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Title:

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

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Global food production depends on phosphorus. Phosphorus is broadly applied as fertilizer but excess phosphorus contributes to eutrophication of surface water bodies and coastal ecosystems[1]. Here we present an analysis of phosphorus fluxes in three large river basins using published data on fertilizer, harvested crops, sewage, food waste and river fluxes[2,3,4]. Our analyses reveal that the magnitude of phosphorus accumulation has varied greatly over the past 30-70 years in mixed agricultural-urban landscapes of the Thames Basin, UK, Yangtze Basin, China, and the rural Maumee Basin, USA. Fluxes of phosphorus in fertilizer, crop harvest, food waste, and sewage dominate over the river fluxes. Since the late 1990s, net exports from the Thames and Maumee Basins have exceeded inputs, suggesting net mobilization of the phosphorus pool accumulated in prior decades. In contrast, the Yangtze Basin has consistently accumulated phosphorus since 1980. Infrastructure modifications such as sewage treatment and dams may explain more recent declines in total phosphorus fluxes from the Thames and Yangtze Rivers[3,4]. We conclude that human-dominated river basins may undergo a prolonged but finite accumulation phase when phosphorus inputs exceed agricultural demand, and this accumulated phosphorus may continue to mobilize long after inputs decline.

Over the past 75 years, agricultural demand has increased the rate of global P mobilization four-fold[5,6,7]. Inefficiencies and large P losses occur at many points in food production, and the majority of P fertilizer originates in mines[8,9], raising concerns about long-term supplies of affordable fertilizer[10,11]. Fluvial P transport 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[1,12]. These widespread inefficiencies in human P use have been characterized as a wholesale disruption of the global P cycle [10] that for ages has supported biological productivity through efficient P recycling.

P 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[13-15]. This relates to the notion that streams and rivers have a chemical memory of the past[16,17], and legacies that delay recovery from water quality impairment. To date there have been few long-term studies of the landscape-level storage, transport, and fate of P accumulated in human-dominated basins (but see [12, 15,18-20]), although there has been much research on P in large basins over shorter time frames [21]. Similarly, there have been few direct comparisons of fluvial versus human modes of P transport at broad scales (but see [22]). Rather, much P research has involved studies of relatively short-term processes at the plot scale or within individual ecosystems, reflecting the long-standing problem that changes in landscape-level P storage and legacy P are 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 examined the dynamics of component P flows involving trade, fluvial transport, and waste transport (food waste disposal, sewage 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 broadscale P dynamics, Haygarth et al.[4] recently proposed 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 P becomes an increasingly important consideration. Here we test this accumulation-depletion framework, 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 fertilizer and food trade as well as food waste and sewage management. 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, 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 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 to 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

P fluxes since pre-industrial times may rival or exceed the changes in the global N and C fluxes that have been reported[5,23]. These major human alterations to the global P cycle are compatible with previous findings for heavier elements[24], whose pre-industrial cycles were controlled mainly by rock weathering, but are now mobilized from the crust through 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[3], possibly combined with improvements in sewage treatment. Nonetheless, like Maumee and Thames, total P transport in 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 P source to Lake Erie, where major algae blooms returned in summer 2014, causing the shutdown of drinking water supplies to Toledo, Ohio[25]. Prior to 1990, and as previously shown[2], gross P input 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 interannual variations in gross P input and output in the 1990s and 2000s had only 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 has a substantial urban population including parts of Greater London. Nevertheless, akin to Maumee, gross P input to Thames Basin greatly exceeded output until the 1990s, demonstrating a prolonged phase of P accumulation. Since the late 1990s, gross annual P outputs from 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 26% ($p<0.001$) while food/feed P export increased 22% ($p=0.044$). Thus, our calculations indicate 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[6], 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[12,15]. Like Maumee and Thames Basins, much accumulated P in 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 demonstrated that large-scale assessments of landscape P storage and dynamics may be achieved by difference, as previously shown in global analyses of P[12,15]. This approach provides a means for estimating the mass of legacy anthropogenic P currently present in the Earth's critical zone, and may inform efforts to exploit it[8]. 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 rarely encompass 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[9,10] are growing worldwide. These kinds of long-term portraits of P storage, mobilization, and legacies 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[19]. While our analysis has focused on a few major P-consuming nations[9], 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[25,30], 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[13], 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 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 examine 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

$$P_{net} = P_{in} - P_{out} \tag{1}$$

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 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

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

where P_{precip} is atmospheric P input from precipitation, $P_{fert,in}$ is gross mineral fertilizer P import, 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 [2], or <1% of mean fertilizer P import over our period of record. Equation 2 simplifies to

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

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

$$P_{out} = P_{food/feed,out} + P_{river} \qquad (4)$$

$P_{food/feed,out}$ 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

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

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

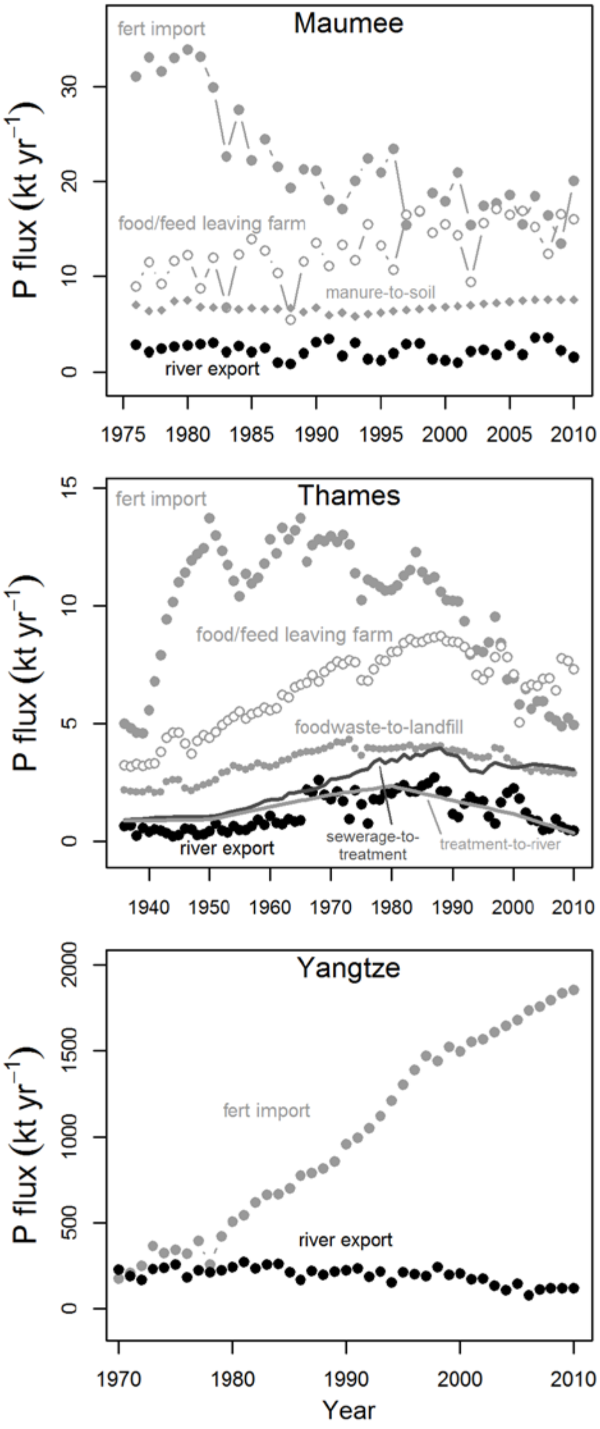
S.M.P. led the writing of the paper, compiled the data, and analyzed the data. Key P data sets were contributed by H.P.J., N.J.K.H., F.W., T.W.B., and J.S. All authors participated in the interpretation of results and the writing and editing process.

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 food waste 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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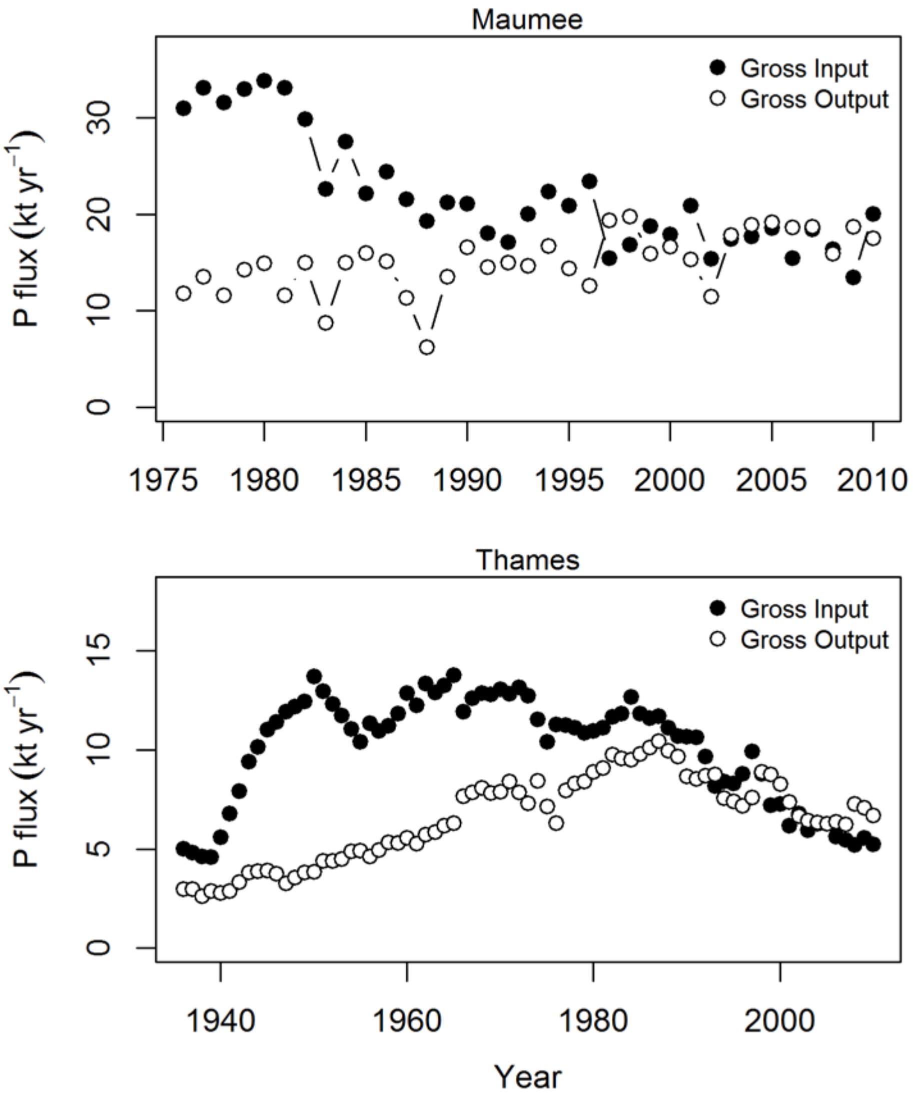

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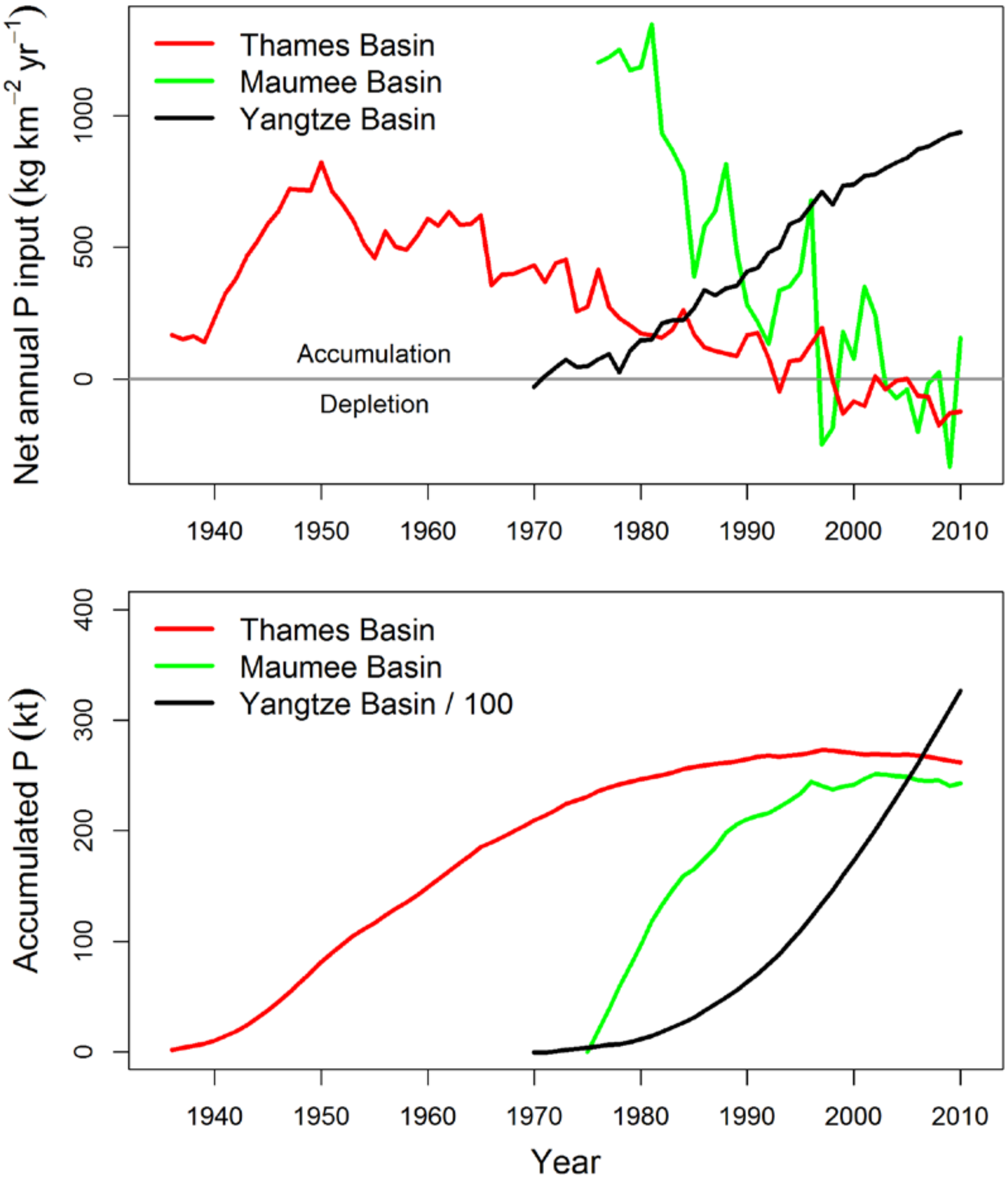

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