (mg L<sup>-1</sup>) at four stations from 2003 to 2013. Observation 1 (brown dots) was observed POC from Le et al. (2017a); observation 2 (brown and black dots) was the observed POC from Dang (2006); simulation (solid grey line) was calculated from Equation 2 based on the simulated suspended sediment concentration (SSC, mg L<sup>-1</sup>) from Wei et al. (2019).

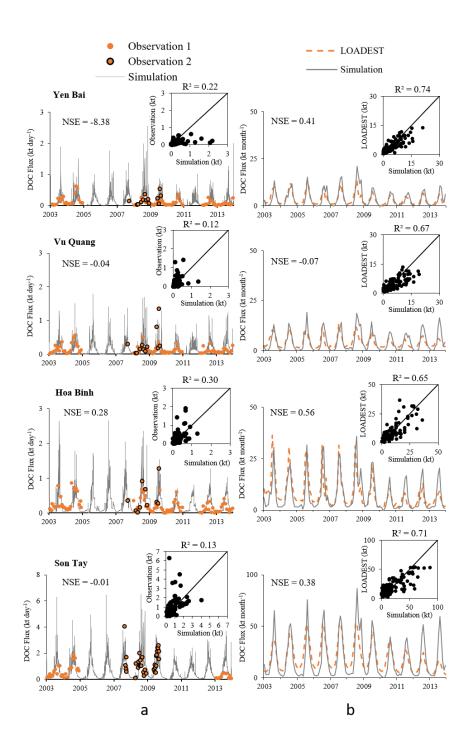


Figure 8. (a) Mean daily variation of dissolved organic carbon (DOC) fluxes (kt day<sup>-1</sup>) at four stations from 2003 to 2013. Observation 1 (orange dots) was calculated from the measured DOC concentration from Le et al. (2017a); observation 2 (orange and black dots) was calculated from the measured DOC concentration from Dang (2006); the solid grey line was the simulated DOC fluxes (kt day<sup>-1</sup>) calculated based on the DOC concentrations from Equation 1 and the Q from SWAT model. (b) Mean monthly DOC fluxes (kt month<sup>-1</sup>) comparison between results from LOADEST and our calculations.

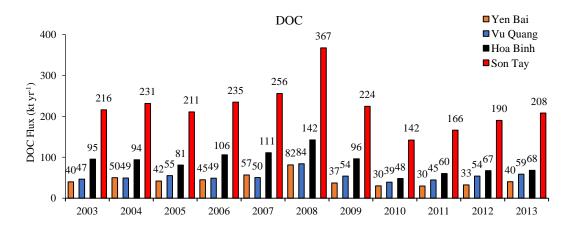


Figure 9. Simulated annual dissolved organic carbon (DOC) fluxes (kt yr<sup>-1</sup>) at four stations from 2003 to 2013.

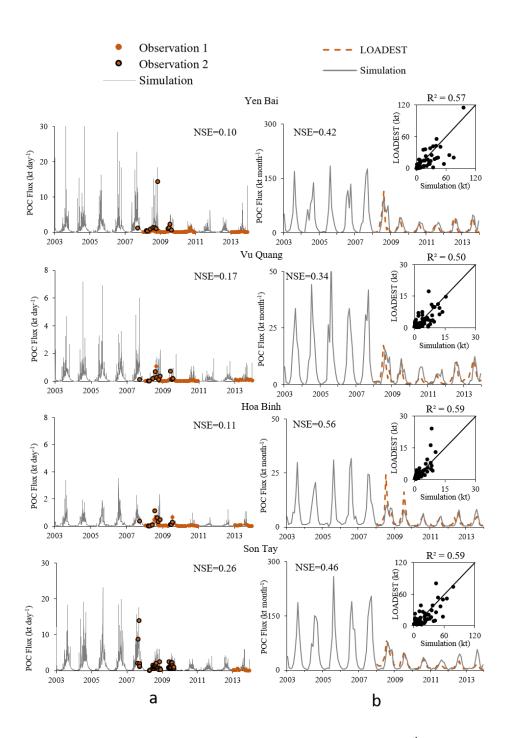


Figure 10. (a) Mean daily variation of particulate organic carbon (POC) flux (kt day<sup>-1</sup>) at four stations from 2003 to 2013. Observation 1 (brown dots) was calculated from the measured POC concentration from Le et al. (2017a); observation 2 (brown and black dots) was calculated from the measured POC concentration from Dang (2006); the solid gray line was the simulated POC flux (kt day<sup>-1</sup>) based on the POC concentrations from Equation 2 and the Q from SWAT model. (b) Mean monthly POC flux (kt month<sup>-1</sup>) comparison between LOADEST results and our calculations during 2008-2013.

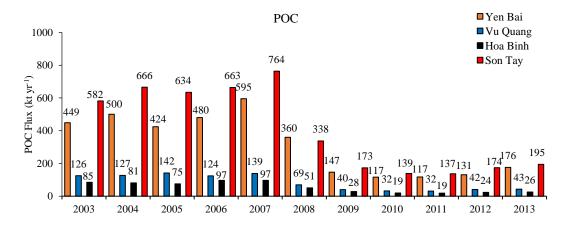


Figure 112. Simulated annual particulate organic carbon (POC) fluxes (kt yr<sup>-1</sup>) at four stations from 2003 to 2013.

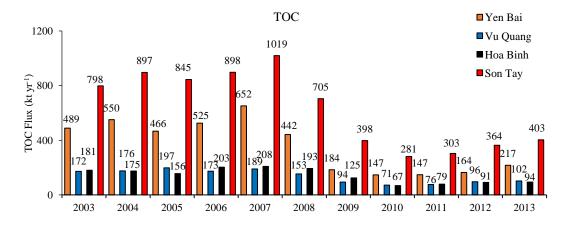


Figure 12. Simulated annual total organic carbon (TOC) flux (kt yr<sup>-1</sup>) at four stations from 2003 to 2013.

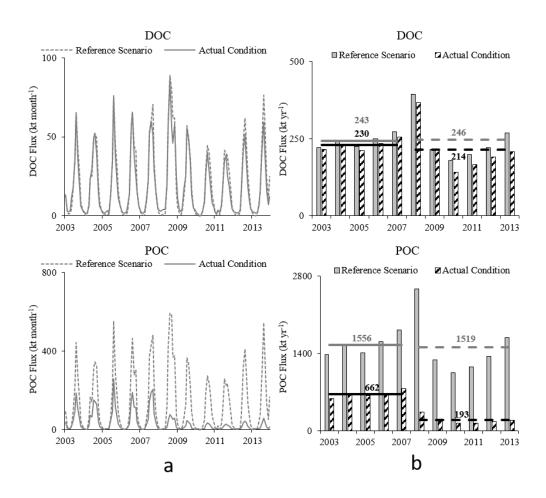


Figure 13. Simulated dissolved organic carbon (DOC) and particulate organic carbon (POC) fluxes at Son Tay station under reference scenario and current conditions: (a) Monthly variations; (b) Annual budgets. The solid black line displays the total decrease caused by short climate variability and dams between 2003-2007 and 2008-2013; the grey dashed line indicates the decrease related to short climate variability, and the black dashed line displays the reduction caused by dams.

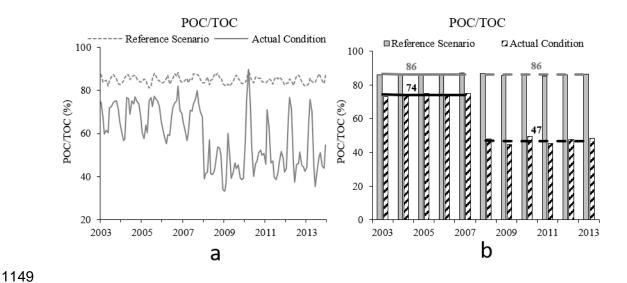


Figure 14. Simulated particulate organic carbon (POC) percentage in total organic carbon (TOC) during 2003-2013 under reference scenario and current conditions: (a) mean monthly variations; (b) mean annual values.

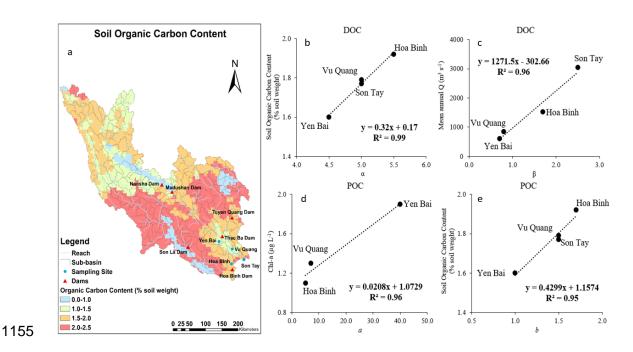


Figure 15. (a) Soil organic carbon content (% soil weight) within each sub-basin; (b) relation between the parameter  $\alpha$  in DOC equation (Equation 1) and the average soil organic carbon content of the drainage area of each station; (c) relation between the parameter  $\beta$  in DOC equation (Equation 1) and the mean annual discharge (Q) of each station; (d) relation between the parameter a in POC equation (Equation 2) and Chl-a ( $\mu$ g L<sup>-1</sup>; Le et al., 2017a); (e) relation between the parameter b in POC equation (Equation 2) and the average soil organic carbon content of the drainage area of each station.

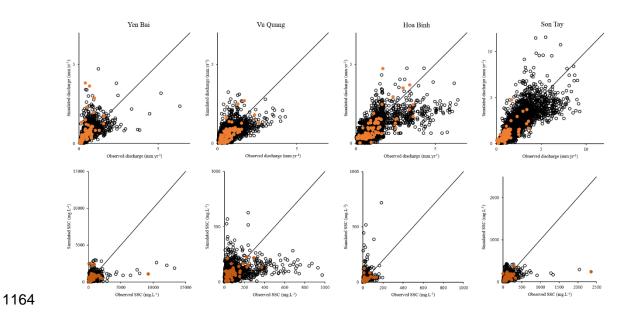


Figure 16. Comparison between observed and simulated discharge (top; mm.yr<sup>-1</sup>) and SSC (bottom; mg.L<sup>-1</sup>). Coloured circles correspond to dates where DOC or POC data are available.

Table 1. Values of the parameters  $\alpha$  and  $\beta$  for dissolved organic carbon (DOC, Equation 1) and of the parameters a, b, and %POC<sub>max</sub> for particulate organic carbon (POC, Equation 2) at different stations, and number (N) of sampling data (DOC and POC) used to calibrate the parameters.

Variables	Parameter	Yen Bai	Vu Quang	Hoa Binh	Son Tay
	N (DOC)	94	94	96	73
DOC	$\alpha$ (mg L <sup>-1</sup> )	4.5	5.0	5.5	5.0
	$\beta$ (mm d <sup>-1</sup> )	0.7	0.8	1.7	2.5
	R <sup>2</sup> (DOC concentrations)	<mark>0.04</mark>	0.00002	<mark>0.02</mark>	0.0001
	N (POC)	63	58	54	49
POC	a (mg L <sup>-1</sup> )	40.0	7.0	5.0	20.0
POC	b (%)	1.0	1.5	1.7	1.5
	%POC <sub>max</sub>	10	15	40	15
	R <sup>2</sup> (POC concentrations)	<mark>0.07</mark>	<mark>0.02</mark>	<mark>0.06</mark>	<mark>0.38</mark>

Table 2. Impacts of the new dams on the organic carbon dynamics (in kt.yr<sup>-1</sup>) in the main tributaries of the
 Red River. The values in parentheses represent the contribution of the three main tributaries.

Variables	Period	Yen Bai	Vu Quang	Hoa Binh	Son Tay
POC	2003-2007	490 ± 66 (69%)	132 ± 8 (19%)	87 ± 10 (12%)	662 ± 66
FOC	2008-2013	175 ± 93 (71%)	43 ± 14 (18%)	28 ± 12 (11%)	193 ± 75
	Difference	-64 %	-67%	-68%	-71%
DOC	2003-2007	44 ± 7 (24%)	53 ± 3 (29%)	88 ± 12 (47%)	222 ± 18
DOC	2008-2013	42 ± 20 (24%)	56 ± 16 (31%)	80 ± 34 (45%)	216 ± 79
	Difference	-5 %	+5%	-9%	-3%

Table 3. Comparisons of organic carbon concentrations and fluxes between the present study and other studies in the Red River and in other rivers

	Station	Drain Area (10 <sup>3</sup> km <sup>2</sup> )	Period -	DOC			POC			
River				Concentration (mg L <sup>-1</sup> )	Flux (kt yr <sup>-1</sup> )	Specific Yield (kg km <sup>-2</sup> yr <sup>-1</sup> )	Concentration (mg L <sup>-1</sup> )	Flux (kt yr <sup>-1</sup> )	Specific Yield (kg km <sup>-2</sup> yr <sup>-1</sup> )	Reference
				1.9	47	969	24.7	274	5649	Dang, 2006
			2008 2000	2.2	44	866	2.6	59	1258	Le et al., 2017a
	Yen Bai	48.50	2008-2009	-	46	-	-	197	-	LOADEST (this study)
				1.51	59	1216	5.21	253	5216	This study
			2003-2013	1.39	44	907	8.35	318	6557	This study
				2.4	78	2568	1.8	84	2766	Dang, 2006
			2008-2009	1.9	49	1613	0.8	47	1218	Le et al., 2017a
	Vu Quang	30.37		-	59	-	-	50	-	LOADEST(this study)
				1.77	69	2272	1.33	55	1811	This study
Red			2003-2013	1.50	53	1745	2.30	83	2733	This study
			2008-2009	2.3	131	2482	1.3	55	1042	Dang, 2006
				1.7	82	1497	0.5	54	758	Le et al., 2017a
	Hoa Binh	52.78		-	98	-	-	58	-	LOADEST(this study)
				1.84	119	2255	0.62	40	758	This study
			2003-2013	1.60	88	1667	0.96	55	1042	This study
		137.23	2008-2009	2.5	263	1916	3.95	243	1771	Dang, 2006
	Con Tour			-	286	-	-	259	-	LOADEST(this study)
	Son Tay			2.03	296	2157	1.66	255	1858	This study
			2003-2013	1.81	222	1618	3.03	406	2959	This study
Mekong	My Thuan (DOC) Phnom Penh (POC)	795	1972-1998 (DOC) 2006 (POC)	n.a.	2200	2767	2.01	1670	2100	Li et al., 2013 Ellis et al., 2012
Pearl	n.a.	452	2005-2006	1.7	380	840	1.5	540	1195	Ni et al., 2008
Yangtze	Datong	1830	2009	2.03	1580	863	n.a.	1520	831	Wang et al., 2012
Godavari	Rajahmundry	313	2003-2005	1.24	130	415	n.a.	756	2414	Balakrishna et al., 2006
Yellow	Lijin	752	2008-2012	3.3	60	80	1.39	410	545	Ran et al., 2013
Amazon	Obidos	6000	1994-2000	7.18	26900	4483	0.85	5800	967	Moreira-Turcq et al., 2003
Congo	Kinshasa-Brazzaville	3700	2009-2010	9.2	12480	3373	1.46	1960	530	Spencer et al., 2016

Table 4. The percentage of particulate organic carbon (POC) in total organic carbon (TOC) in two periods (before and after the new dam constructions) at each station

Variables	Period	Yen Bai	Vu Quang	Hoa Binh	Son Tay
POC/TOC	2003-2007	91%	72%	47%	74%
POC/10C	2008-2013	81%	44%	26%	47%