
Interim Measure 11 Study of Nutrient Reduction Methods: Jar Test Results and Summary Report

Prepared for
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CH2MHILL®

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Acronyms and Abbreviations

BOD	biological oxygen demand
°C	degrees Centigrade
CO ₂	carbon dioxide
COD	chemical oxygen demand
DIP	dissolved inorganic phosphorus
DIW	deionized water
DO	dissolved oxygen
DP	dissolved phosphorus
DRP	dissolved reactive phosphorus
EPA	U.S. Environmental Protection Agency
°F	degrees Fahrenheit
g	grams
KHSA	Klamath Hydroelectric Settlement Agreement
kg	kilograms
L	liter
mg	milligrams
mg/kg	milligram per kilogram
mg/L	milligram per liter (equivalent to parts per million, or ppm)
mL	milliliter
N	nitrogen
NO ₂ -N	nitrite-nitrogen
NO ₃ -N	nitrate-nitrogen
NH ₃	ammonia
NH ₃ -N	ammonia-nitrogen
NH ₄ ⁺	ammonium
NH ₄ -N	ammonium-nitrogen
NO ₂	nitrite
NO ₃	nitrate
Org-N	organic nitrogen
ortho-P	ortho-phosphorus
P	phosphorus
PO ₄ -P	phosphate phosphorus
pH	potential of hydrogen (measurement of acidity of a water sample)

PO ₄	orthophosphate
ppb	parts per billion
ppt	parts per thousand
SRP	soluble reactive phosphorus
TDS	total dissolved solids
TIN	total inorganic nitrogen (ammonia + nitrite + nitrate)
TKN	total Kjeldahl nitrogen
TN	total nitrogen
TP	total phosphorus
TSS	total suspended solids
USGS	United States Geological Survey
VSS	volatile suspended solids
µg/g	microgram per gram
µg/L	microgram per liter (equivalent to parts per billion, or ppb)

Introduction

1.1 Purpose

The Klamath Hydroelectric Settlement Agreement (KHSA) includes Interim Measure (IM) 11 that is intended to address water quality improvement in the Klamath River during the interim period leading up to potential dam removal. Regarding IM 11, the KHSA states “The emphasis of this measure shall be nutrient reduction projects in the watershed to provide water quality improvements in the mainstem Klamath River, while also addressing water quality, algal and public health issues in Project reservoirs and dissolved oxygen in J.C. Boyle Reservoir.”

The IM 11 Study Plan for 2013-2014 (PacifiCorp 2013) includes Activity 7 to investigate potential approaches to reducing nutrient concentrations as a means to improve water quality in Upper Klamath Lake, Keno Reservoir, and the Klamath River downstream. In 2014, Activity 7 included a laboratory-based “jar test” study to assess the potential use of treatment with chemical agents to reduce nutrients, notably phosphorus (P), in selected source waters from the upper Klamath Basin. These agents include commercially-available products that are applied to waters as a method to reduce nutrient concentrations (and associated algae growth and biomass effects) through flocculation, binding, or sequestration.

This report describes the results of the Activity 7 laboratory-based “jar test” study conducted in 2014. The jar test is a common laboratory procedure used to measure the effect of coagulation, flocculation, and sedimentation on nutrients and other water quality constituents, and to determine appropriate or optimal coagulant dosages under controlled test conditions. Coagulation and flocculation are the processes of binding small particles in the water together into larger, heavier clumps (known as “floc”) that settle out relatively quickly, reducing the water’s content of P (and other susceptible constituents).

As described in the following sections of this report, the study included steps to: (1) identify and select appropriate candidate agents; (2) identify and collect appropriate source waters to be tested; and (3) conduct laboratory-based jar tests to assess the effects of various doses of the agents in reducing P (and affecting other water quality changes) in the source waters. These jar test study results may be useful to inform the potential applicability of, and development of further measures using treatments with these agents as a tool for achieving nutrient reductions in the Klamath Basin (for example, in conjunction with other nutrient reduction technologies such as constructed treatment wetlands).

1.2 Context for Study

In the long term, reductions in P loading to waters in the Klamath Basin could be achieved by controlling sources within the upper Klamath Basin through such actions as best management practices (BMPs) and wetlands restoration (e.g., diffuse source treatment wetlands). However, implementing such actions and controlling sources at the basin-scale will take many years before achieving target levels of external P loading, such as recommended in Total Maximum Daily Loads (TMDLs) for the Klamath River (Oregon Department of Environmental Quality 2010, North Coast Regional Water Quality Control Board 2010).

In the interim, other techniques could be employed to reduce P directly in the waters of the Klamath Basin. Treatment with chemical agent applications is one such technology that could be employed to absorb, precipitate, or inactivate P in water and sediments. It is understood that use of agents/amendments for nutrient reduction is not a replacement or substitute for restoration of wetlands or application of other BMPs. However, use of agents/amendments is another “tool in the box”, along with restored wetlands and other BMPs to reduce nutrients and improve water quality in the Klamath River.

For example, agents (also often termed “coagulants”) have been used elsewhere for:

- Application in lakes or reservoirs to strip P from the water column or sequester P in the sediments;
- Use in conjunction with wetlands for a “treatment train” that would enhance P removal efficiencies in wetland outflows;
- Coagulant injection treatment of streams to intercept and inactivate P loads from tributaries.

In an example of chemical treatment specifically proposed in the Klamath Basin, the concept of injection of an alum micro-floc, along with aeration/oxygenation, was identified for potential use in Keno reservoir (downstream of Upper Klamath Lake) in the 2012 Klamath River Water Quality Workshop in Sacramento (Stillwater Sciences et al. 2013). Additionally, the nutrient removal efficiency of treatment wetlands in the Klamath Basin can be increased, and the corresponding wetland facility footprint needed to achieve specific nutrient reduction targets can be reduced, through the application of chemical pre-treatment methods (CH2M HILL 2012).

This study is not intended to recommend or endorse any specific agent or application. This particular study is only the first of several steps that will be needed to determine what chemical treatments may be best to use and to plan how the treatment processes using them could be implemented. The first step consists of that described in this report – that is, laboratory-based jar tests of appropriate candidate agents to assess dosages and likely effectiveness. How this information is used and whether any of these candidate agents are part of a larger restoration project, will be decided by stakeholders (including appropriate authorizing regulatory agencies). For example, additional tests might be conducted to assess effectiveness of agents under field conditions, either within mesocosms or in small wetland test cells (such testing capabilities are an envisioned purpose of the Demonstration Wetland Facility planned under Interim Measure 11 Study 2 [CH2M HILL 2014b]). Thereafter, additional steps would be taken to complete the required planning, design, and permitting of actual treatment projects using selected agents.

1.3 Technical Advisory Committee (TAC) Coordination

PacifiCorp worked with representatives of the KHSAs Interim Measures Implementation Committee (IMIC) to develop plans for the studies and pilot projects to be implemented under IM 11 during 2014, including the Activity 7 study that is the subject of this report. As part of IM 11 Activity 2 (Demonstration Wetland Facility Planning), a Technical Advisory Committee (TAC) was formed to provide input on the demonstration wetland facility concepts and to act as a coordination link to the IMIC and stakeholders. TAC members participated in monthly teleconference calls that began in October 2013 and ended in October 2014. Although the main focus of the TAC was the Demonstration Wetland Facility Planning, the Activity 7 study (that is the subject of this report) was discussed with the TAC on several occasions to solicit input and feedback on the study’s objectives and approach. More details on the TAC participants, process, and outcomes are provided in the recently-completed *Demonstration Wetland Facility Preliminary Research and Implementation Plan* (CH2M HILL 2014b).

Agents and Source Waters Selected for Testing

2.1 Agents Selected for Testing

Four agents were selected for the laboratory-based bench testing, including:

- Lanthanum-modified bentonite clay (Phoslock™)
- Aluminum-modified zeolite (Aqual P™)
- Polyaluminum hydroxychloride (PACl)
- Alum (aluminum sulfate buffered with sodium aluminate)

These four agents were selected from a list of six candidate agents recommended in the study plan for these laboratory-based jar tests (CH2M HILL 2014a). Table 1 summarizes the mode of action and features of the six candidate agents. All are known to be effective at reducing P in natural waters, but have respective advantages and disadvantages. PacifiCorp and CH2M HILL, in consultation with the TAC, selected the four agents to be tested. The four agents actually include five of the six candidate agents, since the two candidate forms of alum (aluminum sulfate and sodium aluminate) were combined to provide a buffered (more circumneutral) form of alum to be tested (as discussed further below).

CH2M HILL (2014a) includes more detailed discussion of the six agents, including mode of effect on nutrients, controlling factors, reported treatment applications and effectiveness, respective advantages and disadvantages, and costs. In addition to the material in CH2M HILL (2014a), extensive literature reviews are available on various agents or coagulants that have been used to reduce nutrients in lakes, reservoirs, wetlands, and other natural waters (Cooke et al. 1993, Douglas et al. 2004, Cooke et al. 2005). In addition, CH2M HILL (2012) provides a detailed review of six categories of supplemental treatment with agents or coagulants that could be used to enhance nutrient removal by wetlands, including the potential applicability of this supplemental treatment to the upper Klamath Basin.

2.1.1 Lanthanum-Modified Bentonite Clay (Phoslock™)

2.1.1.1 Description

Phoslock™ is lanthanum-modified bentonite clay developed by the Australian Federal Government-owned Commonwealth Scientific and Industrial Research Organization (CSIRO) and the Australian Water and Rivers Commission (AWRC) to remove P from natural water bodies and waste water streams (Robb et al. 2003). Phoslock™ is a relatively new commercial product that is emerging as an effective eutrophication and/or blue-green algae management tool. The developers of Phoslock™ consider it an effective alternative to use of alum in natural water bodies (Afsar and Groves 2009). Compared to alum, Phoslock™ is considered to operate effectively over a wider range of pH and alkalinity conditions, and have less risk of potential toxicity in aquatic organisms (Afsar and Groves 2009).

Phoslock™ contains the rare earth element lanthanum in a matrix of bentonite clays and acts to remove dissolved phosphate from the water column by binding it into an insoluble precipitate. The lanthanum ions sorbed to the clay matrix react preferentially with free phosphate compounds in water (removing SRP) and rapidly form a highly stable insoluble species of lanthanum phosphate, or rhabdophane (National Industrial Chemicals Notification and Assessment Scheme 2001, Douglas et al. 2004). This resulting rhabdophane complex has a very low solubility and is not influenced by changes in pH and redox reactions in waterbody sediments, thus is not bioavailable.

2.1.1.2 Reported Effectiveness

In laboratory tests, Douglas et al. (2000) found that Phoslock™ removed 87 to 98 percent of bioavailable P (or SRP) over the range of pH 6 – 8. Flapper (2003) reported on field trials of Phoslock™ applied to mesocosms at Fyshwick Lagoon in Australia. Total P in treated mesocosms was reduced by 83 to 96 percent compared with control mesocosms. The reduction in total P lasted about 9 weeks before total P concentrations began to increase and return to the same level as untreated mesocosms. Flapper (2003) also speculated that Phoslock™ application prevented a bloom of *Microcystis aeruginosa*, which developed in the control mesocosms after the start of the trials.

Robb et al. (2003) reported on two full-scale Phoslock™ applications (in a slurry from a small boat) undertaken in 2001/2002 in impounded sections of the Vasse and Canning Rivers in Australia. Following the first Phoslock™ treatment in the Vasse River, dissolved P concentrations were reduced from 50 µg/L to 20 µg/L. After the second treatment was applied several weeks later, dissolved P concentrations at the control site had reached almost 200 µg/L, but dissolved P concentrations at the treatment site remained low, reaching the detection limit of 5 µg/L. After 194 days, dissolved P concentrations at both the control and treatment sites were of similar magnitude. Similar applications in the Canning River also resulted in reductions in dissolved P concentrations, but of lesser magnitude, thought to be attributable to greater proportional amounts of runoff-related nutrient inputs to the Canning River.

Australia Water Quality Center (2008) reported on a comprehensive single-day application of Phoslock™ in Torrens Lake, Australia in 2008. Concentrations of TP before Phoslock™ treatment ranged from 0.095 to 0.155 mg/L at all sites. Concentrations of TP declined to minima of 0.045–0.061 mg/L within 2 to 3 weeks following the application, then subsequently began to increase again to pretreatment level after 4 to 5 weeks. Some, but not all of these increases were thought to be attributable to increases in runoff to the lake from rain events that occurred 3 to 4 weeks following the application.

Australia Water Quality Center (2008) also reported that the 2008 Phoslock™ treatment in Torrens Lake, Australia appeared to decrease the total algal biomass and cyanobacterial abundance in the water column soon after application. This observation was thought to be attributable to a direct flocculation and sedimentation effect of the bentonite clay on particulate matter, including algal cells, more so than an indirect response on algal growth from nutrient limitation; a process that can reasonably be expected to have a lag time of a few weeks.

2.1.1.3 Reported Key Controlling Factors

In laboratory tests, Douglas et al. (2000) found that when the solution pH was raised above 9, the SRP removal rate of Phoslock™ was slowed, with 40 percent of the SRP removed after the first hour of treatment and 60 percent removed after 24 hours (Douglas et al. 2000). The observed decline was attributed to the formation of the hydroxyl species of the lanthanum ions. Douglas et al. (2000) further comments that if the observed rate of the P uptake at pH 9 were to continue, 99 percent of the SRP could be removed in about 4 days.

Douglas et al. (2004) consider that the use of Phoslock™ to remove phosphate is superior to the use of more conventional use of alum and ferric chloride in several ways: (1) Phoslock™ can achieve greater total removal of phosphates; (2) Phoslock™ is effective over a wider pH range (c. 4.5–8.5) than Fe (III) (c. 3.5–4.5) or Al (c. 5.0–6.5); (3) Phoslock™ precipitates polyphosphates equally well as orthophosphates; and (4) the solubility product of La-phosphate is extremely low, and therefore is not bio-available with less potential for toxicity.

2.1.1.4 Reported Advantages and Disadvantages

The advantages of Phoslock™ include: (1) a relatively high affinity for P compared with conventional treatments; (2) an ability to bind P under both aerobic and anaerobic conditions and over a broader range of pH conditions than most other coagulants (e.g., alum); (3) it does not readily re-release P when physical and

chemical conditions change; and (4) a relatively low toxicity, resulting in safe handling, application and disposal.

The disadvantages of Phoslock™ include: (1) relatively high cost compared with conventional treatments; (2) slow settling of fine particles, and resultant turbidity in waters during the application period; and (3) eventual burial in sediment that reduces efficacy.

2.1.2 Aluminum-Modified Zeolite (Aqual P™)

2.1.2.1 Description

Aqual P™ is an aluminum-amended, proprietary zeolite that is marketed specifically for nutrient removal from lakes and other waterways. Zeolites belong to a family of naturally occurring volcanic minerals with unique physical and chemical characteristics. Natural zeolites consist of a negatively charged three-dimensional aluminosilicate lattice which forms a network of open channels and internal surface area. The channels, typically 0.3 to 0.7 nanometers in diameter (3 to 7 angstroms, slightly larger than a water molecule), selectively screen molecules according to size and exchangeable cations, thus giving rise to the term “molecular sieve”. In general, zeolites provide a substantial cation exchange capacity (CEC). As a cation exchange agent, zeolites have been widely investigated and applied to remove cation contaminants in waters and wastewaters (Widiastutia et al. 2008), and for capping chemically contaminated sediments (Vopel et al. 2008).

In Aqual P™, the aluminum amendment gives the zeolite mineral, which is a strong cation absorber, a strong affinity for, and thus the ability to sequester phosphate. These products were originally developed as a sediment capping material to assist in the reduction of internal P loading in lakes from anoxic sediments during seasonal stratification, and are the only known capping agents that are capable of inactivating both P and N (Gibbs and Ozkundakci 2011, Ozkundakci et al. 2011). Although the modified zeolites have anion exchange properties, the zeolite is still accessible to sorb inorganic cations. It is because the modifying agents are relatively large molecules that remain on the external surface of the zeolite crystal and do not enter the zeolite channels. The internal cation-exchange site of the zeolite remains accessible to sorb inorganic cations.

2.1.2.2 Reported Effectiveness

Gibbs and Ozkundakci (2011) tested the aluminum-amended, proprietary P-inactivation zeolite Z2G1 (which is essentially the same as Aqual-P™) on sediment cores from Lake Okaro, New Zealand for P removal efficacy prior to a whole lake trial to manage internal P loading. Sediment core study results showed that a thin layer of Z2G1 (about 2 mm) could completely block the release of P from the sediment under aerobic and anoxic conditions, and remove P from the overlying water in contact with the capping layer. However, subsequent results from the whole lake treatment study indicated that the sediment P release occurred after the application of Z2G1 (Ozkundakci et al. 2011). Similarly, reduction in N release was lower than expected when compared to the laboratory incubation study. Ozkundakci et al. (2011) concluded that these differences illustrate the difficulty of extrapolating laboratory results to a whole lake, and are likely to be a number of factors, such as the timing of the Z2G1 application after the lake had stratified and the release of SRP from the sediment had begun, and the uneven coating of the capping material on the sediment surface.

Gibbs et al. (2011) assessed the effectiveness of the modified zeolite Z2G1 (which is essentially the same as Aqual-P™) in comparison to alum and Phoslock™ as sediment capping agents to manage P release from sediments. Gibbs et al. (2011) determined that all three products are capable of blocking the release of P from the sediments depending on dosage rates and other factors, such as pH and water hardness. At all levels of treatment the alum and Phoslock™ completely blocked the release of dissolved reactive P (DRP) from the sediments and had the capacity to remove additional DRP from the overlying water column. The Z2G1 at the 50 and 100 percent treatments was not able to block the release of DRP from the sediment. At the 200 percent treatment, which had complete sediment coverage, Z2G1 did completely block the DRP release and had the capacity to remove additional DRP from the overlying water column comparable with

the other capping materials. For NO₃-N, the greatest reduction (48 percent) occurred in the Phoslock™ treatments although similar levels of reduction (43 percent) also occurred in the 100 and 200 percent alum treatments, while Z2G1 caused a 37 percent reduction at the 200 percent treatment.

2.1.2.3 Reported Key Controlling Factors

Zeolites have a high surface area for binding of cations, typical packed bed porosity of 30 to 50 percent, and are stable across a wide range of pH. The ion exchange capacity is of high significance and is typically within the range of 1.65 to 2.5 milliequivalents per gram (mEq/gm).

2.1.2.4 Reported Advantages and Disadvantages

The primary advantages of modified zeolites include: (1) more efficient and effective targeting of nutrient or contaminant removal than natural unmodified zeolites; and (2) the only known nutrient treatment agent that is capable of inactivating both P and N. The primary disadvantages of modified zeolites include: (1) relatively higher costs compared with natural zeolites; (2) effectiveness is dependent on the initial contaminant concentrations, contact time, pH, permeability, and structural stability of the zeolite; and (3) effectiveness may differ among modified zeolite forms and commercial products.

2.1.3 Polyaluminum Hydroxychloride (PACl)

2.1.3.1 Description

Poyaluminum chlorides (PACl) are synthetic polymers that serve as an inorganic aluminum-based coagulant. PACls are a potential substitute for alum because: (1) PACls tend to be more robust than alum with regard to achieving coagulation goals because their precipitates vary less under changing environmental conditions; and (2) PACl has less potential toxicity-related concerns than alum.

PACL products react to form insoluble aluminum polyhydroxides which precipitate in big volumetric flocs similar to those formed with alum to absorb and precipitate suspended pollutants in the water. PACl compounds contain supplemental hydroxide (OH)⁻ ions which cause lower pH depression and alkalinity impacts during coagulation processes. PACL products generally do not require the addition of acid or base to control the pH within the natural water range.

2.1.3.2 Reported Effectiveness

PACls are synthetic polymers designed for coagulation based on optimum charge neutralization and bridge binding. Precipitates formed by alum and ferric salt application are amorphous hydroxides and the exact characteristics of those products and the efficiency of the chemicals used are dependent upon a number of variables such as temperature and mixing energy (Edzwald and Van Benschoten 1990). Engineered polymers like PACls tend to be more efficient and robust with regard to achieving coagulation goals because their precipitates are less variable. PACL modified with silica or sulfate provided consistent removal of P and fine particles in a stormwater treatment study at Tahoe Basin CA (Trejo-Gaytan et al. 2006).

2.1.3.3 Reported Key Controlling Factors

PACls have very good performance over a broad dosing range, and inorganic/organic polymer blends appear to be the most difficult to overdose. Even so, however, more optimal dosing of PACls improves coagulant performance. Thus, more optimal dosing of PACls leads to more efficient coagulant utilization and better performance.

Compared to alum and ferric chloride, the performance of PACls with regard to P and turbidity removal is minimally affected by changes in temperature, mixing regimes, storm water quality and dose. The performance of PACls is also less affected by different rapid or slow mixing specifications.

2.1.3.4 Reported Advantages and Disadvantages

The advantages of PACls include: (1) they reduce total dissolved P as well as alum; (2) typically produce less flocculate than alum; (3) they have a broader range of pH over which they are effective (i.e., optimally effective for waters with pH ranging from 6 – 8, and relatively effective up to a pH of 10); and (4) they

reportedly have ten to twenty times less dissolved aluminum in solution than does alum. PACl has less toxicity potential than sulfate-containing alum. Sulfate loading from alum can be a concern because of the link of sulfur cycling in wetland environments with microbially-mediated methylation of mercury. Methylmercury is toxic, and once formed can bioaccumulate among trophic levels.

The disadvantages of PACls are: (1) they are substantially more expensive than alum, and distributors are more limited; (2) they are available in a wide range of products that are not all equal in performance, which requires an understanding and assessment of their properties in the context of water treatment goals in order to select a preferred PACl coagulants; and (3) it is reported that some PACls are less effective at removing P than alum.

2.1.4 Alum (Aluminum Sulfate Buffered with Sodium Aluminate)

2.1.4.1 Description

Alum, the common name for aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$)¹, has been used in a variety of settings to reduce the P concentrations in water. Removal of P using alum occurs through the formation of either aluminum hydroxide, which subsequently adsorbs P, or precipitation of aluminum phosphate (Metcalf & Eddy 1991, Bottcher et al. 2009). Alum has been used extensively in lakes as a management technique to reduce the amount of P in the water and limit the availability of this nutrient for algae production.

The main mechanism of P removal upon addition of alum involves the formation of aluminum phosphate $\text{Al}_{0.8}\text{H}_2\text{PO}_4(\text{OH})_{1.4}$ (Sedlak 1991). When only moderate P removal is required, and relatively small alum dosages used, aluminum phosphate is the predominant complex formed. However, when lower soluble P concentrations are required, larger alum dosages are required, and the formation of aluminum hydroxide precipitate [$\text{Al}(\text{OH})_3$] becomes an important reaction. The aluminum hydroxide precipitate constitutes a gelatinous “floc”. As the floc settles, the associated bound P is removed from the water. The floc also tends to collect suspended particles in the water and carry them down to the bottom. On the bottom, the floc forms a layer that also can act as a P barrier by combining with P as it is released from the sediments. Alum addition also results in Al^{3+} ions in solution, which can combine with dissolved phosphate to form an AlPO_4 precipitate. In addition to reducing P, alum treatment can also reduce algal blooms in two ways: enmeshment and precipitation of algae in the floc and through reductions in available P for algal growth.

2.1.4.2 Reported Effectiveness

There are a number of case studies of lakes that have undergone nutrient inactivation with alum. Welch and Cooke (1995) evaluated the effectiveness and longevity of alum treatments (based on reduction in TP) on 21 lakes across the U.S. In stratified lakes, percent reduction in controlling internal P loading was continuously above 80 percent over an average of 13 years. Internal loading rate of TP was reduced in six of nine non-stratified lakes by an average of 66 percent over an average of 8 years. However, Welch and Cooke (1995) did find that alum treatment can be less effective or require repeated applications in lakes with high external loading. Welch and Schriever (1994) also found that alum may be completely ineffective, or effectiveness may be short-lived, if much of the lake is covered with macrophytes that senesce during summer and contribute P to the water.

Alum has been tested in a wetland treating municipal wastewater in Florida by Malecki-Brown et al. (2007, 2010) in Florida. Wetland cells treated with alum had significantly lower soluble reactive phosphorus (SRP) than their control counterparts, with removals ranging from 77 to 86 percent depending on the wetland vegetation. On average, alum reduced SRP concentrations to one third of that in the controls.

Ann et al. (2000a; 2000b) investigated the efficacy of alum to increase P retention in highly organic Lake Apopka (Florida) marsh soils under flooded conditions. They found that 12 g of alum was needed for each kilogram of soil to minimize P release from soil to overlying water in the Lake Apopka marsh that had previously been drained and used for intensive agriculture.

¹ The number of water molecules may vary from 14 to 18.

2.1.4.3 Reported Key Controlling Factors

A key controlling factor in the effectiveness, and also the potential toxicity, of alum is the pH of the system (Malecki-Brown et al. 2007). Alum (as aluminum sulfate) has a pH of 2.4 (Beecroft et al. 1995) and therefore tends to decrease the pH of the system to which it is added. When alum is used, alkalinity is consumed as a result of the coagulation process which can result in a decrease in solution pH, depending upon the applied alum dose and the available buffering capacity of the source water.

As long as the pH remains between 6 and 8, P inactivation will result. However, if the pH decreases to between 4 and 6, bound P will be released. Below pH 4 and above pH 8, soluble Al^{3+} dominates which may result in aluminum toxicity (Cooke et al. 1993). The minimum solubility for aluminum phosphate is approximately $10^{-6.5}$ M which occurs at a pH value of approximately 6-6.5. In general, the coagulation process is maximized, and residual metal concentrations minimized, when the coagulated water is maintained within the pH range of minimum solubility for the applied coagulant. For alum, this pH zone is approximately 6-8, since freshly precipitated alum floc has a minimum solubility of approximately 10^{-5} M which occurs in the pH range of 6.2-8.0.

2.1.4.4 Reported Advantages and Disadvantages

An advantage of alum treatment is that it provides rapid, highly efficient removal of P and total suspended solids (TSS). In comparison to other potential coagulants (such as iron and calcium), aluminum compounds are more suitable for coagulation processes under near-neutral pH conditions. Alum is relatively inexpensive compared to other treatment approaches on the basis of unit costs per mass of P removed. The floc of precipitated P from alum treatment is stable and chemically inert, even if there are fluctuations in redox or pH, and it becomes even more stable as it ages (Harper 2007).

Disadvantages of alum use are the potential adverse impacts of alum include excessive acidification in systems with low buffering capacity and potential buildup and development of toxic concentrations of aluminum (Malecki-Brown et al. 2007). The Klamath River is a weakly-buffered system (with alkalinity generally less than 100 mg/L as $CaCO_3$) that is subject to seasonally-elevated pH in response to changes in dissolved CO_2 caused by algal photosynthesis (PacifiCorp 2008). As described above, alum lacks effectiveness as pH exceeds 8. This indicates that pH/buffer control would likely be required for use of alum in the Klamath system. Potential aluminum toxicity is a concern with alum use. Moreover, the association of sulfate from the alum with methylation of mercury in wetland systems warrants further examination prior to implementation. To minimize toxicity risks, careful management and monitoring of dosing levels and resultant water quality effects are needed.

2.2 Source Waters Selected for Testing

Three source waters (from three upper Klamath Basin locations in Oregon) were selected for the laboratory-based bench testing, including:

- Sevenmile Canal (just upstream from Agency Lake)
- Upper Klamath Lake outlet (near Link River dam)
- Keno reservoir (near Miller Island)

PacifiCorp and CH2M HILL, in consultation with the TAC, selected these three source waters to be tested based on the following considerations: (1) these waters typically have quite high nutrient concentrations, notably P; (2) these waters represent a spatial mix of high-nutrient waters both above, within, and below Upper Klamath Lake; and (3) the locations of these waters offer relatively high potential for further future testing or implementation at the field scale.

TABLE 2-1
Treatment Agents Used for Testing

Agent	Mode of Action	Features	References for Use and Effectiveness (see References)
Aluminum Sulfate (Alum) ($\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$)	Removes P through formation of aluminum hydroxide or precipitation of aluminum phosphate.	<ul style="list-style-type: none"> • Most widely used coagulant for P removal • History of effective P reduction in treated lakes, wetlands • Effective in pH range between 6 and 8 • Alkalinity consumed during use, which can result in pH decrease • Addition of buffer may be needed where alkalinity is low • Relatively inexpensive compared to other coagulants • Potential toxicity can be a concern • pH of 1% solution = 3.5 • Available in liquid (4.4% Al) or granular (17% Al_2O_3) form 	Ann et al. (2000a; 2000b), Bottcher et al. (2009), Cooke et al. (1993), Malecki-Brown et al. (2007, 2010), Welch and Cooke (1995), Welch and Schriever (1994)
Sodium Aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$)	Same solubility and precipitation stoichiometry as alum. Sodium aluminate is Al dissolved in sodium hydroxide, so supplies alkalinity when used.	<ul style="list-style-type: none"> • Mainly used in conjunction with alum as buffer for low alkalinity systems • pH of 1% solution = 14 • Available in liquid form (10-13% Al or 20-25% Al_2O_3) 	See above references for alum
Polyaluminum Hydroxychloride (PACl)	Removes P through precipitation of and adsorption by formation of insoluble aluminum polyhydroxides.	<ul style="list-style-type: none"> • Synthetic polymer that serves as inorganic Al-based coagulant • Effective alternative to alum and FeCl_3 for P removal in natural waters • Operates over wider pH and alkalinity range than alum and FeCl_3 • Causes less depression in pH and alkalinity than alum • Less risk of toxicity than alum • Few heavy metal impurities • Substantially more expensive than alum and FeCl_3 • pH of 1% solution varies • Available in liquid form (3-13% Al) 	Gebbie (2001), Pernitsky and Edzward (2006), Trejo-Gaytan et al. (2006)
Lanthanum-Modified Bentonite Clay (Phoslock™) ($\text{La} + \text{Al}_2\text{O}_3 \cdot 4(\text{SiO}_2) \cdot \text{H}_2\text{O}$)	Proprietary modified bentonite clay. La ions sorbed to the clay matrix react preferentially with soluble P compounds in water and rapidly form a highly stable insoluble species of LaPO_4 , or rhabdophane.	<ul style="list-style-type: none"> • Effective alternative to alum and FeCl_3 for P removal in natural waters • Reported to operate over wider pH and alkalinity range than alum and FeCl_3 • P binding capacity not affected by anoxia • Less risk of toxicity than alum • Relatively more expensive compared to other coagulants • Reported to result in noticeable turbidity increases • pH of 1% solution = 7 to 8.5 • Available in granular form (5% La) 	Afsar and Groves (2009), Australia Water Quality Center (2008), Douglas et al. (2000), Flapper (2003), Robb et al. (2003)

TABLE 2-1
Treatment Agents Used for Testing

Agent	Mode of Action	Features	References for Use and Effectiveness (see References)
Modified Zeolite (Z2G1 or Aqual P™) (M ₂ /nO·Al ₂ O ₃ ·xSiO ₂ ·yH ₂ O)	Proprietary Al-amended silicate lattice acts to exchange anions (like P) and absorb cations (like N).	<ul style="list-style-type: none"> • Unlike other coagulants, capable of inactivating both P and N • Limited instances of use for lake, reservoir, and wetland treatments • Relatively more expensive compared to other coagulants • Lack of information on impurities or risk of toxicity • pH of 1% solution not available at time of preparation of this plan • Availability of form not available at time of preparation of this plan 	Bowman (2003), Gibbs et al. (2011), Gibbs and Ozkundakci (2011), Ozkundakci et al. (2011)

Methods

This section describes the methods used to collect the source water sample and conduct the laboratory-based jar tests.

3.1 Source Water Sample Collection and Characterization

In preparation for the laboratory-based bench testing, bulk water samples were collected at the three selected water source locations in pre-cleaned 10-liter polyethylene containers, six (6) containers per site, provided by CH2M HILL's Applied Sciences Laboratory. Subcontractor E&S Environmental Chemistry of Corvallis, OR obtained the three source water samples from the three source water locations on July 29, 2014 at the times listed in Table 3-1.

Source water samples were collected from the three source water locations from a depth of 0.5 meters (m) using a water pump. A 5/8-inch (in) polyethylene hose was attached to intake and output of pump, and the water pump and hose were flushed with distilled water and then with sample water. The set of polyethylene sample containers for the site were then filled in succession and placed in coolers. Water temperature, dissolved oxygen (DO), and pH were measured with a Troll 9500 Sonde placed near the intake hose.

The containers were then transported for next-day delivery by E&S to the Applied Sciences Lab (in Corvallis, Oregon). During transport, the bulk water samples were maintained in larger storage coolers approximately within the diurnal range of water temperatures typical of the source waters at the time of collection.

TABLE 3-1

Source Waters Samples Collection and Subsequent Jar Test Dates and Times

Source	Sampling Date	Approx. Sampling Time	Test Date	Approx. Test Time
Keno Reservoir	7/29/14	12:50	8/2/14	15:00
Sevenmile Canal	7/29/14	16:00	8/1/14	10:30
Upper Klamath	7/29/14	14:00	7/30/14	15:30

When the containers of source waters arrived at the Applied Sciences Lab, samples from each of the source waters were submitted for characterization analysis to understand the ambient (pre-test) chemistry of the source waters. The six (6) containers from each site were homogenized with a drum pump, a sample aliquot was removed for the baseline characterization analysis, and the remaining water was redistributed into the same containers to be held at 5°C until testing. The individual source water sample aliquots were analyzed for the water quality parameters listed in Table 3-2. The Applied Sciences Lab performed the analytical testing of most water quality parameters listed in Table 3-2 with two exceptions. The exceptions included chlorophyll- α , which was analyzed by ALS Environmental laboratory (in Kelso, Washington), and dissolved lanthanum analyzed by Test America (in St. Louis, Missouri).

TABLE 3-2
Parameters, Analytical Methods, and Method Detection and Reporting Limits (MDL, MRL)

Parameter	Analysis Method	MDL	MRL	Units
General Parameters				
Water temperature	In-situ probe	NA	0.1	°C
Hydrogen ion (pH)	In-situ probe	NA	0.1	units
Dissolved oxygen (DO)	In-situ probe	NA	1.0	mg/L
Turbidity	SM2130.B	NA	5	NTU
Alkalinity	EPA310.1	0.5	5	mg/L
Total suspended solids	SM2540D	0.7	2	mg/L
Nutrients				
Total phosphorus (TP)	EPA365.4	0.0078	0.05	mg/L
Orthophosphate (PO ₄ -P)	EPA365.1	0.001	0.01	mg/L
Total nitrogen (TN)	SM4500-N B	0.018	0.20	mg/L
Ammonia nitrogen (NH ₃ -N)	EPA350.1	0.0078	0.10	mg/L
Nitrate+nitrite nitrogen (NO ₃ +NO ₄ -N)	EPA353.2	0.0057	0.01	mg/L
Biological Parameters				
Chlorophyll- α	SM10200H.3	NA	0.02	μ g/L
Other Analytes				
Dissolved aluminum	SM200.7	0.001	0.1	mg/L
Dissolved lanthanum	SW6020	2	0.062	μ g/L
Dissolved organic carbon (DOC)	SM5310B	0.12	0.50	mg/L
Dissolved sulfate	EPA 300	0.032	0.2	mg/L
Silica, soluble	EPA 200.7	0.022	1.1	mg/L

3.2 Laboratory Jar Tests

Jar tests (treatability testing) were subsequently conducted in the CH2M HILL's Applied Sciences Lab as soon as practicable on the dates/times listed in Table 3-1. The tests began with Upper Klamath water because the bulk sample for this site was most "biologically active" with appreciable algae biomatter present (as further discussed in the Results section below). As noted above, the source water containers were held at 5 °C until testing to minimize biological activity and preserve sample character to the extent practicable since arrival to the lab.

3.2.1 Agent Dose Determinations and Ranges Tested

Each of the four agents were tested at dose concentrations of 10, 30, 50, 80, and 120 mg/L (ppm) to evaluate a relatively wide range of potential application doses. Agent doses as used and reported herein are basically expressed in terms of "supplied product", which is the most meaningful way to express doses due to the complex chemical nature and formulations of the agents as supplied². As such, the dose

² In fact, because Phoslock™ and Aqual-P™ are proprietary products, their exact chemical formulations are unavailable.

concentrations between agents are comparable to one another in terms of the dose of supplied product, but are not necessarily directly comparable in terms of the amount of the agent's active ingredient responsible for nutrient reduction, particularly P. Regardless, CH2M HILL has confirmed based on research literature review and inquiries to the manufacturers that the range of doses evaluated in this study are within the range of doses typically used or considered in actual treatment applications using these products.

For example, a dose rate of 50 mg/L (or about 2.5 mg/L La) is reported by the manufacturer as typical for Phoslock™ applications in waterbodies (SePRO 2012). Gibbs (2010) reports a modified zeolite application dosage of about 40 mg/L in a eutrophic lake in New Zealand (using Z2G1, which is similar to Aqual-P™) that resulted in a 60 percent reduction in water-column dissolved P, with a reapplication two years later at a dose of 13 mg/L that resulted in no measurable reduction in dissolved P. Anderson (2012a) used detailed modeling to estimate that modified zeolite dosages (using Aqual-P™) of 21 mg/L and 33 mg/L would result in P reductions of 40 percent and 50 percent, respectively, in Canyon Lake (CA).

Cooke et al. (2005) report alum dosages that have been used in lakes and reservoirs (depending on various factors, such as P-reduction goals and specific lake characteristics) that generally range from about 25 to 250 mg/L (or about 2 to 10 mg/L Al). Alum dose rates of between 50 and 75 mg/L (or 2 to 3 mg/L Al) yielded optimal P removal in similar jar tests recently performed on Canyon Lake (CA) waters (Anderson 2012b). PACl dosages are considered roughly equivalent to alum doses, as PACl is 91 percent of an alum dose on a molar metal-ion concentration basis (Howe and Clark 2002).

For Phoslock™ and Aqual-P™, dose concentrations were obtained by directly adding 10, 30, 50, 80, and 120 mg of product (In powder form) per liter (L) of sample water. The PACl product (PAX-18™) was added neat (undiluted) as received (in liquid form) to sample volumes to reach the target doses of 10, 30, 50, 80, and 120 mg/L on a weight basis.

The alum agent tested was based on a 2:1 mixture of the two alum agents – aluminum sulfate and sodium aluminate (both are listed and summarized in Table 2-1). The resulting buffered alum was intended to maintain pH within a circumneutral range, since the use of aluminum sulfate alone can depress the pH of receiving waters that have low alkalinity (Cooke et al. 2005). The buffered alum agent was prepared in three steps:

1. An aluminum sulfate working solution (at 10,000 mg/L $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$) was prepared by mixing 1.58 mL of neat product (48 percent aluminum sulfate) with 100 mL deionized water (DIW).
2. A sodium aluminate working solution (at 10,000 mg/L $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$) was prepared by adding 1 g of sodium aluminate to 100 mL of DIW.
3. The buffered alum agent was prepared by mixing 66.67 mL of the aluminum sulfate solution with 33.33 mL the sodium aluminate solution to create the 2:1 buffered alum solution used in the testing, which calculated out to 6,667 mg/L $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$.

3.2.2 Laboratory Test Procedures

The jar tests (also referred to as bench-scale treatability tests) were performed at CH2M HILL's Applied Sciences Lab in Corvallis, Oregon. The jar test method allowed for controlled testing of agents across the series of doses (as described in the previous section) to assess total phosphorus (TP) and orthophosphate (PO4) removal efficiency and effects on other water quality constituents in waters from the upper Klamath Basin.

A total of 12 jar tests were conducted that were comprised of a jar test for each of the four agents on each of the three bulk water source samples (four-by-three). All four agents were tested on a source within the same day (on test dates as listed in Table 3-1). Each test consisted of a set of five beakers (jars) to assess the series of the five incremental dosages (i.e., 10, 30, 50, 80, and 120 mg/L), plus the addition of an untreated control beaker (jar).

The procedures for the jar tests were as follows:

1. All glassware were acid-washed and triple-rinsed with deionized water prior to using.
2. Six test beakers (for each of the jar tests) were filled with 2-liter aliquots from the source water containers.
3. Test beakers were brought to constant temperature using a water bath. The target temperature for testing were 20°C.
4. The agents were added to five of the test beakers in amounts equal to the five test dosages (as described in the previous section). The sixth beaker served as a control with no agent added. Addition of agents to the test beakers occurred while mixing at a low speed (20 rpm) just before the start of a 60-second rapid mix stage (100 rpm on the multi-paddle jar test apparatus).
5. The Phoslock™ and Aqual-P™ were added to the jars as a fine, dry powder (as described in the previous section), which rapidly dissolved at the low mix speed (20 rpm) just prior to the 60-second rapid mix stage. The PACl (PAX-18™) and buffered alum were added to the jars in liquid form (as described in the previous section), which mixed quickly at the low mix speed (20 rpm).
6. DO and pH were measured using in-situ probes (Table 3-2) in the control jars prior to starting the test, and in all jars immediately after the rapid mix phase. Turbidity samples were collected at each sampling interval and analyzed later (within 3 hours) via turbidimeter.
7. The treated beakers were then allowed to settle for a period of approximately 24 hours to simulate settling that would occur in source waters at the field scale. The beakers were covered with clear plexiglass during settling. After 1-hour and 24-hour periods of settling, pH, DO, and turbidity were measured (as above).
8. At the end of the 24-hour settling period, the supernatant was drawn off by syphon or syringe and submitted for laboratory analyses of parameters listed in Table 3-2.

No specific toxicity tests were conducted as a part of this study. Rather, the focus of this study was to assess the efficacy of different agents to reduce nutrients in specific source waters. If and when such agents are used in the future, prevention of potential toxicity would be an important factor that would need to be assessed to determine ultimate feasibility for a given proposed application and to acquire approvals from appropriate authorizing regulatory agencies. For example, alum toxicity has been well-studied in the research literature, including the relative effects and potential for toxicity at various dosages and pH levels (e.g., see Appendix A in CH2M HILL [2014a] for detailed discussion on alum). In addition, the lab analyses for this study included some analytes (e.g., dissolved aluminum) in the treated water samples that are used to assess whether concentrations are near to, or exceed, literature-reported reported acute or chronic toxicity values (as described further below in section 4.1.4).

SECTION 4

Results

This section describes the effects of the four testing agents and their doses on nutrient reductions in source waters, particularly P, and further describes the effects of the agents on other water quality constituents in addition to P (as listed in Table 3-2). As discussed in the Introduction, study results are intended to inform the potential applicability of, and development of further measures or treatments that might consider using these agents as a tool for helping to achieve nutrient reductions in the upper Klamath Basin (likely in conjunction with other nutrient reduction technologies).

4.1 Ambient (Pre-Test) Characteristics of Source Waters

As described in the Methods section above, the ambient (pre-test) chemistry of the source waters was determined (for parameters listed in Table 3-2) to understand the baseline characteristics of each of the source waters subjected to the subsequent jar tests. The parameter values for the ambient (pre-test) analyses of the source waters are listed in Table 4-1 and discussed in the following subsections.

TABLE 4-1
Source Water Samples Characterization Results

Parameter	Units	Sevenmile Canal	Upper Klamath	Keno Reservoir
Field Collection				
Water temperature	°C	21.8	22.9	22.8
pH	Units	8.2	9.9	9.0
Dissolved oxygen (DO)	mg/L	7.1	11.3	3.0
Dissolved oxygen (DO)	% saturation	94	152	42
Specific conductance	µgS	81	119	120
Laboratory Arrival				
Water temperature	°C	20.0	20.0	20.0
pH	Units	7.5	9.9	9.4
Dissolved oxygen (DO)	mg/L	8.6	8.8	8.9
Dissolved oxygen (DO)	% saturation	98	100	101
Turbidity	NTU	3.86	44.7	10.0
Alkalinity	mg/L as CaCO3	39.3	52.1	53.0
TSS	mg/L	1.4	26.8	8.30
Total phosphorus (TP)	mg/L-P	0.23	0.35	0.33
Orthophosphate (PO4-P)	mg/L-P	0.16	0.14	0.20
Total nitrogen (TN)	mg/L-N	0.33	3.90	2.22
Ammonia (NH4)	mg/L-N	0.14	0.16	0.41
Nitrate+Nitrite (NO3+NO2)	mg/L-N	0.018	0.034	0.011
Chlorophyll-α	mg/m3	10.7	268	38.6
Dissolved organic carbon (DOC)	mg/L	2.78	6.60	6.20

TABLE 4-1
Source Water Samples Characterization Results

Parameter	Units	Sevenmile Canal	Upper Klamath	Keno Reservoir
Sulfate, soluble	mg/L	0.69	3.15	3.97
Al, soluble	µg/L	9.81	184	66.1
La, soluble	µg/L	<0.031	0.066	0.039
Si, soluble	µg/L	23,300	41,100	41,500

4.1.1 Nutrients

At the outset of this study, it was expected that the nutrient levels in source water samples, particularly P, would be “nutrient-enriched” and at or near seasonal maximum levels. By testing at high nutrient levels, it was assumed that the jar tests would provide a conservative test of the effectiveness of the agents in reducing the “nutrient-enriched” baseline levels that occur in the waters of the upper Klamath Basin (ODEQ 2010).

Indeed, nutrient levels in source water samples were high, particularly for P. Baseline levels of both total phosphorus (TP) and soluble orthophosphate (PO₄) in all three source waters (Table 4-1) were greater than 0.100 mg/L, which approximates the reported threshold for *hypereutrophic* conditions in lakes (i.e., lakes that are very nutrient-rich and characterized by frequent and large algal blooms and low transparency) (Carlson and Simpson 1996). In addition, comparison of the source water samples characterization results for nutrients (Table 4-1) with previous nutrient levels reported for the source water locations (e.g., Walker et al. 2012, Watercourse 2011, Watercourse 2012) indicate that baseline levels in all three source waters were at or above previously-measured peak seasonal mean levels of TP and PO₄ (Table 4-2).

TABLE 4-2
Source Water Samples Characterization Results for Nutrients Compared to Previous Data³

Parameter (Units)		Sevenmile Canal	Upper Klamath	Keno Reservoir
Total phosphorus (mg/L)	Source water	0.23	0.35	0.33
	Previous: Mean (approx.)	0.15	0.13	0.15
	Previous: Peak mean (approx.)	0.28	0.30	0.35
Orthophosphate (mg/L)	Source water	0.16	0.14	0.20
	Previous: Mean (approx.)	0.09	0.05	0.04
	Previous: Peak mean (approx.)	0.15	0.09	0.16
Total nitrogen (mg/L-N)	Source water	0.33	3.90	2.22
	Previous: Mean (approx.)	0.46	1.48	1.90
	Previous: Peak mean (approx.)	1.25	3.15	3.29

³ Sources of previous data information include: (1) Walker et al. (2012) for Sevenmile Canal and Upper Klamath Lake (at Link River (Dam)); and (2) Watercourse (2011) and Watercourse (2012) for Keno Reservoir.

4.1.2 Solids and Algal Matter

Baseline levels of total suspended solids (TSS), chlorophyll- α (CHLA), and turbidity were quite high in the Upper Klamath Lake (Link River Dam) source water sample, moderately high in the Keno Reservoir source water sample, and relatively low in the Sevenmile Canal source water sample (Table 4-1). The higher TSS and CHLA levels in the Upper Klamath Lake and Keno Reservoir source water samples reflect appreciable levels of algae biomatter in the samples, which are not surprising given the high nutrient levels and intense primary production expected in these waterbodies during July when the source water samples were collected.

The appreciable algae biomatter and primary production levels in the Upper Klamath Lake and Keno Reservoir source water samples indicate that these source waters were particularly “biologically active” as a baseline condition underlying the jar tests. Such biological activity is an important factor for explaining other baseline characteristics in the source water samples (such as pH and DO as discussed below) and for interpreting some of the water quality changes observed during the jar tests (as discussed further in sections below).

4.1.3 Alkalinity, pH, and DO

Baseline levels of alkalinity (in mg/L as CaCO_3) were low in source water samples (Table 4-1). Alkalinity is a measure of the ability of water to neutralize acids. In the natural environment, alkalinity comes primarily from the dissolution of carbonate rocks. Carbonate rock sources are rare in much of the Klamath basin due to its volcanic origin. As a result, the Klamath River has a relatively low alkalinity (<100 mg/L) (ODEQ 2010) as reflected in the source water samples (Table 4-1).

The low alkalinity provides for a weak buffering capacity of Klamath Basin water, including the source waters collected for this study. As such, this weak buffering capacity is frequently insufficient to buffer photosynthetically-induced increases in pH. Baseline levels of pH were quite high (alkaline), particularly in the Upper Klamath Lake (Link River Dam) and Keno Reservoir source water samples (9.0 or greater), reflecting the appreciable levels of algae biomatter and primary production in these samples. Photosynthetic activity removes carbon dioxide in the water (in the form of carbonic acid), which increases pH in the water particularly if buffering capacity is low or absent. Therefore, such high pH values (> 9.0) in the source water samples are an indicator of intense primary production activity by algae.

Baseline levels of DO were quite variable in source water samples during the time of field data collection (Table 4-1), ranging from a low (subsaturated) DO level of 3 mg/L in the Keno Reservoir sample, to a near-saturation DO level of 7.1 mg/L in the Sevenmile Canal sample, to a high (supersaturated) DO level of 11.3 mg/L in the Upper Klamath Lake (Link River Dam) sample. As indicated by the pH values discussed above), these DO levels are further indicator of intense primary production activity by algae, particularly in the Upper Klamath Lake (Link River Dam) and Keno Reservoir source water samples.

Algal blooms produce large amounts of oxygen during photosynthesis that may lead to supersaturated levels of DO in the water column (> 110% saturation), particularly during mid-to-late afternoon. Conversely, during respiration, algal blooms remove the DO from the water column which may lead to low levels of oxygen in the water column. Low (subsaturated) DO level conditions, such as observed in the Keno Reservoir source water sample, can also be created when large quantities of algae die and decompose. Keno Reservoir is known as a waterbody where hypoxia (low DO) or anoxia (no DO) in the water column occurs during summer as a result of decomposition of algae biomass emanating from Upper Klamath Lake (ODEQ 2010, Sullivan et al. 2010).

Upon arrival at the laboratory, pH levels were still high compared to field collection measurements (Table 401), particularly in the Upper Klamath Lake (Link River Dam) and Keno Reservoir source water samples (9.0 or greater). However, DO values were moderated, with each of the source water samples measuring 8.6 to 8.9 mg/L and near 100 percent saturation (Table 4-1). These measurements suggest that the direct “biological activity” (i.e., production and respiration) in the source water samples had “quieted” upon arrival at the laboratory, although certain aqueous chemistry effects from prior biological activity (such as related to the carbon dioxide-carbonic acid balance) were still present.

4.1.4 Aluminum and Lanthanum

Dissolved aluminum and lanthanum were analyzed in source water samples and during jar tests (Table 3-2) as indicators of potential toxicity⁴ because alum and PACl agents used in this study contain aluminum and Phoslock™ contains lanthanum.

4.1.4.1 Aluminum

Aluminum toxicity has been well-studied in the research literature, including the relative effects and potential for toxicity at various alum dosages and pH levels (e.g., a thorough review of alum effects on the treated aquatic environment is given in Cooke et al. [2005]). For aluminum, the U.S. Environmental Protection Agency (EPA) national recommended water quality criteria are 750 µg/L and 87 µg/L, respectively, for acute or chronic toxicity values for freshwater aquatic life⁵.

Baseline levels of soluble aluminum were relatively low in the Sevenmile Canal sample, but relatively high in the Upper Klamath Lake (Link River Dam) and Keno Reservoir source water samples (Table 4-1). These results indicate that the Upper Klamath Lake (Link River Dam) and Keno Reservoir samples are already near to, or exceed, the EPA recommended chronic toxicity criteria of 87 µg/L for aluminum as a baseline condition (prior to test applications of aluminum-containing alum and PACl).

Aluminum is one of the most abundant elements on earth, and is constantly leached from soil and bedrock through weathering. However, aluminum is only sparingly soluble in water between pH 6 and 8; therefore, aluminum concentrations are generally low in most natural waters (ATSDR 2008, Snoeyink and Jenkins 1980). Comparative data on dissolved aluminum concentrations in waters of the Klamath Basin are limited, but include previously-measured aluminum concentrations that bracket the baseline aluminum concentrations measured in the source water samples (Table 4-1). For example, dissolved aluminum concentrations were sampled from 2001 through 2005 at several sites along the Klamath River as part of the California Surface Water Ambient Monitoring Program (SWAMP)(NCRWQCB 2008). Aluminum concentrations were measured at 50.7 to 99.2 µg/L at sites from the California-Oregon state line (RM 209) to Iron Gate Dam (RM 190), 26.3 to 280.0 µg/L at sites from Iron Gate Dam to the Salmon River (RM 66), and 8.8 to 565.0 µg/L at sites from the Salmon River to Klamath Glen (RM 6)(NCRWQCB 2008). Although we did not locate previously-measured aluminum concentrations for the water column of Upper Klamath Lake, Eilers et al. (2004) reported high aluminum concentrations in upper layers of sediments in Upper Klamath Lake, which were attributed to accelerated erosional inputs associated with 20th century watershed disturbances.

⁴ No specific toxicity tests were conducted for this study. Rather, the focus of this study was to assess the efficacy of different agents to reduce nutrients in specific source waters. If and when such agents are used in the future, prevention of potential toxicity would be an important factor that would need to be assessed to determine ultimate feasibility for a given proposed application and to acquire approvals from appropriate authorizing regulatory agencies.

⁵ EPA indicates that these criteria values are expressed in terms of total recoverable aluminum in the water column at pH 6.5 – 9.0.

4.1.4.2 Lanthanum

Soluble free lanthanum is considered moderately toxic if sufficient levels are reached (Afsar and Groves 2009). As an approximate chronic toxicity level, Birge et al. (1978) determined that the 28-day LC50⁶ for lanthanum to rainbow trout eggs is 20 µg/L. As an approximate acute toxicity level, Stauber (2000) determined that the 96-hour LC50 for lanthanum to rainbow trout adults is 127 µg/L or greater. Baseline levels of soluble lanthanum were low in all three source water samples (Table 4-1), including levels well below the 28-day and 96-hour LC50 levels described above. We were unable to locate any comparative data on previously-measured dissolved lanthanum concentrations in waters of the Klamath Basin.

Lanthanum is a naturally occurring earth element that can occur in many forms. As used in Phoslock™, the lanthanum (about 5 percent by weight) is embedded inside a clay matrix (about 95 percent by weight) with little ability to release free lanthanum (SePRO 2012). When Phoslock™ is applied to water, the manufacturer reports that the lanthanum associated with the clay preferentially binds with phosphate (PO₄), forming a highly stable mineral called rhabdophane (LaPO₄) (SePRO 2012). This resulting rhabdophane complex has a very low solubility, and is not influenced by changes in pH and redox reactions in the water column or sediments (SePRO 2012).

4.1.5 Other Constituents

Dissolved organic carbon (DOC), sulfate, and silica also were analyzed in source water samples and during jar tests (Table 3-2). DOC serves as an indicator of dissolved organic matter, which has been reported as a factor that can potentially interfere with the removal of P by alum and other chemical agents. For example, Qualls et al. (2009) found that high concentrations of natural DOC (21 to 60 mg/L) inhibited both the short-term removal of PO₄ and the longer-term removal of TP from the water column in wetlands in Florida treated with alum.

Baseline levels of DOC were moderate in the source water samples, with concentrations measured at 2.78, 6.60, and 6.20 mg/L, respectively, for Sevenmile Canal, Upper Klamath Lake (Link River Dam), and Keno Reservoir (Table 4-1). These levels are generally in line with the range in DOC values of 3.1 to 14.0 mg/L, and the mean of 6.5 mg/L, reported by Watercourse (2011, 2012, 2013) for samples collected at Link River Dam and Keno Reservoir during 2010-2012 for the KHSB Baseline Monitoring Program.

Sulfate was tested to identify the potential for increased sulfate concentrations due to alum additions, since the alum formulation included aluminum sulfate. Sulfate is also a natural substance produced in the environment from the oxidation of elemental sulfur, sulfide minerals, or organic sulfur. If alum is considered for potential use in the future, the extent to which sulfate might be increased by alum additions may be an important decision factor related to sulfur and mercury cycling in the potential treatment location. Alum typically includes aluminum sulfate, but non-sulfate alternatives are available.

Baseline levels of sulfate were moderate in the source water samples, with concentrations measured at 0.69, 3.15, and 3.97 mg/L, respectively, for Sevenmile Canal, Upper Klamath Lake (Link River Dam), and Keno Reservoir (Table 4-1). Comparative data on previously-measured sulfate concentrations in waters of the Klamath Basin are sparse and dated. The most recent data from DEQ's LASAR database includes 20 measurements from samples taken in 2001 in the upper Klamath River, including Keno Reservoir, consisting of a range in sulfate values of 3.8 to 7.9 mg/L, and a mean of 5.6 mg/L. DEQ's LASAR database includes 36 measurements from samples taken in Upper Klamath Lake during 1959-1968, consisting of a range in sulfate values of 1.0 to 20.0 mg/L, and a mean of 8.4 mg/L.

⁶ LC50 (or "lethal concentration 50") is a standard measure of the toxicity of the surrounding medium that will kill half of the sample population of a specific test-animal in a specified period through exposure via inhalation (respiration). LC50 is measured in micrograms (or milligrams) of the material per liter, or parts per million (ppm) of water. The lower the amount, the more toxic the material. Also called median lethal concentration.

Silica was tested because the presence of silicates, if sufficiently concentrated, may help to explain dissolved aluminum speciation and bioavailability, which are key factors that control residual aluminum toxicity (e.g., from alum treatments)(Cooke et al. 2005). For example, Birchall et al. (1989) showed that formation of aluminosilicates may be significant in waters containing concentrations of silica above about 2.8 to 14 mg/L, and that this aluminosilicate formation can significantly reduce the bioavailability of aluminum and its toxicity potential.

Baseline levels of soluble silica were moderate in the source water samples, with concentrations measured at 23.3, 41.1, and 41.5 mg/L, respectively, for Sevenmile Canal, Upper Klamath Lake (Link River Dam), and Keno Reservoir (Table 4-1). These levels exceed levels at which Birchall et al. (1989) showed that formation of aluminosilicates may be significant. Comparative data on previously-measured silica concentrations in waters of the Klamath Basin are sparse and dated. Sanville et al. (1974) reported a range in soluble silica values of 9.6 to 49.0 mg/L for over 60 water samples collected in Upper Klamath Lake during 1967-1970. Sanville et al. (1974) also found a distinct seasonal trend in soluble silica values, with lowest values in spring (concurrent with peak presence of diatoms) and highest values in fall and winter.

4.2 Jar Test Results

As described in the Methods section above, the jar tests allowed for controlled testing of the four agents (i.e., Phoslock™, Aqual-P™, PAX-18™, and buffered alum) across the series of doses (i.e., 10, 30, 50, 80, and 120 mg/L) to assess TP and PO₄ removal efficiency and effects on other water quality constituents in the three source waters from the upper Klamath Basin. The results of the jar tests are discussed in the following subsections.

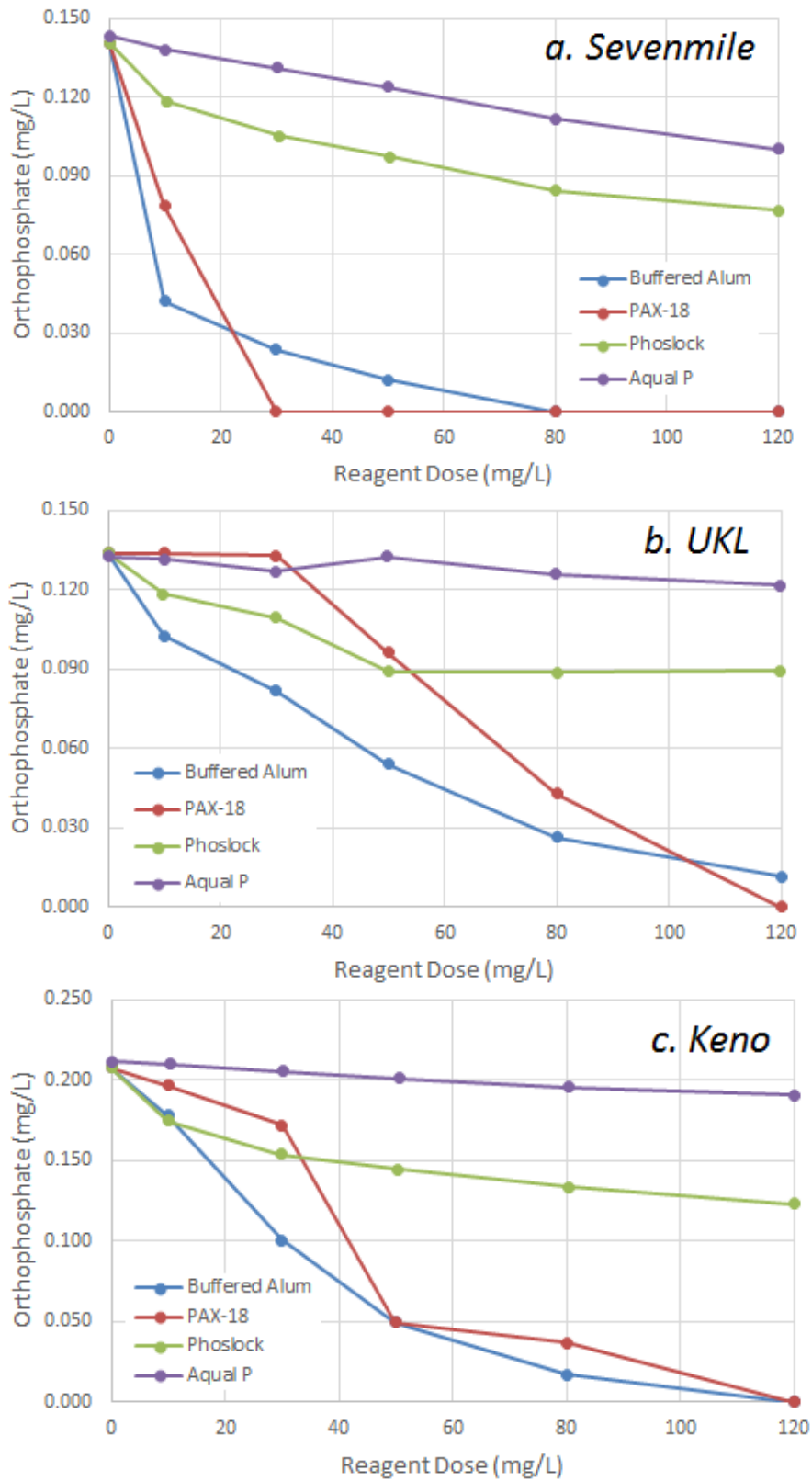
4.2.1 Nutrients

As described in the Introduction section above, the key purpose of the jar tests was to assess the effectiveness of the four agents to reduce nutrients, notably P. The jar test results indicate that all four agents were effective (but to varying degrees) at reducing PO₄, which is considered a positive and important result, given that: (1) P is considered the key limiting nutrient in the Klamath Basin (ODEQ 2002, NCRWQCB 2010, ODEQ 2010); and (2) PO₄ is the soluble, bioavailable fraction of P that is directly taken up by algae, and the concentration of this fraction constitutes an index of the amount of P immediately available for algal growth (Horne and Goldman 1994, Cooke et al. 2005).

Figure 4-1 shows the effect of agent dose on PO₄ concentrations in source water samples following agent applications and 24-hour settling. The agents produced the general trend of increased PO₄ removal with increasing dose. PAX-18™ and buffered alum produced the greatest PO₄ removal (i.e., lowest residual PO₄ concentrations), followed in order by Phoslock™ and Aqual-P™. For example, in the Sevenmile Canal source water sample, PAX-18™ and buffered alum removed all (100 percent) of PO₄ at agent doses of 30 mg/L and 80 mg/L, respectively, while Phoslock™ and Aqual-P™ removed a maximum of 50 percent and 33 percent of PO₄, respectively, at the highest test agent dose of 120 mg/L (Figure 4-1, top plot). In the Keno Reservoir source water sample, PAX-18™ and buffered alum removed all (100 percent) of PO₄ at the highest test agent dose of 120 mg/L, while Phoslock™ and Aqual-P™ removed a maximum of 40 percent and 10 percent of PO₄, respectively, at the highest test agent dose (Figure 4-1, middle plot). In the Upper Klamath Lake source water sample, PAX-18™ and buffered alum removed 100 percent and 95 percent of PO₄, respectively, at the highest test agent dose of 120 mg/L, while Phoslock™ and Aqual-P™ removed a maximum of 33 percent and 7 percent of PO₄, respectively, at the highest test agent dose (Figure 4-1, bottom plot).

FIGURE 4-1

Effect of agent dose (mg/L) on orthophosphate ($PO_4\text{-P}$; in mg/L) in source water samples from Sevenmile Canal (top), Upper Klamath Lake at Link River Dam (middle), and Keno Reservoir near Miller Island (bottom).



The results also revealed that the four agents consistently produced the highest percentage of PO₄ removal in the Sevenmile Canal source water sample, the next highest percentage of PO₄ removal in the Keno Reservoir source water sample, and the least percentage of PO₄ removal in the Upper Klamath Lake source water sample (Figure 4-1). For example, at the 50 mg/L agent dose, an average of about 60 percent of PO₄ was removed by the four agents from the Sevenmile Canal source water sample, an average of 46 percent of PO₄ was removed by the four agents from the Keno Reservoir source water sample, and an average of 25 percent of PO₄ was removed from the Upper Klamath Lake source water sample.

The higher efficiency of PO₄ removal in the Keno Reservoir source water sample and lower efficiency of PO₄ removal in the Upper Klamath Lake source water sample may be due to the much higher algae and particulate matter content in the Upper Klamath Lake source water sample, which likely interfered with the agents' P removal effectiveness. For example, research has shown that algal organic matter can inhibit flocculation or otherwise interfere with removal of particulates by various coagulants resulting in an increase of dosage demand (Henderson et al. 2010, Vandamme et al. 2012).

Figure 4-2 shows the effect of agent dose on TP concentrations in source water samples following agent applications and 24-hour settling. As with PO₄, the agents produced the general trend of increased TP removal with increasing dose, but the percent reduction of TP was consistently less than that observed for PO₄. Reductions in TP were greater with PAX-18™ and buffered alum, particularly at higher doses, while reduction in TP were relatively more modest across all doses for Phoslock™ and Aqual-P™. For example, in the Sevenmile Canal and Keno Reservoir source water samples, PAX-18™ removed a maximum of 100 percent of TP and buffered alum removed a maximum of 75 percent of TP at the highest test dose of 120 mg/L. By comparison, Phoslock™ and Aqual-P™ removed a maximum of 15 percent and 50 percent of TP, respectively, at the test agent dose of 80 mg/L (Figure 4-2, top and bottom plots).

Reduction in TP in the Upper Klamath Lake source water sample was notably less, even more so than described above for PO₄. PAX-18™ and buffered alum removed a maximum of about 40 percent of TP at the highest test dose of 120 mg/L, while Phoslock™ and Aqual-P™ removed a maximum of 20 percent and 5 percent of TP, respectively, at the test dose of 120 mg/L (Figure 4-2, middle plot). The consistently lesser reduction in TP in the Upper Klamath Lake source water sample is likely due to the much higher algae and particulate matter content in the Upper Klamath Lake source water sample, which likely interfered with the agents' P removal effectiveness (described above for PO₄). In addition, the higher amount of particulate and organic matter in the Upper Klamath Lake waters means that TP in these waters consists of a relatively lower percent fraction of PO₄ toward which the agents directly act.

Although PAX-18™ showed the greatest maximum removal of both PO₄ and TP during the tests, particularly at the higher test doses, it is noted that PAX-18™ was relatively much less effective at the low test doses. For example, in the Upper Klamath Lake source water samples, PAX-18™ removed 75 to 100 percent of PO₄ at the higher test doses of 80 to 120 mg/L, but zero to 30 percent of PO₄ at the lower test doses of 10 to 50 mg/L (Figure 4-1, middle plot). In the Keno Reservoir source water samples, PAX-18™ removed 50 to 100 percent of TP at the higher test doses of 80 to 120 mg/L, but only 7 percent or less of TP at the lower test doses of 10 to 50 mg/L (Figure 4-2, bottom plot). Observations in the lab suggested that floc formation from the test applications of PAX-18™ was much more immediate and substantial at the higher test concentrations, which may help explain the relatively abrupt change in PAX-18™ effectiveness across the test doses.

Figures 4-3 and 4-4 shows the effect of agent dose on TN and NO₃+NO₂ concentrations, respectively, in source water samples following agent applications and 24-hour settling. In general, no consistent trends of effects of agent dose on TN and NO₃+NO₂ are evident. Such results were expected as these agents are known to have little or no effect on N specifically. The possible exception is Aqual-P™, which has been observed in other studies as capable of inactivating N (in addition to P), unlike other coagulants (Gibbs and Ozkundakci 2011, Ozkundakci et al. 2011)(see Table 2-1). However, no significant or consistent reductions in

TN and NO₃+NO₂ were observed in our jar tests results using Aqual-P™ (Figures 4-3 and 4-4). Ammonia results are not presented due to unreliable laboratory analysis of samples.⁷

4.2.2 Algal Matter and Suspended Solids

In general, the agents produced inconsistent trends of algal matter and suspended solids reduction with increasing test doses. Algal matter reductions (based on chlorophyll- α) were more evident than reductions in either TSS or turbidity, although results varied by source water sample. For example, Figure 4-5 shows the effect of agent dose on chlorophyll- α concentrations (mg/m³) – a surrogate for algal matter – in the Upper Klamath Lake source water sample following agent applications and 24-hour settling. In the Upper Klamath Lake source water sample, PAX-18™ removed 60 percent of chlorophyll- α at the highest test agent dose of 120 mg/L, while buffered alum, Phoslock™, and Aqual-P™ removed a maximum of 22, 32, and 7 percent of chlorophyll- α , respectively, at the highest test agent dose (Figure 4-5, top plot). In the Keno Reservoir source water sample, PAX-18™ removed 100 percent of chlorophyll- α at the highest test agent dose of 120 mg/L, while buffered alum, Phoslock™, and Aqual-P™ removed a maximum of 20, 30, and 40 percent of chlorophyll- α , respectively, at the highest test agent dose (Figure 4-5, top plot). Baseline chlorophyll- α levels in Sevenmile Canal were relatively low and the effects of test doses (not plotted) were inconclusive.

In general, the agents produced mainly small and inconsistent changes in TSS with increasing test doses. TSS concentrations were generally unchanged across all test doses of buffered alum, Phoslock™, and Aqual-P™ in all samples. The exception was PAX-18™, which was observed to actually increase TSS at higher test doses in each of the three source water samples, although to varying degrees (Figure 4-6). The cause of these increases with PAX-18™ is not clear. A possible factor may be the more immediate and substantial floc formation observed with PAX-18™ at the higher test doses (80 to 120 mg/L). Although jar test analysis samples were taken from the supernatant of the jars, which is presumed to be above settled floc, some residual PAX-18™ floc was perhaps still present in the supernatant if settling was still not complete after 24-hours.

In general, the agents produced mainly small changes in turbidity with increasing test doses, particularly relative to non-dosed control samples (indicated in the plots by the “0 mg/L” test dose). For example, Figure 4-7 shows the effect of agent dose (mg/L) on turbidity (NTU) in source water samples from Upper Klamath Lake after 1-hour settling (top plot) and 24-hour settling (bottom plot). Comparison of the upper and lower plots in Figure 4-7 indicates that turbidity decreased significantly between the 1-hour and 24-hour settling periods, indicating effective settling during the 24-hour settling period. The effect of the agents on turbidity was relatively modest (compared to the non-dosed control samples) at most test doses. In general, turbidities were relatively slightly higher with Phoslock™, which as a finer clay-based material is reported to have relatively slower settling properties and relatively longer residual turbidities in waters when applied (Australia Water Quality Center 2008). Turbidities were relatively slightly less with buffered alum and PAX-18™, but confined mainly to the highest doses.

⁷ Matrix spike recoveries during ammonia laboratory analysis did not meet acceptance criteria of 90-110 percent, possibly due to over-preservation, which would not allow the buffer to correctly adjust the pH of the samples. Also, analyzed ammonia levels exceeded total nitrogen concentrations in many cases, indicating that digestion of the sample may have been incomplete. For these reasons, ammonia laboratory analysis results were deemed unreliable and are not included in this report.

FIGURE 4-2
 Effect of agent dose (mg/L) on total phosphorus (TP; in mg/L) in source water samples from Sevenmile Canal (top),
 Upper Klamath Lake at Link River Dam (middle), and Keno Reservoir near Miller Island (bottom).

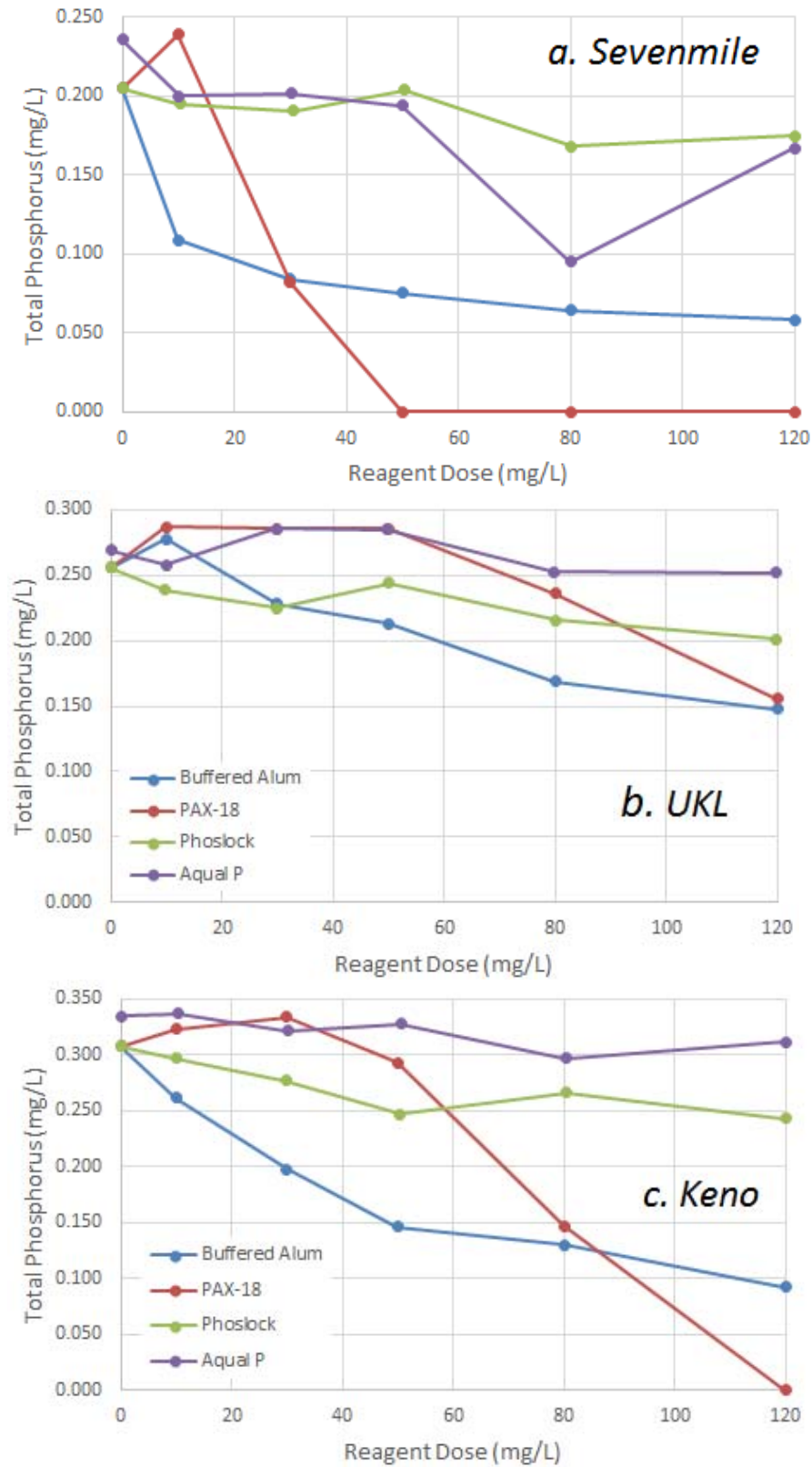


FIGURE 4-3

Effect of agent dose (mg/L) on total nitrogen (TN; in mg/L) in source water samples from Sevenmile Canal (top), Upper Klamath Lake at Link River Dam (middle), and Keno Reservoir near Miller Island (bottom).

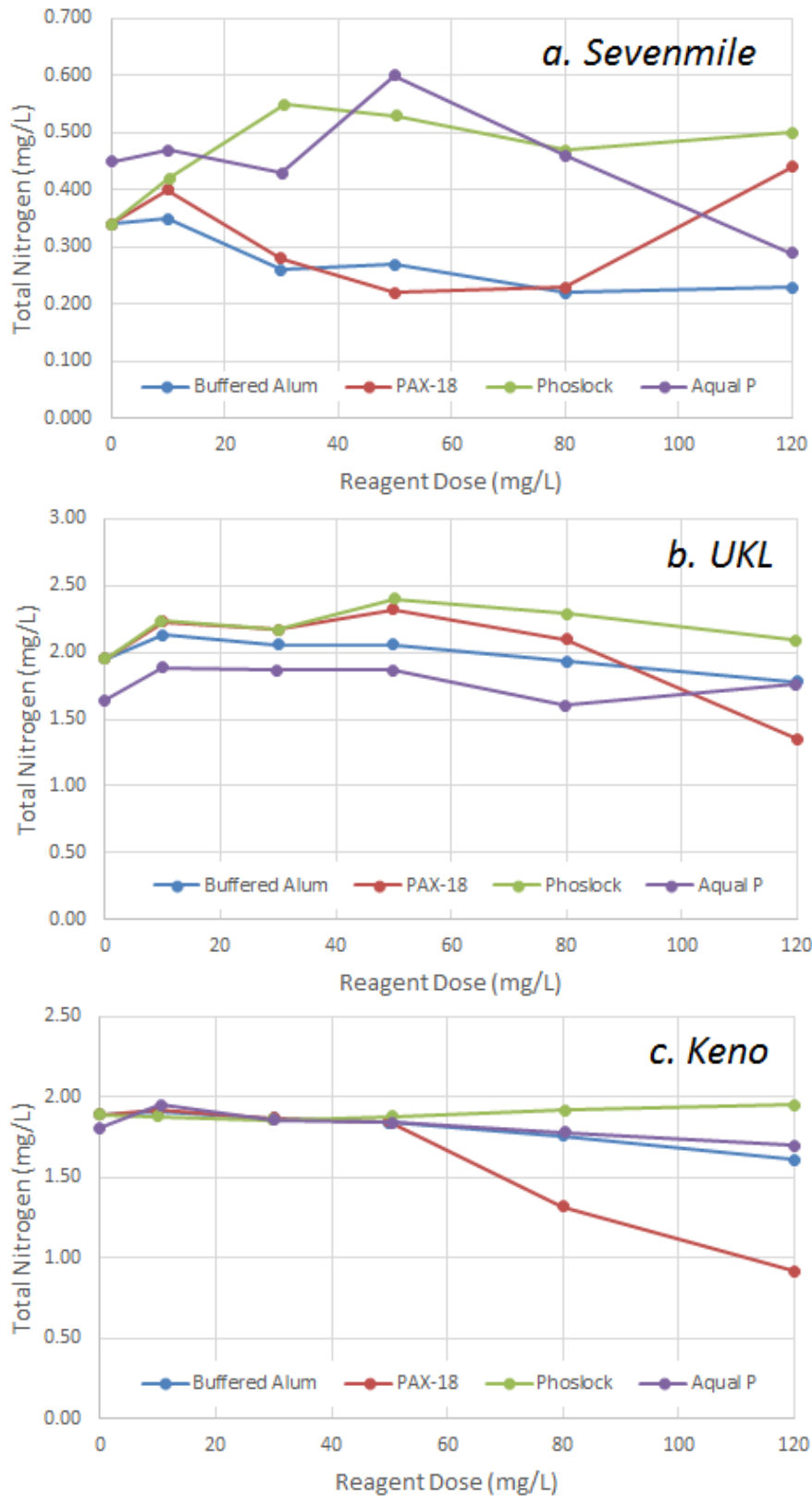


FIGURE 4-4
 Effect of agent dose (mg/L) on nitrate+nitrite (NO₃+NO₂-N; in mg/L) in source water samples from Sevenmile Canal (top), Upper Klamath Lake at Link River Dam (middle), and Keno Reservoir near Miller Island (bottom).

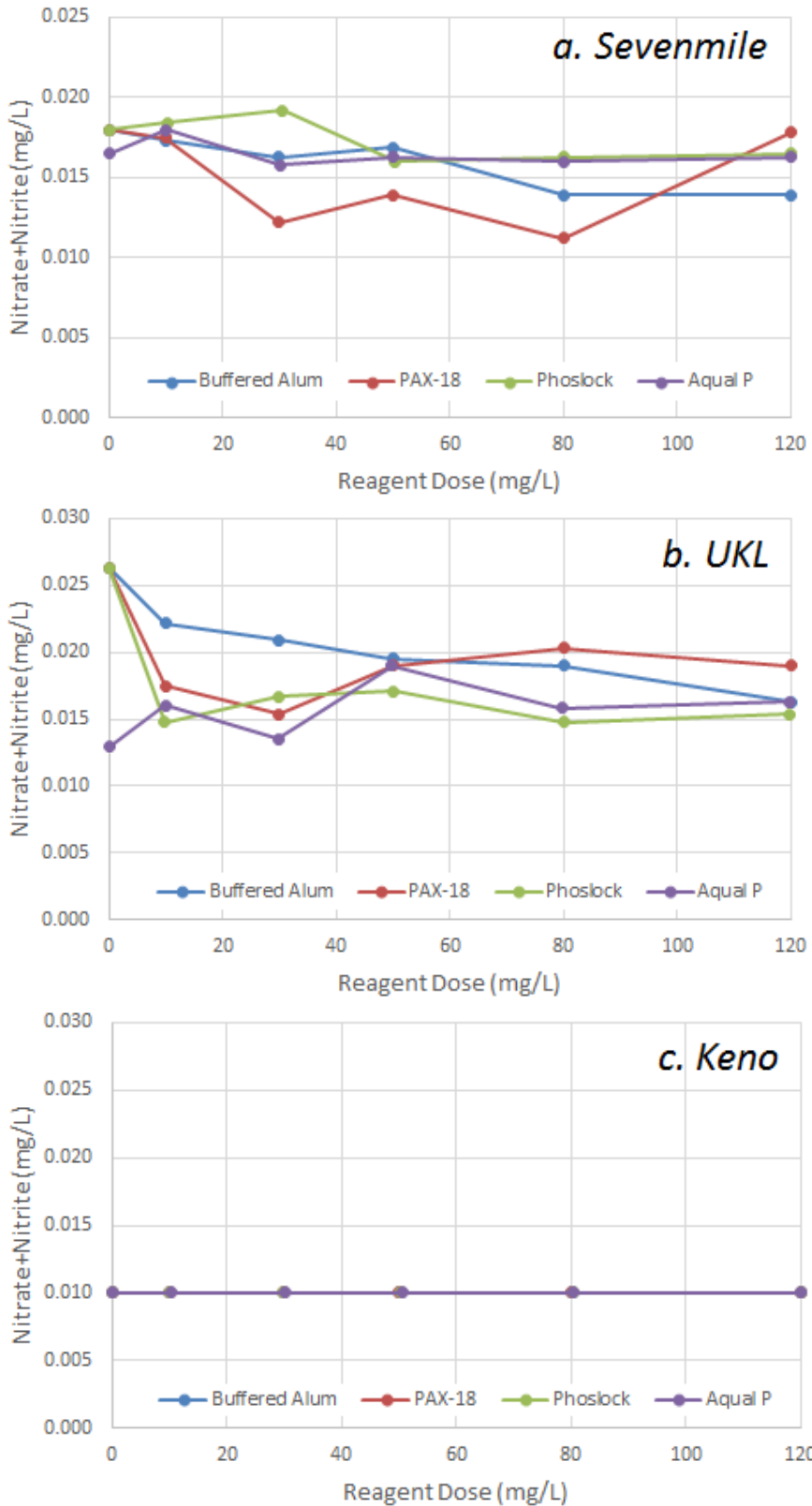


FIGURE 4-5

Effect of agent dose (mg/L) on Chlorophyll- α (mg/m³) in source water samples from Upper Klamath Lake at Link River Dam (top plot) and Keno Reservoir (bottom plot).

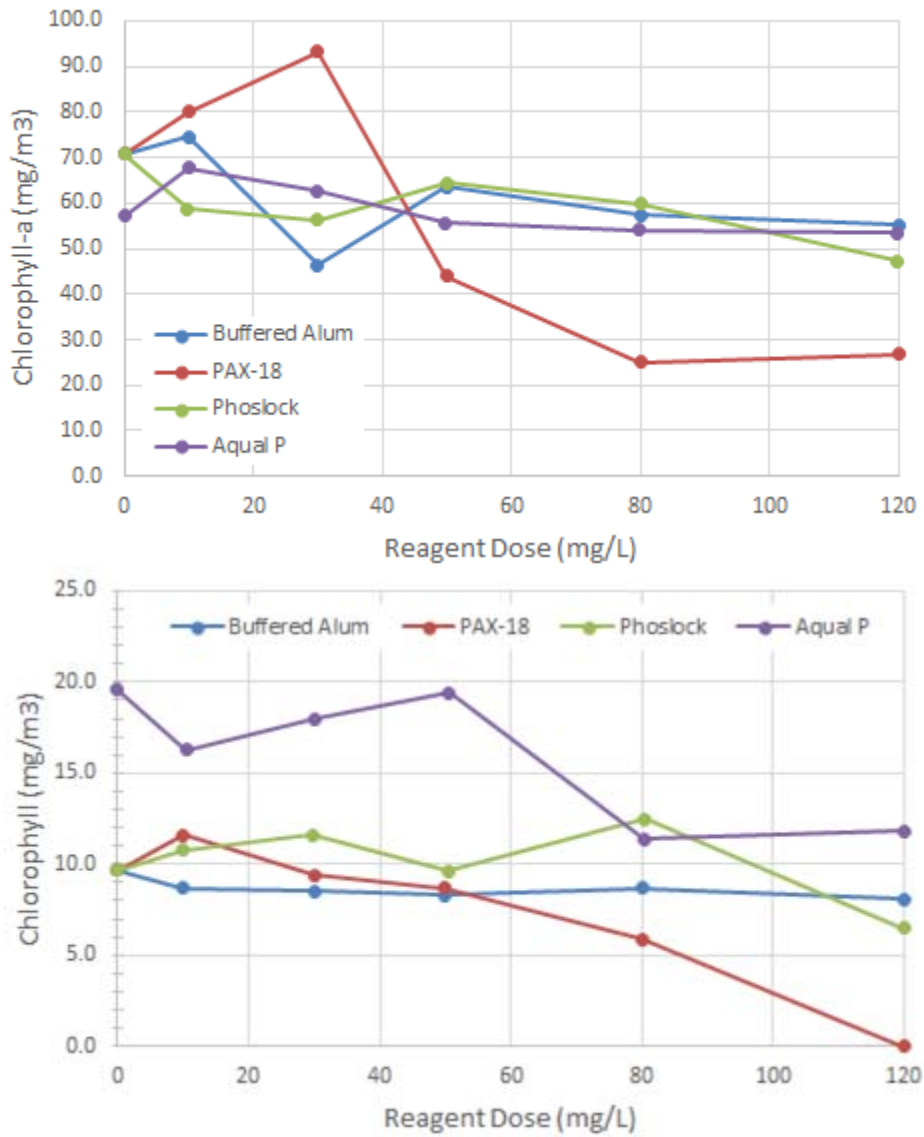


FIGURE 4-6
 Effect of dose (mg/L) of PAX-18 on total suspended solids (mg/L) in source water samples.

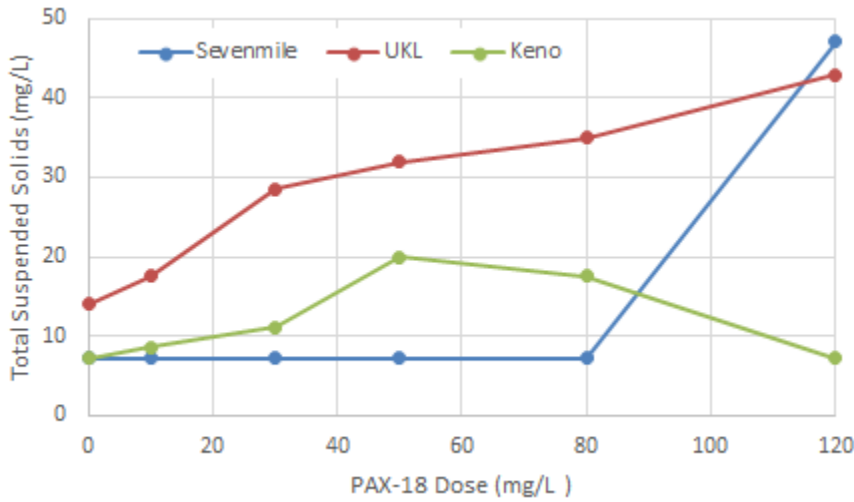
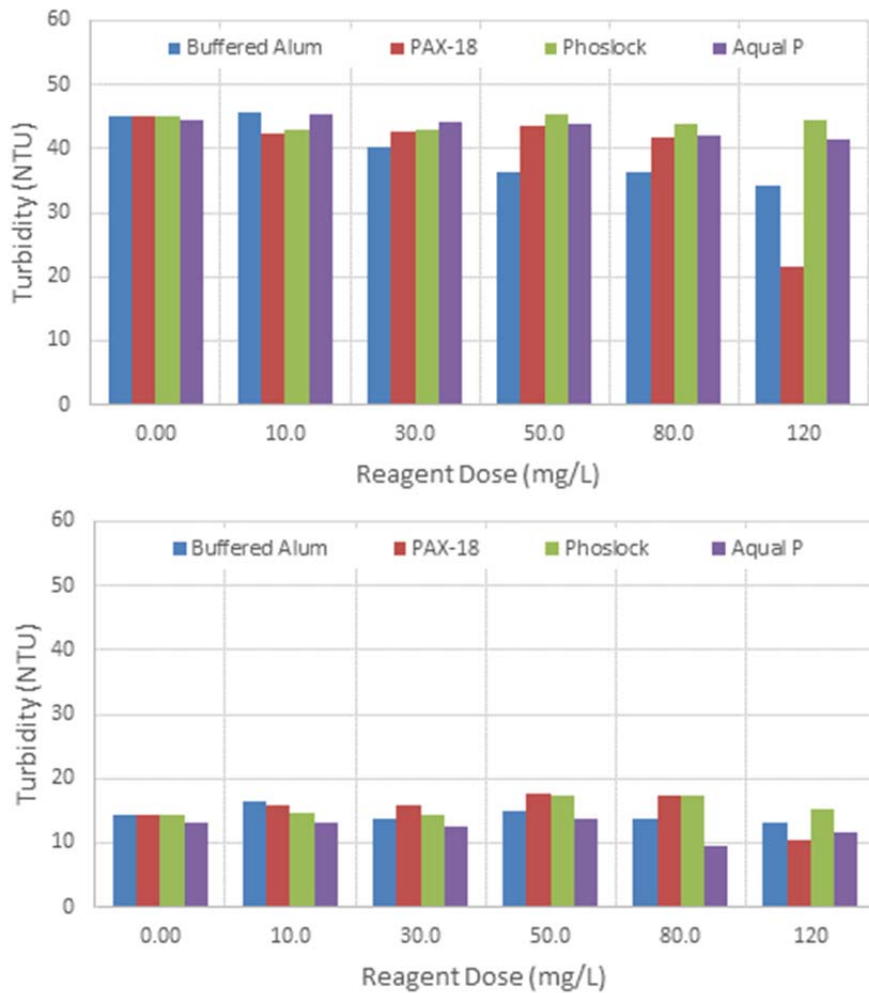


FIGURE 4-7
 Effect of agent dose (mg/L) on turbidity (NTU) in source water samples from Upper Klamath Lake after 1-hour settling (top plot) and 24-hour settling (bottom plot).



4.2.3 pH, Alkalinity, and DO

Figures 4-8 and 4-9 show the effect of agent dose (mg/L) on pH (units) and alkalinity (mg/L as CaCO₃), respectively, in source water samples. As expected, both buffered alum and PAX-18™ depressed pH and consumed alkalinity, while neither Phoslock™ nor Aqual-P™ affected either pH or alkalinity. Upon addition of alum, an insoluble aluminum hydroxide precipitate is formed that are accompanied by a series of hydrolysis reactions that decreases pH and carbonate alkalinity (Cooke et al. 2005). Alum (as aluminum sulfate) has a pH of 2.4 (Beecroft et al. 1995) which further lends to a decrease in the pH of the system to which it is added. However, for this study, aluminum sulfate was buffered with sodium aluminate to obtain a more circumneutral solution and lessen the effect on pH. Even when buffered alum is used, alkalinity is consumed as a result of the hydrolysis reactions as noted above, which still results in some decrease in solution pH, particularly in this case when available alkalinity buffering capacity of the source waters is naturally low. However, even though pH was reduced with increasing dose of buffered alum, the pH remained within the natural water circumneutral range at even the highest buffered alum doses in the jar tests (Figure 4-8).

PAX-18™ is also an acidic solution with low basicity that tends to decrease the pH of the system to which it is added. However, it is reported to cause less depression in pH and alkalinity than alum (Gebbie 2001, Pernitsky and Edzwald 2006, Trejo-Gaytan et al. 2006). However, in these jar tests, PAX-18™ resulted in a greater depressive effect on pH and alkalinity, because it was not buffered like the alum solution that was used. Even though pH was reduced with increasing dose of PAX-18™, the pH remained at or above 6.1, 7.3, and 6.8, respectively, in the Sevenmile Canal, Upper Klamath Lake, and Keno Reservoir source water samples jar tests (Figure 4-8).

As noted above, Phoslock™ and Aqual-P™ doses had no effect on pH or alkalinity (Figures 4-8 and 4-9). Both consist largely of neutral earth materials. Afsar and Groves (2009) report that, unlike alum, the addition of Phoslock™ in low alkalinity water does not reduce pH. Gibb (2010) reports that pH was relatively unchanged in Lake Okaro (New Zealand) after treatments with Z2G1 (essentially the same formulation as Aqual-P™).

In general, the agents produced little or no changes in DO with increasing test doses, particularly relative to non-dosed control samples (indicated in the plots by the “0 mg/L” test dose). For example, Figure 4-9 shows the effect of agent dose (mg/L) on DO (mg/L) in source water samples from Upper Klamath Lake after 1-hour settling (top plot) and 24-hour settling (bottom plot). Comparison of the upper and lower plots in Figure 4-9 indicates that DO decreased significantly (by about 3 mg/L) between the 1-hour and 24-hour settling periods, indicating oxygen demand occurred during the 24-hour settling period. The effect of the agents on DO was generally unchanged (compared to the non-dosed control samples) at most test doses. DO results showed the same trends for Sevenmile Canal and Keno Reservoir source water samples (not shown in graphs), although the decrease between the 1-hour and 24-hour settling periods was not as large (i.e., DO generally decreased by about 1 mg/L or less for both Sevenmile Canal and Keno Reservoir samples). These results indicate that primary production and respiration, including organic matter oxygen demand, are the primary factors affecting oxygen in the source water samples, and not the presence and doses of agents.

FIGURE 4-8
 Effect of agent dose (mg/L) on pH (units) in source water samples from Sevenmile Canal (top), Upper Klamath Lake at Link River Dam (middle), and Keno Reservoir near Miller Island (bottom).

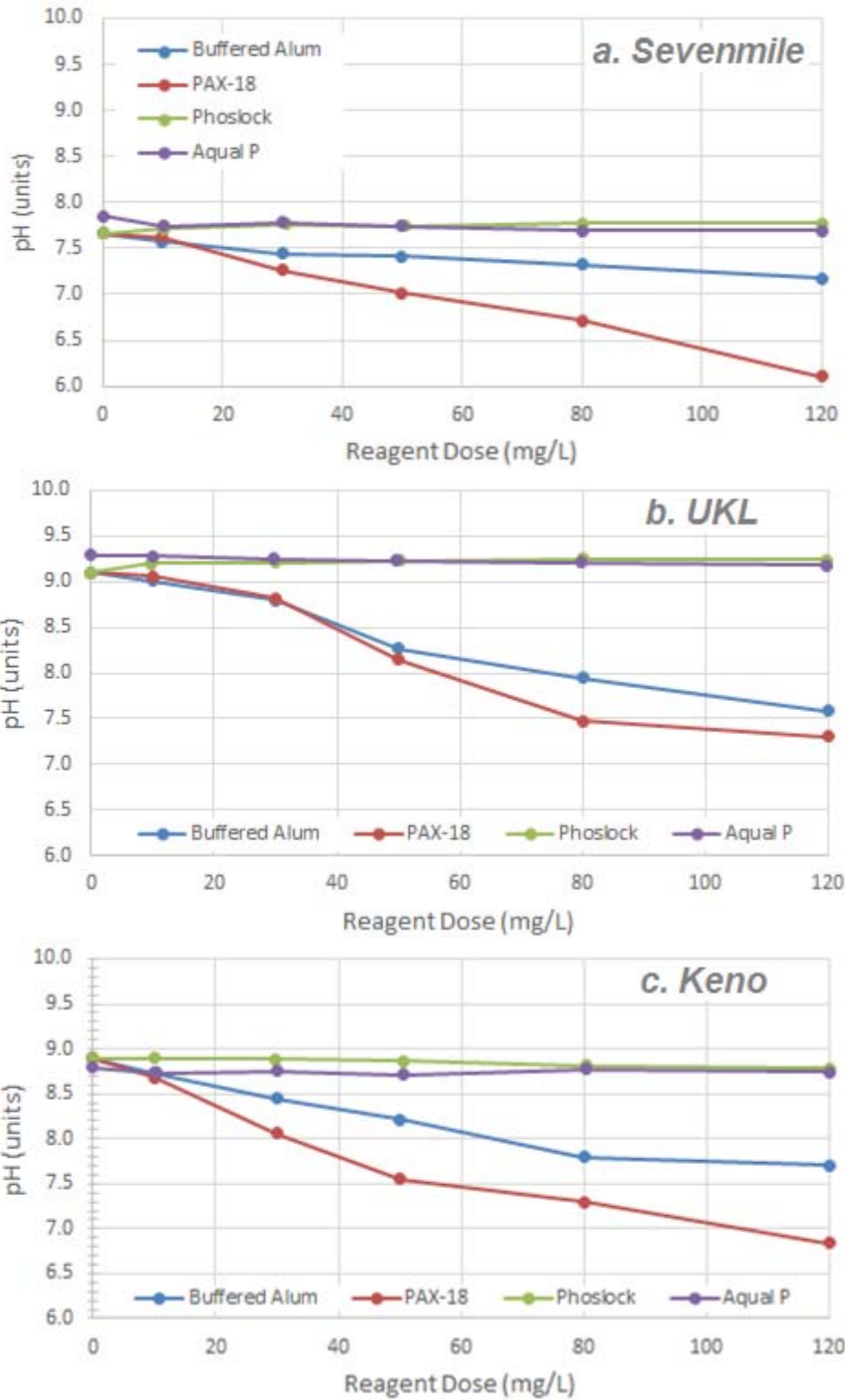


FIGURE 4-9

Effect of agent dose (mg/L) on alkalinity (mg/L as CaCO_3) in source water samples from Sevenmile Canal (top), Upper Klamath Lake at Link River Dam (middle), and Keno Reservoir near Miller Island (bottom).

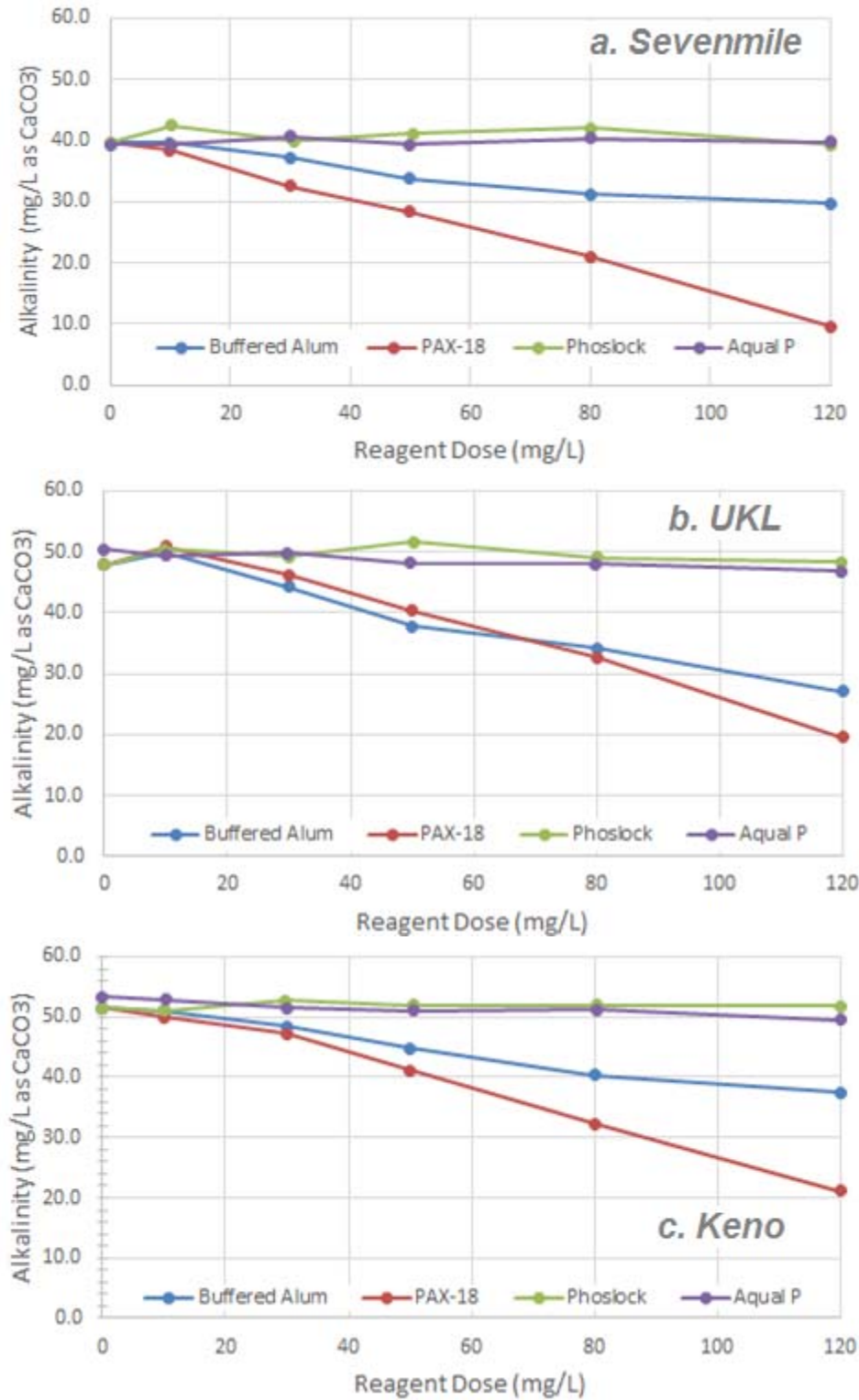
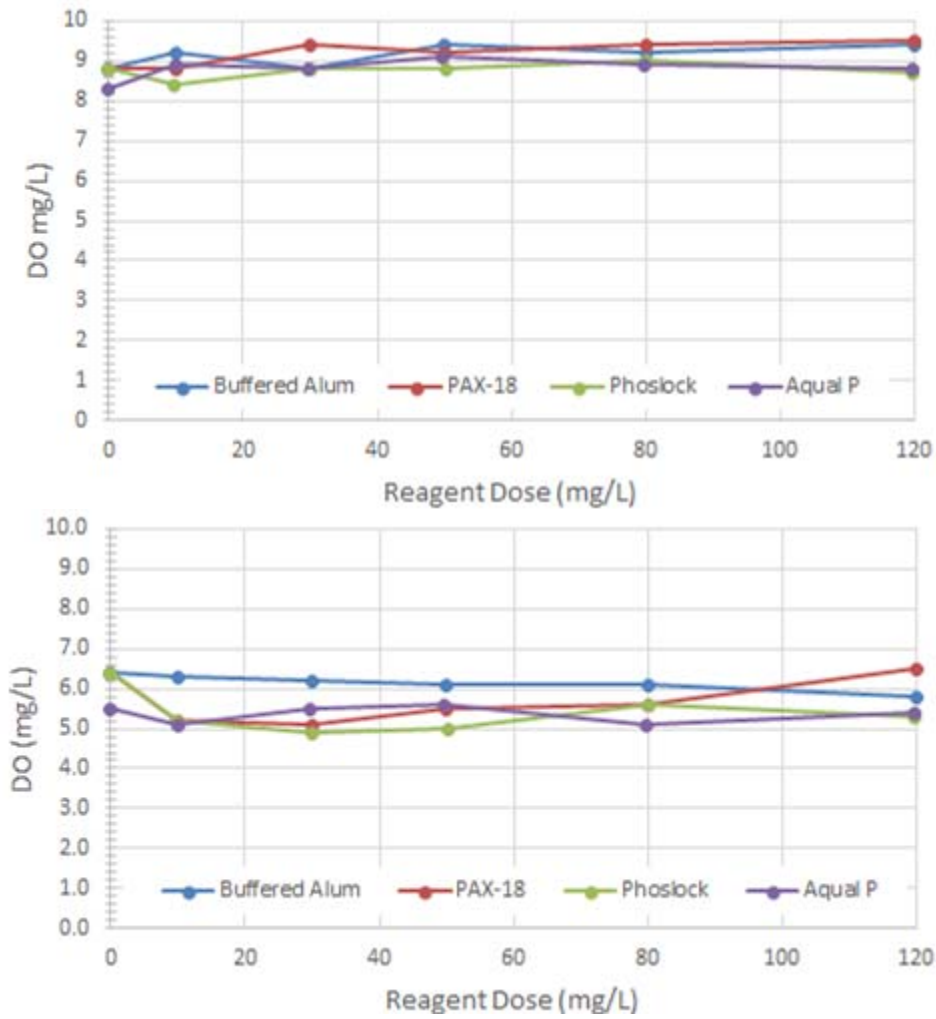


FIGURE 4-10

Effect of agent dose (mg/L) on dissolved oxygen (mg/L) in source water samples from Upper Klamath Lake after 1-hour settling (top plot) and 24-hour settling (bottom plot).



4.2.4 Aluminum and Lanthanum

4.2.4.1 Aluminum

Figure 4-11 shows the effect of doses (mg/L) of PAX-18™ (top plot) and buffered alum (bottom plot) on soluble aluminum (µg/L) in source water samples. Phoslock™ and Aqual-P™ doses had no effect on soluble aluminum (and therefore not shown on graphs or further discussed with regard to soluble aluminum). Soluble aluminum levels were relatively high in the Upper Klamath Lake and Keno Reservoir source water samples, and relatively low in the Sevenmile Canal source water samples.

The substantially higher levels in the Upper Klamath Lake and Keno Reservoir source water samples are due in part to the higher baseline levels of soluble aluminum present in these waters (184 and 66.1 µg/L, respectively, compared to 9.8 µg/L in Sevenmile Canal). However, the higher baseline levels do not fully explain the magnitude of levels observed during the jar tests. For example, maximum soluble aluminum concentrations of 1,350 µg/L, 1,000 µg/L, and 300 µg/L were measured in the Keno Reservoir, Upper Klamath Lake, and Sevenmile Canal source water samples, respectively, during the PAX-18™ jar tests (Figure 4-11). The higher levels in the Upper Klamath Lake and Keno Reservoir source water samples may also be due to the much higher presence of complexing ligands (ions or molecules that bind to metal ions) in these waters, as evidenced by their much higher dissolved organic carbon (DOC) (6.6 and 6.2 mg/L, respectively, compared to 2.8 mg/L in Sevenmile Canal) and much higher silica content (41.1 and 41.5 mg/L, respectively, compared to 23.3 mg/L in Sevenmile Canal).

Aluminum solubility is affected by a wide variety of environmental parameters, including pH, water temperature, DOC content, and the presence and concentrations of numerous ligands (CCME 2003). In the presence of complexing ligands and under acidic (pH < 6) and alkaline (pH > 8) conditions, aluminum solubility is enhanced. DOC and silicates will complex with aluminum in water, forming soluble (or colloidal) aluminum-organic complexes and aluminosilicates (CCME 2003, DHHS 2008).

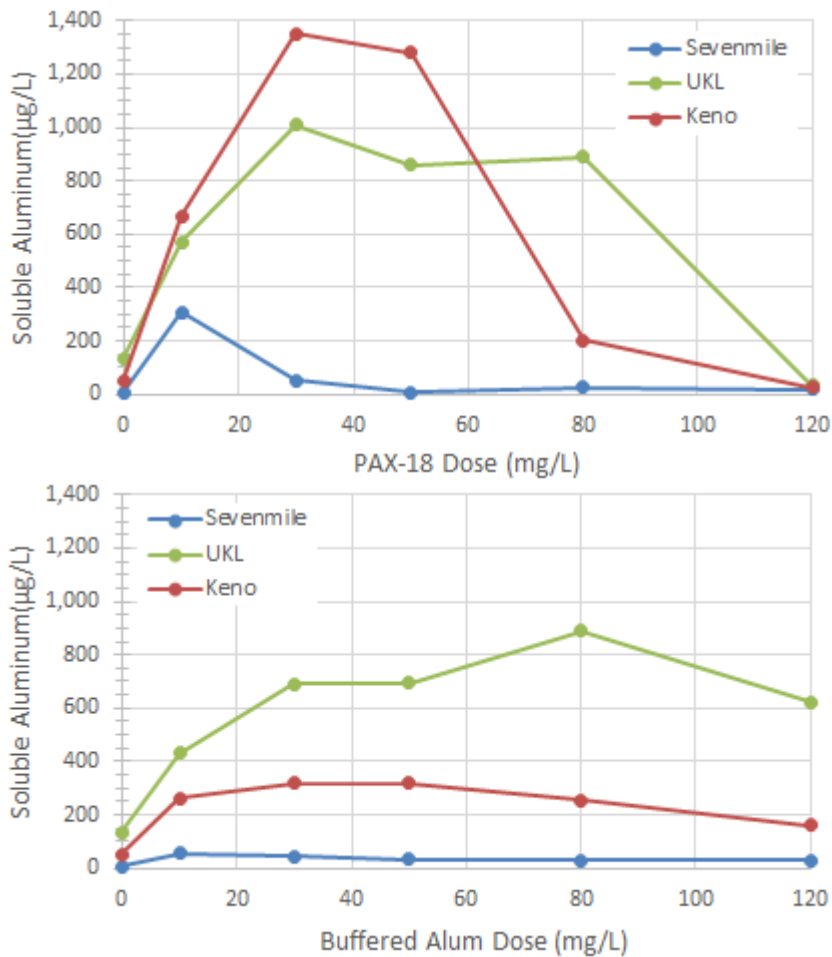
Figure 4-11 also shows that soluble aluminum concentrations were generally highest at the moderate doses of 30, 50, and 80 mg/L of PAX-18™ and buffered alum. This trend likely reflects the changes in pH and precipitate (floc) formation that occurs as doses increase. For example, at doses less than 50 to 80 mg/L, pH remained at or above 8 in the Upper Klamath Lake and Keno Reservoir source water samples (see Figure 4-8), where soluble aluminum predominates and increasing soluble aluminum concentrations reflect increasing PAX-18™ and buffered alum doses. At higher doses, pH drops below 8, where insoluble aluminum hydroxide precipitation predominates and soluble aluminum concentrations decrease.

At nearly all of the PAX-18™ and buffered alum doses in the Upper Klamath Lake and Keno Reservoir jar tests, soluble aluminum concentrations were generally in excess of the EPA national recommended water quality criteria for aluminum of 750 µg/L and 87 µg/L, respectively, for acute or chronic toxicity values for freshwater aquatic life (as discussed above in section 4.1.4.1). In the Sevenmile Canal jar tests, soluble aluminum concentrations were less than the EPA criteria in all cases with the single exception of the lowest PAX-18™ dose (10 mg/L).

Soluble aluminum concentrations in excess of the EPA criteria in the Upper Klamath Lake and Keno Reservoir jar tests indicates potential toxicity concerns with the use of PAX-18™ or alum in these waters. However, if such use is considered in the future for these or similar waters in the upper Klamath Basin, more definitive follow-up analysis of potential toxicity, such as with bioassay tests, would be advisable given the existence of conditions in these waters that may decrease toxicity potential, such as the relatively high DOC and silica levels as described above. Only inorganic monomeric aluminum (Al^{3+}) is highly toxic to fish (Gensemer and Playle 1998, DHHS 2008). DOC and silica complex with inorganic Al^{3+} to create organomonomeric aluminum species and aluminosilicates that are much less toxic than Al^{3+} to fish (Gensemer and Playle 1998, CCME 2003, DHHS 2008). Cooke et al. (2005) also mention that silicates, if sufficiently concentrated, may help reduce residual aluminum toxicity from alum treatments.

FIGURE 4-11

Effect of dose (mg/L) of PAX-18 (top plot) and buffered alum (bottom plot) on soluble aluminum ($\mu\text{g/L}$) in source water samples.



4.2.4.2 Lanthanum

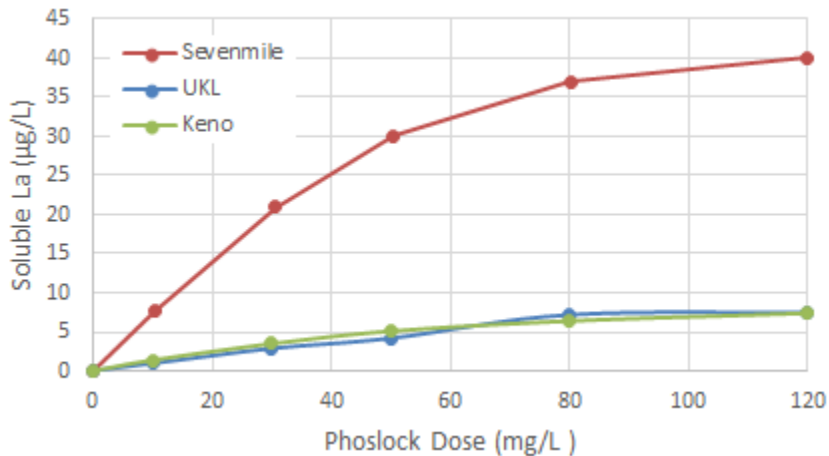
Figure 4-12 shows the effect of doses (mg/L) of Phoslock™ on soluble lanthanum ($\mu\text{g/L}$) in source water samples. PAX-18™, buffered alum, and Aqual-P™ doses had no effect on soluble lanthanum (and therefore not shown on graphs or further discussed with regard to soluble lanthanum). Soluble lanthanum levels were relatively high in the Sevenmile Canal source water samples, and relatively low in the Upper Klamath Lake and Keno Reservoir source water samples.

The relatively lower concentrations of soluble lanthanum in the Upper Klamath Lake and Keno Reservoir source water samples may be related to the much higher DOC in these waters compared to Sevenmile Canal. In this case, the effect of higher DOC is the opposite of that described above for soluble aluminum. In general, monomeric lanthanum (La^{3+}) is only sparingly soluble under normal surface water conditions, and hydrolysis products of lanthanum are also poorly soluble. Solubility is further reduced in the presence of dissolved organic matter, which readily forms complexes with lanthanum (De Vos et al. 2006).

In all jar tests, soluble lanthanum concentrations were less than 127 µg/L cited by Stauber (2000) as the 96-hour LC50 for lanthanum exposure to rainbow trout adults (as discussed in section 4.1.4.2 above). In the Upper Klamath Lake and Keno Reservoir jar tests, soluble lanthanum concentrations also were less than 20 µg/L cited by Birge et al. (1978) as the 28-day LC50⁸ for lanthanum exposure to rainbow trout eggs (as discussed in section 4.1.4.2 above). However, in the Sevenmile Canal jar tests, soluble lanthanum concentrations were greater than 20 µg/L, reaching a maximum of 40 µg/L at the highest test Phoslock™ dose of 120 mg/L. Therefore, if use of Phoslock™ is considered in the future for Sevenmile Canal or similar waters in the upper Klamath Basin, more definitive follow-up analysis of potential toxicity, such as with bioassay tests, may be advisable.

FIGURE 4-12

Effect of dose (mg/L) of Phoslock™ on soluble lanthanum (µg/L) in source water samples.



⁸ LC50 (or "lethal concentration 50") is a standard measure of the toxicity of the surrounding medium that will kill half of the sample population of a specific test-animal in a specified period through exposure via inhalation (respiration). LC50 is measured in micrograms (or milligrams) of the material per liter, or parts per million (ppm) of water. The lower the amount, the more toxic the material. Also called median lethal concentration.

Summary and Conclusions

This report describes the methods and results of laboratory-based jar tests to assess the effects of four coagulation and flocculation agents on nutrients and other water quality constituents in example source waters from the upper Klamath Basin. These jar test results may be useful to inform the potential applicability and development of further measures using treatments with these agents as a tool for achieving nutrient reductions in the Klamath Basin (for example, in conjunction with other nutrient reduction technologies such as constructed treatment wetlands).

The four agents tested were: (1) lanthanum-modified bentonite clay (Phoslock™); (2) aluminum-modified zeolite (Aqual P™); (3) polyaluminum hydroxychloride (PACl); and (4) alum (aluminum sulfate buffered with sodium aluminate). The agents were applied to three source waters (from three upper Klamath Basin locations in Oregon), including: (1) Sevenmile Canal (just upstream from Agency Lake); (2) Upper Klamath Lake outlet (near Link River dam); and (3) Keno reservoir (near Miller Island). These waters have quite high nutrient concentrations, notably P, and represent a spatial mix of high-nutrient waters both above, within, and below Upper Klamath Lake. Each of the four agents were tested at dose concentrations of 10, 30, 50, 80, and 120 mg/L (ppm) to evaluate P removal efficiency and effects on other water quality constituents in the source waters over a relatively wide range of potential application doses.

The jar test results revealed consistent general trends of increased P removal with increasing doses of the four agents. PAX-18™ and buffered alum produced the greatest P removal (i.e., lowest residual PO₄ and TP concentrations), followed in order by Phoslock™ and Aqual-P™. For example, in the Upper Klamath Lake source water sample, PAX-18™ and buffered alum both removed 95 percent or more of PO₄, and about 40 percent of TP, at the highest test agent dose of 120 mg/L. Phoslock™ and Aqual-P™ removed a maximum of 33 percent and 7 percent of PO₄, and 20 percent and 5 percent of TP, respectively, at the highest test agent dose.

The jar test results also revealed that all four agents consistently produced the highest percentage of P removal in the Sevenmile Canal source water sample, the next highest percentage of P removal in the Keno Reservoir source water sample, and the least percentage of P removal in the Upper Klamath Lake source water sample. The lower efficiency of P removal in the Upper Klamath Lake source water sample may be due to the much higher algae and particulate matter content in the Upper Klamath Lake source water sample, which likely interfered with the agents' P removal effectiveness. For example, research has shown that algal organic matter can inhibit flocculation or otherwise interfere with removal of particulates by various coagulants resulting in an increase of dosage demand (Henderson et al. 2010, Vandamme et al. 2012).

No consistent trends of effects of the four agents on N (specifically TN and NO₃+NO₂) were observed in the jar tests. Such results were expected as these four agents are known to have little or no effect on N specifically. Aqual-P™ has been reported in other studies as capable of inactivating N (in addition to P)(Gibbs and Ozkundakci 2011, Ozkundakci et al. 2011), but no significant or consistent reductions in TN or NO₃+NO₂ were observed in these jar test results using Aqual-P™.

The agents produced inconsistent trends of algal matter and suspended solids reduction with increasing test doses. Algal matter reductions (based on chlorophyll- α) were more evident than reductions in either TSS or turbidity, although results varied by source water sample. In the Upper Klamath Lake source water sample, PAX-18™ removed 60 percent of chlorophyll- α at the highest test agent dose of 120 mg/L, while buffered alum, Phoslock™, and Aqual-P™ removed a maximum of 22, 32, and 7 percent of chlorophyll- α , respectively.

The agents produced mainly small and inconsistent changes in TSS and turbidity with increasing test doses. In general, turbidities were relatively slightly higher with Phoslock™, which as a finer clay-based material is reported to have relatively slower settling properties and relatively longer residual turbidities in waters when applied.

As expected, both buffered alum and PAX-18™ depressed pH and consumed alkalinity, while neither Phoslock™ nor Aqual-P™ affected either pH or alkalinity. For this study, aluminum sulfate was buffered with sodium aluminate to obtain a more circumneutral solution and lessen the effect on pH. The jar tests showed that, even though pH was reduced with increasing dose of buffered alum, the pH remained within the natural water circumneutral range at all doses. PAX-18™ had a greater depressive effect on pH and alkalinity, because it was not buffered like the alum solution. However, at all PAX-18™ doses, the pH remained at or above circumneutral values of 6.1, 7.3, and 6.8, respectively, in the jar tests of Sevenmile Canal, Upper Klamath Lake, and Keno Reservoir source waters.

The agents produced little or no changes in DO. The results indicated that primary production and respiration, including organic matter oxygen demand, are the primary factors affecting oxygen in the source water samples, and not the presence and doses of agents.

At nearly all of the PAX-18™ and buffered alum doses in the Upper Klamath Lake and Keno Reservoir jar tests, soluble aluminum concentrations were generally in excess of the EPA national recommended water quality criteria for aluminum of 750 µg/L and 87 µg/L, respectively, for acute or chronic toxicity values for freshwater aquatic life. In the Sevenmile Canal jar tests, soluble aluminum concentrations were less than the EPA criteria in all cases with the single exception of the lowest PAX-18™ dose (10 mg/L).

Soluble aluminum concentrations in excess of the EPA criteria in the Upper Klamath Lake and Keno Reservoir jar tests indicates potential toxicity concerns with the use of PAX-18™ or alum in these waters. However, if such use is considered in the future for these or similar waters in the upper Klamath Basin, more definitive follow-up analysis of potential toxicity, such as with bioassay tests, would be advisable given the existence of conditions in these waters that may decrease toxicity potential, such as the relatively high DOC and silica levels as described above. Only inorganic monomeric aluminum (Al³⁺) is highly toxic to fish (Gensemer and Playle 1998, DHHS 2008). DOC and silica complex with inorganic Al³⁺ to create organomeric aluminum species and aluminosilicates that are much less toxic than Al³⁺ to fish (Gensemer and Playle 1998, CCME 2003, DHHS 2008). Cooke et al. (2005) also mention that silicates, if sufficiently concentrated, may help reduce residual aluminum toxicity from alum treatments.

In all jar tests, soluble lanthanum concentrations were less than 127 µg/L cited by Stauber (2000) as the 96-hour LC50 for lanthanum exposure to rainbow trout adults. In the Upper Klamath Lake and Keno Reservoir jar tests, soluble lanthanum concentrations also were less than 20 µg/L cited by Birge et al. (1978) as the 28-day LC50 for lanthanum exposure to rainbow trout eggs. However, in the Sevenmile Canal jar tests, soluble lanthanum concentrations were greater than 20 µg/L, reaching a maximum of 40 µg/L at the highest test Phoslock™ dose of 120 mg/L. Therefore, if use of Phoslock™ is considered in the future for Sevenmile Canal or similar waters in the upper Klamath Basin, more definitive follow-up analysis of potential toxicity, such as with bioassay tests, may be advisable.

This study is not intended to recommend or endorse any specific agent or type of application using these agents. This study is only the first of several steps that will be needed to determine what chemical treatments may be best to use and to plan how the treatment processes using them would be implemented, if such treatment were pursued.

SECTION 6

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