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Endothall, triclopyr and fluridone granular release profiles under static and aerated water conditions

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ABSTRACT

Granular formulations have been successfully used in aquatic weed management programs for many years; however, information about the characteristics and environmental parameters affecting herbicide release from granules have not been adequately described. Herbicide release from the granule is critical to ensure that in water concentrations reach the critical concentration for the correct concentration exposure time (CET) required for weed control. The release of fluridone from four solid formulations (Sonar Q, Sonar PR, Sonar ONE, and Sonar SRP) was evaluated under static and aerated conditions Similarly, the release characteristics were evaluated for the solid formulations of triclopyr (Renovate OTF) and the dipotassium salt of endothall (Aquathol Super K). Under static conditions, the amount of time required to release 50% (RT_{50}) of fluridone from Q (27 d) and SRP (72 d) formulations were different, but no differences were found between the Q, ONE (39 d), and PR (37 d) formulations. Triclopyr and endothall formulations had RT_{50} values of 12 and 86 h, respectively, under static conditions. Aeration decreased the RT_{50} of fluridone from the Q formulation from 27 d (static) to 16 d (aerated) and from 72 d to 7 d for the SRP formulation. The endothall formulation had an RT_{50} of 86 h in static tests but only 1 h under aerated conditions, and release of triclopyr decreased from 12 h (static) to 1 h (aerated). The very significant impact of gentle water mixing by aeration on herbicide release from solid formulations in these studies have not been previously reported and indicates how little is known about the influence of environmental factors on granular herbicide behavior in the aquatic environment.

Key words: herbicide residue, release time (RT), slow release formulation

INTRODUCTION

Many aquatic herbicides are sold in both liquid and granular or pelleted formulations. Fluridone, triclopyr, and endothall are available in both formulations and widely used in aquatic plant management. Solid formulation carriers are typically clay, but polymers and other materials are also used. They are made by mixing the herbicide with the carrier or spraying it on the outside of the carrier. The release of herbicides from granules depends upon the type of carrier and the manner in which the herbicide is mixed with it. The exact method and specifications of the manufacturing process are proprietary, so more detailed information is unavailable. Hereafter, the term "granule" will be used to generally describe any solid formulation of herbicide, and the term "granule or pellet" will be used when a more specific designation is required.

Registrants that produce granular herbicides often market their products as offering unique and different release profiles, yet there is little independent scientific information regarding herbicide release from these solid formulations. Release characteristics of aquatic herbicides are important because successful plant management is dependent upon maintaining a lethal dose of herbicide in the water for the proper length of time to kill the targeted plant. For example, hydrilla [*Hydrilla verticillata* (L.F. Royle)] biomass was reduced by 85% after 48 h of exposure to 2 mg acid equivalent (a.e.) L^{-1} of endothall or after 24 h of exposure to 3 to 5 mg a.e. L^{-1} (Netherland et al. 1991), while hydrilla requires more than 30 d of exposure to > 12 µg ai L^{-1} of fluridone to achieve a similar reduction in biomass (Netherland and Getsinger 1995). It is important to know how quickly the herbicide releases into the water column from granular formulations in order to know if these critical concentrations will be reached after treatment. For instance, a fast-acting, short-lived contact herbicide would need to be released quickly to ensure that a lethal concentration is maintained during the relatively short exposure time required for control. However, it might be beneficial to have a slow-release granule for a slow-acting, enzyme-inhibiting herbicide so that a lower concentration is maintained for a longer period of time. Much is known regarding aquatic herbicide dilution and degradation in the water, so an understanding of the release characteristics of granular and pelleted herbicides would make concentration/exposure predictions more reliable.

Previous research has evaluated herbicide dissipation and residue stability from liquid treatments in water (Frank and

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Comes 1967) or focused on the interaction between concentration and exposure time (Netherland and Getsinger 1995, Netherland et al. 1991). Surprisingly, few published studies have been conducted that describe the impact of water flow on herbicide release from granules. Reinert et al. (1985) examined the release of endothall from a granular clay formulation under agitation on a shaker table. Under these "agitated" conditions using natural lake water, they found that ca. 50% of the herbicide had released after 3 to 4 h. Although these studies were performed on a formulation that is not commercially available today, it does provide insight into the speed at which herbicide can release under "agitated" or moving water conditions. However, it should be noted that these authors defined this mild agitation as "static conditions". Van and Steward (1986) maintained experimental fluridone "fibers" under static conditions, but the water was gently stirred just prior to taking samples for analysis. Although these studies are useful for demonstrating total potential release, they do not provide quantitative information regarding how water circulation affects the release rate.

Granular herbicide release studies have utilized various methods to stir or mix the water (Mossler et al. 1993, Netherland and Stewart 1994, Van and Steward 1986). For example, Mossler et al. (1993) used "granular" or "pellet" formulations of fluridone that were placed in tubes and agitated on a linear shaker. They reported that there were significant differences in release of fluridone between the two formulations under mild agitation, but that the difference was reduced under vigorous agitation. Complete release of fluridone under mild agitation occurred after ca. 400 h, whereas vigorous agitation resulted in 100% release of fluridone from both formulations by the completion of the 72 h study. Mossler et al. (1993) also cited a personal communication with D. Tarver, which states that slower release of fluridone from Sonar SRP pellets compared to 5P pellets occurs because "the clay binds to itself more tightly than the clay used to make the 5P pellet". These results clearly suggest that the formulation components and water circulation (agitation) greatly influences herbicide release from pellet formulations.

Perhaps the most in-depth study of herbicide release from granules to date was performed by Wilkinson (1964) on various formulations of 2,4-D. Granular 2,4-D formulations have been used for aquatic weed control since the early 1950's (Oborn et al. 1954). Wilkinson evaluated the effects of carrier (clay type), temperature, sediment presence, formulation (2,4-D salts), pH and found that these factors interacted to create unique release profiles, and, in some cases, less than complete release (< 100% recovery). Complete release occurred after as little as several hours or required more than a week. Wilkinson's methods do not mention water circulation, so these experiments were likely performed under static conditions. A possible limitation of this study was the utilization of the cucumber root bioassay. Plants in this assay were exposed to the experimentally treated water and the growth effects compared to results achieved from exposing plants to known concentrations of the herbicide. Although this assay is effective at detecting the impact of treated water on plant growth, instrumental analysis provides much more accurate data. It is possible, particularly in the pH study, that 2,4-D released from the granule, but its form changed due to water chemistry, and the assay could not determine this. The root bioassay is unable to detect if the 2,4-D was in the acid form or remained as the ester. This is a similar problem experienced in our preliminary studies which removed 2,4-D as a candidate for experimentation due to the lack of a quick and reliable method to differentiate between the herbicide residues via immunoassay. Although kits are available for each salt of 2,4-D (amine, acid, ester) these react differently and the results are unreliable if a sample has mixed forms.

The objective of these studies were to determine the release of selected aquatic granular herbicides under static conditions, and compare these results to release under "water circulation" provided by aeration.

MATERIALS AND METHODS

Approximately 500 mg each of fluridone as Sonar Q[1], Sonar PR[1], Sonar ONE[1] and Sonar SRP[1] (hereafter referred to as Q, PR, ONE, and SRP respectively), 650 mg of endothall[2], and 900 mg of triclopyr[3] granules were broadcast over the surface of 15 L of tap water in 19 L plastic buckets resulting in theoretical concentrations of 2, 19, and 8 mg ai L^{-1} of fluridone, endothall, and triclopyr, respectively. The concentrations of herbicide applied to each bucket varied slightly because the solid formulations were taken from the containers and not cut to exact weights in order not to disturb the release profiles. Each treatment was replicated four times. Buckets were sealed with clear plastic wrap secured with a rubber band to prevent evaporation and kept in a darkened temperature controlled room maintained at 20 ± 1 C. Buckets were also covered with black plastic garbage bags to prevent exposure to ambient light.

Samples of treated water were collected periodically over ca. 30 d (endothall and triclopyr) and ca. 90 d (fluridone). Twenty milliliters were taken from the middle of the buckets halfway down the water column and placed in plastic 30 ml scintillation vials which were frozen for later chemical analysis. The volume of the water was replaced after each sampling period with fresh water to maintain a constant volume of 15 L. After final water samples were collected, all granules were crushed using a PVC pipe with a metal flange attached to the end. Three separate grindings were performed, with a 2 to 5 min "rest" between each grind and a final 5-min rest before another 20 ml water sample was collected. This crushed value, or final herbicide concentration, was compared to the concentration applied (based upon the exact weight of granules applied to each bucket) to determine the total amount of herbicide still bound to the granules. All water samples were converted to percent herbicide in the water based on the initial weight of herbicide applied to each bucket.

Four replications each of fluridone as Sonar PR and ONE were also set up, with all granules crushed at the beginning of the experiment and water samples collected over 90 d. This study was designed to determine if any degradation occurred under these experimental conditions and to

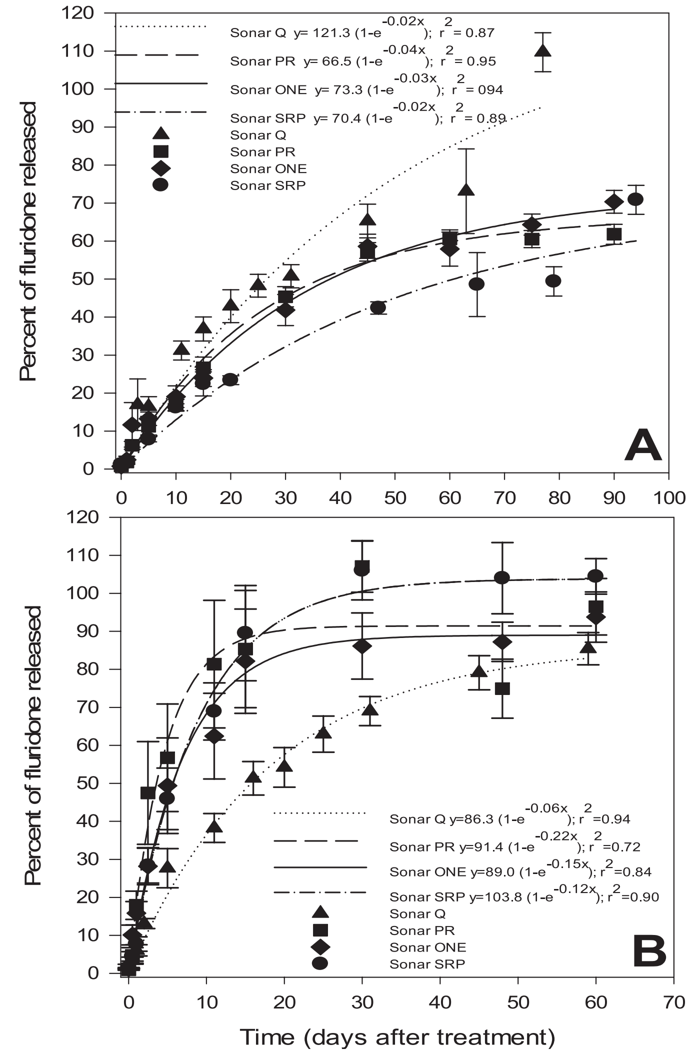

Figure 1. Flurdione release from Sonar Q, PR, ONE, and SRP granules maintained under static conditions for 90 d (A) and under aerated conditions for 60 d (B). Symbols and error bars represent mean ± standard error of 4 replications.

determine if the grinding process resulted in 100% release of the herbicide. Water sample collection and all other procedures were identical to all other granule studies.

Herbicide concentrations in water samples were determined by the ELISA method of immunoassay. Endothall and triclopyr were analyzed utilizing kits manufactured by Strategic Diagnostic Inc.[4], and fluridone kits were manufactured by Envirologix[5]. The limit of quantification (LOQ), or the lowest concentration of a herbicide that will yield a positive test result, is 7 μg ai L^{-1}, 0.1 μg ai L^{-1}, and 0.08 μg ai L^{-1} for endothall, triclopyr and fluridone kits, respectively.

In a companion study, gentle water circulation in the buckets was examined to determine effects on herbicide release. Water circulation was created using aquarium pumps delivering a flow rate of air at 60 mL min^{-1} through an air stone secured halfway down the side of each bucket. Preliminary tests revealed that this flow rate was sufficient to distribute dye throughout the water column within 5 to 10 min, but was not strong enough to physically disturb the granules. The precise amount of water circulation caused by this aeration cannot be determined. All sampling methods for this study were identical to that discussed for the static experiments except the endothall and triclopyr experiments were sampled for ca. 4 d and fluridone for ca. 60 d. These shorter sample periods were used because preliminary sampling showed a much more rapid herbicide release compared to release under static conditions.

Nonlinear regression analysis was used to determine herbicide release of all formulations. The equation used is an exponential rise to max, which provides the generalized equation $y = a \times (1 - e^{-bx})$. This equation is appropriate because the maximum release expected from the granules is 100%. A range of RT (estimated time required to release 25, 50, 75, and 95% of the herbicide) values were calculated for each herbicide from the regression equation.

Table 1. Estimated days required for 25, 50, and 95 percent release of fluridone from granules maintained under static and aerated conditions.

Herbicide	RT_{25}	RT_{50}	RT_{95}	Crushed Value[1]
Static				
Q	12 (9–15)[2]	27 (21–33)	68 (48–88)	108 (98–118)
ONE	14 (11–17)	39 (33–46)	N/A[3]	83 (79–87)
PR	12 (10–15)	37 (31–42)	N/A	78 (76–80)
SRP	24 (16–32)	72 (50–93)	N/A	100 (89–111)
Aerated				
Q	7 (5–8)	16 (12–21)	N/A	96 (90–112)
ONE	2 (1–4)	6 (3–9)	N/A	90 (80–100)
PR	2 (1–2)	4 (2–6)	14 (9–17)	78 (70–86)
SRP	3 (2–3)	7 (5–8)	16 (10–23)	99 (89–109)

RT = release time
[1]Mean percent of total concentration recovered after crushing granules.
[2]Mean (95% Confidence Interval).
[3]N/A = Value could not be calculated from the regression equation, because total release did not attain 95%.

RESULTS AND DISCUSSION

The fit observed for the regression analysis of all four fluridone granules under static conditions was > 0.87, indicating that the regression equation is a good predictor of fluridone release from these granules (Figure 1A). Fluridone release from the granules under static conditions was similar for Q, PR and ONE, whereas SRP had the longest RT_{50} values (Table 1). RT_{25} values for all four fluridone formulations were between 12 and 24 d, with the only difference being between the Q and SRP, and PR and SRP granules. In three of the four formulations, 95% release of fluridone did not occur during the 90 d sampling period. However, after being crushed, almost 100% was recovered from Q and SRP, suggesting that unreleased herbicide remained bound to the ONE and PR formulations after 90 d under static conditions.

Fluridone was released from Q much more rapidly than SRP under static conditions. PR and ONE did not differ from one another and were similar to both Q and SRP, depending on which points of the regression are compared. The reason for low recovery of fluridone from PR and ONE is unknown, but it is unlikely due to degradation. The PR and ONE granules that were crushed at the beginning of the studies and sampled over 90 d showed no fluridone

Table 2. Estimated hours required for 25, 50, and 95 percent release of triclopyr and endothall from granules maintained under static and aerated conditions.

Herbicide	RT_{25}	RT_{50}	RT_{95}	Crushed Value[1]
Static				
Triclopyr	5.1 (4.5–5.9)[2]	11.9 (10.5–13.8)	37.0 (32.6–42.9)	104 (95–113)
Endothall	37.7 (31.6–46.7)	86.2 (72.0–106.7)	237.5 (199.1–294.3)	108 (93–123)
Aerated				
Triclopyr	0.5 (0.4–0.6)	1.1 (0.9–1.5)	4.2 (3.4–5.7)	110 (100–120)
Endothall	0.4 (0.3–0.5)	0.9 (0.7–1.2)	3.4 (2.7–4.6)	95 (85–105)

RT = release time
[1]Mean percent of total concentration recovered after crushing granules.
[2]Mean (95% Confidence Interval).

degradation in this experimental setup (data not shown). It is possible that the subsample of granules used played a role in this result; a limited number of granules were sampled from the formulated product and there is likely variation among the granules, so each granule may include more or less than 5% active ingredient. However, the same low yield of PR also occurred in the aerated studies, so the reason for this discrepancy is unknown.

Water circulation (aerated conditions) greatly altered the release profiles of the fluridone formulations compared to release under static conditions (Figure 1B). The release of fluridone under aerated conditions was similar among the ONE, PR, and SRP formulations, whereas release from Q was slower (Table 1). RT_{50} values for fluridone granules were reduced from a range of 27 to 72 d under static conditions to 4 to 16 d under aerated conditions.

The effect of aeration on fluridone release from the ONE, PR, and SRP formulations was much greater than on the Q. Aeration reduced the RT_{50} time for ONE by 33 d from 39 to 6 d or an 85% reduction, PR from 37 to 4 d (89%), and SRP from 72 to 7 (90%), whereas the RT_{50} for Q decreased by only 11 d (41%). This explains the change in relative position of the Q release profiles between Figures 1A and 1B which appears to be the result of the more rapid release of fluridone by the Q formulation under static conditions.

As expected under static conditions, triclopyr and endothall granules released much more quickly (h) than fluridone formulations (d) (Table 2). Triclopyr granules had 50% release by 12 h and 95% release at 37 h after treatment. In contrast, release of endothall was slower, with an RT_{50} of 86 h and an RT_{95} of 238 h.

Triclopyr and endothall granules were similarly affected by water circulation with release much faster under aerated conditions than static conditions (Figures 2A and 2B). The RT_{50} for endothall and triclopyr under aerated conditions (Table 2) were about 1 h for each, compared to RT_{50} values of 12 h for triclopyr and 86 h for endothall under static conditions. The RT_{95} value for triclopyr was reduced from 37 to 4.2 h or an 89% reduction, whereas the RT_{95} value for endothall was reduced from 237.5 to 3.4 h (99%). Total recovery of triclopyr and endothall under both static and aerated conditions was similar, ranging from 95 to 110% of the concentration of the total herbicide applied.

The results of this research demonstrate large differences in RT values among these six herbicide formulations, with RT_{50} values ranging from 12 h to as long as 72 d under static conditions. The RT_{50} values under aerated conditions were reduced to 1 h (endothall and triclopyr) to a maximum of 16 d for fluridone Q. Both endothall and triclopyr are rapidly taken up by plants, requiring 1 to 2 ppm or higher concentrations for adequate weed management. Control with these two products requires exposure times of several hours

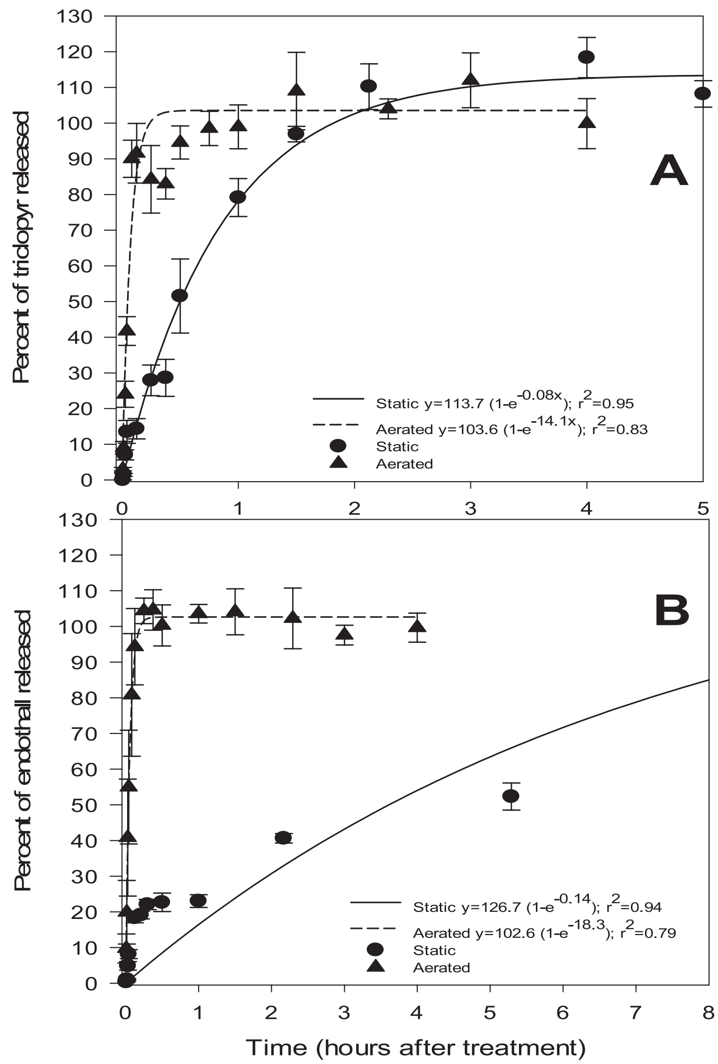

Figure 2. Release of triclopyr from Renovate OTF granules maintained under static and aerated conditions (A) and endothall from Aquathol Super K granules under static and aerated conditions (B). Water sampling for static and aerated treatments for triclopyr were 25 and 4 d, and for endothall 30 and 5 d, respectively. Data collected from samples later than 5 h for triclopyr and later than 8 h for endothall were omitted for graphic presentation. Symbols represent mean ± standard error of 4 replications.

to a few days depending upon concentrations applied. In contrast, fluridone concentration and exposure requirements are ca. 10 ppb for 40 to 90 d. The aqueous half-lives (persistence) of these herbicides are also quite different, with 2 to 10 d half-lives for endothall and triclopyr, and 9 to 20 d for fluridone. Although there are few studies investigating the release of herbicides from granules under static conditions, fluridone has been studied the most. Koschnick et al. (2003) noted that the release of SRP under static conditions in outdoor mesocosms ranged from 25 to 36% after 36 d; which agrees well with results of our study where 36% of fluridone was released from SRP after 36 d (calculated from equation in Figure 1). It therefore seems likely that these values represent the release profile for fluridone that could be expected under static conditions. Reinert et al. (1985) reported that the endothall granules they evaluated released 50% of their herbicide in 3 to 4 h, which is considerably more rapid than the 86 h observed in our study (Table 2). However, Reinert et al. (1985) used a shaker table to mix the water, so that experiment was apparently not conducted under true static conditions. In addition, the endothall formulation they evaluated had a clay carrier whereas the one evaluated in this study had a polymer carrier.

SRP required 16 d for 95% of the fluridone to release under aerated conditions, which is similar to the results reported by Mossler et al. (1993), who noted that SRP required ca. 16.5 d for 100% release of fluridone under mild agitation. Reinert et al. (1985) reported that the endothall granules tested under their parameters (flasks on a shaker table) released 50% in 3 to 4 h which is slightly slower than the 1 h required under the aerated conditions in this study (Table 2).

This research shows a wide range of release profiles among pelleted and granular aquatic herbicide formulations. To achieve 50% release required as little as 12 h for triclopyr and as long as 72 d for SRP under static conditions, and 1 h (endothall and triclopyr) and up to 16 d (Q) to achieve the same release under aerated conditions. There were large differences in herbicide release between the fast acting herbicides (endothall and triclopyr) compared to fluridone, however the release of fluridone from the four formulations was generally quite similar. In summary, there were large differences between herbicide types and release profiles between static and aerated conditions, with much less differences occurring between the granular formulations of one herbicide (fluridone).

The factors that influence the release of herbicides from solid formulations in aqueous solution are numerous and include carrier material, the water solubility of a herbicide, the adsorption or Koc values of the herbicide and the pressure used to compress pelleted formulations, among others. All of these factors will further interact with environmental conditions that are found in the aquatic environment, making predictions on field release difficult. The baseline data on herbicide release reported in this paper will be compared to the effects of sediment on herbicide release in a future publication.

The more rapid release of all the solid formulations under a very gentle flow, compared to the static release, was not anticipated in these studies. All water bodies experience water circulation due to inflowing streams, ditches, wind, or simple thermal gradients created by fluctuating day/night temperature differences. This suggests that release of fluridone from solid formulations over many days would be similar in most waterways to results obtained under the aerated treatments. Weather conditions over a much shorter period of time (h to d) would also affect the release of both triclopyr and endothall.

This study, similar to previously published research on herbicide release from solid formulations, used descriptive or qualitative terms to describe water flow. Likewise, this also raises questions regarding measuring water exchange at the sediment/water interface in natural waters. In addition to better quantifying effects of "flow" on behavior of granular formulations, other studies such as impacts of sediment type, concentration of herbicide in sediment pore water and uptake of herbicide by aquatic plant roots are very poorly understood.

SOURCES OF MATERIALS

[1]Sonar® Q, Sonar® PR, Sonar® One and Sonar® SRP, SePRO Corporation. Carmel, IN 46032.

[2]Aquathol® Super K, United Phosphorus Inc. King of Prussia, PA 19406

[3]Renovate®OTF, SePRO Corporation. Carmel, IN 46032.

[4]Strategic Diagnostics Inc. Newark, DE 19702.

[5]Envirologix. Portland, ME 04103.

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