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Monitoring for National Pollutant Discharge Elimination System Permit Requirements: Algaecides

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Abstract

In the United States, National Pollutant Discharge Elimination System permits were expanded to include algaecide applications and consequently, additional and focused information was needed to provide water resource managers with requisite data to satisfy permit requirements. In the present publication, literature was strategically reviewed regarding National Pollutant Discharge Elimination System permitting requirements and reliable methods were extracted to fulfill these requirements. Pre- and post-application monitoring can provide data necessary for problem identification, to justify or "trigger" algaecide applications, to confirm algaecide exposures, and to measure responses of target and nontarget species to algaecide treatments. Reliable methods to address monitoring are site and situation specific, although the approach for acquiring data is widely applicable.

Key words: algae, algaecide, environmental regulations, environmental sampling, nontarget species

National Pollutant Discharge Elimination System permit requirements have been in place for application of aquatic pesticides since 2011. These requirements for aquatic pesticides resulted from a court decision vacating a United States Environmental Protection Agency rule stating that such applications are exempt from permitting when performed in compliance with the pesticide product's label (The Nat'l Cotton Council of Am., et al. v. EPA, 553 F.3d 927 (6th Cir, 2009)). In accordance with National Pollutant Discharge Elimination System permits, prior to algaecide applications, submission of a Notice of Intent as well as maintenance of a Pesticide Discharge Management Plan are necessary. The Notice of Intent is submitted to the jurisdictional regulatory agency prior to an algaecide treatment, indicating the intent to apply a pesticide. A Pesticide Discharge Management Plan is a record-keeping tool for the operator under the Pesticide General Permit and is not actually submitted to an agency unless requested. Under National Pollutant Discharge Elimination System permitting, post-treatment monitoring of exposures and responses of target and nontarget species is required (USEPA 2016). These data can be analyzed and interpreted to inform decisions about future algaecide applications in terms of increasing efficacy of algaecide treatments and reducing risks for nontarget species (i.e., adaptive water resource management). The purpose of this paper is to provide a strategic review of methods used to compile data for the Notice of Intent and the Pesticide Discharge Management Plan for the use pattern of algae pest control under the National Pollutant Discharge Elimination System.

Algaecides are often used to mitigate density dependent or density independent algal issues for rapid restoration of water resource uses or to alleviate human health and environmental concerns (CAST 2014). Density dependent problems caused by algae include production of total suspended solids (TSS; Ameel et al. 1997); oxygen depletion (Paerl 1988); clogging industrial, municipal, irrigation, and other water intakes and irrigation emitters; and depressing property values. Density independent issues can include production of taste and odor compounds [e.g., 2-methylisoborneol and geosmin (Graham et al. 2008)] and production of toxins [e.g., ichthyotoxins, neurotoxins, and hepatotoxins (Rodgers 2008)], although production of these secondary compounds can also be density dependent (i.e., correlated with cell density of producing cyanobacteria and algae).

Diagnostic symptoms of an algal issue in a water resource may be readily apparent (e.g., production of taste and odor compounds and toxins), although the algal source for these issues can be difficult to locate or confirm. Problematic algae can be established in the water column (planktonic) or adnate to the sediment or substrate (benthic or periphytic) and may not be uniformly distributed throughout a water resource. Examples of problematic planktonic algae include *Microcystis*, *Planktothrix*, *Prymnesium*, and *Euglena* (Graham et al. 2008, Rodgers 2008), and examples of problematic benthic

algae include *Microcoleus* (formerly *Phormidium*), *Didymospenia*, *Oscillatoria*, *Lyngbya*, and *Nitellopsis* (Graham et al. 2008, Bishop and Rodgers 2012, Kipp et al. 2016). The aforementioned algae often have rapid growth rates (some strains of *Microcystis aeruginosa* have doubling times of <2 d; Wilson et al. 2006) and unique abilities to "engineer" their environment (e.g., production of toxins to gain nutrients from an external environment; Graneli and Hansen 2006). Noxious algae tend to rapidly establish and are often challenging to control as well as difficult to extirpate. Therefore, mitigation decisions need to be made expeditiously and corrective actions have to be prompt to be effective.

Due to the rapid establishment of noxious algal growths or 'blooms', swift action is required, therefore, the appropriate regulatory permits need to be in place prior to the onset of a site-specific problematic density of algae, concentration of taste and odor compound or toxin. Components of National Pollutant Discharge Elimination System permits required for algaecide applications include problem definition, confirmation of algaecide concentrations post-treatment, and measurement of algaecide performance and nontarget species' responses (e.g., SC DHEC 2011). Problem definition is the first step and involves answering the following questions: 1) What is the problematic alga or algal assemblage? 2) Where is the problematic alga located? 3) Why is it a problem? 4) What is the action threshold (e.g., SC DHEC 2011)? The problem definition step can be used to establish a mitigation strategy and focus monitoring efforts following algaecide applications.

Given the focus of this review, all of the algaecides considered in this document are registered by the United States Environmental Protection Agency for use in water resources. In the United States, there are six active ingredients used in algaecides that have been registered and approved at the present time (2016). These include acrolein (USEPA 2008), copper (USEPA 2006), diquat dibromide (USEPA 1995), endothall (USEPA 2005), flumioxazin (MDAR and Mass DEP 2013), and peroxy compounds (MDAR and Mass DEP 2010). Acrolein is a potent biocide that is registered as an algaecide for irrigation canals and reservoirs in the western United States (USEPA 2008). Copper algaecides can be applied as liquid or granular copper sulfate pentahydrate or copper chelated with citrate, gluconate, or ethanolamine. Diquat dibromide is commonly used as an algaecide in aquatic environments with little suspended organic material and sediment as the activity of aqueous diquat decreases from sorption by these ligands (USEPA 1995). Endothall is registered for use as an algaecide in the mono (*N*,*N*-dimethylalkylamine) formulation. Flumioxazin was approved for aquatic use in 2010 and is labeled for treatment of filamentous algae (i.e., *Pithophora* and *Cladophora*) (MDAR and Mass DEP 2013). Peroxy compounds include solid formulations as sodium carbonate peroxyhydrate and liquid formulations composed of hydrogen peroxide, peroxyacetic acid, and acetic acid (MDAR and Mass DEP 2010). These active ingredients have different modes of action and contact times (as a function of fate processes) in aquatic systems, resulting in disparate responses in terms of timing and characteristic response end points of target algae.

Selection of appropriate algal response measures is necessary in order to accurately monitor effectiveness of algaecide treatments. Algae have a variety of chemical and physiological responses to algaecide exposures that may not be initially evident by visual observation (Calomeni and Rodgers 2015). Factors to consider for identification of appropriate algal response measures include: 1) time to algal response, 2) relative abundance of target algae relative to nontarget algae, 3) relative sensitivity of target algae, 4) degree of algal control anticipated or desired, and 5) habitat of algae present (i.e., benthic, periphytic, or planktonic). Specificity of algal response measures is necessary to discern responses of a problematic alga from other nontarget species in a natural assemblage.

In addition to target-organism responses, a crucial aspect of National Pollutant Discharge Elimination System permits and the National Pollutant Discharge Elimination System permitting process is to monitor and minimize effects of algaecides on nontarget species. In the context of algaecides applied to control noxious algae, nontarget species can include nontarget algae, heterotrophic microbes, vascular plants, fish, and invertebrates. Additionally, National Pollutant Discharge Elimination System permitting considers minimizing exposure and potential for harm to humans and other vertebrates.

The overall objective of this manuscript is to provide relevant information and a strategic review of methods that are useful for National Pollutant Discharge Elimination System permit requirements in the context of algaecide applications in freshwater resources. Specific objectives are to review 1) information necessary for problem identification, 2) methods for measuring algaecide exposures, 3) methods for measuring algaecide performance (i.e., target algal response), 4) considerations for monitoring nontarget species' responses (i.e., adverse incidents), and 5) a case study that used monitoring sufficient for National Pollutant Discharge Elimination System requirements.

Problem Identification

Strategic monitoring can provide data sufficient for problem definition including identification of target algae, algae location, identification of the water resource uses that are impacted by the algal issue, and action thresholds. Depending on the site and situation, the algal source may be obvious (e.g., algal 'mats' and 'scums'), as is the case for density-dependent algal issues. Alternatively, in the case of density independent algal issues (e.g., toxins and taste and odor compounds), the source may be relatively difficult to identify. The reason for this is that toxins (e.g., microcystin) and taste and odor compounds (e.g., geosmin and 2-methylisoborneol) may not be contained within an algal cell and are therefore influenced by different fate processes (e.g., dilution, volatilization). In situations that the identity and bounds of the algal issue are difficult to locate, strategic sampling is necessary. Knowledge of water movement within the water resource may provide a general location for where to begin strategic sampling. As algae are typically heterogeneously distributed (e.g., 'layered' at a specific depth, benthic, and floating at the surface) sampling should include an array of depths. An additional line of evidence for putative sources of algal issues include literature evidence that a specific genera or species is a producer of toxins or taste and odor compounds. Table 1 provides a brief overview of some algal genera and species that can be problematic in freshwater resources as well as potential issues caused by growths of these algae.

Once the algal issue and source is identified, treatment areas must be determined. In some situations, there may be one treatment area. For example, a relatively small infestation of *Lyngbya wollei* within a cove may necessitate treatment in this one area alone. Alternatively, multiple treatment areas may be designated. This involves knowledge of the distribution of the algae, the designated water resource uses (e.g., drinking water, recreation, industrial) being influenced by the algal issue and stakeholder involvement (e.g., land owners, taxpayers, business owners, and concerned citizens). Often, infested areas may need to be prioritized based on regulatory restrictions, funding, and competing resource uses (Madsen 2014). These considerations are necessary for treatment in both lotic and lentic systems.

Table 1. Some problematic algal genera and species in freshwater resources

Alga	Potential issue	Type (benthic or planktonic)	Citation
Anabaenopsis	Dermatoxin Hepatotoxin Aesthetic	Planktonic	Graham et al. 2008 Codd et al. 2005
Aphanizomenon	Dermatoxin Hepatotoxin Neurotoxin Taste and odor Aesthetic	Planktonic	Graham et al. 2008 Codd et al. 2005
Aphanocapsa	Dermatoxin Hepatotoxin	Planktonic	Graham et al. 2008
Chrysochromulina	Ichthyotoxin Taste and odor	Planktonic	Isaacs et al. 2013
Cylindrospermopsis	Dermatoxin Hepatotoxin Neurotoxin	Planktonic	Graham et al. 2008
Dolichospermum (formerly *Anabaena*)	Dermatoxin Hepatotoxin Neurotoxin Taste and odor Aesthetic	Planktonic	Graham et al. 2008 Codd et al. 2005
Euglena sanguinea	Ichthyotoxin	Planktonic	Rodgers 2008
Lyngbya wollei	Neurotoxin Dermatoxin Taste and odor Aesthetic	Benthic	Mastin et al. 2002 Foss et al. 2012
Microcystis	Dermatoxin Hepatotoxin Neurotoxin Aesthetic	Planktonic	Graham et al. 2008 Rodgers 2008 Codd et al. 2005
Nitelopsis obtusa	Density (extirpating native species)	Benthic	Kipp et al. 2016
Nodularia	Dermatoxin Hepatotoxin Neurotoxin	Planktonic	Graham et al. 2008
Oscillatoria	Dermatoxin Hepatotoxin Neurotoxin Taste and odor	Benthic	Graham et al. 2008
Planktothrix	Dermatoxin Hepatotoxin Neurotoxin Taste and odor Aesthetic	Planktonic	Graham et al. 2008 Codd et al. 2005
Prymnesium parvum	Ichthyotoxin	Planktonic	Rodgers 2008
Pseudanabaena	Dermatoxin Hepatotoxin Taste and odor	Planktonic	Graham et al. 2008
Synechococcus	Dermatoxin Hepatotoxin Neurotoxin Taste and odor	Planktonic	Graham et al. 2008

Action thresholds are specific to the algal issues and situation. The threshold may be a concentration (e.g., of a toxin or taste and odor compound concentration), algal density, or algal mass that necessitates use of an algaecide based on economic or human health effects. An economic threshold is achieved, for example, when taste and odor compound concentrations exceed those that can be treated to concentrations below human detection using the current infrastructure of the drinking water utility (Huddleston et al. 2015). An example of a human health threshold is for the algal toxin microcystin-LR. In 2015, the United Stated Environmental Protection Agency identified a drinking water health advisory of 0.3 µg/liter (<6 yr of age) to 1.6 µg/liter (>6 yr of age) for microcystin-LR (USEPA 2015). Once an action threshold is approached or exceeded for a site, the mitigation plan is triggered. The action threshold is often less than the guidance or criterion value (or a taste and odor compound threshold) to allow sufficient time to trigger a treatment.

Methods for Measuring Algaecide Exposures

Algaecide exposures to organisms in water resources are influenced by a number of factors including; 1) targeted concentration and form, 2) fate processes (e.g., sorption, hydrolysis, precipitation,

dispersion, and dilution), and 3) water characteristics (e.g., dissolved organic carbon, suspended solids, alkalinity, pH, hardness, and conductivity). Under the Federal Insecticide, Fungicide and Insecticide Act, algaecide labels firmly dictate concentrations that can be applied to an aquatic environment and a specific problematic alga. Within these registered label concentrations, the exposure (e.g., duration and concentration) administered to the problematic algae may differ from the targeted concentration. As in situ algaecide concentrations actually achieved can be affected by several factors, targeted algaecide concentrations are insufficient estimates of exposures, therefore measured concentrations are necessary. Responses of target and nontarget organisms in the field that differ from their expected responses are often due to a difference in algaecide exposure (i.e., targeted exposure relative to actual exposure achieved) among other factors (e.g., relative sensitivity). Without measurement of the actual exposure, there are no data to support the magnitude of deviation from the targeted exposure. In order to adjust future algaecide applications to more effectively control the target algae and decrease risks for nontarget species, measured algaecide concentrations achieved in the field are necessary.

Analytical methods for detection of algaecides are listed in Table 2. Generally, algaecide concentrations are measured as the active ingredient (i.e., acrolein, copper, diquat, endothall, flumioxazin, and hydrogen peroxide). Some professional or contract laboratories are available to analyze algaecide concentrations. Hach kits may be used for the analysis of copper, although these methods have limited resolution (Table 2).

Methods for Measuring Algaecide Performance

To determine the effectiveness of an algaecide application, representative samples of targeted algae are collected. A representative sample captures a realistic 'snapshot' of the problem. For example, if the algal issue is density dependent, a sample is collected that is a comparable density to that of the targeted treatment area. Samples are collected, 1) pretreatment, 2) post-treatment within the treatment site, and 3) post-treatment outside of the treatment site. Comparisons of pretreatment and post-treatment (i.e., within treatment site) results provide data regarding responses of the alga, decreases in taste and odor compound concentrations, or declines in toxin concentrations following the algaecide application. Comparisons of pretreatment and post-treatment (i.e., outside of treatment site) algal responses provide data regarding what would have happened if the algaecide application were not used or the consequence of 'no action.'

Adaptive cluster sampling is commonly employed for algal sampling since algae tend to be heterogeneously distributed. This sampling technique involves collection of initial random samples. From these initial random samples, additional sampling is focused in proximity

Table 2. Analytical techniques for algaecides applied in the United States

Dominant ingredient	Label concentrations	Technique and analytical equipment	Method detection limit	Method	Citation
Acrolein	Typical is 8000–15000[a] µg/liter	Purge and trap gas chromatograph	0.7 µg/liter	603	USEPA 1996
		High-performance liquid chromatography with ultraviolet detection	30 µg/liter	8316	USEPA 1994a
Copper	100–2000[bc] µg/liter as copper	Inductively coupled plasma-atomic emission spectrometry	5.4 µg/liter	200.7	USEPA 1994b
		Flame atomic absorption spectrometry	10 µg/liter	NA	APHA 2012
		Graphite furnace atomic absorption spectrometry	1 µg/liter	7010	USEPA 2007
		Hach method 8506 and 8026	40 µg/liter	3500 C or E	
		Hach method 10238	100 µg/liter	Bathocuprione Method adapted from Standard Methods	
Diquat	180–370[d] µg/liter as diquat cation	Liquid solid extraction and high performance liquid chromatography with ultraviolet detection	0.72 µg/liter	549.2	USEPA 1997
Endothall	50–3000[e] µg/liter endothall acid	Aqueous derivatization, liquid-solid extraction and gas chromatography with electron-capture detection	11.5 µg/liter	548	USEPA 1990
Flumioxazin	100–400 µg/liter as flumioxazin[f]	Gas chromatograph/mass spectrometry	9 µg/liter		Ferrell and Vencill 2004
Hydrogen peroxide	300–10,200[g] µg/liter as hydrogen peroxide	I^{-3} spectrophotometry	200 µg/liter	NA	Kinley et al. 2015 Klassen et al. 1994

NA (not applicable).
[a]United States Environmental Protection Agency (USEPA) (2008), Reregistration.
[b]Applied Biochemists Specimen Label, Copper Sulfate Crystals, Germantown, WI.
[c]Applied Biochemists Specimen Label, Clearigate, Germantown, WI.
[d]Syngenta, Reward, for suppression of algae, Greensboro, NC.
[e]United Phosphorus, Inc., Hydrothol 191, King of Prussia, PA.
[f]Valent Specimen Label, Clipper Walnut Creek, CA.
[g]Applied Biochemists Specimen Label, Phycomycin SCP, Germantown, WI.

of a sample or samples containing the alga of interest (Thompson 1990, Isaacs et al. 2013). Planktonic algal samples are collected with Kemmerer, Niskin/ Nansen, or Van Dorn sampling devices (APHA 2012), while benthic algae samples are collected with an Eckman, Ponar or Petersen Dredge (Lind 1974, Wetzel and Likens 2000), or rakes (Kenow et al. 2007). Initial identification of the problematic algae is important to characterize the problem source. To identify the target algae, light microscopy is often used. There are professional or contract laboratories that will identify algae; although, there are also general taxonomic keys such as Prescott (1984), Whitford and Schumacher (1984), Wehr (2011), Dillard (2008), and Wehr (2015) available in print. There are also specific taxonomic keys for algal groups including cyanobacteria (Komárek et al. 2014) and dinoflagellates (Carty 2014). Additionally, many universities and other sources make taxonomic keys publically available on the internet [Greeson 1982, Schneegurt 2002 (cyanobacteria), Shayler and Siver 2006, Spaulding et al. 2010 (diatoms), Baker 2012].

Following an algaecide application, algae manifest different morphological and physiological responses. An important consideration for monitoring studies is the timing after treatment to algal response. Depending on the algae and algaecide formulation applied, the time to manifest a response may differ. Because of the robust structure of algae such as *Lyngbya* (i.e., thick mucilage) and *Nitellopsis,* (i.e., calcium carbonate incrustation) 7 d or more may be required to observe a response (Bishop and Rodgers 2012). For some planktonic algae, as little as 2 to 4 d may be sufficient (Calomeni et al. 2014).

The relative abundance, sensitivity, and magnitude of control of target algae inform the use of individual (i.e., cell density of a specific algal genera or species) or aggregate (i.e., mass, chlorophyll *a* concentration) algal response measures. Individual measures utilize light microscopy to discern the viability of an algal cell on a cell-by-cell basis. By these means, responses of the target alga can be discerned from the responses of nontarget algae. Alternatively, aggregate measures quantify the response of an assemblage. To ensure that the algal response measured is a function of a decrease in targeted algal density, light microscopy is used to corroborate aggregate response measures. In situations dominated by the target alga, aggregate measures of algal responses may be sufficient (Calomeni et al. 2014, Calomeni and Rodgers 2015).

Additionally, algal location can influence algal response measures used and expression (i.e., units) of those measures. Because of the distribution of planktonic algae, response measures are typically expressed per unit volume. For algae associated with the benthic environment, units are expressed per unit mass or surface area. Common planktonic algal response measures include cell density and chlorophyll *a* concentration. Cell density of a target alga is measured using a counting chamber such as a haemocytometer (Rodgers et al. 2010), Palmer-Maloney (Palmer and Maloney 1954), or Sedgewick-Rafter Chamber (Lind 1974) accompanied by light microscopy. If algal samples need to be concentrated prior to enumeration, samples can be centrifuged, filtered (Fournier 1978), or the Utermöhl method can be used with an inverted microscope. Chlorophyll *a* concentrations can be measured using fluorometric or photometric methods (APHA 2012).

Benthic algae can be quantified by scraping a known surface area of an artificial or in situ substrate (Lind 1974). Artificial substrates include etched glass slides (Sládeček and Sládečková 1964), unglazed porcelain tiles and string. Advantages of artificial substrates include decreasing sample variance, although response measures using artificial substrates are relative because the same algae that inhabit substrates in an aquatic environment may not colonize these artificial surfaces. In situ substrates can include rocks, macrophytes, and tree branches. Algal parameters measured using in situ substrates are often associated with relatively high variance, requiring larger sample sizes or additional sample replicates.

Once the algal assemblage has been sampled, it can be analyzed for percent relative abundance (Hunter and Russell-Hunter 1983), species richness, biovolume, biomass, or chlorophyll *a* concentration (APHA 2012). Measurements of percent relative abundance and species richness, in the context of an algaecide application discern shifts in an algal assemblage. Biovolume, biomass, and chlorophyll *a* concentration is typically expressed as ratios using the mass of periphyton or surface area. Using algal responses as ratios with mass may mask responses of the target algae if the mass of the periphyton is consequently altered as a result of the algaecide exposure. Ratios of algal responses with surface area using in situ substrates may mask target algal responses as a result of in situ variability. Weitzel (1979) provides a review of the applications and some limitations of methods used to measure attached algal parameters. Ultimately, multiple algal response measures are likely necessary and a lines-of-evidence approach can discern shifts in the target algae post-treatment. The greatest weight in this approach should be focused on a decrease in the problematic constituent (e.g., algal density, microcystin concentrations, taste and odor compound concentrations, TSS) and will be site-specific.

Considerations for Monitoring Nontarget Species Responses

Following an algaecide application, monitoring for evidence of adverse incidents is required. An understanding of the fate of algaecides can be used to focus data collection. Aspects of fate that may influence nontarget species exposures include the fugacity of active ingredients, exposure durations, and final products (e.g., carbon dioxide, water, copper, oxygen). Acrolein, copper, diquat, endothall, flumioxazin, and hydrogen peroxide have distinctly different fates in aquatic environments. Margins of safety are often used to approximate potential risks for sensitive nontarget species in treated areas. The margin of safety in this context is the difference between the concentration of algaecide applied to control algae in the field and the algaecide concentration that elicits an adverse effect of nontarget species (Murray-Gulde et al. 2002).

Acrolein is a relatively labile organic compound in aquatic environments with biotransformation half-lives of less than 4 d (Callahan et al. 1979). Hydration to β-hydroxypropionaldehyde followed by biological degradation and volatilization (Henry's rate coefficient $=5.66 \times 10^{-5}$) are the major removal pathways for acrolein in aquatic environments (Mabey et al. 1982). Adverse effects for nontarget aquatic species from acrolein exposures are expected to occur rapidly (hours to days) after an application. The 96-h LC_{50} for *Pimephales promelas* is 14 µg acrolein/liter (Holcombe et al. 1987). With application rates of 7.6–14.3 mg acrolein/liter (Magnacide H Herbicide, Alligare, LLC Opelika, AL), acrolein is likely to cause adverse effects for fish; therefore, aquatic use is restricted to irrigation systems. Adverse effects to humans from acrolein exposures have been reported following accidental exposures (USEPA 2008).

Half-lives for copper in the aqueous phase can range from minutes to days (Button et al 1977, Anderson 2003, McNevin and Boyd 2004, Liu et al. 2006). Based on results from conservative laboratory toxicity tests, margins of safety for nontarget species can be minimal, therefore caution is required in the use of copper-based algaecides. Predicted 96-h LC_{50}s in static nonrenewal toxicity tests were between 1180 and 3000 µg Cu/liter for the nontarget alga *Pseudokirchneriella subcapitata* (3×10^6 cells/ml; Calomeni et al.

2014), 34 and 159 µg copper/liter for *Ceriodaphnia dubia* (< 24 h old; Murray-Gulde et al. 2002) and between 201 and 863 µg copper/liter for *P. promelas* (< 24 h old; Murray-Gulde et al. 2002). Generally, nontarget species (*C. dubia* and *P. promelas*) are less sensitive to chelated copper formulations relative to copper sulfate pentahydrate. However, fish (*P. promelas*) may be more sensitive to copper-based algaecides formulated with an adjuvant (d-limonene) (Murray-Gulde et al. 2002).

Copper has a lithic biogeochemical cycle and will partition to the sediment phase following treatment. Sediment characteristics such as percent organic matter (Besser et al. 2003, Milani et al. 2003), acid-volatile sulfides (Allen et al. 1993), cation exchange capacity (Chapman et al. 1999), and particle size distribution (Höss et al. 1997) influence the bioavailability of copper sorbed to sediments. Generally, the bioavailability of copper decreases in sediments with high organic matter, sulfides, and clays because of the strength of these ligands for binding copper. As the bioavailability of copper in sediments is dependent on the aforementioned factors, measurement of sediment copper concentrations alone are often inaccurate indicators of copper bioavailability. The sediment quality triad approach provides multiple lines of evidence to indicate the potential for adverse effects and involves analytical measures of metal concentration to measure contamination, bioassays using sensitive laboratory organisms to measure toxicity, and in situ biological assessments to measure benthic community alterations (Chapman 1990).

Diquat strongly and rapidly sorbs to sediments and organic material in aquatic environments (USEPA 1995). Once diquat has sorbed to organic materials and sediment, it is not considered bioavailable (Ahrens and Edwards 1994). Because of the rapid loss of diquat through sorption with these materials, studies report that diquat achieves nondetect concentrations within 4 to 12 d after application (Frank and Comes 1967, Yeo 1967). Diquat is degraded slowly by biodegradation. Aqueous aerobic and anaerobic half-lives in microcosm experiments for diquat were measured as 32 and 50 d, respectively (Simsiman et al. 1976). Ninety-six–hour static nonrenewal toxicity tests yielded LC_{50}s of 0.75, 3.9, and 4.9 mg/liter as diquat cation for 8- to 10-d old walleye, 6- to 8-d old small mouth bass, and 9- to 13-day old largemouth bass, respectively (Paul et al. 1994). Based on conservative laboratory toxicity tests, concentrations of diquat cation that would elicit adverse effects to nontarget species (e.g., some invertebrates and fish) are approximately an order of magnitude greater than concentrations applied in the field to control algae; therefore, a margin of safety is present (Geer et al. 2016).

Endothall is expected to remain in aquatic environments for approximately 7 d after application (Reinert and Rodgers 1987). Biotransformation and biodegradation play major roles in the fate processes for endothall (Reinert et al. 1986). A biotransformation half-life of 8.35 d was calculated from a laboratory study using water collected from a reservoir (Reinert et al. 1986). Endothall is a relatively labile constituent in aquatic environments with degradation products of carbon dioxide and water. The amine salt, Hydrothol 191 (United Phosphorus, Inc., King of Prussia, PA) is applied for the control of algae at concentrations ranging from 0.05 to 3.0 mg endothall acid/liter. At these concentrations, margins of safety are anticipated to be limited for some fish, invertebrates, and nontarget algae (USEPA 2005).

Flumioxazin is a relatively new (2010) active ingredient in herbicides although the label specifies use for filamentous green algae. This product has a very specific mechanism of action as it inhibits the enzyme protoporphyrinogen oxidase. In studies conducted with plants, the inhibition of protoporphyrinogen oxidase in conjunction with light energy causes the production of reactive oxygen species (MDAR and Mass DEP 2013) that oxidize cellular components. Flumioxazin concentrations dissipate rapidly in the aqueous environment with hydrolysis, photolysis, and biological dissipation half-lives ranging from 0.01 d (hydrolysis at pH 5) to 15 d (aerobic biodegradation). Concentrations of flumioxazin applied to aquatic systems range from 200 to 400 µg flumioxazin/liter. Ninety-six to 48-h laboratory toxicity experiments yielded LC_{50}s for fish (*Oncorhynchus mykiss* (Walbaum, 1792) (Salmoniformes: Salmonidae) and *Lepomis macrochirus* Rafinesque, 1810 (Perciformes: Centrarchidae)) and an invertebrate (*Daphnia pulex* Leydig, 1860 (Cladocera: Daphniidae)) exposed to flumioxazin that ranged from 5500 µg/liter (*D. pulex*) to 21,000 µg/liter (*L. macrochirus*) (MDAR and Mass DEP 2013). Incorporating concentrations of flumioxazin applied in the field and toxicity data, margins of safety are likely to exist for nontarget species (e.g., *O. mykiss*, *L. macrochirus*, and *D. pulex*).

Hydrogen peroxide when applied as an algaecide will rapidly oxidize organic material and also form oxygen and water. Peroxide products are applied from 1–22 mg hydrogen peroxide /liter. Using conservative laboratory toxicity experiments, 4 and 7 d LC_{50}s for an invertebrate (*C. dubia*) and a green alga (*Psudokirchneriella subcapitata*) exposed to sodium carbonate peroxyhydrate are within the concentrations applied in the field (i.e., 1–10 mg hydrogen peroxide/liter as sodium carbonate peroxyhydrate). The value of LC_{50} ranged from 1.3 mg hydrogen peroxide/liter for *C. dubia* (4 d), approximately 7 mg hydrogen peroxide/liter for *P. subcapitata* (7 d), and 22.3 mg hydrogen peroxide/liter for less than 24-h old fathead minnow fry (4 d) (Geer et al. 2016). The authors mention that these laboratory toxicity experiments likely provide conservative measures of concentrations at which organisms are anticipated to respond. A margin of safety could exist for *C. dubia* and *P. subcapitata*, depending on site-specific factors, including target algae as an active site for oxidation by hydrogen peroxide, the initial concentration of sodium carbonate peroxyhydrate applied, the actual exposure concentration of hydrogen peroxide achieved, the proximity of the organisms to the exposure, and the age of the organism(s) (Geer et al. 2016).

Case Study

The following case study of algal issues in a potable water supply provides an example of the site-specific monitoring approach outlined above. The approach used at Lake John Hay, IN, to manage putative taste- and odor-producing algae incorporated sufficient monitoring to fulfill National Pollutant Discharge Elimination System permit requirements. At this site, the taste and odor (i.e., geosmin and 2-methylisoborneol) issues caused by the problematic algae were readily apparent although the source was challenging to identify. Identification of the algal-related issue stemmed from drinking water customer complaints; therefore, the likely source of algal-related issues was in close proximity to the drinking water intake.

Identification of putative taste- and odor-producing algae began by collecting samples at different depths within the section of the reservoir that directly supplies the drinking water intake. Some algae can control their position in the water column (with aerotopes or are motile) and can be located meters below the water surface. This was the case for the two planktonic algae, *Planktothrix* and *Chrysochromulina* at this site that were identified as potential sources of the taste and odor compounds. These algal densities were greatest at approximately 3.7-meter depth.

Following identification of genera and location of problematic algae, an effective algaecide was identified. A laboratory algaecide efficacy experiment was conducted using a series of algaecide concentrations and site collected water containing a representative sample

of the problematic algae. The objective of this experiment was to determine the lowest algaecide concentration that will decrease target algal densities relative to the untreated control and will not elicit a greater algal response with a higher concentration. A copper-based algaecide chelated with gluconate and citrate (Algimycin PWF, Applied Biochemists, Germantown, WI) was applied at 0.2 mg/liter as copper based on results of the laboratory algaecide efficacy experiment. The preliminary laboratory experiment provided defensible data that were used to inform the concentration and formulation used at the field site. Following the algaecide application, algal responses in terms of cell density and taste and odor compound concentrations were measured. Densities of the problematic algae decreased by approximately 90% and geosmin and 2-methylisoborneol concentrations decreased by more than an order of magnitude (50 to > 5 ng/liter) (Isaacs et al. 2013). No adverse effects to nontarget species were observed following treatment.

Following this initial treatment, more refined site-specific action thresholds for algaecide treatments were defined. Action thresholds in this case used multiple lines of evidence as targeted algal cell densities as well as taste and odor compound concentrations were monitored. For this site, cell densities at approximately 40,000 to 50,000 cells/ml (presented as the sum for *Planktothrix* and *Chrysochromulina*) of the target algae collected from 3.7-meter depth corresponded with problematic concentrations of geosmin and 2-methylisoborneol. Site-specific action thresholds in terms of taste and odor compound concentrations can be calculated using a mathematical equation (1) and site-specific parameters. The site-specific parameters include the human detection concentration for geosmin and 2-methylisoborneol (~5–10 ng/liter) and the drinking water facility's removal efficiency for taste and odor compounds. Using conservative assumptions for these parameters may provide sufficient time prior to treatment to implement an algaecide application.

$$T = \frac{\mathrm{HD}}{[1-(\mathrm{PR}/100\%)]} \quad (1)$$

where T is site-specific action threshold (concentration, ng/liter), HD the human detection for geosmin and 2-methylisoborneol (5–10 ng/liter), PR is the percent removal efficiency (%) for the treatment facility.

Characteristics of this case study that are universally applicable include the general approach used. This approach included identification of the algal issue, identification of an effective algaecide, post-treatment monitoring, and identification of action thresholds for future treatments. Characteristics of this case study that were unique included the problematic algae (i.e., *Planktothrix* and *Chrysochromulina*), their location at 3.7 meters depth in the vicinity of the drinking water intake and the effective algaecide treatment (i.e., Algimycin PWF applied at 0.2 mg copper/liter).

Conclusions

This manuscript provides a strategic literature review of several available methods and considerations needed to address National Pollutant Discharge Elimination System permitting requirements in the context of algaecide applications. National Pollutant Discharge Elimination System permitting requires monitoring to address problem formulation, indicators for future treatments (i.e., action thresholds), species responses, and nontarget species responses. Following an algaecide treatment, monitoring is conducted to characterize exposures and responses of target and nontarget species. Methods are available with sufficient detection limits to measure algaecide concentrations within recommended label concentrations. There is no one standard procedure for monitoring algal responses that will be appropriate for all situations. Monitoring methods will be site-specific depending on the alga, algaecide formulation applied, and water resource uses (e.g., fishing, boating, and potable water). Some algaecide formulations have great margins of safety for nontarget species while others have limited to no margin of safety. Therefore, an understanding of intended or designated water resource uses is necessary. Algaecide applications using sufficient product (without excess) necessary to control the problematic algal species will likely reduce risks for nontarget species and decrease cost for a treatment. Algaecide applications in the field require an iterative process or adaptive water resource management in which application decisions can be altered for future treatments to enhance algaecide efficacy and reduce risk to nontarget species. Monitoring in this context provides the knowledge needed to inform that iterative process.

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