

Appendix 3: Source vs Sink (SI3)

In order to quantify the forcings that regulate export of nutrients from watersheds and seaward fluxes of the Changjiang, we elaborate the source vs sink terms on annual basis. In this study, data from National Statistics Bureau of China (Web-site: <http://data.stats.gov.cn>) and previously published results from the literature are referred when dealing with the nutrient budgets, and two types of information are selected, at national level and provincial scale (ca. 20 municipalities, provinces and autonomous regions), for data compilation and statistics. In Table SI3-1 is summarized the information used in this study with a total amount 36.6×10^3 of data sets.

In processing the data, we take into consideration the proportion of individual administrative areas (i.e., provincial scale) in the watersheds of the Changjiang, which is then used to estimate the contributions of given parameters (e.g., synthetic fertilizer) to individual tributaries as well as into the mainstream.

SI3-1. Estimate of Inputs of Nitrogen and Phosphorus

SI3-1.1 Synthetic fertilizers and pesticides

We categorize synthetic fertilizers into N, P and composite groups, and the total applications of nitrogen and phosphorus is calculated by amount of application per square kilometers times the effective concentrations. The annual input of N and P (Fertilizer-N/P) via fertilizer application (Unit: $\times 10^9$ mol/yr) can be estimated by:

$$\text{Fertilizer} - N / P = \frac{1}{n} \times (F_f + a \times F_c) \quad (\text{SI3-1})$$

where a is 0.348 for nitrogen and 0.483, for phosphorus respectively, which is used to transform the amount of composite fertilizers to N and P; n is atomic mass for N (14) and P (31), and F_f and F_c represent the effective amount of application for N, P and composite fertilizers, respectively. The effective amount of fertilizer for N and P is evaluated based on the annual application and percentage of N and P from chemical formulas with the correction of purity.

Application of pesticides also introduces nitrogen and phosphorus into the farmland as well. In the watersheds of the Changjiang application of pesticides in agriculture increased from 0.24×10^9 kg/yr in 1990

to 0.61×10^9 kg/yr in 2014, i.e., by an annual factor of 2.5. However, pesticides application is <3% relative to the amount of chemical fertilizers (e.g., 16×10^9 kg/yr in 2014), and hence is not included for further data analysis.

SI3-1.2 Organic fertilizers

SI3-1.2.1 Manures

Inputs of nutrients (e.g., N and P) through manure releases by livestock and human beings in countryside over the drainage basin is estimated by the product of population and waste excretion rates.

Besides the human population in the countryside, we characterize different types of livestock including poultry, cattle, pig, horse, donkey and mule etc. in data compilation, and following equation is used to calculate the production of manures (Unit: $\times 10^9$ mol/yr):

$$Manure - N / P = \frac{1}{n} \sum_{i=1}^m (E_i \times I_i \times C_i) \quad (SI3-2)$$

where E_i is the excretion rates (kg/ind/yr), I_i is the population of individuals (ind), C_i represents contents (%) of N and/or P, and n is the atomic mass of N (14) and P (31), respectively (Table SI3-2). Manures are separated into two groups, that is feces and urine, and the calculation was made separately, and then combined. It should be noted that manures are traditionally used as organic fertilizer in the agriculture of China.

SI3-1.2.2 Straws used as organic fertilizer

In the drainage basin of the Changjiang, an average 24% of straws materials (i.e., crops residues) is buried in soils and another 35% of the straws is burnt in situ and transformed to plant ash, both are used as organic fertilizers in traditional agriculture, and the rest is used to feed livestock (Gao et al., 2009). The annual input of N and P via application of straws (Unit: $\times 10^9$ mol/yr) was estimated by:

$$Straws - N / P = \frac{1}{n} \sum_{i=1}^m (I_{ci} \times P_{ci} \times R_{ci} \times C_{ri}) \quad (SI3-3)$$

where I_{ci} is the percentage of straws used for fertilizer application, P_{ci} is annual production of crops, R_{ci}

represents the ratio between crops and straws in harvest, and C_{ri} stands for the concentration of N and/or P in straws, n is the atomic mass correction for N (14) and P (31), respectively (Table SI3-3).

SI3-1.3 N-fixation

We refer to the term of “N-fixation” as the sum of nitrogen fixed by cultured crops and plant species of managed and natural ecosystems (e.g., alfalfa-type). Input of nitrogen (Unit: $\times 10^9$ mol/yr) through nitrogen fixation can be estimated by the product of N-fixation rate and the area of coverage, that is:

$$Fixation - N = \sum_{i=1}^m A_i \times k_n^i \quad (SI3-4)$$

where A_i is the area of culture and/or land-mass of N-fixation species, and k_n^i the N-fixation rate (Unit: mol N/km²/yr).

The annual N-fixation rate in the literature ranges from 0.7 mol N km⁻²-71 mol N km⁻² for grass, and 200 mol N km⁻²-2143 mol N km⁻² for green manure at annual scale (Table SI3-4), hence we used the geometric means and corresponding land-area to calculate the N-fixation and then integration for the whole watersheds.

SI3-1.4 Wastewaters

SI3-1.4.1 Aquaculture wastewaters

Freshwater aquaculture is a major part of the Chinese fishery industry. It takes place in ponds, lake, river, reservoir and rice paddy fields, which are widely spread almost across the whole China (Cao et al., 2007). The annual input of N and P as wastes of aquaculture (Unit: $\times 10^9$ mol/yr) can be estimated by:

$$Aquaculture\ wastes - N / P = \frac{1}{n} (P_{aqua} \times R_{aqua}) \quad (SI3-5)$$

where P_{aqua} is the production of freshwater aquaculture, and R_{aqua} is the wastes of N and P released from the freshwater aquaculture (Unit: % fish product). It has been reported that in freshwater aquaculture, production of 1 kg fresh fish results in 0.160 kg of nitrogen and 0.035 kg of phosphorus being released into environment (Guo and Li, 2003).

SI3-1.4.2 Domestic wastewaters

To estimate the nutrients flux originated from the domestic wastewaters, data reported by the National Statistics Bureau of China was adapted and used here in calculation on the basin scale. The annual input of N and P as domestic wastewaters (Unit: $\times 10^9$ mol/yr) can be estimated by:

$$\text{Domestic Wastewaters} - N/P = \frac{1}{n} \times F \quad (\text{SI3-6})$$

where F is the amount of total nitrogen (TN), ammonia (NH_4^+) and phosphorus (TP), respectively, in the domestic wastewaters. Previous studies indicated that in post-treated wastewaters, the majority of nitrogen is in the form of NH_4^+ and NO_3^- , NO_2^- and organic nitrogen were much less and/or negligible (Kong, 2006). Therefore, the difference between TN and NH_4^+ in this study is taken as an estimate of NO_3^- in domestic wastewaters. Similarly, TP is used as an estimate of DIP because PP is negligible in post-treated wastewaters. This may raise the amount of DIN and DIP in the estimate of wastewaters, but it tends to make an overall more conservative budget. However, wastewaters discharged directly into the coastal environment from Shanghai and Jiangsu was excluded in the calculation, because this amount of nutrients is not directly linked to the riverine transport.

Based on the information available, the amount of nitrogen and phosphorus released by the drainage of post-treated domestic wastewaters was 88×10^9 mol/yr and 4.5×10^9 mol/yr, respectively, into the Changjiang watersheds.

SI3-1.5 NO_x emission from combustion of fossil fuels

Based on the conversion factors by Wang et al. (1996), emission of NO_x from combustion of different fossil fuels, such as coal, gasoline, coke, crude oil, kerosene and diesel etc., in the Changjiang watersheds can be estimated as:

$$\text{Fossil fuel} - N = \frac{1}{n} (P_{\text{fossil}} \times C_{\text{NO}_x}) \quad (\text{SI3-7})$$

where P_{fossil} is the amount of combustion of different types of fossil fuels and C_{NO_x} is the conversion factors (%), shown in Table SI3-5.

SI3-2. Export of Nitrogen and Phosphorus

SI3-2.1 Harvests and culture products

SI3-2.1.1 Harvest of crops

Export of nitrogen and phosphorus from the watersheds includes removal along with harvest of crops (Harvest-N/P). Harvest-N/P (Unit: $\times 10^9$ mol/yr) is estimated as products of crops production and concentration of N and P in each of cultured species at annual scale, that is:

$$Harvest - N / P = \frac{1}{n} \sum_{i=1}^m [P_{ci} \times (C_{ci} + C_{ri} \times R_{ci})] \quad (SI3-8)$$

in which C_{ci} stands for the concentration of N and/or P in crops, and harvest of crops and straws are both considered with corrections of the percentage returned to field as fertilizers (Table SI3-3).

SI3-2.1.2 Animal products

Removal of N and P along with livestock and animal products (e.g. meat, egg and milk) and by-products (e.g., bones, guts and furs), as well as from aquatic culture products (e.g., fish, crustaceans and shellfish) in the watersheds of the Changjiang can be estimated by:

$$Production - N / P = \frac{1}{n} \sum_{i=1}^m P_{ai} \times (C_{ai} + R_{ai} \times C_{bi}) \quad (SI3-9)$$

where P_{ai} is the annual production of animal and aquaculture meat, R_{ai} is production ratio between meat and by-products (i.e. $R_{ai}=1$ for meat), C_{ai} and C_{bi} represent the N and P concentration of animal and bi-products, respectively (Table SI3-6).

SI3-2.2 Emission as gas species

SI3-2.2.1 Denitrification

Denitrification can be an important pathway of nitrogen export from the watersheds, but it is difficult, if not impossible, to quantify across the whole Changjiang drainage basin given very limited information and many regulating factors with uncertainty. It has been reported that loss of N-synthetic fertilizers as denitrification in rice paddies can be as high as $(35\pm 3)\%$ (Zhu and Wen, 1992; Zhu, 1997a), while in dry-land tillage loss of carbamide and ammonium bicarbonate is 29% and 13% respectively (Cai et al.,

1998). In this study, we adopt the value of $(28\pm 11)\%$ for denitrification loss of fertilizer nitrogen, and $(14.5\pm 2)\%$ (Range: 13%-16%) for denitrification of manures (Bashkin et al., 2002; Zhu, 1997a-b). Previous studies indicated that the straws back to field as fertilizers has almost no contribution to the denitrification (Zhu, 1997a-b), which is therefore not considered here anymore.

SI3-2.2.2 Volatilization of NH_3

Nitrogen can also be lost from agriculture area via volatilization of fertilizers (e.g., ammonium) as well as human and animal wastes, which can then be a component of atmospheric depositions (i.e., cycling between atmosphere and watersheds). Application of manures as fertilizer is accompanied by a loss of 2.1%-52.7% of NH_3 , and IPCC (1996) recommended a value of 20% for the loss of manures as NH_3 , which was used in the previous studies as well in China (Xing and Zhu, 2002). Based on the data compilation in Table SI3-2, the manures loss as NH_3 is $(124\pm 7)\times 10^9$ mol/yr for the period of 2003-2014, while using the value of 20% from IPCC (1996) generates a rate of $(80.2\pm 5.0)\times 10^9$ mol/yr that seems to be an underestimate.

Another NH_3 loss is along with the application of synthetic fertilizers, which is linked to the type of soils and weather conditions. It is reported that loss of carbamide and ammonium bicarbonate via volatilization can be $(32\pm 19)\%$ and $(40\pm 15)\%$, respectively, from rice paddies, and carbamide loss via volatilization can be $(14\pm 4)\%$ in dry-land tillage (Zhu and Wen, 1992; Zhu, 1997a). In this study a mean value of $(29\pm 14)\%$ is used to account for the volatilization loss of fertilizer-N.

SI3-2.3 Export by the river

Seaward flux of nutrients from the Changjiang includes dissolved and particulate forms. In this study we use data from Xuliujing to examine the export at river mouth. With regards to the nitrogen, the DIN flux is 107×10^9 mol/yr at Xuliujing, and 1.6×10^9 mol/yr for DIP. Transport in dissolved organic nitrogen (DON) is estimated based on the DON/DIN ratio measured in the river course. Measurements made in 1997 (i.e., pre-TGD time), 2009 (i.e., post-TGD time) and 2010 in the river course show DON/DIN of 0.15 ± 0.05 , 0.10 ± 0.03 and 0.14 ± 0.05 , respectively, downstream from Yichang, and there is no systematic difference between middle and lower reaches. Hence, a value of $\text{DON/DIN}=0.12\pm 0.07$ is used to estimate the DON flux. Furthermore, we use the concentration of particulate nitrogen (PN) and annual sediment load at the Datong to calculate the flux in particulate forms, because the relevant information was not available for

Xuliujing in 1990s.

With regards to dissolved organic phosphorus (DOP), we used the DOP/DIP ratio measured in 1997, 2009, and 2010, respectively, which gives a value of $\text{DOP/DIP}=0.94\pm0.11$ ($n=13$), then the DOP flux can be calculated from DIP value.

Data of particulate phosphorus (PP) are rather limited in the literature, and hence we used the measurements of 2009 expedition, which gives a PP concentration of $(0.090\pm0.019)\%$, to calculate the riverine flux.

Similarly, based on the data of DSi at Xuliujing we made estimation of riverine flux from the Changjiang to the East China Sea.

SI3-3. N and P Retention in the Watersheds

SI3-3.1 Farmland

N storage in the farmland is affected by soil type and tillage practice as well as how much fertilizer is applied and/or if N fixation occurs. It has been reported that retention rate of synthetic fertilizer-N is 20% (Range: 12%-30%) for rice paddies and 27% (Range: 11%-68%) from dry-land tillage, respectively (Zhu, 1997a-b; Xing and Zhu, 2002). Retention of N in organic fertilizers (e.g., manures and straws-back to farmland) can be 49% (Range: 27%-78%) in the Changjiang watersheds (Zhu, 1997a-b; Xing and Zhu, 2002). In this study, we use N storage rate of 23%, 49% and 49%, respectively, for synthetic fertilizers, manures and straws as fertilizer in farmland.

Compared to nitrogen, phosphorus is more inclined to be retained in soils because it can combine with calcium, iron and aluminum etc., and hence form insoluble compounds. It is reported that efficiency of P-fertilizers in agriculture is 10%-25% (Cheng et al., 2010; Wang et al., 2011; An et al., 2013). Hence we use a conservative retention rate of 75% for P-containing fertilizers and do not distinguish between manures and synthetic chemicals owing to the gap of knowledge at this time.

SI3-3.2 Forest and grassland

From national-wide research results, including the Changjiang watersheds as well, the biomass accumulation of forests generates an amount of tree leaves at 0.241×10^6 kg/km² annually, concentration of N and P in tree

leaves amounts to 2.08% and 0.28%, respectively (Liu et al., 2006; Wang et al., 2011). Similarly, the forage has concentration of 2.08% and 0.25% for N and P, respectively (Liu et al., 2006; Wang et al., 2011). Therefore, the retention of N and P by biomass accumulation can be estimated by:

$$Storage - N / P = \frac{1}{n} \sum_{i=1}^m (A_f \times M_f \times C_f + M_g \times C_g) \quad (SI3-10)$$

where A_f represents the area for of forest and grassland, C_f and C_g are the concentration of N and P in tree leaves and/or grass, M_f and M_g are the biomass production for tree leaves and/or grass, respectively. The calculation is made separately for the forest and grassland, and then results are combined for the whole watersheds.

SI3-3.3 Three Gorges Reservoir (TGR) trap of sediments

Based on our measurements of 2009 expedition, concentration of PN, PP and BSi in riverine suspended sediments was $(0.24 \pm 0.06)\%$, $(0.090 \pm 0.019)\%$ and $(0.41 \pm 0.28)\%$, respectively. From the national bulletin of river sediments the amount of suspended matter trapped in TGR can be calculated for the period of 2003-2014. This in combination with measured changes in suspended sediment concentrations produces an estimate of $(28 \pm 18) \times 10^9$ mol/yr for N, $(4.7 \pm 3) \times 10^9$ mol/yr for P and $(48 \pm 31) \times 10^9$ mol/yr for Si, respectively, deposited in the reservoir (TGR). It should be noted that the trap of nutrients within the TGR is essentially via the deposition of riverine sediments, while dissolved concentrations of nitrogen and phosphorus (e.g., DIN and DIP) are rather comparable between influx to and outflow from the TGR on an annual scale.

SI3-4. Discussion and Summary

In the watersheds of the Changjiang, input of nitrogen and phosphorus includes atmospheric wet and dry depositions, application of synthetic and organic fertilizers and pesticides, N-fixation, release of organic fertilizer and wastewater and emission from combusting fossil fuel as NO_x , whereas the export incorporates harvests, emission as gas species, as well as seaward flux of river. Role of nutrient retention in the watersheds should also be considered from view point of the adaptive management.

SI3-4.1 Historical trends

Nitrogen. With regards to nitrogen, synthetic fertilizer-N application in the Changjiang drainage basin has

increased from 214×10^9 mol/yr in 1980 to 710×10^9 mol/yr in 2014, i.e., by a factor of 3.5 (Fig. SI3-1). This is followed by organic fertilizers (e.g., Manure-N), which shows a trend of 235×10^9 mol/yr in 1980 to 401×10^9 mol/yr in 2014. After early 1980s, the application of synthetic fertilizer-N over-passed the manure-N in agriculture. Interestingly, N-flux of the Changjiang at Datong showed a rapid increase after early 1980s as well, presumably indicating a response to the large scale applications of chemical fertilizers over the watersheds. Straws-back to field as fertilizers (Straws-N) was 30×10^9 mol/yr in 1980 and then increased slowly to 48×10^9 mol/yr in 2014; nitrogen fixation (Fixation-N) changed from 127×10^9 mol/yr in 1980 to 167×10^9 mol/yr in 2014, i.e., increasing by 5%-10% over a period of 35 years. Aquaculture wastewaters-N has increased from 5×10^9 mol/yr in 1980 to 137×10^9 mol/yr in 2014, i.e., by a factor of 26. NO_x emission from combusting fossil fuel (Fossil Fuel-N) has increased from 41×10^9 mol/yr in 1995 to 188×10^9 mol/yr in 2014, i.e., by a factor of 5. Statistics using the least square method reveal that synthetic fertilizer-N, manure-N, straws-N, fixation-N, aquaculture wastewaters-N and fossil fuel-N have an increase with rates of 15.4×10^9 mol/yr, 5.9×10^9 mol/yr, 0.42×10^9 mol/yr, 1.24×10^9 mol/yr, 3.9×10^9 and 8.4×10^9 mol/yr, respectively, indicating that synthetic fertilizer-N has become the most rapidly growing-up anthropogenic source, followed by fossil fuel-N. It should be indicated that the trend of application of synthetic fertilizers shows a phase-off over the Changjiang watersheds in the 21st Century (Fig. SI3-1).

Among the output terms, harvest of crops, production of animal and aquatic cultures have increased by a factor of 1.8, 6.2 and 22, respectively, in the period of 1980-2014. Loss of nitrogen via emission of gases has been quantified, including denitrification and volatilization, which has increased by 3.1 and 2.5 folds, respectively, in the period of 1980-2014. In the meantime, N-retention in the Changjiang watersheds along with biomass accumulation as forest and grassland has increased by a factor of two in 1980-2014. N-retention in the soils has increased from 178×10^9 mol/yr in 1980 to 387×10^9 mol/yr in 2014, i.e., by a factor of 2.2. Being an independent check, Richter and Roelcke (2000) estimated that nitrogen surplus (retention) rate amounts to 12.5×10^3 kg/km²/yr in soils of China. Similarly nitrogen accumulation rate in farm fields of North China was estimated 11.9×10^3 kg/km²/yr by Ju et al. (2006). If we consider the culture area of 444×10^3 km² of the Changjiang watersheds and use the above mentioned accumulation/surplus rate by Richter and Roelcke (2000), values of N-retention of 378×10^9 mol/yr to 397×10^9 mol/yr can be obtained, which is very comparable to the present study.

Phosphorus. Synthetic fertilizer-P increased from 15×10^9 mol/yr in 1980 to 83×10^9 mol/yr in 2014, i.e., a factor of 5.5 (Fig. SI3-2). Manure-P increased from 39×10^9 mol/yr in 1980 to 60×10^9 mol/yr in 2014. Before 1995 application of organic fertilizers (e.g., Manure-P) was higher than synthetic fertilizer-P over the entire watersheds. It is noted that after mid-1990s, concentration of DIP in the Changjiang has been considerably increased, presumably following the changes in application of fertilizers (i.e., synthetic vs manure products) in agriculture. In the meantime, straws-P increased from 1.7×10^9 mol/yr in 1980 to 3.1×10^9 mol/yr in 2014. Aquaculture wastewaters-P has increased from 0.5×10^9 mol/yr in 1980 to 14×10^9 mol/yr in 2014, i.e., by a factor of 26. Again, statistics reveals that trend for synthetic fertilizer-P, manure-P, straws-P and aquaculture wastewaters-P is 2.2×10^9 mol/yr, 0.90×10^9 mol/yr, 0.031×10^9 mol/y and 0.38×10^9 mol/y, respectively, application of synthetic fertilizer-P is a fast growing-up factor. Similar to nitrogen, the amount of synthetic fertilizer-P in agriculture has been reduced in the 21st Century, shown in Figure SI3-2.

Harvest of crops and animal products has increased by 1.7 and 13.8 folds, respectively, in 1980-2014. In 1980-2014, phosphorus retained by biomass accumulation of forest and grassland has increased by a factor of 2. Our results indicate that P-retention in farmland has increased from 37×10^9 mol/yr in 1980 to 110×10^9 mol/yr in 2014, i.e., by a factor of 3. In the literature, the efficiency (i.e., bioavailability) of phosphorus fertilizers to the crop up-take is 10%-25% (Cheng et al., 2010; Wang et al., 2011; An et al., 2013). Again, if we adopt a value of 75% as the fraction of P-fertilizer storage in farmland, a conservative estimate of 101×10^9 mol/yr can be obtained for phosphorus retention in 2003-2014. Recent studies have shown that P-surplus in soils of middle to lower reaches of the Changjiang drainage basin amounts to 6.1×10^3 kg/km²/yr and 7.4×10^3 kg/km²/yr, respectively (Li et al., 2015), whereas in the North China P-surplus in soils is 5.3×10^3 kg/km²/yr (Vitousek et al., 2009). Using above mentioned agricultural area in the Changjiang watersheds and P-surplus in soils from the literature, values of 76×10^9 mol/yr to 106×10^9 mol/yr can be obtained for P-retention in the farmland along with fertilizer applications, which again compares favorably to our calculation.

SI3-4.2 Budgets for the period of 2003-2014

Based on the data compilation from 1980-2014, we made an average for the period of 2003-2014 in order to compare with seawards flux of nutrients at the river mouth of the Changjiang (i.e., Xuliujing).

With regards to nitrogen, the averages for 2003-2014 show synthetic fertilizer-N amount to $(675\pm40)\times10^9$ mol/yr, which can be a factor of 1.2, 1.5, 3.3, 4.3 and 5.1 higher than atmospheric wet and dry depositions-N, organic fertilizer-N, wastewaters-N, fixation-N and fossil fuel-N, respectively. In the period of 2003-2014, total nitrogen input to the Changjiang drainage basin amount to $(2198\pm65)\times10^9$ mol/yr, of which 77% is accounted for by synthetic fertilizer-N, organic fertilizer-N and atmosphere-N; release from the wastewaters, N-fixation, and emission from fossil fuel accounts for 9%, 7% and 6%, respectively. It should be noted, however, that release of N from aquaculture wastewaters can be as high as $(120\pm20)\times10^9$ mol/yr, which is 30%-40% higher than the drainage from industry and domestic centers.

In 2003-2014, the output of nitrogen from the drainage basin of the Changjiang amounts to $(1260\pm43)\times10^9$ mol/yr, which is $(57\pm3)\%$ compared to the total influx. Retention of nitrogen in the Changjiang watersheds amounts to $(753\pm23)\times10^9$ mol/yr, which is $(34\pm1)\%$ compared to the total influx. The sum of output and retention of nitrogen in the Changjiang watersheds amounts to $(2043\pm49)\times10^9$ mol/yr, which is $(8\pm4)\%$ lower than the total influx and presumably because of uncertainties in data compilation and statistics. Among output terms, harvest of crops and product of animals, gas emission and the seaward export flux of the Changjiang accounts for $(26\pm2)\%$, $(25\pm1)\%$ and $(6\pm1)\%$, respectively. Harvest of crops is $(411\pm32)\times10^9$ mol/yr, with dominance of rice in the Changjiang watersheds. Production from cultures of livestock and aquatic species accounts for $(115\pm10)\times10^9$ mol/yr and $(49\pm8)\times10^9$ mol/yr, respectively, with dominance of poultry and fish. The N loss via gas emissions, including denitrification, volatilization and open water N_2O emission (Zhao et al., 2009) accounts for $(11\pm1)\%$, $(14\pm1)\%$, and 0.03%, respectively. If we use the data from Xuliujing, flux of nitrogen from the Changjiang to the East China Sea, including DIN, DON and PN, are $(107\pm19)\times10^9$ mol/yr, $(13\pm8)\times10^9$ mol/yr and $(18\pm18)\times10^9$ mol/yr, respectively. In detail, N-retention in soils, fixed by biomass in forest and grassland in the watersheds as well as trapped in TGR each is $(374\pm12)\times10^9$ mol/yr, $(351\pm5)\times10^9$ mol/yr and $(28\pm18)\times10^9$ mol/yr, respectively. The N storage in the watersheds, including retention in soils and accumulation of forest and grassland biomass and trap in TGR, represents $(34\pm1)\%$ of the total input.

In 2003-2014, total input of phosphorus to the drainage basin of the Changjiang is on average $(155\pm8)\times10^9$ mol/yr, in which contributions from synthetic fertilizer-P amounts to $(73\pm8)\times10^9$ mol/yr and organic fertilizer-P for $(62\pm3)\times10^9$ mol/yr, accounting together for 87%. The wastewaters-P including aquaculture

and domestic wastewaters is $(17\pm2)\times10^9$ mol/yr, and accounts for 11%, making it the third largest sources for P. Different from nitrogen, the P source via atmospheric depositions is statistically ca. 2% of total input. Weathering and erosion over the watersheds can be an important source of phosphorus in the river. According to Taylor and Lennan (1995), the average P/Si ratio for upper continental crust is 2.3×10^{-3} . If we use measured DSi concentration and above mentioned P/Si ratio, DIP release from weathering would be 0.21×10^9 mol/yr in the Changjiang, which accounts to 0.1% of total P influx over the watersheds, but can be 10%-20% of Changjiang seaward flux. This underlines that anthropogenic forcing becomes dominant factor in driving P cycling in the watersheds as well as the seaward flux of river at sub-continental dimension (e.g., 10^6 km²). Waste drainage of phosphorus from industry and domestic centers amount to 5×10^9 mol/yr, and the amount of P released from aquaculture wastewaters is $(12\pm2)\times10^9$ mol/yr, which can be twice higher than from industry and domestic centers.

The sum of output terms of P from drainage basin of the Changjiang amounts to $(31\pm3)\times10^9$ mol/yr for the period of 2003-2014, which is $(20\pm2)\%$ compared to the total influx. The retention of P in the Changjiang watersheds amounts to $(126\pm7)\times10^9$ mol/yr, which is $(82\pm6)\%$ compared to the total influx. The sum of output and retention of P in the Changjiang is $(157\pm8)\times10^9$ mol/yr, which is $(2\pm7)\%$ higher than the influx and presumably because of uncertainties in data compilation and statistics. Among the export terms, harvest and export by river represent $(15\pm1)\%$ and $(5\pm1)\%$, respectively. Harvest of crops, production of livestock and aquaculture represents $(18\pm2)\times10^9$ mol/yr, $(4\pm0.3)\times10^9$ mol/yr and $(1\pm0.2)\times10^9$ mol/yr, respectively, with a sum of $(23\pm2)\times10^9$ mol/yr. River export of phosphorus of the Changjiang, including DIP, DOP and PP, to the East China Sea are $(1.6\pm0.3)\times10^9$ mol/yr, $(1.5\pm1.7)\times10^9$ mol/yr and $(4.5\pm1.4)\times10^9$ mol/yr, respectively, together for an amount of $(7\pm2)\times10^9$ mol/yr.

The retention of P in soils, fixed by biomass of forest and grassland as well as trapped by the TGR are $(101\pm6)\times10^9$ mol/yr, $(20\pm2)\times10^9$ mol/yr and $(4.7\pm3)\times10^9$ mol/yr, and accounts for $(65\pm5)\%$ and $(13\pm1)\%$, $(3\pm2)\%$, respectively. The considerable P trapped in the Three Gorges Dam relative to the seaward flux is because that a huge amount of sediments (ca. 0.16×10^9 tons/yr) as well P carried by total suspended matter is deposited annually in TGR after 2003.

It should be kept in mind that N-retention from other studies in the literature (cf. Richter and Roelcke, 2000;

Ju et al., 2006) compares well with our results at scale of drainage basin of Changjiang, which provides with an independent check. Similarly, previously reported results on P-retention (cf. Vitousek et al., 2009; Li et al., 2015) are also in agreement with our data.

SI3-4.3 Comparison with other studies

Recently, Xing and Zhu (2002), Bao et al. (2006), Yan et al. (2010), Jiang et al. (2012) and Chen et al. (2016) have reported the data of nitrogen budget of the Changjiang drainage basin for 1980, 1990, 1995, and 2006, respectively, in which N input from composite fertilizers was not considered, however. It has been noted that application of composite fertilizer-N increased from 1% in 1980 to 20% in 2014 of total amount of synthesized fertilizers, which should not be ignored in budgetary calculations. Similarly, with respects of N input from atmospheric pathways previous studies considered only DIN in wet depositions (cf. Xing and Zhu, 2002; Bao et al., 2006; Yan et al., 2010); more recently in the work of Jiang et al. (2012) dry deposition was included in N budget, but the deposition flux was not properly constrained because of data gap for aerosols and gas species. Xing and Zhu (2002), Bao et al. (2006), Yan et al. (2010) and Jiang et al. (2012) did not consider the impact of nutrient release from aquaculture, while it is recognized, for example, that nitrogen from aquaculture wastewaters amounts to 120×10^9 mol/yr.

Another challenge comes to our attention when addressing N flux in the Changjiang is that in the literature N transport was estimated based on assuming that 30% of anthropogenic reactive N and/or 60% of human waste N was discharged into the river, which generated an nitrogen flux of 121×10^9 mol/yr to 271×10^9 mol/yr (Xing and Zhu, 2002; Bao et al., 2006; Jiang et al., 2012). While in our measurements at Xuliujing, the DIN transported by river to the East China Sea is ca. 110×10^9 mol/yr, i.e. 10%-60% lower than values reported in the literature. Consequently, modeling approaches have an effect of over-estimate in the studies of the Changjiang seaward flux of nitrogen (cf. Xing and Zhu, 2002; Bao et al., 2006; Jiang et al., 2012), because source vs sink terms are not properly quantified with historical data; there is also a lack of time-series information at the river mouth to validate the model outputs. Further, our measurements at the river mouth (i.e., Nantong and Xuliujing) illustrate that the increasing trend of DIN of the Changjiang has slowed-down (phase-off) in recent years.

There have been only a few previous studies on the P budgets over the whole watersheds of the Changjiang.

Power et al. (2016) considered only input via synthetic fertilizer-P, while other important contributions, such as manure-P etc. was not included, which is another significant source of P shown in this study. In Li et al. (2011), synthetic fertilizer-P and manure-P were considered, but contributions by other pathways, such as atmosphere-P, straws-P and wastewater-P from aquaculture etc., were ignored. Further our study has shown that input of P via composite fertilizers has increased from 4% of total amount of application of synthetic fertilizer in 1980 to 52% in 2014, while in both Li et al. (2011) and Power et al. (2016), composite fertilizer was not incorporated in their budgetary calculations, which resulted in an under-estimate. Hu et al. (2020) have reported net anthropogenic phosphorus inputs in the Changjiang, but composite fertilizer was also not incorporated. The authors found that growth rates of chemical fertilizer applications in Shanghai, Jiangsu and Zhejiang were negative (Hu et al., 2020). However the composite fertilizers has increased 1.9 times (4.5×10^9 to 8.3×10^9 mol) in those areas from year 2000 to 2015, and the phosphorus fertilizers decreased from 6.0×10^9 to 4.9×10^9 mol, thus the increase of synthetic fertilizer-P is still positive. The amount of composite fertilizers-P has exceeded the phosphorus fertilizers-P in these areas, and should not be overlooked in further studies.

With regards to the outputs of P, Power et al. (2016) considered only the export of phosphorus via riverine pathway, while Li et al. (2011) took into account the factor of harvest of crops in the DIP flux of the Changjiang based on model simulation. For instance, riverine TP flux by Power et al. (2016) was $(3.9 \pm 0.6) \times 10^9$ mol/yr, which is ca. 50% lower than our measurements at Xuliujing, i.e. $(7.7 \pm 2.2) \times 10^9$ mol/yr. Based on the model simulation, Li et al. (2011) indicates that DIP flux of the Changjiang is 0.82×10^9 mol/yr, whereas measurements at Xuliujing show the seaward flux of DIP amounts to $(1.6 \pm 0.3) \times 10^9$ mol/yr, that is doubled. Unlike DIN, time-series data demonstrate that DIP shows a continuous and rapid increase at the river mouth area (e.g., Xuliujing).

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Table SI3-1. Information of parameters used in this study for data compilation. Data are from National Statistics Bureau of China: <http://data.stats.gov.cn>.

Category	Periods	Data Sets
Synthetic Fertilizer	1979-2014	1482
Manure	1979-2014	5752
Straw Fertilizer	1979-2014	8252
N Fixation	1979-2014	5396
Aquaculture Wastes	1980-2014	667
Domestic Wastewaters	2004-2014	361
Harvest of Crops	1979-2014	8892
Production of Animals	1979-2014	6010
Storage in Forest and Grass	1980-2014	200

Table SI3-2. Release of manures and N and P concentrations.

Types	Amount of		Proportion of Feces		Proportion of Urine		Volatilization of NH ₃ (%)
	Excrement		Converted into		Converted into		
	(kg/ind./yr)		Nutrients (%)		Nutrients (%)		
	Feces	Urine	Nitrogen	Phosphorus	Nitrogen	Phosphorus	
Human	90	700	1.00	0.22	0.50	0.057	51.3
Cattle	4646	4055	0.38	0.30	0.50	0.02	12.6
Pig	528	696	0.55	0.40	0.17	0.10	27.9
Horse	3457	1781	0.44	0.30	0.69	0.06	2.1
Donkey/Mule	2040	1051	0.49	0.19	0.71	0.01	2.1
Domestic fowl	24	-	0.82	0.38	-	-	52.7
References	Lin et al., 1994; Wang, 2008						Qian and Lu, 1996

Table SI3-3. Concentration of N and P in the crops of cultivation and straw materials.

Crop Type	Straws	Straws Used for	N/P Content in Crop		N/P Content in Straws	
	and Crop Ratio	Fertilizer Application (%)	N (%)	P (%)	N (%)	P (%)
Soybean	1.6	46	2.66±1.04	0.17±0.077	2.1	0.20
Peanut	0.8	46	1.78±0.76	0.21±0.061	1.8	0.20
Corn	2.0	26	1.57±0.81	0.14±0.062	0.92	0.16
Rice	1	30	1.49±1.01	0.23±0.088	0.91	0.13
Rape-seed	2.0	18	3.98±0.14	0.73±0.03	0.67	0.076
Potato	0.5	19	2.89±0.62	0.195±0.027	3.0	0.28
Cotton	1.2	12.5	1.90±0.51	0.147±0.056	1.24	0.15
Wheat	1.2	44	1.87±0.35	0.095±0.056	0.52	0.08
Maize	1.5	24	1.72±0.86	0.121±0.08	0.58	0.15
Millet	1.6	24	1.78±0.67	0.093±0.055	0.52	0.10
Tobacco	1.2	5.1	2.5	0.31	-	0.169
Fruit	-	-	0.05	0.0043	0.87	0.14
Vegetable	-	-	0.18	0.087	-	-
References	Gao et al., 2009	Gao et al., 2009	Huang et al., 1994; Chen, 2002	Jiang, et al., 1995; Chen, 2002	Jiang, et al., 1995; Wang, 2008	Jiang, et al., 1995; Wang, 2008

Table SI3-4. Comparison of N-fixation (Unit: mol N km⁻²) rates reported in the literature.

Type of Vegetation	N-fixation Rate	N-fixation Rate Used in This Study	References
Leguminous Crops	514-1436		Galloway et al., 1995; Smil, 1999
Soybean	107-3214	571	Galloway et al., 1995; Smil, 1999
Peanut	2657-1471	571	Galloway et al., 1995; Smil, 1999
Green Manure	200-2143	1071	Galloway et al., 1995; Smil, 1999
Rice	113-384	214	Watanabe, 1986
Non-legume Crops		107	Zhu, 1997a
Forest	7-1143	114	Cleveland et al., 1999
Grass	0.7-71	19	Cleveland et al., 1999

Table SI3-5. The conversion factors of NO_x from fossil fuels

Fossil Fuels	Conversion Factor (%)
Coal	0.7
Gasoline	1.82
Coke	0.76
Crude Oil	0.02
Kerosene	1.12
Diesel	1.85
References	Wang et al., 1996

Table SI3-6. Contents of N and P in the culture products of animals and aquatic species (e.g., meat, egg and milk) and by-products (e.g., bones, guts and furs).

Type	Meat Ratio (%)	Bone Ratio (%)	By-products Ratio (%)	N and P in		N and P in		N and P in	
				Meat		Bones		By-products	
				N (%)	P (%)	N (%)	P (%)	N (%)	P (%)
Pig	63	10	27	1.52	0.18	6.29	0.33	6.29	0.07
Cattle	40	10	50	2.83	0.17	6.29	4.2	6.29	0.01
Sheep	54	10	31	2.13	0.17	6.29	5.6	6.29	0.15
Domestic Fowl	75	15	10	2.70	0.16	9.28	2	9.28	0.01
Egg	-	-	-	0.50	0.09	-	-	-	-
Milk	-	-	-	1.52	0.18	-	-	-	-
Fish	52.5	-	47.5	2.9	0.23	-	-	4.6	0.16
Crustaceans	75	-	35	2.7	0.22	-	-	4.1	0.46
Shellfish	-	-	-	1.6	0.18	-	-	-	-
References	Huo, 2002; Wang, 2008; Yang et al., 2009; Ni et al., 2010; Liu and Chen, 2011								

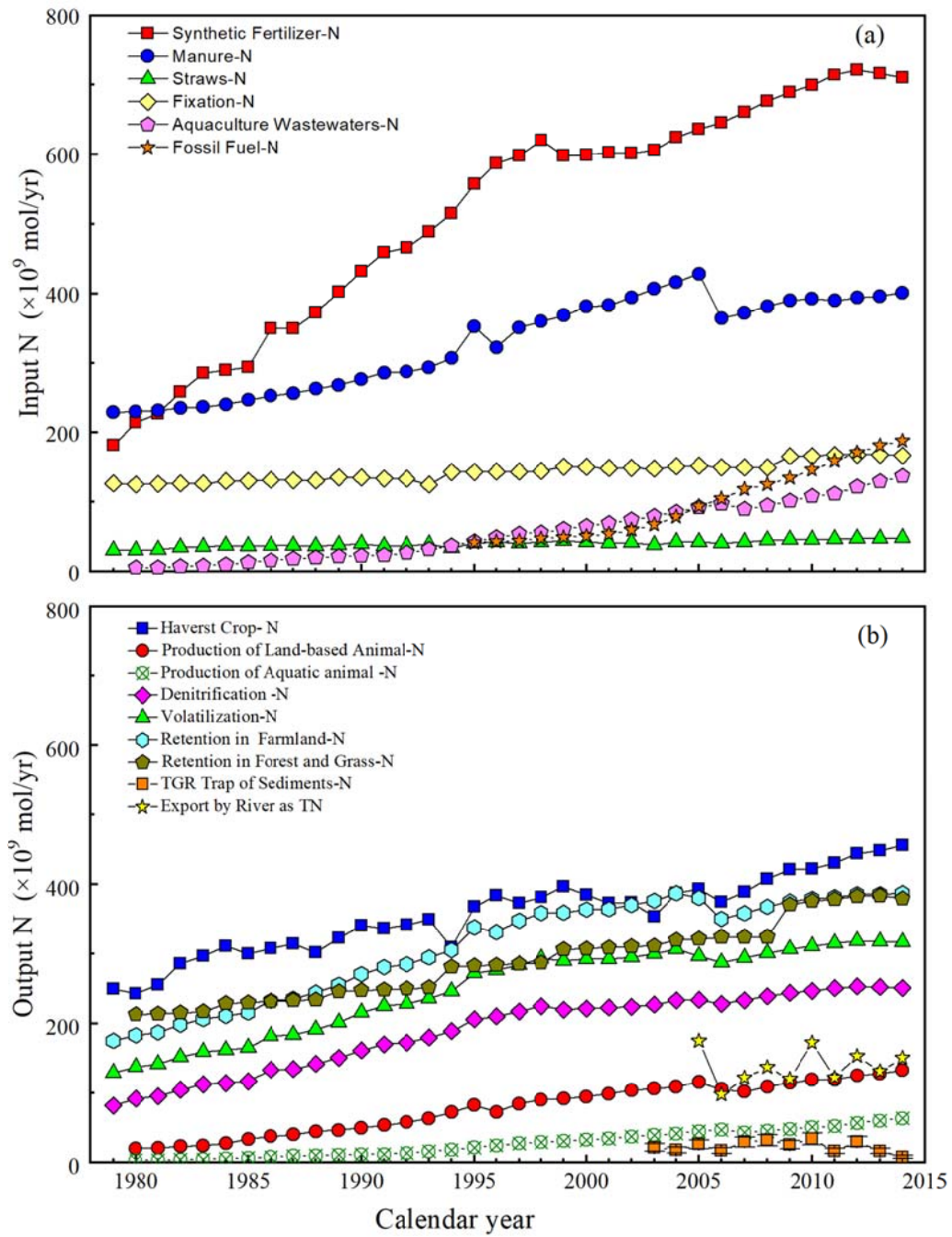


Figure SI3-1. Temporal trends of inputs (a) and outputs (b) for nitrogen from different sources vs sinks and retention/storage in the Changjiang watersheds.

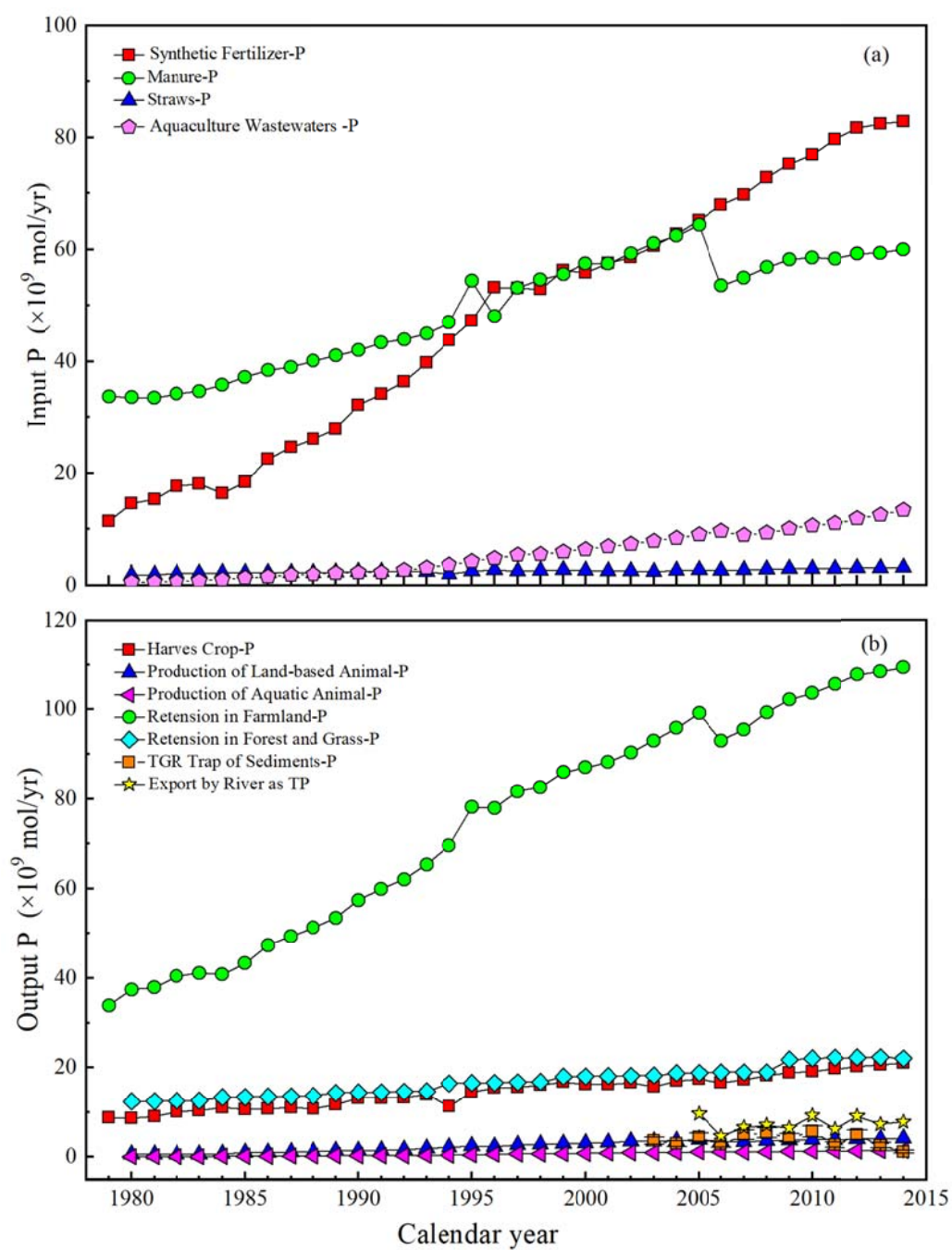


Figure SI3-2. Temporal trends of inputs (a) and outputs (b) for phosphorus from different sources vs sinks and retention/storage in the Changjiang watersheds.