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September 22, 2009

Heather Garvie
Office of Pesticide Programs (OPP)
Regulatory Public Docket (7502P)
U.S. Environmental Protection Agency (U.S. EPA)
1200 Pennsylvania Ave., NW.
Washington, DC 20460–0001

RE: Silver and Compounds Registration Review
(Docket Number EPA–HQ–OPP–2009–0334)

Dear Ms. Garvie:

Thank you for making the preliminary work plan for the upcoming registration review of silver-based pesticides available for public review. We are pleased to have the opportunity to provide U.S. EPA with information from our experience and the scientific literature, with the goal of helping U.S. EPA to ensure that the registration review of silver and compounds is complete and accurate. Our comments focus specifically on the proposed plan to assess the environmental risks of silver discharges to publicly-owned wastewater treatment plants (POTWs).

Tri-TAC is a technical advisory committee representing the League of California Cities, California Association of Sanitary Agencies, and California Water Environment Association. We seek to improve the effectiveness and accountability of environmental programs that affect publicly owned treatment works in California by working with regulatory agencies and interest groups on treatment plant-related issues.

Tri-TAC members are very concerned about the water quality impacts from the discharge of silver ions and particles into our municipal wastewater systems. These concerns have been expressed in our previous letters to U.S. EPA and in letters from our colleagues at the Bay Area Clean Water Agencies (BACWA) and the National Association of Clean Water Agencies (NACWA). We appreciated U.S. EPA's decision to regulate silver ion-generating products like the Samsung "Silver Wash" washing machine. This decision recognized our concerns about the potential water quality impacts of residential pesticide uses—and affirmed U.S. EPA's responsibility to regulate releases of pesticidal silver into the environment.

Tri-TAC's Interest in Silver-Based Pesticides

Silver is highly toxic to aquatic life at low concentrations, is persistent, and can bioaccumulate in some aquatic organisms, such as clams. Due to concerns about

bioaccumulation and the placing of strict silver effluent limits in discharge permits, POTWs have implemented pollution prevention programs to identify and reduce silver discharges to sanitary sewer systems. These programs have been very successful in reducing POTW influent and effluent silver concentrations. These programs have also reduced silver concentrations in biosolids (sewage sludge), ensuring that silver will not limit options for biosolids reuse.

As discussed at length in the enclosed BACWA letter, the enclosed report by the Woodrow Wilson International Center for Scholars (Luoma 2008), and in enclosed scientific papers, ordinary use of silver-containing pesticides releases silver to municipal wastewater treatment systems. Widespread use of household products that release silver ions into sanitary sewer systems could increase silver concentrations in POTW influents, effluents, and biosolids. If silver pesticide product use becomes common, wastewater silver discharges could reach levels not seen in the last two decades—and could have adverse impacts on our wastewater treatment process as well as on the quality of our effluent and biosolids.

POTWs are subject to National Pollutant Discharge Elimination System (NPDES) permits under the Clean Water Act. These permits include toxicity limits and may also include quantitative effluent limitations for silver. Exceeding these limitations has serious consequences, including monetary fines and penalties and the risk of citizen lawsuits. Under California law, our members are liable for daily Mandatory Minimum Penalties should violations of their discharge permits occur.

Preliminary Silver and Compounds Registration Review Work Plan

Tri-TAC greatly appreciates that the preliminary work plan for silver and compounds registration review anticipates conducting an assessment of POTW discharges. This assessment is of tremendous national importance. Since POTWs have little or no practical control over the use of silver biocides, we need U.S. EPA to ensure that water quality standards are not exceeded, that biosolids management is not hindered, and that discharged silver does not interfere with biological wastewater treatment processes at POTWs.

We have the following comments on the preliminary registration review work plan:

- Most silver-based pesticide products will need to be included in the POTW discharge assessment. The preliminary work plan indicates that the assessment would include products "where the active ingredient could potentially pass through WWTPs [wastewater treatment plants]." Since silver does not biodegrade, no special analysis is necessary to determine the potential to pass through POTWs—once discharged to a POTW, silver will definitely enter the environment, either in wastewater effluent or in biosolids. In other words, the scope of the POTW discharge review should include all products that may be discharged to POTWs.

  To assist EPA with the task of identifying which silver-based pesticide use patterns will result in POTW discharges, we have attached a diagram of examples of direct and indirect pathways between pesticide uses and POTWs. On the basis of our review of the use sites in Appendix A of the work plan, all registered silver-containing pesticide active ingredients—and most registered products—will need to be considered in the POTW discharge assessment.

- POTW silver removal efficiency data should be used for the POTW discharge assessment. For assessment of ordinary (non-nanosilver) products, rather than use the computational methods that are mentioned in the preliminary work plan, we recommend the use of real world POTW silver removal efficiency data. Estimates of the efficiency of silver removal by POTWs differ significantly, and if based on solely on the chemical properties of silver, these estimates can be unrealistically high. For example, two of the enclosed papers utilize POTW silver removal efficiency estimates. Benn and Westerhoff (2008) made the unrealistic assumption that 99.8% of silver is removed by wastewater treatment. In contrast, Blaser et al. (2008) used a more realistic approach, recognizing that a range of silver removal efficiencies exist among POTWs. They estimated POTW silver removal efficiencies are in the range of 85% to 99% and considered the implications of both the high end (more silver transferred to biosolids) and low end (more silver in effluent) of the removal efficiency range.

  "Removal efficiency" is really a misnomer. Since silver does not biodegrade, silver "removed" from wastewater is simply transferred to biosolids. POTWs that efficiently repartition silver into biosolids may have lower effluent silver concentrations, but may have higher biosolids silver concentrations.

  On the basis of our POTW management experience, we recommend that U.S. EPA obtain silver removal efficiency data from a representative range of POTW sizes and treatment process designs and use those data to identify the reasonable worst case conditions to use in its environmental risk assessment. Real-world data should not be difficult to obtain. U.S. EPA Office of Water's Office of Wastewater Management may already have these data on file. If these data are not readily available from internal U.S. EPA resources, we would be happy to work with you and our colleagues at NACWA to develop a dataset that meets EPA's needs.

- Leaching studies will be necessary for U.S. EPA to estimate POTW discharges. The work plan should anticipate the need for leaching studies to obtain data on the quantities of silver ions and nanosilver particles discharged to POTWs from ordinary use—including washing and surface cleaning—of silver-containing products. Data from a wide range of product types are needed to account for factors that significantly affect releases to POTWs, e.g., particle size, particle surface area, product use patterns, and the varied characteristics of treated consumer products. The Benn and Westerhoff paper shows the great importance of leaching studies—their measured silver releases from some treated products were much higher than would have been estimated on the basis of desktop estimates.

- Silver surface area measurements are needed. For nanoparticles, surface area has a major affect on product chemistry. Surface area cannot be predicted from particle size alone because particle morphologies vary significantly. Since specific surface area measurements are not difficult or expensive, U.S. EPA should require surface area measurements for nanosilver products.

- End of life product disposal needs evaluation. Since end use products treated with silver biocides may contain relatively high silver concentrations, proper disposal of treated items at end of life in compliance with hazardous waste standards should be considered during registration review. Product silver concentrations can exceed 1,000 parts per million (ppm) (see Benn and Westerhoff, 2008, enclosed), which is twice California's

hazardous waste standard for total silver content (500 ppm, see *California Code of Regulations*, Title 22, Chapter 11, Article 3).

- The scope of the review should include all products in which silver has a pesticidal function. We recognize that U.S. EPA is considering the scope of its registration responsibility concurrent with the initiation of this review. (As we have previously indicated, we believe that U.S. EPA should require registration of all products where silver has a pesticidal function, whether or not a claim is made on the product label.) Since both registered and currently unregistered products contribute cumulatively to POTW silver discharges, we request U.S. EPA include in the environmental risk assessment all consumer products that by design contain silver that functions as a pesticide, whether or not these products are currently registered. We also request that U.S. EPA consult with the Food and Drug Administration regarding similar products that may not be regulated by U.S. EPA and consider these products in the environmental risk assessment.

Nanosilver and POTWs

We support U.S. EPA's plan to address the effects of particle size in the environmental risk assessment. Available scientific information indicates that it will be important for the POTW discharge assessment to include a special assessment of the wastewater discharges from nanosilver products. Silver particle size and form (e.g., zeolite) may significantly alter the way that silver-containing products affect POTWs. For example:

- The quantity and/or nature of silver discharged to POTWs may be affected by the small particle size and large surface area of nanosilver products as compared to other silver biocides. For example, Benn and Westerhoff (2008) found that for certain products, silver losses during washing were so large that most of the silver in these products would be washed into the municipal wastewater system during the products' lifetimes. (A copy of this paper is enclosed.) Where small particles occur in products, the entire particle could be washed down the drain.

- Nanosilver particle may have extraordinary effects on POTW treatment processes. In two related studies, Choi and Hu (2008) and Choi et al. (2008) found that silver particles less than 5 nanometers in diameter are uniquely toxic to nitrifying bacteria, which are critical to biological nutrient removal at POTWs. (Copies of both papers are enclosed).

- Differing removal efficiencies. POTWs tend to be most efficient at removing larger particles from wastewater. Tiny particles and zeolites may have different potential to pass through POTWs than other forms of silver.

- Particle size is known to modify silver's aquatic toxicity. For example, see Griffitt et al. 2008, enclosed.

Widespread Use of Silver-Based Pesticides Is Not Sustainable

It is distressing to POTWs to observe the increasing prevalence of household products that use silver and other toxic chemicals for general antimicrobial purposes. POTWs are proud of our history of taking effective actions that reduce discharges of toxic pollutants to the environment. While POTWs have the authority to regulate industrial and commercial sources of silver and

other toxic pollutants, we have little or no control over the discharge of pollutants from the thousands of households we serve. Silver is a toxic metal that cannot degrade in the environment and is registered for use as a pesticide in numerous products. To allow the unrestricted usage of products that intentionally release silver into the environment would be an irresponsible neglect of the principles of environmental sustainability that should strongly influence U.S. EPA's decisions.

Thank you for your consideration of our comments on the preliminary work plan for registration review of silver-based pesticides. If you have any questions, please contact Gail Chesler, at (925) 229-7294 or chesler.gail@gmail.com.

Sincerely,

Ben Horenstein

Ben Horenstein
Chair

BKH:KM:llb

Enclosures

1. Pla, M. Bay Area Clean Water Agencies (2009). Comment letter – petition for Rulemaking Requesting U.S. EPA Regulate Nanoscale Silver Products as Pesticides. Letter to Nathanael R. Martin, U.S. EPA. March 19.
2. Luoma, S. N. (2008). *Silver Nanotechnologies and the Environment: Old Problems or New Challenges?* Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies. Publication PEN 15. September.
3. Benn, T. M. and P. Westerhoff (2008). "Nanoparticle silver released into water from commercially available sock fabrics." *Environmental Science & Technology* **42**(11): 4133-9 (published correction is included).
4. Blaser, S. A., M. Scheringer, et al. (2008). "Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles." *Science of the Total Environment* **390** (2-3): 396-409.
5. Choi, O. and Z. Hu (2008). "Size dependent and reactive oxygen species related nanosilver toxicity to nitrifying bacteria." *Environmental Science & Technology* **42**(12): 4583-8.
6. Choi, O., K. K. Deng, et al. (2008). "The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth." *Water Research* **42**: 2066-2074.
7. Griffitt, R. J., J. Luo, et al. (2008). "Effects of particle composition and species on toxicity of metallic nanomaterials in aquatic organisms." *Environmental Toxicology & Chemistry* **27**(9): 1972-8.
8. Pesticide Transport to POTWs – conceptual model diagram and diagram of examples of direct and indirect pathways between pesticide uses and POTWs

Note: Enclosures 3 through 7 are copyrighted materials that cannot be posted in the public docket. These have been submitted via email to Heather Garvie. We request that U.S. EPA provide these materials to all staff that are reviewing these comments.

cc: Debra F. Edwards, Director, U.S. EPA Office of Pesticide Programs
William R. Diamond, Director, Field and External Affairs Division
Donald Brady, Director, Environmental Fate & Effects Division
Jack Housenger, Director, Biological and Economic Analysis Division
Lois Rossi, Director, Registration Division
Joan Harrigan-Farrelly, Director, Antimicrobials Division
Betty Shackleford, Associate Director, Antimicrobials Division
Norm Cook, Branch Chief, Antimicrobials Division
Ephraim King, Director, U.S. EPA Office of Water, Office of Science and Technology
James A. Hanlon, Director, U.S. EPA Office of Water, Office of Wastewater Management
Alexis Strauss, Director, Water Division, U.S. EPA Region 9
Patti TenBrook, Life Scientist, U.S. EPA Region 9
Tom Mumley, California Regional Water Quality Control Board, San Francisco Bay Region
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Mary-Ann Warmerdam, Director, California Department of Pesticide Regulation
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Chris Hornback, Senior Director, Regulatory Affairs, National Association of Clean Water Agencies