Activity 7: Pilot Study of Nutrient Reduction Methods in Klamath Basin Waterbodies

Initial Bench Testing Approach and Procedures

Introduction

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 (UKL), Keno Reservoir, and the Klamath River downstream. Activity 7 includes a proposal for a study to assess the effects of treating water from the area using chemical agent applications to reduce nutrient concentrations (and associated algae growth and biomass effects) through flocculation, binding, or sequestration.

This document describes the recommended approach to the initial assessment of the potential use of treatment with agents to reduce nutrients, notably phosphorus (P), in waters in the Klamath Basin. The recommended approach includes steps to: (1) identify and select appropriate candidate agents; (2) determine appropriate doses using laboratory bench testing ("jar tests"); and (3) assess the potential effects of agents on other water quality constituents in addition to P. Bench test study results would inform the potential applicability of, and development of further measures using treatments with agents as a tool for achieving nutrient reductions in the Klamath Basin (in conjunction with other nutrient reduction technologies such as constructed treatment wetlands).

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 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 may 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 indentified for potential use in Keno reservoir (downstream of Upper Klamath Lake) in the 2012 Klamath Basin Workshop in Sacramento (Stillwater Sciences et al. 2013)[1]. 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).

In preparing and implementing this bench testing plan, no specific agents or applications are recommended or endorsed. This testing plan 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. The first step consists of that described in this document, which includes laboratory-based bench testing (jar tests) of appropriate candidate agents to assess dosages and likely effectiveness. How this information is used and where the potential uses of such agents go are later steps down the line to 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 being planned under Interim Measure 11 Study 2). Thereafter, additional steps would be taken to complete the required planning, design, and permitting of actual treatment projects using selected agents.

No specific toxicity tests are proposed as a part of this particular study. Rather, the focus of this study is 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 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. Meanwhile, 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 discussion on alum). In addition, the lab analyses for this study will include some analytes (e.g., dissolved aluminum) in the treated water samples that can be used to assess whether concentrations are near to, or exceed, reported U.S. Environmental Protection Agency (EPA) acute or chronic toxicity values.

Agents Selected for Testing

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

- • Lanthanum-modified bentonite clay (Phoslock™)

- • Aluminum-modified zeolite (Z2G1 or 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 a previous draft of this bench testing plan (CH2M HILL 2013). 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 Technical Advisory

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[1] Based on this workshop discussion, Stillwater Sciences et al. (2013) further outline a possible pilot study to: (1) determine the efficacy of buffered alum dosing in the low alkalinity and seasonally high pH waters of Keno reservoir using bench-scale testing; (2) determine the potential for impacts to aquatic organisms in the project vicinity using toxicity tests; and (3) based on results of the bench-scale tests, to inject alum micro-floc and oxygen into a 40-acre pilot site in Keno reservoir.

Committee (TAC)[2], 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) will be combined to provide a buffered (more circumneutral) form of alum to be tested (as discussed further below).

Appendix A 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 Appendix A, 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.

Source Waters Selected for Testing

Three source waters (from three upper Klamath Basin locations in Oregon) are 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.

In preparation for the laboratory-based bench testing, bulk water samples will be collected at selected water source locations in pre-cleaned 20-liter polyethylene containers. Collection of the samples will occur during a single field day in early summer 2014. During collection of the samples, field measurements will be taken of water temperature, pH, conductivity, and dissolved oxygen at the same point where bulk samples are drawn. The containers will be transported promptly to CH2M HILL's Applied Sciences Lab (in Corvallis, Oregon) so that laboratory treatability testing (jar tests) can commence within 18-24 hours after source water collection. During transport, the bulk water samples will be maintained approximately within the diurnal range of water temperatures typical of the source waters at the time of collection.

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[2] The TAC has been established to provide input on Activity 7 and serve as the coordination link to the Interim Measures Implementation Committee (IMIC).

TABLE 1

Candidate Treatment Agents Considered for Testing

Agent	Mode of Action	Features	References for Use and Effectiveness (see Appendix B)
Aluminum Sulfate (Alum) $(Al_2(SO_4)_3 \cdot 18\ H_2O)$	Removes P through formation of aluminum hydroxide or precipitation of aluminum phosphate.	o Most widely used coagulant for P removal o History of effective P reduction in treated lakes, wetlands o Effective in pH range between 6 and 8 o Alkalinity consumed during use, which can result in pH decrease o Addition of buffer may be needed where alkalinity is low o Relatively inexpensive compared to other coagulants o Potential toxicity can be a concern o pH of 1% solution = 3.5 o 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 Schrieve (1994)
Sodium Aluminate $(Na_2Al_2O_4)$	Same solubility and precipitation stoichiometry as alum. Sodium aluminate is Al dissolved in sodium hydroxide, so supplies alkalinity when used.	o Mainly used in conjunction with alum as buffer for low alkalinity systems o pH of 1% solution = 14 o Available in liquid form (10-13% Al or 20-25% Al_2O_3)	See above references for alum
Ferric Chloride $(FeCl_3 \cdot 6\ H_2O)$	Removes P through precipitation of metal oxyhydroxides and subsequent adsorption of P by ligand exchange.	o Widely used coagulant in wastewater treatment processes o Can be effective for P reduction in treated lakes, wetlands o Strongly affected by redox potential; ineffective where DO is low o Effective in pH range between 8 and 10 o Alkalinity consumed during use, which can result in pH decrease o Addition of buffer may be needed where alkalinity is low o Relatively inexpensive compared to other coagulants o Can contain heavy metal impurities depending on processing quality o pH of 1% solution = 3 to 4 o Available in liquid (10-45% $FeCl_3$) or granular (20% Fe) form	Browne et al. (2004), Cooke et al. (1993), Faithfull et al. (2005), Sherwood and Qualls (2001), Wisniewski (1999)

TABLE 1
Candidate Treatment Agents Considered for Testing

Agent	Mode of Action	Features	References for Use and Effectiveness (see Appendix B)
Polyaluminum Hydroxychloride (PACl)	Removes P through precipitation of and adsorption by formation of insoluble aluminum polyhydroxides.	o Synthetic polymer that serves as inorganic Al-based coagulant o Effective alternative to alum and $FeCl_3$ for P removal in natural waters o Operates over wider pH and alkalinity range than alum and $FeCl_3$ o Causes less depression in pH and alkalinity than alum o Less risk of toxicity than alum o Few heavy metal impurities o Substantially more expensive than alum and $FeCl_3$ o pH of 1% solution varies o Available in liquid form (3-13% Al)	Gebbie (2001), Pernitsky and Edzwald (2006), Trejo-Gaytan et al. (2006)
Lanthanum-Modified Bentonite Clay (Phoslock™) $(La + Al_2O_{3.4}(SiO_2)\cdot H_2O)$	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.	o Effective alternative to alum and $FeCl_3$ for P removal in natural waters o Reported to operate over wider pH and alkalinity range than alum and $FeCl_3$ o P binding capacity not affected by anoxia o Less risk of toxicity than alum o Relatively more expensive compared to other coagulants o Reported to result in noticeable turbidity increases o pH of 1% solution = 7 to 8.5 o 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)
Modified Zeolite (Z2G1 or Aqual P™) $(M_2/nO.Al_2O_3.xSiO_2.yH_2O)$	Proprietary Al-amended silicate lattice acts to exchange anions (like P) and absorb cations (like N).	o Unlike other coagulants, capable of inactivating both P and N o Limited instances of use for lake, reservoir, and wetland treatments o Relatively more expensive compared to other coagulants o Lack of information on impurities or risk of toxicity o pH of 1% solution not available at time of preparation of this plan o 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)

Laboratory Treatability Testing

Source Water Characterization

Upon arrival of bulk samples at the laboratory, samples from each of the source waters will be submitted for characterization analysis to understand the ambient chemistry of the source waters. The individual source water samples will be analyzed for the water quality parameters listed in Table 2.

TABLE 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	In-situ probe	NA	1.0	mg/L
Turbidity	In-situ probe	NA	5	NTU
Alkalinity	EPA310.1	0.5	5	mg/L
Total suspended solids	EPA160.2	0.7	2	mg/L
Nutrients				
Total phosphorus (TP)	EPA365.1	0.0078	0.05	mg/L
Orthophosphate (PO4-P)	EPA365.1	0.001	0.05	mg/L
Total nitrogen (TN)	SM4500-N B	0.018	0.20	mg/L
Ammonia nitrogen (NH3-N)	EPA350.1	0.0078	0.10	mg/L
Nitrate+nitrite nitrogen (NO3+NO4-N)	EPA353.2	0.0057	0.01	mg/L
Biological Parameters				
Chlorophyll *a*	SM10200H.3	NA	0.02	µg/L
Other Analytes				
Dissolved aluminum	SM3500-Al E.	0.001	0.01	mg/L
Dissolved lanthanum	SW6020	2	0.062	µg/L
Dissolved organic carbon	SM5310B	0.12	0.50	mg/L
Dissolved sulfate	EPA 300	0.032	0.2	mg/L
Silica	EPA 200.7	0.022	1.1	mg/L

Laboratory Bench Testing (Jar Tests)

The four agents will be subjected to bench testing (jar tests) in the laboratory to assess the effectiveness of treatment on the source water samples. In addition to determining the effectiveness of the agents, the jar tests will provide information on optimum doses, agent strength and stability, required mixing intensity and duration, and follow-up considerations for possible subsequent testing. The results from the jar tests will also provide insights to help anticipate and plan the functioning of potential field-scale treatment or wetland pre-treatment applications using these agents.

The bench-scale treatability testing (jar tests) will take place at CH2M HILL's Applied Sciences Lab in Corvallis, OR. Jar tests are a standardized and controlled laboratory procedure used to determine the optimum operating conditions of agents for water treatment. Figure 1 shows the jar test setup at the Applied Sciences Lab. The jar test method allows for controlled adjustments in coagulant dose, pH, or alkalinity to investigate total phosphorus (TP) and orthophosphate (PO4) removal efficiency and effects on other water quality constituents.

Treatability testing (jar tests) will be conducted using a range of dosages of each of the four agents on each of the three bulk water source samples for a total of 12 tests (four-by-three). Each test will consist of a set of six beakers (jars) to assess a series of five incremental dosages in addition to an untreated control. Agents will be tested at media dose concentrations of 10, 30, 50, 80, and 120 mg/L (ppm) to evaluate a relatively wide range of potential application doses[3]. Consistent dose concentrations between agents will also allow direct comparison of the relative effectiveness of the agents – one to another. The alum agent to be tested will be based on an approximate 2:1 mixture of the two alum agents – aluminum sulfate and sodium aluminate – listed in Table 1. The resulting buffered alum should 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).

FIGURE 1
Jar testing setup at CH2M HILL's Applied Sciences Lab.

The general procedures for the treatability testing (jar tests) will be as follows:

- All glassware will be acid-washed and triple-rinsed with de-ionized water prior to using.

- Six test beakers will be filled with 2-liter aliquots from the source water containers.

- Test beakers will be brought to constant temperature using a water bath. The target temperature for testing will be 20°C.

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[3] 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). 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). Gibbs (2010) reports a modified zeolite application dosage of about 40 mg/L in a eutrophic lake in New Zealand 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 of 21 mg/L and 33 mg/L would result in P reductions of 40 percent and 50 percent, respectively, in Canyon Lake (CA). 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).

- The agents will be added to five of the test beakers in amounts equal to the five test dosages. The addition of agents to the test beakers will occur at the start of a 60-second rapid mix stage at 100 rpm (on the multi-paddle jar test apparatus).

- The sixth beaker will serve as a control with no agent added. The sixth beaker (control) will be measured for pH, DO, and turbidity using in-situ probes (Table 2) just prior to starting the tests (just before adding the agents to the five test beakers).

- Following the 60-second rapid mix stage (at 100 rpm), pH, DO, and turbidity will be measured using in-situ probes (Table 2) in all five test beakers, and again in the control beaker.

- The treated beakers will then be allowed to settle for a period of approximately 24 hours to simulate settling that would occur in source waters at the field scale. After 1-hour and 24-hour periods of settling, pH, DO, and turbidity will be measured in the beakers. Visual observations (including photos at the 1-hour and 24-hour periods) will be recorded during the settling process for each beaker (dose).

- At the end of the 24-hour settling period, the supernatant will be decanted from each of the five test beakers for subsequent laboratory analyses of parameters listed in Table 2.

Reporting of Testing Results

The final task of this assessment will be to produce a report of the results of the treatability testing (jar tests). The report will describe the effects of various chemical doses on nutrient reductions in source waters, particularly P, and assess the effects of the chemical agents on other water quality constituents in addition to P (as listed in Table 2). Study results would inform the potential applicability of, and development of further measures using, treatments with these agents as a tool for helping to achieve nutrient reductions in the Klamath Basin (in conjunction with other nutrient reduction technologies).

References

See Appendix B for the complete list of references that are cited above and in the attached review of candidate chemical agents (Appendix A).

Appendix A

Review of Potential Treatment Agents for Testing

Alum

Description

Alum, the common name for aluminum sulphate $(Al_2(SO_4)_3 \cdot 18\ H_2O)$[4], has been used in a variety of settings to reduce the P concentrations in water. Removal of phosphate 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.

Mode of Effect on Nutrients

The main mechanism of P removal upon addition of alum involves the formation of the metal phosphate $Al_{0.8}H_2PO_4(OH)_{1.4}$ (Sedlak 1991). When only moderate P removal is required, and relatively small alum dosages used, the metal 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 [$Al(OH)_3$)] 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.

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 Schrieve (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.

Bottcher et al. (2009) provide an extensive summary and evaluation of alum treatment of agricultural runoff to reduce P loading to marsh and wetland areas in Florida. Table 13 provides a general summary of changes in water

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[4] The number of water molecules may vary from 14 to 18.

chemistry of agricultural runoff with increasing alum dose reported by Bottcher et al. (2009). Based on these data, P removal in agricultural runoff is most significant at alum dosages greater than 10 mg Al/L.

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 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. 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 aluminium 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. However, over a period of several months, the alum floc ages, eventually forming gibbsite, which has a minimum solubility of approximately 10^{-9} M in the pH range of approximately 5-7.

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. However, the alkalinity consumption during coagulation is less with alum than with ferric coagulants (discussed below). This suggests that at equal doses the addition of alum will have less impact on pH than would be observed using iron-based coagulants.

Temperature may also have an impact on the coagulation process. Under cold temperatures, floc formation and the removal efficiency achieved using metal salts for coagulation decreases substantially. Colder temperatures often require a change in coagulant or change in dose to maintain acceptable settling characteristics and removal efficiencies. In the seasonally variable climate conditions in the Upper Klamath basin, temperature likely is an insignificant parameter impacting coagulation processes during the warmer period of the year, but may be a significant factor during colder months.

Advantages and Disadvantages

Advantages

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. For example, aluminum coagulation occurs in a neutral pH environment, while iron precipitation occurs under more alkaline 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

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 adverse impacts of alum include potential buildup and development of toxic concentrations of aluminum, and excessive acidification in systems with low buffering capacity (Malecki-Brown et al. 2007). Unlike iron, aluminum compounds do not undergo reduction-oxidation reactions under anaerobic conditions. However, there is some concern regarding the effect of aluminum and sulfate ions on the plant and animal communities. Potential toxicity can be 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 is needed.

Another potential disadvantage of using alum is that the alum floc produced from alum treatment can over time produce a sludge that may require removal and disposal. For example, Bottcher et al. (2009) indicate that sludge production is about 0.28 percent of the volume of the treated flow (or 374 ft^3 alum sludge per mgd of water treated) after a 30-day settling period at a dosage of 10 mg Al/L. Settled fresh floc will dewater naturally over a period of 30-60 days, with a 95 percent reduction in volume compared to fresh floc (Bottcher et al. 2009).

Costs

Reported treatment costs using alum in lakes and reservoirs are highly variable, ranging from about $280/acre to $7,000/acre (BCWMC 2011, Burghdoff and Williams 2012. Cooke et al. 2005, WDNR 2003). Costs of alum application vary depending on the form of alum used, dosage rate, area treated, equipment rental or purchase, and labor. This includes the cost of the aluminum sulfate and/or sodium aluminate at $2.50 to $4.00 per gallon. However, in general, alum is relatively inexpensive compared to other coagulants, resulting in relatively low unit costs per mass of pollutant removed (Cooke et al. 2005, Harper 2007). For alum use in conjunction with treatment wetlands, Bottcher et al. (2009) estimates that P removal costs using alum treatment range from approximately $75-250/kg of P removed over a 20-year life-cycle cost (i.e., initial capital costs plus 20 years of O&M). Costs may be higher with the pH/buffer control likely to be required for use of alum in the Klamath system.

Ferric Chloride

Description

Ferric chloride (FeCl$_3$) is the most widely used iron salt in North America, and is second only to alum for use in chemical coagulation. Ferric chloride has been widely used in wastewater treatment processes to reduce P concentrations. Ferric chloride has been successfully used to remove phosphates from sewage effluent by precipitation with a mixture of ferric salt and lime, but precipitated P is strongly affected by changes in redox potential (Ann et al. 2000b). The addition of this iron compound is also a method that is used to regulate P availability and control eutrophication in lakes and reservoirs (Cooke et al. 1993). More recently, ferric chloride is garnering more attention as a potential treatment within wetland and marshes, and associated soils (Sherwood and Qualls 2001, Faithfull et al. 2005).

Mode of Effect on Nutrients

The main mechanism of P removal upon addition of ferric chloride involves the precipitation of metal oxyhydroxides and subsequent adsorption of P by ligand exchange. The precipitates remove P by similar primary mechanisms previously discussed for alum. Removal of suspended solids, algae, P, heavy metals, and bacteria occurs primarily by enmeshment and adsorption onto the metal hydroxide precipitate. Removal of additional dissolved P occurs as a result of formation of FePO$_4$.

In the cases of lakes and wetlands, the water body itself serves as a settling basin, not only removing P from the settling of precipitates though the water column, but also forming a blanket of precipitated metal oxyhydroxides covering the top layer of sediment, blocking the release of P from the sediment.

Effectiveness

Sherwood and Qualls (2001) evaluated ferric chloride additions to agricultural runoff entering the northern Everglades in Florida as a means for enhancing natural mechanisms of P removal from wetlands. In this study, ferric chloride was added to Everglades water spiked with soluble phosphate in microcosms simulating the Everglades ecosystem. Results indicated that on average less than 1 percent of the added soluble phosphate was measured in the water column during the 139-day testing period. Based on these results, Sherwood and Qualls (2001) suggested that ferric chloride addition thus might prove an effective means of long-term P retention in the Florida Everglades and perhaps other wetland systems.

Wisniewski (1999) undertook laboratory and in situ experiments in two hypertrophic lakes in Poland to determine the possibilities for the effective SRP precipitation by means of FeCl$_3$, applied directly to organic sediments (at a specific depth) previously subject to resuspension. Mesocosms treated with FeCl$_3$ showed either negligible or slight reduction of SRP in surface water, but SRP in interstitial water in lake sediments and water overlying sediments was reduced by 59 to 69 percent.

Browne et al. (2004) found that a 10 mg/L dose of $FeCl_3$ removed 79 and 73 percent of SRP and total P, respectively, from laboratory tests of enriched stream waters in New Zealand. Higher doses of 100 mg/L $FeCl_3$ removed 92 and 95 percent of SRP and total P, respectively. These tests relied on maintaining oxic conditions for Fe to bind to P.

Key Controlling Factors

When using ferric chloride, the impact of pH on the coagulation and floc-forming process is significant, as it is with other common coagulants. 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 ferric chloride, this pH zone is approximately 8-10, since the resultant floc has a minimum solubility of approximately 10^{-9} M which occurs in the pH range of approximately 8-10. The stability of the floc decreases substantially and the solubility of Fe^{+3} increases substantially at pH values both lower and higher than this range. Unlike floc produced by alum, the iron oxyhydroxide floc does not undergo a significant aging process or shift in solubility characteristics over time. In addition to P removal by absorption onto metal hydroxides, ferric chloride can also precipitate SRP directly as ferric phosphate ($FePO_4$). The minimum solubility for ferric phosphate is approximately $10^{-5.8}$ M which occurs at a pH value of approximately 4-5.

Iron hydroxides have been shown to be very sensitive to changes in redox potential (Sherwood and Qualls 2001). Under anaerobic conditions, phosphate adsorbed to iron oxyhydroxide complexes or precipitated ferric phosphate complexes will re-dissolve as Fe^{+3} to Fe^{+2} reduction occurs. However, the potential release of P under reducing conditions depends not only on redox conditions, but also on the solubility of the various iron oxyhydroxide-phosphate complexes formed. Lack of easily mineralized organic matter could retard the development of reduced conditions and subsequent Fe reduction.

Under reducing conditions, which exist in conditions where dissolved oxygen is low or absent, Fe (III) is reduced microbially to Fe (II), with the release of adsorbed P. Thus, Fe (III) absorbents are likely to be ineffective unless oxic conditions are present and maintained. Addition of ferric iron will also result in reduced water alkalinity with precipitation of ferric hydroxide and the efficiency of water column phosphate removal may be low with both reactions occurring. Addition of a suitable buffer may be necessary in situations where alkalinity is low. The alkalinity consumption during coagulation is higher with ferric coagulants than with alum. This suggests that at equal doses the addition of ferric chloride will have a more significant impact on pH than would be observed using alum. In contrast, alkalinity is added to the source water during coagulation with alkaline coagulants, such as lime, sodium hydroxide, or sodium aluminate.

Temperature may also have a significant impact on the coagulation process. Under cold temperatures, floc formation and the removal efficiency achieved using metal salts for coagulation decreases substantially. Colder temperatures often require a change in coagulant or change in dose to maintain acceptable settling characteristics and removal efficiencies. In the seasonally variable climate conditions in the Upper Klamath basin, temperature likely is an insignificant parameter impacting coagulation processes during the warmer period of the year, but may be a significant factor during colder months.

Advantages and Disadvantages

Advantages

The primary advantages of using ferric iron are: (1) it is considered a "natural" product; (2) it is readily available and potentially of lower cost compared to other chemical treatment alternatives; and (3) provides hydrogen sulfide binding and precipitation (in addition to phosphates).

Disadvantages

The primary disadvantages of using ferric iron are: (1) binding efficiency may be lower than anticipated based on stoichiometry, including the potential for reversible binding of P (redox-dependent); (2) reduction in alkalinity associated with dosing (may require alkalinity addition); and (3) low floc retention in turbulent conditions. Iron precipitation occurs under more alkaline conditions compared to coagulation with alum, which occurs in a neutral pH environment. Iron is unstable in a reduced environment, and the collected floc must be stored in an aerobic

environment at all times. Because of this instability, use of FeCl$_3$ in wetlands may not be desirable since precipitated P could potentially become soluble as water levels and redox fluctuate.

The addition of ferric chloride for P precipitation can have an impact on other biological processes. The formation of metal hydroxides consumes alkalinity, and maintaining pH stability is important in biological systems. Also, ferric chloride is produced by dissolving iron ore in hydrochloric acid. As a result, heavy metals are common contaminants. Strict control of chemical characteristics of ferric chloride is necessary when using this compound in treating surface or drinking waters.

Costs

Information is not readily available on costs associated with use of ferric chloride in lakes or constructed treatment wetlands. However, reviews of cost-effectiveness of chemical coagulants to treat storm water indicate that ferric chloride is similar in cost to alum (Narayanan and Pitt 2006, Peluso and Marshall 2002). Ferric chloride is slightly more expensive than the same volume of alum; however, the iron-based coagulants are more concentrated, therefore the cost to treat water is similar.

Lanthanum-Modified Bentonite Clay (Phoslock™)

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. Although information on the use of Phoslock™ in treatment wetlands is lacking, it is included in this report because 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).

Mode of Effect on Nutrients

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 (K_{sp} < 10^{-27}) and is not influenced by changes in pH and redox reactions in waterbody sediments, thus is not bio-available.

As a general rule, Phoslock™ is applied at the rate of 100:1; that is, 100 g Phoslock™ is required to remove 1 g of bioavailable P (Afsar and Groves 2009). Phoslock™ is generally supplied in a granular form (in 25kg bags) and can be applied to the water body both as a slurry and as granules.

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.

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 hrs (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.

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.

Costs

As a proprietary product, cost of treatment using Phoslock™ is only readily available by specific request from the manufacturer or designated representatives. Such a request has not yet been made for this study.

Zeolites

Description

Zeolites belong to a family of naturally occurring volcanic minerals with unique physical and chemical characteristics. There are over forty-eight varieties of natural zeolite minerals with similar structures and molecular makeup, each with its own particular attributes – some subtle and some more obvious (Coombs et al. 1998, Flanigen et al. 2010). 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".

Mode of Effect on Nutrients

Zeolites provide a substantial cation exchange capacity (CEC). Positively charged cations (sodium, calcium, potassium, and magnesium) are loosely bound at the junctures of the negatively charged aluminosilicate lattice structure. Cation exchange occurs when two or more positively-charged compounds or elements exchange places on a negatively charged host. 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). A classic example of cation exchange in zeolite is the removal of NH3 from water and wastewater. When a molecule of NH3 is hydrated, the reaction produces NH4+, which is readily exchanged for all or part of the calcium, potassium and magnesium cations contained in zeolite and adsorbed on to its stable aluminosilicate lattice.

"Modified zeolites" have been developed that allow for more efficient and effective targeting of nutrient or contaminant removal. One form of modified zeolite includes modification with a surfactant to reverse the surface properties of natural zeolite from negative to positive. Surfactant-modified zeolite (SMZ) is capable of simultaneous sorption of anions, cations, and non-polar organic molecules from water, making it amenable to various water treatment applications (Bowman 2003). These include applications of SMZ as a sub-surface permeable reactive barrier to control contamination of groundwater, removal of petroleum hydrocarbons from oilfield wastewaters, and removal of nutrients and pathogens from wastewater (Bowman 2003).

Another form of modified zeolite includes an aluminum-amended, proprietary zeolite (Z2G1 or Aqual P™ by Minsorb) that is marketed specifically for nutrient removal from lakes and other waterways. The aluminium 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.

Effectiveness

Most of the research regarding the effectiveness of zeolites, particularly with regard to nutrients, has occurred relative to applications to remove nutrient in waters and wastewaters (Bowman 2003, Widiastutia et al. 2008), and for capping nutrient releases from sediments (Vopel et al. 2008). Research by Widiastutia et al. (2008) on the use of SMZ to remove phosphate (PO_4^{3-}) from greywater indicates that SMZ using cethylpyridinium chloride could remove phosphate ranging from 50 to 90 percent depending upon variables such as the initial phosphate concentration, contact time, and initial pH.

Gibbs and Ozkundakci (2011) tested the aluminum-amended, proprietary P-inactivation zeolite Z2G1 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 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 NO_3-N, the greatest reduction (48 percent) occurred in the Phoslock[TM] 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.

Use of zeolites in treatment wetlands has been more limited than the applications described above, but research to date indicates considerable effectiveness of zeolite use in conjunction with treatment wetlands. Shuib et al. (2011) assessed the removal of nutrients and TSS from moderate strength wastewater in a horizontal subsurface flow constructed wetland using natural zeolite (unmodified) as a substrate. During a study period of 39 weeks, the constructed wetland with zeolite achieved significant removal of COD, NH_4-N, TN, and TSS compounds. Removals for COD, NH_4-N, TN, and TSS were found to be 89, 99, 96, and 95 percent, respectively, at 4 days hydraulic residence time (HRT) in the wetlands, and 85, 99, 91, and 91 percent, respectively, at 3 days HRT. Based on these results, Shuib et al. (2011) concluded that zeolite as a substrate media can substantially improve the effluent quality of the constructed wetlands.

Stefanakis and Tsihrintzis (2012) tested gravity filters containing zeolite (unmodified), bauxite, and carbonate material that were operated for 3 years to treat the effluent of a pilot-scale vertical flow constructed wetland. Results showed a significant improvement of effluent quality at an HRT of 1 day. Zeolite was more effective in N and organic matter removal, while bauxite in P retention. The carbonate material had the lowest efficiency among all filter materials used. The filter containing a 50:50 mixture of zeolite and bauxite showed the highest efficiency in pollutant removals. The increase of the residence time from 1 to 2 days did not show a respective statistically significant increase in removal rates.

Hillsborough County, Florida operated a zeolite (unmodified) filter pilot plant over a 216-day period to evaluate its ability to enhance N removal in stormwater from a pre-sedimentation pond prior to discharge to a post-filtration wetland (Smith et al. 2006). When operated at steady or simulated storm-event flow rates, the zeolite filter was highly effective at removing NH3, producing an effluent about a 90 percent or greater reduction in NH3-N concentration and removing more than 95 percent of the applied NH3 mass. The effluent also had about a 32 percent reduction in total inorganic N concentration. These results demonstrated that the zeolite filter performance was much superior to a parallel sand filter operated under similar conditions. The zeolite filter had limited or no removal effectiveness for dissolved organic N (DON) and NO3-N. DON removal in the zeolite filter was 25 percent or less. Nitrate-N was actually increased in the zeolite filter effluent (compared to influent), which Smith et al. (2006) indicate would require treatment or containment by other measures if TN removal were to be the goal.

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)[5].

Advantages and Disadvantages

The primary advantages of natural zeolites include: (1) they are relatively inexpensive and abundant natural products; and (2) a relatively high affinity for cation removal, particularly NH4+. The primary disadvantages of natural zeolites include: (1) they lack affinity for anion removal, including phosphate; (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 various zeolite forms and commercial products.

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[5] The mEq is one-thousandth of a compound's or an element's equivalent weight. The equivalent weight is the amount of a substance that combines with or displaces 8.0 g of oxygen (or 1.008 g of hydrogen); it is the ratio of the molecular weight to the number of protons (acid/base reactions) or electrons (redox reactions) involved in the reaction.

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.

Costs

Natural zeolites are relatively inexpensive, costing in bulk about $200.00 per ton from large manufacturers, such as Bear River Zeolite Co. in Idaho (http://www.bearriverzeolite.com/) or the St. Cloud Mining Co. in New Mexico (http://www.stcloudmining.com/). Modified zeolites are more expensive due to the additives and processing required. For example, Bowman (2003) reports that surfactant-modified zeolites are about cost 7-10 times as much as unmodified zeolites.

Costs of treatment using aluminum-amended, proprietary modified zeolites (Z2G1 or Aqual P™ by Minsorb) are only readily available by specific request from the manufacturer or designated representatives. Such a request was not made for this study given unknowns regarding if and how proprietary modified zeolites might be used in conjunction with potential constructed treatment wetlands in the study area.

Polyaluminium Chloride (PACl)

Description

Polyaluminum 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.

Mode of Effect on Nutrients

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.

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). The effectiveness of this approach is described in the following section 5.2.6 *Low Intensity Chemical Dosing (LICD)*.

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.

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.

Costs

Generally, PACl coagulants are more costly than alum on an equivalent Al basis (Pernitsky and Edzwald 2006). On the other hand, PACls are pre-neutralized and are less acidic than alum. For low and moderate alkalinity waters, lower amounts of base would be used to control coagulation pH, thus reducing costs. Sludge quantities, dewatering characteristics and treatment and disposal are also important considerations in evaluating the overall cost of PACl versus alum (Pernitsky and Edzwald 2006). For example, Gebbie (2001) reported that chemical costs using PACl were about 10 percent higher than alum per unit volume of treated water. However, Gebbie (2001) also reported that treatment effectiveness of PACl was more robust than alum and produced less sludge requiring disposal. As a result, the overall treatment costs using PACl were about 14 percent less than alum per unit volume of treated water.

Appendix B

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