# Passive Chemical Treatment Monitoring Guidance and Study Plan Development

Recommendations to Inform Guidance and Requirements for Stormwater Runoff Management

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**Prepared for** 

# STATE WATER RESOURCES CONTROL BOARD

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This report contains the findings and recommendations of the Office of Water Programs and does not represent the conclusions or opinions of the State Water Board.

The literature review, guidance flowcharts, and study plan included in this project report were developed in 2021. As such, these items represent the best available information at the time, and any new guidance documents, studies, or regulatory requirements developed after 2021 are not included within this report. California construction stormwater professionals should reference the 2022 California CGP for additional requirements related to the use of passive treatment technologies.

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## **Acronyms and Abbreviations**

- ac acre
- ASTM American Society for Testing and Materials
- ATS Active Treatment System
- **BMP** Best Management Practice
- CASQA California Stormwater Quality Association
- CGP Construction General Permit
- DOT Department of Transportation
- EPA US Environmental Protection Agency
- gpm gallons per minute
- IGP Industrial General Permit
- L liter
- lbs pounds
- LC50 Concentrations that are lethal to 50% of organisms
- LOEC Lowest Observed Effects Concentration
- mg milligrams
- NAL Numeric Action Levels
- NPDES National Pollutant Discharge Elimination System
- NRCS National Resource Conservation Service
- NTU Nephelometric Turbidity Unit
- PAC Poly Aluminum Chloride
- PAM Polyacrylamide
- TAC Technical Advisory Committee
- USDA United States Department of Agriculture

## **Executive Summary**

Chemical flocculants are used on construction sites and in certain industrial facilities to enhance the effectiveness of erosion control and sediment control practices. Some data exist on the environmental impact of flocculant chemicals, but data on the amount of chemical in stormwater discharges from construction and industrial stormwater applications are lacking.

The goals of this project were the following:

1) Report the conditions in which passive use of flocculants is known to cause toxicity, identify data gaps, and develop interim deployment and monitoring guidance.

2) Develop a study plan to fill the data gaps so that appropriate application techniques to control toxicity in the receiving water can be identified. The study plan identifies data that can be collected by dischargers as a condition of chemical use.

This project accomplished four tasks:

- 1. Performed a literature review on the use of particle-binding chemicals to enhance erosion control and stormwater runoff treatment from construction sites and industrial land uses. Toxicology and state-of-practice guidance were reviewed and summarized.
- 2. Developed interim chemical deployment guidance for system design, basin operations, and monitoring that decreases the risk of impacts to the aquatic environment. Guidance includes a mass-balance calculator for estimating discharge concentrations.
- 3. Proposed interim requirements for system design, basin operations, and monitoring to minimize impacts from discharges, while using available monitoring tools to identify underperforming systems. Interim requirements allow the conservative and cautious use of chemicals while data are being collected.
- 4. Developed study plans to address the critical data gaps needed to ensure environmentally safe use.

## Literature and State-of-Practice Review

This project found substantial toxicity data, especially for establishing concentrations that are lethal to 50% of test organisms (LC50 concentrations). Lowest observed effect concentrations (LOEC concentrations) were not always available. Data on sediment toxicity due to the presence of settled floc was almost universally lacking. The most common chemical to enhance erosion and sediment control was polyacrylamide (PAM). Interestingly, the LOEC (growth inhibition) toxicity value for exposure of the water flea to PAM was substantially lower than for fish species and often within the target treatment concentration for enhanced flocculation within sedimentation control basins. Successful and safe use was anecdotally reported as an absence of fish kills or visible instream sludge deposits; however, impacts to benthic organisms and water flea in the water column would be difficult to casually observe following typical inspection protocols.

Oft-cited NRCS application guidance (NRCS 2016) and supporting references to the environmental safety of PAM (Weston et al. 2009; Kerr et al. 2014) were found to be of limited value for stormwater applications because of 1) documentation that water flea growth impacts have occurred at PAM concentrations as low as 1 mg/L (Acharya et al. 2010) and those impacts

were not attributed to particular PAM formulations, 2) increased erosion potential of construction sites and industrial facilities with little or no topsoil, 3) potentially different preferential binding between PAM and agricultural topsoil and PAM and erosion control matrix, 4) unknown correlation of USDA research to the nonarable California soils where construction occurs, 5) steeper slopes on certain construction sites and industrial facilities, and 6) NRCS guidance, which limits spray application to 4 lbs/ac to limit crusting while typical construction site rates are typically 20 to 30 lbs/ac. Crusting is concerning, and further study is needed to determine if this increases runoff or leaves a surface of PAM that is unbound to the soil and therefore available for dissolution and wash off.

Literature was also explored to see if guidance, particularly limits on application rates, could be correlated to maximum allowable runoff concentrations. Several states provide substantial guidance on various classes of chemicals, often with application rates for specific chemicals within classes. However, very limited data measuring chemical loss and correlating to dose and site factors exist (Kang et al. 2014; Manning et al. 2021). Peer reviewed research on dose and residual occurrence in conditions similar to West-Coast hydrology, topography, and soils could not be found. Also, calibrated and verified calculators that translate application rates to discharge concentrations of unreacted chemical or floc-bound chemical were not found. Wisconsin appears to use an internal calculator to determine application rates that could be helpful, but the calculator was not reviewed as a part of this study. However, an open source calculator was developed for estimating discharge concentrations (Section 3.3).

Primary factors that lend to high variability and low confidence in concentration estimates include the following: 1) storm runoff volume; 2) storm intensity; 3) sediment load; 4) soil variability by excavation depth, area, and off-site import; 5) dissolution rates of solid-state chemicals; and 6) level of chemical-particle binding for both erosion control and sediment control applications. Simple mass balance (no losses) shows that the mass of chemical applied using existing guidance is sufficient to result in a toxic impact (e.g., water flea growth), so further investigation of fate and transport is critical to ensuring safe use. The lack of a calibrated, verified, and field-applicable residual test for PAM has likely hampered data collection for this particular flocculant.

## **Recommendations Overview: Interim Guidance and Proposed Interim Requirements**

This report differentiates recommendations as either 1) guidance, or 2) requirements. Practices are grouped by 1) system design, 2) basin operations, and 3) monitoring. Recommended practices then fall into the following groups, each listed with recommendations:

#### Guidance

- Interim system design
  - Perform jar testing for formulation and dose
  - Use mass-balance calculator developed in this study to predict chemical concentrations in discharge for likely storm characteristics
  - Cationic chemicals are not recommended
  - o Design basins with baffles to provide slow mixing
- Interim basin operations

- Consider additional turbidity or residual monitoring of slope runoff and sedimentation basin influent
- Perform site reassessment when turbidity in basin exceeds 50 NTU or water shows toxic
- Interim monitoring
  - Perform field measurements of rainfall, drainage area, runoff rate, runoff flow, and sediment load in basin influent
  - Collect sedimentation basin influent and rerun jar test, adjusting formulation and dose with each storm event

### **Proposed Requirements**

- Interim system design
  - Only use chemicals with known toxicity thresholds
  - Use sedimentation basins for erosion control or sediment control applications
  - PAM product should not contain more than 0.05 percent acrylamide monomer, must be free of surfactants such as nonylphenol (NP) and nonylphenol ethoxylates (NPE), and must have an LC50>100 mg/L for pimephales promelas (fathead minnow) in standard EPA WET test
  - Size basin area per CASQA Construction BMP Handbook (2019), Option 1
  - Size basin volume per CASQA Construction BMP Handbook (2019) (capture the 2-yr 24-hr event)
  - Design basins with outlet controls
  - Use basin liners for long-term installations, such as at industrial sites, to prevent risk of groundwater impacts
- Interim basin operations
  - Hold water for a minimum of 24 hours
  - For non-cationic chemicals, only discharge when basin effluent is less than 50 NTU prior to release. If not,
    - Hold water and assess options to lower NTU, including recirculation, if appropriate, and additional treatment through filtration or other means
    - Follow local vector control requirements
    - If 50 NTU turbidity target is unachievable, drain basin and discharge contents to sewer
  - For cationic chemicals, or at the discretion of the operator using non-cationic chemicals, use a toxicity test of the most sensitive species and discharge only nontoxic water.
- Interim monitoring
  - Measure basin effluent turbidity, pH, and temperature; 24-hr and daily thereafter if extended holding time is needed to meet 50 NTU
  - Perform a visual assessment of floc (photographs)
  - For each site discharge location that is sampled per the CGP, record the quantity and type of flocculent chemical used for erosion control
  - For each site discharge location that is sampled per the CGP, record the percent of the drainage treated with chemical for erosion control
  - Record the quantity and type of flocculent chemical used to enhance sediment control (water treatment)

• For each site discharge location that is sampled per the CGP, record the percent of drainage area treated by basins using chemicals to enhance sediment control

All recommendations are offered for consideration by the State Water Board and stakeholders in setting policy. Guidance is also offered for consideration by stormwater practitioners, professional and trade associations, and trainers to inform improvements to existing guidance. Recommended guidance will assist practitioners engage in more efficient management strategies that minimize the risk of chemical impacts; this guidance should be adapted by others as practices continue to evolve and improve. Proposed interim requirements are, in the view of the Study Team, needed to ensure environmentally safe use of chemicals at this time. Proposed requirements should also be considered interim, as requirements will evolve as the data identified in the study plan are gathered.

The proposed requirements herein are an outcome of the narrow task of addressing impacts of chemicals. One mechanism to institute requirements is permit language; however, regulators should consider the interim nature of these proposed requirements and whether a permit reopener would be nimble enough for a timely update of the requirements to avoid unnecessary costs. The caveat section below should also be considered before instituting the proposed interim requirements into permit language.

Final policy decisions should consider tradeoffs between the discharge of sediment and discharge of flocculent. Tradeoffs are discussed generally below under "Caveats" and more thoroughly throughout the report. While disallowing chemical use leads to the least impact, the Study Team believes a reasonable balance is to allow the continued, but more cautious, use of passively dosed flocculant chemicals accompanied by 1) concurrent study of toxicity impacts, and 2) field monitoring designed to determine residual discharge concentrations and relate those to key site variables.

## **Study Plan**

The following Study Plan research topics address the assessment tools and data needed to ensure the environmentally safe use of treatment chemicals:

- Protocols for jar and effluent tests
- Protocol for residual tests
- Field water quality monitoring
- Field sediment toxicity and bioassessment monitoring

Other research topics useful to optimizing the effectiveness of chemical use are not covered in the study plans because they are not critical to the immediate task of ensuring safe environmental use. These topics include the following:

- Chemical dissolution rates
- Chemical-binding to coapplied erosion control matrices, crusting, wash off, and redissolution
- Calibration and verification of a mass-balance concentration prediction calculator
- Settling velocity and optimized basin sizing
- Determining if nonionic PAM effectiveness in certain soils justifies its higher dose

### **Caveats**

#### Adapting Policy to New Data

Adapting policy to new data is important in order to allow more cost-effective practices to be implemented once they are confirmed environmentally safe. If the data demonstrate that following certain practices results in environmentally safe discharge, then many proposed requirements can be relaxed. However, the data may also indicate that certain system design practices are required rather than recommended in some situations. Data collected in future studies will help establish minimum inspection and monitoring requirements to identify these site practices.

The literature review, guidance flowcharts, and study plan included in this project report were developed in 2021. As such, these items represent the best available information at the time, and any new guidance documents, studies, or regulatory requirements developed after 2021 are not included within this report. California construction stormwater professionals should reference the 2022 California CGP for additional requirements related to the use of passive treatment technologies.

#### **Risk Tradeoffs and Unknown Impacts**

Risk is defined here as the likelihood of occurrence of impact as well as the severity and persistence of impact. It is difficult to compare risk between construction site discharge with chemical use and construction site discharge without chemical use in California environments. The project Technical Advisory Committee (TAC) could not find universal agreement on addressing the risks posed by passively treated discharges, partly due to tradeoffs between untreated sediment impacts and the impact of chemical use (Table ES-1). This balance is a difficult one. A less severe and less persistent impact that is more likely to occur is not necessarily more favorable than an impact that is more severe and more persistent but less likely to occur.

Discharged Pollutant	Toxicity	Habitat Impact	Persistence
Sediment (no chemical treatment)	Salmonid egg and larvae sublethal at prolonged and high exposure	Yes, depending on stream hydraulics	Toxicity: Low Habitat: Medium (several events)
Turbidity (no floc)	Limited toxicity; correlates to suspended sediment and depends on species	Yes, good and bad, depending on species	Toxicity and Habitat: Low/Medium (depending on residence time and particle size; lower in streams and higher in lakes)
Chemical residual	Water flea; unknown sediment toxicity	Indirectly, when bound with receiving water sediments	Toxicity: Low (single event) Habitat: High for settled floc (seasonal to multiyear)
Floc	Unknown sediment toxicity	Yes	Toxicity and Habitat: High (seasonal to multiyear)

Table ES-1: Environmental	risk tradeoffs	of pollutants	as	expressed	by	severity	type	of	impact	and
persistence										

## **1** Background and Goals

Treatment chemicals are coagulants or flocculants used to enhance Best Management Practice (BMP) performance. BMPs that use these coagulants and flocculants include sediment controls and erosion controls. They are most commonly used on construction sites and in industrial facilities. They are also used in advanced treatment systems that employ other removal mechanisms, such as filtration. Advanced systems typically employ metered dosing of chemical directly into water, which is considered active dosing in this report. These advanced systems are described in Attachment F of the California Statewide Construction General Permit (CGP) as active treatment systems (ATS), which includes residual chemical monitoring for flow-through systems and toxicity testing for batch systems (SWB 2009).

Chemicals used with traditional sediment control and erosion control BMPs that dose or apply chemicals prior to the occurrence of rainfall are considered passive dosing in this report. Passive dosing with sedimentation BMPs includes floc logs within flow paths to basins or silt fence impoundments. Erosion control applications include chemical use in hydraulic or bonded matrices, soil binders, stabilized fiber matrices, and/or tackifiers. Chemical properties and levels of toxicity vary widely depending on the quantity of active ingredients and dissolution rates, which are, in turn, dependent on the manufacturer. Internationally, industries use treatment chemicals in water purification, food production, and other industrial applications to reduce turbidity and the concentration of target constituents. Construction site operators regularly use treatment chemicals in passive and active applications to reduce turbidity levels in stormwater runoff (also referred to as site discharge) to achieve the numeric action level (NAL) of 250 NTU. Industrial sites may also be candidates for chemical use, particularly aggregate mining and landfill locations where erosion and sediment discharge are more likely to occur.

Preliminary research into commonly used chemicals indicates that many are toxic or contain toxic components and have the potential to negatively impact aquatic organisms and habitats when discharged to surface waters. Overdosing of treatment chemicals can also result in ineffective systems. Regulation is inconsistent.

The State Water Board is not currently regulating a discharger's passive dose of treatment chemicals in the CGP. The Industrial General Permit (IGP) does not regulate active or passive dosing (SWB 2014). The United States Environmental Protection Agency's (EPA) current National Pollutant Discharge Elimination System (NPDES) General Permit for Stormwater Discharges from Construction Activities (EPA 2017) became effective on February 16, 2017 and regulates construction sites in states not designated to manage their own stormwater program. The EPA requires construction sites planning to use cationic treatment chemicals to provide site-specific use information before applying for permit coverage and outlines requirements for the use of treatment chemicals (in passive and active dosing systems). The EPA has developed more detailed requirements for chemical use at industrial sites, but it does not require toxicity or residual testing (EPA 2021).

Active dose recommendations are not addressed in this report.

## 1.1 Data Gaps

Quantitative data on the negative impacts on receiving waters from the use of stormwater treatment chemicals (passively and actively) are limited and not centrally compiled. Studies examining the impacts of these chemicals on aquatic communities may be necessary to effectively regulate their use at construction sites and industrial facilities.

The California Stormwater Quality Association (CASQA) provides limited specifications for the use of polyacrylamide-based flocculants or coagulants in fiber rolls, hydraulic mulch, and ATS. The construction industry supports the use of treatment chemicals because these products provide a cost-effective method to comply with the turbidity numeric action levels in the CGP.

Despite the available technical information and guidance, questions remain about appropriate dosing of chemicals, given the variability in solids loading and toxicity when these chemicals are used in excess. Flocculants have known toxicity, for the most part, so questions about their use focus on concentration prediction, floc management, and long-term ecological impact. Many commonly used anionic flocculants have relatively lower toxicity than nonionic and cationic flocculants, but use rates are often higher. Also, questions remain regarding anionic chemical toxicity after molecular breakdown and the deleterious effects of flocculated solids that may escape the site or form after unconsumed flocculant leaves the site.

## **1.2 Report Goals**

The goals of this report include the following:

- 1) Report the conditions in which the passive use of chemicals is known to cause toxicity (Section 2.3), identify data gaps (Section 2.4), and develop interim deployment (Sections 3.1 and 3.2) and interim monitoring guidance (Section 4.1).
- 2) Develop a study plan (Section 5) to fill the data gaps so that appropriate application techniques to control toxicity in receiving waters due to the passive use of flocculants can be identified. The study plan will identify data that can be collected by dischargers as a condition of chemical use.

## **1.3 Technical Advisory Committee**

A Technical Advisory Committee was solicited from CASQA Industrial and Construction subcommittees. After some literature review, invitations were extended to researchers who have recently contributed to the state-of-knowledge. There were three virtual meetings: the first reviewed literature, the second reviewed draft guidance, and the third reviewed the mass-balance calculator developed in this project. In addition, the Study Team is indebted to several TAC members who shared their experiences in conversations outside of the group meetings.

Anecdotal observations from TAC members could not all be verified in the literature given time constraints to complete this report. The TAC was given an opportunity to provide comment letters, but no formal comments were received. Table 1 identifies TAC members, the company or organization they work for, as well as their affiliation type (permittee, consultant, supplier, regulator, or academic).

#### Table 1: TAC members

Name	Company	Affiliation Type	
Beth Smiley	Independent	Consultant	
Dave Mercier	Michael Baker International	Consultant	
Eddie Snell	Applied Polymer Systems Inc.	Vendor/Manufacturer	
Kyla lwinski	Applied Polymer Systems Inc.	Vendor/Manufacturer	
Hamid Hakim	Caltrans	Permittee	
Heaven Moore	North Coast Regional Water Quality	Regulator	
	Control Board		
Jeff Endicott	CASC Engineering and Consulting Inc.	Consultant	
Joe Gannon	Clear Creek Systems	Consultant/Supplier	
Kadi Whiteside	Southern California Edison	Permittee	
Liisa Doty	Water Tectonics	Consultant/Supplier	
Lucas Paz	Terraphase Engineering	Consultant	
Mark Naugle	Golder Associates Inc.	Consultant	
Marvin H. Sachse	Brash Industries	Consultant/Supplier	
Matt Hromatka	Clear Water Services	Consultant/Supplier	
Melanie Sotelo	CASC Engineering and Consulting Inc.	Consultant	
Mike Chase	MC Environmental Solutions	Consultant	
Mike Perez	Auburn University	Academic	
Patrick Galvin	GSI Environmental Inc.	Consultant	
Rich McLaughlin	North Carolina State University, Crop	Academic	
	and Soil Sciences		
Rich Muhl	Central Valley Regional Water Quality	Regulator	
	Control Board		
S. Wayne Rosenbaum	The Environmental Law Group, LLP	Consultant	
	Varco and Rosenbaum		
Tanya Bilezikjian	Michael Baker International	Consultant	
TJ Mothersbaugh	Water Tectonics	Consultant/Supplier	

## 2 Literature Review

## 2.1 Common Usage

The use of treatment chemicals for sediment and erosion control purposes varies throughout the country. In an article published in the 2021 Fourth Quarter IECA Connect newsletter, Billur Kazaz, Michael A. Perez, and Wesley N. Donald summarized nationwide flocculant usage. Surveys were sent to all state departments of transportation (DOTs) to identify common use practices of flocculants on construction sites. Survey results identified that "31 DOTs (61%) are hesitant on using flocculants on construction sites, with only 20 DOTs (39%) using flocculants" (Kazaz, Perez, and Donald 2021, 15). These survey results highlight the hesitancy of DOTs to use flocculants on construction sites due to a lack of guidance and understanding regarding proper usage and toxicity risks.

Fifty percent of the agencies surveyed also considered their current traditional stormwater treatment practices adequate for treating construction stormwater to meet water quality objectives. For agencies that do allow the use of chemical flocculants, the vast majority (92%) use these chemicals for sediment control while a smaller population (31%) use these flocculants for erosion control. The survey results also indicated that the most common flocculant types preferred include PAM (62%), chitosan (38%), and polyaluminum chloride (PAC) (23%). These studies were focused on DOTs. Residential developments were not addressed.

California usage has not been centrally reported, though TAC reported usage throughout the state.

## 2.2 Existing Guidance and Permits

Guidance documents and existing permits outlining the safe use of passive chemical treatment on industrial and construction sites provide an opportunity to review current best management practices. The following sections provide an overview of guidance for optimizing traditional erosion and sediment control practices, product selection, application guidance, and maintenance standards. While this subsection provides an overview of existing permit requirements, guidance documents, and practices, Section 3 of this report provides the Study Team's recommended practices.

### Summary of Guidance

Existing guidance documents were reviewed as a part of this project to identify the state-ofpractice for the use of passive treatment chemicals at industrial and construction sites. Guidance from professional member associations, vendor application handbooks, and testing procedures, as well as government guidance are included for discussion in this section.

#### **Optimization of Traditional Sediment and Erosion Control Practices**

The guidance documents reviewed emphasize that chemical treatment of stormwater to meet water quality objectives should not be used as a substitute for the proper planning and implementation of traditional sediment and erosion control practices. Traditional erosion and sediment control BMPs should first be maximized before evaluating the feasibility of using chemical treatment options to meet water quality objectives. However, some soils with clay and silt content may require the use of chemically enhanced treatment techniques to reach the NAL of 250 NTU.

Found in this literature review, the following quote emphasizes the importance of first maximizing the use of traditional erosion and sediment control practices prior to exploring the feasibility of passive chemical treatment options: "Chemical Treatment shall not be substituted for proper planning, phasing, sequencing, and the design of appropriate erosion and sediment control practices" (New York State Department of Environmental Conservation 5-2).

#### Product Selection

A large number of chemical formulations are available for passive erosion and sediment control applications. Selecting the appropriate treatment chemical for a given site dictates performance, toxicity risk, and the overall cost of treatment. Jar tests are most commonly used to select an appropriate treatment chemical for a construction or industrial site. The guidance documents reviewed emphasize the need for site-specific soil testing, and, in some states, lists of preapproved chemicals have been developed with recommended application rates. Table 2 provides the chemical name, manufacturer, allowable usage rate, and the state in which the chemical is approved for use. Some chemicals are preapproved by multiple states at the same maximum recommended concentration.

#### Table 2: List of state-approved passive treatment chemicals

Manufacturer	Product Name	Maximum Concentration	Unit	State Agency
				Maryland Department of the Environment
Aquamark, inc	AQ109	180	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Aguamark, inc	AQ 224	1	mg/L	Maryland Department of the Environment
			Ŭ	Maryland Department of the Environment
Ashland Hercules Water Tech (Solenis)	Ashland ChargePac 55	10	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Biostar	CH Chitosan Acetate	220.8	mg/L	Maryland Department of the Environment
Biostar	CH Chitosan Lactate	263.9	mg/L	Maryland Department of the Environment
Halo Source / now Dober Chem 4-4-16	3% LiquiFloc	9.4	mg/L	Maryland Department of the Environment
Halo Source / now Dober Chem 4-4-16	HaloKlear 4900 DBF	1.4	mg/L	Maryland Department of the Environment
Halo Source / now Dober Chem 4-4-16	Haloklear BHR-P50	78.4	mg/L	Maryland Department of the Environment
				Maryland Department of the Environment
Halo Source / now Dober Chem 4-4-16	HaloKlear GelFloc	2.56	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Applied Polymer Systems	APS 702b Floc Log	42	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 702c Floc Log	42	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 703d # 3/806 Floc Log	51.8	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 703d # 3/806 Floc Log	Not Specified	na	North Carolina Department of Environmental Quality, Division of Water Resources
Applied Polymer Systems	APS 703d Floc Log	38.3	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 703d Floc Log	Not Specified	na	North Carolina Department of Environmental Quality, Division of Water Resources
Applied Polymer Systems	704f Floc Log	42	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 705 Floc Log	27.7	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 705 Floc Log	27.7	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Applied Polymer Systems	APS 706b Floc Log	42	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 706b Floc Log	Not Specified	na	North Carolina Department of Environmental Quality, Division of Water Resources
Applied Polymer Systems	APS 712 Floc Log	59.3	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 712 Floc Log	59.3	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Applied Polymer Systems	APS 730 Floc Log	5.6	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 730 Floc Log	5.6	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Applied Polymer Systems	APS 740 Floc Log	5.2	mg/L	Maryland Department of the Environment
Applied Polymer Systems	APS 740 Floc Log	5.2	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Halo Source / now Dober Chem 4-4-16	HaloSource DBP-2100	84	mg/L	Maryland Department of the Environment
Halo Source / now Dober Chem 4-4-16	HaloSource LBP-2101	500	mg/L	Maryland Department of the Environment
Halo Source / now Dober Chem 4-4-16	HaloSource LBP-2101	500	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Innovative Turf Solutions (ITS)	EnviroPAM	200	mg/L	Maryland Department of the Environment

Manufacturer	Product Name	Maximum Concentration	Unit	State Agency
Innovative Turf Solutions (ITS)	EnviroPAM	200	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Innovative Turf Solutions (ITS)	Erosion Guard Powder, Erosion Guard Logs, Erosion Guard Flats	200	mg/L	Maryland Department of the Environment
Innovative Turf Solutions (ITS)	Erosion Guard Powder, Erosion Guard Logs, Erosion Guard Flats	200	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Innovative Turf Solutions (ITS)	FLOC (granular)	400	mg/L	Maryland Department of the Environment
Innovative Turf Solutions (ITS)	FLOC	650	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Innovative Turf Solutions (ITS)	FLOC BAG	400	mg/L	Maryland Department of the Environment
Innovative Turf Solutions (ITS)	FLOC SOC	400	mg/L	Maryland Department of the Environment
NEO Solutions	NS 6850P / NS 9179 Tablet	1.3	mg/L	Maryland Department of the Environment
NEO Solutions	NS 6850P / NS9181 Logs	1.3	mg/L	Maryland Department of the Environment
NTU	GeoScrub 10, 13, 20, 23, 34	10	mg/L	Maryland Department of the Environment
NTU	GeoScrub 10, 13, 20, 23, 34	10	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
NTU	GeoScrub Bubbles	1	mg/L	Maryland Department of the Environment
NTU	GeoScrub Bubbles	1	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Soil Net LLC	EM 1000(OL 1000)	41.3	mg/L	Maryland Department of the Environment
Soil Net LLC	EM 1240	28	mg/L	Maryland Department of the Environment
Soil Net LLC	EM 1340	15	mg/L	Maryland Department of the Environment
Soil Net LLC	S1000-SAL	8.1	mg/L	Maryland Department of the Environment
Soil Net LLC	S550W	18	mg/L	Maryland Department of the Environment
Soil Net LLC	Soil Net - TRIPAM	123	mg/L	Maryland Department of the Environment
	SoilNet Disk A	39	mg/L	Maryland Department of the Environment
Soll Net LLC		100	mg/L	Maryland Department of the Environment
ZINKan	ADS702 Silt Stop	1.1	mg/L	Maryland Department of the Environment
Applied Folymer Systems	APS702 Silt Stop	61 75	mg/L	Maryland Department of the Environment
Dober HaloKlear		152 75	mg/L	Maryland Department of the Environment
Dober HaloKlear		4 37	mg/L	Maryland Department of the Environment
Aquamark, inc	AQ100	39.7	mg/L	North Carolina Department of the Environmental Environmental Quality, Division of Water Resources
Ashland Hercules Water Tech (Solenis)	Ashland Zalta MC 9500	10	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Cape Fear Consulting	PAX-CFC39A	5	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Cape Fear Consulting	CFC-4330	4.5	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Carolina Hydrologics	HYDROLOC PAM	3	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Carolina Hydrologics	Floc Roll/Line/Flat	50	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Chemical Solutions, Inc.	CS-1234 and/or CS- 1234D	500	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources

Manufacturer	Product Name	Maximum Concentration	Unit	State Agency
Chemical Solutions, Inc.	MK7154DP	10	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Green Techniques	Soil Defender	0.008	%	North Carolina Department of Environmental Quality, Division of Water Resources
Hanes Geo Components	TerraGuard Granular PAM	3.25	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Leaner Meaner Greener, Inc	L.M.G. Dust Magnet 281 Solution	0.05	%	North Carolina Department of Environmental Quality, Division of Water Resources
Leaner Meaner Greener, Inc	L.M.G. Dust Magnet 163 Powder	0.5	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Leaner Meaner Greener, Inc	DBP-2100	28.125	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Nalco	Nalco 8187	100	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Paschal Associates Sales	PFR P251	25	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Southeastern Laboratories	SEL FLOC 6026	7.5	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Storm Klear	3% Liqui-Floc	9.4	mg/L	North Carolina Department of Environmental Quality, Division of Water Resources
Terra Novo	EarthGuard	0.000625	mL/L	North Carolina Department of Environmental Quality, Division of Water Resources

ASTM D 2035-19 jar test method has been commonly referenced for use to select site-specific treatment chemicals for use in passive applications. In the TAC meetings, practitioners stated that they make substantial modifications to this method in the field. While the ASTM method can be used for stormwater applications, it has shortcomings due to differences between construction site controls and the treatment plants for which the ASTM method was developed. In addition to 20 minutes of slow mixing, the ASTM method requires an additional 15-minute settling time prior to checking for the appearance of floc. While some systems may be designed to accommodate these extended mixing and settling times, size limitations of most stormwater sediment control applications require a reaction to occur in a much shorter period of time (30–60 seconds), as illustrated in the tailgate procedures from Minnesota and the *State of Florida's Erosion and Sediment Control Designer and Reviewer Manual* discussed below.

In 2017 a research project funded by the Minnesota Department of Transportation was completed to develop a tailgate test kit for determining appropriate sediment-reducing chemicals and dosing rates for construction sites. In addition to selecting an appropriate chemical, a methodology for estimating appropriate dosing rates was also developed (Toso 2017).

The first step in the procedure involves intentionally overdosing a sample to determine if a reaction occurs. The second step requires adding a dose or a mixing step and waiting for 30–60 seconds for a reaction to occur. If a reaction occurs, then after 5 minutes a turbidity test is taken from the sample and compared against target turbidity. The dose/mixing steps and recorded turbidities are used to develop a dose-turbidity curve to determine the appropriate dose rate. If multiple chemicals are found to be equally effective, then floc size as well as the total respective cost of the product to be used can be selected for use.

The *Erosion and Sediment Control Designer and Reviewer Manual* developed by the State of Florida provides guidelines on selecting appropriate treatment chemicals for a particular construction or industrial site. The first step involves obtaining a representative sample from the site. Next, a test needs to "demonstrate that within 60 seconds at least 95% of all sediment and suspended colloidal particles found in 29-inch (735 mm) high vertical water column are captured and accelerating downward. More than likely, performance-based tests will have to be completed while construction activities continue to ensure optimal capturing capabilities of the polymer remains viable" (State Erosion and Sediment Control Task Force 2013 IV-36).

This test emphasizes a much shorter reaction and settling time than the ASTM standard discussed earlier in this section. A clearer definition of "particle capture" and "downward acceleration" would provide practitioners with the tools necessary to select chemicals based on more quantitative observations though. The Florida Manual also states the need to continue jar testing to confirm the correct chemical type is selected as representative soil and water samples may change in a construction application (AIII-48).

#### <u>Training</u>

Erosion and sediment control plans that identify the use of passive treatment chemicals should also identify professionals who are qualified in the use of passive treatment chemicals in a given application. According to the *Anionic PAM Application Guide for Urban Construction in Ontario*, an individual will be considered "qualified" based on training and prior experience in the application of passive treatment chemicals (Toronto and Region Conservation 4). It is recommended that

- Safe handling and spill prevention practices be developed and implemented to ensure safe application practices are followed, and
- California IGP and CGP Training Teams consider additional training requirements to address passive chemical treatment use in erosion and sediment control applications.

#### Inspection, Monitoring, and Maintenance

A summary of the guidance documents included in this literature review is listed in Table 3. The document title, author, and highlights from each guidance document are included. The main categories of guidance documents include professional organizations, vendor application handbooks, as well as government guidance. As with any BMP, regular inspections, monitoring, and maintenance are commonly recommended both to ensure efficient operation and to minimize toxicity risks to downstream aquatic environments.

#### Table 3: Existing guidance summary

Category	Document Title	Author	Highlights
Professional	BMP Construction		Soil Binders - PAM treated soils should pass through Sediment Control BMP prior to discharge (>5 acres = sed basin) (< 5 acres sediment trap or series of check dams)
Member Association	Handbook	CASQA	No cationic; do not discharge to water body
			Not stand alone
Vendor Guidance	Applications Using Turbidity Reducing Polymers in Florida	R.H. Moore and Associates, Inc.	Focus on APS products and methodology. Pages taken from APS BMP application guide
Vendor Guidance	Polymer Enhanced BMP Application Guide	Applied Polymer Systems, Inc.	Focus on anionic polyacrylamide with both erosion and sediment control application types
	Stormwater Best		Highlights anionic PAM over Cationic
Federal Guidance	Management Practices;	EPA	Site specific soil testing should be performed
	r orymer r rocculation		Emphasizes jute matting or other surface to promote bonding and particle capture
Regional Guidance	Anionic Polyacrylamide Application Guide for Urban Construction in Ontario	Toronto and Region Conservation	Discussion of product selection, qualifications of professionals, documentation, safe handling, spill response, and application for erosion and sediment control
		Notural Pasaurasa	Emphasis on Anionic PAM
Federal Guidance	Anionic Polyacrylamide (PAM) Application	Conservation Service	Focus on agricultural applications
		Conservation Practice Standard	Some criteria discussed: percent of acrylamide / molecular weight / mixed according to OSHA Safety Data Sheet
			Cationic PAMs not permitted
State	Alaska SWPPP Guide	Alaska DOT and Public	Operators must provide notification on the Notification of Intent (NOI)
Guidance		Facilities	Site personnel must be trained in the proper handling and use of specified chemicals
			Proper site storage in leakproof containers under storm-resistant covers surrounded by secondary containment
Testing Guidance	ASTM D 2035–19	American Society for Testing and Materials	This practice covers a general procedure for evaluation of a treatment to reduce dissolved, suspended, colloidal, and nonsettleable matter from water or wastewater by chemical coagulation–flocculation, followed by gravity settling
			Requires use of sediment pond
State	BMP C 126: BMP Polyacryamide (PAM) for Erosion Protection	Washington State	No direct application to water or allowed to enter water body
Guidance		Department of Ecology	Dissolved application preferred

			Cationic PAM shall not be used
			Application rates provided (maximum 80mg/L) per 1 acro of bare soil
			Formal approval from ecology is required for use of chemical treatment
State	BMP C 250: Construction Stormwater Chemical	Washington State	Must be nontoxic to aquatic organisms. Only approved chemicals are allowed
Guidance	Treatment	Department of Ecology	Compliance monitoring required every 15 minutes for influent and effluent pH, flocculent chemical concentration, and turbidity
State	Construction Site Best		Discussion in soil binders of Polymeric Emulsion blends. Specifically:
Guidance	Management Practice (BMP) Manual	Caltrans	Linear copolymer polyacrylamide is packaged as a dry-flowable solid. When used as a stand-alone stabilizer, it is diluted at a rate of 1 lb/100 gal of water and applied at a rate of 5 lb/ac
Chata	State of Florida Erosion and	Chata English and Cadimont	Appendix 3 and IV-35 includes description of use of polymers or alum
Guidance	Sediment Control Designer and Reviewer Manual	Control Task Force	Product selection based on performance standards. Dissolution rates used as basis for maximum expected concentration calculator developed for this project (Section 3)
			Only anionic polyacrylamides shall be used
State Guidance	Manual for Erosion and Sediment Control in Georgia	Georgia Soil and Water	Application shall conform to manufacturer's guidelines
		Conservation Commission	In all cases where treatment chemicals are used, it is essential to use a sediment basin or sediment trap unless a "pump and treat" system is used
		Maryland Department of the Environment	Must compose additional SWPPP Documentation
State Guidance	Standards for Use of Chemical Additives for		Basis for the use of chemical additives
	Sediment Control		Specific additive information (Safety Data Sheets, jar test results, proposed dosing rates)
State Guidance	Procedures for Review of Chemical Additives for Sediment Control	Maryland Department of the Environment	Includes description of restrictions and limitations of chemical additives as well as an outline of procedures for reviewing and approving chemical additives for use in sediment control applications
State Guidance	List of Approved Chemical Additives	Maryland Department for the Environment	The Maryland Department of the Environment keeps an updated list of approved chemical additives. Information includes manufacturer/distributor, product name, max concentration, type of polymer, and any applicable limitations
			The following PAMs not allowed: non-food grade, cationic PAM; emulsion-based PAMs.
State	Polyacrylamide Products and Soil Erosion and Sedimentation Control	Michigan Department of Environment, Great Lakes, and Energy	Ensure proper chemical is matched to site-specific soil type
Guidance			Land application generally 10 lbs/ac
			List of regulatory approvals provided. Less than one acre, follow technical guidance. PAM applied to land or stormwater retention ponds, follow technical guidance

State Guidance	Protecting Water Quality: A Field Guide to Erosion, Sediment, and Stormwater Best Management Practices for Development Sites in Missouri and Kansas	Missouri Department of Natural Resources	Section 6-125 discusses chemical application Effluent should be monitored for residual chemical products or aquatic toxicity Keep records of chemical use; do not use cationic PAM, unformulated chitosan, alum, or ferric iron compounds Do not use in areas with shallow groundwater table or highly permeable soils
State Guidance	Tailgate Test Kit for Determining Appropriate Sediment Reducing Chemicals and Dose Rates	Minnesota Department of Transportation	This study focuses on developing a test kit to be used in the field to test flocculants for reducing turbidity in construction stormwater discharge. Identify appropriate chemical as well as optimal dose Identifies the need to investigate methods for identifying residual/unreacted products
State Guidance	North Carolina DWR List of Approved PAMS/Flocculants	North Carolina Resources Environmental Quality	This reference provides a list of approved PAMs/flocculants as well as the company manufacturing the product and maximum recommended concentrations
State Guidance	New York State Standards and Specifications: Section 5 Sediment Control	New York State Department of Environmental Conservation	Chemical treatment will not be substituted for proper planning, phasing, sequencing, and design of appropriate erosion and sediment control practices No polymer application will take place without written approval from NYSDE Field tests must be conducted on the proposed site at the design basin locations with tributary soils to establish polymer dosing rates and verify settling performance Treated water discharged from sediment basins with polymer treatment will be tested to determine that any residual polymer meets standards set by NYSDEC. Daily inspection of systems is required
State Guidance	Water Application of Additives for Sediment Control	Wisconsin Department of Natural Resources Technical Standard	Rates will not exceed manufacturers written application rates Additive mixtures should achieve at least 95% sediment reduction
State Guidance	e List of Previously Reviewed Wisconsin Department Additives for Sediment Natural Resources Standard		This list includes product names, manufacturers, and allowable rates for both acute and chronic usage in mg/L. This list is current as of April 2020
State Guidance	Erosion Control and Storm         Water Product Acceptability         Wisconsin Department           idance         Lists User Guide and         Transportation		Installation according to manufacturer's instructions. All products are required to be approved and undergo toxicity testing to determine a maximum usage rate restriction from WDNR

#### Summary of Permit Requirements

State CGP and IGP with delegated authority (see Figure 1) from EPA and EPA permits were reviewed. Requirements or restrictions relative to usage of PAM, polymer, coagulant, and water treatment chemicals are summarized in Table 4. States not represented in the table may allow chemical use, but it is not explicitly addressed in the permit reviewed.



#### Figure 1: Status of state authorization for NPDES administration (Image courtesy EPA, Office of Water)

On comparing permits, a disclaimer is necessary because terminology varies greatly among states. In one example, an active treatment system is defined as one that uses chemicals, regardless of the manner of application. Differences in terminology require careful reading of the permit; misinterpretation in the summaries here is almost inevitable.

Overall, it appears observations indicate that only a few states ask for additional care in the use of chemicals. These tend to be more recent permits, and more may follow as the latest EPA permits address chemical use. A few noteworthy observations may be instructive for the evolution of policy in California. Areas of interest include the required use of sedimentation basins, residual monitoring, prohibition of certain chemicals, and use restrictions. Arizona and Utah CGPs call out treatment chemicals as potential on-site pollutants, and Arizona requires monitoring in some watersheds. In North Dakota, the CGP requires monitoring of discharge from chemically treated dewatering operations, though monitoring of sedimentation basin

effluent was not explicitly addressed. The draft Maryland CGP leaves residual testing an open question that is resolved when approval is granted. Many permits require downstream sediment control, though most of them allow silt fence to fulfill this requirement. Mississippi requires minimum basin sizing and specifies that baffles must be used. Prohibition of cationic PAM is common, though some states allow it under special approval. Most permits did not address restrictions on chemical use in erosion controls, though the draft Maryland permit specifically "does not authorize use of additives for bank or soil stabilization" (19). Where chemical restrictions were in place, the focus was usually sediment control applications. Upstream dosing was often specified. In no case was direct water application specified as an approved method unless within an active treatment-type system as defined by the California CGP.

States	Year	Permit Type	Erosion Control Highlights	Water Treatment Highlights
Alabama	Draft	CGP	Polyacrylamide (PAM) and chitosan listed as common. Basin or perimeter sediment control required	Polyacrylamide (PAM) and chitosan listed as commonly used. Basin or perimeter sediment controls required
Alabama	2017	IGP	Not addressed	Must identify use of coagulants in permit application
Alaska	2016	CGP	Dissolved in nonaqueous emulsions are not recommended. Consider appropriateness of usage of these materials where sensitive or protected aquatic organisms exist	Polyacrylamide (PAM), chitosan, alum, polyaluminum chloride, and gypsum allowed, but chitosan only with ATS. Approval by EPA or the states of California, Minnesota, Oregon, Washington, or Wisconsin for use in controlling erosion or sediment runoff from agricultural land or construction projects. Nonaqueous emulsions are not allowed
Alaska	2020	IGP	No specific requirements	Only upstream dosing. Training required. 14-day notice for cationic. 100-ft minimum ditch length prior to receiving waters
Arizona	2020	CGP	No specific requirements	Must justify use. Specify dosage. Provide "adequate settling time." Describe training. Present schematics. Treatment polymers are identified as possible pollutants for "pollutant- generating activities." and these may

 Table 4: EPA and state permits with explicit references to chemical use for erosion control or sediment control

States	Year	Permit Type	Erosion Control Highlights	Water Treatment Highlights
				require monitoring in "Outstanding Arizona Waters"
Arizona	2017	IGP	Identify polymers in SWPPP	Identify polymers in SWPPP
Arizona	2021	IGP	Identify polymers in SWPPP	Identify polymers in SWPPP
California	2009	CGP	No specific requirements	ATS requires residual monitoring, filtration, and residual concentrations less than 10% of average of NOEC and LOEC
Delaware	2021	CGP	No specific requirements	Similar to EPA. Contractors must be extensively trained by experienced personnel. Operational monitoring should include pH, conductivity (as a surrogate for alkalinity), turbidity, and temperature of untreated stormwater. Other quantities include total volume treated, amount of polymer used, and settling time
EPA	2017	CGP	"Chemically enhanced stormwater control" implies chemical use for erosion control; if so, then permit requires downstream sedimentation control, which includes perimeter controls	"Chemical treatment systems" implies water treatment; if so, then permit requires downstream sedimentation control, which includes perimeter controls. Cationic chemicals require approval; cationic polymer require site-specific approval. Chemical containment BMP required. Spill kits required
EPA	2021	MSGP 2021 1- 7, and 8	Identify polymers and/or other chemical treatments in SWPPP	Must use traditional EC and SC before/after chemicals are applied. Requires training. Follow manufacturer's guidelines. Select chemicals suited to soil type, and expected turbidity, pH, flow rate
Georgia	2018	CGP	Flocculants or coagulants encouraged for soils still disturbed after 7 days	Flocculants or coagulants encouraged in all ditches upstream of sedimentation basins
Georgia	Draft	IGP	Identify polymers and other chemical treatments and chemical storage locations in SWPPP	Identify polymers and other chemical treatments and chemical storage locations in SWPPP

States	Year	Permit Type	Erosion Control Highlights	Water Treatment Highlights
Illinois	2018	CGP	Identify polymers and other chemical treatments and chemical storage locations in SWPPP	Identify polymers and other chemical treatments and chemical storage locations in SWPPP
Kansas	2017	IGP	Not addressed	Show water treatment chemical storage on site map
Kentucky	2019	CGP	Not addressed	Not allowed by CGP; requires individual permit for "construction project that plans to use any treatment chemicals (polymers, flocculants, coagulants)" (5)
Louisiana	2021	IGP	List polymers and other chemicals in SWPPP, and state purpose	List polymers and other chemicals in SWPPP, and state purpose
Maryland	Draft	CGP Draft	Does not authorize use of additives for bank or soil stabilization	Only allowed when conventional BMPs cannot meet WQS. Must follow separate guidance document. Selection of additives and dosing rates should be determined based on site-specific test results. Only use preapproved additives. Must use traditional EC and SC before/after chemicals are applied. Test for residuals or other components may be required when applying for approval, depending on chemical type. Other requirements similar to EPA
Minnesota	2013	CGP	Not addressed	Similar to EPA MSGP
Minnesota	2020	IGP	Not addressed	Must report: a) a 48-hour LC50 or EC50 acute study for a North American freshwater planktonic crustacean (either <i>Ceriodaphnia</i> or <i>Daphnia sp</i> .); and b) a 96-hour LC50 acute study for rainbow trout, bluegill, or fathead minnow or another North American freshwater aquatic species other than a planktonic crustacean. Other requirements similar to EPA MSGP
Mississippi	2017	CGP > 5 acre	Not addressed	Upstream dosing. Only anionic PAM. Minimum sedimentation basin sizing: 2-yr, 24-hr; baffles required

States	Year	Permit Type	Erosion Control Highlights	Water Treatment Highlights
Montana	2018	IGP	Not addressed	Passive or active dose encouraged. No specific requirements
Nebraska	2016	IGP	Not addressed	Passive or active dose encouraged. No specific requirements
Nevada	2015	CGP	Not addressed	Cationic requires individual permit. No other specific requirements/prohibitions
Nevada	2019	IGP	Identify polymers and treatment chemicals	Identify polymers and treatment chemicals
North Carolina	2019	CGP for areas exclusi vely under state law jurisdict ion	Must use approved products	Must use approved products. Flocculant use can be used to justify smaller basins
North Carolina	2020	CGP other areas	Must use approved products	Must use approved products Flocculant use can be used to justify smaller basins
North Dakota	2020	CGP	Not addressed	Requires description of monitoring point for product [treatment chemical] discharge. 48-hour LC50 or EC50 for a North American freshwater planktonic crustacean ( <i>Ceriodaphnia sp.</i> , <i>Daphnia sp.</i> , or <i>Simocephalus sp.</i> ). Results for a toxicity test for one other North American freshwater aquatic species (other than a planktonic crustacean)
Ohio	2017	IGP	Not addressed	Similar to EPA
Oklahoma	2011	IGP	Not addressed	Identify water treatment chemical storage on site map
Oregon	2020	IGP	Not addressed	Similar to EPA. O&M plan required for active dose; routine maintenance standards for passive dose
Oregon	2018	CGP	Not addressed	Passive dose not addressed. Detailed ATS requirements. Plan and approval required
Pennsylvan ia	2021	IGP	Not addressed	Requires written permission

States	Year	Permit Type	Erosion Control Highlights	Water Treatment Highlights
Rhode Island	2020	CGP	References the state's handbook	References the state's handbook
Rhode Island	2019	IGP	Must identify chemical used	Must identify chemical used
South Carolina	2016	IGP	Not addressed	Similar to EPA MSGP. Cationic requires individual permit. Passive and active treatments are encouraged
South Dakota	2021	CGP	Polymer definition includes chemicals used for erosion control. Must use traditional erosion and sediment controls	Similar to EPA MSGP. Downstream sediment control (e.g., sediment basin, perimeter control) required. Cationic requires letter of approval from EPA
Tennessee	2021	CGP	Not addressed	Update SWPPP with changes in dosage
Tennessee	2020	IGP	Not addressed	Show treatment chemical storage on site map. State's erosion control manual is referenced. Cationic polymers are prohibited
Utah	2018	CGP	Polymer definition includes chemicals used for erosion control. Requires downstream sediment controls	Similar to EPA MSGP. Cationic use must be authorized, and additional requirements are within the authorizations. Treatment polymers listed under potential pollutant-generating activities
Vermont	2011	IGP	Not addressed	Show treatment chemical storage on site map. Passive and active dose encouraged
Vermont	2019	CGP	Not addressed	Active treatment systems require approval. "Active Stormwater Treatment" means the treatment of construction stormwater using chemical additions, including coagulants and flocculants [Note different definition of ATS in California CGP]
Vermont	2020	EPA < 5 ac	Not addressed	Similar to EPA CGP. Cationic requires an approved site- specific plan
Washington	2020	CGP	Recognizes PAM; no special requirements	Requires written permission
Washington	2019	IGP	Not addressed	Requires application to regulator

States	Year	Permit Type	Erosion Control Highlights	Water Treatment Highlights
West Virginia	2019	CGP	Not addressed	Recognizes "Polymers, flocculants, or other treatment chemicals." No specific requirements beyond manufacturer's guidelines. Cationic prohibited
Wyoming	2020	CGP	Not addressed	60-day notice required. Must include in SWPPP. Must report dosage. May require a separate permit

### 2.3 Toxicity of Passive Chemical Treatment

Flocculants have been implemented for many years to treat stormwater and reduce erosion and sediment transport in construction sites. Polymer flocculants are water-soluble polymers that can adsorb on suspended particles, creating larger aggregates through bridging and/or charge neutralization. These chemicals, which include polyacrylamides, copolymers, and biopolymers, refer to a vast class of chemical compounds with soil stabilization properties. This section reviews the aquatic toxicity, pervasiveness, and reactivity of various types of treatment chemicals used in erosion control and stormwater management.

#### **Polyacrylamide**

Polyacrylamide (PAM) chemicals are formed by polymerization of acrylamide monomers. Hundreds of PAM formulations exist, but all consist of acrylamide (AMD) monomers. The number of AMD monomers in the polymer chain directly impacts the chemical properties of the PAM. Polyacrylamide chemicals are categorized into four different treatment groups: anionic PAM, cationic PAM, nonionic PAM, and copolymer blends. Toxicity, pervasiveness, and reactivity of these chemicals are discussed in the following section.

#### Anionic PAM Toxicity

Anionic polyacrylamide is relatively nontoxic to humans, animals, fish, and plants, particularly in the dose levels typically used in stormwater management. In addition, due to the very large molecular size of PAM chains, polyacrylamide cannot transport across biological membranes, and anionic PAM is generally considered to be nontoxic to humans and other mammals. In general, previous studies on acute toxicity to fathead minnow (Weston et al. 2009), rainbow trout (Kerr et al. 2014), Atlantic cod (Hansen et al. 2019), and freshwater mussels (Buczek et al. 2017) revealed no adverse effect when exposed to anionic PAM at doses up to 100 mg/L. Furthermore, Acharya et al. (2010) showed that limited exposure of Daphnia magna did not show significant difference in their growth, onset to reproduction, fertility, and mortality. In the same study, acute toxicity tests on *D. magna* showed LC<sub>50</sub> at 152 mg/L for a linear, anionic PAM product (Tack Dry®, Precision Polymer Corporation) with less than 0.05% residual acrylamide. However, Acharya et al. (2010) showed adverse impact on D. magna at levels as low as 1 mg/L and growth reduced by 37% at this concentration for prolonged exposure. Furthermore, fecundity and onset to reproduction was also impaired at 10 mg/L. It is proposed that the viscous properties of PAM result in mechanical and physiological impairments, leading to reduction in the biological life cycle of the invertebrate.

Although PAM is considered to be relatively nontoxic, PAM degradation releases residual monomers such as acrylamide (due to incomplete polymerization process), which is a known

neurotoxin and potential carcinogen (LoPachin 2004). Exposure of mammalian species to acrylamide at a dose of 0.5–50 mg/kg per day has shown neurotoxicity characterized by ataxia, skeletal muscle weakness, and numbness of hands and feet (LoPachin 2004). Other potential adverse effects include carcinogenicity, toxicity to the reproductive organs, and impairments based on substantial data from animal studies (Friedman 2003). Acrylamide is highly soluble in water and very unlikely to adsorb to organic and inorganic soil components.

The amount of acrylamide in PAM significantly depends on the degree of polymerization in the PAM manufacturing process. Krautter et al. (1986) determined the acute toxicity of acrylamide monomer to two species of aquatic macroinvertebrates (*D. magna*, midges) and three species of fish (rainbow trout, fathead minnows, and bluegill), revealing acute toxicity of greater than 100 mg/L in all species. Although acrylamide has shown neurotoxicity when organisms are exposed to considerable concentrations, due to the very low concentration of acrylamide in PAM (0.05% w/w), Krauth et al. (2008) reported no significant decrease in survival when fathead minnows and water fleas were exposed for 48 hr to stormwater from irrigation and rainstorm events treated with granular PAM pellet at concentrations of 30 and 45 mg/L, respectively (Ciba Specialty Chemicals Corporation, Sulfolk, VA). In addition, several studies showed biodegradation of acrylamide to nontoxic products such as ammonia and carbon dioxide within days (Shanker et al. 1990; Labahn et al. 2010).

Various types of PAM formulations, including oil-based, water-based, granular, and tablet products exist. In a study conducted by Weston et al. (2009), five different species (*Hyalella azteca, Chironomus dilutus, Ceriodaphnia dubia, Pimephales promelas,* and *Selenastrum capricornutum*) were evaluated for toxicity testing; acute toxicity was observed in 80% of species when PAM was applied as an oil-based product at concentrations less than 10 mg/L. This study showed minimal toxicity (with only 16% reduction in the fathead minnows population) associated with non-oil-based PAM products even at concentrations as high as 100 mg/L. Granular products are nearly pure PAM and contain few ingredients other than polyacrylamide (approximately 97% purity). In toxicity tests with granular product (SoilFloc® 110D, Hydrosorb), Weston et al. observed no evidence of toxicity at high concentrations below 100 mg/L in 80% of species. The only invertebrate that showed lethality in concentrations below 100 mg/L was *Ceriodaphnia dubia* with LC<sub>50</sub> of 28.7 mg/L. The substantially lower toxicity results for non-oil-based PAM suggest that toxicity in oil-based PAM is mainly due to other inert ingredients and agents in the oil-based formulation such as surfactants or emulsifiers.

Significant variation in toxicity is reported in published literature, and this inconsistency can be attributed to differences in chemical characteristics of polyacrylamides as well as environmental factors such as presence of organics. As PAM can be produced by different reactions, it can result in various pH and oxidation states in the final product. Therefore, toxicity of PAM products can vary as a function of product formulation. For instance,  $LC_{50}^{48}$  (i.e., adverse effects on 50% of the test population of *D. magna* after 48 hours of exposure) for Dow® AP-30 (Dow Chemicals) has been reported at a high concentration of 345 mg/L (Biesinger et al. 1976), while  $LC_{50}^{96}$  (i.e. adverse effects on 50% of the test population of *D. magna* after 96 hours of exposure) for Magnafloc® E10 (Brenntag Canada Inc.) has been reported at levels as low as 14.1 mg/L (Beim and Beim 1994).

#### Anionic PAM Pervasiveness

Once polyacrylamide is applied to soil, it is adsorbed to soil and clay mineral surfaces in a rapid and irreversible reaction. Tekin et al. (2006) showed a direct correlation of pH and ionic strength on the adsorption of PAM to soil and clay particles. Due to the irreversibility of the PAM adsorption process, an insignificant amount of adsorbed PAM (less than 3%) may be removed from the soil minerals (Deng et al. 2006). Polyacrylamide molecules are remarkably stable, but a variety of mechanical, chemical, thermal, photolytic, and biological degradation mechanisms can degrade high molecular weight PAM molecules into monomers. Chemical degradation of PAM includes a chain scission involving activation of the polymer molecules by free radicals, which are generally hydroxyl radicals generated from Fenton reactions (i.e., interaction between oxygen and dissolved iron) in the environment (Seright and Skievrak 2015). The release of free iron molecules from pyrite minerals or other iron-bearing clay soils can generate hydroxyl radicals. As Fenton reactions occur under acidic conditions, the presence of alkaline minerals such as calcite can reduce the chemical degradation of PAM. Thermal degradation of PAM requires a very high temperature (above 300°C) and is therefore unlikely to occur in soil or water environments. Photolytic degradation of PAM occurs when hydroxyl radicals created in the presence of light and oxygen lead to activation and chain scission of polymer molecules (Vijayalakshmi and Madras 2006). Similar to chemical degradation with Fenton reaction, presence of dissolved iron (Fe<sup>3+</sup>) in acidic conditions can enhance photolytic degradation (Larson et al. 1991). About 10% PAM degradation per year can occur to chemicals incorporated into soil, while application of PAM near the soil surface enhances its photodegradation (Barvenik et al. 1996). Polyacrylamide is typically considered to be relatively recalcitrant to biological decomposition, and biodegradation of PAM occurs in lower rates compared to chemical and photolytic degradations since it is much harder for microorganisms to use the carbon backbone in PAM as their sole carbon source. PAM biodegradation can occur in the presence of amidase enzyme converting polyacrylamide to polyacrylate and ammonia. Amidase activity has been identified in several genera of bacteria and fungi, and studies have demonstrated that acrylamide-specific amidase activity increases in PAM-treated soil (Kay-Shoemake et al. 1998), which eventually enhances the PAM biodegradation rate.

#### Anionic PAM Reactivity

The acidity condition of soil and water when PAM is applied can affect the adsorption mechanism of PAM on soil surfaces and consequently influence the residual PAM concentration. Increasing pH in the soil and water results in decrease of the adsorption of anionic PAM due to large electrostatic repulsions (Lee et al. 1991). Ionic strength and electroconductivity can also affect the adsorption capacity in PAM and soil interaction. Aly and Letey (1988) demonstrated that increasing salinity (i.e., electroconductivity) reduces the adsorption of cationic and nonionic PAM but enhances the adsorption of anionic PAM. Temperature is another environmental factor that can affect the adsorption of PAM. Some studies have shown that high temperature can enhance the adsorption of anionic PAM on clay minerals such as kaolinite and sepiolite (Mpofu et al. 2004; Tekin et al. 2006), which may be due to polymer–polymer interaction promoted by disruption of polymer-water hydrogen bonds at high temperature.

As mentioned earlier, chain scission and degradation of PAM by hydroxyl radicals under acidic conditions can release acrylamide monomers. The concentration of dissolved iron can affect the amount of released acrylamide, and at low levels of iron (less than 0.02 mg/L) under an alkaline condition (pH 7.5–8.5), an insignificant amount of acrylamide is released (Woodrow et al. 2008). Temperature can also affect acrylamide degradation, and a higher temperature increases the rate of degradation (Smith et al. 1996). The hydrolysis rate of acrylamide is also dependent on pH; it increases in an alkaline condition but is relatively slow in acidic pH (Barvenik et al. 1996). In general, smaller particles have more affinity for PAM than larger particles (Lu et al. 2002).

#### Cationic PAM

Cationic (positively charged) polyacrylamide (CPAM) consists of acrylamide monomers that are copolymerized with trimethyl ammonium monomers. Cationic PAM can adsorb on suspended particles and create larger aggregates through charge neutralization and bridging mechanisms

and, therefore, they are most preferred for applications such as removal of organic matter from wastewaters.

#### Cationic PAM Toxicity

Cationic PAM polymers are relatively toxic to aquatic organisms and are not recommended for erosion and sediment control applications. The main reason for the high toxicity of cationic polymers is binding with anionic sites on fish gills, resulting in mechanical suffocation (Bervenik et al. 1996). A study conducted by Goodrich et al. (1991) showed acute toxicity of  $LC_{50}^{96}$  (i.e., adverse effects on 50% of rainbow trout after 96 hours of exposure) between 661 µg/L (for 39% charge density) and 1,733 µg/L (10% charge density) for cationic polyacrylamide. Chronic toxicity assessment for CPAM with 10% charge density showed LC<sub>50</sub> as low as 303 µg/L for a 28-day exposure period. In another study conducted by Duggan et al. (2019), a majority of zebrafish embryos died or had lethal phenotypes after exposure to 30 mg/L cationic PAM for 7 days. This study also evaluated the residual coagulant after treating the water with optimum dose and overdose of cationic polymers, and demonstrated that 50% overdose of cationic PAM results in 17.4 mg/L residual concentration, while cationic starch produces substantially lower residual concentrations and results in only 3.8 mg/L residual in the released liquid.

#### **Cationic PAM Pervasiveness**

Due to the higher toxicity of cationic PAM, only a limited number of studies focus on cationic PAM pervasiveness. In a study conducted by Hennecke et al. (2018), the fate of PAM in dewatered sludge applied to soil was evaluated by investigating the degradation of <sup>14</sup>C-radiolabelled PAM. Based on the total recovered radioactivity, Hennecke estimated that cationic PAM degrades in soil at a very slow rate, showing a half-life of 5.4 years and a rate constant of 0.00035/day. It should be noted that the half-life in this study was determined using a conservative approach based on polymer mineralization that does not consider any other processes such as degradation of polymer backbone or hydrolysis of the side chains that could contribute to the degradation. Another study by Chang et al. (2001) demonstrated partial degradation of cationic PAM under aerobic and anaerobic conditions. This study showed partial destruction of pendant cationic moieties but no destruction of polymer's backbone as a result of oxygen production under aerobic conditions and methane production under anaerobic conditions. Similarly, a study conducted by Wang et al. (2018) demonstrated degradation and depolymerization of cationic PAM under anaerobic conditions, which resulted in conversion of PAM to methane and generation of acrylamide and acrylic acid.

#### **Cationic PAM Reactivity**

Cationic PAM is considered to be highly toxic to fish and invertebrates, but under normal environmental conditions its toxicity decreases significantly as PAM irreversibly binds to soil particles (Zhang and Miller 1996); therefore, residual cationic PAM concentration is largely reduced. However, adsorption of cationic PAM to soil particles has been observed to decrease as the electrolyte concentration of soil suspension increases (Aly and Letey 1988). Other environmental conditions including temperature and pH can also affect cationic PAM reactiveness. An increase in pH and temperature can accelerate cationic PAM hydrolysis, and therefore reduce the duration of effectiveness of toxic chemical agents (Seo et al. 2018).

#### **Copolymer Blends**

Blends of acrylamide and sodium acrylate result in copolymer alternatives that can be used as erosion control chemicals. Acrylamide-co-sodium acrylate is a sodium salt of a polymer that contains acrylic acid, methacrylic acid, or one of their simple esters. Sodium polyacrylate copolymer, also known as waterlock, is another coagulant aid used in sediment control practices.

#### **Copolymer Toxicity**

Copolymer of sodium acrylate and acrylamide has very high molecular weight and low water solubility, and is therefore considered relatively nontoxic to aquatic organisms compared to cationic PAM. Toxicity assessment of Polyfloc AE1115P (GE Betz Inc., PA) based on the manufacturer's material safety data sheet (MSDS) showed  $LC_{50}^{96}$  of 75.2 mg/L for rainbow trout, 25.8 mg/L for fathead minnow, and 3.9 mg/L for *D. magna*. Another product, Floerger<sup>TM</sup> AN 900 reported  $LC_{50}^{96}$  of greater than 100 mg/L for rainbow trout and  $EC_{50}^{48}$  of 54 mg/L for *D. magna*. The variation in toxicity level resulted from charge density and molecular weight that can vary in different copolymers. Low charge density and high molecular weight polymers demonstrate lower toxicity to aquatic organisms and microorganisms.

Sodium polyacrylate copolymer dispersant is another coagulant aid used in sediment control. As sodium acrylate copolymer contains no acrylamide, and thus no residual acrylamide monomer, the copolymer is considered less problematic in terms of environmental impact. In addition, sodium acrylate copolymer is generally considered immobile in soil, and once it is adsorbed onto the soil it does not leach into aquifers. In toxicity tests with *D. magna*, the most sensitive aquatic species tested in the study, Freeman and Bender (1993) determined that the LC<sub>50</sub> of sodium polyacrylate copolymer is greater than 100 mg/L and the chronic NOAEL (no observed adverse effect level) is 5.6 mg/L.

#### **Copolymer Pervasiveness**

Due to high molecular weight of copolymer blends ranging from 10,000 to more than 1,200,000 Da (Wu et al. 1991), bioaccumulation and biodegradation of acrylamide/sodium acrylate is limited. In addition, copolymer blends have very low octanol / water partition coefficient (K<sub>ow</sub>), which makes them very hydrophilic and highly soluble in water; therefore, they have very limited potential to bioaccumulate to organic materials such as cell tissues. In a study conducted by Hayashi et al. (1994), a UV-irradiated sodium polyacrylate copolymer demonstrated biodegradability following photolytic degradation, suggesting that the copolymer might be utilized and degraded by microorganisms in natural environments. Although the copolymer is considered immobile due to strong ionic and van der Waals interaction between acrylamide-sodium acrylate and organic matters and minerals, degradation can occur to smaller and more mobile monomers such as acrylamide; so caution is warranted when applying this copolymer.

#### **Copolymer Reactivity**

As acrylic acid has negatively charged carboxylic groups, copolymer of sodium acrylate and acrylamide can be impacted by cations as they are attracted to carboxylic acid groups, which increase the flexibility of the molecule and reduce the apparent viscosity of copolymer (Zhang et al. 2008). Ma et al. (2019) observed a noticeable decrease in the apparent viscosity of the copolymer solution in the presence of NaCl, KCl, and CaCl<sub>2</sub>. Also, the copolymer showed no resistance to temperature; increasing temperature significantly reduces the apparent viscosity of the copolymer. However, the addition of different salt ions (NaCl, KCl, and CaCl<sub>2</sub>) improved the temperature resistance of the copolymer.

#### **Biopolymer-Based Soil Stabilizer**

Biopolymers are polymers produced from naturally occurring resources such as proteins, polysaccharides, and monomers derived from microbial activities. As biopolymers are environmentally friendly with minimal toxicity, they can be considered for soil stabilization and erosion control when environmental concerns are paramount. In this section, some common biopolymers used in erosion control application and their toxicity, pervasiveness, and reactiveness are discussed.
#### **Gum Biopolymers**

A variety of gum biopolymers such as guar and xanthan gum are available for soil strengthening, dust control, and erosion reduction. Guar gum is a neutrally charged polysaccharide that hydrates rapidly in cold water producing a highly viscous solution, while xanthan gum is an anionic polysaccharide biopolymer that can be also used for soil stabilization. Chitosan is considered a cationic polysaccharide biopolymer and is discussed later in this section.

#### Gum Biopolymers Toxicity

Guar and xanthan gums provide high viscosity at low concentrations and show excellent stability at varying temperatures and over a wide pH range (Zohuriaan and Shokrolahi 2004; Mudgil et al. 2014). Due to their outstanding physicochemical properties, these gums are essentially nontoxic and have many applications in the food industry. Very limited information on aquatic toxicity for gum biopolymers exists; most toxicity assessment is based on chemical structure, not actual toxicity studies. According to MSDS,  $LC_{50}^{96}$  of 218 mg/L and 320–560 mg/L are assessed for aquatic toxicity of guar gum and xanthan gum to rainbow trout, respectively (Sigma-Aldrich, MO).

#### **Gum Biopolymers Pervasiveness**

Gum biopolymers are naturally extracted polymeric molecules and are therefore readily biodegradable. Microbial degradation is the major pathway of transformation in the environment, and their natural decomposition results into simple sugars and water. Biodegradation can occur to xanthan gum under aerobic conditions. In a study conducted by Muchova et al. (2009), carbohydrates in xanthan gum were used by microbial communities in activated sludge. Isolation of degrading bacteria revealed the critical role of *Paenibacillus*, which is a facultative bacterium found in a variety of environments such as soil, water, and the rhizosphere. Biopolymers have great potential to adsorb to soil particles, and negligible amounts are expected to reach surface water dissolved in runoff. Due to very low octanol / water partition coefficient ( $K_{ow}$ ), the potential of bioaccumulation for gum biopolymers is very low.

#### Gum Biopolymers Reactivity

Due to the presence of hydroxyl groups in the chemical structure of guar gum, the biopolymer readily interacts with soil particles (Sharma et al. 2018). As guar gum shows uncharged behavior due to its nonionic molecular structure, it is stable over a wide pH range of 4 and 10.5 (Gupta et al. 2009). The viscosity of guar gum increases with decreasing temperature (Mudgil et al. 2014). In addition, the presence of salt also changes the charge density of solution and affects the viscosity of guar gum by contributing to the intermolecular interactions. The viscosity of guar gum solution increases with increasing salts (Srichamroen 2007). Xanthan gum is also stable over a wide range of pH, and its viscosity is not significantly affected by pH changes between pH 1 and 13 (Garcia-Ochoa et al. 2000). The presence of salts in xanthan gum affects the viscosity of xanthan solution. In xanthan gum solution with low polymer concentration, the viscosity decreases in the presence of small amounts of salt, but the viscosity of solution increases with large amounts of salt.

#### Chitosan

Chitosan is a cationic soil stabilizer derived from chitin that enhances interparticle cohesion by charge neutralization and bridging between soil particles. Chitin, an important low-cost biopolymer, is abundant in nature, derived from crustacean shells that are a byproduct of the food industry. Chitosan is the most important derivative of chitin and is obtained by demineralization followed by partial deacetylation of chitin.

## <u>Chitosan Toxicity</u>

Chitosan is reported by some to be a nontoxic and biodegradable polymer (Thanou et al. 2001; Renault et al. 2009). Nichols (2010) has argued that chitosan has limited toxicity due to its composition of primary amines, resulting in a weaker cationic charge compared to cationic polymers made up of quaternary amines. Acute and chronic toxicity assessment using various concentrations of ChitoVan<sup>™</sup> (Dungeness Environmental, WA) showed NOAEL and LC<sub>50</sub> concentrations greater than 100 mg/L for the most sensitive studied organisms. Acute toxicity assessment demonstrated that NOAEL and LC<sub>50</sub> for rainbow trout is 125 and 173 mg/L, respectively. In addition, chronic toxicity assessment revealed LC<sub>50</sub> of 154 mg/L for rainbow trout (ChitoVan MSDS). Toxicity assessment tests conducted using D. magna showed NOAEL and LC<sub>50</sub> of 1,000 mg/L and 1,369 mg/L, respectively. In a field study conducted by Bachand et al. (2010), a chitosan product (Liqui-Floc<sup>™</sup>) was used to treat stormwater runoff, and its toxicity on Ceriodaphnia dubia was evaluated. The study investigated the effects of coagulant under optimally-dosed (evaluated by streaming current detector) and overdosed conditions. The optimum doses of coagulant in this study were between 100 and 300 mg/L (depending on the site). The study demonstrated that C. dubia brood sizes significantly increased with optimallydosed runoff, showing that there are no adverse effects.

Although chitosan has been generally considered to be nontoxic, several studies showed alarming results regarding its toxicity to various aquatic organisms. A study conducted by Bullock et al. (2000) showed high toxicity of soluble acidified chitosan (dissolved in 1% acetic acid) to rainbow trout (*Oncorhyncus mykiss*) even at low concentration of 0.075 mg/L. The acute toxicity assessment in this study estimated that 0.75 mg/L and 0.075 mg/L concentrations of acidified chitosan kills 80% and 40% of the fish over a 24-hour exposure, respectively. In another study, rainbow trout (*Oncorhyncus mykiss*) exposed to 10 mg/L of chitosan acetate showed an irreversible toxicity after 30 to 60 min of exposure, resulting in respiratory stress and death by hypoxia (Valenzuela et al. 2003). It should be noted that toxicity tests on various fish species demonstrate that rainbow trout are the most sensitive species. While toxicity tests on rainbow trout using StormKlear<sup>TM</sup> Liqui-Floc<sup>TM</sup> (chitosan acetate) showed LC<sup>96</sup><sub>50</sub> of 1.68 mg/L (Nautilus Environmental, 2004), toxicity tests on fathead minnow using Gel-Floc<sup>TM</sup> (chitosan acetate) polymer showed significantly more tolerance to chitosan with LC<sup>96</sup><sub>50</sub> of 23.6 mg/L (MACTEC 2005).

#### Chitosan Pervasiveness

Although chitosan is generally a biodegradable material, Sawaguchi et al. (2015) demonstrated that each chitosan-treated soil tested had a distinctive degradation rate depending on microbial communities available for biodegradation. While chitosan applied to silty soil showed complete degradation after 30 days of incubation at 25°C, chitosan applied to sandy soil did not significantly degrade. Wieczorek et al. (2014) also reported that chitosan was not degraded in an agricultural soil. In addition, a study by Kavazanjian et al. (2009) showed photodegradation of chitosan, where sunlight degraded chitosan by approximately an order of magnitude over a period of two weeks.

# Chitosan Reactivity

The chemical properties of chitosan depend on degree of deacetylation, but chitosan has been shown to be completely soluble in acidic conditions at pH below 6 (Rinaudo 2006). Aiba (1991) suggested that chitosan with 50% deacetylation can be soluble at neutral pH. Ratajska et al. (2003) demonstrated that the rate of chitosan degradation increases with an increase in temperature; optimum degradation occurs at 40°C. The degree of deacetylation changes chitosan's chemical properties, and as the degree of deacetylation decreases, the decomposition rate of chitosan also decreases.

#### Sediment Toxicity Discussion

Discharge of floc particles and the strong adsorption of dissolved PAM to suspended solids can lead to transfer to the sediment compartment and increase sediment toxicity risk (Dell'Ambrogio 2019). PAM degradation to acrylamide is of greater concern under acidic conditions and high dissolved iron concentrations (Woodrow et al. 2008). The persistence of acrylamide in aquatic systems is unknown. Some studies suggest complete degradation of acrylamide likely occurs within 2 weeks (Brown et al. 1982; Shanker et al. 1990). However, a recent study that monitored a sand/gravel aggregate quarry found acrylamide contamination of a nearby pond and in groundwater (Touzé 2015).

#### **Toxicity Summary**

A variety of chemicals available for soil stabilization and erosion control were reviewed in this project. Although some of these chemicals, particularly cationic polyacrylamides and chitosan, showed environmental concerns in terms of toxicity to aquatic organisms, any residual PAM is expected to be adsorbed to suspended soil particles (Lentz et al. 2002) and its toxicity reduced by complexation with organic matter originating from soil particles (Goodrich et al. 1991).

Several factors determine the selection of appropriate chemicals for erosion and sediment control. Although efficacy and product cost are important, environmental toxicity risks must be primary when selecting the most appropriate formulation. Relative to other available products, guar-based and water-based anionic PAM products present relatively low aquatic toxicity risks when used to manage construction stormwater and minimize erosion in construction sites. Although biopolymer-based products cannot compete with PAM products in terms of efficacy and cost, their nontoxic characteristic makes them more appropriate when strict regulations or exceptionally sensitive and risky application scenarios prohibits using PAM products. The relative toxicity of these products in the field depends on their concentration in runoff, which is a function of predicted storm size, required application rate, particle availability, particle attachment rates, and product loss (via erosion), as well as water chemistry.

A critical component for establishing the safe use of a chemical is toxicity information for aquatic organisms. At minimum,  $LC_{50}$  concentrations must be known. Ideally, the lowest observable effect concentration (LOEC) is also known, which will allow for better assessment of toxicity risks. Table 5 is a partial list of available erosion control and water treatment products and their  $LC_{50}$  concentrations. This table can serve as a starting point for future expansion and update by the regulatory community, chemical manufacturers, researchers, and practitioners.

Table	<b>5:T</b>	oxicity	summary	

	Chemical	Product/Supplier	Acute Toxicity (LC <sub>50</sub> )	Formulation Notes	Reference
		Tack Dry, Precision Polymer Corporation	152 mg/L <i>Daphnia magna</i> (academic study) >100 mg/L various aquatic species (supplier information)	Granular linear anionic PAM, > 0.05% residual acrylamide	Acharya et al.2010 Tack Dry MSDS
	Superfloc A110, Kemira	>100 mg/L various aquatic species (supplier information)	Solid high molecular weight anionic PAM with less than 500 mg/L residual acrylamide	SuperFloc MSDS	
	Anionic PAM	SoilFloc 110D, Hydrosorb	28.7 mg/L <i>Ceriodaphnia dubia</i> (academic study) >100 mg/L various aquatic species (supplier information)	Granular anionic PAM, 97% purity, USDA certified (>0.05% residual acrylamide, 6-24 mg/mole, 10–50% charge density)	Weston et al. 2009 SoilFloc MSDS
		FlocLoc, Profile Products*	>5000 mg/L <i>Daphnia magna</i> (supplier information)	100% granular linear anionic PAM, water soluble, > 12 mg/mol, >30% anionicity	GHS FlocLoc Safety Data Sheet

Treatment Chemical	Product/Supplier	Acute Toxicity (LC <sub>50</sub> )	Formulation Notes	Reference
	SAP 400, Rantec*	No ecotoxicity information provided	Cross-linked, medium anionic PAM, granular	APS Floc Log Data Sheet
Cationic PAM	Cationic PAM, Applied Specialties	10–100 mg/L Oncorhynchus mykiss and Daphnia magna (supplier information)	Liquid emulsion with 39–40 weight % cationic PAM	Cationic Acrylamide Safety Data Sheet
	Sodium acrylate, COATEX	>100 mg/L various aquatic species (supplier information)	100% sodium acrylate	COATEX Sodium polyacrylate Safety Data Sheet
Copolymer	TerraTack, Reinco	No specific eco-toxicity data provided	Blend of acrylamide and sodium acrylate, contains < 0.05% acrylamide monomer	TerraTack Safety Data Sheet
Blends	Soil Binder DC, Simplot	>500 mg/L Daphnia magna (supplier information)	90% sodium acrylate/acrylamide blend, 10% inert ingredients	Soil Binder DC MSDS
	700 Series Floc Log, APS*	>420 mg/L Daphnia magna	Semisolid block anionic PAM blend with around 40% moisture content	
Chitosan	StormKlear LiquiFLoc, Natural Site Solutions	2–93 mg/L various aquatic species (supplier information)	LiquiFloc 1% concentration; Storm-Klear Gel-Floc is a fabric "sock" containing a dry form of chitosan	Storm-Klear Fact Sheet
Guar	Supercol Guar Gum, Ashland	42 mg/L <i>Daphnia magna</i> (supplier information) 218 mg/L <i>Onchorhynchis mykiss</i> (supplier information)	Most guar-based soil binders are blends with other natural polysaccharides and ecotoxicity data is not provided; these numbers are for guar gum intended for use in personal care products	Supercol™ U2 Guar Gum Safety Data Sheet
Starch	Non specified	No ecotoxicity data available	Not available	
Psyllium	Non specified	No ecotoxicity data available	Not available	
Lignin Sulfonate	Lignosite 458, Georgia- Pacific	2,125 mg/L (academic study)	Solid sodium lignosulfonate	
Aluminum Salts	FennoFloc, Kemira	3–80 mg/L (academic study) 1189 mg/L (supplier information)	Aluminum chloride and polyaluminum chloride 45- 50% aqueous solution	Gostomski 1990 FennoFloc safety data sheet
Ferric Salts	Ferric chloride, Hill Brothers Chemical Company	Limited chronic toxicity data available, EC <sub>20</sub> 's between 0.2– 0.5 mg/L >1000mg/L <i>Daphnia magna</i>	Aqueous solution with 39–44 wt% ferric chloride	Cadmus et al. 2018 Ferric chloride MSDS
Gypsum	x	No ecotoxicity data available	X	
DADMAC	Diallyldimethylammonium chloride, Santa Cruz Biotechnology	0.5–10 mg/L (academic study) >1.0 mg/L (supplier information)	Solid powder >98% purity	Cumming et al. 2008 DADMAC MSDS

# 2.4 Factors Affecting Performance and Environmental Safety and Associated Data Gaps

Toxicity assessments on treated stormwater effluent are often carried out in controlled environmental conditions. While this methodology is helpful in understanding basic toxicities, it provides limited information on the effects of additional variables such as formulation types, environmental conditions, and residual concentrations. Natural conditions in the environment such as temperature, pH, turbidity, and hardness can vary significantly, which may affect the toxicity of chemicals on aquatic organisms. In this section, formulation factors, field variables, and residual tests are discussed. Because PAM does not have an accepted residual test and residual concentrations are seldom measured, factors affecting the performance of PAM are focused on in this section as they are critical to identifying field tests for further study. Key factors that are quantifiable are included in Section 4 as monitoring recommendations. Factors that are not quantifiable are also appropriate for further study and are addressed in Section 5 Study Plan.

Tables 6, 7, and 8 summarize literature findings on formulation factors, field variables, and residual tests, respectively. These tables show that a large number of uncontrolled factors and variables can impact treatment effectiveness and therefore have the potential to impact toxicity due to passive system discharges. Given the large number of uncontrolled factors and variables, it is not possible to develop general guidance applicable to all sites. The study plan therefore focuses on developing reliable residual tests and identifying factors that result in actual receiving water toxicity and habitat impacts.

## Table 6: Formulation factors affecting toxicity

Factor	Controlled	Effect on Floc Size/Settling Rate	Included in Study Plan?
Type (anionic, non-ionic)	Yes	Optimal dose anionic much lower than for non-ionic. Restrict use of non-ionic PAM even if anionic ineffective (i.e., ATS only option)?	No
Molecular Weight (MW)	Yes	High MW produces denser and faster settling floc when mixing intensity is high. However, when mixing intensity is mild, low MW produces denser and faster settling floc High MW (>1x10^5 g/mol) best, but very high MW can result	Yes, field monitoring
		In viscous solution In land application, low molecular weight PAM (<7.5x10^4 g/mol) could move to about the same depth as the wetting front and may not be restricted to surface layer of soil	-
		MW more important than charge density (CD) in determining flocculation efficiency	-
		Effect of MW dependent on CD of PAM	
		High MW PAM less affected by calcium ions. Medium MWs are best in terms of the trade-off between the number of chains available (more in low MW PAM) and chain length (more in high MW PAM) and perform best over the widest range of mixing conditions	-
Charge density (CD)	Yes	Increase in charge density results in smaller flocs	Yes, field monitoring
		Increase in charge density reduces treatment efficiency	-
		Overall, anionic PAM with a CD of 3% was most effective at reducing turbidity	-
Chain length	Yes	Chain length in solution more important than amount of PAM adsorbed to particles. Increasing the number of OH groups (hydrolysis level) in formulation increases chain length providing a pH not below 6	No
Chain type (branched, linear)	Yes	Branched results in lower settling rate than linear for same MW	No
Additives (e.g., oil-based)	Yes	Oil-based PAM shows significantly higher toxicity than non- oil-based PAM	No

#### Table 7: Field factors affecting toxicity

Factor	Controlled	Effect on Floc Size / Settling Rate	Included in Study Plan?
Polymer concentration	No	Optimal dose after which overdose reduces flocculation efficiency. Optimal is about 1 mg/L. In general, the farther away from optimal dose, the more impact environmental variables have on flocculation efficiency. If using lower-than-optimal dose (reduced toxicity risk), then may need longer mixing time and settling time to compensate (larger basin size) Overdose can reduce flocculation by stabilizing suspensions at high doses. Depends on several factors including molecular weight, charge, and conformation of the molecule; size and chemistry of the dispersed solids; and chemistry of the water Target field dosing typically much higher than lab entimal at 5 = 10 mg/l	Yes, lab testing
Water temperature	No	Higher turbidities at lower temperatures	Yes, field monitoring
		Flocs at high temperature are larger, but can be more fragile and sensitive to mixing intensity	
		Low temperatures cause smaller, less-dense, and more fragile flocs. Impact of low temperatures greater at relatively lower PAM doses	
Water pH	No	Increase in pH reduces flocculation efficiency	Yes, field monitoring
		Optimal pH about 6. pH lower than 6 less optimal	
		At high pH, flocs formed are smaller, and they settle slowly	
Mixing intensity	Partial	Lower-than-optimal PAM doses require higher mixing intensity to achieve better turbidity reduction	Yes, lab testing
		Optimal is 100 rpm (velocity gradient of 130 s-1). Higher intensity results in reduction in viscosity, which indicates shearing of PAM molecules into smaller chains	
		Jar test turbidity removal efficiencies are more variable than hand-shake method. Hand-shake method for field application: shake manually for 10 seconds, allow 30 seconds settling, and measure turbidity	
		May not need both fast and slow mixing, making simple hand-shake method effective	
Mixing time         Yes         Floc si time, floc		Floc size depends on mixing time. After optimal mixing time, floc size decreases	Yes, lab testing
		Longer, slow mixing results in better flocculation efficiency. Final turbidity levels decline rapidly with increasing slow mixing time from 0 to 5 minutes, and only moderate decreases in turbidity observed when further increasing the mixing time to 10 minutes. Longer	

		mixing time would be needed to effectively reduce turbidity levels when low doses of PAMs are used	
Settling time	Yes	Longer settling time provides greater floc removal	Yes, field monitoring and lab testing
		Effect of overdosing disappears if sufficient settling time available. So, maximize settling time in pond (at least 24 hrs)	
Floc and treated water properties (visual assessment)	No	As the polymer dose approaches the optimal dose, floc size increases until, at the optimal dose, there is essentially just a single "megafloc." After this dose is surpassed, floc size again diminishes At low mixing speed and time, the sediment is partially present as fine powder due to lack of flocculation	Yes, field monitoring and lab testing
		Assessment of floc size and shape an indicator of treatment effectiveness. If treated water feels "slimy or viscous," this indicates an overdose. When solution starts to feel "slippery," then overdose likely	
Soil type (clay, silt, etc)	No	PAM effectiveness high for soils >14% clay and 22% silt Anionic PAM ineffective for some soil types due to significant amounts of smectite and vermiculite (>20%) present	Yes, field monitoring and lab testing
Organic matter content	No	High organic matter reduces flocculation effectiveness High charge density PAM better when organic matter	Yes, field monitoring
Water hardness	No	Calcium ions promote flocculation through bridging mechanism. Effect of hardness on floc settling only noticeable at lower-than-optimal PAM doses and calcium concentrations below about 50 mg/L	Yes, field monitoring
Water iron content	No	Dissolved iron interacts with oxygen to create free radicals that promote PAM degradation to acrylamide monomer	Yes, field monitoring
Soil spatial variability	No	Representativeness of soil sample used in jar tests	Yes, field monitoring
Product type for erosion control (granular, liquid)	Yes	Loss of PAM higher in granular application. Minimize groundwater contamination by only allowing liquid application? Granular PAM potentially more toxic than liquid form, due to poorer control of dosing and reduced reactivity with soils prior to rainfall	Yes, field monitoring

Basin size	Yes	Base on optimal jar test settling rate? Size could be reduced in size (surface area) by 2-to-4 times standard due to high floc settling rates	Yes, field monitoring
		Effect of overdosing disappears if sufficient settling time available. So, maximize settling time in pond (at least 24 hrs)	

#### Table 8: Residual tests

Factor	Controlled	Effect on Floc Size / Settling Rate	Included in Study Plan?
Hyamine	-	Hyamine method strongly affected by total organic carbon (TOC). The sensitivity of the hyamine method in soil extracts decreases with decreasing charge density. There is a maximum TOC concentration (< 5 mg/L TOC) beyond which interference from TOC renders the test not useful	Yes, field monitoring and lab testing
Flocculation -		Test whether addition of soil results in flocculation. Samples need to be centrifuged to remove existing turbidity and tested at multiple sediment concentrations (added as synthetic stormwater). Control could be centrifuged and filtered supernatant assuming filtering removes PAM	Yes, field monitoring and lab testing
Spectrometry	-	UV-Vis spectrometry. Absorbance curves using DI water, rainwater, and source (retention pond) water. Absorbance for each concentration measured at 200 nanometers	No
		Use of kaolin mineral standard that is mixed with a PAM- amended water sample. Absorbance measured at 560 nm using a spectrophotometer	
Sensitivity Method	-	Sensitivity to flocculation variables/factors increases further away from optimal dose. Use principle to test for sensitivity to: - mixing intensity - mixing time - addition of product (liquid form)	Yes, field monitoring and lab testing

Other research topics useful to optimizing the effectiveness of chemical use are not covered in the study plans because they are not critical to the immediate task of ensuring safe environmental use. These topics include the following:

- Chemical dissolution rates
- Chemical-binding to coapplied erosion control matrices, crusting, wash off, and redissolution
- Calibration and verification of a mass-balance concentration prediction calculator

- Settling velocity and optimized basin sizing
  Determining if nonionic PAM effectiveness in certain soils justifies its higher dose

# 2.5 Unknown Impacts and Risk Tradeoffs

Risk, defined here as the likelihood of occurrence of impact and the severity and persistence of impact, is difficult to compare for construction site discharges with and without chemical use in California environments. The project TAC could not find universal agreement on addressing the risks posed by passive treated discharges, partly because of trade-offs between untreated sediment impacts and the impact of chemical use. This balance is a difficult one. A less severe impact that is more likely but less persistent may not be clearly worse or better than a more severe impact that is less likely but more persistent.

Direct comparison of risks for chemical and nonchemical treatment scenarios for construction site discharge were not found in literature, so a discussion of discharge characteristics that affect risk is provided for short-term policy considerations.

# **Clean Sediment and Turbidity**

Clean depositional sediment (no floc) can impact spawning habitat, specifically by inhibiting dissolved oxygen penetration. However, spawning fish tend to pick locations where hydraulics scour out sediment (Kondolf 2000), and sediment sizes that impact spawning habitat (1 to 10 mm) are so large that they would be very unlikely to be discharged from construction sites with traditional erosion control and sediment control. Benthic organisms usually adapt (Maurer et al. 1986). Suspended sediment has possible physiology effects at fairly high concentrations (Wilber and Clarke 2001) with severity increasing with exposure and concentration. For example, severity was low for concentrations below 55 mg/L TSS and exposure less than 2 days (Newcombe and Jensen 1996). Levels of NTU toleration as measured by feeding rate varies by species (Rowe and Dean 1998). High NTU has been linked to food web degradation due to reduction of light penetration; however, salmonids were found to have optimal feeding in the range of 35–150 NTU (Gregory and Northcote 1993). Many species (e.g., small pelagic fishes) rely on turbid water to avoid predation, though turbidity actually appeared to reduce the effectiveness of physical cover (Gregory and Levings 1996).

# **Chemical Residual and Floc**

Though adverse impacts of chemical use are rarely reported, chemical use can theoretically impact both toxicity and habitat. However, based on preliminary modeling from an unverified mass-balance calculator, chemical toxicity may be limited to invertebrates such as water flea for polyacrylamide chemicals. Fish toxicity is expected to be very rare and result only from a chemical spill or gross negligence in application. Habitat and sediment toxicity from discharge of residual chemical and floc are not well studied.

#### Persistence

Policy development should consider persistence as a component of impacts. Persistence of sediment discharge from sites using traditional sediment and erosion control should be compared to the persistence of impacts of residual or floc from sites using chemical dosing. Though not found in literature, it is plausible that escape of chemically-bound floc could have the longest lasting impact to benthic habitats.

Sediment discharge and deposition from a site not treated with flocculant is possibly mitigated by the scour of episodic high flow in the receiving water that is expected a few times a year. Persistence of sediment-caused turbidity correlates to the residence time of the waterbody. Water column toxicity caused by discharge of residual chemical would likely be short-lived and mitigated by dilution in the receiving water; however, more data are needed on formation of the acrylamide monomer. Discharge of floc could cause toxic habitat impacts that are more difficult for natural environmental conditions (e.g., high flows) to mitigate due to much higher critical shear force required to detach chemically-bond floc from the receiving water streambed. Floc could also have a sediment toxicity to the benthic community either by chemical impact or the reduction of oxygen transmissivity in the streambed sediments. Relative persistence and impact of pollutant types are summarized in the Table 9.

Discharged Pollutant	Toxicity	Habitat Impact	Persistence
Sediment (no chemical treatment)	Salmonid egg and larvae sublethal at prolonged and high exposure	Yes, depending on stream hydraulics	Toxicity: Low Habitat: Medium (several events)
Turbidity (no floc)	Limited toxicity; correlates to suspended sediment and depends on species	Yes, good and bad, depending on species	Toxicity and Habitat: Low/Medium (depending on residence time and particle size; lower in streams and higher in lakes)
Chemical residual	Water flea; unknown sediment toxicity	Indirectly, when bound with receiving water sediments	Toxicity: Low (single event) Habitat: High for settled floc (seasonal to multiyear)
Floc	Unknown sediment toxicity	Yes	Toxicity and Habitat: High (seasonal to multiyear)

Table 9: Environmental risk tradeoffs of pollutants as expressed by severity type of impact and persistence

# 3 System Design and Operations Guidance & Requirements

To determine appropriate guidance and proposed requirements for monitoring, system design was considered first. Allowing flexibility in system design adds variability and unknown outcomes, which will then affect what monitoring is required. For system design, following typical practices for passive dose for either erosion control or sediment control and using conservative mass-balance calculations and available performance data will not ensure with certainty that discharge of chemicals and chemical-bound floc would not escape in environmentally impactful quantities. This suggests site-specific monitoring is required regardless of the system design practices used. If monitoring is required because use on any site cannot be automatically deemed safe, then more flexibility should be given to system design practices. In essence, universal monitoring allows for a performance standard rather than a prescribed site solution. Unfortunately, residual tests for chemical and floc escapement are not well established for all chemicals. However, other performance metrics (e.g., turbidity) theoretically help identify poor performing systems. Because monitoring of actual chemical is not possible, a hybrid of interim guidance and requirements is suggested for both deployment and monitoring.

As data are collected, many requirements can be relaxed if the data demonstrate that following certain practices results in environmentally safe discharge. However, the data may also indicate that certain system design practices are required rather than recommended in some situations.

Data collected in future studies will help identify minimum inspection and monitoring requirements to identify these site practices.

Interim system design and basin operations guidance and proposed requirements are presented in the following subsections. Flowcharts are provided in Sections 3.1 and 3.2 to assist in understanding and applying the proposed requirements for sediment control design and operations, respectively. Both factsheets have the flexibility to address both industrial and construction sites. This project offers recommendations for erosion control, but no requirements are suggested beyond the requirement that erosion control be implemented. Consequently, a flowchart for erosion control is not provided.

# 3.1 System Design

# System Design Guidance: General

# Maximize Traditional Erosion and Sediment Control Practices

Traditional erosion and sediment control practices should always be maximized first prior to evaluating the feasibility of passive chemical treatment in an erosion or sediment control application. Traditional erosion control will reduce sediment loads that may interfere with operation of the chemical dosing systems and reduce erosion of chemicals used for erosion control. Uncontrolled sediment also introduces added variability that will make design of dosing to basins more difficult.

# Perform Site Specific Jar Testing

Jar tests are critical when using passive treatment chemicals to optimize system performance. Optimal chemical coagulant type is selected as well as the proper dosage. Soil samples are often sent to manufacturers to perform appropriate tests. Overapplication can increase costs, reduce performance, and pose an elevated toxicity risk. Jar testing may need to be repeated when unanticipated soil types are exposed.

For industrial sites, the IGP requires TSS sampling, and historic TSS data should be readily available for a given site. The presence of adequate sediment load should be confirmed before using passive treatment chemicals in an industrial sediment control application. Jar tests can be based on actual runoff flow, rather than relying on site soils. Also, if other constituents require treatment, jar test samples should be analyzed for those constituents.

# Formulation Selection and Dose

Perform jar testing to select formulation and determine optimal dose. Test multiple formulations and confirm selected chemical provides treatment that is at least 80% more effective than an untreated control within 5–10 minutes of dosing. Cationic chemicals are not recommended. Note that if cationic chemicals are used, toxicity testing is required prior to discharge.

#### **Recommended PAM Formulation**

Recommendations for PAM include the following:

- Low-to-moderate charge density (<35% by weight)
- High molecular weight (1–24 mega-g/mol)

# Erosion Control and Sediment Control (Basin) Discharge Concentration Estimation

All sites should use the calculator developed in this study (Section 3.3) or an equivalent method to determine the maximum likely concentration that may result from a particular application. Perform event-specific analysis to identify when dosing should be adjusted. The proposed calculator in Section 3.3 requires further calibration and verification; until then, results are informational. For longer-term projects, site-specific verification of the calculator may justify its use in comparison to toxicity thresholds. Document calculator inputs, including adjustments to default values, that result in calculator output concentrations that are below toxicity thresholds, and ensure any BMPs that are assumed in the final design are implemented in the field.

# Follow State-of-Practice

State-of-practice guidelines should be followed once the maximum likely concentration calculator has been used and the calculated values are below the acceptable limit. These guidelines are often provided by the manufacturer, but California-specific guidance may provide additional detail (e.g., Caltrans and CASQA) based on experiences in this state. Timing of application is particularly important because most chemical coagulants used for erosion control require time to set (typically at least 24 hours). Information on safe chemical storage, handling, and loading is lacking in many guidance documents and is of particular concern for liquid chemicals in the construction site environment. Maximum slope is also critical, and it depends on the type of erosion control applied with or after application of the chemical.

#### System Design Guidance: Erosion Control

# Use of Dissolved Chemical in Erosion Control

Because dry application to land can result in greater product loss than wet application, wet application is recommended for industrial and construction sites. Safe product handling procedures should also be developed specific to the chemicals used to enhance erosion control. Mass-balance calculations indicate theoretical concentrations can be quite high under certain conditions (high percentage of area treated, high particle detachment, low particle binding). Industry standards should be followed to prevent these high concentrations.

#### Additional Cover

Additional ground cover methods used in combination with a wet application of chemical coagulants further reduces the likelihood of discharging chemicals from an industrial or construction site. Geotextile matting, mulch, or straw is commonly used in combination with treatment chemicals. This additional layer of cover provides slope protection and helps further prevent high particle detachment.

# System Design Guidance: Basins

# Application into Drainage Pathways

Pre-storm application into drainage pathways provides several advantages. First, dosing into upstream drainage paths reduces the burying of treatment chemicals with sediment that commonly occurs in stagnant or slow-flowing water. Naturally occurring drainage pathways that are wet between storm events may require additional analysis and consultation to determine their status as receiving waters and address application of chemicals to those waters. Prewetting of treatment blocks is recommended prior to storm events to promote effective dissolution.

# <u>Mixing Zone</u>

All use of a flocculent or soil-binding chemical should be far enough upstream of a sedimentation basin to allow for adequate mixing prior to entering the basin.

#### **Recirculation of Flows**

Flows can be recirculated if treatment is poor and underdosing is suspected. If flows are recirculated, variables such as flow rate, turbidity, and treatment volume can be better defined than uncontrolled flow scenarios. Practitioners may also consider elevating the product off of the channel invert to reduce the likelihood of overdosing.

#### **Proposed Interim System Design Requirements**

These requirements should be revised as studies identified in Section 5 are completed and alternative analysis tools are developed. System design requirements are proposed for sedimentation basins. There are no requirements for erosion control proposed.

#### Toxicity Thresholds for the Most Sensitive Species

To ensure environmentally safe use of treatment chemicals, toxicity thresholds must be known. Any chemicals used must have available toxicity data including the LC50 and LOEC based on standard EPA WET methods. The application of any chemicals to water without this information is not allowed.

#### Anionic PAM Formulation

If anionic PAM is used, PAM products must not contain more than 0.05 percent acrylamide monomer, must be free of surfactants such as nonylphenol (NP) and nonylphenol ethoxylates (NPE), and must have an LC50>100 mg/L for pimephales promelas (fathead minnow) in a standard EPA WET test. LC50 and LOEC must be available prior to use for both fish and water flea species.

# <u>Use Sedimentation Basins Downstream of Any Treatment Chemical Use</u>

Sedimentation basins must be used at all sites using chemicals. Runoff capture allows for uncertainty in dosage that results from variability in storm runoff volume, storm intensity, sediment load, and soil type. When chemicals are used with erosion control, there is no assurance of high chemical-soil binding nor assurance that chemical wash off will not occur with slope failure. The use of a downstream sediment basin reduces the likelihood of discharging high chemical concentrations by decreasing spike concentrations that may be experienced in erosion control applications. Even with the use of sedimentation basins, the amount of product applied in a watershed for erosion control is likely higher than what is typically used to enhance sedimentation in a basin, so the theoretical risk remains for residual discharge in basin effluent; the proposed monitoring requirements in Section 4.1 are aimed at identifying poorly performing systems that may be discharging chemical residual or unsettled floc.

#### **Basin Sizing and Features**

Basin area dimensions must be designed to achieve an overflow rate conducive to the settling of a small particle (10 micron), as specified in the CASQA Sediment Basin Factsheet SE-2 (CASQA 2019). Sedimentation volume must be sufficient to capture volume of a moderate storm of likely occurrence, such as the volume from a 2-yr, 24-hr storm depth. (Note: sedimentation basins are often sized for larger events, but this recommended minimum is for the narrow task of addressing high chemical concentrations. So, while larger storms are less

impactful due to dilution, they may still be preferred to manage high sediment loads in conditions where erosion control is more likely to fail.)

Basins must have adequate upstream channel length to provide fast mixing, and they must also include baffles within the basin to provide slow mixing. Long-term installations, such as at industrial sites, must incorporate liners until the risk of groundwater impacts from long-term chemical use is better understood. Sedimentation basins must have outlet controls to enable batch operations (see Section 3.2) and prevent the discharge of toxic residual chemical or unsettled floc.

# Passive Chemical Dosing Design and Basin Design Flowchart

Figure **2** presents a flowchart for dosing system design for basins. The flowchart guides the user through key recommendations and proposed requirements described above.



- Items in **bold font** are proposed interim requirements, which should be revisited as studies are completed and alternative analysis tools are developed.
- Toxicity data for chemical coagulant used must include LC50 and LOEC for both fish and water flea species. Must have an LC50>100mg/L for pimephales promelas (fathead minnow) in a standard EPA WET test.
- 3. The formulation of a given product is designed to bind to different soil types. Performance testing is necessary to determine the appropriate formulation that will be the most effective for a particular site. For industrial sites, perform test with range of prior TSS values. For polyacrylamides, moderate charge density (<35% by weight) and high molecular weight (1–24 mega-g/mol) is recommended. PAM products must not contain more than 0.05 percent acrylamide monomer and must be free of surfactants such as nonylphenol (NP) and nonylphenol ethoxylates (NPE).</p>
- 4. For uncontrolled flow, consider elevating some product off the channel invert to reduce the likelihood of overdose for lessthan-predicted storm size and intensity. For controlled flow (e.g., recirculated flow), calculate flow depth in the channel and arrange dosing configuration within the predicted depth.
- 5. Use mass-balance calculator to determine the maximum likely concentration based on selected dosage and site characteristics.
- See Passive Chemical Dosing Basin Operations flowchart. Regular inspections and monitoring will be required to determine the need to adjust dosing, mixing, flocculation, or sedimentation zone design.

Note: Check local regulations for additional guidance and prohibitions.

Figure 2: Passive chemical dosing and basin design flowchart

# 3.2 Basin Operations

# Interim Operational Guidance

#### **Regular Inspections**

After final design is complete, regular inspections are still recommended to ensure the system is functioning properly. Inspection frequencies can vary depending on how often the system is used, but at minimum systems should be inspected before and after wet weather events to evaluate maintenance needs and potentially adjust dosing, mixing, flocculation, or sedimentation zone design. Inspection of block form chemicals is also critical as blocks may develop a sediment layer or get buried in sediment that reduces dissolution rates, which may result in an underdosed system. Wiping off sediment on blocks may be necessary, and repositioning blocks may help reduce submergence in sediment.

#### <u>Basin Cleanout</u>

Basin cleanout may need to be more frequent to keep sufficient sediment capture volume and maintain the clarifier function of the basin.

Sediment removal may be required more frequently when high influent turbidities are experienced as previously settled sediment and floc may be resuspended if proper inspection and clean out activities are not performed.

#### **Corrective Action**

If basin turbidity is above 50 NTU, additional NTU or residual monitoring is recommended to be completed for 1) runoff from slopes receiving chemically-enhanced erosion control, and 2) sedimentation basin influent and effluent.

Finally, sites with exceedances are also recommended to be reassessed for all of the following:

- Adequacy and function of traditional erosion control and sediment control BMPs on site;
- Formulation, dosage calibration, and dosage reduction (sedimentation basins);
- Increased in-channel mixing zone; and
- Increased basin area.

Turbidity above 50 NTU could be indicative of several design issues, so the following actions should be taken to determine the cause of the deficiency:

- 1) A swirl test can identify if mixing is inadequate. If floc forms during a swirl test, then additional slow mix baffles and/or recirculation may be necessary to achieve a target turbidity below 50 NTU.
- 2) Visual inspection may identify unsettled floc within the system. Under this circumstance, practitioners should confirm that the proper chemical formulation is used, the target dosage is achieved, and the system is experiencing adequate settling times.
- 3) Unexpected leftover product within the channel is an indication that the system is not reaching the target dose. In this case, practitioners may consider recirculation or the use of additional treatment chemical to achieve the target dose.

Basins that cannot be returned to service in time for subsequent storm events may hamper the ability of the site to meet CGP or IGP NALs. In these cases, off-site disposal, ATS, or temporary detention should be explored while remediation of the basin performance is pursued.

### **Proposed Interim Basin Operational Requirements**

These requirements should be revised as studies identified in Section 5 are completed and alternative analysis tools are developed.

#### **Batch Operation**

Basins must operate in batch mode, with a minimum hold time of 24 hours for sites applying chemicals as either erosion control or water treatment.

# <u> Basin Effluent – Toxicity Threshold</u>

For basin operations that use cationic chemicals or that use non-cationic chemicals and wish to use toxicity testing instead of checking turbidity against the NAL of 50 NTU, several actions must be taken prior to discharge. First, water samples must be collected and analyzed for toxicity for the most sensitive species based on known toxicity thresholds. Measurements for pH, turbidity, and temperature must all be taken in the field. While samples are being analyzed for toxicity, flows must be held within the basin. Because toxicity testing will require an extended hold time, local vector control guidance must be followed for hold times exceeding 72 hours. Water with toxicity cannot be discharged; treatment enhancements or alternative disposal methods will need to be pursued for water with measured toxicity.

While no established standards exist for measurement of floc, visual assessments can be made and documented. At minimum, confirm if visible floc is present and submit a photograph taken of a sample of the discharge collected in a clear glass jar (after mixing to ensure minimal floc settling).

#### Basin Effluent - Turbidity Threshold

For basin operations that are not performing toxicity testing, water in the basin must reach below 50 NTU prior to discharge. Field samples must be taken for pH, turbidity, and temperature.

If no storms are forecast within the next 24 hours, practitioners must continue to identify system deficiencies and implement the appropriate corrective action, which may include recirculation, increased settling time, and additional slow mix baffles.

#### **Bypassing Forecast Storms**

For systems that use non-cationic chemical, storms forecast within the corrective action period (after results show turbidity > 50 NTU) should bypass the basin, including the chemical dosing (or the chemicals should be removed). This will prevent potentially toxic discharges.

For systems holding water pending toxicity results, any storm that would cause bypass of collected water should also be bypassed. This will likely require an offline basin.

# Discontinued Use

For failure of either toxicity or turbidity thresholds, chemical products should be removed from the channel immediately, and further use should be discontinued until performance issues are identified and remediated.

# **Basin Operations Flowchart**

Figure 3 presents a flowchart for basin operation. The flowchart guides the user through the key requirements described previously. Proposed interim requirements specified in flowchart should be revisited as studies are completed.

The key decision affecting operations is whether cationic chemicals are used. If used, toxicity tests are required prior to discharge. If anionic or nonionic chemicals are used, the user has the option of toxicity tests or analysis of turbidity prior to discharge.



- Items in **bold font** are proposed interim requirements, which should be revisited as studies are completed and alternative analysis tools are developed.
- 2. The toxicity test will require extended hold time prior to discharge.
- Hold water and assess options to lower NTU. Follow local vector control guidance if cumulative hold time will extend beyond 72 hours. Examples of corrective action may include recirculation, additional settling time, and adding additional slow mix baffles. Troubleshooting tests include the swirl test to identify inadequate mixing; visual floc assessment to identify inadequate formulation, mixing, or settling; and measurement of undissolved chemical to identify inadequate dosing.

Note: Check local regulations for additional guidance and prohibitions.

Figure 3: Flowchart of proposed basin operations requirements

# 3.3 Estimating Residual Concentration from Quantity of Chemical and Site Factors

A set of Excel-based, mass-balance calculators were developed to predict the maximum likely concentration of erosion control treatment chemical(s) in effluent water following a user-defined pre-storm application for erosion control or enhanced treatment of runoff via sedimentation. The tool is available here: <u>https://www.owp.csus.edu/passive-chemical-dose.php</u>.

The calculator was developed using information gathered from a literature review of existing empirical data and existing best management practices, manufacturer and vendor guidance, and input from the TAC. Calculator input variables include chemical product dissolution rate, chemical product characteristics (i.e., block- or granular-form product size and other properties), chemical-soil reactivity rate, storm event volume, duration, and flow pattern, and application type (land or water). Using a timestep modeling approach, the calculator predicts both chemical concentration over time and average concentration over the duration of and at the culmination of a storm or flow event, with options for comingled treated and untreated flows in cases where the treatment area does not cover an entire watershed.

The calculator demonstrates the benefits of using basins by accounting for attenuation of spikes in concentration over a higher volume. This allows users to determine if a planned treatment is likely to exceed predetermined environmental toxicity limits as well as to estimate the impact of the detention basin to reduce channel effluent concentrations. The calculator also reports the amount of chemical product expected to remain unused at the end of the storm or flow event, which may alert a user to potential unnecessary or excessive use of costly chemicals. While initially designed for use with polyacrylamide erosion control products, user inputs allow for customization of the calculator for use with similar-functioning chemical products where sufficient product data are available. The resulting calculator assists users in designing environmentally safe erosion and sediment controls that use treatment chemicals at construction sites and industrial facilities.

# **Dissolution Rate Data Sources**

In the calculator, the effluent concentration of an erosion or sediment control chemical product is approximated primarily as a function of the "dissolution rate" of the chemical product. This variable describes the rate of mass loss of product per unit area of product. Because product dimensions decrease with dissolution, the chemical dosage will be highest when the chemical product is first used and the surface area of the product is at its greatest. As the product dissolves or erodes in flow, losing mass and decreasing available surface area, the dosage rate decreases.

The dissolution rate may depend on many factors, both known and yet to be identified across a variety of erosion and sediment control products. For polyacrylamide-based products, the TAC reports that the dissolution rate and resulting dosage can be affected by how wet the product is. However, numerous additional potential factors may affect the dissolution rate of polyacrylamide as well as other erosion and sediment control chemicals, including soil composition, iron content, pH, temperature, velocity, and chemical reactivity with other constituents that may exist in runoff.

A literature review of existing research as well as manufacturer guidance was performed; however, publicly available information on dissolution or dosage rates appears sparse, and

inadequate data exist to verify the few data points that were located. Two approaches were used to estimate dissolution. One uses manufacturer information detailing the expected lifespan of a block-form polyacrylamide product. The other approach uses results from a lab-scale dosage experiment performed on three types of polyacrylamide polymer logs (State Erosion and Sediment Control Task Force 2013).

For estimating dissolution, expected lifespan of a block-form product was considered first. Applied Polymer Systems, Inc. indicated that their Floc Log products typically treat one million gallons of flow before completely dissolving. Additionally, product information sheets for the 700 Series Floc Log products indicate that one Floc Log should be used for every 60 gpm of flow (approximate). In conjunction, these two pieces of data imply that one Floc Log will last approximately 277.8 hours. These data can be transformed into a dissolution rate using the following steps:

- 1. Determine "linear erosion rate" into the block-form product in each dimension (length, width, and height) such that each dimension erodes at a constant rate and reaches zero (full dissolution, no product remaining) at 277.8 hours.
- 2. Over a hypothetical 1-hour time period, use the dimensional linear erosion rates to determine the total eroded volume as well as the average surface area of the block over the 1-hour time period.
- 3. Finally, use the known density of the block to convert this volumetric loss to mass and divide the mass loss by the average surface area. This gives a dissolution rate in units of mass per surface area per time, in this case 0.154 g/in^2/hr (grams per square inch of surface area per hour).

Lab dosing results were also used to estimate a dissolution rate. Dosage in a controlled lab environment using filtered water, resulted in similar dissolution rates: 0.096 g/in^2/hr (APS 703d Floc Log), 0.166 g/in^2/hr (APS 703d#3 Floc Log), and 0.194 g/in^2/hr (APS 706b Floc Log). In this case, a reversal of the above steps was employed using Excel's Solver add-in tool to determine the effective linear erosion rates from the dissolution rates.

# **Calculation Methods**

The calculator addresses for four application types:

- Sediment control (water) application 1: Block-form chemical placed within a channel
- Sediment control (water) application 2: Granular-form chemical, applied in defined patches located at check dams/berms within a channel
- Sediment control (water) application 3: Granular-form chemical, distributed throughout a channel
- Land erosion control application: Granular-form chemical, distributed across an area (no channel)

While both data sources for dissolution rate discussed above provide information on block-form polyacrylamide products, the calculator applies the same dissolution rate principles to granular product at the grain level. That is, while the block-form calculator calculates mass dissolved over time from each block unit, the granular-form calculator calculates mass dissolved over time from each individual grain unit. Because granular product has an exponentially greater surface area than block product for the same mass, granular product tends to exhibit a much higher initial effluent concentration spike. For the sediment control (water) application of granular form chemical applied at check dams or berms within a channel, the calculator treats each

application "patch" or "pad" as a custom-sized, thin "block." Wetted granular product applied in patches is assumed to form a congealed, semisolid mass in which the surface area of every individual grain is no longer fully in contact with flow, thus behaving more like a block-form product.

For all calculator applications, the user is prompted to input data describing the storm or flow event (volume determined using SCS method or user-defined, hydrograph shape, and duration), the chemical application (for block-form applications, block shape, number, mass, percent chemical, and percent of dissolved chemical bound to sediment; for granular-form applications, mass applied, grain size, density, and application patch size if applicable), toxicity data for graph visualization (selected from prepopulated, known data, or user-defined data), modeling timestep, and dissolution rate option need to be inputted.

# Sediment Control Example Calculation

To demonstrate the calculator function, the following is an example of a single timestep of a model using the following inputs:

- SCS Curve Number Method determined volume of 36,929 L (1-inch precipitation over a 1-acre watershed, soil group C)
- Storm duration of 6 hours, constant flow hydrograph shape
- 100% of the watershed runoff is treated/flows through the application site (no bypass of untreated flow)
- 1 APS 700 Series PAM block chemical application (12 in by 6.5 in by 3.5 in, starting mass of 9 lbs)
- 100% erosion control (EC) chemical in block
- 10% of dissolved chemical bound to sediment
- 60 min modeling timestep
- Dissolution rate of 0.194 g/in^2/hr, representative of an APS 706b product

Calculation steps are as follows:

- 1. The calculator populates the known linear erosion rate corresponding to the selected dissolution rate, which in this case is as follows:
  - Lengthwise linear erosion rate of 0.027 in/hr
  - Widthwise linear erosion rate of **0.015 in/hr**
  - Heightwise linear erosion rate of 0.008 in/hr
- 2. Calculate volume of water over the timestep using the total storm volume and duration (calculation varies in the case of a triangular-shape hydrograph):

 $Timestep \ runoff \ volume = \frac{Total \ storm \ volume}{Storm \ duration} \times timestep = \frac{36,929 \ L}{6 \ hrs} \times 1hr = 6,155 \ L$ 

3. Calculate starting and ending length, width, and height over the timestep using the linear erosion rates, assuming the blocks dissolve from all directions:

Ending length = Starting length - 2 \* lengthwise erosion rate \* timestep =  $12.00 \text{ in} - 2 * \frac{0.027 \text{ in}}{hr} * 1hr = 11.95 \text{ in}$ 

Ending width = Starting width - 2 \* widthwise erosion rate \* timestep =  $6.50 \text{ in} - 2 * \frac{0.015 \text{ in}}{hr} * 1hr = 6.47 \text{ in}$ 

Ending height = Starting height - 2 \* heightwise erosion rate \* timestep =  $3.50 \text{ in} - 2 * \frac{0.027 \text{ in}}{hr} * 1hr = 3.48 \text{ in}$ 

4. Determine volume eroded:

$$Volume \ eroded = Starting \ volume - ending \ volume$$
$$= (12in)(6.5in)(3.5in) - (11.95in)(6.47in)(3.48in) = 3.68in^{3}$$

5. Convert to mass eroded using calculated density:

Mass eroded = Volume eroded \* density =  $3.68in^3 * \frac{9lbs}{(12in)(6.5in)(3.5in)} = 55.09g$ 

6. Calculate mass of chemical eroded:

Mass of chemical eroded = Mass eroded \* % chemical in product = 55.09g \* 100% = 55.09g

7. Calculate total chemical concentration in treated channel:

 $Total chemical concentration = \frac{Mass of chemical eroded}{Timestep runoff volume} = \frac{55.09g}{6,155L} = 8.95 mg/L$ 

8. Calculate unbound (or unreacted) chemical concentration in treated channel: *Unbound chemical concentration* 

$$= Total chemical concentration * (100\% - \% bound chemical)$$
$$= \frac{8.95mg}{L} * (1 - 0.1) = 8.06 mg/L$$

Since this example shows only the first timestep, the result represents both the channel concentration and the downstream pond concentration. For subsequent timesteps, the channel concentration is calculated again, and the pond concentration is calculated using the total mass eroded over all previous timesteps divided by the total runoff volume over all previous timesteps. As discussed, a concentration spike occurs at the start of the simulation due to the maximum available surface area of product, and in cases where a triangular hydrograph is used, low volumes at the start of a storm. Existence of a downstream pond allows for attenuation of concentration spikes and will be a necessary part of the passive chemical application design in order to ensure concentrations remain below the aquatic toxicity limit for a given product.

The resulting pond and channel concentrations are then plotted along with the user-selected or defined-toxicity limit, allowing the user to visualize whether their planned chemical application is expected to exceed the aquatic toxicity limit. In cases where less than 100% of the watershed is treated, the calculator also reports a comingled basin concentration that includes all treated runoff as well as untreated runoff.

#### Additional Research Needs

While the calculator provides a data-driven model to predict maximum likely outflow concentration for a passive chemical application, the available data is minimal and the lack of case studies for comparison reveals a strong need for additional research in order to verify its accuracy and underlying principles. In its current state, the calculator functions off of essentially four data points for dissolution rate, all of which apply only to a single manufacturer's block-form polyacrylamide product. While the calculator applies these data to granular-form products as well as block-form products other than polyacrylamide, it is likely that differences in chemical composition between products may cause other products to behave very differently than the calculator predicts.

A one-at-a-time (OAT) sensitivity analysis was performed for the block application, revealing high model sensitivity to variables such as dissolution rate, modeling timestep, number of chemical blocks (dosage), duration of runoff, and rainfall variables affecting treated volume and flow. In an OAT sensitivity analysis, a "base case" is defined for every variable, then each input variable is varied across an expected range, returning to the base case before varying the next variable. This type of analysis by nature does not capture potential interaction between variables and any model sensitivities that may arise from those interactions, which could be significant. Additionally, due to a lack of case study information and availability, the expected range for many variables may not be representative of the range of real-world applications.

# 4 Recommended Monitoring

# 4.1 Monitoring Guidance and Proposed Requirements

Guidance supports better system design, but data does not support that system design practices commonly recommended will always be protective of water quality. Proposed monitoring requirements aim to identify underperforming systems that are more likely to have negatively impactful discharges. Proposed monitoring that is not well established is further addressed in the Study Plan.

# Interim Monitoring Guidance

This monitoring is encouraged to support better system design. In particular, data are needed to 1) calibrate and validate design calculators that predict discharge concentrations, and 2) improve operation of basins for subsequent storm events. The recommended monitoring is:

- Field measurement of rainfall, drainage area, runoff rate, runoff flow, and sediment load in basin influent, which are critical to concentration estimation.
- Collection of sediment basin influent to use to repeat jar tests for subsequent events.

# **Proposed Interim Monitoring Requirements**

Basin effluent monitoring will be conducted for turbidity or one of the in-development residual tests as described in the Study Plan. Minimum field conditions should also be reported, including the following:

- Basin effluent turbidity, pH, and temperature; 24-hr and daily thereafter if extended holding time is needed to meet 50 NTU
- % drainage treated with chemical for erosion control
- Quantity and type of chemical used for erosion control
- Quantity and type of chemical used to enhance sediment control (water treatment)
- % of site discharge treated by basins using chemicals to enhance sediment control
- Soil texture analysis of representative soil sample

# 4.2 Residual and Toxicity

Because conservative mass-balance calculations indicate toxic release of chemical is possible, residual monitoring is recommended. For some chemicals, particularly PAM, no known direct methods to measure concentrations exist. Surrogate options are further explored in Section 5.

# 4.3 Floc Monitoring

Visual assessment of floc size and shape can provide additional information on treatment effectiveness, including the presence of fine suspended floc ("pin floc") that may not be effectively removed by sedimentation. Photographs should be taken of floc in clear sample bottles immediately after sample collection.

# 5 Study Plan

This section comprises four studies that address all of the factors identified in Section 2.4 as critical to understanding impacts to the aquatic habitat. These studies include the following:

- Developing protocols for jar and effluent tests
- Developing protocols for residual tests
- Field water quality monitoring (using residual testing protocols)
- Field sediment toxicity monitoring and bioassessments

The goal of these studies is to identify system design practices and site conditions that, as verified with monitoring data, can be deemed environmentally safe use without the need for discharge-specific monitoring. In these cases, inspections to verify proper system design are sufficient to identify problematic situations. Water quality monitoring would only be triggered where improper system design is identified. These studies should also identify questionable practices and conditions that should always be monitored.

In the development of monitoring methods, study of the viability of inspection-based and lowcost field monitoring is prioritized over costlier laboratory-based analysis.

Soil type is a critical variable in all proposed studies. Soils selected for study should be similar to those on sites where chemicals are commonly needed to achieve NALs. Soils with substantial clay fit this category because, though less erosive than silts, they are more difficult to settle. Selected soils should also target a substantial silt component, as erosivity is most sensitive to silt. Coagulant binding to silts is also more problematic than to clays, so designing a site for more clay than is present could result in more impactful discharge. Consequently, soils in the silt-clay spectrum are addressed in these studies. These include the following:

- Silt
- Silt loam
- Silty clay loam
- Silty clay
- Clay

# 5.1 Protocols for Jar and Effluent Tests

# Introduction

A jar test is typically used to select PAM formulation. Although there is currently an ASTM protocol (ASTM D2035-19) for conducting jar tests, the protocol was not specifically developed for stormwater and has not been widely used at construction sites. A relatively simple effluent test is also sometimes used to assess treatment effectiveness and identify the need for additional mixing or dosing before discharge of treated water. No standard protocols for this effluent test currently exist, so conducting additional studies to develop a standard jar test and a standard effluent test for construction sites is needed.

#### **Background**

# <u>Jar Test</u>

A jar test is a laboratory or field procedure in which the effectiveness of a given chemical is determined by simulating the flocculation process at different chemical doses for different formulations. The purpose of the procedure is to estimate the optimal coagulant dose required to maximize turbidity reduction.

In a jar test, samples of water to be treated are placed in jars, and different amounts of chemicals are added to each jar. The samples are then stirred, and the settling of solids is observed. The dose of chemicals that provides the maximum flocculation and settling is the optimal or target dose. The ATSM jar test protocol (D2035-19) requires a "flash mix" speed of 120 rpm for a duration of 1 min, followed by a "slow mix" speed sufficient to keep floc particles suspended in the water. The recommended duration of the slow mix speed is 20 min. Discussions with the project TAC suggest that flash mix and slow mix durations as short as 15 sec and 5 min, respectively, may be sufficient for construction site runoff.

#### <u>Effluent Test</u>

The objective of the effluent test is to determine whether discharge water requires additional measures prior to discharge to ensure treatment is optimal (e.g., additional chemical, additional mixing, additional settling). The test is based on the observation that factors such as mixing intensity, mixing time, and dose have an effect on final turbidity removal.

In the effluent test, a sample of treated discharge water is collected in a flask, and its turbidity is measured. A subsample is taken and mixed for a short period of time, followed by a period of gentle mixing by swirling. If the turbidity of the subsample is significantly different from the original sample, mixing is assumed to have been inadequate, and recirculation and/or other measures are required. If turbidity differences between the original sample and test sample are minor, an incremental amount of product relative to the original target dose (e.g., about 1 mg/L for PAM) is added to the sample to see if there is an improvement in turbidity removal. An improvement in turbidity removal compared to the control indicates underdosing.

# **Study Goals**

The overall goals of the study are to determine mixing intensity and mixing time protocols for the following:

- 1. A standard jar test
- 2. A standard effluent test

# **Research Questions**

The following are the key research questions that are addressed by the study:

- Is the ASTM jar test protocol appropriate for construction site runoff?
- What modifications, if any, are required to the ASTM jar test protocol for application to construction site runoff?
- Is there an effluent test that is sufficiently sensitive to changes in mixing intensity, mixing time, and dose?
- o Is the effluent test sufficiently reliable to determine the need for additional measures?
- Are controls required for the tests? If so, what type of water is used for the controls?
- How many tests are required on each sample?

# **Study Variables**

- Table 10 lists the study variables for the jar and effluent tests, how they are expected to affect test results, and how each is accounted for in the study design.
- The primary objective of the study is to identify optimal mixing intensity and duration of mixing for each test. Therefore, a number of flash and slow mix times are tested:
  - Jar test

Flash mix for 15 sec, 30 sec, or 1 min, and slow mix for 5 min or 20 min (1 min flash mix and 20 min slow mix based on ASTM D2035-19)

• Effluent test

Rapid swirling/shaking for 15 sec or 30 sec and slow swirling for 1 min or 5 min (no standard mixing protocols available in literature)

In order to keep the number of tests manageable, only two types of PAM and soil are tested, and most environmental factors affecting performance are held constant (i.e., temperature, pH, hardness, TOC). Consequently, this study plan is a proof of concept that may require testing under a wider range of environmental conditions prior to adopting as a standard protocol. The two PAMs and soils selected are those expected to "bookend" a wide range of turbidity reductions. A high-molecular-weight, low-charge-density PAM that provides good treatment and a low-molecular-weight, high-charge-density PAM that provides relatively poorer treatment are selected for the two PAMs. For soils, a clay soil and a silty/sandy soil are selected.

# Methodology

# <u>Jar Test</u>

Equipment: Standard jar test equipment (see Figure 4) and turbidimeter Control: None Core experiments: 2 PAMs x 2 Soils x 3 Doses x 6 mixing protocols = 72 experiments Quality control: Repeat experiments with best and worst turbidity reductions for each mixing protocol = 12 experiments Total number of experiments: 72 + 12 = 84 experiments

Total number of experiments: 72 + 12 = 84 experiments

# <u>Effluent Test</u>

Equipment: Standard lab flasks Figure 5 and turbidimeter

Control: Water that is same as test water but does not undergo additional mixing or dosing Core experiments: 2 PAMs x 2 Soils x 3 Doses x 4 mixing protocols = 48 experiments Quality control: Repeat experiments with best and worst turbidity reductions for each mixing

protocol = 8 experiments

Total number of experiments: 48 + 8 = 56 experiments

#### Table 10: Study variables for jar and effluent tests

Variable	How does it affect test results?	How is it accounted for?
Formulation	Turbidity reduction depends on molecular weight (MW) and charge density (CD)	<u>All Tests</u> : Use various formulation liquid anionic PAMs. Perform tests on 2 PAMs (high MW low CD, low MW high CD). PAM/Soil combinations must show sensitivity to mixing intensity and time

Variable	How does it affect test results?	How is it accounted for?
Soil type	Turbidity reduction best for clay and silt soils and worst for sandy soils	<u>All Tests</u> : Use two soils (clay soil, silty/sandy soil). Soil/PAM combinations must show sensitivity to mixing intensity and time
Dose	Optimal dose typically 1 mg/L. Turbidity reduction poorer at nonoptimal doses	<u>All Tests</u> : Use 3 different doses (0.1 mg/L, 1 mg/L, 10 mg/L). Range of doses must include optimal dose for PAM/soil combination
Temperature	Turbidity reduction poorer at lower temperatures	<u>Jar Test:</u> Ensure all jar tests at same temperature <u>Effluent Test</u> : Compare results to control at same temperature
рН	Optimal pH about 6. Turbidity reduction poorer at nonoptimal pH	<u>Jar Test:</u> Ensure all jar tests at same pH <u>Effluent Test</u> : Compare results to control at same pH
Hardness	Turbidity reduction poorer at low hardness when PAM dose is nonoptimal	<u>Jar Test:</u> Ensure all jar tests at same hardness <u>Effluent Test</u> : Compare results to control at same hardness
TOC/DOC	Turbidity reduction poorer at high organic matter concentrations	<u>Jar Test:</u> Ensure all jar tests at same TOC/DOC <u>Effluent Test</u> : Compare results to control with same TOC/DOC
Mixing intensity	Turbidity reduction poorer at nonoptimal mixing intensity	<u>Jar Test:</u> Use a flash mix speed of 120 rpm and a slow mix speed sufficient to keep floc particles suspended in the water <u>Effluent Test</u> : Use rapid swirling/shaking followed by gentle swirling sufficient to keep floc particles suspended in the water
Mixing time	Turbidity reduction poorer at nonoptimal mixing intensity	<u>Jar Test:</u> Use flash mix durations of 15 sec, 30 sec, 1 min, and slow mix durations of 5 min and 20 min <u>Effluent Test</u> : Use rapid swirling/shaking durations of 15 sec and 30 sec, and slow swirling durations of 1 min and 5 min
Settling time	Turbidity reduction poorer if settling time insufficient	<u>All Tests</u> : Measure turbidities at the end of slow mixing and each minute of settling time until below 30 NTU



Figure 4: Standard jar test equipment



Figure 5: Standard lab flasks

# 5.2 Protocols for Residual Tests

#### Introduction

No approved tests to determine polyacrylamide residual concentrations in treated stormwater discharging from construction sites exist. A residual test that is both reliable and practical is required to assess downstream toxicity risk from treated construction site discharges.

# **Background**

The following potential field tests have been identified based on a review of tests published in the literature and knowledge of PAM properties:

- Turbidimetric Test using Hyamine (Hyamine Test)
- Turbidimetric Test using Soil Addition (Flocculation Test)

# Turbidimetric Test Using Hyamine (Hyamine Test)

The objective of the Hyamine Test (Kang et al. 2013) is to provide an estimate of residual PAM concentration. This test is conducted after the effluent test (Section 5.1). The Hyamine Test uses a cationic reagent that reacts with anionic PAMs to produce insoluble colloids that remain suspended in solution. The turbidity resulting from the colloids is directly proportional to the concentration of PAM in solution.

The most commonly used turbidimetric reagent for anionic PAMs is Hyamine 1622 (benzethonium chloride). Methods based on hyamine have been found to have detection limits of 0.5 to 1 mg/L for dissolved PAM indeionized (DI) water.

In the Hyamine Test, a small volume of treated water is collected and its turbidity measured. The treated water is then centrifuged, and the supernatant is separated for further testing. The supernatant water is reacted with hyamine solution and, after a short reaction time, the sample turbidity is measured again. The PAM concentration is estimated from predetermined PAM calibration curves developed with untreated (blank) water samples. This method is known to be strongly affected by organic carbon (TOC/DOC) present in water samples, the charge density of the PAM used, and the type of soil. The maximum recommended TOC concentration is about 5 mg/L, beyond which there is significant interference from TOC (McLaughlin et al. 2014).

# Turbidimetric Test Using Soil Addition (Flocculation Test)

The objective of the Flocculation Test (Becker et al. 2000) is to provide an estimate of residual PAM concentration. This test is conducted after the effluent test (Section 5.1). The Flocculation Test involves addition of known quantities of a standard soil extract to treated water to see if significant turbidity reductions occur within a set time. The standard soil used is one known to be effectively treated by the PAM (>80% turbidity reduction at optimal dose).

In the Flocculation Test, a sample of treated water is collected and its turbidity measured. Since treated water contains sediment, flocs, and residual PAM, the water is first settled or centrifuged to separate out solids. A known quantity of standard soil extract is added to the supernatant, and the resulting water is mixed, transferred to a settling cylinder, and allowed to settle for <5 minutes. The turbidity is measured after a set time and used to estimate PAM concentration from predetermined calibration curves for the same soil (Becker et al. 2000). If required, dilutions can be performed to increase sensitivity to higher concentrations outside the range of the calibration curves.

# Study Goal

The overall goal of the study is to develop a PAM residual test(s) that is practical to use in the field and has a sensitivity of 1 mg/L.

# **Research Questions**

The following are the key research questions that are addressed by the study:

- Is the residual test practical for use at construction sites?
- o What is the minimal detectable concentration relative to toxicity thresholds?
- How sensitive is the test to changes in PAM concentration?
- o Do the residual tests show that the residual concentrations occur at the optimal dose?
- Is a control required for the test? If so, what type of water is used for the control?
- Is there interference from dissolved constituents in water such as dissolved salts and organic matter? If so, can these interference effects be minimized?
- What environmental factors have a significant effect on test results, and how can they be controlled?
- o How many repeat tests are required to address test variability?
- o If no single test is sufficient, can a combination of tests satisfy the study goal?
- How closely must soils used for calibration curves match soils at the site?

# **Study Variables**

• Table 11 lists the study variables for the residual tests, how they are expected to affect test results, and how each is accounted for in the study design.

The primary objective of the study is to develop a reliable field test(s) for estimating PAM residual concentration in treated water; therefore, a number of different PAMs, soil types, and doses are tested to ensure the test(s) is (are) applicable throughout California:

• PAMs

Use various formulation liquid anionic PAMs. Perform tests on a minimum of 6 PAMs (3 different MWs and 3 different CDs). Include a high MW low CD PAM that provides good treatment and a low MW high CD PAM that provides relatively poorer treatment.

Soils

Use 5 varied soils representative of California soil types. Include a high clay content soil that shows good treatment and a silty/sandy soil that shows relatively poor treatment at nonoptimal doses. Perform jar tests to ensure PAM-soil combination provides effective turbidity reduction at optimal dose (>80%).

Doses

Use 3 different doses (1, 10, 100 mg/L). Concern is with overdosing so doses < 1 mg/L do not need to be tested.

In order to keep the number of tests manageable, the effect of variables such as temperature, hardness, etc., are not tested. However, tests are conducted at two different pH values (pH 6 and pH 9) to account for the potential for higher pH in runoff during periods of active construction. Mixing protocols are based on those determined in the jar and effluent test method development (Section 5.1).

In order to apply the residual tests in the field, PAM manufacturers will be required to provide standard concentration-turbidity "calibration curves" for varying levels of temperature, pH, and

hardness using deionized water and standard soils (various clays and silts). These calibration curves provide an indication of how sensitive treatment is to these variables and how field results should be interpreted in light of this sensitivity. For the Hyamine Test, manufacturer calibration curves are required by performing the Hyamine Test in deionized water without the addition of soil. (See example in Figure 6.)

#### Table 11: Study variables for residual tests

Variable	How does it affect test results?	How is it accounted for?
Formulation	Turbidity reduction depends on molecular weight (MW) and charge density (CD)	<u>All Tests</u> : Use various formulation liquid anionic PAMs. Perform tests on a minimum of 6 PAMs (3 different MWs and 3 different CDs)
Soil type	Turbidity reduction best for clay and silt soils and worst for sandy soils	<u>All Tests</u> : Use 5 varied soils representative of California soil types. Perform jar tests to ensure PAM-soil combination provides effective turbidity reduction at optimal dose (>80%)
Dose	Optimal dose typically 1 mg/L. Turbidity reduction poorer at nonoptimal doses	All Tests: Use 3 different doses (1, 10, 100 mg/L)
Temperature	Turbidity reduction poorer at lower temperatures	<u>All Tests</u> : Ensure temperature fixed for all experiments
рН	Optimal pH about 6. Turbidity reduction poorer at nonoptimal pH	All Tests: Test at two different pH (pH 6 and pH 9) to determine sensitivity
Hardness	Turbidity reduction poorer at low hardness when PAM dose is nonoptimal	<u>All Tests</u> : Ensure hardness fixed for all experiments. Measure hardness using simple field test
TOC/DOC	Turbidity reduction poorer at high organic matter concentrations	<u>Hyamine Test</u> : Ensure TOC/DOC fixed for all experiments. The maximum recommended TOC concentration is about 5 mg/L. Ensure turbidity response is sensitive to addition of PAM (positive linear response to PAM additions with slope comparable to calibration curve for TOC <5 mg/L). Measure TOC/DOC using portable sensor
		<u>Flocculation Test</u> : Ensure TOC/DOC fixed for all experiments. Measure TOC/DOC using portable sensor
Reagent	Reagent must effectively react with PAM to produce insoluble solids	<u>Hyamine Test</u> : Multiple literature studies have shown hyamine to be an effective reagent. No additional reagents considered. Add reagent to supernatant after samples are centrifuged
		Flocculation Test: Not applicable
Mixing intensity	I urbidity reduction poorer at nonoptimal mixing intensity	All Lests: Use same mixing intensity in all experiments. Mixing intensity determined in jar and effluent test method development (Section 5.1)
Mixing time	Turbidity reduction poorer at nonoptimal mixing intensity	<u>All Tests</u> : Use same mixing time in all experiments. Mixing times determined in jar

Variable	How does it affect test results?	How is it accounted for?
		and effluent test method development (Section 5.1)
Settling time	Turbidity reduction poorer if settling time insufficient	<u>All Tests</u> : Measure turbidities at the end of slow mixing and each minute of settling time until below 30 NTU

In order to apply the residual tests in the field, PAM manufacturers will be required to provide standard concentration-turbidity "calibration curves" for varying levels of temperature, pH, and hardness using deionized water and standard soils (clay soil, silty/sandy soil). These calibration curves provide an indication of how sensitive treatment is to these variables and how field results should be interpreted in light of this sensitivity. For the Hyamine Test, manufacturer calibration curves are required for deionized water (see example in Figure 6).

# *Methodology*

# **Hyamine Test**

Equipment: Conical tubes, standard turbidimeter, centrifuge Control: None Core experiments: 6 PAMs x 5 Soils x 3 Doses x 2 pH values = 180 experiments Quality control: Repeat highest and lowest residual experiments for each PAM type = 12 experiments Total number of experiments: 180 + 12 = 192 experiments

# Flocculation Test

Equipment: Standard jar test equipment (see Figure 4) and turbidimeter Control: None Core experiments: 6 PAMs x 5 Soils x 3 Doses x 2 pH values = 180 experiments Quality control: Repeat highest and lowest residual experiments for each PAM type = 12 experiments

Total number of experiments: 180 + 12 = 192 experiments


Figure 6: Example Hyamine Test PAM calibration curves in deionized water (Reproduced from McLaughlin et al. 2014)

# 5.3 Field Water Quality Monitoring

#### **Introduction**

Most field passive treatment studies have focused on turbidity reduction and its dependence on variables such as formulation and mixing conditions. Field data on residual concentration, which directly indicates toxicity risk, and its dependence on site-specific variables such as temperature, pH, hardness, and organic matter content are lacking. Monitoring of critical field variables and their effect on residual concentrations is needed to better assess site-specific toxicity risk.

#### **Background**

Laboratory and field studies have shown that a great number of variables can affect turbidity removal and, as a result, have the potential to affect residual concentrations. In passive application, there is little or no control over most of these variables, and data are lacking on how these variables affect residual concentrations. Given the large number of uncontrolled variables, regulatory standards are likely to be most effective when targeted at measures that apply to the water in sedimentation basins and not at system design or operation where greater flexibility is required to allow for site-to-site and storm-to-storm variation.

Sediment basins enable significant control over final treatment (i.e., site discharge). Laboratory studies have shown that extended settling times can overcome the effects of nonoptimal dosing or mixing on turbidity removal (McLaughlin and Knappe 2018) and therefore may have the

potential to reduce residual concentrations prior to discharge. However, PAM degradation into acrylamide monomer may also be a concern in some waters with high dissolved iron concentrations that are exposed to sunlight over periods of days (Woodrow et al. 2008). Sampling of water in a sand/gravel quarry settling basin showed acrylamide concentrations as high as 0.41  $\mu$ g/L (Touzé et al. 2015), suggesting that exceedance of the EPA MCL of 0.5  $\mu$ g/L may be possible. A recent modeling study identified dissolved iron, soil site pH, and soil bacterial health, among other factors, as major considerations in the potential release of acrylamide monomer in stormwater runoff (Maloney 2021).

The current CASQA construction site sediment basin sizing methodology (CASQA 2019) is recommended until additional field data are collected that may justify modifications. This sizing methodology uses a peak runoff flow rate based on the peak rainfall intensity for the 10-year, 6-hour rain event and a particle settling velocity for a 0.01 mm silt particle. Basin outlets are designed to drain basins within 24 to 96 hours, with the higher limit specified to mitigate vector control concerns.

The field monitoring proposed assumes the following:

- Sediment basins are required at all sites.
- Minimum hold time in sediment basins is 24 h.
- Monitoring and residual tests are required at select sites until sufficient data are collected to justify reducing monitoring at sites deemed low risk.
- Residual tests, once developed, are required at select sites for 5 storms each season until measured residual concentrations are at or below 1 mg/L. The 1 mg/L residual limit is based on the LOEC for *Daphnia magna* (Acharya et al. 2010).

# Study Goals

The goals of the study are the following:

- 1. Monitor residual concentrations and critical site variables at select construction sites with varying soil types.
- 2. Correlate residual concentrations to site variables to identify sites with high toxicity risk.
- 3. Field verify residual test(s) developed in Section 5.2.

### **Research Questions**

The following are the key research questions addressed by the study:

- o Is the residual test(s) practical for field use or are modifications required?
- Does the residual test(s) confirm laboratory results for the relationship between dose and residual concentrations?
- Which field variables have the most impact on residual concentrations?
- o Can data on soil type and field variables be used to identify sites with high toxicity risk?
- Is the current CASQA sediment basin sizing criteria appropriate for minimizing floc and residual discharge?
- o Is there a need to maximize sediment basin hold time to 96 h?
- How is PAM degradation to acrylamide affected by sediment basin hold time?
- o Can visual assessments of flocs and water be used to assess toxicity risk?

### **Study Variables**

Study variables and corresponding monitoring plan for sampled storm events are presented in Table 12. Study variables for field water quality monitoring are presented in Table 13.

#### **Methodology**

### Selected Sites

An estimate of the number of sites required is made assuming that there will be a sufficient number of sites available with varied types of PAM for each soil type. Sites should be selected to accommodate monitoring of a minimum of 3 different MWs and 3 different CDs and 5 varied California soils:

number of sites:  $6 \times 5 = 30$  sites

The number of sites could be reduced where more than one variable occurs within a single site.

Field Measurements/Field Analysis at Selected Sites

- Equipment: Turbidity meter, pH/temperature meter, residual test apparatus (conical tubes, centrifuge; see Section 5.2)
- Control: Only if required for residual tests (see Section 5.2)
- Quality control: Assume 1 additional measurement for each parameter
- Total number of measurements / storm at each site: 4 temperature + 4 pH + 7 turbidity + 3 QC = 18 (see Table 12)

Table	12 <sup>.</sup> Field	water	quality	monitoring	sampling	ner	sampled	storm	event
Iable	12. I ICIU	water	quanty	monitoring	Samping	hei	Sampleu	3101111	event

TIme	Temperature	рН	Turbidity
0 h (end of storm or basin full, whichever	1	1	1
comes first)			
24 h	1	1	2
48 h (if residual at 24 h > 1 mg/L)	1	1	2
72 h (if residual at 48 h > 1 mg/L)	1	1	2
Total	4	4	7

Number of storms/site: 5 storms

Total number measurements/site:  $18 \times 5 = 90$  measurements Total number of measurements at all sites:  $90 \times 30 = 2,700$  measurements

Field Samples/Laboratory Analysis at Select Sites

Equipment: Standard stormwater sampling equipment Quality control: Standard control samples for target constituents Number of samples / storm at each site: 1 hardness + 1 TOC + 1 dissolved iron + 1 acrylamide monomer + standard QC = 4 + standard QC

Number of storms/site: 5 storms

Total number samples/site: 4 x 5 + standard QC = 20 + standard QC

Total number of samples at all sites: 20 x 30 + standard QC = 600 samples + standard QC

#### Table 13: Study variables for field water quality monitoring

Variable	How does it affect field results?	How is it accounted for?
Formulation	Turbidity reduction depends on molecular weight (MW) and charge density (CD)	Require residual monitoring at select sites until sufficient data collected. Monitor a minimum of 3 different MWs and 3 different CDs
Soil type	Turbidity reduction best for clay and silt soils and worst for sandy soils	Require soil texture analysis and jar test at select sites. Monitor 5 varied soils representative of California soil types
Dose	Optimal dose typically 1 mg/L. Turbidity reduction poorer at nonoptimal doses	Not applicable. Dosing cannot be accurately monitored and is assumed optimal based on basin effluent test (see Section 5.1)
Temperature	Turbidity reduction poorer at lower temperatures	Record temperature for each residual test. Ensure selected sites include sites in colder regions of California
рH	Optimal pH about 6. Turbidity reduction poorer at nonoptimal pH. PAM degradation by free radicals highest under acidic conditions	Record pH for each residual test. Ensure selected sites include sites likely to produce low pH runoff (pH < 6)
Hardness	Turbidity reduction poorer at low hardness when PAM dose is nonoptimal	Collect and analyze field sample for hardness at end of hold time in sedimentation basin. Ensure selected sites include sites likely to produce low hardness runoff (< 100 mg/L)
Turbidity	High turbidity may indicate high residual concentrations	Measure at beginning of hold time (end of storm or basin full, whichever comes first) and each residual test
TOC/DOC	Turbidity reduction poorer at high organic matter concentrations.	Collect and analyze field sample for TOC at end of hold time in sedimentation basin
Iron	Interacts with oxygen to create free radicals that degrade PAM to acrylamide monomer	Collect and analyze field samples for dissolved iron and acrylamide monomer at end of hold time in sedimentation basin. Ensure selected sites include sites with high iron soils
Mixing intensity	Turbidity reduction poorer at nonoptimal mixing intensity	Not applicable. Mixing intensity cannot be accurately monitored and is assumed optimal based on effluent test
Mixing time	Turbidity reduction poorer at nonoptimal mixing intensity	Not applicable. Mixing intensity cannot be accurately monitored and is assumed optimal based on effluent test
Settling time	Turbidity reduction poorer if settling time insufficient	Perform residual test at: - 24 h - 48 h (if residual at 24 h > 1 mg/L) - 72 h (if residual at 48 h > 1 mg/L)

# 5.4 Field Sediment Toxicity and Bioassessments

#### Introduction

Polyacrylamide-treated discharges from construction sites have the potential to be toxic to aquatic organisms. There are two potential concerns in aquatic waters: relatively short-term water column toxicity due to discharge of residual flocculant, and longer-term sediment toxicity due to settlement of floc and floc degradation in the vicinity of the discharge location. Although sufficient literature data on short-term aquatic toxicity exists, data on long-term toxicity of floc sediments are lacking, so the ecological significance of treated construction site discharges is largely unknown.

#### **Background**

Most toxicity studies to date have focused on short-term impacts of PAM in the water column. Discharge of dissolved PAM is expected to pose low water column toxicity risk because of rapid dilution in the receiving water, adsorption to suspended solids, and complexation with organic matter that is naturally present in the water. However, discharge of floc particles and the strong adsorption of dissolved PAM to suspended solids can lead to transfer to the sediment compartment and increase sediment toxicity risk (Dell'Ambrogio 2019).

Flocs settled on sediment may form a "blanket" that restricts oxygen transfer to benthic organisms. In addition, degradation of PAM floc releases acrylamide monomers that are toxic. PAM degradation to acrylamide is of greater concern under acidic conditions and high dissolved iron concentrations (Woodrow et al. 2008). The persistence of acrylamide in aquatic systems is unknown. Some studies suggest complete degradation of acrylamide likely occurs within 2 weeks (Brown et al. 1982; Shanker et al. 1990). However, a recent study that monitored a sand/gravel aggregate quarry found acrylamide contamination of a nearby pond and in groundwater (Touzé 2015). Information on the environmental persistence is used for determining whether subchronic (10-day) or chronic (28-to-60-day) whole sediment toxicity tests are appropriate (EPA 2015). Since subchronic (10-d) sediment tests do not involve life cycle exposures or consider effects on reproduction, chronic (28 to 60-day) are recommended (Figure 7). The recommended freshwater test species are the amphipod *Hyalella azteca* and the waterflea *Daphnia magna, Daphnia pulex, or Ceriodaphnia* (EPA 2000).

To evaluate ecological significance, benthic macroinvertebrate (BMI) bioassessments are appropriate because BMI assemblages can be found in most waterbodies and are reliable indicators of biological health. These can be supplemented with bioassessments of benthic algae, which are sensitive to environmental stressors because of their short lifespans and rapid reproduction rate. Ode et al. (2016) provides standard operating procedures for performing BMI and algae bioassessments.

### **Study Goals**

The overall goals of the study are to determine if PAM-treated discharges result in

- 1. Sediment toxicity in receiving waters and, if so, what combinations of chemical type, chemical quantity, soil, receiving water characteristics present the greatest toxicity risks.
- 2. Habitat and population changes to benthic macroinvertebrates and algae.

### **Research Questions**

The key research questions addressed by the study are the following:

- Are passive treatment discharges toxic to benthic and aquatic life?
- Do discharges present the greatest risk for water column toxicity or sediment toxicity?
- o What formulation/soil type characteristics show the greatest toxicity risk?
- o What receiving water characteristics show the greatest toxicity risk?
- How does toxicity relate to floc age?
- Are there long-term habitat changes for BMI and algae (seasonal, annual, or longer)?

### Study Variables

Table 14 lists the variables for the toxicity monitoring study. The study can be phased by looking first at worst-case scenarios. If they are found benign, no further study is needed. Worst-case scenarios can be chosen by selecting, with bias, sites whose variables increase likelihood of finding an impact. For this study, sites with high relative chemical quantity contributions and low receiving water dilution are suggested as initial study sites.

#### **Methodology**

### <u>Sediment Toxicity</u>

Equipment: Follow guidance in EPA (2000)

Reference site: One site upstream of discharge (minimum distance 30 ft)

Quality control: 4 replicates per site

Total number of tests: 6 formulations x 5 soil types x 2 sites/location x 3 times/yr = 180 tests/yr + quality control (the need for multiyear tests should be determined after each year of sampling)

### <u>Bioassessments</u>

Equipment: Follow guidance in Ode et al. (2016)

Reference site: One site upstream of discharge (minimum distance 30 ft)

Quality control: 4 replicates per site

Total number of assessments: 10 locations x 2 sites/location x 4 replicates/site x 3 times/yr = 240 assessments/yr + quality control (the need for multiyear assessment should be determined after each year of sampling)

Variable	How does it affect field results?	How is it accounted for?
Formulation	Floc strength depends on flocculant properties (e.g., molecular weight, MW, and charge density, CD). Toxicity of chemical increases with increasing charge density	Flocculant varies site-to-site. Monitor toxicity at minimum of 6 sites with different formulations (3 different MWs and 3 different CDs). All flocculants must meet minimum NOEC/LOEC toxicity thresholds (see Section 5.3)
Basin efficiency	Poorly performing basin discharges more floc due to improper mixing, a lack of sedimentation, or a mismatch of chemical formulation and soil particle	Because finding sites with floc discharge should be rare, given the conservative guidance presented, site selection should bias toward sites more likely to have impacts. Sites should be screened by the occurrence of high NTU. The residual test and effluent tests developed previously should be used to further confirm discharge of floc. This bias must not be inappropriately extrapolated to sites with lower risk factors.
Relative chemical quantity	Floc strength in discharge depends on the quantity of chemical product applied to the site relative to the drainage area	Because finding sites with floc discharge should be rare, given the conservative guidance presented, site selection should bias toward sites more likely to have impacts. Sites should be screened by the relative quantity applications per discharge drainage should be selected. This bias must not be inappropriately extrapolated to sites with lower risk factors
Soil type	Floc strength depends on soil properties (e.g., texture and type). Toxicity of acidic soils may be higher because of lower pH in runoff	Soil type varies site to site. Monitor toxicity at minimum of 5 sites with different soils representative of California soil types
Temperature	PAM/Floc degradation rate higher at higher temperatures	Measure receiving water temperature prior to toxicity sample collection. Follow guidance in Ode et al. (2016)
рН	PAM/Floc degradation higher at low pH. Treated discharges may change receiving water pH	Measure receiving water pH prior to toxicity sample collection. Follow guidance in Ode et al. (2016)
Dissolved iron	Promotes degradation of PAM to acrylamide in the presence of dissolved oxygen	Measure dissolved iron in samples collected for toxicity analysis
TOC/DOC	Organic carbon may reduce toxicity by reacting with residual or leached flocculant	Measure DOC in samples collected for toxicity analysis

## Table 14: Study variables for sediment toxicity and bioassessments

Variable	How does it affect field results?	How is it accounted for?
Dissolved	Promotes degradation of PAM to	Measure DO in receiving water prior to
oxygen	acrylamide in the presence of	toxicity sample collection. Follow
	iron. Treated discharges may	guidance in Ode et al. (2016)
	change receiving water DO	
Hardness	Floc strength may be affected by	Measure hardness in samples collected
	hardness	for toxicity analysis
Alkalinity	Flocculant may lower pH in low	Measure alkalinity in samples collected
	alkalinity waters	for toxicity analysis
Salinity	Floc properties and flocculent	Measure salinity in receiving water prior
	effectiveness affected by salinity	to toxicity sample collection
Flow	Affects floc accumulation,	Ensure sites selected have varied flow
turbulence/	resuspension, and potential for	characteristics (turbulence levels that
scour in	floc breakdown	affect floc settling and accumulation).
receiving water		Evaluate scour following guidance in
		Ode et al. (2016).
		Select at least 5 "worst-case" sites with
		low scour/turbulence
Dilution	Reduces risk of exposure at toxic	Ensure sites selected have varied
	levels	dilution factors (mixing in receiving
		water). Select at least 5 "worst-case"
		sites with low dilution.
		Focus site selection in N. California
		because of more frequent storms and
		higher risk of sediment basin overflows
Sampling	Floc accumulation and age of	Collect sediment samples for toxicity
frequency	settled floc dependent on	analysis at beginning, middle, and end
	sampling frequency	of season at each site.
		Do not sample at least two weeks after
		any storm event that has generated
		enough stream power to scour stream
		substrates (Ode et al. 2016).
		Collect reference site sediment samples
		at undisturbed site upstream of
		discharge point (minimum distance 30
		ft)
Habitat	Receiving water	Perform BMI and algae bioassessments
assessment		following Ode et al. (2016). Select 10
		locations with low scour and verified floc
		accumulation. Perform assessments at
		one site upstream and one site
		downstream of the discharge point
		Perform 4 replicates per site.
		Consider additional toxicity sample
		collection based on physical function of
		aqualic/semiaqualic life (e.g.,
		amphibians), impacts to seasonal
		species presence, and the timing of



\* Sediment testing may be required when evidence suggests available water column invertebrate test species are not adequate surrogates for risk assessment purposes (see Section 2.2).

\*\* Chronic (life cycle) tests may be required as part of a tiered approach based on results of subchronic 10-d tests (see Section 3.2.1).

Figure 7: Conceptual framework for requesting sediment toxicity data (Reproduced from EPA 2015)

#### 5.5 Implementation Recommendations

Staffing, timing, and phasing are discussed below and summarized in Table 15.

#### Staffing

The studies described largely require experienced researchers, so participation may be limited to consultants, university, and State Water Board staff. The noted exception is the Field Water Quality Monitoring Study. Depending on the success of protocol development, this could be carried out by on-site CGP or IGP compliance personnel. If laboratory analysis is required, sample preservation and shipping need to be covered in training, but this should not be substantially different from the training required to implement sampling of nonvisible pollutants.

### **Timing**

Development of jar tests and residual protocols should proceed immediately. Field Water Quality Monitoring and Field Sediment Toxicity Monitoring and Bioassessment studies will both benefit from standardization of jar tests, effluent tests, and residual tests.

#### **Phasing**

The studies to develop protocols should not be phased. They should address the likely scenarios found in California soils. The field tests can be phased, starting with the highest-risk applications. If found safe or easily mitigated, other less risky scenarios may not require study.

Study	Staffing	Timing	Phasing
Developing protocols for jar	Researchers (consultant or	Immediate	No
and effluent tests	university)		
Developing protocols for	Researchers (consultant or	Immediate	No
residual tests	university)		
Field water quality monitoring	On-site CGP compliance	After protocol	Yes, focus
(using residual testing	personnel; data reported	development	on high-
protocols)	via SMARTS		risk sites
Field sediment toxicity	Researchers (consultant or	After protocol	Yes, focus
monitoring and	university), in coordination	development	on high
bioassessments	with Regional Board staff		risk sites

#### Table 15: Staffing, timing, and phasing of recommended studies

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