COMMONWEALTH OF MASSACHUSETTS
EXECUTIVE OFFICE OF ENERGY & ENVIRONMENTAL AFFAIRS
DEPARTMENT OF ENVIRONMENTAL PROTECTION
OFFICE OF APPEALS AND DISPUTE RESOLUTION

IN THE MATTER OF
MASSACHUSETTS DEPARTMENT OF CONSERVATION AND RECREATION
Docket No. WET-2009-039
DEP FILE #233-0641
NATICK, MA

TESTIMONY OF WARREN J. LYMAN, Ph.D.

I, Warren J. Lyman, do hereby swear and affirm the following:

1. I am an environmental chemist with over 30 years of experience. I am now retired, but conduct occasional studies on projects of interest. I received my Bachelor of Arts degree from Williams College in 1964 and my Ph.D. in chemistry from the University of Rochester in 1969.

2. For 27 years, I was employed as an environmental consultant first by Arthur D. Little Inc. (Cambridge, MA) and then by Camp Dresser & McKee, Inc. (Cambridge, MA). I then worked as an independent consultant for several years. My recent studies have focused on site remediation, development of risk-based cleanup goals for hazardous waste sites, hazardous waste treatment, chemical property estimation, chemical fate and transport in the environment (including chemical fate modeling), water quality problems, sediment quality problems, risk assessments and litigation support.

3. My experience includes a study in 2006 of the proposed treatment of Lake Cochituate's South Pond with fluridone for invasive plant control. (Lyman, 2006) The main question addressed in that study was: "What is the potential for fluridone to migrate through soils between the lake water column and the public drinking water supply wells, designated as the Springvale well field, just south of Route 9 in Natick?" I did this study for the Massachusetts Department of Conservation and Recreation (DCR) at the request of the Natick Board of Health.

4. Recently, the DCR has proposed a program of invasive plant removal from Lake Cochituate's Middle Pond that involves, in part, the use of an herbicide. The Town of Natick's Evergreen well field – part of their public water supply - is located (on land) across the Pond from the proposed herbicide application area, with a distance of about 300 to 400 yards between the application area and the well heads. I have been retained by the Petitioners in this matter to determine the likelihood of the migration of the herbicide diquat dibromide ("diquat") from Lake Cochituate's Middle Pond to groundwater, and subsequently to the nearby Evergreen well field. I have undertaken this work on a *pro*

bono publico basis. My opinions, as set forth herein, are stated to a reasonable degree of scientific certainty.

5. I have examined several documents as part of my study. Key documents are listed in a reference section at the end of my testimony.

Technical Issues Relating to Diquat Migration Potential

6. In general terms, for diquat to move from the DCR's designated treatment area in Middle Pond to the Evergreen well field, the following four conditions must hold:

- Recharge Conditions: Surface water in the treatment area must move down into the pores of the underlying sediments and soil (i.e., the groundwater is recharged by the pond water);
- Groundwater Flow Regime: Groundwater must move, by natural forces or by influence of groundwater withdrawals by the Evergreen wells, from the treatment area to the well field area;
- Environmental Persistence: Diquat, which will be dissolved in water before and after application, must not be completely degraded by natural processes such as biodegradation, hydrolysis, or photolysis (i.e., its "lifetime" in the water/sediment environment must at least as long as the time it takes groundwater to travel from the treatment area to the well field).
- Adsorption to Sediments and Soils: Diquat must not be completely adsorbed by the pond sediments (suspended and settled) or by the underlying soils (typically comprised of materials like silt, sand and gravel).

7. The following technical section will provide information suggesting that all four conditions could hold. A proper and rigorous assessment of the overall migration potential for diquat would require studies of the four conditions listed above using site-specific information and studies. (Examples of such studies are provided in a subsection below.) Where possible, all this information should then be combined in a site-specific fate and transport model that would provide quantitative estimates of the likely diquat concentrations in the Evergreen wells. Unfortunately, neither the DCR nor their selected Middle Pond treatment contractor (Aquatic Control Technology, Inc. [ACT]) have undertaken such studies. Rather they have cited literature data, including those from both laboratory experiments and full-scale diquat treatments at other locations, to claim that Middle Pond can be treated without impacting the Evergreen well field. Given the potential risks to the residents of Natick (i.e., from contamination of their wells), it is not appropriate to rely on the data – perhaps subjectively selected - from generic laboratory experiments or from other treatment sites. For the DCR's proposed treatment to proceed, they should provide a site-specific assessment that demonstrates, with a high level of scientific certainty, that diquat cannot reach the Evergreen well field in concentrations of concern. The assessment should consider the possible impacts of repeated applications over a period of years. Such repeat treatment is usually necessary for herbicidal control of invasive plants. In fact, the Massachusetts Department of Environmental Protection has

issued a Superseding Order of Conditions that allows diquat treatment annually for a period of five (5) years in the designated Middle Pond treatment areas. (Freed, 2009)

8. Before proceeding to a discussion of the four conditions mentioned above, it is worth considering what a concentration of concern might be for diquat, and what dilution factor would be required to dilute the initial target treatment concentration below the concentration of concern. The US Environmental Protection Agency (EPA) has set a drinking water standard of 0.02 mg/L (0.02 ppm) for diquat. (EPA-a, undated) The DCR's target treatment concentration is 0.185 – 0.28 ppm, which is roughly a factor of ten above the drinking water standard. However, in assessing risks to large populations (e.g., all of Natick's residents), the EPA's risk assessment guidance for non-carcinogens suggests that exposure concentrations be at least a factor of ten below applicable health standards. This helps provide protection in case of environmental variability, sensitive individuals in the population, or other unknowns. The net result of the above is that the DCR should have to prove a minimum dilution factor of 100 for diquat traveling between the treatment area and the well field (i.e., that well head concentrations would be below 0.002 ppm). Since risk management is traditionally left to local (affected) individuals and their chosen representatives, higher levels of protection – i.e., more dilution – might be stipulated.

Discussion of the Selected Technical Issues

Recharge Conditions

9. I am not aware of any site-specific data that indicate whether or not water from Middle Pond recharges the underlying groundwater. However, a 2001 field study by the US Geological Survey (USGS, 2001) did determine that – for the nearby South Pond (which is hydraulically connected to Middle Pond) – there was such discharge to the groundwater. The velocity of downward flow from South Pond into the pond-bottom sediments was reported to range from 0.5 to 1.0 feet per day. Because of the proximity of the two sites (about 1 mile) and the similarities of the local topography and groundwater hydrology (considering both natural and well-induced flows), it is reasonable to assume that water in Middle Pond also recharges to groundwater.

Groundwater Flow Regime

10. I am not aware of any site-specific data that indicate whether or not groundwater under Middle Pond travels, by natural forces or by influence of groundwater withdrawals by the wells, from the proposed treatment area to the Evergreen well field area. However, following a detailed site-specific study by the USGS (2001), such a conclusion was reached for South Pond area groundwater movement to Natick's Springvale well field. Using measured data and a model, the USGS estimated that 64 (± 15) percent of the water withdrawn at the public-supply wells was derived from South Pond. The USGS (2001) estimated the travel time for groundwater flowing between South Pond (at test well NCW77) and the Springvale wells to range from 1 to 8 months. They noted that

water infiltrating from other locations might take shorter or longer times that could range from days to more than a year. Because of the proximity of the two sites (about 1 mile) and the similarities of the local groundwater hydrology (considering both natural and well-induced flows), it is reasonable to assume that groundwater beneath Middle Pond also flows to the Evergreen well field area. This view is also apparently held by the Massachusetts Department of Environmental Protection (DEP). In a Superseding Order of Conditions relating to the proposed herbicidal treatment of Lake Cochituate, the DEP stated that: "Although not studied, by the way of comparison, the Natick Evergreen well field bordering Middle Pond should have similar hydrologic characteristics as the Springvale well field." (Tomczyk, 2006) The clear implication of this statement is that the Evergreen well field likely draws a substantial portion of its water from Middle Pond.

Environmental Persistence

11. Using data from generic laboratory experiments or from other test sites, the DCR's consultant, Aquatic Control Technology, Inc. (ACT, 2009), has stated that:

> *"In natural environments, Diquat has a short half-life ranging between 1-4 days."* (ACT, 2009)

And they have further stated that:

> *"Although Diquat is ....generally non-detectable within 1-4 days of treatment, Diquat does bind with sediments and can persist for some time. In most instances Diquat is only detectable in soils for short periods following treatment and is generally broken down by photolysis and microbial breakdown, but in more extreme cases has been found to persist up to 1000 days. Although somewhat persistent in soils long-term field studies have nevertheless shown degradation rates of the order of 5-10% per year."*(ACT, 2009)

12. What is notable about ACT's statements is that they are general in nature, are not based on any site-specific data, and – further – do not provide a balanced assessment taking local conditions into account. They also give an insufficient evaluation of the possibility of long-term persistence. It is especially important to note that the environmental degradation of a chemical is extremely site- and situation-specific, with the degradation rate (and, thus, persistence) potentially changing by orders of magnitude between sites, or with different conditions at the same site. With these limitations, the ACT, 2009 statements cannot be relied upon.

13. Based upon a review of other documents[1], it appears that diquat can persist as a dissolved substance in surface waters for a few days following applications. Removal mechanisms involve: (a) transport of the treated water out of the treatment area, including movement into the groundwater zone; (b) adsorption to plants, and to suspended and bottom sediments; (c) photolysis (molecular alteration due to sunlight exposure); and

1. California EPA, 1994; Emmett, 2002-a and –b; EPA-a and –b (undated); and EXTOXNET, 1996.

(d) biodegradation (shown to be facilitated by adsorption to plant surfaces and severely hindered by adsorption to soils). Diquat that is adsorbed to bottom sediments, or that is not exposed to sunlight, may persist much longer. Photolysis will not be important in turbid waters or in sediments where sunlight penetration is blocked. Adsorbed diquat is also resistant to photolysis. (EPA-b, undated) The importance of adsorption immediately after diquat applications is limited by the fact that the adsorption process can be slow for some soil types (e.g., sandy sediments) (Emmett, 2002-a), thus allowing greater amounts to be transported to the groundwater zone.

14. Given the above, it appears reasonable to assume that once diquat has entered the groundwater zone (as a dissolved substance), that it can persist for very long times as photolysis is blocked (no sunlight) and biodegradation is limited by the paucity of degrading microbes and their necessary nutrients. Adsorption will continue to take place, but, as discussed below: (a) the adsorption will be relatively weak if – as expected - the soils are primarily sand and gravel (lacking significant amounts of clay and/or organic matter); and (b) desorption also will take place continuing to leave some diquat in solution and capable of migrating with flowing groundwater. Given the above, it is not unreasonable to assume that some diquat could persist in the groundwater long enough to be transported to from Middle Pond to the Evergreen well field.

Adsorption to Sediments and Soils[2]

15. The extent to which diquat is adsorbed to the soils and sediments (and suspended particulate matter) following an application to surface waters is, perhaps, the most import question in assessing movement into, and through, the groundwater zone. It is important to note that diquat is weakly adsorbed to some natural materials, and strongly adsorbed to others. Adsorption coefficients for diquat (a measure of the strength of adsorption) have been reported to range over three to four orders of magnitude.[3] Thus, assumptions about adsorption at specific sites can be severely in error if site-specific data are not used.

16. Using data from generic laboratory experiments or from other test sites, the DCR's consultant, Aquatic Control Technology, Inc. (ACT, 2009), has stated that:

- "*Following application, diquat is rapidly absorbed by green plant tissue;*
- *Diquat not absorbed by plant material is shown to quickly and readily bond with sediments and suspended particulate matter.*"

17. They also quote other documents which present a misleading or incorrect assessment of diquat adsorption. These quotes lead the reader to understand that diquat

2. In this discussion, "sediments" refers to the material recently deposited on the bottom of a water body (e.g., a pond), and "soils" refers to the solid material (excluding any bedrock) beneath the sediments deposited over geologic time.

3. For example, Emmett (2002-b) shows one type of adsorption coefficient (Kd_{ads}) to range from 15 L/kg for a sandy sediment, to 60,000 for a silty clay loam, to 92,000 for unspecified sediments or soils. Emmett (2002-b) also shows values of the organic-carbon-normalized adsorption coefficient (K_{oc}) ranging from 205 L/kg to 7,900,000 L/kg.

adsorption to soils is extremely strong and irreversible. Again, ACT's statements are general in nature, are not based on any site-specific data, and – further – do not provide a balanced assessment taking local conditions into account.

18. Based upon my review of other documents[4], the facts are that: (a) very strong adsorption is only seen for limited classes of material (e.g., organic matter and certain clays); and (b) the adsorption process is reversible to a significant extent. In addition, the second bullet quote listed above seems to assume that the sediments contain the special materials (e.g., clays and organic material) that have high adsorption potential. This assumption ignores the fact that in shallow waters (subject to wave action and human activity), there may be little net deposition of the small particles of silt and organic material that commonly accumulate in deeper, undisturbed waters. In such shallow water areas, the surface "sediments" are likely to be coarse grained (e.g., sand and gravel). Such coarse grained materials have a low adsorption potential for diquat. It seems likely that some portions of the proposed Middle Pond treatment area will contain such coarse grained sediments which would only weakly adsorb diquat, thus allowing more of the chemical to enter the groundwater zone.

19. Of all soil types, diquat is adsorbed most weakly to sandy soils; with very clean sands, sorption is weak enough to allow migration of diquat through the sand. (Emmett, 2002-b) If the proposed Middle Pond application area has sediments that are mostly sandy, then migration of diquat to ground water would be facilitated. In a sand and gravel aquifer, transport of diquat with flowing groundwater would also be facilitated due to the weak adsorption. It is noted that Natick's Springvale wells are screened in a sand and gravel layer (at depths of up to 75 feet below land surface), (USGS, 2001) and it is likely that the Evergreen wells are also screened in such material. The USGS report (USGS, 2001; see Figures 2 and 3 in that report) also show that the fine-grained sediments such as those containing clays and organic matter (which would have a higher adsorption capacity for diquat) are primarily located in the deeper waters in the center of South Pond. It seems likely that Middle Pond would similarly have most of the fine-grained sediments in the deeper waters, and less in the shallow waters that will be treated with diquat. The shallow waters with minimal fine-grained sediments would be less likely to hinder diquat migration to the groundwater zone.

20. The topic of irreversible chemical adsorption to soils is technically complex with few, if any, absolutes. While most early adsorption studies (on organic chemicals in general) appeared to be consistent with a concept of equilibrium adsorption (i.e., equal rates of adsorption and desorption after an apparent steady state was reached), more recent studies with some chemical-soil combinations have found that a fraction of the chemical appears to become sequestered (i.e., permanently bound to the soil) after the passage of significant time. This phenomenon is likely more important with large, strongly-adsorbed chemicals and high-surface-area soils. It likely is not so important with low-surface-area soils such as sand and gravel. In a practical sense, this partial sequestration may be manifested by having measured desorption coefficients being

4. California EPA, 1994; Doucette, 2000; Emmett, 2002-b; Schwarzenbach *et al.*, 1993-a and 1993-b; Lyman, 1982.

higher than the adsorption coefficient for the same chemical-soil combination.[5] But the studies I have seen have never shown 100% sequestration; there is always some desorption. In sandy soils with reasonably short exposure times, I would not expect significant amounts of sequestration.

Importance of Findings from Other Diquat Pond Applications

21. The applicants for Lake Cochituate's Middle Pond treatment program have pointed out that reports from other states, and from other publications, have apparently never shown a problem with diquat migration in groundwater (and no well contamination) after numerous field tests or full-scale applications. (ACT, 2009) While appearing to provide a significant weight of evidence, in my opinion this body of evidence must be discounted as essentially no evaluation was undertaken to show: (a) that the results were from properly designed scientific studies; and (b) that the conditions of the treatment applications (e.g., soil types, groundwater flows, etc.) for the cited studies were very similar to those at Middle Pond. Because the concern in this case is the possible contamination of public water supply wells, a higher burden of proof (of no migration and no risk) is required. The highest level of proof would come from the use of site-specific data in a rigorous mathematical model of diquat fate and transport at the Middle Pond-Evergreen well field site. This would provide quantitative estimates of diquat concentrations reaching the wells. A lower level of proof, one based only on site-specific data (but no modeling), might be acceptable if assessments of individual fate and transport properties (e.g., sediment and soil adsorption, biodegradation, photolysis) led to a "no migration" conclusion with a high degree of scientific certainty. In my opinion, the applicants have not come close to the level of proof required. Thus the applicants need to go beyond the citation of other program findings and conduct a site-specific evaluation which includes the measurement of site-specific data. (Examples of such data are given below.)

22. Examples of Some Site-Specific Studies

- Collect, in the proposed treatment area, several Middle Pond sediment/soil cores (extending down several feet from the sediment surface) and conduct:
  - Soil type and grain size analyses on samples from different depths in the cores.
  - Analyses for cation exchange capacity and organic matter of samples from different depths in the cores.
  - Batch adsorption and desorption tests (and/or soil column mobility tests) with diquat on samples from different depths in the cores. (Also, if possible, conduct similar adsorption/desorption test on deep soil samples representing likely flow pathways between the application area and the Evergreen well field.)

5. For example, data cited by the California EPA (California EPA, 1994) list an adsorption coefficient (Kd) for diquat on sand of 36, and a desorption coefficient of 39.

- Conduct measurements of the rate of surface water recharge to groundwater in the proposed application areas.
- Conduct investigations of the deeper soils that lie between the application area and the Evergreen well field. The studies should include assessments of soil types and stratification, as well as adsorption and desorption tests for samples from the most conductive layers.
- Conduct an investigation of the groundwater flow regime between the application area and the Evergreen well field. (To be done while the water supply wells are operating at normal pumping rates.)
- Using the site-specific data generated by the above, model the possible transport of diquat from the application area to the Evergreen well field.

23. Conclusion

I believe that it is possible for diquat to migrate from an application area on Middle Pond to Natick's Evergreen well field. This belief is based on:

- The likely similarities of the hydrology at this site to the nearby South Pond-Greenvale well field site where detailed site-specific studies by the US Geological Survey showed significant recharge of surface water into the groundwater zone, and a strong hydrologic connection (between pond and well field) with an estimated 64 (± 15) percent of the water withdrawn at the public-supply wells being derived from South Pond. (USGS, 2001);
- The likelihood that some of the diquat applied to Middle Pond surface waters would migrate to the groundwater zone before chemical or biological degradation could take place, and that – once in the groundwater zone – diquat would not be subject to any significant degradation; and
- The likelihood that the sediments and soils, through which the diquat would have to migrate, would not completely retard or bind the chemical. This statement reasonably assumes that sands, or sand and gravel mixtures, constitute a significant fraction of the sediment/soil material at the treatment area, and in the more conductive aquifer layers connecting the groundwater under the treatment area with the Evergreen well field. Sands (and sand and gravel mixtures) have – of all tested soils – the lowest tendency to adsorb diquat from solution, and diquat adsorption to such materials is not irreversible (i.e., desorption also takes place).

I reject the applicant's assertion - based on studies of diquat's limited mobility in sediments and soils, and studies at other diquat application sites – that "there is negligible risk for infiltration of diquat into Natick's nearby Evergreen Wells." My rejection is based on the fact that the data they cite and rely on come from generic laboratory studies or from field studies at other sites, with no effort being made to evaluate conditions at the Middle Pond site and to compare them to the conditions for the laboratory tests or at the sites where the other tests were conducted. The reasoning here is based on the fact that the fate and transport of a chemical in the environment is extremely dependent on site-specific conditions, and extrapolation of results from one site to another – without careful evaluation of differing site conditions – can easily lead to erroneous conclusions. To properly evaluate diquat fate and transport at the Middle Pond site, the applicants must obtain data on sediment, soil and groundwater conditions at the site, and on the interaction (i.e., adsorption/desorption) of diquat with sediments and soils from the site. Site-specific studies on degradation mechanisms (e.g., photolysis and biodegradation) would also be helpful.

References

Aquatic Control Technologies, Inc. (ACT), 2009. "Treatment of Non-Native Eurasian Watermilfoil at the Department of Conservation & Recreation [Middle Pond] Beach and Boat Ramp." Public information material supplied to the Natick Conservation Commission at their Public Hearing on March 19, 2009.

California EPA, 1994. "Diquat Dibromide: Risk Characterization Document," issued by the Department of Pesticide Regulation, California Environmental Protection Agency. Available at: www.cdpr.ca.gov/docs/risk/rcd/diquat.pdf.

Doucette, W.J., 2000. "Soil and Sediment Sorption Coefficients," Chapter 8 in: *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*." Eds: R.S. Boethling and D. Mackay. Lewis Publishers, Boca Raton, FL.

Emmett, K., 2002-a. "Final Supplemental Environmental Impact Statement for Diquat Dibromide." Publication number 02-10-052 of the Washington State Department of Ecology, The Water Quality Program, Olympia, WA. Available at: www.ecy.wa.gov/biblio/0210052.html.

Emmett, K., 2002-b. "Appendix A: Final Risk Assessment for Diquat Dibromide." Publication number 02-10-046 of the Washington State Department of Ecology, The Water Quality Program, Olympia, WA. Available at: www.ecy.wa.gov/biblio/0210046.html.

US Environmental Protection Agency (EPA-a), undated. "Consumer Factsheet on: DIQUAT." Available at: www.EPA.gov/safewater/pdfs/factsheets/soc/diquat.pdf.

US Environmental Protection Agency (EPA-b), undated. "Technical Factsheet on: DIQUAT." Available at: www.EPA.gov/safewater/pdfs/factsheets/soc/tech/diquat.pdf.

Extension Toxicology Network (EXTOXNET), 1996. "Diquat Dibromide," a Pesticide Information Profile compiled by a multi-university cooperative program with files maintained and archived at Oregon State University. Available at: http://extonet.orst/edu/pips/diquatdi.htm.

Freed, R., 2009. Personal communication (including a Superseding Order of Conditions for the subject site) from Rachel Freed, Section Chief: Wetlands and Waterways

Program, MA Department of Environmental Protection (Wilmington, MA) to Martin Levin, Esq., Stern Shapiro, Weissberg and Garin, LLP (Boston, MA) dated August 4, 2009.

Lyman, W.J., 2006. Letter report to Mike Gildesgame, Acting Director, Massachusetts Office of Water Resources, Department of Conservation and Recreation, Boston, MA. (March 7, 2006).

Lyman, W.J., 1982. "Adsorption Coefficient for Soils and Sediments," Chapter 4 in: *Handbook of Chemical Property Estimation Methods, Environmental Behavior of Organic Compounds*, Eds: Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. McGraw Hill Book Co., New York, NY, 1982. [Book subsequently published by the American Chemical Society, Washington, DC.]

Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden, 1993-a. "Organic Acids and Bases: Acidity Constant and Partitioning Behavior," Chapter 8 in: *Environmental Organic Chemistry*. John Wiley & Sons, Inc., New York.

Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden, 1993-b. "Sorption: Solid-Aqueous Solution Exchange," Chapter 11 in: *Environmental Organic Chemistry*. John Wiley & Sons, Inc., New York.

Tomczyk, R., 2006. Personal communication (including a Superseding Order of Conditions for the subject site) from Richard Tomczyk, Section Chief: Wetlands Program, MA Department of Environmental Protection (Wilmington, MA) to Sandra Brennan (Wayland, MA) and Eileen Samels (Natick, MA) dated November 2, 2006.

US Geological survey (USGS), 2001. "Pond-Aquifer Interaction at South Pond of Lake Cochituate, Natick, Massachusetts," prepared by P.J. Friesz and P.E. Church. Water Resources Investigation Report 01-4040 by the US Geological Survey. Available at http://pubs.usgs.gov/wri/wri014040/.

Signed under the pains and penalty of perjury this 26th day of October, 2009.

Warren J. Lyman