Modeling biogeochemical processes of phosphorus for global food supply

Marion Dumas [a,*], Emmanuel Frossard [b], Roland W. Scholz [a]

[a] Institute for Environmental Decisions (IED), Natural and Social Science Interface, ETH Zurich, Universitätsstrasse 22, 8092 Zurich, Switzerland
[b] Institute of Plant, Animal and Agroecosystem Sciences, ETH Zurich, Eschikon 33, CH-8315 Lindau, Switzerland

ARTICLE INFO

ABSTRACT

Harvests of crops, their trade and consumption, soil erosion, fertilization and recycling of organic waste generate fluxes of phosphorus in and out of the soil that continuously change the worldwide spatial distribution of total phosphorus in arable soils. Furthermore, due to variability in the properties of the virgin soils and the different histories of agricultural practices, on a planetary scale, the distribution of total soil phosphorus is very heterogeneous. There are two key relationships that determine how this distribution and its change over time affect crop yields. One is the relationship between total soil phosphorus and bio-available soil phosphorus and the second is the relationship between bioavailable soil phosphorus and yields. Both of these depend on environmental variables such as soil properties and climate. We propose a model in which these relationships are described probabilistically and integrated with the dynamic feedbacks of P cycling in the human ecosystem. The model we propose is a first step towards evaluating the large-scale effects of different nutrient management scenarios. One application of particular interest is to evaluate the vulnerability of different regions to an increased scarcity in P mineral fertilizers. Another is to evaluate different regions' deficiency in total soil phosphorus compared with the level at which they could sustain their maximum potential yield without external mineral inputs of phosphorus but solely by recycling organic matter to close the nutrient cycle.

1. Introduction

Despite its vital importance to all life forms and the global scale of its flows, no biogeochemical cycle model exists for phosphorus (P) to quantify the temporal and spatial patterns of its distribution on Earth. Yet, due to the small size of the known P-bearing rock deposits (Jasinski, 2009), concerns are rising about future provision of mineral P fertilizer to agro-ecosystems. At the same time as these concerns are voiced, tens of millions of tons of P harmfully make their way to aquatic systems annually (Liu et al., 2004). While in most ecosystems, P cycles several hundred times from the soil to the biomass to the zoomass back to the soil before finding its way to the aquatic systems (Smil, 2000), most human-managed systems are much less efficient as P cycles rarely more than once. P is a constitutive element of basic cellular processes and structures and as such is a non-substitutable ingredient to plant growth. Finally, P is distributed via global markets, traded in the form of food and mineral, the latter being supplied only by a handful of countries which hold more than ninety percent of the known world terrestrial P-bearing rock reserves (Cordell et al., 2009). In a precautionary perspective, we should investigate the vulnerabilities for global food production that are associated with the usage patterns sketched above. We should also examine the impact on food production, cost and pollution of different scenarios of P supply – from the current extractive model to a potential closed cycle. To achieve this, we need a quantitative understanding of P stores and flows and their dynamics on a global scale.

As a first step towards quantifying the P cycle, the objective of this paper is to present a model of P flows through arable soils and the resulting effect on crop yields. This model is based on substance-flow analyses proposed by other authors (e.g. Liu et al., 2004) but it is dynamic. We seek to develop a simple probabilistic formulation that can be applied at different scales. We argue for a simple solution to the scaling of the complex dynamics of P cycling in soils, usually handled by deterministic models that cannot easily be scaled because of the site-specific parameterization needed to implement them (e.g. Jones et al., 1984). One application of our model will be to simulate the evolution of food production when suppressing the inflow of mineral P fertilizer, as a way to evaluate our level of dependence on P-bearing rocks. The model will have wider applications: for example, to quantify the amount of P fertilizer necessary to transition to a long-term steady-state closed-loop cycle. This paper may contribute to methodologies for integrating LCA and biogeochemistry for the successful management of biogeochemical-cycles.

* Corresponding author. Address: 535 W 113th Street #73, New York, NY 10025, USA. Tel.: +1 212 537 6673.
E-mail address: mmd2172@columbia.edu (M. Dumas).

2. Modeling the *P* cycle

2.1. Formalizing how *P* cycles through the "human ecosystem"

Evaluating the impact on crop yields is one way to translate different states of the *P* cycle in terms of units that matter to society. Correspondingly, we built a simple model of *P* cycling whose output variable is total food production (Fig. 1). The boundaries drawn in Fig. 1 represent a particular agricultural region, typically composed of both cropland and grassland. Although Fig. 1 represents a large number of pathways, the dynamics can be summarized as follows:

$$\frac{dy}{dt} = \frac{dy}{dP_a}\frac{dP_a}{dP_T}\frac{dP_T}{dt} \tag{1}$$

where *y* is the yearly yield per hectare, P_T is the total concentration of all *P* compounds in the soil and P_a (plant-available *P*) is the concentration of *P* that is loosely bound to the soil and can enter the soil solution to be taken up by roots.

In Eq. (1), dP_T/dt represents the balance of *P* flows in and out of the soil. It is composed of: (1) x_{er}, the out-flux from the land to the river network, principally due to soil erosion but influenced by human activities; (2) out-fluxes of *P* contained in harvested crops $(x_{y_c}), (x_{y_f})$ and grass (x_{y_g}); 3) in-flux of *P* from the application of *P* fertilizers (null if we consider a scenario of shortage) and the application of manure (x_{ma}), crop residues (x_{re}), and human waste (x_{hw}). Clearly, these flows, associated with our management of the cycle, affect P_T, the total stock of *P* in soils. Crop yields, on the other hand, are affected by P_a, the fraction of soil *P* that is bioavailable. Indeed, the term dy/dP_a can be modeled by what agronomists call the yield response function of a crop, which indicates as a function of P_a how

much a plant can achieve of its maximum potential yield. Hence, to understand how the large-scale fluxes of *P* through society and across the landscape affect food production, one needs to understand the relationship between P_a and P_T.

In the next two sections of this paper, we present our main contribution to the quantitative understanding of the cycle depicted in Fig. 1, that is, to propose a way to model the term dP_a/dP_T such that it can be integrated with the balance of flows dP_T/dt and the crop responses dy/dP_a.

2.2. Probabilistic modeling of the bioavailability of *P* in the landscape

From the soluble or loosely bound state (P_a), *P* is taken up by the biomass but also reacts reversibly with a wide range of minerals. As a result, *P* is present in soils in myriads of chemical compounds, which can broadly be categorized in three classes: organic compounds, mineral precipitates and surface complexes with metal oxides and clays (Frossard et al., 2000).

The relative importance of the three main classes of compounds (precipitates, metal oxides and organics) varies with some degree of predictability with the types and properties of soils (Sharpley and Cole, 1987). This observation explains the following key patterns (examples can be found in Syers et al., 2008). First, some soils in the northern latitudes that have been fertilized for long periods of time can be left unfertilized for decades without showing any change in the levels of P_a: the *P* supplied as fertilizer has been stored in stable forms and is being re-supplied over time to the plants in the absence of new fertilizer inputs (for e.g., Otabbong et al., 1997). Second, and in contrast, on highly weathered soils in the tropics, yields may decline very rapidly if fresh *P* in the form of mineral fertilizer is not applied on a regular basis (for e.g., Beck
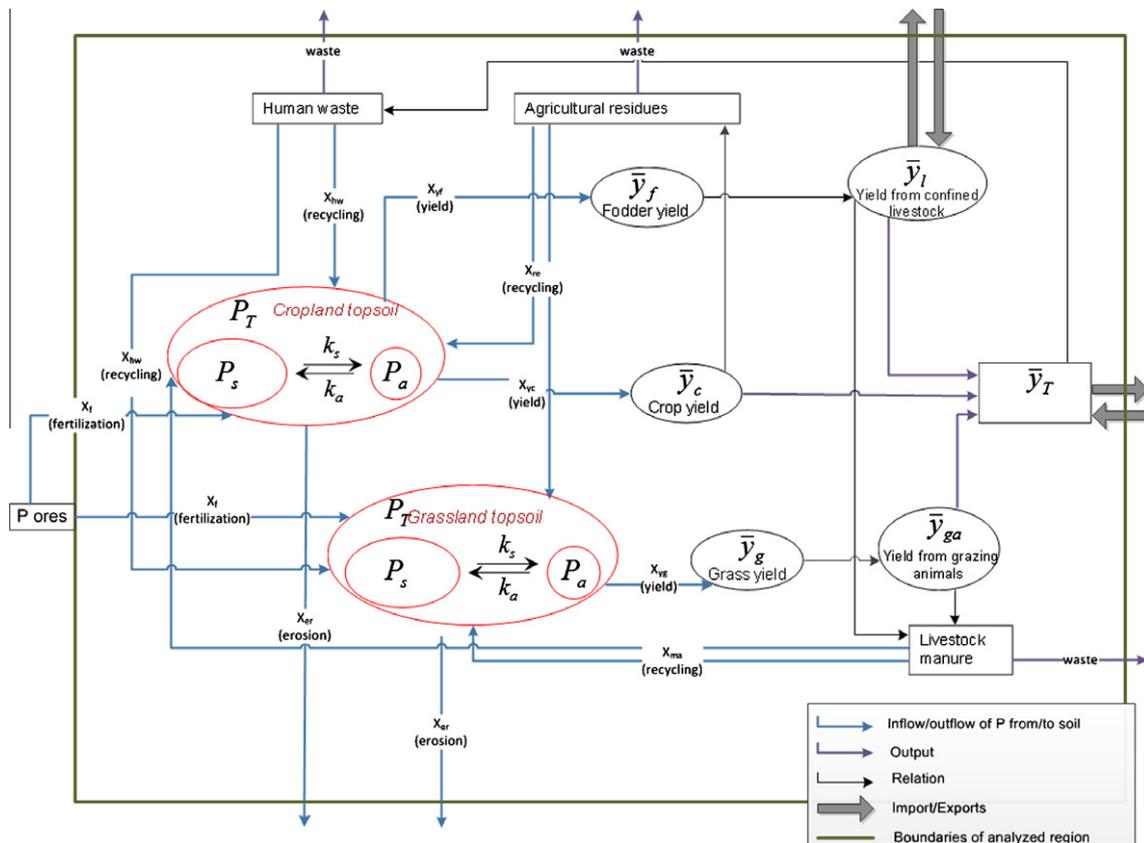
Fig. 1. Phosphorus cycling through the human ecosystem. A region composed of grassland and cropland. Food production consists of crops, confined livestock fed by fodder and grazing animals fed by grass. $\bar{y}_\bullet$ signifies the total yield of crops, animals etc. and $x_\bullet$ stand for the different fluxes (e.g. x_{hw} for Human waste) in or out of the pool of P_T. The terms P_s, P_a, k_s and k_a are elucidated in the article.

and Sanchez, 1996). In these soils, the predominant reaction is adsorption of P to metal oxides forming very stable bonds. As a result of the high activation energy needed for desorption, the P_a pool is only very slowly replenished. These examples illustrate why the soil P cycle and the relationship between P_a and P_T are so important: they modulate the impact of P fluxes on biological productivity.

With few exceptions (Rothman and Forney, 2007), chemical transformations of elements such as P in soils or water are typically modeled deterministically by arbitrarily breaking the continuum of chemical forms into discrete compartments, usually connected by first-order reactions, the coefficients of which require site-specific parameterization (e.g. the P-module of EPIC by Jones et al. (1984), or of DSSAT by Daroub et al., 2003). Such models are ill suited for large-scale modeling, as they would require long time series, which are unavailable, and highly uncertain extrapolations of the fitted parameters.

Instead of a discrete compartmentalization, the non-bioavailable compounds can be thought of as a single pool of P bonded reversibly by a continuum of bond strengths (Frossard et al., 2000). We call it the slow-release pool P_s (such that $P_s = P_T - P_a$) and model it as reacting with the P_a pool through a reversible first-order reaction whose rate coefficients, k_a and k_s, change as a function of the chemical composition of P_s. This change is due to the fact that P_s and P_a are in fact composed of a continuum of species, with transfers between these two pools happening through a continuum of first-order reactions. k_s is the effective observed rate coefficient of transfer from P_s to P_a and is thus an integral over the continuum of underlying rate coefficients of the species in P_s. As a result, the rate coefficient of the largest dynamic class of compounds in P_s must dominate the value of k_s. As these compounds react and disappear from P_s, k_s changes. At any point in time, if there is equilibrium, it can be described by the equilibrium constant $K_s = \frac{P_a}{P_s} = \frac{k_s}{k_a}$. With this physical model in mind, we turn to long-term experiments (LTEs) and remark that, indeed, P pools isolated by sequential fractionations are typically in a quasi-equilibrium (Supplementary material Fig. 1). Model simulations and field experiments where P_a is frequently measured corroborate this quasi-equilibrium. Both show that perturbations in P_a, due to input or harvest, decay rapidly and that P_a re-equilibrates with P_s within a year (e.g. Ayodele and Agboola,1982; Daroub et al., 2003, Supplementary material Figs. 2 and 3). This fact implies that on a yearly time scale, P_a and P_s can be thought of as two pools in dynamic equilibrium.

Based on the discussion above, we postulate the existence of a non-linear function that can describe the relationship between P_a and P_T. In this relationship, P_a can be any routine extractions of soil P (such as Olsen or Bray). As this relationship is only expected to hold in a statistical sense, on large scales, we express it as a conditional distribution function of P_a with respect to P_T, $f(P_a|P_T)$ with $E(P_{\alpha|P_T}) = g(P_T)$ and call $g(P_T)$ the bioavailability function. We think of the bioavailability function as representing the pseudo-equilibrium K_s. Over the range of P_T, the underlying distribution of chemical species in P_s changes and thus so must k_s, which explains why the bioavailability function is non-linear. Indeed, in a scenario of P depletion, as the more reactive pool is used up to replenish P_a, a more stable pool must eventually dominate the equilibrium, thus causing k_s to decrease.

2.2.1. Hypothesized bioavailability function

Sharpley and Cole (1987), motivated by similar issues of P behavior in soils, proposed a classification of soils in three classes: calcareous soils (CS), slightly weathered soils (SWS) and highly weathered soils (HWS). Each one of these classes displays typical properties that influence which reactions should predominate. In addition, Walker and Syers (1976) proposed a theory predicting which chemical form of P should predominate in a soil according to its pedogenetic development stage. With the help of these broad classifications, we found some strikingly regular patterns amongst the dozens of LTEs tended around the world. These patterns lead us to hypothesize specific functional forms for the bioavailability function of each of the three soil classes, which are illustrated and explained in Fig. 2. Mathematically, they can be expressed for example by the generalized logistic function, with a different set of parameters for each class of soil:

$$g(P_T) = \frac{h}{1 + Q\exp(r(P_T - M)^{1/\alpha})} \qquad (2)$$

where h is the asymptote, r is akin to a growth rate, M is the point of fastest increase, Q normalizes the lower bound and v governs the skew of the curve. It has been argued that concentration of minerals and contaminants in soil should follow a log-normal distribution (Limpert et al., 2001). Assuming a marginal log-normal holds for both P_a and P_T, the bioavailability function gives us the following joint probability distribution for P_a^t and P_T^t, indexed by time in anticipation of the dynamic model:

$$f(P_a^t|P_T^t) = \frac{1}{P_a^t \sigma_a \sqrt{2\pi}} \exp\left(-\frac{\left(In(P_a^t - \mu_a)^2\right)}{2\sigma_a^2}\right)$$

where

$$\mu_a = \ln\left(g(P_T^t)\right) \qquad (3)$$

$$f(P_a^t, P_T^t) = \frac{1}{P_a^t \sigma_a \sqrt{2\pi}} \exp\left(-\frac{\left(\ln(P_a^t - \mu_a)^2\right)}{2\sigma_a^2}\right) \times \frac{1}{P_T^t \sigma_T \sqrt{2\pi}}$$
$$\times \exp\left(-\frac{(\ln\left(P_T^t\right) - \mu_T)^2}{2\sigma_T^2}\right) \qquad (4)$$

2.2.2. Empirical evidence for the bioavailability function

Testing the hypothesis of the bioavailability function requires a large and homogeneous data set spanning major soil types and land uses, containing simultaneous measures of P_a and P_T, plus a set of soil properties to classify soils appropriately. In waiting for the availability of such a data set, we tested the plausibility of the hypothesis using a small data set of native soils from around the world whose soils were already categorized in the three weathering classes "CS", "SWS" and "HWS" (data and classification from Sharpley and Cole, 1987). We furthermore compiled data from LTEs to see whether the evolution of P_a and P_T over time at a given site follows the hypothesized pattern. Fig. 3a,b and c constitute a phase space diagram in $P_a \times P_T$ space for each of the three types of soil classes, in which the survey data of uncultivated soils from Sharpley and Cole (1987) and time series from some of the LTEs are plotted.

Far from representing a proper test of the validity of our statistical model, Fig. 3a–c demonstrate its plausibility. The time series fall within the same statistical ensemble as the survey data, which form a curvilinear pattern. As hypothesized, the HWS show limited availability with build-up at high levels of P_T and the CS seem to exhibit a plateau. A proper implementation of the model requires a much more extensive data set and non-parametric analyses to identify the exact dependence structure between P_a and P_T, and the proper classification scheme for a robust categorization of soils according to their P behavior. Indeed, we do not expect the hypothesis drawn in Fig. 2 to hold exactly; rather we expect that we can find a classification of soils for which there exists a well-defined non-linear function $f(P_a|P_T)$ describing P's behavior. Assembling

Hypothesized bioavailability curves

Parameter values for CS, SWS and HWS:
-h=(100,150,200)
-r=(0,005,0.0027,0.0008)
-M=(45,150,200)
-nu=(0.25,0.10,0.15)

Fig. 2. Sketch of the hypothesized bioavailability functions for the three soil classes. Common patterns of *P* behavior in the three classes of soils are summarized to explain the hypothesized bioavailability function. The hypothesis concerns the overall shape and relative position of the functions, not the exact values.

Calcareous soils (CS)

P undergoes both adsorption to the surface of non-carbonate clays and precipitation with carbonate, the latter predominating at high P concentrations. These reactions are easily reversible, so moderate additions of P can quickly build-up the Pa pool, which must reach a plateau due to precipitation with carbonates. Thus we can postulate a sigmoid showing adsorption to clays at low levels of PT, quick build-up of Pa subsequently and an asymptote corresponding to saturation of the soil solution and precipitation.

Highly Weathered Soils (HWS)

These soils are often old soils with low pH and high clay and metal oxide content, much of the P is found in occluded pools and on very stable metal oxide bonding sites. Beyond a certain level of PT, these sites become saturated, P adsorbs on weaker bonding sites and Pa can build-up. When present, organic matter can improve the bioavailaility of P. With such a behavior, we can hypothesize an increasing exponential curve with a long lower tail showing the strong adsorption to weathered minerals.

Slightly Weathered Soils (SWS)

These soils display a behavior that is intermediate between CS and HWS: like CS, they have high replenishment power because they are too young to have large proportions of occluded P of pedogenetic origin and the adsorption sites are of lower energy than in HWS. Unlike CS, Pa does not seem to be as clearly controlled by precipitation reactions at higher concentrations. And like HWS, bioavailability of P is improved by organic matter. Therefore, the bioavailability function is expected to be a sigmoid with a higher plateau than CS and an accelerating growing limb with larger slope than HWS.

the data set that is needed to characterize these probabilistic functions is currently work in progress.

2.3. Integrating soil cycling, crop response and the large-scale fluxes

In this section, we show how the bioavailability function is integrated to the mass balance fluxes in Fig. 1 and Eq. (1). Since several processes are non-linear functions of P_a or P_T, we cannot rely on averages and instead must integrate Eq. (1) over the full scale of variability of the system (environmental heterogeneity) and of our knowledge of the environment (uncertainty). Hence, throughout, we are interested in describing the probability distributions of our model's variables over time, denoted by $f(\bullet)$. For sake of simplicity, consider a catchment with homogeneous arable soil with, at time $t = 0$, initial soil P content $f(P_a^0, P_T^0)$ and whose land-use consists of cropland, feedlots and a few human settlements. We assume further that its river network is monitored for nutrient and sediment load so that we can infer $f(x_{er}^t|(P_a^t, P_T^t))$, the probability distribution of P losses to the aquatic systems over the catchment area, conditional on $f(P_a^t, P_T^t)$. Then, in a scenario of no mineral P

fertilization, we model the changes in soil P and crop yields in discrete time steps of a year:

$$f(P_T^t) = f\left(P_T^{t-1} + \frac{1}{\rho D}(-x_y^{t-1} - x_{er}^{t-1} + x_{ma}^{t-1} + x_{hw}^{t-1})\right) \quad (5)$$

$$f(P_a^t) = \int f(P_a^t|P_T^t)f(P_T^t)dP_T^t \quad (6)$$

$$f(y^t) = \int f(y^t|P_a^t)f(P_a^t)dP_a^t \quad (7)$$

where y is the yield of a given crop, ρ and D are soil density and soil rooting depth, needed for conversion from mass (kg ha^{-1} yr^{-1}) to P concentrations. x_y^t is the P exported from the soil, per hectare, by the plant yields and is equal to $c_P y^t$, the product of the yield with the crop's concentration in P (c_P)[1]. As a reminder, x_{er}, x_{ma}, x_{re} and x_{hw} are, respectively, P losses to aquatic systems, P application rates of manure, plant residues and human waste in kgP ha^{-1} yr^{-1}. Since each variable is random, Eqs. (5)–(7) are implemented by a Monte Carlo simulation.
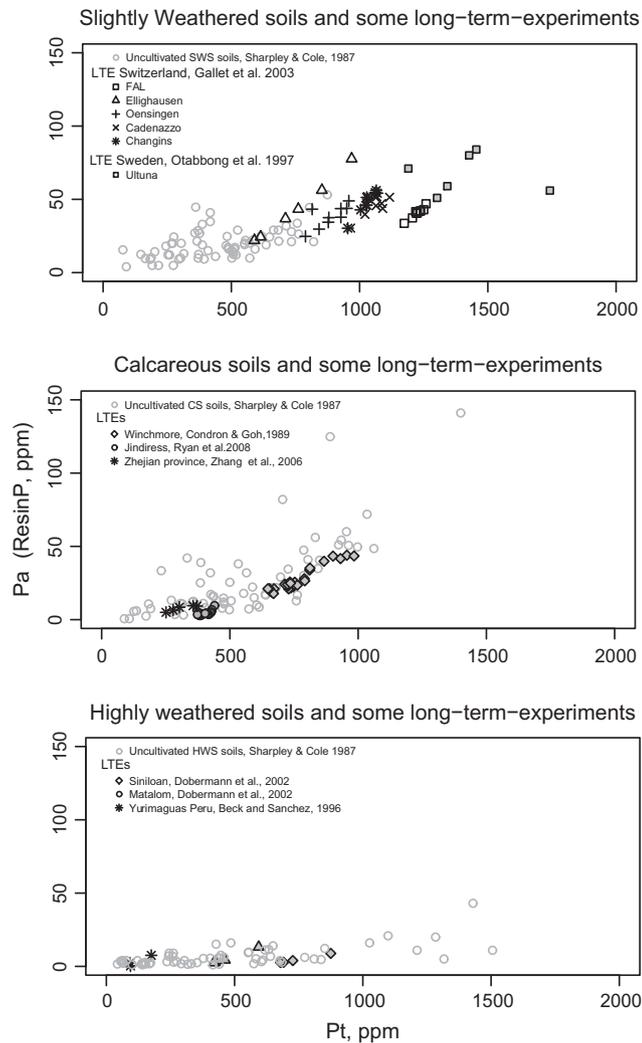
Fig. 3. Plots of (P_a, P_T) for the three soil classes. In grey are the data points from Sharpley's data set of uncultivated soils. Over these are plotted time series of LTEs. Together, they draw a statistical envelope in which the system evolves. (see above-mentioned references for further information.)

Eq. (7) is the yield response of the crop to a given level of P_a. The yield response can be expressed as follows (Johnston, 2005):

$$f(y^t|P_a^t) = f(y_{max})y_r^t(P_a^t) \tag{8}$$

$$y_r^t(P_a^t) = 1 - ae^{b \times P_a^t} \tag{9}$$

where y^r is the yield achieved by a plant at a given level of P_a relative to its potential yield y_{max}. The relative yield is expressed as an increasing exponential function of P_a that reaches 1 once P_a is no longer a limiting factor. The coefficients a and b are crop and soil specific, while the potential yield y_{max} reflects the aggregate effect of other limiting factors, primarily soil fertility and climate, whose variability within an area is captured by the distribution $f(y_{max})$.

To close the mass balance, we must constrain the feedback flows. First, we require that $A_{ma} \int x_{ma} f(x_{ma}) dx_{ma} = k_{ma}(f_{1_p} \bar{y}_l)$, where A_{ma} is the area of manured land, k_{ma} is the recycling rate of manure, f_{l_p} is the P waste flow generated for each head of livestock per year, the total livestock being denoted by $\bar{y}_l$. This means that the total manure applied in the area must be equal to the recycling rate of manure times the total volume of manure produced by the live-stock. Similarly we require that $A_{hw} \int x_{hw} f(x_{hw}) dx_{hw} = k_{hw}(f_{hw_P} Y)$, where A_{hw} is the area over which human wastes are applied, k_{hw}

is the recycling rate of human waste, f_{hw_p} is the P waste flow generated by each person per year and Y is the population. Furthermore, the number of grazing animals $\bar{y}_{ga}$ and of livestock $\bar{y}_l$ should depend on the amount of grass $\bar{y}_{ga}$ and of fodder $\bar{y}_f$. Similarly, the flux of P in the waste stream from the human population must be related to the P contained in the total food supply. Locally, these feedbacks are non-binding because changes in production can be compensated by exports and imports, but globally, these feedbacks must be included.

Eqs. (5)–(7) give a flexible framework to represent the way soil chemistry mediates the response of the biomass to P fluxes at various scale and the resulting mass balance feedbacks. Its probabilistic formulation can accommodate heterogeneity and uncertainty associated with different levels of spatial aggregation. For example, even if the spatial resolution of the model is coarse, the fact that in some areas people apply manure at high and localized concentrations can be represented by a skewed or heavy-tailed distribution of manure application rates. In such a scenario, P losses to aquatic systems are much greater than if the manure was spread evenly over the whole area, as would be implied by use of averages.

In the next section we outline applications of the model and their associated challenges.

3. Discussion: From simple toy-model applications to information-rich simulations

The first application of Eqs. (5)–(7) is as a toy model: after making meaningful simplifying assumptions, it can help us answer important questions. Indeed, in the absence of appropriate data on recycling, runoff and erosion fluxes we can meaningfully re-place the true values by hypothetical values reflecting management scenarios.[1] With these scenario assumptions, if we simply knew the spatial distribution of $f(P_a, P_T)$ with some degree of spatial resolution, we could answer the following questions: (1) In the ab-sence of P fertilizers, given the distribution $f(P_a, P_T)$ in a region, what is the time until crop productivity diminishes by half, assum-ing other factors stay constant? (2) How much P would need to be added to bring arable soils everywhere to a stable productive le-vel? How does this amount compare with current economically exploitable reserves of P-bearing rocks? By stable productive level, we mean a level where P_a does not need to be artificially increased above its equilibrium level $f(P_a|P_T)$ by sudden inputs of highly-sol-uble inorganic P fertilizer, but can instead be maintained at the le-vel $f(P_a|P_T)$ by inputs of recycled organic matter? (3) How does the spatial distribution of soil P match with the future expected distri-bution of other critical factors of crop production?

As an example of this toy model's behavior, Fig 4 shows how yields and soil P content change over time in the absence of fertil-ization for six hypothetical regions whose soil types and distribu-tion of initial P_T and erosion rates differ. The graphical trends alone can answer question (1) above. Moreover, the distributions $f(P_a, P_T)$ can tell us by how much the P_T content of soils should be enriched for these soils to obtain an expected P_a value compatible with maximum potential yield, thus answering question (2). Figs. 4 and 5 in the supplementary material show some of these distribu-tions and how they inform question 2).

The second application is to build realistic simulations of the P cycle on large scales. The model can accommodate increasing com-plexity, such as a distinction between grassland and cropland and

---

[1] Indeed, even the natural fluxes (erosion and runoff) are in large part determined by human management. Montgomery (2007) illustrated this point in a compelling way by compiling rates of soil loss from a variety of land uses around the world. This data set suggests that conventional agriculture generates rates of soil loss that are two orders of magnitude larger than either conservation agriculture or background geologic erosion rates.
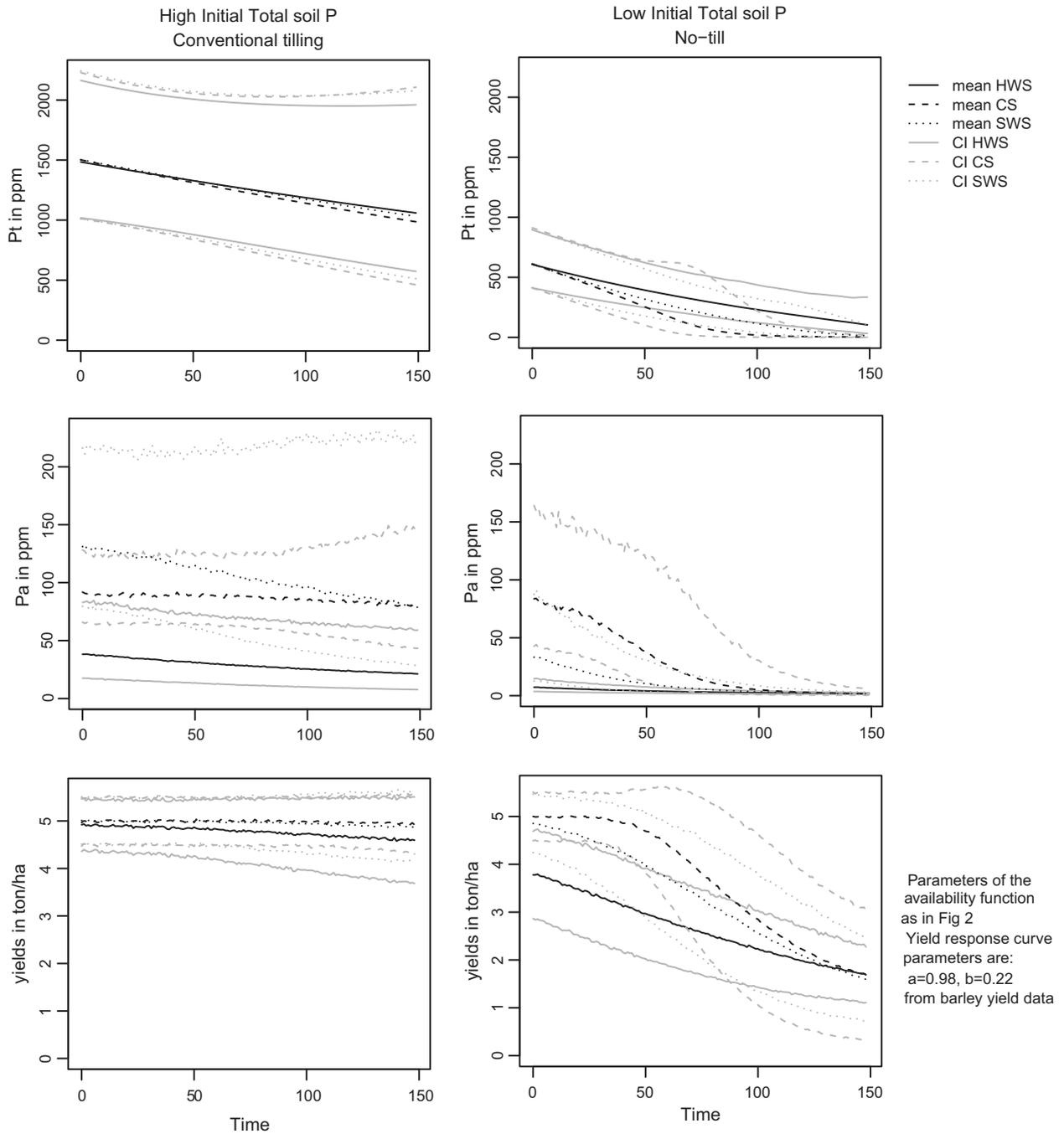
Fig. 4. Evolution in time of the distributions of P_T, P_a and y for the three soils classes. Scenario 1: high initial P_T and high erosion rates. Scenario 2: low initial P_T and low erosion rates (erosion rates sampled from data set in Montgomery, 2007). The underlying joint probability distributions are in Supplementary Material Figs. 4 and 5 and can help answer question 2).

the representation of heterogeneous soil types and multiple crops, either by doing an area-weighted combination of the distributions in Eqs. (5)–(7), or by increasing the spatial resolution to obtain more homogeneous units. This full implementation of the model will require a quantity of detailed information: in addition to data on soil P content, it needs information on fertilization and livestock farming practices, agronomic experiments from which yield response curves can be estimated for each major crop and the distribution of cropland and grassland. It is also necessary to quantify $f(x_{er}|P_a, P_T)$, a delicate task because of its sensitivity to spatial scaling. A full implementation of the model (i.e. with a realistic representation of all fluxes) would have value at large scales such as that of a basin, from headwaters to ocean, or on the global scale.

Indeed, the full implementation prompts us to include import and export fluxes of P through food and fodder between regions and to represent the variation of $f(x_{er}|P_a, P_T)$ with different farming practices (till vs. no-till, extensive vs. intensive manuring). Including these additional fluxes would reveal the extent to which some regions subsidize other regions in P and evaluate quantitatively the contribution of different farming systems to its waste. *In fine*, such a model would give a good estimate of the resulting vulnerability and contribution of different regions to the issue of P availability for food production. It would also allow us to model the macro-scale impacts of changing farm practices.

At such scales, lack of data will not be the only challenge in obtaining a realistic simulation. There are also conceptual difficul-

ties in deciding how to discretize space because defining spatial units requires that we can model the interaction between them. The two main interactions are the transport of *P* in the landscape due to surface and subsurface hydrology and the transport of *P* due to the spatial allocation of food, feed and waste. Correctly representing the latter is critical for the *P* cycle. For example, consider the export in the USA of thousands of tons of maize from the monocultures of the Great Plains to the feedlots of Oklahoma or Texas. The resulting flow of manure is not sent back to the cropland but instead is in part drained by the river network, contributing to the poisoning of the Gulf of Mexico and to dispersion of *P* (Alexander et al., 2008). This pattern is recurrent (e.g. China and the Ganges Basin, Gerber et al., 2005). To correctly represent these transfers, it is important to identify regions that span farming systems that are similar in terms of their *P* management and use these units as a minimal spatial resolution. Yet, depending on the available data, the hydrological transport of *P*, described by $f(x_{er}|P_a, P_T)$, may best be quantified taking the catchment as a spatial unit[2], which creates a spatial misalignment of the input data. These issues will best be resolved on a case-by-case basis depending on the availability of data and the organization of the landscape. For example, in the case of the Mississippi basin, the Sparrow model provides a spatially explicit distribution of *P* losses per hectare and per year throughout the basin that is consistent with the measured river loads (Alexander et al., 2008) and this could simply be fed into our *P* cycle model. Because of the model's flexibility, it allows different approaches to solving these problems, with varying degrees of spatial resolution.

4. Conclusion

The model presented in this paper suggests how to integrate natural processes with human-managed flows to investigate the long-term consequences, in terms of food production, of various scenarios of *P* management. Furthermore, it proposes a solution to the challenge of capturing the large-scale effect of multiple micro-scale soil cycling processes. However, this model is only a first step towards being able to assess the sustainability of the *P* cycle. Indeed, implementation of the model at meaningful scales is made very challenging by the current scarcity of data needed to quantify the different fluxes and pools. In particular, the model highlights the role of the soil as an active store that must be understood on a macro-scale. In a world with no net inputs of *P* (arising because affordable *P*-bearing rock deposits are exhausted or because organic agriculture has become the norm), soil *P* constitutes the nutrient reserve for agriculture, constraining the time before exhaustion in an open-loop *P* cycle (no recycling), as well as setting an upper-limit to the fluxes and to food production in a closed-loop *P* cycle (with complete recycling). Yet, there exists few soil surveys with measures of P_T so we can do little more than guess the total size of this pool, especially for specific agricultural regions (see global estimate in Smil (2000)). Second, there has not been any careful tracking of recycling fluxes. Cordell et al. (2009) provided rough estimations on a global scale, which suggest that we recycle about 30% of *P* taken up by crops. Yet, we would be much better equipped

with a systematic survey of farming and urban waste treatment practices. Finally, we also lack good records of nutrient loads in rivers, needed to quantify total losses of *P* to the oceans.

From a societal point of view, *P* may not yet be on the political radar, but this means that, unlike in the case of C or water, we have time to understand and maneuver the cycle before the scarcities and imbalances outlined in the Introduction become critical. In particular, this modeling exercise suggests to us that in assessing the sustainability of the *P* cycle we should focus on the adequacy and maintenance of reserves of *P* in arable soils rather than on the conservation of *P*-bearing rocks. Indeed, *P* in soils is more useful than *P* in rocks if we know how to minimize losses to the environment. Perhaps we can think of the recent history of fertilization as a transition from a recycling system with small throughput (state of vulnerability and ecological stress, but where the *P* cycle was in some places successfully closed, as reported for example in King, 1911) to a recycling system with large throughput after the enrichment of sufficient areas of arable soil by mineral fertilizers.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.02.039.

References

Alexander, R.B., Smith, R.A., Schwarz, G.E., Boyer, E.W., Nolan, J.V., Brakebill, J.W., 2008. Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. Environ. Sci. Technol. 42, 822–830.

Ayodele, O., Agboola, A., 1982. An attempt to evaluate phosphorus fertilizer requirements of western Nigeria savanna soils. Fert. Res. 3, 293–302.

Beck, M.A., Sanchez, P.A., 1996. Soil phosphorus movement and budget after 13 years of fertilized cultivation in the Amazon basin. Plant Soil 184, 23–31.

Condron, L.M., Goh, K.H., 1989. Effects of long-term phosphatic fertilizer applications on amounts and forms of phosphorus in soils and irrigated pastures in New Zealand. J. Soil Sci. 40, 383–395.

Cordell, D., Drangert, J., White, S., 2009. The story of phosphorus: global food security and food for thought. Global Environ Change 19, 292–305.

Daroub, S., Gerakis, A., Ritchie, J., Friesen, D., Ryan, J., 2003. Development of a soil-plant phosphorus simulation model for calcareous and weathered tropical soils. Agric. Syst. 76, 1157–1181.

Dobermann, A., George, T., Thevs, N., 2002. Phosphorus fertilizer effects on soil phosphorus pools in acid upland soils. Soil Sci. Soc. Am. J. 66, 652–660.

Frossard, E., Condron, L.M., Oberson, A., Sinaj, S., Fardeau, J.C., 2000. Processes governing phosphorus availability in temperate soils. J. Environ. Qual. 29, 15–23.

Gerber, P., Chilonda, P., Franceschini, G., Menzi, H., 2005. Geographical determinants and environmental emplications of livestock production intensification in Asia. Bioresource Technol. 96, 263–276.

Haygarth, P.M., Condron, L.M., Heathwaite, A.L., Turner, B.L., Harris, G.P., 2005. The phosphorus transfer continuum: linking source to impact with an interdisciplinary and multi-scaled approach. Sci. Total Environ. 344, 5–14.

Jasinski, S.M., 2009. Phosphate Rock, USGS Mineral Commodity Summaries.

Johnston, A.E., 2005. Phosphorus nutrition of arable crops. In: Sims, J.T., Sharpley, A.N. (Eds.), Phosphorus: Agriculture and the Environment. American Society of Agronomy.

Jones, C.A., Cole, C.V., Sharpley, A.N., Williams, J.R., 1984. A simplified soil and plant phosphorus model. Soil Sci. Soc. Am. J. 48, 801–805.

King, F.H., 1911. Farmers of Forty Centuries: Organic Farming in China, Korea and Japan. Dover Publications, New York.

Limpert, E., Stahel, W.A., Abbt, M., 2001. Log-normal distributions across the sciences: keys and clues. Bioscience 51, 341–352.

Linquist, B.A., Singleton, P.W., Cassman, K.G., Keane, K., 1996. Residual phosphorus and long-term management strategies for an Ultisol. Plant Soil 184, 47–55.

Liu, Y., Mol, A., Chen, J., 2004. Material flow and ecological restructuring in china – the case of phosphorus. J. Ind. Ecol. 8, 103–121.

---

[2] Indeed, losses of *P* from land to water can either be assessed at the moment of mobilization by erosion and runoff plots (plot-level scale measure), or at the moment of delivery to receiving waters by measurements of *P* loads in water (catchment-scale measure). On the one hand, plot level measures over-estimate the loss of *P* because *P* can be retained in multiple ways during its routing through the catchment, thus remaining available to future biological productivity (Haygarth et al., 2005). On the other hand, estimates of aggregate export of *P* from a given catchment obtained by measurements of *P* loads in rivers do not inform us on the contribution of individual slopes to this loss. An ideal approach would combine both types of measurements and use inference methods that estimate $f(a_{er})$ of individual slopes such that they are consistent with the flux measured at the catchment scale.

Montgomery, D., 2007. Soil erosion and agricultural sustainability. P Natl. Acad. Sci. USA 104, 13268–13272.

Otabbong, E., Persson, J., Iakimenko, O., Sadovnikova, L., 1997. The Ultuna long-term soil organic matter experiment. Plant Soil 195, 17–23.

Rothman, D.H., Forney, D.C., 2007. Physical model for the decay and preservation of marine organic carbon. Science 316, 1325–1327.

Ryan, J., Ibrikci, H., Singh, M., Matar, A., Masri, S., Rashid, A., Pala, M., 2008. Response to residual and currently applied *P* in dryland cereal/legume rotations in three Syrian Mediterranean agroecosytems. Eur. J. Agron. 28, 126–137.

Sharpley, A., Cole, C., 1987. Soil phosphorus forms extracted by soil tests as a function of pedogenesis. Soil Sci. Soc. Am. J. 51, 362–365.

Smil, V., 2000. Phosphorus in the environment: natural flows and human interferences. Annu. Rev. Energy Environ. 25, 53–88.

Syers, J., Johnston, A., Curtin., D., 2008. Efficiency of Soil and Fertilizer Phosphorus Use. Technical Report, FAO.

Walker, T., Syers, J., 1976. The fate of phosphorus during pedogenesis. Geoderma 15, 1–19.

Zhang, Q., Wang, G.H., Feng, Y.K., Sun, Q.Z., Witt, C., Dobermann, A., 2006. Changes in soil *P* fractions in calcareous paddy soil under intensive rice cropping. Plant Soil 288, 141–154.