Phosphorus in the river corridor

Rosemary M. Records ^a, Ellen Wohl ^b, and Mazdak Arabi ^c

^a Integrated Water, Atmosphere, Ecosystems Education and Research Program, Department of Geosciences, Colorado State University, 1482 Campus Delivery, Fort Collins, CO 80523-1482, USA, rosemarymrecords@gmail.com (Corresponding author)

^b Department of Geosciences, Colorado State University, 1482 Campus Delivery, Fort Collins, CO 80523-1482, USA, Ellen.Wohl@colostate.edu

^c Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO 80523-1372, USA, Mazdak.Arab@colostate.edu

Abstract

River corridor protection has been adopted by government agencies and non-governmental organizations to try to control nonpoint nutrient loading to rivers. Yet, river corridor protection and modeling strategies developed on a national basis may not fully account for dynamics that have proven to be important controls on phosphorus in river corridors. These sources of uncertainty may have economic and environmental costs, yet we know of no previous works that have proposed a broad conceptual model of phosphorus dynamics in river corridors. In this review, we develop a conceptual model of phosphorus in the river corridor under natural conditions based on existing research by: (i) evaluating how processes and controls vary among distinct landscape characteristics and among distinct segments within river networks (e.g., in confined channels versus wide valleys); and (ii) determining whether some processes and controls are generally more dominant for some landscape types and river reaches. Finally, we provide an example application of the conceptual model, and identify key areas for future research. The review suggests that phosphorus dynamics in the river corridor, and their controls, may vary substantially across different landscape types and river reaches. However, the conceptual model outlined here illustrates how certain characteristics of landscape type, and abundance, transport, and transformation of phosphorus and reactive compounds, may help to predict important river corridor phosphorus dynamics. Use of this conceptual model can better inform numerical modeling of phosphorus dynamics and management of river corridors.

Keywords

Phosphorus; river corridor; riparian; floodplain; conceptual models

1. Introduction

Phosphorus loading to the oceans is approaching levels that have caused massive marine extinction in the past [Rockstrom, 2009]. Modern loading rates are nearly eight times the natural background rate of ocean influxes [Lerman *et al.*, 2000; Bennett *et al.*, 2001]. Efforts to control widespread marine “dead zones” below estuaries like the Mississippi River are commonly focused on reducing inputs of nitrogen from upstream farms; however, control of phosphorus may also be important in reducing eutrophication of these zones [Mitsch *et al.*, 2001; Carpenter, 2008]. High phosphorus loads also impact the rivers and lakes in which these loads are transported or stored. Phosphorus is the limiting nutrient in freshwaters and can cause eutrophication at 0.02 mg/L or higher [Correll, 1998]: levels far below river concentrations in many managed watersheds. The costs of eutrophication in water treatment investments, public health, ecological integrity, traditional food sources, and recreational opportunities are well documented [Carpenter *et al.*, 1998; Boyd *et al.*, 2002].

In the United States, water quality impacts from point sources (such as industrial effluent or wastewater treatment) have generally improved [Carpenter *et al.*, 1998]. “Nonpoint” inputs are the majority of nutrient inputs to rivers [Carpenter *et al.*, 2009; Son *et al.*, 2013], but have proved extremely difficult to control through regulatory means [e.g., Jones, 2014]. Restoration, rehabilitation, or conservation of the river corridor (which we subsequently call “river corridor protection”) is one approach government agencies and non-governmental organizations have used to try to control nonpoint nutrient loading to rivers [Wohl *et al.*, 2015].

We use the term “river corridor” to include areas outside of the active channel that are directly affected by river processes such as flooding (i.e., the floodplain and riparian zone), and “landscape” to refer to the hillslope and river corridor across larger spatial scales than a particular hillslope or river reach [Harvey and Gooseff, 2015]. Although we do not discuss other in-channel dynamics, we briefly

touch on hyporheic processes because they are an important means of exchange between the river and river corridor in some watersheds. Where wetland research is described, it is because these findings are assumed to have similarities with reaches of the river corridor (e.g., saturation and related effects, such as accumulation of organic matter and occurrence of redox processes).

Earlier work focused on surface transport of particulate phosphorus to receiving waters [King *et al.*, 2015], yet more recent studies show that phosphorus dynamics in the hillslope and river corridor can be quite complex. For example, groundwater can also transport significant phosphorus loads to rivers and lakes [Peterjohn and Correll, 1984; Vanek, 1993; Sims *et al.*, 1998; Djodjic *et al.*, 2004; Holman *et al.*, 2008]; the river corridor may be a large sink of phosphorus from the hillslope [Peterjohn and Correll, 1984] or the river [Noe and Hupp, 2009], but can also release soluble phosphorus under some conditions [Dillaha *et al.*, 1989]; and the net role of the river corridor as a source or sink of phosphorus may sometimes be driven by exchanges with the river rather than with the hillslope (e.g., by the balance of sediment deposition with floods and bank erosion at the river channel-river corridor interface) [Noe and Hupp, 2009].

Further, such processes affecting phosphorus fluxes in the hillslope and river corridor may vary significantly along the river network [Noe *et al.*, 2012]; in acid versus alkaline systems [Carignan and Vaithiyathan, 1999]; and in different soil types, climates or land use histories [Macdonald *et al.*, 2012]. Guidelines for river corridor protection strategies are commonly developed on a national basis [e.g., USDA NRCS, 2015a], and so may not yet fully account for such place-specific phosphorus dynamics.

Environmental phosphorus models may not include dynamics that have proven to be important controls of river corridor phosphorus in field studies (e.g., only some models simulate different sorption rates for calcareous and non-calcareous soils, although lab studies show there is marked difference between the two) [Darke *et al.*, 1996; McGeachan and Lewis, 2002; Havlin *et al.*, 2005; Robson, 2014].

78 These place-specific variations in phosphorus dynamics may influence how sensitive distinct watersheds
79 are to future human activities (whether river corridor protection or urbanization) and climate change,
80 and the time scales over which such responses may occur; yet place-specific variations may not be
81 reflected explicitly either in management or decision support tools such as environmental models.

82 These sources of uncertainty may have economic and environmental costs. River restoration
83 supports a multibillion dollar industry and is particularly widespread in the United States, Europe and
84 Australia [Wohl *et al.*, 2015]. Although many restoration activities are focused on channels, riparian
85 [Osborne and Kovacic, 1993] and floodplain [Brookes, 1996; Hughes *et al.*, 2001; Roley *et al.*, 2012;
86 Koebel and Bousquin, 2014; Marks *et al.*, 2014] restoration have been considered important for river
87 water quality improvements for some time, and such projects are increasingly being evaluated for their
88 water quality benefits [Wohl *et al.*, 2015]. River corridor protection has been implemented for water
89 quality improvements [Hoffmann *et al.*, 2009], at national [Palmer and Filoso, 2009], regional [Buffering
90 the Bay - Forestry Workgroup, 2013], and local [California Department of Forestry and Fire Protection,
91 2013] levels in diverse countries [Muotka and Laasonen, 2002; Brooks and Lake, 2007; Campana *et al.*,
92 2014]. However, most floodplain and riparian restoration intended to improve water quality has not yet
93 been effective. Possible reasons include the small areas restored relative to altered areas within the
94 contributing watershed [Palmer *et al.*, 2005; Wohl *et al.*, 2015], and “legacy” phosphorus from past
95 management that is mobilized when the river corridor is hydrologically reconnected to rivers, or when
96 external phosphorus loads to the river decrease [Sharpley *et al.*, 2013]. Water quality trading, another
97 increasingly popular mechanism for river water quality improvements, commonly relies on
98 environmental models to set transaction costs [US EPA, 2008]. The success of these approaches—
99 riparian and floodplain restoration, and water quality trading—is contingent on place-specific scientific
100 understanding of the river corridor and its relationships with the landscape.

Conceptual models are an important way to synthesize scientific knowledge into testable hypotheses about a system. Such models are an important component of river restoration and management [Wohl *et al.*, 2005] and are essential to improving environmental model capabilities and appropriate use of environmental models [Jakeman *et al.*, 2006; Gupta *et al.*, 2012]. A number of previous works have synthesized key phosphorus processes and human influences on phosphorus dynamics in watersheds [e.g., Walbridge and Struthers, 1993; Axt and Walbridge, 1999; Reddy *et al.*, 1999; Hendricks and White, 2000; Reddy and DeLaune, 2008; Withers and Jarvie, 2008; Hoffmann *et al.*, 2009; Vidon *et al.*, 2010; Noe, 2013; Sharpley *et al.*, 2013]. Other investigators have used a phosphorus index approach to indicate the susceptibility to phosphorus loading of watersheds with certain characteristics [e.g., Andersen and Kronvang, 2006]. Several works have assessed lateral and longitudinal variations in phosphorus cycling [Noe *et al.*, 2012; Noe, 2013 and references therein]. The effect of storms and short-term meteorological events on phosphorus fluxes have been well studied [e.g., Jarvie *et al.*, 2011]. However, we are unaware of any broad conceptual model of phosphorus dynamics in the river corridor, particularly in a whole-watershed context.

Humans have altered phosphorus cycling at global scales, and at the watershed level in many regions [e.g., Withers and Jarvie, 2008; Rockstrom, 2009]. Human activities (e.g., fertilizer application) may be a much greater source of phosphorus in the environment than background sources [Newman, 1997], and phosphorus from such activities may accumulate in the hillslope only to be released to waterways later [Sharpley *et al.*, 2013]. This “legacy phosphorus” is a key concern in managing watersheds for long-term water quality. Although much phosphorus loading to rivers may be from anthropogenic sources [Withers and Jarvie, 2008], how and when this phosphorus is transported and transformed between the landscape and river corridor is greatly affected by the natural characteristics of the landscape (i.e., climate and geology, as noted below). In some watersheds, these natural drivers of biogeochemistry may be substantially altered by humans (e.g., tile drains have changed historic

hydrologic flow paths), or may be currently undergoing anthropogenic change (e.g., increased flooding and export of organic matter with climate warming) [Tetzlaff *et al.*, 2013; King *et al.*, 2015]. Yet, without a clear understanding of background processes, it is not possible to determine the nature and extent of alteration in phosphorus dynamics, or to implement process-based river restoration for water quality or other goals [e.g., Beechie *et al.*, 2013]. Therefore, place-specific conceptual models of natural phosphorus dynamics are key to understanding and managing phosphorus in a particular landscape; and to assessing the extent of anthropogenic change and guiding river restoration where these natural processes have been altered. The goal of this paper is to develop a conceptual model of key controls and processes shaping phosphorus dynamics in the river corridor under background (natural) conditions. Our motivating questions are: what controls whether a reach or watershed is a net source or sink of phosphorus to rivers? And, what are implications for place-specific river corridor management and monitoring, and existing environmental modeling approaches? These questions guide our development of the conceptual model. However, they cannot be fully answered in this review, as answers are likely to vary substantially with landscape characteristics, time scales, and the management goals under consideration.

We develop the conceptual model based on existing research by: (i) evaluating how processes and controls vary among distinct landscape characteristics, and among distinct segments within river networks (e.g., in laterally confined channels versus wide valleys); (ii) determining whether some processes and controls are generally more dominant for some landscape types and river reaches; and (iii) synthesizing how drivers of phosphorus dynamics in distinct landscape types and locations along the river network may respond to disturbances. Finally, we provide an example application of the conceptual model, and identify key areas for future research.

Although river nutrient cycling is important to phosphorus dynamics in rivers [Ensign and Doyle, 2006], we have chosen not to address it here as our focus is the river corridor and surrounding landscape. For the same reason, we do not discuss the effects of point sources on phosphorus dynamics.

2. Phosphorus Dynamics

We consider phosphorus dynamics across diverse spatial scales. For convenience, we group phosphorus dynamics into abundance (the amount of phosphorus or compounds important for phosphorus dynamics present in some part of the landscape), transport (movement through or storage in the landscape), and transformation (broadly, alteration of the chemical formula, lability, or solubility). In this discussion we consider not only phosphorus, but the compounds which bind to phosphorus or influence its transformations and transport. Although we have selected the terminology of abundance, transformation, and transport, these correspond well to terms in other works on phosphorus. Approximately corresponding terms in these works [Beven *et al.*, 2005; Haygarth *et al.*, 2005] are as follows, with our terminology shown in parentheses: source (abundance); mobilization (transformation); transport and delivery (transport).

Forms of phosphorus in soil may be broadly divided into dissolved inorganic, particulate inorganic, dissolved organic, and particulate organic phosphorus (Table 1; Reddy and DeLaune, 2008). However, phosphorus literature does not consistently use this terminology; commonly, terminology derived from fractionation schemes (such as oxalate-extractable phosphorus) is used instead, sometimes without explicit description of the physical meaning of these fractions. We attempt to standardize terminology to follow the common forms and availability of these compounds summarized in Table 1 as described in Reddy and DeLaune [2008]. However, where the phosphorus fraction described does not neatly map to the terminology of Table 1, we use the original phrasing and attempt to describe its physical meaning when the phrase is first introduced.

2.1. Other compounds influencing phosphorus dynamics

Several compounds strongly affect retention of phosphorus in soil and sediments. In acid soils, iron and aluminum oxides and oxyhydroxides, aluminum minerals, and amorphous oxides may bind phosphorus, or release it into solution. In calcareous soils, some investigators attribute this binding primarily to calcium carbonate [Reddy *et al.*, 1999], whereas others suggest that reactions with iron oxide impurities are equally or more important [e.g., Havlin *et al.*, 2005], or that the importance of iron versus calcium varies under aerobic versus anaerobic conditions [Moore and Reddy, 1994]. Under anaerobic (or reducing) environments, the presence of manganese, nitrate, ferric phosphates, and/or sulfate may also become important [Richardson and Vepraskas, 2000; Reddy and DeLaune, 2008].

We subsequently refer to aluminum oxides and oxyhydroxides, aluminum minerals and alumino-silicates (clays), amorphous oxides and non-crystalline materials, calcium carbonate, iron oxide impurities in calcareous soils, and other compounds that undergo (de)sorption, precipitation and dissolution with phosphorus as “phosphorus-binding compounds”. Such a general term is chosen to signify that phosphorus immobilization with these compounds occurs in many distinct ways [Reddy and DeLaune, 2008; Withers and Jarvie, 2008]. The form as well as the abundance of these compounds is important for phosphorus dynamics. Less crystalline iron and aluminum oxides have more sorption sites (buffering or sorption capacity) for phosphorus, but hold phosphorus sorbed to their surfaces with lower bonding energy (less tightly) than do more crystalline forms, meaning that the potential for desorption is higher. The type of minerals present is closely related to abundance of iron and aluminum oxides. For example, 1:1 clay minerals more common in highly weathered soils have more iron and aluminum oxides than 2:1 clays and so can sorb more phosphorus. Similarly, acid soils can sorb up to five times more phosphorus, and five times more tightly, than calcareous soils or soils at neutral pH [Havlin *et al.*, 2005].

193 Additionally, the ratios of carbon and nitrogen to phosphorus, as well as the availability of these
194 elements, are strong controls on biotic immobilization or release of phosphorus [*Sylvia et al.*, 2005].
195 These processes may in turn indirectly affect other phosphorus dynamics (e.g., by affecting biological
196 oxygen demand and redox potential) [*Withers and Jarvie*, 2008]. Organic matter may also inhibit
197 phosphorus sorption to aluminum and iron, increasing phosphorus in solution [*Havlin et al.*, 2005].

198 **2.2. Landscape-scale controls**

199 The abundance and dominant forms of background phosphorus in hillslope soil reflect
200 concentrations and forms of phosphorus and other compounds in the original parent material (geology),
201 as well as the degree of weathering [*Yang et al.*, 2013] and, in some cases, atmospheric deposition
202 [*Peterjohn and Correll*, 1984; *Crews et al.*, 1995; *Hoffmann et al.*, 2006]. These controls, together with
203 hydrogeomorphology, biota, and human influences, dictate what transformations take place in the
204 hillslope and river corridor. Abundance, transformations, and transport—and their controls—may vary
205 over years, or even seasons. For example, *Dupas et al.* [2015a] found that river concentrations of
206 phosphorus were controlled by rainfall intensity in spring, but by river corridor groundwater rise and
207 near-channel sources during the rest of the year. *Darke and Walbridge* [2000] reported that non-
208 crystalline iron abundance increased in the river corridor in winter. *Mulholland et al.* [1990] surmised
209 that the river corridor released dissolved inorganic phosphorus to rivers during summer oxygen
210 depletions in groundwater, but that the river corridor was likely a sink for dissolved inorganic
211 phosphorus at other times.

212 Hydrogeomorphology affects the connectivity of the hillslope and the river corridor, what
213 hillslope processes dominate deliveries of water and sediment to the corridor, the responsiveness of
214 specific reaches to disturbances [*Montgomery and Buffington*, 1997; *Montgomery*, 1999], and dominant
215 plant and microbial communities or biogeochemical processes in a given part of the river corridor

[Merritt *et al.*, 2009; Noe *et al.*, 2012]. For example, in a wide, low-gradient, floodplain connected to the channel, overbank deposition may store a significant proportion of the annual sediment and phosphorus in within-river loads [e.g., Noe and Hupp, 2009]. If the water table in the floodplain is high for extended time periods, this may inhibit growth of woody plants [e.g., Rasmussen, 2011], limiting potential of long-term biological phosphorus storage, and promote release of phosphorus from sediments through desorption or redox processes [Richardson and Vepraskas, 2000]. Hydrologic connectivity within the river corridor, and its relation to hydrogeomorphology and biogeochemistry, is reviewed extensively by Harvey and Gooseff [2015].

Transformations in turn affect the mobility of hillslope soil phosphorus [Beven *et al.*, 2005] and are interlocked with when, how, and in what form phosphorus is delivered to lower areas of the hillslope or to the river corridor, thus affecting abundance in the hillslope. Although abundance, transformation, and transport are inter-related and mutually influence each other, if one of these is optimal for phosphorus loading from the hillslope, it may be unimportant if the others minimize the probability of phosphorus delivery to the river corridor or river. For example, soils with high phosphorus saturation may leach far less phosphorus to groundwater than soils with little phosphorus saturation (low abundance) but preferential flow paths (high transport) [e.g., Djodjic *et al.*, 2004].

Phosphorus-related transformations in the river corridor as well as the hillslope are dependent on the loads received with respect to the abundance and form of phosphorus, as well as the compounds with which phosphorus reacts, and other nutrients (such as carbon and nitrogen). For example, watersheds with calcareous soils will have more abundant calcium and magnesium in the river corridor and hillslope. When pH in these river corridor sediments lowers through natural floodplain conditions, the solubility of calcium compounds increases and these compounds can release phosphorus into solution. However, the river corridor of non-calcareous, neighboring watersheds may show no such

releases of phosphorus [e.g., *Carignan and Vaithiyathan*, 1999]. Because soil classifications can capture many of these aspects of a watershed, we note below the soil taxa for which we expect these attributes to be maximized. All classifications are based on USDA [*USDA NRCS Soil Survey Staff*, 1999].

2.2.1. Abundance

Most research on nonpoint sources of phosphorus to rivers is in intensively managed watersheds that have been repeatedly fertilized with mineral phosphorus [*Haygarth et al.*, 2005]. Weathering of the parent material and subsequent soil development strongly shape the background total phosphorus in the hillslope, phosphorus partitioning among particulate, dissolved, organic or inorganic forms (Table 1), and phosphorus distribution in the soil profile. However, human activities, such as fertilizer applications to farm land, can have far greater influence on observed phosphorus levels than background phosphorus made available through weathering [*Newman*, 1997].

Parent material total phosphorus concentrations are highest in volcanic rock (where concentrations can reach 1000 ppm) and shale formations [*Gray and Murphy*, 2002]. The latter materials are prevalent in the Pacific Ring of Fire, parts of southern Asia and Africa, and central North America, northern Europe, and Asia, respectively [*Yang et al.*, 2013]. Parent material phosphorus concentrations tend to be lower in some ultra-mafic igneous rocks, sandstones, and carbonate parent material [*Gray and Murphy*, 2002].

The influence of background soil phosphorus levels and concentrations in parent material is apparent in river loads. Over California and a few neighboring watersheds of Oregon and Nevada, background contributions of phosphorus to rivers were found to be nearly equal to diffuse contributions from cultivated lands, with the remainder comprised of point sources (38% and 39%, respectively) [*Domagalski and Saleh*, 2015]. Even near the mouth of the Sacramento River, which drains the intensively cultivated California Central Valley, as much as 14% of the river phosphorus load may be

from background sources. The contribution of volcanic regions (such as those with andesite lithology) to background phosphorus loads may be markedly higher than exports from regions with lithologies low in phosphorus (such as slates, sandstones, and other kinds of metamorphic and igneous rock) [Domagalski and Saleh, 2015]. Where geologic sources of phosphorus are low and soluble phosphorus is readily removed from solution (e.g., removal through calcium carbonate precipitation in the Everglades, USA), surface waters may have extremely low concentrations of phosphorus. In these oligotrophic ecosystems, microbial processes, periphyton activity, and biotically mediated changes in pH are key controls on phosphorus transport and transformation (sections 2.2.2 and 2.2.3). These ecosystems are also especially sensitive to anthropogenic phosphorus additions [Noe et al., 2001; Gaiser et al., 2005].

Primary mineral phosphorus (mostly calcium apatite) is generally highest in least weathered soils, with the exception of desert Aridisols (due to secondary calcium phosphate mineral formation) and Andisols [Yang and Post, 2011]. As weathering and ecosystem succession occur, this phosphorus is dissolved and taken up by biota or sorbed onto secondary mineral surfaces. This secondary mineral inorganic phosphorus is a greater proportion of total phosphorus in highly weathered, more acid soils with more abundant iron and aluminum oxides (Ultisols and Oxisols). As soils become progressively more weathered, more phosphorus becomes occluded or surrounded by iron and aluminum hydrous oxides; most of this phosphorus is biologically unavailable. Organic phosphorus commonly peaks at intermediate soil weathering until primary mineral phosphorus is depleted, and then declines [Walker and Syers, 1976; Crews et al., 1995; Zehetner et al., 2008; Yang and Post, 2011; Yang et al., 2013]. The percent of total phosphorus in labile (biologically available) inorganic form is similar for most soil orders and stages of weathering [Yang et al., 2013]. Weathering also influences the abundance and form of phosphorus-binding compounds. Literature [Walker and Syers, 1976; Crews et al., 1995; Havlin et al., 2005; Schaetzl and Anderson, 2005; Zehetner et al., 2008; Yang and Post, 2011; Macdonald et al., 2012; Yang et al., 2013] suggests the following generalizations based on the broad grouping of soil order.

In highly weathered soils (e.g., Ultisols and Oxisols), background total and percent organic phosphorus are lower, and more phosphorus is occluded. These soils are abundant in clays such as kaolinite, which is rich in iron and aluminum oxides and common in weathered environments; but iron and aluminum oxides are commonly in a lower sorption capacity, crystalline form, possibly representing a “tradeoff” in the soil’s ability to sorb phosphorus. The response of these soils to agriculture is a reduction in total phosphorus (Oxisols, Alfisols), and reduction or no change in labile phosphorus, implying that phosphorus may be lost to surface or ground water.

Moderately weathered soils have intermediate amounts of background total phosphorus and the highest percentage of organic phosphorus. The fraction of phosphorus in primary and occluded (secondary mineral) form, and the proportion of crystalline versus non-crystalline iron and aluminum oxides, are intermediate between highly weathered and poorly weathered soils. Clays (such as montmorillonite and other 2:1 clays) may not be as abundant in iron and aluminum oxides as more weathered soils, and adsorption rates, even for soils with the equivalent amount of clay, may be much lower than for highly weathered or volcanic soils [*Havlin et al.*, 2005, citing Sanchez and Uehara, 1980]. If developed on calcareous parent material, calcium and magnesium-related transformations may occur alongside or predominate over iron and aluminum-related transformations (see section 2.2.3, below). Moderately weathered and low clay content soils (Spodosols) have elevated total phosphorus after agricultural abandonment. Note that elevated total phosphorus after agriculture implies phosphorus is retained in the hillslope (at least in sediments, which may later be transported to the river corridor).

Poorly weathered soils such as Entisols and Inceptisols have the greatest background total phosphorus concentrations of mineral, non-volcanic soils, and the largest percentage of phosphorus in primary mineral form (e.g., apatite). They have a lower percentage of organic phosphorus than intermediately weathered soils. Iron and aluminum oxides are less prevalent than in more weathered

soils, but a larger fraction is likely to be non-crystalline—as for highly weathered soils, this may represent a “tradeoff” in phosphorus sorption capacity. These soils show higher labile phosphorus following the cessation of agriculture (e.g., Entisols), which could imply more potential for dissolved inorganic phosphorus transport.

Two soil types are special cases. Volcanic soils have the highest background total phosphorus concentrations of any soil type, and abundant non-crystalline material that yields high sorption capacities [Shoji *et al.*, 1993]. Soils with volcanic properties may have very high adsorption even compared to soils with equal, or lesser, amounts of clay [Havlin *et al.*, 2005, citing Sanchez and Uehara, 1980]. Volcanic soils may be acidic (rhyolite, dacite), intermediate (andesite, basaltic andesite), or basic (basalt) [Shoji *et al.*, 1993]. Soil phosphorus responses to agriculture are the same as those for other poorly weathered soils (above). The second special case is organic soils. These have the second-highest background total phosphorus concentrations of all soil types. Most phosphorus is organic, so organic transformations likely predominate over inorganic retention mechanisms such as sorption (see section 2.2.3, below). Because concentrations of aluminum, iron, magnesium and calcium are small, the soil has very little phosphorus sorption capacity and fertilizer applications are likely to result in high rates of phosphorus leaching. Cultivated organic soils may be large sources of phosphorus in another way. When these soils are drained, oxidation and more rapid decomposition of organic matter can release large amounts of phosphorus into labile form [e.g., Snyder and Morace, 1997].

Weathering, along with biological processes, also influences how surface and subsurface phosphorus are partitioned vertically in the soil. Phosphorus values in unmanaged, less weathered soils are generally highest in surface mineral horizons from organic matter accumulation. In more weathered soils, concentrations are lowest in horizons just below the surface (likely due to vegetative uptake and leaching) [Walker and Syers, 1976].

Atmospheric and marine sources of phosphorus may be important in some landscapes. Atmospheric inputs of phosphorus are commonly considered to be negligible [Hendricks and White, 2000]. However, these inputs may maintain relatively constant soil total phosphorus levels even after high rates of weathering [Crews *et al.*, 1995], and have been shown to contribute up to a third of phosphorus inputs to the river corridor in a small watershed [Andersen *et al.*, 2006], while contributing only 4% of phosphorus inputs to river corridors in other systems [e.g., Peterjohn and Correll, 1984]. Atmospheric inputs of phosphorus may be important where there is deposition of large amounts of wind-eroded fine soil (e.g., dust from the Gobi and Saharan deserts) or volcanic ash; coal and oil burning rates are locally high; large amounts of biomass are burned (e.g., forest fires or shift agriculture); and potentially where pollen grains are abundant, such as wind-pollinated trees and grasses [Newman, 1995]. Even comparatively small amounts of atmospheric phosphorus deposition may have greater ecological impacts in oligotrophic systems that have developed from phosphorus-poor geology (e.g., the Everglades, USA) [Noe *et al.*, 2001]. In Alaska, Russia, Japan, and Canada, fish returning from the ocean to spawn can provide a large percentage of nutrients to the river and river corridor, despite heavy reductions relative to pre-development runs [Gresh *et al.*, 2000; Naiman *et al.*, 2005].

Abundance in the river corridor presumably reflects abundance in the contributing hillslopes. However, transport and transformation may alter the abundance of phosphorus and binding compounds in the river corridor. Eroded sediments usually have a greater proportion of fine particles and so have a higher phosphorus concentration than in situ soils [Sharpley, 1980]. Areas of sediment deposition (for example, at the foot of hillslopes) [Noe *et al.*, 2012] have the potential to become hotspots of legacy phosphorus [Sharpley *et al.*, 2013]. Sediment eroded from the hillslope may become increasingly finer as it is deposited closer to the river corridor [Cooper and Gilliam, 1987], presumably because flow energy in surface runoff decreases with distance from the toe-slope, or surface soil texture

may remain relatively similar laterally across the floodplain [Noe *et al.*, 2012]. River corridor environments near the river, such as levees and splays, may have coarser soil material [Wohl, 2014b].

Iron and aluminum oxides and oxyhydroxides may be more abundant closer to the river, and flooding appears to result in accumulation of non-crystalline iron oxides in the river corridor [Darke and Walbridge, 2000]. These spatial patterns are relevant because iron and aluminum oxides are key phosphorus-binding compounds, and sorption capacity is generally greater for finer soil textures and amorphous materials (as noted above).

In fact, variation in deposition of fine soil can explain much of the variation in total phosphorus in river corridor soils [Cooper and Gilliam, 1987]. Some characteristics of the river corridor may alter the importance of sorption and other transformations relative to the hillslope, as described below in section 2.2.3. Floodplains with high available soil phosphorus also tend to have large nutrient loads in the adjoining river [Spink *et al.*, 1998]. Despite this apparent correlation, disconnection with the river via levees may or may not influence phosphorus cycling in adjacent floodplains [Sánchez-Pérez and Trémoières, 2003; Zehetner *et al.*, 2008].

Therefore, we expect background total phosphorus abundance to be highest in volcanic and organic soils and in soils with little weathering. We expect background phosphorus with higher potential for release in the river corridor (sorbed onto mineral surfaces or in labile organic matter) to be more abundant in Andisols (parent material and little weathering mean high total phosphorus, and amorphous volcanic materials retain large amounts of phosphorus) and organic or drained organic soils (Histosols) because of their high total phosphorus content and the potential for oxidation to release large amounts of labile phosphorus. Fertilizer or waste application to Andisols, or to nutrient-poor Oxisols and Ultisols rich in iron and aluminum oxides, could create potential large phosphorus sources if the enriched sediment is transported to the river corridor. We expect Aridisols and other calcareous

soils to have higher potential for release of phosphorus to rivers if fertilized or cultivated, because of their relatively low sorption capacity and lower-energy bonds with phosphorus.

We expect the river corridor to generally follow the trends described above for its contributing hillslopes. However, depositional environments (such as the toe-slope and backswamps) may contain concentrated levels of soil phosphorus, particularly where background levels or fertilizer application rates of phosphorus in the hillslope are high. These general expected trends are summarized in Figure 1.

2.2.2. Transport

Transport of phosphorus is inter-related with phosphorus abundance and transformations, as noted above. Present-day phosphorus abundance is the product of background and anthropogenic phosphorus sources and past transformation and transport. Transformations are highly affected by the dominant transport mechanisms in a given location. For example, phosphorus mineralization rates in floodplains may vary strongly with the depositional environment of the floodplain, such as in backswamps versus levees [Noe *et al.*, 2012], although mineralization as a *percent* of the total nutrients did not vary significantly in this study. Rates of sorption of phosphorus from water to soil are lower in faster flows [Fuchs *et al.*, 2009] and redox conditions promoting release of phosphorus from iron are less likely to develop in fast-flowing, oxygenated waters [e.g., Hendricks and White, 2000]. Similarly, abundance and transformation impact the effectiveness of phosphorus transport in flow: i.e., if most phosphorus in the hillslope remains tightly sorbed to sediments, even high subsurface flow rates may not deliver much phosphorus to the river corridor.

Transport or delivery may be one of the most poorly understood aspects of phosphorus transfer from hillslopes to soils, as compared to sources, mobilization, and impacts to waters receiving phosphorus fluxes [Haygarth *et al.*, 2005]. Most studies of phosphorus transport have used relatively brief plot experiments, and it is doubtful whether findings from plot simulations “scale up” to processes

over a hillslope or watershed [Dougherty *et al.*, 2004; Haygarth *et al.*, 2005]. Further, it is commonly not possible to distinguish the destination to which mobilized phosphorus will be transported: i.e., is dissolved inorganic phosphorus measured in shallow groundwater in the hillslope being subsequently transported to the river? This uncertainty reflects difficulty in linking the mobilization of phosphorus at a specific point to delivery to rivers [Haygarth *et al.*, 2005], and the destination of these fluxes is partly a question of the time scale considered [Sharpley *et al.*, 2013].

Phosphorus transport may be surface or subsurface, in matrix flow or concentrated in channels or preferential flow paths. In this discussion, we group phosphorus transport into surface, matrix flow in the subsurface, and subsurface preferential flowpaths. Particulate forms of phosphorus are usually believed to dominate surface runoff, as reflected in the equation structure of commonly used hydrologic models such as the Soil and Water Assessment Tool [Neitsch *et al.*, 2009], but dissolved phosphorus fluxes may sometimes comprise the majority of total phosphorus in surface runoff [e.g., Heathwaite and Dils, 2000; Buda *et al.*, 2009]. Finer sediments (e.g., silt and clay) have a greater specific surface area to sorb phosphorus, and may be more readily transported than coarser particles [Sharpley *et al.*, 2013]. Therefore, landscape characteristics and uses, and episodic events such as floods that enhance fine sediment transport, have potential to move large amounts of phosphorus, as described in more detail below. Most of the dissolved constituents in groundwater are commonly inorganic [Freeze and Cherry 1979], and dissolved phosphorus generally dominates subsurface transport [e.g., Heathwaite and Dils, 2000] except in preferential flow paths, which readily transport particulate and dissolved phosphorus [Sims *et al.*, 1998].

Gradients of gravitational and pressure potential energy control water flow between the hillslope, river, and river corridor, and dissolved phosphorus diffusion is governed by concentration gradients in soils, sediments, and water [Withers and Jarvie, 2008], but actual rates of transport depend

on local conditions. High transport rates can lead to high phosphorus loading to rivers, even when hillslope concentrations of phosphorus are low. Therefore, understanding the main sources and transport mechanisms of phosphorus in runoff is very important, and is reflected in the idea of “critical source areas” in phosphorus literature [e.g., *Buda et al.*, 2009].

Phosphorus may be transported from the hillslope to the river corridor; from the river corridor to the river; from the river into the river corridor; and from the hillslope directly to the river (for example, via preferential flow paths, or via tile drainage, canals, etc.). In some instances, nutrient transport may also occur from the river or river corridor to the hillslope (for example, as animals that feed in the river corridor move to the hillslope, e.g. *Baxter et al.* [2005]; *Naiman et al.* [2005]). Because of the multi-directional nature of transport, we begin each of the three sections (surface, matrix flow in the subsurface, and preferential flow) by describing conditions that generally enhance that particular transport pathway. Then, we note conditions that may enhance transport specifically within the hillslope or river corridor, or from one element of the landscape to another (e.g., from the river to the river corridor). For example, surface runoff in general tends to be higher in fine soils with poor drainage, but retention in the river corridor of material deposited in surface transport (floods) may be greater in low-gradient floodplains [*Noe and Hupp*, 2009]. River corridor segments of lower gradient tend to have more areally extensive and finer-grained floodplain sediment than higher gradient reaches (e.g., *Marren et al.*, 2006; *Sutfin*, 2016) and thus have a higher potential for adsorption and particulate storage. Lower gradient segments are also more likely to be altered by activities such as channelization, construction of artificial levees, and wetland drainage, which cumulatively enhance conveyance within the channel and decrease channel-floodplain and channel-hyporheic connectivity for water, sediment, and solutes (e.g., *Schoof*, 1980; *Wohl*, 2014a). Many of the human alterations of nitrogen dynamics in river corridors, which are relatively well documented in the literature (e.g., *NSTC*, 2000; *Galloway et al.*, 2004; *Boyer et*

al., 2006; Ranalli and Macalady, 2010), have also likely influenced phosphorus dynamics in river corridors, although there are few references on this topic for phosphorus.

The conditions enhancing various types of transport are also summarized in Figure 2 and Table 2. Human influences (tile and surface drains and ditches, damming, land cover changes, etc.) also have potential to greatly alter phosphorus transport, but are not addressed in this review.

Surface transport

As noted above, phosphorus concentrations are higher in fine-textured soils and sediments [Dougherty *et al.*, 2004]. By implication, particulate phosphorus loads in surface runoff from the hillslope are enhanced where fine sediment is also readily transported. In the hillslope, the primary control on fine sediment production is likely the presence of clastic sedimentary rock parent material, such as sandstones, shales, and siltstones [e.g., Wohl *et al.*, 2007]; and in the river corridor, main controls are likely lithology and valley and channel geometry, as they affect valley width and channel gradient, and thus transport capacity versus deposition of varying grain sizes [Montgomery and Buffington, 1997; Wohl *et al.*, 2007; Livers and Wohl, 2015].

In addition to having higher phosphorus concentrations, finer-textured, less permeable soils could decrease infiltration and thus increase dissolved and/or particulate phosphorus loading in surface runoff. Domagalski and Saleh [2015] noted that phosphorus yields from the more clayey soils of the western San Joaquin Valley, California, were higher than yields from the sandier eastern side of the valley, although their study did not distinguish between subsurface and surface transport mechanisms. They proposed a potential third effect of finer soils on phosphorus loads: as a finer particle, clays are more susceptible to erosion and entrainment. However, erodibility is usually believed to be highest in silty-textured soils [Wischmeier *et al.*, 1971]. Additional factors affecting the erodibility of a given soil include rainfall erosivity, slope length and steepness, vegetation cover, and conservation practices

[*Wischmeier and Smith, 1978*], and these or related factors are commonly reported as important controls on phosphorus in surface runoff [*Wetzel, 2001*, and references therein].

The effects of lithology and other factors on erosion are partially reflected in the total suspended solid fluxes in rivers globally, which are commonly very low downstream from major depositional areas such as lakes or abundant wetlands and in low-relief, humid environments, and progressively higher in areas with greater topographic relief, a greater proportion of erodible rocks that weather to fine sediments, and/or semiarid regions [*Meybeck et al., 2003*]. Although particulate phosphorus loads also depend on the concentration of phosphorus in the sediments, these types of environments have the potential to enhance surface phosphorus transport. Phosphorus loads in surface runoff and/or particulate phosphorus loads also tend to be greater in agricultural watersheds [*Vidon et al., 2010*] and in urbanized watersheds [*Withers and Jarvie, 2008; Sharpley et al., 2013*].

Various studies imply that runoff volume and mass of water and phosphorus from the river corridor may be greater than from the hillslope [e.g., *Buda et al., 2009*]. Hydrologic modeling studies show that the primary source of nutrient runoff (in this case, modeled nitrate and dissolved organic nitrogen and carbon) may be the riparian zone, and that higher water table rise leads to greater solute export [*Weiler and McDonnell, 2006*].

These observations are consistent with several field study findings. For example, *Kleinman et al. [2006]* noted that the foot-slope had higher runoff volumes and so produced higher total phosphorus loads than the mid-slope because the foot-slope was moister and more easily generated runoff. *Buda et al. [2009]* found that the river corridor had much higher phosphorus runoff rates compared to the hillslope (in this case, because of a fragipan or poorly permeable layer) and *Dupas et al. [2015]* noted that the largest peaks of dissolved inorganic phosphorus occurred when river corridor groundwater dominated over upland subsurface sources.

Surface transport from the river corridor to the river may occur through overland flow, particularly where it is concentrated or channelized, and through bank erosion at the interface of the channel and river corridor [e.g., *Vidon et al.*, 2010]. The balance between sediment and sorbed phosphorus deposition in the river corridor, versus erosion at the channel banks, dictates whether the area is a net source of sediment-bound phosphorus [*Noe and Hupp*, 2009]. In large floodplains that are highly connected to the channel, and have slow velocities and small loads of sediment, floodplains can store a significant amount of the river's annual sediment and phosphorus loads [*Noe and Hupp*, 2009] and net deposition likely exceeds net erosion. Most sorbed phosphorus is in the clay and fine silt fraction, which settles in backwaters and floodplain basins [*Dougherty et al.*, 2004; *Wohl*, 2014b]. In oligotrophic environments such as the Everglades wetlands, transport of phosphorus downstream may occur primarily via biotic transformations (e.g., through periphyton and flocculent detritus) [*Gaiser et al.*, 2005].

Bank erosion may contribute large fractions of the total annual suspended sediment and total phosphorus loads in some rivers. *Laubel et al.* [2003], for example, report that 15-40% of total phosphorus loads were from bank erosion. However, bank erosion may not be included in environmental models [*Kronvang et al.*, 2012]. Bank erosion is more prevalent in coarse-textured soils [*Knighton*, 1998], whereas phosphorus concentrations are greater in fine-textured sediment, so areas of rapid bank erosion are not necessarily large contributors to phosphorus loads downstream. Sediment and/or phosphorus export from the river corridor to rivers may be greater where the river corridor is vegetated with grass rather than trees and shrubs [*Kronvang et al.*, 2012]; in the middle of river reaches or where stream power is highest [*Knighton*, 1999]; and where finer-textured soils are layered over gravel and coarser-textured soils that can be readily undermined by low flows [*Miller et al.*, 2014 and references therein].

Transport through subsurface matrix flow

Subsurface contributions of phosphorus to rivers are typically assumed to be small and so have received little study compared to surface transport [Holman *et al.*, 2008]. Much of the current understanding of subsurface phosphorus transport is based on measured concentrations of subsurface phosphorus [e.g., Carlyle and Hill, 2001; Young and Briggs, 2005], and an important uncertainty is what these observations mean for transport to rivers and surface water [Holman *et al.*, 2008, citing House, 2003]. Clarification of these processes may require additional methods such as the use of conservative tracers (such as Rhodamine WT) [e.g., Fuchs *et al.*, 2009]; statistical modeling of phosphorus concentration time series with predictor variables such as hillslope and river corridor groundwater levels [e.g., Assegid *et al.*, 2015; Dupas *et al.*, 2015]; and physically-based modeling of nutrient dynamics in the river corridor [e.g., Helton *et al.*, 2014; González-Sanchis *et al.*, 2015].

Subsurface transport through preferential flowpaths, such as through naturally occurring cracks or “piping” in the soil, animal burrows, and root channels, can be a major control on soil hydraulic conductivity [Dingman, 2002] and subsurface phosphorus transport [Fuchs *et al.*, 2009], and is addressed below. In summarizing subsurface phosphorus literature, we assume that preferential flow paths do not occur unless they are specifically noted, and we draw particularly from the work of Holman *et al.* [2008] and Sims *et al.* [1998].

Higher subsurface phosphorus transport or higher phosphorus concentrations in subsurface soil solution can occur where soils are coarse and permeable, and in some cases where impermeable layers occur near the soil surface [Carlyle and Hill, 2001; Vidon *et al.*, 2010]. Fine-textured and poorly drained mineral soils are reported to have lower potential for phosphorus leaching through matrix flow, unless the soil has already sorbed high levels of phosphorus [King *et al.*, 2015, citing Reid *et al.*, 2012]. River

538 corridor floodplains commonly include alluvial deposits with gravel layers whose hydraulic conductivity
539 promotes subsurface phosphorus transport [*Fuchs et al.*, 2009].

540 Others have reported that poorly drained soils (e.g., more clayey soils) may have higher
541 dissolved and particulate phosphorus concentrations in groundwater, in cropped hillslopes and river
542 corridors alike [*Carlyle and Hill*, 2001; *Young and Ross*, 2001]. This may be due to multicollinear factors
543 associated with poor drainage or finer textured soils, including higher organic matter content and
544 greater abundance of amorphous materials in soil; shallower groundwater more prone to intersect soil
545 layers close to the surface, which typically have higher phosphorus concentrations, as noted in section
546 2.2.1, and lower redox potentials [*Young and Ross*, 2001]. Regardless of the higher concentrations in
547 fine-textured soils, flow velocities will be higher in coarser material [*Carlyle and Hill*, 2001].

548 Somewhat paradoxically, slower flow pathways (such as those through fine-textured soil) may
549 have potential for higher phosphorus loading rates despite lower velocities, because reducing conditions
550 may have developed and released dissolved phosphorus to solution. Conversely, higher flows are more
551 likely to be oxygenated. *Hendricks and White* [2000] propose a conceptual model in which upwelling,
552 oxygen-poor hyporheic waters increase the dissolution of phosphorus-iron compounds through redox
553 reactions and release of soluble phosphorus to the river bed, whereas phosphorus in downwelling,
554 oxygenated waters (for example, at the heads of riffles) is controlled primarily by sorption processes.

555 Organic soils and mineral soils poor in phosphorus-binding compounds also tend to have higher
556 rates of phosphorus leaching. Organic soils may leach accumulated organic phosphorus where
557 groundwater rises into these layers [e.g., *Evans et al.*, 2004]. This is presumably most important where
558 organic material is present in more decomposable forms (e.g., naturally low lignin content, or oxidized
559 by diking and draining in the river corridor). However, leaching of organic phosphorus or of mineral
560 phosphorus fertilizers may be exacerbated by the lack of binding compounds that slow the downward

velocity of phosphorus, such as iron, aluminum, and calcium, and by complexation of organic compounds with iron and aluminum, preventing sorption of phosphorus [Sims *et al.*, 1998; Havlin *et al.*, 2005; Reddy and DeLaune, 2008].

Although calcareous and neutral soils bind phosphorus, their sorption capacity is substantially lower than acid soils on the basis of per-unit-surface-area of soil (as noted in 2.2.1) [Havlin *et al.*, 2005]. Therefore, it is possible that these soils are more vulnerable to phosphorus leaching if fertilized, although we are not aware of any comparative studies that test this hypothesis. In soils with calcareous parent material, low calcium abundance may correlate with higher phosphorus concentrations in soil pore water [Young and Ross, 2001]. Higher background phosphorus levels have also been correlated with particular lithologies, notably in andesitic regions [Domagalski and Saleh, 2015]. The effect of land cover on groundwater phosphorus concentrations is less clear than the influence of geology, but there may be significant differences between croplands and forest [Young and Briggs, 2005].

Phosphorus concentrations in groundwater may increase when storms follow dry periods [Young and Briggs, 2005], but the ecological importance of groundwater phosphorus contributions to rivers may increase during dry periods when most stream flow is baseflow [Dupas *et al.*, 2015].

Preferential flow transport

Landscapes with preferential flowpaths are susceptible to high phosphorus exports from the hillslope to rivers [Holman *et al.*, 2008]. Preferential flowpaths may increase loading directly by increasing flow velocity and thus the volume transported per unit time. These flowpaths may indirectly increase loading because less phosphorus sorption occurs [Fuchs *et al.*, 2009], likely because there is insufficient time for equilibrium between sediment and water phosphorus concentrations to occur. This lack of sorption caused by higher flow velocities may mean that phosphorus concentrations in preferential flow are higher than in subsurface matrix flow in the river corridor [Fuchs *et al.*, 2009], and presumably in the

hillslope. Preferential flowpaths may yield a greater flux of phosphorus even when concentrations of phosphorus in the leaching soil are relatively low [Djodjic *et al.*, 2004].

Here we discuss only flow occurring in natural preferential flowpaths, as described above (e.g., cracks, animal burrows, piping, etc.). Preferential transport in surface [Kröger *et al.*, 2013] and tile drains [King *et al.*, 2015] may be a major means of phosphorus transport to rivers in agricultural watersheds.

Preferential flow, and accompanying phosphorus leaching, is greater in clayey soils with poor drainage and/or an abundance of minerals that swell and shrink on wetting and drying (such as vermiculite) [Sims *et al.*, 1998, citing Nolin *et al.*, 1991; King *et al.*, 2015]. Preferential flow is likely exacerbated when such soils become dry, or rapidly wetted and dried, causing cracking [Sims *et al.*, 1998 and citations therein; Turner and Haygarth, 2000].

Summary of phosphorus transport environments

From the above, and additional literature [e.g., Schumm, 1960; Stanford and Ward, 1993; Hendricks and White, 2000; Hill, 2000; Thomas *et al.*, 2000; Meybeck *et al.*, 2003; Wohl, 2014b], we draw the following generalizations regarding transport rates of phosphorus (Table 2; Figure 2). In the hillslope, there will be higher *potential* for surface transport of dissolved and particulate phosphorus in clayey soils; active mountain ranges and semi-arid regions, particularly those with erodible or clastic sedimentary rocks, such as sandstones, shales and siltstones, or those derived from loess; highly agricultural or urbanized watersheds; and in smaller, humid rivers, where the aquifer is perched, or of thin to intermediate thickness and feeding ephemeral rivers; and confined headwater reaches in mountainous watersheds [Schumm, 1960; Montgomery and Buffington, 1997; Meybeck *et al.*, 2003; Domagalski and Saleh, 2015]. However, the river corridor may have higher volumes of water runoff than the hillslope and/or may be the primary source area of nutrients, particularly where river corridor soils overlie a shallow impermeable layer [Hooper *et al.*, 1998; Kleinman *et al.*, 2006; Weiler and McDonnell, 2006; Buda *et al.*,

2009; *Dupas et al.*, 2015]. Alluvial and hillslope aquifer thickness may be an important control on riparian runoff volume [*Hooper et al.*, 1998; *Hill*, 2000]. The conceptual model of *Hill* [2000] was originally developed for sulfate in humid Canadian valley bottom wetlands but can be used as a starting framework for other landscapes.

For surface exchanges of particulate phosphorus between the river and river corridor, storage of river fluxes in the river corridor will tend to dominate the exchange in low-gradient floodplains with wide valleys [*Noe and Hupp*, 2009]. However, where bank erosion is high *and* the eroded bank material has higher phosphorus concentrations (for example, where finer soils have a coarser, erodible “toe”), fluxes of phosphorus from the river corridor to the river may be high [*Miller et al.*, 2014].

Phosphorus transport rates in subsurface matrix flow may be increased by any or all of the following conditions, which are somewhat inter-related (Table 2): (1) sorption capacity in the soil is low; (2) (saturated) hydraulic conductivity is high; and (3) phosphorus concentrations are higher. The first condition is likely to occur where soils have a high organic content; are coarser and so have fewer sorbing clays; or otherwise have low abundance of phosphorus-binding compounds (i.e., iron, aluminum, calcium and magnesium and amorphous materials) [*Sims et al.*, 1998; *Young and Ross*, 2001].

The second condition is also met in coarser mineral soils [*Dingman*, 2002] and peats [*Siegel*, 1988]. In the river corridor, these conditions may occur in the alluvial floodplains of larger rivers [*Fuchs et al.*, 2009]. For coarser sediment, this may include natural levees and splays where coarser material is deposited [*Wohl*, 2014b]. Organic carbon stocks tend to be greater in regions with relatively high primary productivity and seasonal cold periods that limit organic decomposition, including mountainous regions and arctic or boreal regions [*Sutfin et al.*, 2015]. The third condition may be met in the hillslope or river corridor if the soil already has a high concentration of phosphorus from background sources (e.g., the soil orders described in section 2.2.1) or fertilizer applications; or if phosphorus is otherwise

released to the groundwater by redox or other processes (see section 2.2.3 below). Zones of slower flow are more conducive to high phosphorus concentrations in solution because they tend to have lower redox potentials. This may be evident in leachate from fine-textured soils in the hillslope [Young and Briggs, 2005] and in upwelling regions of the hyporheic zone [Hendricks and White, 2000], such as at bedrock outcrops or areas where the aquifer becomes constricted by less permeable sediments [Stanford and Ward, 1993]. Besides their influence on phosphorus through redox potentials, fine sediments also tend to have higher phosphorus concentrations, as described in section 2.2.1. In the river corridor, finer-textured sediments commonly occur in backswamps and floodplain basins [Noe et al., 2012; Wohl, 2014b].

The third condition that can increase phosphorus transport in subsurface matrix flow may also be met where groundwater intersects the surface soil, a zone in which phosphorus concentrations are generally higher. Subsurface connectivity between the hillslope and river corridor will also tend to be higher where the hillslope aquifer is of intermediate to large thickness. Connectivity directly from the hillslope to the river will be enhanced where thick aquifers in the hillslope are paired with a river corridor with permeable, deep soils: here, deep groundwater flow effectively bypasses the river corridor.

Preferential flowpaths will tend to be more prevalent in soils with shrink-swell clays, such as Vertisols, and some poorly drained soils with carbonate, mafic, or metamorphic shale parent material [Thomas et al., 2000]. Preferential flowpaths occur in soils with large macropores, such as those underlying well vegetated hillslopes in steep terrain with abundant biological activity [Wohl, 2014b].

These flowpaths are particularly common in more arid regions, where shrink-swell clays or erosion of macropores give rise to larger soil “pipes”. Preferential flowpaths also occur in karst environments

developed in limestone geology [Wohl, 2014b] and along joints and fractures in any type of bedrock [Onda et al., 2001].

Animals and plants can also transport phosphorus from the river to the river corridor, or to the hillslope. For example, marine-derived phosphorus from salmon carcasses may be consumed by predators or invertebrates in the riparian zone, and then be incorporated into soils and vegetation of the river corridor or further upslope [Naiman et al., 2005]. This may be particularly important in the phosphorus dynamics of small headwater streams in the Pacific Northwest of North America, although marine-derived phosphorus from returning salmon may have decreased by 90% or more compared to predevelopment levels [Gresh et al., 2000].

2.2.3. Transformation

Transformations in the hillslope and river corridor are controlled by the factors described under section 2.2.1. These multicollinear factors include concentration and form in soil of phosphorus, phosphorus-binding compounds, other compounds whose stoichiometry influences decomposition (carbon and nitrogen), electron acceptors (such as oxygen, nitrate, iron, manganese, and in some cases, sulfate) and redox potential, and pH. Also important are the concentrations of phosphorus and phosphorus-binding compounds in inflowing waters relative to concentrations in the soil, which are a product of past and present loading rates. These in turn are affected by the hydrologic pathways through which the runoff arrives, the ratio of the area contributing runoff relative to the receiving area, and the flow velocity and residence time, described in more detail under section 2.2.2. Anaerobic subsurface pathways often deliver higher loads of dissolved inorganic phosphorus [Hendricks and White, 2000; Carlyle and Hill, 2001]. River corridors or wetlands with large hillslope areas relative to the receiving area or faster flow-through tend to have shorter residence times of water [e.g., Jencso et al., 2010], and so to have lower phosphorus retention rates [Richardson and Vepraskas, 2000; Woltemade, 2000].

These hydrologic factors also influence phosphorus transformations by affecting the length of saturation and thus the soil's ability to (de)sorb phosphorus, develop redox conditions, and increase or slow rates of organic matter decomposition. Therefore, transformation (or mobilization) and delivery to the river corridor or river are closely linked [Beven *et al.*, 2005].

Common phosphorus biogeochemical processes include mineralization and uptake of organic phosphorus; mineral precipitation and dissolution; sorption (abiotic retention of inorganic phosphorus in soils); and molecular diffusion [Sharpley *et al.*, 2013]. Oxidation-reduction (redox) processes indirectly affect movement of phosphorus between sediment and solution [Reddy and DeLaune, 2008]. Processes commonly occur together. For example, phosphorus released from reduced iron may then be adsorbed to the soil surface, only to be precipitated with iron as vivianite, or as ferric phosphates when diffused to an oxidized zone [Moore and Reddy, 1994; Reddy and DeLaune, 2008].

In general, the variations in transformations of phosphorus among different landscape characteristics (such as geology) are not as well studied as abundance and transport. Individual studies have described phosphorus transformations in different watersheds with distinct mineralogies [e.g., Darke *et al.*, 1996; Litaor *et al.*, 2003; Lapworth *et al.*, 2011]; evaluated the correlation of phosphorus with abundance of phosphorus binding compounds or other soil characteristics [e.g., Vanek, 1993; Evans *et al.*, 2000; Prior and Johnes, 2002]; or (in a few cases) proposed conceptual models of the effects of redox level gradients on phosphorus release, or of landscape-scale hydrologic characteristics on the development of redox conditions or an index-based susceptibility to phosphorus loss [e.g., Hill, 2000; Andersen and Kronvang, 2006; Reid *et al.*, 2012].

However, to our knowledge, a conceptual model has not yet been put forward to predict what transformations tend to dominate phosphorus dynamics based on distinct landscape, hillslope, or river corridor characteristics, such as mineralogy in combination with hydrologic regime (although some

aspects are described in *Vidon et al.* [2010]; *Noe et al.* [2012]; and *Sharpley et al.* [2013]). Lab [e.g., *McLaughlin et al.*, 1981] and field [e.g., *Carignan and Vaithiyathan*, 1999] studies, however, suggest that such broad generalizations are possible.

We suggest that developing and testing hypotheses about these broad variations in phosphorus dynamics, such as the generalizations we outline below, would be an important contribution to the understanding of river water quality, river and river corridor protection, nutrient management, and conservation practices. Testing could occur through paired watershed studies, modeling, laboratory experiments, meta-analysis from published literature, or some combination of these methods. Testing will likely be most fruitful where it crosses disciplines, such as soil science, biogeochemistry, geomorphology, river ecology, and hydrology [*Haygarth et al.*, 2005]. We outline key areas of potential future work and possible approaches in section 4.

Below, we discuss some of the main processes and controls for transformations of phosphorus. This discussion is also summarized in Table 3 and in Figure 3. Although any of these processes may occur in the hillslope and river corridor, the controls and therefore the rate of processes are likely to vary spatially. We attempt to describe possible general trends in this variation. Where it is not noted whether findings are for the river corridor or the hillslope, we expect the statement to be generally applicable to hillslope and river corridor alike (i.e., plain font in Table 3). Findings more specific to the river corridor are noted as such in the text, and in bold font in Table 3.

Net immobilization and mineralization

As noted above, a large fraction of soil phosphorus is commonly in organic form, and most is not readily decomposable. The balance between net mineralization (release of phosphorus) and net immobilization (storage of phosphorus) is controlled by hydrologic characteristics (soil moisture and oxygen availability); the organic carbon to organic phosphorus ratio (net mineralization is enhanced at lower

ratios, and net immobilization at higher); organic matter quality (particularly lignin content and particle size); pH; soil temperature; the biotic communities present; and associated enzyme activities [Richardson and Vepraskas, 2000; Havlin et al., 2005; Sylvia et al., 2005; Reddy and DeLaune, 2008]. Riparian and hillslope vegetation are clearly a strong control on many of these variables, and are also greatly influenced by the geomorphic, lithologic, climatic, and hydrologic setting [Tabacchi et al., 1998; Polvi et al., 2011]. However, details on the influence of vegetation type on phosphorus transformations are beyond the scope of this work.

Most mineralization of organic phosphorus in wetlands is biotic, but organic phosphorus can also be mineralized abiotically to dissolved organic form by leaching from dying plant tissue, hydrolysis, and photolysis (breakdown via ultraviolet light) [Reddy and DeLaune, 2008]. Decomposition rates are much slower in anaerobic conditions [Richardson and Vepraskas, 2000], are commonly most rapid where there is frequent wetting and drying [Noe, 2013], and are optimized at near-neutral pH and hot soil temperatures (30-45°C) [Sylvia et al., 2005]. Mineralization is likely particularly important where there are “pulses” of organic phosphorus to nutrient-poor rivers, as for small streams in the Pacific Northwestern United States where spawning salmon provide a large percentage of annual phosphorus (see section 2.2.1, above), and in oligotrophic systems such as the Everglades [e.g., Noe et al., 2001].

Key processes and controls for inorganic phosphorus cycling

Dissolved inorganic phosphorus is biologically available and rapidly taken up by biota, normally maintaining low soluble phosphorus concentrations in the soil profile [Reddy and DeLaune, 2008]. Adsorption and precipitation are the important inorganic phosphorus retention mechanisms in acid and alkaline soils under aerobic conditions. Similarly, desorption and dissolution are key mechanisms releasing inorganic phosphorus to solution. Adsorption governs phosphorus uptake from solution at

lower phosphorus concentrations. At higher concentrations, above the soil's adsorption capacity, precipitation reactions dominate [Havlin *et al.*, 2005].

The term “sorption” is used to refer to a variety of reversible and non-reversible combinations of phosphorus with other compounds. As McGechan and Lewis [2002, p. 19] state: “The processes of sorption of [phosphorus] in soil are very complex, and the very extensive literature on the subject can present a very confusing picture regarding the mechanisms of sorption. Nevertheless, there are some broad trends and some general comments can be made.” Sorption requires contact between soil and water to occur [Reddy *et al.*, 1999; Richardson and Vepraskas, 2000]. Sorption may occur in several steps, beginning with relatively fast adsorption via reversible surface tension attraction of a molecule to the surface, or chemical, non-reversible bonds, and followed with slower absorption of phosphorus via penetration of molecules or atoms of one phase by another [Reddy and DeLaune, 2008].

(De)sorption

First-order controls on phosphorus sorption direction (whether release to water or retention in the sediment) and rate are commonly reported as phosphorus concentrations in sediment versus influent; mineralogy, which is related to texture because of the higher sorption capacity of clay minerals; flow velocity; and in certain environments, the effect of redox on phosphorus concentrations in sediment and pore water and on soil sorption capacity and intensity (described below). Soil moisture content has also been reported as important for *net* phosphorus mineralization—encompassing release of phosphorus through breakdown of organic matter—and from sorption, redox, and other processes [Noe *et al.*, 2012].

A key control on sorption is the concentration of phosphorus in inflowing waters to concentrations in soil pore water. If inflowing phosphorus concentrations are substantially higher, sorption of phosphorus and retention in the sediment commonly occur. If inflowing concentrations are low, soils or

sediments commonly release phosphorus into the surrounding waters [Reddy *et al.*, 1999]. Paradoxically, this may mean that as phosphorus concentrations in inflowing waters are lowered (for example, by nutrient management plans uphill of a riparian zone) or as natural hydrology of an area is restored (for example, by levee breaching), areas that were once phosphorus sinks may become net sources for some time [e.g., Wong *et al.*, 2011; Sharpley *et al.*, 2013]. Mineralogy controls the amount of inorganic phosphorus that may be sorbed (sorption capacity) and the strength with which that phosphorus is held (“buffer intensity”, as noted above in “Abundance”) [Reddy *et al.*, 1999]. Organic soils typically contain few phosphorus-binding compounds, and may complex with iron and aluminum, preventing sorption of phosphorus. Therefore, (de)sorption is likely not an important process in most organic soils.

In acid soils, most phosphorus sorption is by iron and aluminum oxides and oxyhydroxides. In alkaline soils, phosphorus sorption occurs chiefly by calcium carbonate [Reddy and DeLaune, 2008], with variations in the sorption capacity and buffer intensity by mineralogy—e.g., amorphous materials commonly sorb more phosphorus but less tightly. A third control on sorption is the residence time or flow velocity. Sorption is limited in fast flows [Fuchs *et al.*, 2009] because these reactions take hours to days to come to equilibrium [Reddy and DeLaune, 2008].

Other controls include pH, organic matter, and temperature. Sorption decreases with increasing pH in acid soils [Noe *et al.*, 2012]. Organic matter tends to inhibit adsorption. Adsorption increases with hotter temperatures [Havlin *et al.*, 2005].

As described above in section 2.2.1, the river corridor may have a higher concentration of iron and aluminum oxides and amorphous materials than the hillslope due to preferential erosion and deposition of fine soil particles and the tendency of flooding to decrease the crystallinity of iron oxides. Although these traits in general may increase sorption capacities in the river corridor, there are substantial

789 variations within the corridor itself (e.g., backswamps and floodplain basins may have finer textures and
790 so different sorption capacity than levees).

791 ***Precipitation and dissolution***

792 The controls on precipitation and dissolution are the concentration of phosphorus in soil and inflowing
793 water, the particular minerals present in the soil and their solubility, and pH. At higher influent
794 concentrations of phosphorus that exceed the adsorption capacity of the soil (dictated by the
795 phosphorus solubility of the specific soil minerals), precipitation may dominate inorganic phosphorus
796 dynamics. Precipitation has been described as an important means of phosphorus retention in
797 calcareous river corridors and wetlands, in particular [House and Denison, 2000; Noe et al., 2001;
798 Sánchez-Pérez and Trémolières, 2003; Evans et al., 2004; Lapworth et al., 2011]. Precipitation appears to
799 be less frequently described as important in acid soil phosphorus dynamics, with some exceptions: for
800 example, House and Denison [2000] report precipitation of phosphorus as vivianite as an important
801 control under highly reduced conditions.

802 However, at higher phosphorus concentrations, it is not always possible to distinguish
803 adsorption and precipitation [Reddy and DeLaune, 2008], so it is possible that this retention mechanism
804 may occur more frequently in acid soils than is commonly reported in field studies. In calcium- and iron-
805 dominated soils, Moore and Reddy [1994] suggested that precipitation of phosphorus with calcium
806 minerals controlled the amount of phosphorus in solution under anaerobic conditions in a lake, whereas
807 precipitation as ferric phosphates dominated in aerobic conditions.

808 Additionally, when pH in the hillslope or river corridor changes, precipitation and dissolution
809 may occur [Havlin et al., 2005]. Decreases in pH release calcium-bound phosphorus into solution,
810 whereas increases in pH generally increase solubility of iron- and aluminum-associated phosphorus

[Reddy and DeLaune, 2008]. Conversely, increases in pH in calcareous soils and decreases in pH in acid soils decrease phosphorus solubility [Havlin et al., 2005].

The river corridor environment may be particularly conducive to changes in pH through photosynthesis, which can greatly increase pH in standing water (as in a floodplain) over diurnal timescales, or via decomposition of organic matter and redox reactions, which decrease pH in the river corridor [Reddy and DeLaune, 2008]. Such reductions in pH in the river corridor may cause calcareous sediments deposited on the floodplain to release soluble phosphorus, whereas neighboring acid soil floodplains sequester phosphorus under similar conditions [Carignan and Vaithiyanathan, 1999].

Oxidation-reduction (redox) and effects of wetting and drying on phosphorus dynamics

Perhaps one of the least well understood yet most critical aspects of phosphorus dynamics in the river corridor is the influence of changes in iron under redox conditions [Zhang et al., 2010 and references therein], and the associated effects of saturation via flooding or elevated water tables on phosphorus dynamics. Redox processes are relevant to phosphorus cycling where iron is available; the soil is saturated; organic matter is present that can be decomposed and oxidized; and most available oxygen, nitrate and manganese have already been reduced (more or less in this order) [Richardson and Vepraskas, 2000]. Other controls on the effects of redox and sustained saturation on phosphorus dynamics are pH (phosphate release from iron minerals appears to increase with lower pH) [Noe et al., 2012]; the presence of iron-reducing microbial communities [Reddy and DeLaune, 2008]; the degree of crystallinity (amorphous forms of iron are preferentially reduced) [Richardson and Vepraskas, 2000]; and the means by which most phosphorus is bound in the soil (e.g., as ferric phosphates, sorbed to amorphous material).

Some work suggests redox processes are a “tradeoff” in inorganic phosphorus retention in the river corridor [e.g., Darke and Walbridge, 2000], whereas other studies suggest redox processes may be

834 responsible for (sometimes large) fluxes of phosphorus from the river to the river corridor in oxygen-
835 depleted groundwater [e.g., *Mulholland, 1992; Carlyle and Hill, 2001*]. Yet other studies indicate
836 increases in phosphorus sorption under reducing conditions [e.g., *Zhang et al., 2010*]. The ambiguity
837 regarding effects of redox conditions on phosphorus may reflect the diverse mechanisms through which
838 these effects occur, and the fact that field studies may identify changes in phosphorus flux under
839 reducing conditions, but rarely identify the particular mechanism through which this occurs.

840 Specific mechanisms that enhance phosphorus release to water under redox conditions include
841 the dissolution of ferric phosphate compounds in iron-dominated soils and of phosphorus protected by
842 iron coatings of soil particles as the reduced iron becomes soluble. Increased desorption potential as the
843 bonding energy of reduced iron with phosphorus weakens also enhances phosphorus release to water,
844 as does adsorption of dissolved organic matter in place of phosphorus. If saturation persists and redox
845 levels become low, the reduction of sulfate and accompanying reactions with iron releases phosphorus
846 [*Reddy and DeLaune, 2008; Zhang et al., 2010*]. Although not specifically associated with redox
847 conditions, phosphorus release to water in the river corridor under saturation or wetting may be
848 enhanced by desorption if inflowing waters are of lower phosphorus concentration. Flushing of organic
849 phosphorus built up in the soil, particularly in spring or winter, can enhance phosphorus release [*Fabrel*
850 *et al., 1996; Prior and Johnes, 2002*]. Phosphorus can be released via soil cracking under repeated
851 wetting and drying, and development of preferential flow paths [*Heeren et al., 2010; Mittelstet et al.,*
852 *2011*], whose higher flow velocities may limit sorption of phosphorus from solution into soil. Greater
853 crystallinity of iron oxides with repeated wetting and re-oxidation of soils can also release phosphorus
854 because less phosphorus is held by sediments, but more tightly [*Darke and Walbridge, 2000*]. Finally,
855 saturation that lasts for long periods selects for a microbial community with lower demand for dissolved
856 inorganic phosphorus, potentially allowing phosphorus release to water in the river corridor [*Reddy and*
857 *DeLaune, 2008*].

Phosphorus uptake from solution by sediments is enhanced under reduced conditions by the larger number of sorption sites provided by ferrous (reduced) iron, despite the lower bonding energy with phosphorus and so higher potential for desorption. Similarly, increasing abundance of amorphous or non-crystalline iron may persist after flooding, providing more sorption sites with lower bonding energy. Also important are reactions with the reduced, ferrous iron, such as the formation of vivianite (in iron- and phosphorus-rich soils), that remove phosphorus from solution [Darke and Walbridge, 2000; Reddy and DeLaune, 2008]. Phosphorus storage in sediments may be enhanced under flooded or wet conditions (without relation to redox processes) by deposition of coarse sediment with lower sorbed phosphorus concentrations in high-energy portions of the floodplain [Fabrel et al., 1996]. If saturation persists for a long time, phosphorus storage in sediments may also be enhanced via decreasing biotic breakdown of phosphorus by inhibiting fungi and activity of phosphorus enzymes [Reddy and DeLaune, 2008].

In addition to these “tradeoffs” in phosphorus retention, another complication in understanding redox effects is that soil phosphorus made soluble through reduction of iron may be removed from solution again before it is transported to rivers. Where reduced waters are subsequently oxidized, ferrous iron may re-precipitate at the soil-water interface and remove phosphorus from solution [e.g., Moore and Reddy, 1994; Young and Ross, 2001]. This may be a critical control on phosphorus dynamics in some environments [Moore and Reddy, 1994].

The role of reducing conditions in phosphorus dynamics of calcium-rich soils appears even less clear than for acid soils, although small amounts of iron may govern phosphorus dynamics in calcareous soils [Havlin et al., 2005]. Besides the work of Moore and Reddy [1994] in iron- and calcium-dominated lakes, little research appears to have been conducted on this topic, but this could be a useful area of future research to better understand phosphorus retention in calcareous river corridors. An additional

complication is that phosphorus enrichment in calcareous, oligotrophic systems (e.g., the Everglades) may shift soils from oxidized to reduced conditions [Noe *et al.*, 2001]. It is unclear how this mechanism may be related to feedbacks in (de)sorption or other phosphorus transformations.

Another area that has been poorly studied is the influence of nitrate on redox-related release of phosphorus in the river corridor. Although work in wetlands and lab studies show that denitrification must be more or less complete before reduction of iron begins [Reddy and DeLaune, 2008], we are aware of only two studies noting the effects of nitrate removal on soluble phosphorus release under potentially reducing conditions in the river corridor [Young and Briggs, 2005; Hoffmann *et al.*, 2006]. To our knowledge, the effect of the presence of nitrate on redox-related release of phosphorus is not yet included in river corridor biogeochemical models. This would be a useful component of future research and modeling, especially as restored or rehabilitated riparian buffers in the river corridor intended to remove nitrate may also inadvertently promote redox-related releases of phosphorus [Vidon *et al.*, 2010].

Summary of phosphorus transformation environments

Generalizing from the literature described above, we hypothesize the following spatial variations in phosphorus transformations (Table 3, Figure 3). Assuming that net phosphorus immobilization or mineralization tracks organic carbon decomposition trends, phosphorus immobilization will tend to be enhanced in colder, wet climates with prolonged saturation (examples from the carbon literature are arctic or boreal areas, and the mountainous region of river networks) [Sutfin *et al.*, 2015]. Physical retention of organic matter in the river corridor will tend to be greater in flatter regions (such as larger floodplains) versus steeper river reaches. Decomposition will tend to be more rapid in warmer environments with abundant moisture, such as some tropical regions [Sutfin *et al.*, 2015], and areas with frequent wetting and drying [Noe, 2013]. Such rapid dry and moist cycles may occur more commonly in

regions with perched or thin aquifers [Hill, 2000]. These processes may be especially important in moderately and highly weathered mineral soils because (1) a higher fraction of total background phosphorus is in organic form; and (2) more of this organic phosphorus is recalcitrant, so decomposition may have greater biological importance [e.g., Crews *et al.*, 1995].

Sorption and desorption will both tend to be enhanced in conditions where soils are mineral with lower organic content, acid and/or volcanic, and moist; flow is not rapid (e.g., not in preferential flowpaths and not in coarse-textured soils with extremely high hydraulic conductivity); and finer-textured soils are present, such as backswamps and other lower-energy environments of the river corridor (see sections 2.2.1 and 2.2.2). Flow conditions may be more likely to be met where the groundwater table does not fluctuate rapidly throughout the year—potentially in intermediate to thicker aquifers. Sorption will generally be enhanced where inflowing waters have higher phosphorus concentrations than in the soil (given that the soil is not saturated with phosphorus), such as some river corridor reaches [Darke and Walbridge, 2000] and deeper in the hillslope soil profile [Walker and Syers, 1976]. Sorption will also tend to be an important control on phosphorus in the oxygenated, faster-flowing, downwelling hyporheic zones (e.g., at the heads of riffles) [Hendricks and White, 2000]. Because of greater abundance of iron and aluminum oxides in weathered soils, and warmer temperatures [Havlin *et al.*, 2005], sorption may be enhanced in areas with a more moist and warm climate, such as the humid tropics.

Desorption will generally be enhanced where inflowing water has lower concentrations of phosphorus than soil. This may occur more commonly where soil phosphorus concentrations are already high, such as surface hillslope soils [Walker and Syers, 1976; Jobbágy *et al.*, 2001], some reaches of the river corridor where hillslope soils with higher phosphorus concentrations have been deposited, and

926 historically heavily cultivated areas that have been (re)flooded or where upstream nutrient loads have
927 been lowered (as noted above).

928 Precipitation and dissolution will tend to influence phosphorus dynamics more heavily where
929 nutrient loads in rivers are already high [*Spink et al.*, 1998], such as the river corridors of larger rivers
930 which drain more urban and agricultural lands [*Spink et al.*, 1998; *Withers and Jarvie*, 2008]. Larger
931 rivers might be more prone to natural fluctuations in pH than smaller rivers through accumulation of
932 organic matter in the river corridor, as noted above, and heightened photosynthesis from greater
933 availability of light. Precipitation and dissolution may be an especially important mechanism in
934 calcareous watersheds and in highly reduced soils with substantial amounts of both iron and
935 phosphorus (as noted above) [*Moore and Reddy*, 1994; *Reddy and DeLaune*, 2008], but the importance
936 of this mechanism will depend on the mineral composition of the specific soil and present and past
937 loading rates of phosphorus.

938 Redox-related processes are more likely to dominate inorganic phosphorus dynamics in areas
939 where saturation lasts for some time; flow velocities are relatively slow and flow is oxygen-depleted;
940 denitrification rates are high relative to nitrate loading rates; and iron and organic matter are relatively
941 abundant. Redox processes presumably have little impact on phosphorus dynamics in calcareous soils
942 unless significant amounts of iron are also present [e.g., *Moore and Reddy*, 1994]. The necessary flow
943 conditions are more likely to be met in landscapes with intermediate to large aquifers that maintain
944 relatively constant groundwater supply to perennial streams, with smaller fluctuations in water table
945 elevation, and where the river corridor soils are not so deep and permeable as to cause “bypass flow”
946 from the hillslope to rivers [*Hill*, 2000]. Redox processes in this kind of “bypass flow” would likely be
947 limited by the common trend in soils of decreasing carbon concentrations with depth [*Jobbágy and*

948 *Jackson, 2000*], as well as being limited where fine-textured soils occur [e.g., *Carlyle and Hill, 2001*;
949 *Young and Ross, 2001*].

950 Other conditions necessary for the occurrence of redox processes are more likely to be met in
951 the surface soils of the river corridor than the hillslope, particularly in the low-energy environments and
952 finer-textured soils along the river corridor that promote poor drainage, such as reaches with wider
953 valleys and lower gradients. Redox is more likely to occur in river corridors than in hillslopes because the
954 riparian water table is generally closer to the surface, organic matter has accumulated, and there may
955 be more iron and aluminum oxides and oxyhydroxides because of deposition from the hillslope and river
956 (as noted in section 2.2.1). Upwelling, oxygen-poor hyporheic waters will also tend to increase the
957 dissolution of phosphorus-iron compounds through redox reactions and release of soluble phosphorus
958 to the river bed [*Hendricks and White, 2000*].

959 **3. Conceptual model**

960 The conceptual model we outline below represents hypotheses about average, long-term patterns
961 of phosphorus dynamics and their drivers over space and time, and what conditions may enhance
962 certain dynamics (Figure 4). These hypotheses are based on field and modeling studies from multiple
963 disciplines, with diverse measurements and spatiotemporal resolution. We suggest that these
964 hypotheses be tested; a variety of approaches are possible (see section 4).

965 To apply the conceptual model, users could begin by characterizing the components outlined in
966 Figure 4, using the regional- or global-level databases, references and models in Table 4 as a starting
967 point. We illustrate such an application of the conceptual model below. Most of these data sources have
968 a relatively coarse spatial resolution, so site-specific, higher resolution data are preferable where
969 available. Data sources in Table 4 may be used to generally characterize abundance, but these sources
970 only suggest important controls on transport and transformation for particular environments.

Characterizing underlying transformation and transport processes may also require modeling, monitoring, and additional approaches (section 4).

We recognize that humans have altered the global phosphorus cycle [Rockstrom, 2009] and the transport and transformation of phosphorus from hillslopes and through river networks in many watersheds [Withers and Jarvie, 2008]. The effect of biota and in-stream processes on nutrients in the river and river corridor is also important, but has been addressed extensively elsewhere [e.g., Reddy et al., 1999; Ensign and Doyle, 2006; Reddy and DeLaune, 2008; Withers and Jarvie, 2008; Noe, 2013]. Our conceptual model considers phosphorus river corridor dynamics in the context of the surrounding larger landscape without explicitly evaluating the effects of human alteration, detailed biotic interactions, or in-stream processes. We recommend that future work develop a conceptual model of the effects of human alteration on river corridor phosphorus dynamics, building on work such as Sharpley et al. [2013] to include impacts of flow regulation, channelization, and river management. As a starting point for future work, we note select human activities with potential to affect river corridor phosphorus dynamics, and the possible effect of these activities on soluble phosphorus in the river corridor (Figure 4). The anthropogenic influences listed are divided into abundance [Carpenter et al., 1998; Sims et al., 1998; Gresh et al., 2000; Withers and Jarvie, 2008; Macdonald et al., 2012], transport [Austin et al., 1996; Sánchez-Pérez and Trémolières, 2003; Withers and Jarvie, 2008; Zehetner et al., 2008; Ciotti et al., 2010; Kronvang et al., 2012; Sharpley et al., 2013; King et al., 2015], and transformation [Snyder and Morace, 1997; Macdonald et al., 2012]. However, a single human activity may influence any of these three aspects of phosphorus dynamics (e.g., levee construction may reduce phosphorus transport between the river and river corridor, as well as redox transformations). We also illustrate in the example application (section 3.5.5) how the conceptual model of natural processes may highlight sensitivity of phosphorus dynamics to anthropogenic change.

Our conceptual model is as follows (Figure 4): delivery of phosphorus from the hillslope or river corridor downslope and to the river will tend to be greater where at least some of these conditions are met: background phosphorus is more abundant; transport rates are higher; and phosphorus transformations (or their lack) coincide in form and timing with the type of flow paths (e.g., surface runoff, preferential flow). In some cases, any of the above conditions (abundance, transport, or transformation) may be elevated without leading to high present-day phosphorus deliveries downslope and to the river. In other cases, only one condition may need to be “optimal” to lead to high phosphorus loading to the river corridor or river. For example, water draining from soil profiles may have higher phosphorus concentrations where there are preferential flowpaths (high transport), but not where soil phosphorus concentrations are higher (high abundance) [Djodjic *et al.*, 2004]. Areas where phosphorus is abundant but present-day transport rates minimal can represent a “hot spot” for high future rates of phosphorus export to rivers [Sharpley *et al.*, 2013]. Human influences have the potential to alter natural river corridor phosphorus dynamics by changing abundance, transport, and/or transformation of phosphorus and reactive compounds.

3.1. Role of geology and climate

At the landscape level, geology and climate control rates and mechanisms of weathering and soil types, as well as partially determining the biota of a given region. Geology and climate also control hydrogeomorphology and hydrologic connectivity among different elements of the landscape (e.g., hillslope and river corridor) at regional and local scales [Beechie *et al.*, 2013].

Lithology and weathering are major controls on phosphorus abundance in soils and aquifers, and the potential for phosphorus transport and transformations. Geology and climate are also an important control on transport mechanisms of phosphorus. Stream fine sediment loads (and so potential for sorbed surface phosphorus transport) tend to be greater in tectonically active mountain

1017 ranges and semi-arid zones, particularly where there are erodible or clastic sedimentary rocks.
1018 Lithologies with higher potential for preferential flow transport may include limestone, in which karst
1019 develops; bedrock with joints and fractures; and a range of rock types from which shrink-swell clays
1020 tend to weather, such as carbonates, mafic rocks, or shale. Preferential flow may also be promoted in
1021 soils resulting from diverse lithologies and in which macropores develop through high biological activity
1022 or soil cracking, or where soil piping occurs. Preferential transport increases subsurface phosphorus
1023 deliveries to the river corridor and river in two ways: larger volumes transported per unit time, and lack
1024 of sorption due to higher flow velocities.

1025 Where sediment production is lower and preferential flow less dominant, higher rates of
1026 phosphorus loading in subsurface matrix flow may be enhanced where phosphorus-binding compounds
1027 are lower (e.g. organic soils) and the matrix is coarser and has higher hydraulic conductivity. Examples of
1028 the latter may include volcanic tephra; peat; sand; and gravel. Phosphorus transport in subsurface
1029 matrix flow may also be enhanced in areas where phosphorus abundance is greater (organic, volcanic,
1030 and less weathered soils, sites of fine sediment deposition, and surface soil horizons), and where redox
1031 conditions develop in finer-textured soils (see below).

1032 Climate also directly influences transformations through temperature. Net immobilization is
1033 enhanced in cold climates such as at higher latitudes and higher elevations. Net mineralization,
1034 particularly where moisture is available, and sorption rates are generally greater in warmer
1035 environments.

1036 **3.2. Role of soil type**

1037 Geology and climate also influence soil type (mineralogy and soil texture) and degree of
1038 weathering. In special circumstances, atmospheric and marine inputs may be important in the

1039 background total phosphorus budget of a landscape. Examples include where ash, wind-eroded fine soil,
1040 or biomass burning is high, or where there are large influxes of fish from the ocean to rivers.

1041 Soil type and degree of weathering are major controls on background abundance of
1042 phosphorus; phosphorus binding compounds and their ability to sorb or release phosphorus; availability
1043 of electron acceptors; and on transport and transformations of these compounds. Together with past
1044 phosphorus loading rates, these factors control the likelihood that soluble phosphorus concentrations
1045 will change with particular environmental alterations (such as the development of reducing conditions
1046 and changes in pH).

1047 Volcanic, organic, and little weathered soils commonly have higher background total
1048 phosphorus concentrations, whereas highly weathered soils have the least background total
1049 phosphorus. Finer soils have greater sorption capacity and generally higher phosphorus concentrations.
1050 Because they are typically slower to drain, these soils may also influence phosphorus transformations
1051 through development of reducing conditions under the right hydrologic and chemical settings.
1052 Therefore, geologic settings (active mountain ranges, clastic sedimentary rocks, loess-derived soils) and
1053 geomorphic settings (toe-slopes, backswamps, etc.; see below) that give rise to finer sediments are
1054 important controls of phosphorus dynamics.

1055 Soils that are high in organic content or predominantly organic have little capacity for
1056 phosphorus (de)sorption or precipitation and dissolution due to a lack of phosphorus-binding
1057 compounds. Although the existence of high organic content suggests net immobilization dominates
1058 phosphorus dynamics, soils high in organic matter may also leach phosphorus into solution where
1059 groundwater intersects organic layers. Some organic soils such as peats may have high hydraulic
1060 conductivities (as noted above), which together with the minimal sorption in these soils may lead to
1061 high subsurface transport rates.

1062 Phosphorus in acid and calcareous mineral soils is sensitive to transformation via sorption
1063 (desorption) where inflowing waters have a higher (lower) concentration of phosphorus than sediments.
1064 Of mineral soils, volcanic soils and highly weathered soils are particularly rich in phosphorus-binding
1065 compounds. These iron and aluminum oxides have a lower sorption capacity, but bind phosphorus more
1066 tightly. Conversely, less weathered soils are less abundant in iron and aluminum oxides, and have a
1067 higher sorption capacity but lower bonding energy with phosphorus. Therefore, desorption potential
1068 from less weathered soils could be higher.

1069 Mineral calcareous soils sorb less phosphorus per unit surface area of soil than mineral acid
1070 soils. They are susceptible to precipitation reactions (e.g., when pH increases or phosphorus
1071 concentrations are high) and dissolution reactions (e.g., from pH decreases as organic matter
1072 decomposes in the floodplain), but saturated conditions likely do not induce redox-related changes in
1073 phosphorus in solution unless the soils also have significant amounts of iron.

1074 Acid soils can sorb a greater quantity of phosphorus per unit surface area of soil. Acid soils are
1075 susceptible to phosphorus transformations through changes in pH and through redox-related processes
1076 under the right hydrologic and soil conditions (see below). Acid soils are also susceptible to
1077 precipitation, particularly in conditions that are both reduced and iron-rich, and to dissolution under
1078 increases in pH (e.g., via photosynthesis).

1079 In acid mineral soils where reducing conditions develop, the literature is not clear on the net
1080 effect on soluble phosphorus. Many field studies reviewed for this paper suggest reducing conditions
1081 cause releases of soluble phosphorus to streams and groundwater. This may not be the case where
1082 reduced waters from the hillslope or river corridor are re-oxygenated before entering the river (e.g.,
1083 where iron and phosphorus can diffuse and re-precipitate in the oxygenated zone) and where significant

amounts of phosphorus and iron are present for vivianite formation. However, the net effect of reducing and wetting conditions on river corridor phosphorus needs more study (see section 4).

3.3. Role of hydrogeomorphology

Another important landscape level control is hydrogeomorphology, also dictated by landscape-scale controls. Hydrogeomorphology affects transport mechanisms by influencing the degree, timing and duration of hydrologic connectivity among hillslope, river corridor, and river. Hydrogeomorphology also dictates the depositional and erosional environments, and physical and chemical characteristics of aquifers and flow paths. These characteristics are key controls on transformations of phosphorus, and include: frequency and duration of wetting; velocity; depth of flowpaths; and concentration of dissolved constituents in surface and groundwater (see section 3.4, below). However, the effect of similar hydrologic conditions on phosphorus transformations may be different for distinct soil types and conditions. *Noe* [2013] provides an excellent review of the effects of hydrogeomorphology on floodplain nutrient cycling. *Harvey and Gooseff* [2015] concisely review the role of fluvial geomorphology in hydrologic exchanges and biogeochemistry within the river corridor.

Confined, steeper channels or headwater streams may occur within landscapes of sediment production as hillslope surface fluxes are quickly delivered to rivers, with little transport from the river to the river corridor, coarser grain sizes [*Montgomery and Buffington*, 1997], and potentially higher soil organic content in the river corridor [*Noe et al.*, 2012].

Wider valleys with shallower gradients may promote higher rates of surface transport from the river into the river corridor and net retention of total phosphorus--unless, perhaps, bank erosion exceeds deposition of sediment in the river corridor [*Noe and Hupp*, 2009]. In this case, surface transport of phosphorus from the river corridor to the river may be high if banks are erodible and also

1106 have fine sediments with higher phosphorus concentrations, e.g. banks with coarser toes overlain with
1107 clayey soils.

1108 In the river corridor, lower-energy depositional sites for fine sediment (such as backswamps,
1109 floodplain lakes, and toe-slopes) will tend to have higher phosphorus concentrations as well as greater
1110 abundance of phosphorus-binding compounds (e.g., clays). With the right hydrologic conditions (below),
1111 finer soils have higher potential for (de)sorption, and/or may promote redox-related transformations of
1112 phosphorus (as noted above) because of slower drainage. Redox-related transformations may occur in
1113 the hillslope, but are likely more prevalent in river corridors, where organic matter content and
1114 groundwater levels are typically higher. Sand splays, natural levees, and higher-energy depositional
1115 environments in the river corridor promote higher rates of subsurface matrix flow, and thus may have
1116 lower (de)sorption rates and lower likelihood of redox-related phosphorus transformations.

1117 Geomorphic setting is also related to local and regional hydrology. Aquifer thickness and
1118 variability may be used to conceptualize the frequency and duration of wetting; depth of flowpaths; and
1119 development of redox conditions in the river corridor [Hill, 2000]. The response of each landscape to
1120 these conditions depends on soil type, influent versus soil phosphorus concentrations, and other factors.
1121 In the river corridor, surface-dominated transport and more frequent wetting and drying may occur
1122 where there are perched or thin aquifers. These aquifers may be due to climatic conditions, or to the
1123 presence of thin soils with shallow impermeable layers (for example, soils on steep, convex slopes).
1124 These aquifers give rise to ephemeral rivers and a river corridor that is only periodically hydrologically
1125 connected with uplands, with little groundwater contribution. Such conditions promote storm- and
1126 snowmelt-driven high surface transport rates, and may enhance net mineralization of organic
1127 phosphorus through frequent wetting and drying.

River corridors linked to intermediate and thick aquifers are more likely to have sustained subsurface flows to the river corridor, less variability in groundwater elevation, and longer periods of saturation. These conditions may promote net immobilization (in any soil), development of redox-related processes in acid mineral soils or calcareous soils with significant amounts of iron, and enhancement of (de)sorption in mineral soils in general due to slower flows. Long, sustained floods, as in large rivers like the Amazon or in regions with a sustained snowmelt peak flow, might result in similar conditions, particularly in unconfined river reaches. Where river corridor soils are also deep, transformations of any kind may be minimal because flows bypass the river corridor.

Local groundwater flow patterns may also affect phosphorus transformations. In upwelling hyporheic zones, as at bedrock outcrops or areas where the aquifer becomes constricted by less permeable sediments, flows may be slower, anaerobic, and enriched in soluble phosphorus from redox-related processes. In faster, oxygenated downwelling hyporheic zones, such as at the heads of riffles, sorption may dominate soluble phosphorus transformations.

3.4. Role of water quality

Water quality relative to abundance of phosphorus, phosphorus binding compounds, and other nutrients in soils is an additional control on phosphorus dynamics. Nutrient-rich inflowing waters, such as floodwaters from highly urbanized or heavily agricultural watersheds or runoff from agricultural fields, may result in sorption or precipitation of phosphorus in uncultivated or less heavily fertilized hillslopes and river corridors, especially in subsurface soils, or enhance net mineralization [e.g., via subsidies of inorganic nitrogen; *Noe et al.*, 2012]. Where inflowing waters are low in phosphorus but soil concentrations high, desorption is more likely to occur. Examples include where the river corridor has been pastured or cultivated, then re-flooded (as in reconnection of the river to a floodplain through levee breaching or removal) [e.g., *Wong et al.*, 2011].

3.5. Example application of conceptual model

We illustrate an example application of the conceptual model to the Sprague River watershed of Oregon, USA. Sediment cores in Upper Klamath Lake, downstream of the Sprague River, appear to show increased rates of sediment deposition during approximately the last 150 years. People within the drainage basin are concerned that increased phosphorus loads have shifted the historically eutrophic lake to hypereutrophic conditions [Boyd *et al.*, 2002], as lake cores appear to be enriched in nitrogen and phosphorus near the surface relative to underlying layers [Eilers *et al.*, 2004]. We have developed this model by working systematically through Figure 4, referencing Figures 1-3 and Tables 2-4 as needed. An illustration of the example application is shown in Figure 5.

3.5.1. Example: Landscape controls

In the Sprague River watershed, landscape-level controls of phosphorus are the volcanic and Basin and Range geology and a semi-arid climate with cold winters [Records *et al.*, 2014]. Lithology is predominantly recent basalt and basaltic andesite [Gannett *et al.*, 2007], which are associated with higher background phosphorus concentrations [Domagalski and Saleh, 2015]. These geologic conditions give rise to a well-developed, permeable aquifer [Gannett *et al.*, 2012], which substantially affects regional hydrogeomorphology (below) and may cause mostly herbaceous river corridor vegetation in the mainstem Sprague River due to frequent saturation [Rasmussen, 2011].

3.5.2. Example: Abundance

The landscape-level controls also shape abundance of phosphorus and reactive compounds in the watershed. Young parent material (from recent volcanic eruptions) and lower annual precipitation give rise to poorly weathered volcanic soils, which are high in background total phosphorus as well as phosphorus-binding compounds. There are no present marine inputs, as dams downstream of Upper Klamath Lake prevent migration of fish from the Pacific Ocean [Eilers *et al.*, 2004]. To our knowledge,

atmospheric inputs are likely small because the basin is isolated from coal-burning zones or wind-borne fine sediment sources. Global maps shown low atmospheric deposition rates of phosphorus in the region [Mahowald *et al.*, 2008]. Soils are loamy or more coarsely textured in much of the basin [Cahoon, 1985]. However, mainstem river corridor soils are fine, sedimentary fill that result in fine-grained banks and channel beds [O'Connor *et al.*, 2014], with greater potential for high abundance of phosphorus concentrations and phosphorus-binding compounds.

3.5.3. Example: Transport

In lower tributaries and the Sprague River mainstem, most river valleys are wide and filled with fine-grained, low permeability sedimentary deposits derived from volcanic material and diatomite and deposited through overbank flooding [Cahoon, 1985; USDA NRCS Soil Survey Division, 2006, 2009; Gannett *et al.*, 2007; Rasmussen, 2011; O'Connor *et al.*, 2014]. These soils are generally deep, slightly acid to somewhat alkaline in pH, enriched in organic matter in the surface horizon, with iron and manganese masses throughout, and with no large pores or cracks reported [Cahoon, 1985; USDA NRCS Soil Survey Division, 2006, 2009]. Confined (canyon) river reaches are sources of coarse sediment from colluvial surface transport [O'Connor *et al.*, 2014].

These wider river corridors can store significant depths of sediment from overbank floods, including silt and silty sand [O'Connor *et al.*, 2014]. Potential retention of sorbed phosphorus may be somewhat offset by natural erosion via lateral migration and chute cutoffs [NewFields River Basin Services and Kondolf, 2012], and human-associated erosion. The latter may include channel erosion from bank instability attributed to cattle grazing [Rasmussen, 2011; NewFields River Basin Services and Kondolf, 2012] and channel straightening in some reaches [O'Connor *et al.*, 2014], possibly accounting for increased rates of sediment deposition downstream.

River reaches in the lower mainstem Sprague River generally have significant groundwater components from springs and baseflow [Gannett *et al.*, 2007], may have near-surface saturation during much of the year, and have soil horizons with visibly reduced iron (gleying) [Cahoon, 1985; USDA NRCS, 2006, 2009]. Overbank flooding may have a return interval of 2-3 years [Chapin *et al.*, 2002]. Surface transport also occurs from the river corridor to the river. River corridors in the mainstem Sprague River are commonly flood-irrigated as cattle pasture during the growing season, with large amounts of return flow, mostly as surface runoff [USDA NRCS, 2009].

Despite high groundwater contributions in the lower mainstem, the upper, volcanic parts of the watershed have many runoff dominated streams [Gannett *et al.*, 2007] with thin soils [Cahoon, 1985]. (In the conceptual model, these areas have a thin aquifer.) However, the watershed has low sediment yields at the watershed outlet, possibly because of in-stream storage in the low-gradient Sprague River mainstem, and low rates of hillslope erosion due to gentle slopes and snowmelt-dominated hydrographs [Graham Matthews & Associates, 2007].

3.5.4. Example: Transformations

Flood-irrigated river corridors have net retention of dissolved phosphorus in surface irrigation applications [Ciotti *et al.*, 2010], but high concentrations of dissolved nutrients in shallow groundwater [USDA NRCS, 2009]. We speculate that the landscape controls, abundance, and transport conditions described above affect transformations in the Sprague mainstem river corridor as follows. High water tables, natural and managed flooding, and cold winters promote net immobilization of organic phosphorus. Lack of woody vegetation means relatively little of the river corridor phosphorus is stored long-term in plants. Volcanic soils with higher amounts of amorphous materials as well as slower groundwater flows promote high sorption capacity in the river corridor. These conditions mean that

1218 soils have potential to sorb high quantities of dissolved phosphorus from surface irrigations and manure
1219 from pasture use.

1220 Hillslope soils in the upper watershed, which are mostly basalt-derived [Cahoon, 1985], have
1221 high background phosphorus concentrations. These hillslope soils release phosphorus to the local and
1222 regional groundwater systems through desorption when rainfall or snowmelt percolates through the soil
1223 and aquifer, resulting in the observed high background phosphorus levels in springs and baseflow to
1224 rivers (an average of 77 µg/L) [Boyd *et al.*, 2002]. In the river corridor, high groundwater contributions
1225 from a large aquifer lacking preferential flowpaths promote subsurface matrix flows slow enough to
1226 allow (de)sorption. Where soil phosphorus concentrations in the river corridor are high from
1227 background soil levels or management, the river corridor may release rather than reduce inflowing
1228 phosphorus from the hillslope, at least in the short term [e.g., Wong *et al.*, 2011].

1229 Prolonged saturation near the soil surface, greater organic matter availability, and presence of
1230 iron throughout the soil profile may promote release of soluble phosphorus under reducing conditions.
1231 However, amorphous materials from volcanic lithology and flooding could re-sorb released phosphorus.
1232 If reducing conditions release phosphorus to the groundwater, or pastured river corridors are flooded
1233 with waters of lower phosphorus concentration than soils (for example, diked areas re-connected with
1234 the river; prolonged irrigation of phosphorus-enriched pastures), they may be a phosphorus source to
1235 streams, at least in the short term.

1236 **3.5.5. Example: Management and climate sensitivity**

1237 Interpreting the Sprague River case study within the framework of the conceptual model has
1238 implications for sensitivity of the watershed to altered management and climate. For example, a
1239 previous study of the river corridor in a nearby watershed shows large removal rates of phosphorus
1240 from surface irrigation water [Ciotti *et al.*, 2010]. However, since the river corridor of the lower Sprague

mainstem is frequently under reducing conditions, there is greater potential for the river corridor to transform phosphorus stored in the surface into soluble phosphorus. River corridors in the lower mainstem may store significant amounts of sorbed phosphorus in larger overbank floods because the river remains largely unincised, but the river corridor may not be a net sink of sorbed sediment if bank erosion rates exceed storage capacity. Where the river corridor has been diked and pastured or cultivated, floodplain reconnection might increase storage potential of sorbed phosphorus, but could release large amounts of dissolved phosphorus for some time when flooded.

Projections of an increased proportion of precipitation as rain, warmer temperatures, and greater evapotranspiration [Records *et al.*, 2014] may imply: potential to alter phosphorus dynamics by accelerating net mineralization and sorption; altering sorbed phosphorus dynamics through changes in frequency of overbank flooding, rates of erosion in the hillslope and channel, and geomorphic responses to alterations in supply of flow and sediment; and lowering river corridor water tables through greater evapotranspiration, thus affecting redox processes.

4. Knowledge gaps and future work

We have identified several knowledge gaps and possible key areas of future work to clarify river corridor phosphorus dynamics and environmental models (Table 4; Table 5). We follow Haygarth *et al.* [2005] in suggesting researchers adopt a multi-disciplinary approach to investigate these and other questions. For example, studies of rice cultivation have been effectively adapted to better understand floodplain phosphorus dynamics [e.g., Wright *et al.*, 2001]. Studies of cranberry production may provide insight into phosphorus in river corridors, but to our knowledge these have not yet been applied to river systems. As an example, one study found that reduced phosphorus fertilizer inputs and short floods of cranberry bogs greatly reduced phosphorus yields in outflow [DeMoranville *et al.*, 2009].

The conceptual model we propose does not explicitly account for human influences on river corridor phosphorus dynamics. Although a number of these influences have been addressed in individual works (e.g., the effects of fertilizer applications of mineral phosphorus, atmospheric deposition, or subsurface drainage), we are not aware of a comprehensive review and synthesis on this topic. We have included in our conceptual model an example list of these activities (Figure 4). Future work expanding on this topic would be a useful addition to the model we have proposed. We suggest that this work also include treatment of the effects of increased channel conveyance on river corridor phosphorus dynamics. As we note above, this topic has been studied extensively for nitrogen but there appears to be relatively little research for phosphorus.

We have also provided potential data sources for conceptual model applications to specific sites (Table 4). To our knowledge, there are no regional or global databases of fluvial geomorphology, or of inputs of marine-derived phosphorus to rivers. These databases could be useful resources for future river corridor phosphorus studies.

The net effect of river corridors on phosphorus from hillslopes and rivers is difficult to assess from the literature, because very few studies provide comprehensive, detailed river corridor phosphorus budgets. More research with detailed documentation of phosphorus inputs and outputs, such as *Peterjohn and Correll* [1984] and *Hoffmann et al.* [2006], would help to clarify the net role of river corridors on phosphorus. Studies quantifying only some phosphorus inputs and outputs are likely to be more economical, however, and can still yield useful information about the relative importance of different exchanges or transformations [e.g., *Mittelstet et al.*, 2011].

Despite much previous work, it is ambiguous whether redox conditions and associated wetting and drying cause long-term net increases in soil soluble phosphorus [reviewed in *Wright et al.*, 2001; *Zhang et al.*, 2010], and if so, by what mechanism(s). This is an important management consideration

because many river corridor restoration projects are intended to remove nitrate by denitrification, and so may reach redox potentials that can reduce iron, thus releasing soluble phosphorus. A literature meta-analysis quantitatively assessing the mechanisms affecting phosphorus in reduced river corridors, and the net effect on soluble phosphorus, could clarify this. An important aspect not commonly evaluated in field studies is the effect of river corridor moisture regime on microbe populations and community composition, and the subsequent effects of microbes on phosphorus dynamics.

The literature used in developing this conceptual model is biased towards temperate climates in North America and Europe. There are comparatively few river corridor phosphorus studies in other climates such as tropical, semi-arid or arid, and sub-arctic or arctic, or in volcanic soils. Additionally, we know of very few studies that have systematically evaluated the relative importance of different phosphorus transformations among distinct river corridor geomorphic, chemical, or other characteristics. For example, it is difficult to evaluate longitudinal trends of nutrient cycling in river corridors because of a lack of published studies [Noe *et al.*, 2012], just as it is difficult to evaluate trends in nutrient dynamics in iron-rich versus calcareous landscapes.

These comparisons could be made quantitatively. Potential techniques include modeling-based approaches [e.g., Seibert and McDonnell, 2002; Weiler and McDonnell, 2006; Helton *et al.*, 2011; González-Sanchis *et al.*, 2015], comparison of explanatory variables for time series analyses of frequent river corridor measurements [e.g., Dupas *et al.*, 2015] or of long-term averages of phosphorus river loads [e.g., Domagalski and Saleh, 2015], rigorous meta-analysis of existing works on phosphorus to investigate prevalence of certain transformations and important controls [e.g., extending the work of Fisher and Acreman, 2004], multi-site comparisons of phosphorus dynamics based on common metrics [Shenker *et al.*, 2005], paired watershed studies to compare the relative importance of various processes and controls in river corridor phosphorus cycling [Carignan and Vaithiyanathan, 1999; House and

Denison, 2002], and systematic examination of nutrient cycling in distinct geomorphic units of the river corridor and along the river network [e.g., *Noe et al., 2012*].

Some candidate environmental models are shown in Table 6. These models are developed at basin- or site-scales to assess effects of wetlands or river corridors on water quality. Comprehensive reviews are also available of phosphorus modeling in aquatic systems [*Robson, 2014*] and nutrient modeling in wetlands [*Min et al., 2011; Hantush et al., 2013*] and river basins [*Shoemaker et al., 2005*]. Models such as these are used to predict effects of management, land use and climate change on stream phosphorus loads, and are increasingly relied on for water quality trading. These models, however, may not simulate apparently important controls or processes, such as distinct adsorption based on soil type (e.g. calcareous versus acid), effects of reducing conditions on phosphorus, and changes in pH (e.g. as a result of decomposition or photosynthesis) and associated effects on phosphorus dynamics. Model selection also generally requires a tradeoff: as process representation becomes more detailed (complexity increases), data requirements also typically increase.

Steps to adapt these models to simulate landscape level variations in phosphorus dynamics could include model structure approaches, such as ensemble equations; and the Bayesian Estimation of Structure [*Gupta et al., 2012*]. Model parameterization approaches could include evaluation of progressively more complex models at finer time steps; assessment of groundwater and tracer data to identify important hydrologic processes to include in the model; and an ensemble model approach, with models weighted based on performance to derive prediction uncertainty [*Gupta et al., 2012*].

5. Conclusions

To our knowledge, no previous works have proposed a broad conceptual model of phosphorus dynamics in river corridors under natural conditions, particularly in the context of landscape-scale controls and processes. Our motivating questions in developing this review and conceptual model were: to

determine what dictates whether a river corridor segment is a sink or source of phosphorus; and evaluate implications for place-specific river corridor management, monitoring, and modeling. Although guided by these overarching considerations, we cannot answer these questions in such a broad review, as the answers are likely to be highly context-specific. However, we believe that the conceptual model we propose may be adapted to answer these questions for specific applications—or, where this is not possible, to more clearly identify and address important knowledge gaps. In regions where human activities have substantially affected abundance, transport, and transformation of phosphorus and reactive compounds, this conceptual model may be adapted to account explicitly for anthropogenic effects. We note some of these human activities in Figure 4 and provide an example of such evaluation in the example application (Section 3.5.5.). We suggest that future work include a comprehensive review of the effects of human activities on river corridor phosphorus dynamics.

We are aware of few field studies that provide a phosphorus budget sufficiently detailed to evaluate whether a river corridor reach has net retention or release of phosphorus. This is an important area of future research. However, the conceptual model outlined here illustrates how certain characteristics of landscape type, and abundance, transport, and transformation of phosphorus and reactive compounds, may help to predict important river corridor phosphorus dynamics (Figure 4). As illustrated in the example, the conceptual model may also suggest sensitivities of the river corridor to change (e.g., alterations in management or hydroclimatic regime). Use of this conceptual model can also better inform numerical modeling of phosphorus dynamics and management of river corridors.

The review suggests that phosphorus dynamics in the river corridor, and their controls, may vary substantially across different landscapes and river reaches. Where river corridor management or modeling practices do not reflect some of these variations, results may be incomplete or perhaps costly. Examples of incomplete management or modeling include neglecting the influence of reducing

conditions on soluble phosphorus release in acid soils, or variations in sorption capacity among organic and mineral soils. This highlights the importance of place-specific modeling and management of phosphorus dynamics within river corridors. The conceptual model presented in this paper can provide a framework for evaluating potential controls on phosphorus dynamics in a particular river segment, and for identifying what are potentially the most important controls on phosphorus abundance, transport, and transformations within that segment. We suggest that future work is needed on phosphorus dynamics in relation to saturation and redox processes; variation across diverse- and little-studied systems; sensitivities to site-specific modeling schemes; and development of conceptual models of human influences on abundance, transport, and transformation of phosphorus and reactive compounds. An interdisciplinary approach and use of diverse modeling, field and laboratory studies is particularly important.

Acknowledgements

This research is based upon work supported by National Science Foundation Grant No. DGE-0966346 “I-WATER: Integrated Water, Atmosphere, Ecosystems Education and Research Program” at Colorado State University. This publication was made possible by USEPA grant RD83557001. Its contents are solely the responsibility of the grantee and do not necessarily represent the official views of the USEPA. Further, USEPA does not endorse the purchase of any commercial products or services mentioned in the publication. This work was also supported by funding from the USDA Natural Resources Conservation Service to the California Cooperative Fish and Wildlife Research Unit. We thank two anonymous reviewers who provided valuable feedback on this work. We appreciate the assistance of Jacob McDaniel in clarifying phosphorus availability. The following people provided useful comments at early stages of the work on phosphorus conceptual and environmental models: Walter Duffy and Sharon

1378 Kahara of the California Cooperative Fish and Wildlife Research Unit; William Effland and Mari-Vaughn
1379 Johnson, USDA-NRCS; Kris Fischer of the Klamath Tribes Research Station; Ryan T. Bailey of Colorado
1380 State University; Jeff Arnold, Mike White, and Kate Behrman of the Grassland, Soil & Water Research
1381 Laboratory, USDA-ARS; and James Ascough II of the USDA-Agricultural Research Service, Plains Area.

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Phosphorus in the river corridor (abstract)

Rosemary M. Records ^a, Ellen Wohl ^b, and Mazdak Arabi ^c

^a Integrated Water, Atmosphere, Ecosystems Education and Research Program, Department of Geosciences, Colorado State University, 1482 Campus Delivery, Fort Collins, CO 80523-1482, USA, rosemarymrecords@gmail.com (Corresponding author)

^b Department of Geosciences, Colorado State University, 1482 Campus Delivery, Fort Collins, CO 80523-1482, USA, Ellen.Wohl@colostate.edu

^c Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO 80523-1372, USA, Mazdak.Arabi@colostate.edu

1 River corridor protection has been adopted by government agencies and non-governmental
2 organizations to try to control nonpoint nutrient loading to rivers. Yet, river corridor protection and
3 modeling strategies developed on a national basis may not fully account for dynamics that have proven
4 to be important controls on phosphorus in river corridors. These sources of uncertainty may have
5 economic and environmental costs, yet we know of no previous works that have proposed a broad
6 conceptual model of phosphorus dynamics in river corridors. In this review, we develop a conceptual
7 model of phosphorus in the river corridor under natural conditions based on existing research by: (i)
8 evaluating how processes and controls vary among distinct landscape characteristics and among distinct
9 segments within river networks (e.g., in confined channels versus wide valleys); and (ii) determining
10 whether some processes and controls are generally more dominant for some landscape types and river
11 reaches. Finally, we provide an example application of the conceptual model, and identify key areas for
12 future research. The review suggests that phosphorus dynamics in the river corridor, and their controls,

13 may vary substantially across different landscape types and river reaches. However, the conceptual
14 model outlined here illustrates how certain characteristics of landscape type, and abundance, transport,
15 and transformation of phosphorus and reactive compounds, may help to predict important river
16 corridor phosphorus dynamics. Use of this conceptual model can better inform numerical modeling of
17 phosphorus dynamics and management of river corridors.

Table 1. Terminology, examples, composition, and availability of phosphorus fractions in wetland soils, assuming no changes in pH or redox potential of the system. Derived from Reddy and DeLaune [2008].

Type	As % of TP in wetlands		General fractions	Common compounds or measures	Availability
	Organic soil	Mineral soil			
Inorganic phosphorus	20-50	50-80	Dissolved inorganic	Dissolved/soluble reactive P (orthophosphate: H_2PO_4^- , HPO_4^{2-} , PO_4^{3-})	Labile/bioavailable
			Particulate inorganic	Phosphate sorbed on clays, precipitates of PO_4^{3-} with Ca, Mg, Fe or Al	"Readily available" (present in exchangeable P pool), "slowly available" (recently formed with Ca, Mg, Fe &/or Al); "very slowly available" (present in Ca, Al or Fe phosphates)
Organic phosphorus	50-80	20-50	Dissolved organic	Sugar phosphates, phospholipids	Variable
			Particulate organic	Various decomposing microbial and plant tissues	Refractory

Table 2. Controls and conditions that tend to enhance phosphorus transport in surface, subsurface matrix flow, and subsurface preferential flow. Regular typeface indicates conditions that generally promote transport from higher to lower land surface elevations in hillslope and river corridor, unless another direction of transport is noted. Bold font denotes conditions more specific to the river corridor. References are noted in the text. Aquifer conditions may be more applicable to humid landscapes.

Control	Surface	Subsurface matrix	Preferential flow
<i>Lithology / soil</i>	Clastic sedimentary rocks; higher clay	<i>Low sorption</i> : highly organic, or low abundance in Fe, Al, Ca and Mg, and moderate sorption (calcareous); <i>high phosphorus</i> : labile organic or drained organic soils; little weathered mineral soils / finer textures	Shrink-swell clays (Vertisols), poorly drained soils from carbonate, mafic or metamorphic shale; limestones (karst)
<i>Flow characteristics / aquifer</i>	Perched aquifer; thin to intermediate thickness; ephemeral rivers; shallow impermeable layers	<i>High flow</i> : high hydraulic conductivity (coarser soils, peats); <i>high phosphorus</i> : groundwater table intersects surface soils; <i>low sorption</i> : "bypass" flow from thick hillslope aquifers and deep, permeable river corridor soils	Varies; soil and geomorphic controls likely dominate
<i>Geomorphology, biota and climate</i>	Active mountain ranges; semi-arid; confined channels / steeper valleys; small drainages in humid zones; low gradient, wide valley (river to river corridor); erodible banks with fine-textured soil (river corridor to river)	<i>High flow and low sorption</i>: levees, splays, and higher-energy environments with coarser texture; <i>high phosphorus</i>: upwelling hyporheic zones, toeslopes and backswamps with finer textures	Karst landscapes; jointed and fractured bedrock; piping, particularly in (semi) arid regions; rapid wetting and drying in shrink-swell clays; high biologic activity, large macropores in steep vegetated terrain

1 Table 3. Controls and conditions that may enhance various phosphorus transformations in the hillslope or river corridor, or for which certain
 2 transformations may be more important for phosphorus dynamics. Bold font denotes conditions more specific to the river corridor alone.
 3 References are noted in the text. *Refers only to physical retention (not necessarily decomposition rates). Aquifer conditions are likely more
 4 applicable to humid landscapes.

	Net immobilization	Net mineralization	(De)sorption			Precipitation and dissolution	Redox-related
			Sorption & desorption	Sorption only	Desorption only		
Lithology / Soil	Organic; moderately and highly weathered mineral soils and other soils with higher organic content	Moderately weathered mineral soils	Finer-textured, low organic content mineral, acid soils, particularly highly weathered (Ultisols, Oxisols); volcanic soils (Andisols)	Inflowing P concentrations > soil P concentrations	Inflowing P concentrations < soil P concentrations	Calcareous soils (aerobic); acid and iron-dominated soils when highly reduced	Finer-textured mineral soils with substantial iron; not organic matter limited (e.g., surface soils, river corridor); nitrate supply <denitrification
Flow / aquifer	Wet, prolonged saturation; intermediate to thick aquifers	Frequent wetting and drying; perched or thin aquifers	Slower flows; intermediate and thicker aquifers	Downwelling hyporheic zones	Flow nutrient loads reduced (re-flooded river corridor , fertilizer or hillslope nutrient load reductions)	Nutrient-rich flows, such as highly urbanized/cultivated watersheds	Longer saturation, slow flow (intermediate to large aquifers, perennial rivers); shallower subsurface flow through river corridor; upwelling hyporheic zones
Geo-morphology and climate	Cold, wet climates (higher latitudes, higher elevations); flatter channels*	Warmer, moist environments (e.g., tropics); frequent wetting and drying; steeper channels*	Variable	Uncultivated areas; deeper soil horizons; warmer climates; some river corridors if fine soils, lower soil P; riffle heads (downwelling)	Cultivated areas/waste applications; warmer climates; surface soil horizons	River corridor of larger rivers where pH changes are large (through decomposition or photosynthesis)	River corridor, especially low-energy environments such as wider valleys with smaller slopes; pools (upwelling)

Table 4. Potential sources for development of river corridor phosphorus conceptual models. Bold type indicates global data sources, and plain font indicates sources only for specific regions (United States unless otherwise noted). Underlined font indicates that no known databases are available, and that modeling and monitoring may be necessary to obtain these data.

Grouping	Data type	Potential Sources
<i>Geology</i>	--	*Geology [USGS Energy Resources Program, 2015]; parent material [Yang et al., 2013]
<i>Climate</i>	--	†Schneider et al. [2014]; NOAA Earth System Research Laboratory Physical Sciences Division [2015]
<i>Biota</i>	--	Vegetation [Channan et al., 2014; Global Land Cover Facility, 2014]
<i>Hydrogeomorphology</i>	--	Hydrology: See Transport and Transformations in table below; Geomorphology: No global databases. See example geomorphic analysis and reach classifications from elevation data [Wohl et al., 2007; Livers and Wohl, 2015]
<i>Abundance</i>	Soil type, mineralogy & degree of weathering	‡Approximate soil classification, texture, drainage class, cracks/pores, mineralogy and erosion risk for US [National Cooperative Soil Survey, 2015; USDA NRCS, 2015b, 2015c; USDA NRCS Soil Survey Division, 2015] and globally [FAO/IIASA/ISRIC/ISSCAS/JRC, 2012]; concentrations and fractions of P by soil order [Yang and Post, 2011]
	Soil texture, erosion / deposition, proximity to river Atmospheric & marine sources	Soil texture and erosion‡; Proximity: May be measured in satellite imagery [Aerometrex, 2013] Atmospheric: [Mahowald et al., 2008]; Marine: No databases. See estimates in Gresh et al. [2000] (western US and Canada) and eastern Russia [Murota, 2012]
<i>Transport</i>	Soil texture & mineralogy; cracks, joints & pores	Soil characteristics, cracks and pores‡; joints*
	Tectonic setting & valley type; erosion & deposition	Tectonic setting*; Valley type: See Hydrogeomorphology; Erosion‡
	Wetting frequency/duration	§Identify soil classification, approximate wetting frequency by drainage class and Soil Surveys by State description [USDA NRCS, 2015c]; SSURGO [USDA NRCS, 2015b], and Official Series Descriptions [USDA NRCS Soil Survey Division, 2015]
	Hydraulic conductivity, flow velocity	Relative surface hydraulic conductivity can be approximated from soil drainage class‡; <u>Flow velocity: Modeling [e.g., Brunner, 2010] & monitoring</u>
	Flow path type & depth	<u>Modeling (basin-scale models, see Shoemaker et al. [2005])</u>

9 Table 4 (concluded).

Grouping	Data type	Potential Sources
<i>Transformations</i>	Valley & reach type; erosion & deposition	Valley type: See Hydrogeomorphology; erosion‡
	Wetting frequency/duration; flow velocity; temperature	Wetting frequency/duration§; <u>Velocity: Modeling [e.g., Brunner, 2010]</u> <u>& monitoring; Temperature†</u>
	Soil type (acid, calcareous, organic), texture & mineralogy	Soil type, texture & mineralogy‡
	pH changes; P concentration in soil vs water	<u>Modeling (Table 6; Robson [2014]) & monitoring</u>
	Electron acceptors & organic matter	Modeling, monitoring (Table 6; Robson [2014]); N, Fe, and organic matter may be available‡

10 Table 5. Potential areas of future work on river corridor phosphorus dynamics, and select references.

Theme	Topic	Selected References
<i>Detailed P budgets</i>	Effect of the river corridor on P export to streams (e.g., P budget for different inputs and outputs, and/or from different components of the landscape)	Studies providing a river corridor P budget (mass or % total): <i>Buda et al.</i> [2009]; <i>Noe and Hupp</i> [2009]; <i>Mittelstet et al.</i> [2011]; Most detailed P budget studies (including atmospheric inputs): <i>Peterjohn and Correll</i> [1984]; <i>Hoffmann et al.</i> [2006]
<i>Saturation and redox processes</i>	“Tradeoffs” in soluble P release and retention from saturation and reducing conditions, including effects on microbial community	<i>Ellis</i> [1998]; <i>Baldwin and Mitchell</i> [2000]; <i>Wright et al.</i> [2001]; <i>Reddy and DeLaune</i> [2008]; <i>Turner et al.</i> [2003]
<i>Landscape-level variation</i>	P dynamics of river corridors in less well-studied systems (tropical, arctic and sub-arctic, volcanic, arid and semi-arid)	Tropical: <i>Chacon et al.</i> [2008]; volcanic: <i>Wong et al.</i> [2011]; (semi)arid: <i>Litaor et al.</i> [2003]; <i>Fuchs et al.</i> [2009]; <i>Mittelstet et al.</i> [2011]; (sub)arctic: <i>Giblin et al.</i> [1991]
	Variation in P transformations among landscape types/characteristics	<i>Carignan and Vaithiyanathan</i> [1999]; <i>Vidon et al.</i> [2010]; <i>Noe et al.</i> [2012]
<i>Computer modeling</i>	Sensitivity of biogeochemical model P predictions to distinct routines in calcareous vs acidic systems	Distinct adsorption equations based on soil type (e.g., Ca abundance, pH, clay) for EPIC, GLEAMS, and CREAMS environmental models summarized in <i>McGechan and Lewis</i> [2002]
	Sensitivity of biogeochemical model P predictions to effects of reducing conditions on P	River corridor models approximating Fe reduction by oxygen depletion and/or saturation: <i>van der Peijl and Verhoeven</i> [1999]; <i>Hantush et al.</i> [2013]; aquatic models with redox conditions related to O, Fe, Ca, abundance summarized in <i>Robson</i> [2014]
	Environmental influences on pH, and pH effects on P	No known modeling studies

Table 6. Select models of effects of wetlands or river corridor processes on phosphorus in surface or groundwater at site- or basin scales. “Data-driven” models use mostly empirical or statistically-based approaches, such as regression or principal component analysis. “(Semi) physically based” models rely more heavily on physics-based equations of hydrologic and/or biogeochemical processes.

Comprehensive reviews are available of phosphorus modeling in aquatic systems [Robson, 2014] and nutrient modeling in wetlands [Min et al., 2011; Hantush et al., 2013] and river basins [Shoemaker et al., 2005].

	Wetland	River corridor	Basin
(Semi) physically based	<i>Jorgensen et al.</i> [1988]; <i>Kadlec and Hammer</i> [1988]; <i>Mitsch and Reeder</i> [1991]; <i>Paudel et al.</i> [2010]; <i>Hantush et al.</i> [2013]	Riparian Ecosystem Management Model (REMM) [<i>Lowrance et al.</i> , 2000]; Wetland Solute Transport Dynamics (WETSAND) [<i>Kazezyilmaz- Alhan et al.</i> , 2007]; <i>van der Peijl and Verhoeven</i> , [1999]; <i>Wang and Mitsch</i> [2000]; <i>González-Sanchis et al.</i> [2015]	Soil and Water Assessment Tool (SWAT), basin-level river corridor applications reviewed in <i>Gassman et al.</i> [2007]
Data-driven	Wetlands Water Quality Model (WWQM) [<i>Chavan and Dennett</i> , 2008]	<i>Dupas et al.</i> [2015]	SPAtially Referenced Regressions On Watershed attributes (SPARROW) [<i>Smith et al.</i> , 1997]; <i>Johnston et al.</i> [1990]

Figure 1. Major controls on abundance of phosphorus (italics), phosphorus binding compounds (bold), or both (bold italics) in the hillslope and river corridor. Boxes show major controls, with those believed to be more important at the top of the figure. Curved arrows show the effect of one control (at the start of the arrow) on another control (at the end of the arrow). An asterisk notes that seemingly contradictory results are due to differences in sediment and particulate phosphorus depositional patterns reported in literature.

Figure 2. Some characteristics that may enhance phosphorus transport in (a) surface transport, (b) subsurface matrix flow, and (c) preferential flow. An asterisk shows that the seeming contradiction is because finer soils have higher concentrations of phosphorus, but coarser soils have higher rates of flow and lower phosphorus sorption. Aquifer schematics are based on those in Hill [2000].

Transport is towards the river, unless signified by an arrow.

Figure 3. Characteristics that may enhance particular phosphorus transformations in the river corridor. Symbols represent specific processes affecting phosphorus. Symbol position indicates the combined conditions that enhance this process in the flow/aquifer and either lithology/soil or geomorphology/climate. For example, immobilization may be enhanced in cold areas and in highly organic areas where there is long saturation.

Figure 4. Conceptual model of phosphorus dynamics in the river corridor. Circles show landscape-scale controls on phosphorus abundance, transport, and transformations in the hillslope and river corridor. The term “landscape” refers to both hillslope and river corridor at larger spatial scales than a particular hillslope or river corridor reach. Boxes show controls important in both the hillslope and river corridor.

Potential human influences on the conceptual model are noted, and whether these activities are believed to increase (+), decrease (-), or have unknown effect (?) on river corridor soluble phosphorus.

References are noted in the text.

Figure 5. Example application of the conceptual model of river corridor phosphorus (Figure 4) to the Sprague River basin, Oregon, USA. Italics refer to controls specific to the mainstem Sprague river corridor, and bold italics to controls important in river corridor and hillslope. Plain font shows controls specific to the hillslope only.