Phosphorus Retention in Lakes: A Critical Reassessment of Hypotheses and Static Models**

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Abstract

Various hypotheses and models for phosphorus (P) retention in lakes are reviewed and 39 predictive models are assessed in three categories, namely mechanistic, semi-mechanistic, and strictly-empirical models. A large database consisting of 738 data points is gathered for the analyses. Assessing four pairs of competing hypotheses used in mechanistic models, we found that (i) simulating lakes as mixed-flow reactor is superior to plug-flow reactor hypothesis; (ii) modeling P loss as a second-order reaction outperforms the first-order reaction; (iii) P loss is better explained as a removal process throughout the lake volume than as a settling process across the sediments; and (iv) considering a fraction of P loading is associated with fast settling particles enhances lake total phosphorus (TP) predictions. Due to the systematic approach used for combining the hypotheses, some models are for the first time developed and assessed. For instance, the preeminent mechanistic model combines, for the first time, the second-order reaction hypothesis with the hypothesis that a specific proportion of P loading settles rapidly at the lake entrance. Results also showed that semi-mechanistic models outperform both mechanistic and strictly-empirical models since they take the form of a mechanistic model based on the physical
representation of the lakes and utilize statistically acquired equations for unknown parameters. The best-fit model is a semi-mechanistic model that adopts the mixed-flow reactor hypothesis with a second-order volumetric reaction rate that is calculated as a non-linear function of inflow TP concentration, lake average depth, and water retention time. This model predicts 77.8% of the variability of log10-transformed lake TP concentration, which is 4.2% higher than the best mechanistic model and 0.8% higher than the best strictly-empirical model. The findings of this study not only shed light on the understanding of P retention in lakes but also can be useful for assessment of data-limited lakes and large-scale hydrological models to simulate the P cycle.

**Keywords:** Phosphorus, Lake, Modeling, Retention, Eutrophication

**List of symbols**

\( A = \) Surface area of the lake (m\(^2\))
\( L = \) Areal loading of TP (mg TP m\(^{-2}\) yr\(^{-1}\))
\( Q_{in}, Q_{out} = \) Hydraulic inflow, outflow rate (m\(^3\) yr\(^{-1}\))
\( q_s = Q/A = \) Areal hydraulic loading rate (m yr\(^{-1}\))
\( R_{TP} = \) Lake TP retention
\( TP_{in}, TP_{out} = \) Average inflow, outflow TP concentration (mg TP m\(^{-3}\) or \( \mu g\) TP L\(^{-1}\))
\( \alpha = \) Fraction of \( TP_{in} \) that does not settle fast in lake entrance
\( TP_{lake} = \) Average lake TP concentration (mg TP m\(^{-3}\) or \( \mu g\) TP L\(^{-1}\))
\( v = \) Settling velocity of TP containing materials (m yr\(^{-1}\))
\( v_2 = \) Second-order settling coefficient of TP containing particles (m\(^4\) mg TP\(^{-1}\)yr\(^{-1}\))
\( V = \) Lake volume (m\(^3\))
\( \bar{z} = V/A = \) Average lake depth (m)
\( \bar{w} = \) Average width of the lake (m)
\( \tau_w = V/Q = \) Water residence time (yr)
\( \rho = 1/\tau_w = \) Lake flushing rate (yr\(^{-1}\))
\( \sigma = \) First-order volumetric reaction rate constant (yr\(^{-1}\))
\( \sigma_2 = \) Second-order volumetric reaction rate constant (m\(^3\) mg TP\(^{-1}\) yr\(^{-1}\))
\( m_{TP} = \) Mass of TP in lake water (mg TP)
\( m_s = \) Mass of TP incorporated into sediments (mg TP)
1. Introduction

By providing relatively reliable storage of water for consumption during water deficit periods and attenuation of floods, lakes and reservoirs play an important role in societies (Jørgensen et al., 2005). Due to generally lower water velocity, longer water residence time, and lower flushing rate, lakes tend to trap the sediments they receive from tributaries. The accumulation of these sediments from the watershed, as well as the deposition of detritus to the lake bottom, will eventually lead to the filling of the lake, i.e. lake aging. As the lake ages, nutrients, especially nitrogen (N) and phosphorus (P) accumulate in the water column, and lake productivity increases which is referred to as eutrophication (Vinçon-Leite and Casenave, 2019). However, human activities have accelerated the eutrophication process by increasing the nutrients delivery to the aquatic systems (Mekonnen and Hoekstra, 2018). Thus, anthropogenic eutrophication is one of the most important elements of fresh and marine water quality deterioration (Hu et al., 2019; Smith and Schindler, 2009). One direct consequence of anthropogenic eutrophication comes in the form of massive algal blooms (Granéli et al., 2008; Heisler et al., 2008), which are predicted to be intensified under warmer water temperatures as climate changes (Gobler, 2020; Mukundan et al., 2020).

Eutrophication is a “wicked” problem, which is the consequence of various processes that operate cumulatively. Considering the uniqueness of each lake and its surrounding area, there is no broadly applicable set of best management practices that can be applied in watersheds to mitigate phosphorus loading and its impact on all lakes (Thornton et al., 2013). Hence, eutrophication management and lake restoration need integrated plans that are not only scientifically valid but also socio-economically satisfying (Gibson et al., 2000). To that end, Khorasani et al., (2018) developed a fourfold comprehensive framework that considers the upstream and downstream interactions for the management of eutrophication in lakes and uses a social choice voting method.
to choose the best set of practicable actions. Lake eutrophication management includes a wide range of approaches, from the reduction in external nutrient loading to sediment capping and control of internal loadings (Hickey and Gibbs, 2009; Zamparas and Zacharias, 2014) to biological and hydrological manipulations and end-of-the-pipe methods (Cooke et al., 2016; Lürling et al., 2016). However, a successful management plan needs to be accompanied by a reduction in external nutrient loading to achieve sustainable results (Cooke et al., 2016).

Predicting lake response to manipulative scenarios is of crucial importance for the selection of best management practices. Various models for the simulation of ecological processes in lakes have been developed during the last decades, from mechanistic (or process-based) models to empirical models (Vinçon-Leite and Casenave, 2019), and from static models to dynamic models, to agent-based models (Jørgensen and Bendoricchio, 2011). Although the static models are based on simplifying assumptions, their low computational demand is an advantage in the large-scale assessments of eutrophication and P retention (Maavara et al., 2015; Radomski and Carlson, 2018; Wu et al., 2021; Xu et al., 2020), optimization of reservoir operation rules (Chen et al., 2019; Deng et al., 2020; Xu et al., 2021; Zmijewski and Wörman, 2017), the evaluation of manipulative plans for lakes with the risk of eutrophication (Estalaki et al., 2016; Kasprzak et al., 2018), and paleolimnological studies (Moyle and Boyle, 2021). Though N and P are both vital for algae growth in the aquatic environment (Lewis and Wurtsbaugh, 2008; Liang et al., 2021), it is widely believed that the control of P seems the most promising approach for reduction of algal blooms in freshwater systems (Kazmierczak et al., 2021; Le Moal et al., 2019; Schindler, 2012; Smith and Schindler, 2009; Tong et al., 2017). Hence, predicting the P concentration in lakes is of crucial importance, and static models can provide valuable estimates for the lake management goals.
Phosphorus is subject to various biochemical transformations in lakes. Simple static models (as explained in section 2) generally incorporate these transformations into a loss term in different ways with the assumption that a certain fraction of the external P loading retains in a lake (i.e. lake P retention). The objective of this paper is to review and assess the static models, particularly four pairs of competing hypotheses that are suggested for the lake P retention problem using a large dataset of northern temperate lakes (n=738). Although researchers have done extensive work to evaluate some of the hypotheses (e.g. Walker 1985; Brett and Benjamin 2008), to our knowledge this research is the first known comprehensive and systematic assessment of all four competing hypotheses (see Table 1).

2. Static Lake Phosphorus Models

A general TP mass balance model for the lakes, assuming that in the long-term the lake is estimated as a Continuously Stirring Tank Reactor (CSTR), is as follows:

\[
\frac{\Delta m_{TP}}{\Delta t} = \text{Input} - \text{Output} - \text{Loss}
\]  

(1)

Based on some previous models in the early 1960s and using the data of 8 Swiss lakes, Vollenweider (1969) hypothesized that the loss of the TP from the lake water column to the sediments is a linear function of the TP mass in water as follows:

\[
\frac{\Delta m_S}{\Delta t} = \sigma m_{TP}
\]  

(2)

Using Vollenweider’s assumptions, that (i) the concentration of TP in output (\(TP_{out}\)) is equal to the lake-averaged TP concentration (\(TP_{lake}\)), (ii) the water input and output of the lake are equal (i.e., \(Q_{in} = Q_{out} = Q\)) and lake volume is constant (\(\Delta V = 0\)), (iii) the lake is in steady-state
(ΔTP_{lake}/Δt = 0), and (iv) there is no net internal loading of TP, the mass balance equation (Eq. 1) can be rewritten as follows:

\[ V \frac{ΔTP_{lake}}{Δt} = Q \cdot TP_{in} - Q \cdot TP_{lake} - \sigma \cdot V \cdot TP_{lake} = 0 \]  \hspace{1cm} (3)

By assuming that the mean water residence time (τ_w) in lakes is calculated as τ_w = V/Q, rearranging Eq. (3) takes the following form:

\[ TP_{lake} = \frac{TP_{in}}{1 + \sigma \tau_w} \]  \hspace{1cm} (4)

where all the parameters except \( \sigma \) can be directly measured for a lake. Eq. (3) assumes that there are two outputs for the TP after entering the lake, i.e. it either is washed out of the lake or is retained in the water column or is removed from lake volume via several reactions that are lumped and simplified as a first-order reaction. However, other researchers (e.g., Chapra, 1975; Imboden, 1974; Lorenzen, 1973) treated the TP removal through the lake mainly as the sedimentation process of P-containing particles with the settling velocity (v) to the sediment surface (which is assumed to be equal to lake surface area). In this approach Eqs. (2) and (4) take the following form:

\[ \frac{Δm_s}{Δt} = v \cdot A \cdot TP_{lake} \]  \hspace{1cm} (5)

\[ TP_{lake} = \frac{TP_{in}}{1 + \frac{v}{\bar{z}} \tau_w} \]  \hspace{1cm} (6)

With a slightly larger database (n=31), Vollenweider (1975) also suggested that the loss rate constant (\( \sigma \)) “depends on mean depth to a high degree” and obtained an approximation of \( \sigma = (10 m \ yr^{-1})/\bar{z} \).
In an attempt to find an alternative for the Vollenweider’s model with parameters that are all directly measurable, Dillon and Rigler (1974) used the areal loading of TP \( L \) (see Eq. 7) to introduce the lake TP retention \( R_{TP} \) which is defined in Eq. (8).

\[
L = \frac{Q \cdot TP}{A} \tag{7}
\]

\[
R_{TP} = 1 - \frac{L_{out}}{L_{in}} = 1 - \frac{(Q_{in} \cdot TP_{in})/A}{(Q_{out} \cdot TP_{out})/A} = 1 - \frac{TP_{out}}{TP_{in}} \tag{8}
\]

The input areal loading of TP is the sum of all the external loads of TP that enter the lake from different sources and the output load is the output of TP loads through the lake outlet. Using this approach, the loss term and the Vollenweider equation takes the following forms:

\[
\frac{\Delta m_S}{\Delta t} = R_{TP} \cdot Q \cdot TP_{in} \tag{9}
\]

\[
TP_{lake} = TP_{in} (1 - R_{TP}) \tag{10}
\]

Replacing the \( R_{TP} \) from Eq. (8) into Eq. (10) results in the basic assumption of the well-mixed lake where the TP concentration in the outlet is equal to the average lake TP concentration suggested by Vollenweider:

\[
TP_{lake} = TP_{in} (1 - R_{TP}) = TP_{in} \left[1 - \left(1 - \frac{TP_{out}}{TP_{in}}\right)\right] = TP_{out} \tag{11}
\]

However, this is undeniable that further attempts to develop equations for the prediction of \( R_{TP} \) have resulted in a better understanding of the TP retention problem in lakes. One of the general forms of \( R_{TP} \) prediction equations is \( R_p = a/(a + b) \). It can be shown that if \( b \) is equal to lake flushing rate \( (\rho) \) then \( a \) is essentially the loss rate constant \( (\sigma) \), while if \( b \) is equal to areal hydraulic loading \( (q_s) \), then \( a \) is essentially the settling velocity \( (v) \) (Chapra, 1975; Dillon & Kirchner, 1975;
Kirchner & Dillon, 1975). There are also other forms of empirical equations for $R_{TP}$ in the literature as shown in next sections.

Prior research has interestingly enough suggested that empirical models of lake TP retention may subsequently be explained with a mechanism. For instance, Jones and Bachman (1976) observed that the Vollenweider model would perform better when $TP_{in}$ is multiplied by a constant coefficient ($\alpha$) (See Eq. 12). They estimated $\alpha = 0.84$ using a database of 51 lakes, and they also observed that after removal of urban lakes from the database, $\alpha$ increases to 0.97 and the model performs slightly better. Hence, they speculated that $\alpha$ is associated with the different sedimentation properties of TP loadings. Canfield and Bachman (1981) hypothesized that after sedimentation of fast settling particulate P, $(1 - \alpha)TP_{in}$, near the inlet of lakes, $\alpha$ is a constant fraction of $TP_{in}$ that reaches the open waters and has slower removal rate. Chapra (1982) also used two pools for rapidly settling and slowly settling fractions of P, and showed that if $v_{rapidly-settling} \gg v_{slowly-settling}$ then the constant coefficient in the numerator ($\alpha$) represents the P fraction that has slower removal in the main basin of lake.

$$TP_{lake} = \frac{\alpha TP_{in}}{1 + \sigma \tau_w} \quad \text{or} \quad \frac{\alpha TP_{in}}{1 + \frac{v}{z} \tau_w}$$

Higgins and Kim (1981) proposed the hypothesis to simulate the lakes as a Plug Flow Reactor (PFR) as an alternative to the CSTR approach, to consider the longitudinal TP concentration gradient. Assuming that the lake is a rectangular channel with uniform width and depth, the mass balance equation in Eq. (3) in steady-state is as follows:

$$\bar{w} \bar{z} \Delta x \frac{dT_{P}\Delta x}{dt} = CQ - (C + \Delta C)Q - \sigma TP_x \bar{w} \bar{z} \Delta x = 0$$
where $\bar{w}$ and $z$ are width and depth of the lake, respectively, $x$ is the distance from lake entrance and $TP_x$ is the TP concentration in cross-section $x$. By simplifying and integrating Eq. (13), the PFR lake model is as follows:

$$TP_x = TP_{in} \exp\left(-\frac{\sigma \bar{w} z x}{Q}\right) = TP_{in} \exp\left(-\sigma \tau_{wx}\right)$$  \hspace{1cm} (14)

where $\tau_{wx}$ is the mean water retention time from lake entrance to cross-section $x$. If $x$ is equal to the length of the lake then $\tau_{wx} = \tau_w$. By integration of Eq. (14), the mean $TP_{lake}$ is calculated as follows:

$$TP_{lake} = \frac{TP_{in}}{\sigma \tau_w} (1 - \exp(-\sigma \tau_w))$$ \hspace{1cm} (15)

However, Higgins and Kim (1981) did not compare the overall performance of the CSTR model and the PFR model with any dataset. Walker (1985) compared the two types of models and concluded that the CSTR models generally outperform their PFR counterparts, suggesting a completely mixed hypothesis might be generally better than the plug flow hypothesis for lake TP concentrations.

Another important hypothesis in the development of the Vollenweider model is that the loss term is linearly correlated to TP mass in the water column, which implies that the TP loss is the first-order reaction. This hypothesis was initially based on the data of four lakes in Vollenweider (1968). Dillon (1974) theoretically investigated the use of a second-order reaction form. Walker (1985) performed a more comprehensive study and investigated the case in which the loss term per unit volume of the lake is a quadratic function of $TP_{lake}$:

$$\frac{1}{V} \frac{\Delta m_s}{\Delta t} = \sigma_2 \cdot TP_{lake}^2$$  \hspace{1cm} (16)
The steady-state mass balance equation, in which terms are expressed per unit volume of the lake, is as follows:

\[
\frac{1}{V} \frac{\Delta m_{TP}}{\Delta t} = \frac{Q \cdot TP_{in}}{V} - \frac{Q \cdot TP_{lake}}{V} - \sigma_2 \cdot TP_{lake}^2 = 0
\]  

By simplifying the aforementioned equation, the second-order version of the Vollenweider model is as follows:

\[
TP_{lake} = \frac{-1 + \sqrt{1 + 4\sigma_2 TP_{in} \tau_w}}{2\sigma_2 \tau_w}
\]

It is noteworthy to mention that in the second-order models, the dimension of loss/sedimentation parameter (\(\sigma_2\)) is no longer only the inverse of time (e.g., \(yr^{-1}\)), but the inverse of TP concentration and time (e.g., \((mg \ m^{-3})^{-1} \ yr^{-1}\) or equivalently, \(m^3 \ mg^{-1} \ yr^{-1}\)). Also, it should be mentioned that due to the dimension of \(\sigma_2\), the terms of the mass balance equation need to be expressed per volume of the lake. For the first-order reaction, even if the terms are expressed as per volume of the lake, the derived equation will not differ. The derivation of the first-order model using the per volume terms is presented in Supplementary Materials (Text S1).

After a comprehensive review of the literature (see Table 1), we found that there are mainly four pairs of competing hypotheses: mixed vs. plug flow, volumetric reaction vs. areal sedimentation, first-order vs. second-order reaction, and fraction \(\alpha < 1\) vs. \(\alpha = 1\). In addition to mechanistic models, researchers have developed different semi-mechanistic and empirical models. Semi-mechanistic models take their forms from mechanistic models, but their unknown parameter is a non-linear function of lake characteristics. Although Empirical models do not necessarily explain the mechanisms with lake TP retention (See Table 4 for their list), we decided to include them in this study and assess the performance of all different types of models.
Table 1. Summary of the static lake TP retention models developed and the databases used in the studies as well as comparison with the current study.

| Author (Year)                  | Mechanistic | Semi-mechanistic | Empirical | Mixed Flow | Plug Flow | First Order | Second Order | Areal Settling velocity | Volumetric loss rate | $\alpha$-fraction $< 1$ | Database size¹ |
|-------------------------------|-------------|------------------|-----------|------------|-----------|-------------|---------------|------------------------|---------------------|---------------------|------------------|
| Vollenweider (1969)           | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 8 Lakes          |
| Lorenzen (1973)               | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 4 Lakes           |
| Dillon (1974)                 | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 4 Lakes           |
| Imboden (1974)                | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 13 Lakes          |
| Dillon and Rigler (1974)      | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 17 Lakes          |
| Dillon (1975)                 | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 27 Lakes          |
| Vollenweider (1975)           | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 31 Lakes          |
| Kirchner and Dillon (1975)    | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 15 Lakes          |
| Chapra (1975)                 | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 15 Lakes          |
| Dillon and Kirchner (1975)    | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 28 Lakes          |
| Snodgrass and O’Melia (1975)  | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 11 Lakes          |
| Larsen and Mercier (1976)     | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 20 Lakes          |
| Vollenweider (1976)           | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | (194 Obs.)        |
| Jones and Bachman (1976)      | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 51 Lakes          |
| Chapra (1977)                 | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 5 Lakes           |
| Ostrofsky (1978)              | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 53 Lakes          |
| Schindler et al. (1978)       | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 60 Lakes          |
| Yeasted and Morel (1978)      | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 128 Lakes         |
| Reckhow (1979)                | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 47 Lakes          |
| Chapra and Reckhow (1979)     | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 117 Lakes         |
| Reckhow and Chapra (1979)     | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 15 Lakes          |
| Utormark and Hutchins (1980)  | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 23 Lakes          |
| Canfield and Bachman (1981)   | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 704 Lakes (723 Obs.) |
| Higgins and Kim (1981)        | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 18 Artificial Lakes |
| Chapra (1982)                 | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 13 Lakes          |
| Nurnberg (1984)               | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 90 Lakes          |
| Stauffer (1985)               | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 20 Lakes          |
| Walker (1985)                 | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | (696 Obs.)        |
| Reckhow (1988)                | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 70 Lakes          |
| Prairie (1989)                | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 112 Lakes         |
| Foy (1992)                    | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 10 Lakes          |
| Dillon and Molot (1996)       | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 7 Lakes           |
| Hejzlar et al. (2006)         | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 212 Lakes         |
| Bryhn and Håkanson (2007)     | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 41 Lakes          |
| Brett and Benjamin (2008)     | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 305 Lakes         |
| Köiv (2011)                   | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 54 Lakes          |
| Abell et al. (2019)           | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | 84 Lakes          |
| Current Study                 | ✓           | ✓                | ✓         | ✓          | ✓         | ✓           | ✓             | ✓                      | ✓                   | ✓                   | (738 Obs.)        |

¹ The numbers inside parentheses are the number of observational (Obs.) points. If the measurements in one lake are repeated in different years, the number of observations in the database surpasses the number of lakes.
3. Materials and Methods

This section presents the materials, including the models and their classification criteria, and the database of the lakes. The methods for fitting the models and their evaluation as well as the Bayesian Information Criterion (BIC) used for the comparison of the models are presented in Appendix 1.

3.1. Model Development and Classification

Lake phosphorus models generally can be divided into three categories, i.e., mechanistic, semi-mechanistic, and strictly-empirical. Mechanistic models are explicitly based on theoretical representations of lake mixing and TP dynamics and are derived from first principles. The hypotheses reviewed in section 2 are combined to derive different mechanistic models as presented in Table 2. The dimension of unknown parameters in mechanistic models lies in the integer combination of base units that hold physical meanings. Each of the mechanistic models has one or two unknown parameters. It is noteworthy to mention that, to our best knowledge, this is the first time that the combination of the second-order reaction hypothesis and $\alpha$-fraction hypothesis is considered and assessed. Moreover, this is the first time the average forms of the plug-flow models and their combination with $\alpha$-fraction hypothesis are tested with a large dataset.

Empirical models, on the other hand, are obtained from statistical analysis and do not rely on the conceptual representation of the lake. Semi-mechanistic models partly rely on the physical representation of the lake and partly benefit from the statistical analysis (Braake et al., 1998). In this paper, semi-mechanistic models adopt their basic structure from mechanistic models but the unknown parameters, i.e., the P removal rates, are obtained by fitting an empirical equation to the
data. Overall, 39 different models are assessed in this study including 16 mechanistic (see Table 2), 13 semi-mechanistic (see Table 3), and 10 strictly-empirical models (see Table 4). Considering that most of the semi-mechanistic and strictly-empirical models are non-linear, the refitting of the models is conducted using the Genetic Algorithm heuristic search method in MATLAB programming language (Appendix 1).

Table 2. List of mechanistic models and their basic hypotheses

| Overall Model No. | Intra-type model No. | Model                                      | Formulation ($TP_{in} = $)                                | Description                           |
|-------------------|----------------------|--------------------------------------------|----------------------------------------------------------|---------------------------------------|
| 1                 | 1                    | Plug-Flow, First-Order, Constant Loss Rate | $TP_{in} k_1 \tau_w [1 - \exp(-k_1 \tau_w)]$            | $k_1 = \sigma$ is the volumetric loss rate (1/yr) |
| 2                 | 2                    | Plug-Flow, First-Order, Constant Settling Velocity | $TP_{in} k_1 \tau_w [1 - \exp(-k_1 \tau_w)]$            | $k_1 = \nu$ is the settling velocity (m/yr) |
| 3                 | 3                    | Plug-Flow, First-Order, Constant Loss Rate for Constant Fraction of $TP_{in}$ | $aTP_{in} k_1 \tau_w [1 - \exp(-k_1 \tau_w)]$            | $k_1 = \sigma$ is the volumetric loss rate (1/yr), $a$ is a constant fraction of $TP_{in}$ |
| 4                 | 4                    | Plug-Flow, First-Order, Constant Settling Velocity for Constant Fraction of $TP_{in}$ | $aTP_{in} k_1 \tau_w [1 - \exp(-k_1 \tau_w)]$            | $k_1 = \nu$ is the settling velocity (m/yr), $a$ is a constant fraction of $TP_{in}$ |
| 5                 | 5                    | Plug-Flow, Second-Order, Constant Loss Rate | $\frac{\ln(k_1 TP_{in} \tau_w + 1)}{k_1 \tau_w}$        | $k_1 = \sigma_2$ is the effective second-order loss rate (m²/(mg.yr)) |
| 6                 | 6                    | Plug-Flow, Second-Order, Constant Settling Coefficient | $\frac{ln(k_1 TP_{in} \tau_w + 1)}{k_1 \tau_w}$        | $k_1 = \nu_2$ is the effective second-order settling coefficient (m²/(mg.yr)) |
| 7                 | 7                    | Plug-Flow, Second-Order, Constant Loss Rate for Constant Fraction of $TP_{in}$ | $\frac{ln(k_1 TP_{in} \tau_w + 1)}{k_1 \tau_w}$        | $k_1 = \sigma_2$ is the effective second-order loss rate (m²/(mg.yr)), $a$ is a constant fraction of $TP_{in}$ |
| 8                 | 8                    | Plug-Flow, Second-Order, Constant Settling Coefficient for Constant Fraction of $TP_{in}$ | $\frac{ln(k_1 \frac{aTP_{in} \tau_w + 1)}{a \tau_w}}{k_1 \tau_w}$ | $k_1 = \nu_2$ is the effective second-order settling coefficient (m²/(mg.yr)), $a$ is a constant fraction of $TP_{in}$ |
| 9                 | 9                    | Mixed, First-Order, Constant Loss Rate     | $\frac{TP_{in}}{1 + k_1 \tau_w}$                       | $k_1 = \sigma$ is the volumetric loss rate (1/yr) |
| 10                | 10                   | Mixed, First-Order, Constant Settling Velocity | $\frac{TP_{in}}{1 + k_1 \tau_w}$                       | $k_1 = \nu$ is the settling velocity (m/yr) |
| 11                | 11                   | Mixed, First-Order, Constant Loss Rate for Constant Fraction of $TP_{in}$ | $\frac{aTP_{in}}{1 + k_1 \tau_w}$                       | $k_1 = \sigma$ is the volumetric loss rate (1/yr), $a$ is a constant fraction of $TP_{in}$ |
| 12                | 12                   | Mixed, First-Order, Constant Settling Velocity for Constant Fraction of $TP_{in}$ | $\frac{aTP_{in}}{1 + k_1 \tau_w}$                       | $k_1 = \nu$ is the settling velocity (m/yr), $a$ is a constant fraction of $TP_{in}$ |
| 13                | 13                   | Mixed, Second-Order, Constant Loss Rate    | $\frac{-1 + (1 + 4k_1 \tau_w TP_{in})^{0.5}}{2k_1 \tau_w}$ | $k_1 = \sigma_2$ is the effective second-order loss rate (m²/(mg.yr)) |
| 14                | 14                   | Mixed, Second-Order, Constant Settling Coefficient | $\frac{-1 + (1 + 4k_1 \tau_w TP_{in})^{0.5}}{2k_1 \tau_w}$ | $k_1 = \nu_2$ is the effective second-order settling coefficient (m²/(mg.yr)) |
| 15                | 15                   | Mixed, Second-Order, Constant Loss Rate for Constant Fraction of $TP_{in}$ | $\frac{-1 + (1 + 4k_1 \tau_w aTP_{in})^{0.5}}{2k_1 \tau_w}$ | $k_1 = \sigma_2$ is the effective second-order loss rate (m²/(mg.yr)), $a$ is a constant fraction of $TP_{in}$ |
| 16                | 16                   | Mixed, Second-Order, Constant Settling Coefficient for Constant Fraction of $TP_{in}$ | $\frac{-1 + (1 + 4k_1 \tau_w aTP_{in})^{0.5}}{2k_1 \tau_w}$ | $k_1 = \nu_2$ is the effective second-order settling coefficient (m²/(mg.yr)), $a$ is a constant fraction of $TP_{in}$ |
### Table 3. List of semi-mechanistic models and their effective loss rate description

| Overall Model No. | Intra-type Model No. | Model | Formulation ($TP_{in,k} = 1$) | Description |
|-------------------|----------------------|-------|-------------------------------|-------------|
| 17                | 1                    | Plug Flow, First-Order | $\frac{TP_{in}}{k_{1}T_{w}} \left[1 - \exp\left(-k_{1}T_{w}\right)\right]$ | The effective loss rate is $\sigma = k_{1}T_{w}z_{w}^{-1}$ |
| 18                | 2                    | Plug Flow, First-Order | $\frac{TP_{in}}{k_{1}T_{w}T_{P_{in,k}}} \left[1 - \exp\left(-k_{1}T_{w}T_{P_{in,k}}\right)\right]$ | The effective loss rate $\sigma = k_{1}T_{w}z_{w}^{-1}TP_{in,k}$ |
| 19                | 3                    | Plug Flow, First-Order | $\frac{TP_{in}}{k_{1}T_{w}T_{P_{in,k}}^2} \left[1 - \exp\left(-k_{1}T_{w}T_{P_{in,k}}^2\right)\right]$ | The effective loss rate $\sigma = k_{1}T_{w}z_{w}^{-1}TP_{in,k}z_{k}$ |
| 20                | 4                    | Plug Flow, Second-Order | $\frac{\ln\left(k_{1}T_{w}T_{P_{in,k}} + 1\right)}{k_{1}T_{w}}$ | The effective loss rate $\sigma_2 = k_{1}T_{w}z_{w}^{-1}$ |
| 21                | 5                    | Plug Flow, Second-Order | $\frac{\ln\left(k_{1}T_{w}T_{P_{in,k}} + 1\right)}{k_{1}T_{w}T_{P_{in,k}}}$ | The effective loss rate $\sigma_2 = k_{1}T_{w}z_{w}^{-1}TP_{in,k}$ |
| 22                | 6                    | Plug Flow, Second-Order | $\frac{\ln\left(k_{1}T_{w}T_{P_{in,k}}^2 + 1\right)}{k_{1}T_{w}T_{P_{in,k}}^2}$ | The effective loss rate $\sigma_2 = k_{1}T_{w}z_{w}^{-1}TP_{in,k}z_{k}$ |
| 23                | 7                    | Mixed, First-Order | $\frac{TP_{in}}{1 + k_{1}T_{w}}$ | The effective loss rate $\sigma = k_{1}T_{w}z_{w}^{-1}$ |
| 24                | 8                    | Mixed, First-Order | $\frac{TP_{in}}{1 + k_{1}T_{w}T_{P_{in,k}}}$ | The effective loss rate $\sigma = k_{1}T_{w}z_{w}^{-1}TP_{in,k}$ |
| 25                | 9                    | Mixed, First-Order | $\frac{TP_{in}}{1 + k_{1}T_{w}T_{P_{in,k}}^2}$ | The effective loss rate $\sigma = k_{1}T_{w}z_{w}^{-1}TP_{in,k}z_{k}$ |
| 26                | 10                   | Mixed, Second-Order | $\frac{-1 + \left(1 + 4k_{1}T_{w}TP_{in,k}\right)^{0.5}}{2k_{1}T_{w}^2}$ | The effective loss rate $\sigma_2 = k_{1}T_{w}z_{w}^{-1}$ |
| 27                | 11                   | Mixed, Second-Order | $\frac{-1 + \left(1 + 4k_{1}T_{w}TP_{in,k}^2\right)^{0.5}}{2k_{1}T_{w}^2TP_{in,k}}$ | The effective loss rate $\sigma_2 = k_{1}T_{w}z_{w}^{-1}TP_{in,k}z_{k}$ |
| 28                | 12                   | Mixed, Second-Order | $\frac{-1 + \left(1 + 4k_{1}T_{w}TP_{in,k}^4\right)^{0.5}}{2k_{1}T_{w}^2TP_{in,k}^3z_{k}}$ | The effective loss rate $\sigma_2 = k_{1}T_{w}z_{w}^{-1}TP_{in,k}z_{k}^4$ |
| 29                | 13                   | Mixed, Second-Order | $\frac{-1 + \left(1 + 4\sigma_2T_{w}TP_{in}\right)^{0.5}}{2\sigma_2T_{w}}$ | The effective loss rate $\sigma_2 = k_{1}T_{w}z_{w}^{-1}TP_{in,k}z_{k}$ |

* Overall model numbers continued from Table 2
** Obtained from Walker Jr. (1985)
Table 4. List of strictly-empirical models and their references

| Overall Model No.* | Intra-type Model No. | Model Name | Formulation \((TP_{\text{in}} =)\) | Reference |
|--------------------|----------------------|------------|-----------------------------------|-----------|
| 30                 | 1                    | K&D        | \(1 - \left(k_1 \exp\left(-k_2 \frac{Z}{\tau_w}\right) + (1 - k_3) \exp\left(-k_3 \frac{Z}{\tau_w}\right)\)\) | Kirchner and Dillon (1975) |
| 31                 | 2                    | Ostrofsky1 | \(1 - \left(k_1 \exp\left(-k_2 \frac{Z}{\tau_w}\right) + k_3 \exp\left(-k_4 \frac{Z}{\tau_w}\right)\)\) | Ostrofsky (1978) |
| 32                 | 3                    | Ostrofsky2 | \(1 - \frac{k_1}{k_2 + \frac{Z}{\tau_w}}\) | Ostrofsky (1978) |
| 33                 | 4                    | L&M1       | \(1 - \left(k_1 - k_2 \ln\left(\frac{1}{\tau_w}\right)\right)\) | Larsen and Marcier (1976) |
| 34                 | 5                    | L&M2       | \(1 - \left(k_1 - k_2 \ln\left(\frac{Z}{\tau_w}\right)\right)\) | Larsen and Marcier (1976) |
| 35                 | 6                    | OECD       | \(k_4 \left(\frac{TP_{\text{in}}}{1 + \sqrt{\tau_w}}\right)^{k_2}\) | Vollenweider (1976) |
| 36                 | 7                    | Foy1       | \(\frac{k_5 \left(\frac{TP_{\text{in}}}{TP_{\text{in}} - k_1 \ln\left(\frac{1}{\tau_w}\right)}\right)^{k_2}}{\left(k_1 TP_{\text{in}}\right)^{k_2}}\) | Foy (1992) |
| 37                 | 8                    | Foy2       | \(\frac{k_5 \left(\frac{TP_{\text{in}}}{TP_{\text{in}} - k_1 \ln\left(\frac{1}{\tau_w}\right)}\right)^{k_2}}{\left(k_1 TP_{\text{in}}\right)^{k_2}}\) | Foy (1992) |
| 38                 | 9                    | B&B        | \(k_5 \left(\frac{TP_{\text{in}}}{TP_{\text{in}} - k_1 \ln\left(\frac{1}{\tau_w}\right)}\right)^{k_2}\) | Brett and Benjamin (2008) |
| 39                 | 10                   | Köv et al. | \(TP_{\text{in}}[k_1 + k_2 \log(TP_{\text{in}}) + k_3 \log \tau_w]\) | Köv et al. (2011) |

* Overall model numbers continued from Table 3

3.2. Database Development

The database used in this paper is a compilation of three data sets and has 738 observation data points. The largest database of the three is the National Eutrophication Survey (NES) dataset conducted by the U.S. Environmental Protection Agency (EPA) from 1972 to 1975 across the contiguous United States (USEPA, 1975). The NES database has 775 lakes and to our best knowledge is the largest database that includes the phosphorus data of lake input, in-lake, and output. Stachelek et al. (2018) digitized the NES tables and we carefully examined the digital database and corrected some faulty entries by comparing the reported and recalcualted water retention time, TP and TN retention values, and the extreme values for TP and TN concentrations (data available at [https://github.com/ReproducibleQM/NES](https://github.com/ReproducibleQM/NES)). The second database is from Hejzlar et al. (2006) and includes 264 observations of which 6 observations for the West Point Lake in
Georgia state are the results of simulation rather than direct measurements. After the removal of West Point Lake, 258 observations of which two-thirds are located outside of the US (mostly Europe and Canada) are added to our database. The third database is from Brett and Benjamin (2008) which includes 305 lakes of which 178 lakes overlap with the other two datasets. Hence, only 127 lakes from Brett and Benjamin (2008) are added to our database of which 22% are located in Europe and the rest is equally distributed between the US and Canada.

In total, 1160 data points are obtained after combining the three databases of which 122 were excluded due to the lack of data for water retention time. Then, 42 lakes were removed because of inaccurate water retention time (5% outliers in the ratio between calculated and reported values), while another 23 lakes were removed because of suspicious problematic $T_{P_{lake}}$ (5% outliers in the ratio of $T_{P_{out}}$ and $T_{P_{lake}}$). Seventy-one lakes did not have data for $T_{P_{in}}$ and 149 lakes without data for $T_{P_{lake}}$ were also removed. Next, 5 lakes with a surface area greater than 10,000 km² (4 Laurentian Great Lakes and Lake Winnipeg in Canada) were excluded. Lake Tahoe in Nevada, US, was also removed since its retention time ($\tau_w = 700 \text{ yrs}$) is 11 times larger than the second largest lake in the database ($\tau_w = 60 \text{ yrs}$ for Lake Okanagan in British Columbia, Canada).

Considering that the net annual TP retention in lakes is assumed to be positive (i.e. $T_{P_{out}} = T_{P_{lake}} < T_{P_{in}}$) (Hamilton et al., 2018), about 10% of the lakes had negative $R_{TP}$ values. A negative $R_{TP}$ value may result from: 1) a lake is in transient condition after external loading reduction but not in steady-state condition as static models assume (Jensen et al., 2006); 2) a lake receives persistent internal P loading from the sediment (Søndergaard et al., 2013); and/or 3) the measurements of $T_{P_{in}}$ and $T_{P_{lake}}$ have errors due to short water retention time of a lake (Brett and Benjamin, 2008). Considering that the errors resulting in negative TP retention probably spread through the whole database, we decided to follow the same practice as Brett and Benjamin (2008).
to retain most of the lakes with negative $R_{TP}$. Hence, only 9 lakes with $R_{TP} < -0.85$ were excluded from the database. Eventually, 738 observations (348 natural and 390 artificial lakes) remained in the database (Fig. 1). All lakes are located in the northern hemisphere between latitude $25^\circ$ – $60^\circ$ N, specifically in Europe and North America.

Figure 1. A representation of the data points (n=738) in the database.

While some lakes have more than one measurement in the database, stating the number of lakes with repeated measurement is a subjective issue. For example, Lake Sammamish in Washington has three different measurements from three different surveys. However, for some lakes, e.g., Lake Memphremagog in Quebec and Lake Päijänne in Finland, the whole lake basin is divided into several sub-basins and each sub-basin is considered as a different observation data point in the original databases. As a result, we refrain from the differentiation between the number of observations and that of individual lakes and consider each data point as independent.
The probability density distribution plot of six characteristics, i.e., water retention time, $TP_{in}$, $TP_{lake}$, lake surface area, mean depth, and TP retention are shown in Fig. 2. Although the number of natural lakes is slightly smaller than artificial lakes, they both cover a wide range of hydroclimate and landscape characteristics. Generally, artificial lakes have relatively narrower ranges with $TP_{in}$, $TP_{lake}$, lake surface area, and mean depth than natural lakes, while their mean values of $TP_{in}$, $TP_{lake}$, and lake surface area are higher than in natural lakes. Though the water retention time of artificial lakes tends to be significantly smaller than that of natural lakes, the TP retention of natural and artificial lakes seems to follow a similar distribution. The mean depth of artificial and natural lakes is also quite similar. Table S1 presents the extremum and the measures of the central tendency of the database variables.
Figure 2. The probability density distribution of lake characteristics for the database divided by artificial or natural lakes. The black lines represent the box plots. The z-score (z) and p-value (p) of the two-tailed hypothesis test is carried out on the log-transformed data of water retention, $TP_n$, $TP_{lake}$, lake surface area, mean depth, while the $R_{TP}$ values are not log-transformed.

4. Results and Discussion

This section presents the results of the models' calibration and comparison of different hypotheses followed by a comparison of the best performing models and a discussion on the retention of $P$ in different models. For the explanation of the Bayesian Information Criterion (BIC) used to make the comparison between different hypotheses as well as between models the reader is referred to Appendix 1.
Table 5. Final goodness of fit results for the mechanistic, semi-mechanistic, strictly-empirical. The intra-type $\Delta BIC$ is the difference to the minimum $BIC$ within one type of models and the overall $\Delta BIC$ is the comparison to the minimum of all 39 models (See Appendix 1). Please note that in each model type, the best model(s) is(are) highlighted. The overall best model(s) is(are) also highlighted in the last column.

| Overall Model No. | Intratype Model No | Calibrated Parameters | ESS | $\hat{R}^2_{adj}$ | BIC | Intra-type $\Delta BIC$ | Overall $\Delta BIC$ |
|-------------------|---------------------|-----------------------|-----|-----------------|-----|------------------------|---------------------|
| 1                 | 1                   | $k_1 = 1.029 \pm 0.097$ | 76.44 | 1 | 0.578 | -1666.8 | 398 | 440 |
| 2                 | 2                   | $k_1 = 7.318 \pm 0.680$ | 79.91 | 1 | 0.559 | -1634.0 | 431 | 473 |
| 3                 | 3                   | $\alpha = 0.566 \pm 0.021, k_1 = 0.242 \pm 0.061$ | 55.54 | 2 | 0.693 | -1895.9 | 169 | 211 |
| 4                 | 4                   | $\alpha = 0.563 \pm 0.016, k_1 = 1.890 \pm 0.275$ | 55.98 | 2 | 0.690 | -1890.0 | 175 | 217 |
| 5                 | 5                   | $k_1 = 0.019 \pm 0.002$ | 61.16 | 1 | 0.662 | -1831.3 | 233 | 276 |
| 6                 | 6                   | $k_1 = 0.090 \pm 0.013$ | 78.90 | 1 | 0.564 | -1643.4 | 421 | 464 |
| 7                 | 7                   | $\alpha = 0.620 \pm 0.019, k_1 = 0.008 \pm 0.002$ | 47.86 | 2 | 0.735 | -2005.7 | 59 | 101 |
| 8                 | 8                   | $\alpha = 0.560 \pm 0.017, k_1 = 0.024 \pm 0.006$ | 55.21 | 2 | 0.695 | -1900.3 | 164 | 207 |
| 9                 | 9                   | $k_1 = 0.786 \pm 0.070$ | 68.80 | 1 | 0.620 | -1744.5 | 320 | 362 |
| 10                | 10                  | $k_1 = 5.816 \pm 0.513$ | 72.76 | 1 | 0.598 | -1703.1 | 362 | 404 |
| 11                | 11                  | $\alpha = 0.597 \pm 0.021, k_1 = 0.207 \pm 0.044$ | 53.62 | 2 | 0.703 | -1921.9 | 143 | 185 |
| 12                | 12                  | $\alpha = 0.582 \pm 0.017, k_1 = 1.390 \pm 0.222$ | 55.37 | 2 | 0.694 | -1898.1 | 167 | 209 |
| 13                | 13                  | $k_1 = 0.027 \pm 0.003$ | 48.73 | 1 | 0.731 | -1999.0 | 66 | 108 |
| 14                | 14                  | $k_1 = 0.148 \pm 0.019$ | 63.90 | 1 | 0.647 | -1799.0 | 266 | 308 |
| 15                | 15                  | $\alpha = 0.702 \pm 0.024, k_1 = 0.011 \pm 0.002$ | 44.18 | 2 | 0.756 | -2064.7 | 0* | 42 |
| 16                | 16                  | $\alpha = 0.605 \pm 0.020, k_1 = 0.032 \pm 0.008$ | 52.85 | 2 | 0.708 | -1932.5 | 132 | 174 |
| 17                | 1                   | $k_1 = 2.038 \pm 0.077, k_3 = 0.311 \pm 0.024$ | 48.54 | 2 | 0.732 | -1995.3 | 112 | 112 |
| 18                | 2                   | $k_1 = 0.531 \pm 0.076, k_2 = 0.307 \pm 0.023, k_3 = 0.296 \pm 0.031$ | 41.86 | 3 | 0.768 | -2098.0 | 9 | 9 |
| 19                | 3                   | $k_1 = 0.324 \pm 0.078, k_2 = 0.263 \pm 0.024, k_3 = 0.344 \pm 0.038, k_4 = 0.137 \pm 0.048$ | 41.18 | 4 | 0.772 | -2103.5 | 3 | 3 |
| 20                | 4                   | $k_1 = 0.026 \pm 0.002, k_2 = 0.501 \pm 0.048$ | 52.19 | 2 | 0.711 | -1941.8 | 165 | 165 |
| 21                | 5                   | $k_1 = 0.353 \pm 0.106, k_2 = 0.432 \pm 0.031, k_3 = 0.579 \pm 0.044$ | 41.76 | 3 | 0.769 | -2099.8 | 7 | 7 |
| 22                | 6                   | $k_1 = 0.261 \pm 0.086, k_3 = 0.369 \pm 0.033, k_4 = 0.507 \pm 0.053, k_5 = 0.202 \pm 0.066$ | 41.06 | 4 | 0.772 | -2105.7 | 1* | 1** |
| 23                | 7                   | $k_1 = 1.354 \pm 0.062, k_2 = 0.371 \pm 0.028$ | 48.53 | 2 | 0.732 | -1995.5 | 111 | 111 |
| 24                | 8                   | $k_1 = 0.269 \pm 0.046, k_2 = 0.366 \pm 0.026, k_3 = 0.356 \pm 0.037$ | 41.81 | 3 | 0.768 | -2098.9 | 8 | 8 |
| 25                | 9                   | $k_1 = 0.149 \pm 0.042, k_2 = 0.313 \pm 0.028, k_3 = 0.414 \pm 0.045, k_4 = 0.166 \pm 0.056$ | 41.13 | 4 | 0.772 | -2104.4 | 3 | 3 |
| 26                | 10                  | $k_1 = 0.030 \pm 0.002, k_2 = 0.623 \pm 0.050$ | 45.24 | 2 | 0.750 | -2047.3 | 60 | 60 |
| 27                | 11                  | $k_1 = 0.257 \pm 0.067, k_2 = 0.575 \pm 0.042, k_3 = 0.432 \pm 0.058$ | 41.72 | 3 | 0.769 | -2100.4 | 7 | 7 |
| 28                | 12                  | $k_1 = 0.095 \pm 0.041, k_2 = 0.489 \pm 0.043, k_3 = 0.333 \pm 0.071, k_4 = 0.288 \pm 0.088$ | 40.99 | 4 | 0.773 | -2106.9 | 0* | 0** |
| 29                | 13                  | $k_1 = 0.008 \pm 0.022, k_2 = 0.104 \pm 0.046$ | 43.49 | 2 | 0.759 | -2076.3 | 31 | 31 |
| 30                | 1                   | $k_1 = 0.257 \pm 0.067, k_2 = 0.575 \pm 0.042, k_3 = 0.432 \pm 0.058$ | 53.27 | 3 | 0.705 | -1920.1 | 173 | 187 |

* selected intratype best models based on $\Delta BIC$

** selected best models based on $\Delta BIC$
4.1. Hypotheses Assessment

The BIC estimate of mechanistic models (model #1-16 in Table 5) is used for the pairwise comparison of the different hypotheses underlying the models. These comparisons include the particle settling approach versus volumetric reaction approach; the hypothesis that lakes behave as a plug-flow reactor versus a mixed flow reactor; the first-order reaction of phosphorus in lakes versus the second-order reaction; and the hypothesis that a constant fraction of input phosphorus participates in the reactions inside the lake versus the hypothesis that all the input phosphorus goes under the same loss reactions. Fig. 5 presents the results of the pairwise comparison of the different hypotheses. The BIC estimate of model #15 ($R^2_{adj} = 0.756$) suggests that it is the best mechanistic model. The pairwise comparison of the hypotheses that are used for the development of models, as presented below, shows that the hypotheses underlying model #15 also outperform their competitors.
Figure 5. The pairwise comparison of mechanistic models considering their underlying hypotheses using \( \Delta BIC \) values.

(a) Comparison of settling velocity approach versus the volumetric reaction approach, (b) comparison of the plug-flow hypothesis versus the mixed-flow hypothesis, (c) comparison of first-order reaction hypothesis versus the second-order reaction hypothesis, and (d) comparison of the hypothesis that all input TP participates in the reactions versus the hypothesis that a fixed proportion of input TP participates in reactions.

4.1.1. Particle settling vs. volumetric loss

As shown in Fig. 5a, the volumetric reaction approach for simulating TP performs better than the particle settling approach in all of the comparisons. Brett and Benjamin (2008) made a similar conclusion that their findings do not support the “widespread acceptance of the constant settling velocity model in the limnological literature”. The volumetric loss rate of TP in model #1 is found to be equal to \( k_1 = \sigma = 0.786 \pm 0.070 \, yr^{-1} \) which is similar to the reported value of \( \sigma = 0.65 \, yr^{-1} \) by Jones and Bachman (1976) but larger than the \( \sigma = 0.45 \pm 0.04 \, yr^{-1} \) reported by
Brett and Benjamin (2008) and smaller than $\sigma = 4.09 \text{ yr}^{-1}$ reported by Walker (1985). Generally the value of first-order volumetric loss rate of TP in mixed-flow models are found to be between $0.1 \text{ yr}^{-1}$ and $1 \text{ yr}^{-1}$ (Vollenweider, 1976).

Even though our results do not support the particle settling approach, reporting the settling velocities and comparing them with the literature might be of use for other modeling purposes. The apparent settling velocity in a mixed-flow reactor (model #2) is calibrated to $k_1 = v = 5.816 \pm 0.513 \text{ m yr}^{-1}$ which is very comparable to $v = 5.1 \pm 0.6 \text{ m yr}^{-1}$ reported by Brett and Benjamin (2008). Vollenweider (1975) reported the approximate value of $v = 10 \text{ m yr}^{-1}$; however, these values depend on the database that is used for calibration and may significantly vary. For instance, Higgins and Kim (1981) argue that the Vollenweider’s settling velocity of 10 m yr$^{-1}$ is for natural lakes and for a database of 10 Tennessee Valley Authority reservoirs with $TP_{in} > 25 \text{ mgTP m}^{-3}$, they found the average settling velocity $v = 92 \text{ m yr}^{-1}$.

### 4.1.2. Plug flow reactor vs. mixed flow reactor

Based on the $\Delta BIC$ values (Fig. 5b), there is strong to very strong evidence that the mixed-flow reactor hypothesis performs better than the plug-flow reactor hypothesis. In the literature, we found only two studies that consider or compare these two hypotheses. Although Higgins and Kim (1981) seem to be the first researchers proposing the use of the plug-flow model, they did not perform a full comparison between the two models and postponed it to a later occasion, when more data become available. They only discussed that the plug-flow model should be more appropriate for long and narrow reservoirs. Walker (1985) compared the plug-flow and mixed-flow models for 60 reservoirs and concluded that the mixed-flow models perform better than plug-flow ones. Note that Walker (1985) calibrated the models for the outflow TP concentration ($TP_{out}$), while we used
the in-lake TP concentrations \((TP_{lake})\) and made the same conclusion as that of Walker (1985). In the previous considerations of plug-flow and mixed-flow models, the numerical value for loss rate or settling velocity of plug-flow models is smaller than that of mixed-flow model counterparts, while in this analysis the P removal coefficients of plug-flow models are slightly larger than that of mixed-flow models. For example, the first-order volumetric loss rate found by Walker (1985) is \(\sigma = 4.09 \text{ yr}^{-1}\) for mixed-flow model and \(\sigma = 1.66 \text{ yr}^{-1}\) for plug-flow model. In this analysis, these values are \(\sigma = 0.786 \text{ yr}^{-1}\) and \(\sigma = 1.029 \text{ yr}^{-1}\), respectively. This seems to be due to the fact that while \(TP_{lake}\) and \(TP_{out}\) are not significantly different \((p < 0.00001, n = 540)\), the formulae of the plug-flow model for \(TP_{out}\) and \(TP_{lake}\) differ from each other. The ambiguity in which form of the plug-flow model should be used can be another reason that the plug-flow models are less reliable.

4.1.3. First-order vs. second-order reactions

As presented in Fig. 5c, second-order reaction models are found to be better than first-order reaction models. Using the data of only 4 alpine lakes and observing a linear relationship between \(TP_{lake}\) and their annual sedimentation, Vollenweider (1969) hypothesized the removal of TP as a first-order reaction, henceforth making this hypothesis widely accepted. However, similar to Walker (1985), our results show that assuming TP removal as a second-order function of \(TP_{lake}\) is performing better. The second-order volumetric loss rate of mixed-flow model in our study is \(k_1 = \sigma_2 = 0.027 \pm 0.003 \text{ m}^3 \text{ mgTP}^{-1} \text{ yr}^{-1}\), which is smaller than \(\sigma_2 = 0.10 \text{ m}^3 \text{ mgTP}^{-1} \text{ yr}^{-1}\) in Walker (1985). It is noteworthy to mention that the use of the second-order reaction models does not add to the number of unknown parameters while increasing the prediction power. Another difference between first-order and second-order models is that the second-order reaction model associates the TP retention not only with average water retention time but also with \(TP_{in}\). The
conventional approach for the calculation of $R_{TP}$ is the substitution of the developed models for $TP_{lake}$ into Eq. (8) instead of $TP_{out}$. In the first-order reaction models, the $TP_{in}$ is canceled in the calculation of $R_{TP}$. For example, the $R_{TP}$ for model #9 is as follows:

$$R_{TP} = 1 - \frac{TP_{lake}}{TP_{in}} = 1 - \frac{TP_{in}/(1 + \sigma \tau_w)}{TP_{in}} = \frac{\sigma \tau_w}{1 + \sigma \tau_w}$$

(19)

As seen in Eq. (19), $R_{TP}$ under the hypothesis of the first-order reaction only depend on the loss rate constant and water retention time. If the loss rate is assumed to be constant but not a function of $TP_{in}$, this independency of $R_{TP}$ and $TP_{in}$ can be doubtable (Søndergaard et al., 2013). Tammeorg et al. (2018) also show that $TP_{in}$ is an important factor affecting the retention of TP in Finnish lakes. In second-order reaction hypothesis, $TP_{in}$ still remains in the $R_{TP}$ equation. The $R_{TP}$ estimates by the first-order reaction model (model #9) and the second-order reaction model (model #13) are presented in Figs. 6a and 6b. The $R_{TP}$ in model #13 is a surface that is dependent on $TP_{in}$ and $\tau_w$. Therefore, while the model #9 is able to predict about 20% of variability of $R_{TP}$, model #13 improves to 26%.
4.1.4. Rapid sedimentation fraction

As presented in Fig. 5d, there is always very strong evidence that considering the fraction of rapid sedimentation generates better models. The TP removal coefficients in the models considering \( \alpha \)-fraction are smaller than those in the models without considering rapid sedimentation. This is because when considering \( \alpha \)-fraction, a portion \((1 - \alpha)\) of the input of TP is removed at the
entrance of the lake and does not participate in the reactions. The values previously used for $\alpha$ are respectively $\alpha = 0.84$ (Jones and Bachmann, 1976), $0.49 < \alpha < 0.80$ (Canfield and Bachmann, 1981), $\alpha = 0.50$ (Chapra, 1982), $\alpha = 0.754 \pm 0.023$ (Prairie, 1989), and $\alpha = 0.65 \pm 0.03$ (Brett and Benjamin, 2008). Based on our analysis (Table 5), the mean value of $\alpha$ generally ranges from 0.55 to 0.70, depending on the choices of other hypotheses. It indicates that a significant proportion (30 – 45%) of the TP loading into the lakes may be removed rapidly and the rest reaches to main basin of the lake. The TP removal coefficients for the remaining P loading is smaller than that for the total loading and their value is generally between 20% and 45% of the original coefficients, as shown in Fig. S1. Using the constant $\alpha$-fraction hypothesis forces a minimum value to the simulated $R_{TP}$, regardless of the lake morphologic characteristics. The $R_{TP}$ under this hypothesis will always be $R_{TP} \geq (1 - \alpha)$ which can be seen as an upward shift in simulated $R_{TP}$ toward higher values, especially in lakes with lower water retention time (Figs. 6b and 6d). This shift results in an overestimation of $R_{TP}$ in lakes with water retention time smaller than a month. As shown in Fig. 6, the predictive power of $R_{TP}$ in models that utilize $\alpha$-fraction hypothesis, is reduced in comparison to their counterpart models without $\alpha$-fraction hypothesis. Although model #9 and #13 can respectively predict 20% and 26% of variation in $R_{TP}$ values, their $\alpha$-fraction counterparts, i.e., models #11 and #15 can predict 16% and 23% respectively. However, models #11 and #15, respectively perform about 2% and 8% better than models #9 and #13 in predicting the variation of $TP_{lake}$. 
4.2. Mechanistic, Semi-mechanistic, or Strictly-empirical Models?

Using the $\Delta BIC < 2$ criterion, the best intratype as well as the best overall models are chosen. Among the mechanistic group, the mixed-flow, second-order, constant loss rate for constant $\alpha$-fraction of $TP_{in}$ model (model #15) outperforms others. The second best in this group is model #7 which has the same hypotheses as model #15, except that the lake is assumed a plug-flow reactor. However, with an intratype $\Delta BIC_{7-15}$ of 59, there is very strong evidence that model #15 is the best mechanistic model.

Among the semi-mechanistic group, model #28, with the form of a mixed reactor with a second-order reaction rate estimated by $\tau_w$, $TP_{in}$ and $\bar{z}$ is selected as the best model. However, with $\Delta BIC_{22-28} = 1$, model #22 which is the plug-flow reactor version of model #28 is chosen as the second-best model and comparable to model #28. The fact that the first two best performing models in both the mechanistic and the semi-mechanistic group utilize second-order hypothesis merely emphasizes the importance of this hypothesis. With an intra-type $\Delta BIC$ of 3, models #25 and #19 are the first-order reaction versions of models #28 and #22, respectively, which also use a combination of $\tau_w$, $TP_{in}$ and $\bar{z}$ for the estimation of the volumetric reaction rate. The next two models #27 and #21 with $\Delta BIC$ equal to 7 also utilize the same hypotheses of models #28 and #22, except that $\bar{z}$ is not used for the estimation of the TP loss rate. Generally, the performance of the semi-mechanistic group is better than mechanistic models.

Among the strictly-empirical group, the recalibrated OECD model (model #35) is selected as the best performing and there is not any other candidate in this group with $\Delta BIC \leq 2$. The first five models in this group (models #30-34) use $R_{TP}$ for simulating $TP_{lake}$. Hence, there is a challenge in calibrating these models because $R_{TP}$ might be estimated larger than one for some lakes, which
will result in a negative prediction for $TP_{lake}$ (note that $TP_{lake} = TP_{in}(1 - R_{TP})$). Considering that the $TP_{lake}$ values are log-transformed for the calculation of the estimated sum-of-errors ($ESS$), a penalty is applied for the unknown parameters that result in negative simulated $TP_{lake}$.

The overall comparison of the groups is also presented in Fig. 7. The semi-mechanistic models generally outperform the other two types. The top 8 models are all from the semi-mechanistic group, while the best performing outside of the semi-mechanistic group is the OECD model with an overall $\Delta BIC$ of 14. The mechanistic models mainly rely on the assumptions to explain the variation of $TP_{lake}$ without the privilege of the other two types to use statistical terms for improving their prediction power. Hence, as shown in Fig. 7, the mechanistic models have a wider range of $R^2_{adj}$ in comparison to the other two types. The strictly-empirical models generally perform better than the mechanistic group because they are not limited to the physical representation of the system. The comparison of the semi-mechanistic and strictly-empirical models also shows that generally, the semi-mechanistic models perform better than empirical models with the same number of unknown parameters. This can be because semi-mechanistic models have the form of a physical model, which helps them to better explain the changes in comparison to their strictly-empirical counterparts. For example, models #38 and #39 are two strictly-empirical models that use three parameters (i.e., $k_1$, $k_2$ and $k_3$) as well as two variables $TP_{in}$ and $\tau_w$. Semi-mechanistic models #18, #21, #24, and #27 have similar characteristics, except that they have the form of physical models. The $\Delta BIC$ of these semi-mechanistic models and the two similar strictly-empirical models is more than 10, indicating that in comparison there is very strong evidence against the strictly-empirical models.

The performance of the best models from each type are presented in Fig. 8, including the simulated $TP_{lake}$ versus the measured $TP_{lake}$ as well as the relative errors of simulated $TP_{lake}$. While model
#28 has the highest $R^2_{adj}$, the closest median of relative errors to one is observed in model #22 and the smallest Inter Quartile Range (IQR) which is the difference between the third and first quartile is observed in model #35. The distribution of the parameters of the best performing models is presented in Fig. S2.

Figure 7. The $R^2_{adj}$ values of the models grouped by the model types as mechanistic, semi-mechanistic, and strictly-empirical models.
Figure 8. Observed lake TP concentrations plotted against the simulated lake TP concentration for the four best models in panels (a) to (d). The perfect fit is shown by using a diagonal line in these panels. The frequency distribution of the relative error of the four best models is also shown in panels (e) to (h) where the dashed line shows the perfect 1:1 fit. The median and the Inter Quartile Range (IQR) of the relative errors are also presented in the corresponding panels.

The comparison of the mechanistic and semi-mechanistic models performance shows that the use of constant values for the unknown parameters is a limitation for mechanistic models. Previous studies have shown correlations between the TP loss rate and the lake and landscape characteristics (Cheng and Basu, 2017; Hejzlar et al., 2006). The most prevailing type of relation between removal rate and lake characteristics in the literature is from Larsen and Mercier (1976) with the form of \( \sigma = k_1 \tau_w^{k_2} \) where \( k_2 \) has been repeatedly found to be around -0.5 by different researchers. This relationship implies that TP loss rate is proportional to the lake flushing rate (\( \sigma \propto \rho^{0.5} \)). Canfield and Bachmann (1981) found it unclear that a higher flushing rate correlates to a higher sedimentation rate. They hypothesized that higher TP loading may accelerate algal growth and consequently increase the loss of TP from water by the settlement of algae. Assuming \( \sigma \propto \rho^{0.5} \).
which is equivalent to $\sigma \propto k_1 \left( TP_{in} / \tau_w \right) k_2$ they found $k_2$ is approximately equal to 0.5 which is in line with Larsen and Mercier (1976)’s assumption. Hejzlar (2006) showed the loss rate is correlated to all three $TP_{in}$, $\tau_w$ and $\bar{z}$ and as shown in Table 5, all four best performing models are semi-mechanistic models whose TP removal rate is a function of these variables. The first-order and second-order volumetric loss rate of model #25 and #28 are as follows:

$$\sigma = 0.149 \frac{(TP_{in})^{0.414}(\bar{z})^{0.166}}{(\tau_w)^{0.687}(\bar{z})^{0.288}}$$

$$\sigma_2 = 0.095 \frac{(\tau_w)^{0.511}(TP_{in})^{0.333}}{}$$

As seen, the first-order volumetric reaction rate is proportional to $TP_{in}$ while the second-order volumetric reaction rate is proportional to the inverse of $TP_{in}$. While in the semi-mechanistic models, these rates are dynamically changed by different lake characteristics, in their mechanistic counterparts, only the constant values of $\sigma = 0.786 \text{ yr}^{-1}$ and $\sigma_2 = 0.027 \text{ m}^3 \text{ mgTP}^{-1} \text{ yr}^{-1}$ are used. The phosphorus loss term (i.e., $\sigma TP_{lake}$ for the first-order and $\sigma_2 TP_{lake}^2$ for the second-order) for mixed-flow models using the constant and dynamic volumetric reaction rates is shown in Fig. 9. The comparison of Fig. 9a and 10b show that the mechanistic models, especially the first-order mechanistic model, have a limited range of TP loss prediction. This range, for the mechanistic first-order model, is between 3 and 1200 $mgTP \text{ m}^{-3} \text{ yr}^{-1}$ while the second-order mechanistic model is from 0.4 to 62000 $mgTP \text{ m}^{-3} \text{ yr}^{-1}$ the limited range of TP loss prediction in the first-order hypothesis is solved when using the dynamic loss term calculation in the semi-mechanistic models, as the loss terms of first-order and second-order models in Fig. 9b are similar. However, it is apparent that as the TP loss term increases (with the increase of lake TP concentration) the behavior of the TP loss term in first-order and second-order models slightly differ. The first-order
model tends to predict a higher TP loss than the second-order model for lakes with lower $TP_{lake}$ and a lower TP loss for lakes with higher $TP_{lake}$.

Figure 9. The comparison of the TP loss term (i.e., $\sigma TP_{lake}$ for the first-order and $\sigma_2 TP_{lake}^2$ for the second-order hypothesis) for the mixed flow models. The first-order model TP loss term is plot versus the second-order model TP loss term. The loss term is shown for (a) the mechanistic models #9 and #13 and (b) the semi-mechanistic models #25 and #28.

5. Conclusion

The main objective of this paper was to assess four pairs of competing hypotheses that are suggested for retention of TP in lakes using a large database. For this reason, 16 mechanistic models are developed explicitly based on the physical representation of lakes. Specifically, this research found that the best performing mechanistic model considers the lake as a mixed-flow reactor where 30% of the input TP is rapidly settled in the entrance and the remaining participates in a second-order reaction over the volume of the lake. It is worth highlighting that the $\alpha$-fraction has been generally overlooked in previous studies and the combination of this hypothesis with second-order reaction hypothesis and plug-flow models is for the first time conducted in this study. Though the $\alpha$-fraction hypothesis is supported by the data, this fraction does not seem to be constant for all lakes and this hypothesis overestimates TP retention for lakes with relatively short
water retention time (e.g., $\tau_w < 1$ month). Estimation of $\alpha$-fraction as a function of the lake and river characteristics should be further investigated in the future. Using the lake and river characteristics to calculate the unknown parameter of the mechanistic model results in the development of a semi-mechanistic model, which is found to be the best performing type. Modeling the TP removal as a second-order reaction outperformed the first-order reaction models both in mechanistic and semi-mechanistic groups. The well-known strictly-empirical models not only failed to perform better than the tested semi-mechanistic models but also they do not necessarily provide any information about the retention mechanism. The results of this study provide more insight into the P retention in lakes and can be used for large-scale hydrological models to simulate P cycle and assessment of lakes eutrophication status.

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Appendix 1: Statistical Analysis

The objective function of the fitting process is minimizing Error Sum-of-Squares (ESS) between the log10-transformed $TP_{lake}$ observations and simulations (See Eq. A.1). We used the bootstrap resampling method (sampling with replacement) to measure the accuracy of the fitted parameters. The fitting process was repeated many times (1000 times in this study) and each time the used database was a resampled dataset of the complete database (n=738). Selection of the samples
followed the uniform distribution and replacement was allowed (Efron, 1979). The calculation of ESS and the adjusted coefficient of determination ($R_{adj}^2$) are as follows:

$$ESS = \sum [\log_{10}(TP_{\text{lake,observed}}) - \log_{10}(TP_{\text{lake,predicted}})]^2 = \sum \left(\log_{10}\frac{TP_{\text{lake,observed}}}{TP_{\text{lake,predicted}}}\right)^2$$  \hspace{1cm} (A.1)

$$R_{adj}^2 = 1 - \frac{(n - 1) ESS}{(n - p - 1) TSS}$$  \hspace{1cm} (A.2)

where $n$ is the number of data points, $p$ is the number of unknown parameters in the model $TSS$ is the Total Sum-of-Squares of population defined as follows:

$$TSS = \sum \log_{10}\left(\frac{TP_{\text{lake,observed}}}{TP_{\text{lake,observed}}}\right)$$  \hspace{1cm} (A.3)

For finding the best models, the Bayesian Information Criterion (BIC) is used (Schwarz, 1978), which take into account both the best fit and the number of calibrated parameters as follows:

$$BIC = n \ln\left(\frac{ESS}{n}\right) + p \ln(n)$$  \hspace{1cm} (A.4)

As can be seen in this equation, larger errors in the simulation ($ESS$) as well as the greater number of dependent variables ($p$) increases BIC estimate. Hence, the minimum BIC value indicates the best model. The difference between the BIC estimates ($\Delta BIC$) is used to compare different models, as follows:

$$\Delta BIC_{i-j} = BIC_i - BIC_j$$  \hspace{1cm} (A.5)

where the $i$ and $j$ are the indicator number of the model and, in this paper, $j$ is the model of lower BIC estimate, i.e., the better model. By using the similarity to the likelihood ratio testing statistics, Kass and Raftery (1995) have suggested the values in Table A.1 to be used for describing the evidence against the model with higher BIC as a better model.
Table A.1. Guideline for the interpretation of the $\Delta \text{BIC}_{i-j}$ in the comparison of the models (adopted from Kass & Raftery, 1995).

| $\Delta \text{BIC}_{i-j}$ | Evidence against $i$th model as a better model to the $j$th model |
|--------------------------|-------------------------------------------------------------|
| 0 - 2                    | Not worth more than a bare mention                          |
| 2 - 6                    | Positive                                                    |
| 6 - 10                   | Strong                                                      |
| > 10                     | Very strong                                                 |

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