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Title:

Long-term accumulation and transport of anthropogenic phosphorus in three river basins

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Abstract:

Global food production depends on phosphorus (P) and in agricultural and urban landscapes much P is anthropogenically cycled through trade. Here we present a long-term, large-scale analysis of the dynamics of P entering and leaving soils and aquatic systems via a combination of trade, fluvial transport and waste transport. We report net annual P inputs, and the P mass accumulated over several decades, for three large river basins. Our analyses reveal historical P accumulation for two mixed agricultural-urban landscapes (Thames Basin, UK; Yangtze Basin, China), and one rural agricultural landscape (Maumee Basin, USA). We also show that human modes of P transport involving trade and waste massively dominate over fluvial transport in these large basins, and we illustrate linkages between fluvial P dynamics and infrastructure such as wastewater treatment and dams. For Thames and Maumee Basins, recently there was modest P depletion/drawdown of the P pool accumulated in prior decades, whereas Yangtze Basin has consistently accumulated P since 1980. These first estimates of the magnitude of long-term, large-scale P accumulation in contrasting settings illustrate the scope of management challenges surrounding the storage, fate, exploitation and reactivation of legacy P that is currently present in the Earth's critical zone.

Phosphorus (P) is a key requirement for food production and over the past 75 years, agricultural demand has increased the rate of global P mobilization four-fold [1-3]. Inefficiencies and large losses of P occur at many points in food production, and the great majority of P fertilizer originates in mines [4, 5], raising concerns about long-term supplies of affordable fertilizer [6, 7]. Fluvial transport of P from agricultural land, and release of P-rich animal and human wastes into the environment, have degraded lakes, rivers, reservoirs, and coastal waters with excess P, causing costly damages [8, 9]. These widespread inefficiencies in human P use have been characterized as a wholesale disruption of the global P cycle [6] that for ages has supported biological productivity through efficient recycling of P.

Phosphorus inputs to agriculture initially increase soil fertility and crop yields, but continued P application in excess of plant uptake increases the risk of P loss from land to water bodies. Following storage in soils and aquatic sediments, the associated time lags for P mobilization and transport can last years to decades [10-12]. This relates to the notion that streams have a chemical memory of the past [13, 14] that delay recovery from water quality impairment. There have been few long-term studies of the landscape-level storage, transport, and fate of P accumulated in human-dominated basins (but see [8, 12, 15-17]), although there has been much research on P in large basins over shorter time frames [18]. Similarly, there have been few direct comparisons of fluvial vs. human modes of P transport at broad scales (but see [19]). Rather, much research on P has involved studies of relatively short-term processes at the plot scale or within individual ecosystems. This reflects the long-standing problem that changes in landscape-level P storage and legacy P are very difficult to measure directly. To address these needs, we synthesized diverse agronomic, urban, and river data sets, and examined the long-term dynamics of P accumulation in three large river basins using a difference approach. In advance of our calculations for long-term P accumulation, we also examined the dynamics of component P flows involving trade, fluvial transport, and waste transport (food waste disposal, sewer infrastructure) which have not been frequently juxtaposed over the long-term at large scales.

Our synthesis of long-term P fluxes involves: cropland-dominated Maumee River basin, USA, tributary to Lake Erie, southernmost of the Laurentian Great Lakes; mixed agricultural-urban Thames River basin, UK, which drains parts of the London metropolitan area *en route* to the North Sea; Yangtze River basin, the largest in China, which has undergone rapid population growth and economic development. To conceptualize these broad-scale P dynamics, Haygarth et al. [21] recently hypothesized that human-dominated catchments consist of an accumulation phase, when P gradually builds up, and a depletion phase (Fig. S1, Supplementary Information), when P inputs decline and mobilization of accumulated "legacy" P becomes an increasingly important consideration. Here, we test this accumulation-depletion hypothesis, posing three questions: 1) Which P fluxes drive the long-term dynamics in human-dominated river basins? 2) How do gross P inputs and outputs, and net P inputs, change over the long-term? 3) How can understanding of long-term accumulation inform management of P trajectories, regionally, nationally, and internationally? The Maumee, Thames, and Yangtze Basins differ substantially in terms of socio-economic history and physiographic features but are linked by common interests of water security, food security, and resource management that transcend geopolitical hierarchies and provide lessons about P.

Biogeochemical studies of watersheds and landscapes commonly focus on fluvial fluxes but, in the Anthropocene, the P cycle has become increasingly dominated by human fluxes via trade of fertilizer and food as well as management of food waste and sewage. Our analysis provides new evidence that, indeed, human P fluxes massively dominate over the fluvial fluxes, even for large basins. In the agricultural Maumee Basin, both annual fertilizer P import and food/feed P export exceeded fluvial P export by 5- to 20-fold (Fig. 1), depending on the year. In the Thames Basin, between World War II (1940) and 1980, fertilizer P import averaged >15-fold higher than river P export; food/feed P export from farms >7-fold higher; food waste P to landfills >4-fold higher; and P input from sewage treatment works >2-fold higher. Likewise, even during the era of highest sewage P effluent and highest river P export in Thames Basin

(1970-1990), mean fertilizer P import, food/feed P export from farms, total sewage production, and food waste P to landfills were 11, 8.0, 4.0, and 3.3 kilotons (kt) per year, respectively, compared to only 1.9 kt yr^{-1} for river P export. These results for Maumee and Thames Basins suggest the changes in global fluxes of P since pre-industrial times may rival or exceed the changes in the global fluxes of N and C that have been reported [1, 21]. These major human alterations to the global P cycle are compatible with previous findings for heavier elements [22], whose pre-industrial cycles in the biosphere were controlled mainly by rock weathering but now are being mobilized more rapidly from the crust via mining.

In the Yangtze River, dissolved P export increased by 10-fold between 1970 and 2010 but our calculations indicate a 44% decline in river total P export between 1970 and 2010 ($p<0.001$, Fig. S5). This reflects a long-term decline in particulate P export that is likely linked to lower suspended sediment following the construction of large dams [23], possibly combined with improvements in sewage treatment. Nonetheless, like the Maumee and Thames, total P transport in the Yangtze River was dwarfed by annual fertilizer P application, which increased by more than 10-fold over this period of record. We suggest the dominance of human P fluxes over fluvial fluxes extends to many other agricultural and urban basins of the world.

The highly agricultural Maumee Basin is the primary source of P to Lake Erie, where the return of major algae blooms in summer 2014 resulted in the shutdown of the drinking water supply to Toledo, Ohio [24]. Prior to 1990, and as previously shown [25], gross P input greatly exceeded gross output (Fig. 2), consistent with expectations for P accumulation (Fig. S1). Since the late 1990s, gross P input and output have converged towards a common value between 15 and 20 kt yr^{-1}. Our analyses reveal that inter-annual variations in gross P input and output in the 1990s and 2000s had only a minor influence on the >200 kt pool of P that accumulated mostly during the 1970s and 1980s (Fig. 3). While annual P output has exceeded input for certain years (1997-1998, 2006, 2009), our calculations up to 2010 indicate there has not yet been meaningful P depletion.

Unlike Maumee Basin, the Thames Basin includes a substantial human population including parts of London. Nevertheless, akin to the Maumee, gross P input to the Thames Basin greatly exceeded output until the 1990s, demonstrating a prolonged phase of P accumulation. Since the late 1990s, gross annual P outputs from the Thames Basin have slightly exceeded the inputs. During the 2000s, Thames River P export declined by 86 % (p=0.001) in association with a reduced flux from sewage treatment to river, reflecting higher sewage treatment efficiency motivated partly by the European Union's Urban Waste Water Directive. Over the same recent period, fertilizer P import declined by 26% ($p<0.001$), while food/feed P export increased by 22% (p=0.044). Thus the Thames Basin shifted to modest depletion around 1998, following a long-term decline in fertilizer P import that began around 1960 (Fig. 1 and 3).

In contrast to the slowing rates of P accumulation in Maumee and Thames Basins, the available P data for Yangtze reveal a consistent phase of rapid P accumulation, especially since 1980. We were unable to determine Yangtze Basin sewage inputs ($P_{sewage,in}$) or exports of food and feed ($P_{food/feed,out}$) needed in Eq. 5 (Supplementary Information), so we did not estimate gross P input and output for this basin. Nevertheless, we provide estimates of net P input based on the assumption of $P_{sewage,in} = P_{food/feed,out}$. Our calculations reveal that Yangtze Basin, one of Earth's largest, was accumulating legacy P at a remarkable rate of 1.7 Tg yr^{-1} (1700 kt yr^{-1}) in 2010 (Fig. 3). On an areal basis, Yangtze Basin net annual P input of 940 kg km^{-2} yr^{-1} in 2010 approaches the maximum historical rate of P accumulation in Maumee Basin (1300 kg km^{-2} yr^{-1} in 1981) and exceeds the maximum historical rate of Thames Basin (820 kg km^{-2} yr^{-1} in 1950). This annual rate of accumulation is also equivalent to about 8% of the global rate of P production from phosphate rock, or 43% of the national rate of P production by China [2], suggesting that Yangtze Basin alone accounts for 17% of the annual P increment of 10 Tg yr^{-1} that has been reported for erodible soils globally [8, 12]. Like the Maumee and Thames basins, much accumulated P in the Yangtze Basin occurs in arable upland soils [26] and eventually could be delivered to water bodies, adding to the more immediate effects of population change, dam construction, and sewage treatment on dissolved or particulate P transport by rivers globally [27]. Research is still needed to understand how interactions between land use change and climate variability affect the mobilization of legacy P from soils as well as from river channels, reservoirs, floodplains, wetlands, and natural lakes occurring within hydrologic networks.

Here we have demonstrated that large-scale assessments of landscape P storage and dynamics may be achieved by difference, as previously shown in global analyses of P [8, 12]. This approach provides a means for estimating the mass of legacy anthropogenic P that is currently present in the Earth's critical zone, and may inform efforts to exploit it [4]. Contributing challenges to the direct measurement of change in P storage are that soil P is notoriously heterogeneous in space and with soil depth, while historical soil sampling efforts have rarely targeted the entire landscape P pool. Thus, while P flux data are often lacking during early stages of P accumulation, even in intensively monitored basins such as Maumee, there are pathways for long-term analysis through linkages between the P cycle and documented human activities.

Concerns about excess P, its mobilization, and the lack of robust P recycling pathways [5, 6] are growing worldwide. These kinds of long-term portraits of P storage, mobilization, and transfers are needed to help understand the true causes and consequences of P transport. We suggest an important role for new technologies and land practices that specifically target legacy

P in terms of storage, fate, exploitation/recovery, and reactivation to more plant-available forms [16] . While our analysis has focused on a few major P-consuming nations [5], the need for robust P recycling pathways extends to developing nations, especially those where mineral P is scarce [28]. In regions of intense P surplus [29], managed drawdown of excess soil P represents an increasingly viable option. As demonstrated by the return of algae blooms to Lake Erie [24, 30], P dynamics are complex, requiring vigilance to incorporate both new and historical information into adaptive management. Improved understanding of long-term time lags for transport [10] , and more timely updates to spatially- and temporally-explicit data sets on traded goods and wastes containing P, may help identify strategies that sustain food production while protecting water quality.

Methods

We used both published and new data on major P fluxes across the boundaries of the landscape P pool (soils+aquatic systems), as well as within-basin P transfers. Methods for the net annual P input calculations were informed by known properties of each basin, including physiographic setting, human population, and size (Table S1). A summary of the sources of P flux data and calculations is provided in Table S2. The time series for each P flux, and net annual P inputs, are provided in Table S3 (Maumee), Table S4 (Thames), and Table S5 (Yangtze), and we used discrete time in annual intervals. Three linked reasons for our focus on Maumee, Thames, and Yangtze Basins are: 1) each basin has major human influences that may relate to the long-term P dynamics; 2) there have been major management, monitoring, and research efforts in these basins for several decades, leading to the P data sets that provide a unique opportunity to reconstruct the long-term net P inputs to soils and aquatic systems; 3); the basins differ substantially in terms of socio-economic history and physiographic features but are linked by common interests of water security, food security, and resource management.

We define the basin-level net annual P input (P_{net}, mass per year) as

$$P_{net} = P_{in} - P_{out} \quad (1)$$

where P_{in} is gross annual input and P_{out} is gross annual output to/from the landscape P pool. In our conceptualization, human systems such as markets, waste treatment facilities, and landfills are not components of the landscape P pool, but still may greatly influence it through exchange. Note that the calculations of P_{net}, P_{in}, and P_{out} were not merely the summation of the simple component fluxes plotted in Fig. 1, which includes internal transfers within the basin. Rather, the net/gross calculations required more thorough book-keeping of new/exogenous P inputs and permanent outputs across the basin boundaries, not double-counting of the same P mass moved internally. Gross inputs from equation 1 may be broken down further as

$$P_{in} = P_{fert,in} + P_{sewage,in} + P_{precip} \quad (2)$$

where P_{precip} is atmospheric P input from precipitation, $P_{fert,in}$ is gross mineral fertilizer P import via trade, and $P_{sewage,in}$ is the subset of sewage P production that originates from imported products (food + household cleaners) and enters the environment either as effluent from sewage treatment or as biosolids/sludge waste applied to soils. The new landscape P input represented by $P_{sewage,in}$ is not to be confused with total sewage P production plotted in Fig 1. Rather, total sewage P production contains internally produced food P already accounted as fertilizer input. P_{precip} in agricultural basins is often small relative to fertilizer use, as evidenced by Maumee River Basin, where P_{precip} was reported to be 0.2 kt per yr [25], or <1% of mean fertilizer P import over our period of record. Equation 2 simplifies to

$$P_{in} = P_{fert,in} + P_{sewage,in} \quad (3)$$

under the assumption of P_{precip}=0. The outputs may be broken down further as

$$P_{out} = P_{food/feed,out} + P_{river} \tag{4}$$

$P_{food/feed,out}$ is gross P export via food/feed trade and waste transport to landfills, and P_{river} is P exported via fluvial transport. Note that un-mined rock-P is not a part of the landscape pool in our conceptualization, so there is no need to include an export term for fertilizer P. Substituting equations 3 and 4 into equation 1 gives

$$P_{net} = P_{fert,in} + P_{sewage,in} - P_{food/feed,out} - P_{river} \tag{5}$$

and we used equation 5 as the central basis for constructing time series of net annual P input. Accumulated P stores were quantified by taking the cumulative sum of the P_{net} (t) time series, across years.

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Author Contributions

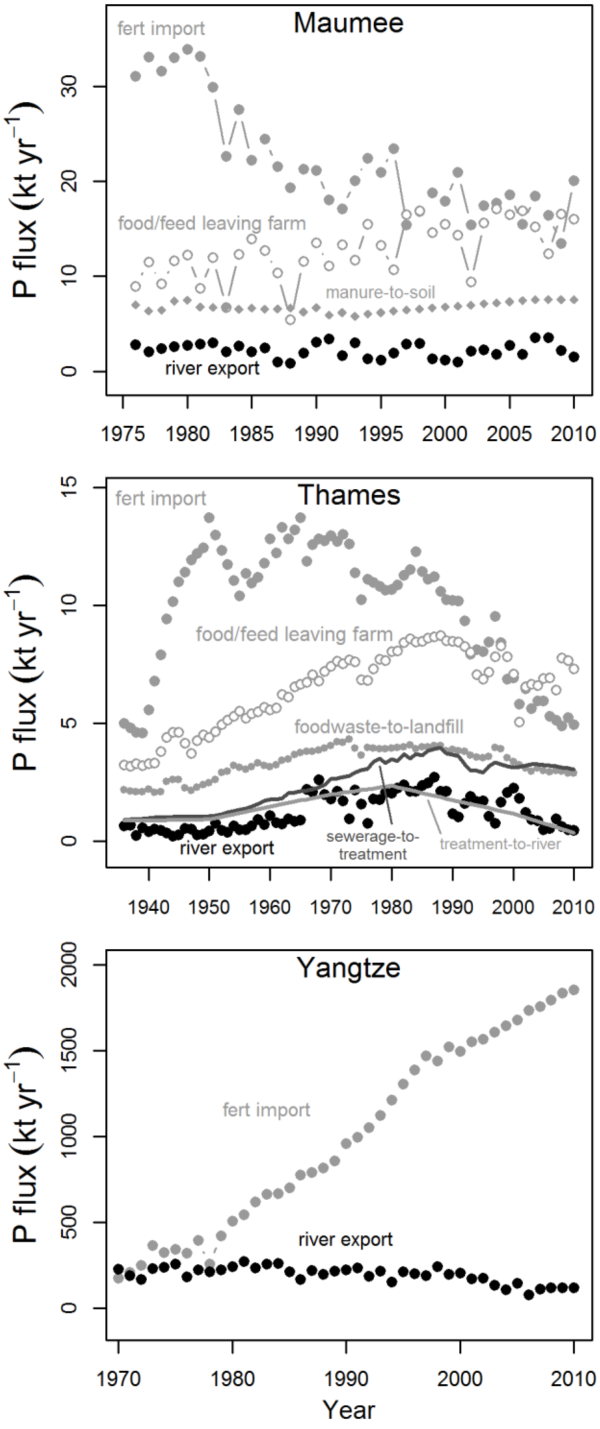
S.M.P. led the writing of the paper, compiled the data, and analyzed the data. Key P data sets were contributed by H.P.J., N.J.K.H., F.W., T.W.B., and J.S. All authors participated in the interpretation of results and the writing and editing process.

Figure legends

Figure 1. Component P fluxes used in calculating the net annual P inputs for the three river basins (Maumee R. USA, Thames R. UK, Yangtze R. China).

Figure 2. Gross P inputs and outputs to/from the landscape P pool (soils + aquatic systems) of Maumee and Thames Basins. Gross P input includes fertilizer import, and for Thames only, detergent import. Gross P output includes river export, food/feed exported from the basin via trade, and for Thames only, disposal of foodwaste to landfill and disposal of sewage biosolids to landfill, sea, or incinerator.

Figure 3. Net annual P input and accumulation curves for landscape P pools (soils+aquatic systems) of three river basins (Maumee R. USA, Thames R. UK, Yangtze R. China). Accumulated P is the cumulative sum of net annual P input over time.



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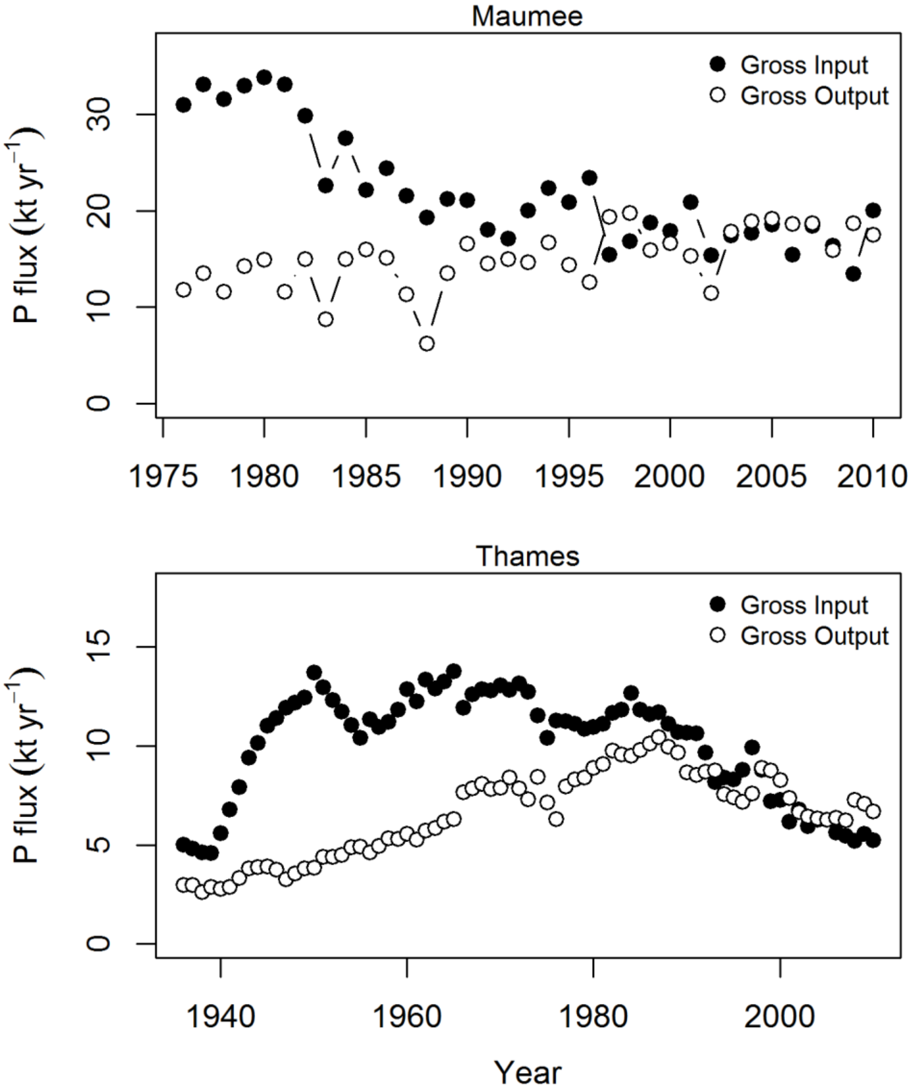

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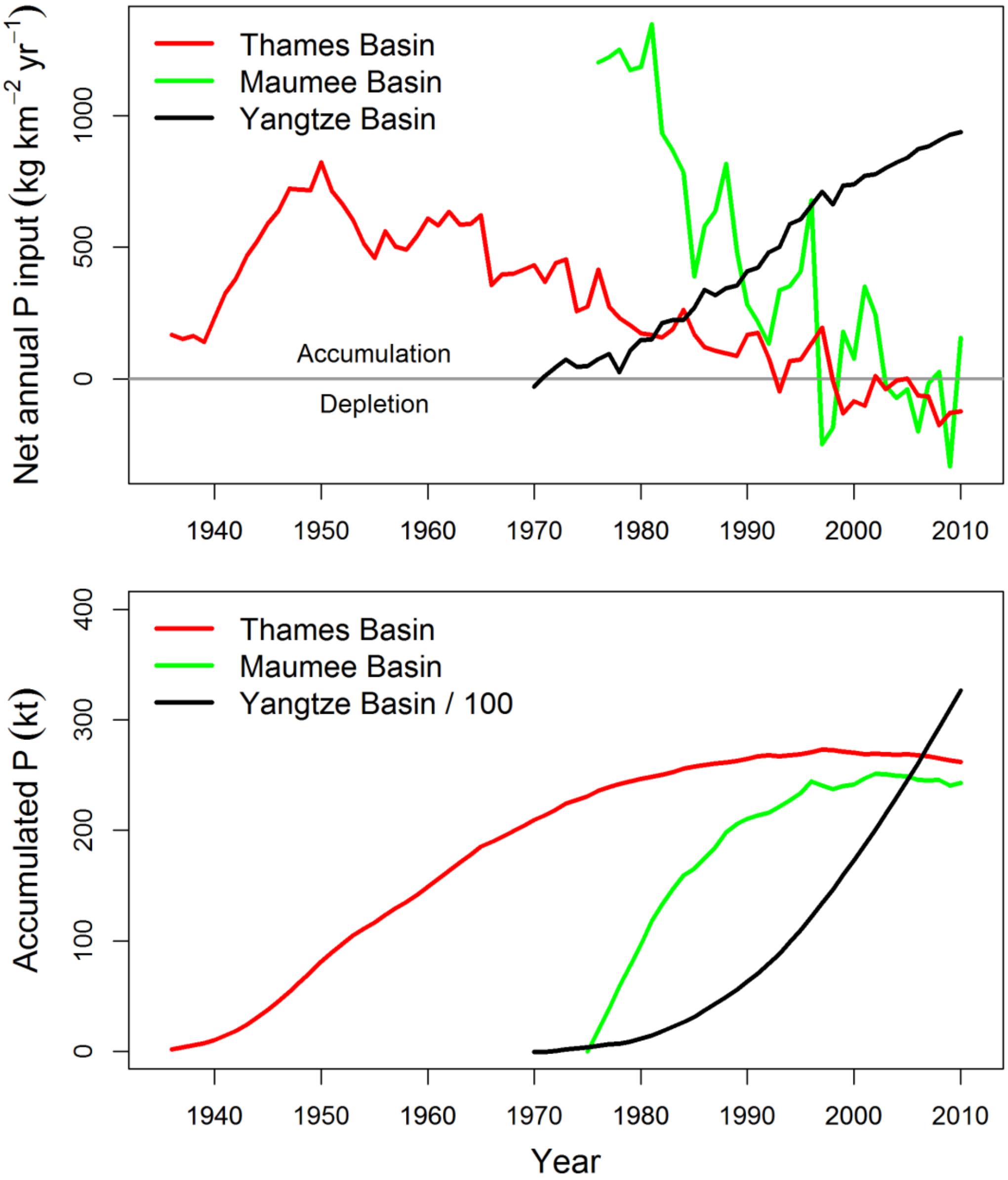

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