Summary of the August 27, 2012 Meeting of the Sulfate Ad hoc Workgroup of the Water Resources Advisory Committee (WRAC)

This special Ad hoc workgroup meeting of WRAC was called to order at 9:40 a.m. by Chairperson Don Bluedorn on Monday, August 27, 2012 in Room 105 of the Rachel Carson State Office Building, Harrisburg, PA.

The following committee members were present:

Myron Arnowitt, Clean Water Action Gary Merritt, NSG Chuck Wunz, Wunz Associates Robert Cavett, Merck & Co. Don Bluedorn, Babst, Calland, Clements, Zomnir, P.C.

The following DEP staff members were present:

Duke Adams, DEP Office of Water Management Sean Gimbel, Policy Office Theia Hofstetter, Bureau of Point/Non-Point Source Management Paul Curry, Bureau of Point/Non-Point Source Management Diane Wilson, Bureau of Conservation and Restoration Jesse Shull, Bureau of Point/Non-Point Source Management Chuck Thurner-Diaz, Bureau of Conservation and Restoration Olivia Carlson, Bureau of Conservation and Restoration Kevin Kelly, Bureau of Conservation and Restoration Michelle Moses, Bureau of Regulatory Counsel Joshua Graybeal, DEP Intern Tom Barron, Bureau of Point/Non-Point Source Management Tom Bold, Bureau of Waterways Engineering and Wetlands Jason Oyler, Bureau of Regulatory Counsel Kristen Schlauderaff, Bureau of Point/Non-Point Source Management Rodney McAllister, Bureau of Point/Non-Point Source Management Lee McDonnell, Bureau of Point and Non-Point Management Bonita Moore, Bureau of Point/Non-Point Source Management Rod Kime, Bureau of Point/Non-Point Source Management

The following guests were also present:

Nancy Evans, PPL Sarah Miller, Independent Regulatory Review Commission Alisha Wells, PA Chamber of Business and Industry Jeff Shanks, Waste Management Josie Gaskey, PA Coal Association Jim Richenderfer, Susquehanna River Basin Commission John Burglund, Wallace & Pancher Gary Geisinger, Wallace & Pancher Daniel Ryan, PA Fish & Boat Commission Scott Schalles, Independent Regulatory Review Commission Michelle Elliott, Independent Regulatory Review Commission Jake Smeltz, Electric Power Generating Association

Overview of Workgroup Objectives: Don Bluedorn and Duke Adams

After some brief discussion, it was agreed that the workgroup would attempt to develop a "consensus position" but, if that was not possible, the workgroup instead would prepare a summary report of the discussions for the broader WRAC membership.

DEP overview of public comments received: Rod Kime & Tom Barron

Eight entities provided specific comments on Sulfates. There were three basic themes of the comments that are related to the science.

The first being that Dr. Soucek's Illinois study is not transferable to Pennsylvania. The commenters noted that emerging science shows that the combinations of different ions in water have association to the toxicity of different ions such as sulfate. The study utilized sodium sulfate making sodium the dominant ion in that study and PA streams are primarily calcium dominated.

The second is that recent testing has shown that there are chronic impacts of sulfates on aquatic life as well that should be considered. The results show that chronic criteria are lower than acute criteria. The criterion DEP was proposing was based on acute tests so that to have a complete set of sulfate criteria, DEP should add a chronic component as well.

The third comment was a study that collected macroinvertabrate and sulfate concentrations above and below NPDES discharges. They concluded that there was minimal to no difference or effect on aquatic life between compliant and non-compliant sulfate limits. DEP has concern with the analysis and believe this conclusion is misleading.

Influence of hardness and chloride on the acute toxicity of sodium sulfate: Development of the Illinois sulfate standard: Dr. David Soucek, University of Illinois

Dr. Soucek's Power Point presentation is attached. He explained the research and how the data was used to establish the Illinois standard for sulfates. General Use Standards of 500 mg/L for sulfate and 1000 mg/L for TDS were adopted in 1972, but little scientific data was available at that time for support. In 1984, a special sulfate standard of 3500 mg/L was adopted specifically for mine related waters. In 2003, the Illinois EPA began the process of developing updated sulfate standard. The chloride standard was and remains 500 mg/L.

The objective of Dr. Soucek's study was to 1) generate acute toxicity data for several invertebrates, 2) determine influence of chloride on sulfate toxicity, and 3) determine

influence of hardness on sulfate toxicity. Dr. Soucek noted that invertebrates were chosen for the study because literature research showed that data on invertebrates was sparse and we know from other data that fish are much less sensitive to changes in sulfates. Tests were conducted at appropriate temperatures for the species and in moderately hard reconstituted water (MHRW) developed as a U.S. EPA standard for lab testing. The test species were *Ceriodaphnia dubia, Chironmus tentans, Sphaerium simile,* and *Hyalella Azteca.*

Lethal concentrations to 50% of a sample population (LC50) are geometric means of all Spearman-Karber values generated for a given organism using measured sulfate concentrations. Lethal concentrations to 10% of a sample population (LC10) values were generated using probit analysis with the combined data from all tests for a given species. Control group survival was >90% in all exposures. Tests produced similar LC50s and because the values were so high, a third test was not conducted on *Chironomus tentans*.

Species	n	Mean LC50 $(mg SO^{2-}_4/L)$	Range $(\text{mg SO}^{2-}_{4}/\text{L})$	$\frac{LC10}{(\text{mg SO}^{2-}_{4}/\text{L})}$
Ceriodaphnia dubia	3	2,050	1,869 - 2,270	1,759
Chironomus tentans	2	14,134	14,123-14,146	11,682
Spaerium simile	3	2,078	1,901 - 2,319	1,502
Hyalella azteca	3	512	431 - 607	262

The data that stood out was that *C. tentans* was very insensitive and *C. dubia* and *S. simile* shared similar sensitivities, while *H. azteca* had very low LC50. It didn't seem that *H. azteca* should be that much more sensitive than the other organisms. Some additional literature research revealed that a reformulated moderately hard reconstituted water (RMHRW) was developed exclusively for use with *Hyalella* in the lab. The major difference in MHRW and RMHRW is chloride concentration which is 1.9 mg/L and 33.9 mg/L respectively; and magnesium and calcium ratios with RMHRW having more calcium, but less magnesium.

The RMHRW resulted in increased LC50 for both *H. azteca* and *C. dubia*. Based on additional research it appeared the calcium and magnesium ratio had little impact and the greatest factor in this change is the increase in chloride concentration. Based on this, Dr. Soucek developed an additional experiment to look at changes in the chloride concentration, beginning with 1.9 mg/L from the original MHRW and increasing incrementally to 500 mg/L. The reconstituted water had a hardness constant at ~100 mg/L and calcium:magnesium mass ratio of 2.33

The results of this study showed that over the low end of the range from nominal chloride concentrations up to about 33 mg/l there is a slight increase in LC50 for *C. dubia* and a strong increase for *H. azteca* at the low end of the chloride scale. At the upper end of the range for chloride concentration from about 33 mg/L to 500 mg/L there is a decrease in

LC50 and sulfate toxicity, some of this is likely due to an increase in chloride toxicity at these levels.

Next Dr. Soucek looked at the effect of hardness in the water. The literature shows that sodium and calcium were not significant variables, suggesting toxicity of sodium and calcium salts attributable to corresponding anions and the toxicity of chlorides, sulfates, and potassium were reduced in solutions enriched with more than one cation, mainly magnesium and calcium. Dr. Soucek tested *C. dubia* and *H. azteca* at nominal hardnesses of 100, 200, 300, 400, 500, and 600 mg/L. There is a strong decrease in toxicity as hardness increases. All the data above led to the development of the Illinois standard which is as follows:

-If hardness \geq 100 but \leq 500, and Cl \geq 25 mg/L but \leq 500 mg/L: sulfate criterion = [1276.7 + 5.508(hardness) - 1.457(Cl)]*65

-If hardness \geq 100 but \leq 500, and Cl \geq 5 mg/L but \leq 25 mg/L: sulfate criterion = [-57.478 + 5.79(hardness) + 54.163(Cl)]*65

-If hardness <100 or Cl < 5: sulfate criterion = 500 mg/L

-If hardness >500 and Cl >5: sulfate criterion = 2000 mg/L

A question was posed if Dr. Soucek believes that there is enough information to transfer the Illinois information to Pennsylvania

Dr. Soucek noted that PA streams are more calcium dominated and not sodium dominated like Illinois streams. He stated a belief that calcium concentrations should be less than sodium concentrations for the Illinois criteria to apply. He suggested that more research would be beneficial to determine if the criteria Illinois as established and his research would be over protective or under protective in Pennsylvania's calcium dominated streams.

In response to a question about the use of plants for toxicity studies, Dr. Soucek noted that some work is being done with blue-green algae, but plant data is not typically used in the development of water quality standards. Minnesota has looked closely at wild rice and does have a more stringent standard than Illinois.

Another question was posed if we are getting the most accurate picture of what is happening in PA streams if we do not talk about chlorides as well. Dr. Soucek responded that Illinois has incorporated the use of chlorides in their standard and also has a standalone chloride standard. Iowa has recently developed an acute and a chronic standard and there is talk of a move at the federal level to update the chloride standard.

Acute and chronic sulfate toxicity to select freshwater organisms in water-only exposures: Dr. Ning Wang, U.S. Geological Survey

Dr. Wang's PowerPoint presentation is attached. The objective of the study was to generate acute and chronic sulfate toxicity data for four freshwater organisms that might be used by USEPA to develop national water quality criteria and by states and tribes to develop water quality standards for sulfate. The test material for Dr. Wang's studies was sodium sulfate.

Their studies looked at both acute and chronic conditions and concluded the following:

- The cladoceran and the mussel were more acutely sensitive to sulfate than the fathead minnow and midge
- Fathead minnow (especially the embryonic life stage) were extremely sensitive to sulfate (acute-chronic ratio of 34)
- The mussel was more chronically sensitive to sulfate than the cladoceran and the midge
- Further study is planned to determine the influence of water quality (hardness or chloride) on chronic sulfate toxicity to fathead minnow and C. dubia

Dr. Wang noted that he intends to do future sulfate studies for toxicity related to sodium, calcium, and potassium dominated systems in the near future.

A question was posed on studies that look at sulfate in other forms such as sulfides. Dr. Wang noted that they have not but believes that there is merit to study of other sulfate ions.

The point was clarified that this is lab study as opposed to field study, and questioned if there were any plans to conduct study in the field. Dr. Wang noted that there are no plans to do so, but it would be useful information.

PA Coal Association (PCA) presentation: Josie Gaskey, Gary Geisinger, John Burglund

PCA's PowerPoint presentation is attached. The field study conducted by Wallace & Pancher to determine if the proposed criteria were the appropriate aquatic life benchmarks for sulfate and chloride.

The study looked at two watersheds and placed 47 sample stations upstream and downstream of known regulated discharge points. The study was conducted from August 2010 thru June 2011. The number of samples taking at each site varied from as few as two to as many as 17 for a total of 157 total samples. The USEPA Rapid Bioassessment Multi-habitat Protocol was utilized for collection. In the lab samples were sorted to $200(\pm 20\%)$ organisms according to USEPA protocols. Macroinvertebrates were identified by certified taxonomists to lowest practicable level and water quality samples collected concurrently and tested by a certified laboratory. The eight biological metrics were chosen to evaluate diversity, composition, and pollution tolerance:

- Taxa richness
- Ephemeroptera richness

- Modified Ephemeroptera richness
- Modified % Ephemeroptera
- Modified Ephemeroptera, Plecoptera, Trichoptera richness
- Modified % Ephemeroptera, Plecoptera, Trichoptera
- Number of pollution intolerant taxa
- Equitability index

Modified taxa were chosen to exclude intolerant taxa

The study evaluated the compliance of sites with proposed sulfate and chloride criteria. Looking at all the sites 10% would not be in compliance with one or both criteria, as proposed. Of the non-compliant samples, 3% were non-compliant with sulfate and 94% were experiencing low flow conditions, compared to other sampling events.

The study used principal coordinate analysis and cluster analysis as a way to show that the samples meeting the criteria with sites not meeting the criteria indicating similarity. Both analyses grouped the samples meeting the criteria with sites not meeting the criteria indicating similarity.

PCA believes that in order to set a water quality standard the following information should be collected: biological integrity data, chemical data, physical data, habitat assessment, and toxicity testing. PCA's recommendation is for DEP to take a step back and collect the needed biological integrity, chemical and physical data, and conduct habitat assessments and toxicity testing across the state to determine that a state-wide water quality standard for sulfate and chloride is actually needed.

DEP staff voiced concerns about the analysis. The biggest concern was the study did not control for co-variables, such as habitat, sedimentation, and seasonality. To determine the impact of sulfate on macroinvertebrates, the effects of the co-variables must first be understood. The ordination graph based on macroinvertebrates to show there were no sulfate impacts on macroinvertebrates was misleading because the form of the resultant graph could easily have been due to any number of co-factors other than sulfate. Impaired sites with low sulfate but impaired by habitat would have clustered with sites impaired by high sulfate. Ordinations that include taxa, other chemical constituents beside sulfate, habitat metrics, and land use patterns would likely produce different results than what was presented.

DEP reviewed the data that PCA provided in a spreadsheet and noted that everywhere there were high sulfates above the proposed criteria the macroinvertebrates were impaired. The study relied heavily on various forms of the EPT index which all probably correlate because they are measuring the same subgroup of taxa in slightly different ways.

PCA noted that this study was not meant as a definitive analysis, but was more intended to look at these indices to see if there are sites that meet the criteria and don't meet the criteria. PCA noted that more study needs to be done.

PCA asked what does DEP's data show. DEP noted that our data shows that sulfate impairments can begin between 50 and 200 mg/L. Whenever field data is used, there are many co-variables that need to be teased out. This is precisely why toxicity tests are done in lab settings because the variables can be controlled to truly see the effects of a given constituent. The lab studies DEP has reviewed and those presented as part of this meeting show that sulfates at increased levels kill aquatic organisms. DEP noted that we collect field data regularly and will share that information with PCA, and that DEP would appreciate PCA's data that was used as part of this study. PCA indicated they were not sure if they could share this data, and would get back to DEP on that.

Conclusions and Path Forward: Don Bluedorn and Duke Adams

After some discussion, it was determined that the workgroup could not agree to a "consensus position" and that a summary report would be prepared for the broader WRAC membership.