

Recirculating Dynamics of Conventional Recreational Water Algaecides

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The dynamics of conventional algaecides were studied in a recirculating tank equipped with filtration devices capable of housing various filtration media (silica sand, diatomaceous earth, perlite, zeolites, fibrous cellulose and polyester cartridges). Two distinct groups of algaecides were studied. The first group was the quaternary ammonium compounds (linear and polymeric quats) and the second group, was copper-based products (ionic and complexed). Results revealed that under dynamic (recirculating) conditions none of the quats adsorbed onto (un-fouled) silica sand, diatomaceous earth, synthetic polyester cartridges, or perlite. Significant algaecide sorption was observed with zeolite-1 and zeolite-2 (clinoptilolite) after 21 filter passages. Additional studies revealed that under static/passive conditions (no-recirculation), all filter media tested demonstrated sorption properties with all algaecides tested. Further studies under static conditions demonstrated that soil had a dramatic impact on residual algaecide levels as compared to residual levels when products were exposed to packed algal cells. Our experimental results indicate that the longevity or half-life of selected test algaecides in a recirculating system most likely is predominantly due to the level or degree of trapped organic particles such as soil, algae cells and other organic and/or inorganic debris. Certain filter media has also intrinsic sorption properties for algaecides, such as zeolites. Based on our results, copper-based products appear to be more susceptible to be taken out of circulation with most conventional filter media than quaternary ammonium products.

Introduction

The separation of solid particulates from water has been in practice since early Chinese history. However, the first documented use of sand filtration dates back to only the 1800's. Since the early days, filtration systems have evolved into sophisticated, efficient designs and into a large selection of filtration media. There is no doubt that filtration systems will continue to evolve and play an important role in the cleanliness and safety of recreational water systems. An essential aspect for new innovations, is a clear understanding of the basic operational aspects of each system. In addition to understanding of the basics of a filtration system, it is necessary to investigate if there are possible physical or chemical incompatibilities with filter systems and common chemical additives. Recreational water systems, such as pools and spas are typically exposed to conditions conducive to the introduction of airborne, waterborne and bather contaminants. These contaminants can be either soluble or non-soluble materials. To date, filtration is the only practical means of removing most non-soluble particulates that find their way into each system. Typical filtration media employed to remove non-soluble materials include silica sand, diatomaceous earth (D.E.), and polyester cartridges. Most recently, due to environmental and regulatory concerns, numerous new filter media choices have become available to the recreational water industry. Among the new choices are perlite, zeolites, and fibrous cellulose. Most of these new alternatives have already been in the marketplace in other industries and have not been evaluated for potential chemical incompatibilities.

Although filtration removes most non-soluble particulates from the body of water, the material re-

tained by the filter remains in the recirculation loop until the filter medium is either cleaned, backwashed or replaced. Since filtration is an integral element for a clean recirculating system, inevitably chemical additives such as algaecides will also be subjected to the rigors of such systems. Little information is available today on the impact of filtration and its media components and typical contaminants on the bio-availability of pool chemicals such as algaecides. Early studies conducted by Debussy (1952), Jung (1954), and Fitzgerald (1960 & 1963) on filtration dynamics with algaecides indicated that quaternary ammonium and copper algaecides were removed from a recirculating system by conventional filter media such as silica sand and D.E. In addition, older service manuals (Swimming Pool Operation Handbook, U.S. Army, 1986) also have alluded to the removal or sorption of selected algaecides by filter media. Based on the experimental conditions in which these studies were conducted, it was difficult to discern with certainty, if the reported loss of algaecide was due to the actual filtration media (silica sand) or due in part to dirt (soil, algae, leaves...etc) particles trapped within the filter medium. In addition, the experiments were conducted in pools with significant bather loads.

We felt that the results obtained in these early studies were not clear enough to attribute the algaecide loss to filter media, therefore, our objective was to carefully dissect all possible elements that might impose a demand on the bio-availability of selected algaecides. In order to accomplish this task, we looked first at clean filter media to determine the intrinsic demand of each filter medium on low levels of algaecides. The second tier of experiments focused on the demand that soil, halogens and packed algae cells have on residual algaecide levels in a laboratory controlled environment.

Materials and Methods

Test Algaecides

All dynamic and static experiments were conducted in "balanced" (not chlorinated) water per NSPF (Pool and Spa Operators Handbook, 1990) and NSPI chemical water balance guidelines. Chemical adjustments were made with conventional products known to the trade. Algaecides were purchased from selected pool outlet stores from the Memphis, TN area. Experiments were conducted with the following test algaecides: Quaternary ammonium algaecides: (1) LinQ-1, alkyl dimethyl ammonium chloride (10% ai). (2) LinQ-2, Didecyl dimethyl ammonium chloride (50% ai). (3) Poly-1, Poly[oxyethylene(dimethyliminio)-ethylene-(dimethyliminio)ethylene dichloride] (60% ai). (4) Poly-2, 1,2-ethanediamine, polymer with (chloromethyl) oxirane and N-

methylmethanamine (50% ai). Copper based algaecides: (5) Ccu, ethanolamine complexed copper (7.41%) and (6) Icu, cupric sulfate (copper II sulphate pentahydrate, 99.0% ai). Test algaecides, with the exception of product #4, an experimental algaecide, are commercially available. Stock algaecide solutions were made in "balanced" water the day of the assay. For dynamic (recirculating) experiments, the test algaecides were added directly to the system, by-passing all filtration equipment for optimal product dispersion. Residual levels of quaternary ammonium chloride were monitored with the titrimetric PVSAK method. The LaMotte test kit model QAC, code 7057 was employed for monomeric quats (1 & 2). The LaMotte test kit model PQ-DC, code 3629 was utilized for polymeric quats (3 & 4). To monitor residual copper-based products, the Zeneca portable Baqua Spa test kit (Model STC-K) was employed, which utilizes the spectrophotometric bicinochoninic method. Algaecide levels during our assays were slightly higher than recommended (14 ppm ai) for quaternary ammonium products, because of test kit sensitivity (drop equivalence). For copper-based products, concentration levels during all assays did not exceed 1.5 ppm active ingredient. Residual algaecide determinations were conducted after 1,3,6,9,12,15,18 and 21 turnovers (1 TR = 9-10 minutes). Although numerous measurements were taken during a filter run, only the last measurement (21 TR) was taken in account for product loss calculations. Loss of residual levels were calculated by subtracting starting concentration by the final measurement, divided by starting concentrations times 100. Each value in each table represents the average of two separate individual experiments performed under identical conditions.

Filter And Filter Media

For the recirculating studies, a Hi-Rate sand filter was employed to evaluate the permanent filter media, silica sand and zeolite. Silica sand was purchased from a local pool supply store in the Memphis, TN area. Approximately fifty pounds (50 lbs.) of silica sand was charged to the housing unit leaving the required headboard space. The same Hi-Rate filter housing was also employed to test two types of zeolite filter media. The zeolite-1 (WaterKlean™) filter medium was purchased from Imtek Environmental Corporation, (Alpharetta, Ga). A second source of zeolite media (Zeolite-2) was purchased from Ecosmarte (Richfield, MN.) distributors of Zeoclere-30™ (British Zeolite Company). Non-permanent filter media such as diatomaceous earth (D.E.) was also evaluated under dynamic conditions and purchased from a Greater Memphis, TN pool supply store. The D.E. filter housing system was utilized to evaluate other non-permanent filter medium such as fibrous cellulose and Perlite. Cellulose media, Cel-1 (CF-138)

was kindly donated by S.W.I.M. (Santa Ana, CA.) A second source was obtained (Cel-2) from a pool distributor that markets Purifiber™ (Swimpure Corp), a third source (Cel-3) was kindly donated by Zeneca Pool Products (Wilmington, DE) under the trade name BAQ AID™. Perlite (SILKLEER™) was kindly donated by Silbrico Corporation (Hodgkins, Ill). All filter media was charged according to the supplier's and manufacturer's recommendations. Finally, two types of cartridge filtering systems were evaluated under dynamic conditions. The first cartridge filter evaluated was a typical REEMAY® polyester-type filter, while the second was a blend of polyester and cotton blend (SuperTuf™) sold by Harmsco (Miami, FL). Both cartridges were purchased locally.

Recirculating System Experiments

Recirculation studies were conducted in an outdoor rectangular mobile tank on a steel frame (9.5 ft long x 6 ft width x 6.5 ft high) that simulates a typical modern recirculating system. The system was modeled after a similar system described in the Environmental Protection Agency, Pesticide Assessment Guidelines [(1982: EPA 540-82-026). Subdivision G., Product Performance. Efficacy of aquatic pest control agents (92-20f) swimming pool algaecides (section 2) simulated pools] The water holding capacity of the tank is approximately 350 gallons (7 ft long x 3 ft wide x 2.2 ft. deep) and is embedded within a steel framework with plexiglass sides. The system has 2 inch PVC on the suction side and 1.5 inch PVC on the discharge side. The system is equipped with two bottom drains, a flow meter, a skimmer, and a 1 hp pump. The system also has three types of filtration devices. One device typically houses (Hi-Rate) silica sand (filtration area: 1.4 sq. ft.), the second is a pre-coat type D.E. device (filtration area: 30 sq. ft.), and the third is a device to house cartridges (filtration area: 50 sq. ft.). The total volume of water in recirculation takes into account the water capacity within each device and PVC system. The EPA test guidelines mentioned above recommend a 6 hour turnover cycle (standard for pools). To obtain a 6 hour turnover cycle with our 350 gallon system a flow rate of approximately 1.0 gpm is required. Due to the total water volume in the system and the pump output capacity, the actual pump flow rates (meter) varied between 35-38 gallons per minute (depending on the filter system in use). Based on our calculations, the turnover rates observed in our system fluctuated between 9-10 minutes. Therefore, our system in a three and a half hour period would be expected to have about 21 turnovers (equivalent to 5 standard days with 24 hour filtration). In contrast, a conventional pool with 6 hour turnover rate with continuous filtration, we would expect 4 turnovers/24 hour period.

Static (non-recirculating) Experiments

Static experiments were conducted in the laboratory with (250 ml) glass beakers containing 200 ml of test algaecide solution in balanced water. Pre-weighed amounts of "composite" soil, packed algal cells and filter media were added to each test solution. The composite soil was made as follows: dried soil samples of loam, silt loam, clay, silt, and sand were obtained from an agriculture soil testing facility (Memphis, TN). Each type of soil was blended in equal amounts to make our "composite" test soil. Varied amounts of soil (0.1, 0.2, 0.4, 1.0, 2.0, & 3.0 grams) were added to beakers containing the test algaecide (200 ml). After 30 minutes contact time, a 30 ml aliquot was removed from each flask, centrifuged and the supernatant (top layer) analyzed for remaining residual algaecide level. In the second soil experiment, only one concentration of soil was employed (0.2 gram/200 ml) per algaecide and residual algaecide levels measured at timed intervals (30 min, 1, 2, 3, 4 & 24 hours). To determine the algaecide demand of algae, four algae species were selected and grown in Allens medium for 14 days at 25°C (room temperature) before the assay. The four algae species selected were *Chlorella vulgaris* (UTEX 26), *Eustigmatos vischeri*, (UTEX 310) *Scenedesmus obliquus* (UTEX 78) and *Phormidium faveolarum* (UTEX B-427). Equal amounts of each algae culture were mixed and the mixture centrifuged and washed in balanced water. Cells were re-suspended in balanced water to total cell density of approximately 3.2×10^9 cells/filaments/ml. One milliliter of washed algae cells was added to 200 ml of test algaecide. After 30 minutes contact time, a 30 ml aliquot was obtained, centrifuged and supernatant analyzed for residual algaecide level. To determine filter medium demand on algaecides (static conditions), 2.0 grams of test media (sand, D.E. cellulose (1, 2 & 3), perlite and zeolite (1 & 2) was added to a 200 ml solution containing the test algaecide. After 30 minutes contact time, a 30 ml aliquot was transferred to a centrifuge tube and centrifuged for 5 min at 4,000 rpm (Sorvall Instruments, Model RC-3B). The supernatant was analyzed for residual algaecide as outlined above. The halogen demand of selected quaternary ammonium compounds was determined in solutions containing 10 and 20 ppm (ai) - "balanced" water. For the ethanolamine complex copper product solutions of 3.0 and 6.0 ppm (ai) were also prepared in "balanced" water. Calcium hypochlorite was employed as the source of hypochlorous acid, and 1,2 dibromodimethyl hydantoin as the source of hypobromous acid.

To determine the chlorine demand of selected algaecides, a solution of 3 ppm free available chlorine solution was prepared in "balanced" water the day of the assay. For bromine demand, a 5.0 ppm free avail-

able bromine solution was also prepared in balanced water. Total and free halogen determinations were made with the DPD titrimetric method (Standard Methods for the Determination of Water and Waste Water, 9th Edition). Contact time between halogen and test algaecides was 1 hour at room temperature (25°C).

Charge characterizations

Charge characterizations were done by employing a MUTEK PCD 02 (West Germany) particle charge detector. All filter media (except sand and zeolite-2), and all test algaecides were analyzed quantitatively to determine degree of positive (cationic) or negative (anionic) charge. Five milliliters of each test algaecides was made as 5% active ingredient in deionized water. Five milliliters of a 1.0% by weight sample of each filter media was made in deionized water and tested. Charge neutralizations were performed by adding PES-Na 10X-3 N for cationic samples and PDDAC 10X-3 N for anionic samples.

Results

Studies employing the recirculating system revealed that conventional filter media, such as D.E., sand, perlite and polyester cartridge filters had no measurable impact on residual levels of LinQ-1, LinQ-2, Poly-1 and Poly-2 (Table 1). The complexed copper product on the other hand, showed some affinity (15% sorption) towards diatomaceous earth media and perlite (19.0% sorption) media. Among the newer recreational water filter media, cellulose-1 medium had no measurable impact on LinQ-1, LinQ-

2, and Ccu products after 21 filter passages. Cellulose-1 did have a slight to moderate impact on Poly-1, Poly-2 and Icu with 1,11 and 32% decrease in residual levels. The zeolite-1 filter medium appears to have the highest rate of sorption towards all test algaecides (Table-1). Zeolite-1 sorption rates were the highest for Poly-1, (85%) followed by Icu (68.0%), LinQ-1 (67%), LinQ-2 (60.0%), Ccu and Poly-2 (22.0%). The zeolite-2 filter medium also demonstrated measurable sorption rates for most algaecides evaluated. Based on these experiments, ionic copper (Icu) was retained by the majority of the tested filter media. The highest sorption rates for ionic copper (Icu) were obtained with zeolite filter media (68.0%).

Similar experiments were conducted under static conditions with the listed filter media and test algaecides. Based on our experimental results, all algaecides tested had demonstrable sorption rates with all filter media (Table 2). Sand and D.E. demonstrated the least sorptive properties of all filter media evaluated in these tests. Cellulose-3 filter medium demonstrated the highest sorptive rates of all the tested filter media. Sorption rates with cellulose filter media approximated sorption rates obtained with activated carbon, which was used as the positive control.

Based on our laboratory results (Figure 1), the composite soil had a dramatic impact on residual algaecide levels. Removal values increased as soil concentration increased. Poly-2 appeared to be the least affected by soil. Figure 2 depicts the effect of predetermined soil concentrations over time.

Based on the next set of experiments, contact time had an effect on residual levels of test algaecides. Poly-2 appeared to have the lowest sorption rate of the test algaecides.

Recirculating Dynamic Assay (percent sorption) after 21 filter passages						
Media	LinQ-1	LinQ-2	POLY-1	POLY-2	CCU	ICU
Control (-)	No loss	No loss	No loss	No loss	No loss	22.0%
SAND	No loss	No loss	No loss	No loss	No loss	Nd
D.E.	No loss	No loss	No loss	No loss	15.0%	66.0%
Zeolite-1	67.0%	60.0%	85.0%	22.0%	45.0%	68.0%
Zeolite-2	No loss	37.0%	27.0%	24.0%	32.0%	59.0%
Cellulose-1	No loss	No loss	1.0%	11.0%	No loss	32.0 %
Perlite	No loss	No loss	No loss	No loss	19.0%	56.0%
Cartridge-1	No loss	No loss	No loss	No loss	No loss	42.0%
Cartridge-2	No loss	No loss	No loss	No loss	10.0%	38.0%

Control (-), indicates system recirculated but bypassed all filtration elements. Nd: not determined

Percent algaecide sorption calculated as:

$$\frac{\text{starting residual concentration} - \text{residual concentration after 21 passages}}{\text{Starting residual concentration}} \times 100$$

Table 1 – Filter media effect on conventional recreational water algaecides under dynamic conditions.

**Static Beaker Assay (Percent sorption after 30 minutes exposure)
2.0 grams media/200 ml test algaecide**

Media	LinQ-1	LinQ-2	POLY-1	POLY-2	CCU	ICU
Control (-)	17.0%	0	0	0	0	9.0%
Control (+)	40.0%	67.0%	64.0%	62.0%	92.0%	79.0%
SAND	2.5%	17.0%	5.0%	0	16.0%	27.0%
D.E.	10.0%	0	17.0%	25.0%	42.05%	8.0%
Zeolite-1	31.0%	50.0%	18.0%	12.0%	28.0%	43.0%
Zeolite-2	15.0%	17.0%	12.0%	50.0%	17.0%	32.0%
Cellulose-1	16.0%	33.0%	46.0%	37.0%	31.0%	39.0%
Cellulose-2	20.0%	17.0%	46.0%	50.0%	52.0%	40.0%
Cellulose-3	62.0%	50.0%	70.0%	50.0%	67.0%	48.0%
Perlite	13.0%	17.0%	51.0%	50.0%	26.0%	39.0%

Control (+): Activated charcoal was employed as a positive control

Control (-): No filter media

Percent algaecide loss calculated as:

$$\frac{\text{starting residual concentration} - \text{residual concentration after 30 minutes}}{\text{Starting residual concentration}} \times 100$$

Table 2 – Filter media effect on conventional recreational water algaecides under static conditions

Figure 1 – Soil Interaction with Test Algaecides
t = 30 min

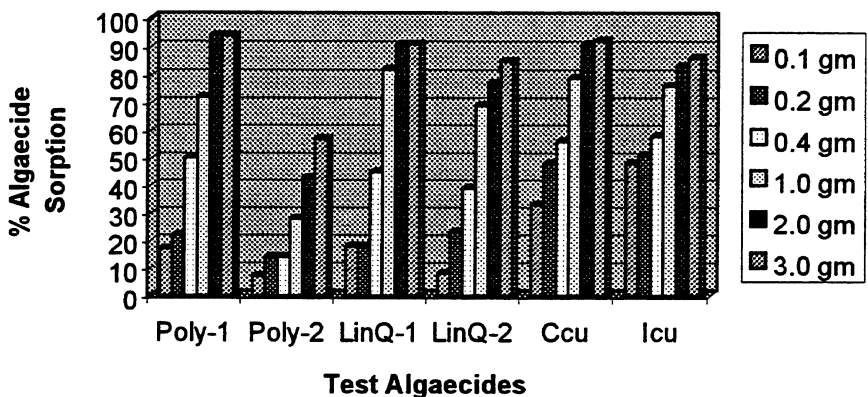


Figure 2 – Soil Interaction with Test Algaecides
0.2 grams soil/200 ml

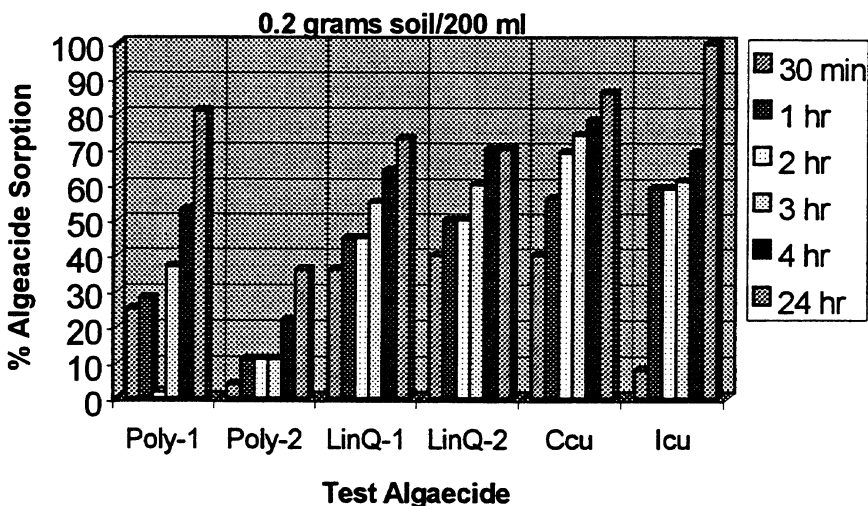


Figure 3 depicts the sorption rates obtained with an algae mixture. Our results indicated that algae has an impact on residual levels of test algacides. Ionic copper (Icu) had the highest sorption rates in the presence of algal cells. All products tested had some degree of sorption to the algal mixture, but sorption rates were not as dramatic as soil sorption rates.

The next set of information obtained was the degree of interaction (demand) that test algacides have on maintenance levels of hypobromous (5 ppm) and hypochlorous acid (3 ppm). The oxidizer concentrations chosen are those typically employed as maintenance levels. Experiments were only conducted with the polymeric algacide (Poly-1), a monomeric algacide (LinQ-1) and a complexed copper (Ccu) product. Our observations revealed that, at chlorine levels of 3 ppm, all products tested had some chlorine demand. Chlorine demand did not change dramatically as the levels of test algacide increased from 10 to 20 ppm. The highest chlorine demand was observed with complexed copper (Ccu). Both polymeric (Poly-1) and mono-quats have similar chlorine demand values (combined chlorine), when tested at 10 ppm (Poly-1; 8.53%, LinQ-1; 10%). Hypobromous acid (5 ppm), on the other hand, had little or no effect on complexed copper. In other words, no bromamines were formed with 6 ppm complexed copper. Quaternary ammonium products, on the other hand (Poly-1 and LinQ-1), when tested at 20 ppm, demonstrated bromamine values of 7.85% for Poly-1, and 10% for LinQ-1.

Finally, charge assays were performed on all test algacides and filter media (Table 3). Based on our observations, all algacides tested registered as cationic, with the exception of Ccu (complexed copper). Test algacide LinQ-2 demonstrated the highest cationic reading (1,975 mV), followed by LinQ-1 (1,000 mV), Poly-1 (972 mV), Poly-2 (800 mV) and Icu (267 mV). Complexed copper (Ccu) was neutral in charge. All filter media, with the exception of Cel-1, were anionic in charge.

Conclusion and Discussion

Based on our recirculating dynamic experiments, conventional filter media such as silica sand, D.E. and cartridge polyester elements do not appear to significantly retain or bind quaternary ammonium compounds such as alkyl dimethyl benzyl ammonium chloride (LinQ-1) and polymeric quats (Poly-1, Poly-2). Our results are in disagreement with Fitzgerald's (1963) field results and conclusions. Fitzgerald's studies concluded that algacide residuals were lost in recreational systems as a result of either adsorption of the chemical to the filter medium (sand) or to physical filtration of an insoluble form of the chemical. A possible reason for such discrepancies could be due to variations in experimental conditions such as the use of a fully functional public pool with significant bather loads, versus an experimental tank with no bather loads. Conditions of one of two test facilities observed about 100-200 children plus motel guests as typical

Sample	millivolts	Charge
Cel-1	230	cationic
Cel-2	408	anionic
Cel-3	800	anionic
Perlite	650	anionic
Zeolite-1	1238	anionic
D.E.	1259	anionic
Poly-1	972	cationic
Poly-2	800	cationic
LinQ-1	1005	cationic
LinQ-2	1975	cationic
Ccu	0	neutral
Icu	267	cationic

Zeolite 2 and silica sand were not evaluated.

Table 3 - Charge Assays of Test Algacides and Filter Media

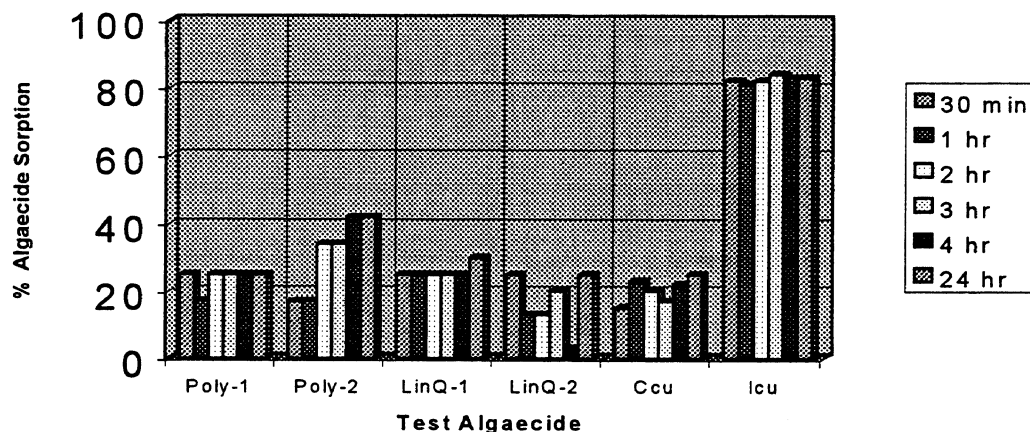


Figure 3 - Algae Interaction with Test Algacides

bather loads per day. Furthermore, the degree of cleanliness of the filtration system in use at each test site during the actual evaluations was not known. We believe these early studies failed to consider other possible elements which could have caused a loss of algaecide. In addition, in the textile and cosmetics industries the "conditioning" effects that quaternary ammonium products have on surfaces is well known (Lawrence, 1957). Although we have not demonstrated the effects these surfaces or materials have on algaecide residuals, we should not discount the possibility that these interactions could occur. We have shown that a mixture of soil has a dramatic impact on algaecide residuals. It is important to note that we are not questioning the fact that algaecide reduction did not take place in a "real" life scenario, we only question the true cause of such product losses.

Can we predict with some certainty the half-life of algaecides in a recreational water system? The answer: it is very difficult to predict, unless we are in a laboratory setting conducting an experiment with controls and known variables.

The underlying reason for our studies and the early studies conducted by Fitzgerald is in determining how often to dose an algaecide to a system. Swimming pools are subject to a plethora of environmental conditions, (sunlight, temperature, evaporation, and bather loads, etc.) which will exert a varied demand on pool chemicals, including algaecides. We believe that no system is identical, nor will it have identical chemical needs. Therefore, we cannot predict how often to add a chemical without additional site specific information. The optimal and probably the most logical approach to adequately dosing a system, is simply to test for residual algaecide levels and adjust accordingly.

It is possible for a residential system with low bather load to have too much product present at one time by following use label recommendations of dosing every 3-7 days. Our experience (data not shown) has indicated that in residential pools employing polyquats with low bather loads, residual levels were still present 3-4 weeks post-application. We believe that by optimizing residual algaecide levels by pool-side assays, as part of a total maintenance regime, less product would be consumed unnecessarily, proving to be a cost-effective measure. Rather than dosing blindly every 3 to 7 days, as most use labels recommend, algaecide levels could be adjusted as needed. It is also possible to have to dose more frequently than recommended, especially in a heavily used pool with heavy organic loads. Although from a regulatory aspect this might not be possible, manufacturers might need to re-visit use label recommendations to reflect use rates based on residual active levels, rather than on weekly slug doses. The downside of having to measure algaecide residuals is that it is another poolside measurement. Measuring algaecide levels in certain

situations is a "must-do" practice, especially when employing copper based products. There are certain implications associated with the use of ionic copper-products such as possible staining of pool surfaces. It is our opinion that we need to become smarter chemical users, and that algaecide testing is a reasonable practice. This extra effort, as compared to other pool-side chores, like brushing, is relatively easy and not extraordinarily time consuming. There are several commercial companies marketing portable test kits (i.e. LaMotte Co, Taylor Technologies). Unfortunately, the only problem with present test kit technology, especially with quats, has been the difficulty in accurately discerning titration end points with the PVSAK methodology. These types of test kits have a very subtle color change (blue to violet) that can be difficult to discern, even to the trained eye.

The observed sorption levels observed in our static laboratory experiments were in agreement with Fitzgerald's (1960) laboratory results. Fitzgerald's research concluded that celite (analytical grade diatomaceous earth) under static conditions bound or retained quaternary ammonium products as determined indirectly by the ability of treated algaecides to inhibit or not inhibit algae growth. Fitzgerald (1960) also observed that quaternary ammonium products retained by celite were eluded back after treatment with distilled or hard water. These observations as well as our dynamic experiments appear to indicate the electrostatic forces seen under static conditions with D.E. are not a factor under high shear conditions experienced with our system. The same phenomenon could also be true for quats exposed to perlite, cartridge elements and silica sand while under dynamic conditions. Among the results obtained with the newer filter media, zeolites had the most consistent sorptive properties of all filter media evaluated. The zeolite's highly sorptive properties appear not only to be related to its anionic charge alone, but also to its porosity. It is unknown, without further experimentation, whether or not bound algaecides to zeolites are eluded or desorbed back into the system, under longer operating conditions. It is known, however, that natural zeolites can, upon ionic saturation, be re-activated by exposure to a saline environment. The zeolite products evaluated in this study did not reach a saturation point, as the medium was not changed or re-activated between product evaluations. There is a possibility that retention values could have been higher if new zeolite filter media were replaced for each individual algaecide. If saturation were to be achieved, algaecide levels might have been maintained during the 21 cycle evaluation, but ionic exchange for ammonia and other undesirable contaminants, (we speculate), could have been compromised. Among the copper based products evaluated in this study, complexed copper (ethanolamine) and inorganic copper (copper sulphate) were among the al-

gaecides that most frequently were retained by filter media, compared to quaternary ammonium products.

The information presented here brings to light some basic issues concerning the retention and/or sorption of selected commercial algaecides to filter media. It is imperative for us, the chemical industry, as well as the service sector, to have some idea of the interactive forces that might be present in a recreational water setting that affects the bio-availability of algaecides. Previously we have shown (del Corral and Johnson, 1996) the importance of maintaining residual algaecide levels, as it pertains to algae control. Information such as we have presented here and in past publications will allow a clearer understanding of the factors associated with the loss of product and its ability to exert its biological activity (del Corral and Johnson 1996). It is also important to distinguish between product failure, by either a physical loss of product through sorption mechanisms, or product failure due to the inability of a product to exert toxic effects. In most cases that we have observed, a significant amount of treatment failures are not necessarily due to ineffectiveness of a particular product, but rather due to the physical loss of product by excessive contaminants.

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