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December 7, 2018

Ms. Elena Guilfoil
Washington Department of Environmental Quality
PO Box 47600
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Dear Ms. Guilfoil:

The Washington Department of Ecology (Ecology) has initiated a process to look at changes to WAC 173-460, Controls for New Sources of Toxic Air Pollutants. Associated with this regulatory process, the Far West Agribusiness Association (Far West) has submitted a petition to Ecology to remove ammonium sulfate as a toxic air pollutant.

The J.R. Simplot Company (Simplot) is a privately held agribusiness company headquartered in Boise, Idaho. Simplot has extensive operations in the State of Washington, including food processing, farming, beef cattle, fertilizer distribution and warehousing and fertilizer retail operations. In particular, Simplot is one of the largest manufacturer and supplier of phosphate nutrients in the western United States.

Simplot supports the petition to remove ammonium sulfate as a toxic air pollutant as is currently listed in WAC 173-460. A review of the relevant technical studies that were used as the basis for classifying ammonium sulfate as an air toxic has shown that such a determination was likely made in error. The primary study referenced (Utell et al. 1983), *did not* show an effect from exposure to ammonium sulfate in the study conducted with asthmatics. The attached technical report reviews the Utell et all study and other relevant documents.

Please let me know if you have any questions. We do sincerely appreciate the opportunity to provide comments on this matter to Ecology.

Sincerely,

Alan L. Prouty
Vice President
Environmental & Regulatory Affairs

Attachment

C:
Association of Washington Business
Far West Agribusiness
Food Northwest

J.R. Simplot Company

TECHNICAL REPORT SUPPORTING PETITION TO REMOVE AMMONIUM SULFATE FROM THE TOXIC AIR POLLUTANT LIST

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Acronyms and Abbreviations

DOE	Department of Ecology
FEV_1	forced expiratory volume in one second
MMAD	Mass Median Aerodynamic Diameter
MPR	Maximum Permissible Risk
NAAQS	National Ambient Air Quality Standard
NOAEL	No Observed Adverse Effect Level
OEHHA	Office of Environmental Health Hazard Assessment
PEL	Permissible Exposure Level
REL	Reference Exposure Level
RIVM	National Institute for Public Health and the Environment of the Netherlands
TAP	Toxic Air Pollutant
TLV	Threshold Limit Value
USEPA	United States Environmental Protection Agency

TECHNICAL REPORT SUPPORTING PETITION TO REMOVE AMMONIUM SULFATE FROM THE TOXIC AIR POLLUTANT LIST

The Washington Department of Ecology (DOE) has listed ammonium sulfate as a "toxic air pollutant" under WAC 173-460-150 based on the California Office of Environmental Health Hazard Assessment (OEHHA) 1-hour acute Reference Exposure Level (REL) from 2008. The Far West Agribusiness Association has petitioned the DOE to remove ammonium sulfate from the Toxic Air Pollutant (TAP) list or specifically exempt ammonium sulfate fertilizers from the requirements of the rule.

This document provides technical support to the petition of the Far West Agribusiness Association to remove ammonium sulfate from the TAP list based on the most recent, best available health effects information.

1 Ammonium Sulfate Did Not Cause Adverse Health Effects in the Study Cited as the Basis for the REL for Sulfates, and Subsequently as a Toxic Air Pollutant in Washington

The California OEHHA derived an Acute REL for particulate sulfate aerosols in ambient air of 120 µg/m³ to protect against a decrease in airway conductance, which was described as a "mild adverse" effect. The REL is based on a study by Utell et al. (1983) with 17 volunteer human asthmatics who were exposed to small particle aerosols of 100, 450, or 1,000 µg/m³ of sulfuric acid or other sulfates of varying acidities for 16 minutes. OEHHA derived the REL by defining 450 µg/m³ as a No Observed Adverse Effect Level (NOAEL) for "sulfates," because it was a NOAEL for ammonium bisulfate. Given that the exposure time in this study was 16 minutes, OEHHA used Haber's Law to prorate the exposure to 60 minutes for the 1-hour REL.

The Utell et al. (1983) study tested five types of aerosols: sodium chloride (negative control), sulfuric acid, ammonium bisulfate, sodium bisulfate, and ammonium sulfate. A key aspect of this study was that it was focused on small particle aerosols associated with airborne emissions from combustion sources. The introduction of the paper starts with these two sentences:

> "The burning of fossil fuels results in the release of sulfate and sulfuric acid aerosols into the environment. Several recent epidemiologic studies have emphasized the relationship between elevated levels of sulfate air pollutants and symptoms in asthmatics (1-3)."

To simulate the aerosols emitted from combustion sources in urban areas, the researchers created laboratory aerosols with an average Mass Median Aerodynamic Diameter (MMAD) of 0.8 micrometers, which would fall into the $PM_{2.5}$ category. The particle concentrations of 100-1,000 µg/m³ were considerably higher than the United States Environmental Protection Agency's (USEPA's) National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$, which is 12 µg/m³ as the annual mean averaged over 3 years and 35 µg/m³ as the 98th percentile averaged over 3 years (https://www.epa.gov/criteria-air-pollutants/naaqs-table).

The study authors took two measurements, specific airway conductance (SGaw) and forced expiratory volume in one second (FEV_1) in 7 to 15 of the volunteers (*n* varied by test substance and dose). The measurements were compared to tests with a sodium chloride aerosol, which was the negative control. As noted in the table below that summarizes the data in Table 3 of Utell et al. (1983), ammonium sulfate did not affect the ventilatory function in asthmatic volunteers at 1,000 µg/m³, a concentration considerably higher than the NAAQS of 12 µg/m³ for $PM_{2.5}$ or the California REL of 120 µg/m³. The authors did not even bother to test the lower doses because of the lack of response at the maximum dose.

The authors claim to test 17 asthmatics, but sodium chloride was tested in 13 to 17 subjects and the four test substances were tested in only 7 to 15 subjects. No explanation is provided for why all 17 subjects were not tested for each substance at each dose, and the tested subjects were not identified. The 17 individuals varied considerably in their pre-testing pulmonary function. The [forced expiratory volume (1-sec)/forced vital capacity] varied from 62% to 79% and the specific airway conductance varied from 0.112 to 0.275 (cm H_2O^{-1} s^{-1}). Thus, which subjects were tested with which test dose is important information for evaluating this study, and this information is missing. The study does say that it was double-blind and randomized, but the use of differing numbers of subjects in each group adds considerable uncertainty to the results.

Table 1. Specific Airway Conductance Results of Utell et al. (1983)

Dose	Sulfuric Acid	Ammonium Bisulfate	Sodium Bisulfate	Ammonium Sulfate
1,000 µg/m³	Significant	Significant	Not Significant	Not Significant
450 µg/m³	Significant	Not Significant	Not Significant	*
100 µg/m³	Not Significant	Not Significant	Not Significant	*

* Not Tested

Table 2. Forced Expiratory Volume (1-second) Results of Utell et al. (1983)

Dose	Sulfuric Acid	Ammonium Bisulfate	Sodium Bisulfate	Ammonium Sulfate
1,000 µg/m³	Significant	Not Significant	Not Significant	Not Significant
450 µg/m³	Not Significant	Not Significant	Not Significant	*
100 µg/m³	Not Significant	Not Significant	Not Significant	*

* Not Tested

The study authors acknowledge that ammonium sulfate aerosol had no effects on the breathing of the asthmatic volunteers: "Exposure to the less acidic sulfate aerosols, $NaHSO_4$ [sodium bisulfate] and $(NH_4)_2SO_4$ [ammonium sulfate], caused no significant change in lung function." They theorize that the reason that certain "sulfates" cause adverse effects in asthmatics and certain ones do not is the acidity of the species. The pH of equal molar solutions at the concentrations used in the studies are as follows:

Table 3. Effects of Sulfates Depend on Acidity, Utell et al. (1983)

Species	pH of 0.01 Molar Solution
Sulfuric Acid	1.8
Ammonium Bisulfate	2.2
Sodium Bisulfate	2.5
Ammonium Sulfate	4.8

Utell et al. (1983) did not report that ammonium sulfate caused bronchoconstriction in asthmatic subjects. However, their general conclusions may have misled some readers into thinking that adverse effects were seen with ammonium sulfate. For instance, in the abstract, they stated:

> "These data indicate that asthmatics demonstrate bronchoconstriction after brief exposures to common acidic sulfate pollutants."

They did not further state that only *two* of the four compounds tested were "common acidic" sulfates. Further, in the Results section, they stated:

> "The present study demonstrated significant responses in asthmatic subjects to short-term inhalation of acidic sulfates at 450 µg/m³ and 1,000 µg/m³ for 16 min."

Again, they did not state that only *two* of the tested compounds fell into the category of "acidic sulfates." One has to read the entire paper carefully to see that ammonium sulfate was not an "acidic sulfate," and it did not cause bronchoconstriction in asthmatic subjects.

2 OEHHA (2008) Made an Honest Mistake When They Added Ammonium Sulfate to the Dossier on "Sulfates"

OEHHA (2008) intended for the REL for "Sulfates" to be used to assess sulfates in the atmosphere as fine aerosols, as evidenced by the documentation provided in Appendix D of the Technical Support Document for the Derivation of Noncancer Reference Exposure Levels:

> "Sulfates, including sulfuric acid, are produced in ambient air through oxidation of the SO_2 and SO_3 formed from fuel combustion (CARB, 1976). Atmospheric ammonia reacts with sulfuric acid to form the ammonium salts $(NH_4)_2SO_4$ and $(NH_4)HSO_4$."

There is no reference to ammonium sulfate fertilizer in the documentation for the REL for "Sulfates," and solid ammonium sulfate or dissolved ammonium sulfate fertilizers were not the subject of the REL derivation exercise in 2008.

OEHHA (2008) initiated its discussion of the toxicity of "sulfates" by acknowledging that the acidity of certain sulfate species causes their adverse effects in the respiratory system. In Section IV. (Acute Toxicity to Humans), they state:

> "The hydrogen ion content of the acid sulfate exposure provides a stimulus for bronchoconstriction, especially in asthmatics (Balmes et al., 1989)."

Ammonium sulfate has no hydrogen ion content, so it cannot act like some other sulfate species that do have donor hydrogen ions. In fact, ammonium sulfate is a neutralization product of atmospheric sulfuric acid and acidic sulfates, such as sulfuric acid and ammonium bisulfate, that renders them less toxic as noted by Schlesinger and Graham (1992) and cited in OEHHA (2008).

OEHHA's (2008) discussion of the Utell et al. (1983) study mentions the positive results for sulfuric acid and ammonium bisulfate at the highest dose tested, but it does not mention the negative results for sodium sulfate or ammonium sulfate. Because the Utell et al. (1983) study showed no effects for ammonium sulfate and only showed effects for ammonium bisulfate, the derived REL is relevant for ammonium bisulfate fine aerosols, but it is not relevant or appropriate for ammonium sulfate. In addition, ammonium sulfate did not exhibit any adverse effects in any other studies cited.

Table 4. Other Human Studies Cited in OEHHA (2008)

Study	Test Compounds	Results on Airways Function
Amdur et al. (1952)	Sulfuric Acid	Adverse effects
Amdur et al. (1989)	Sulfuric Acid	Adverse effects
Avol et al. (1979)	Sulfuric Acid, Ammonium Bisulfate, Ammonium Sulfate	No adverse effects
Koenig et al. (1989)	Sulfuric Acid	Adverse effects
Avol et al. (1990)	Sulfuric Acid	No adverse effects
Kleinman et al. (1981)	Ferric Sulfate	No adverse effects
Utell et al. (1982)	Sulfuric Acid, Ammonium Bisulfate, Sodium Bisulfate, Ammonium Sulfate	Adverse effects for sulfuric acid

The Utell et al. (1982) study is duplicative of the Utell et al. (1983) study and uses the same chemicals, the same volunteers, and the same general protocol. The data presented in Utell et al. (1982) are also presented in Utell et al. (1983) with the addition of data from a new 450 $\mu g/m^3$ dose group. It appears that the later study is an extension of the earlier study. This assumption is supported by the fact the study authors in Utell et al. (1983) referred to their earlier study only with regard to sulfuric acid. They were silent on how their 1983 results for the other test chemicals compared to the preliminary results from the 1982 study because of the duplication within the two studies.

3 Other Studies with Human Volunteers Showed that Ammonium Sulfate Does Not Cause Adverse Effects on Pulmonary Function

Two summary toxicology reports have summarized the literature on ammonium sulfate's effects on human pulmonary function:

- BMU (Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit). 2004. SIDS Initial Assessment Report for SIAM 19. Ammonium Sulfate.

- Weinburg Group. 2003. Health & Environmental Safety Data Summary Document; Ammonium Sulfate CAS #7783-20-2.

Several additional studies that were not discussed in OEHHA (2008) were summarized in these two summary documents.

Table 5. Other Human Studies Cited in BMU (2004) or Weinburg (2003)

Study	Test Compounds	Results on Airways Function
Stacy et al. (1983)	Ammonium Sulfate	No adverse effects
Kulle et al. (1984)	Ammonium Sulfate	No adverse effects
Koenig et al. (1993)	Ammonium Sulfate	No adverse effects
Frank et al. (1977)	Ammonium Sulfate	Adverse effects

Only one of the studies reported effects on pulmonary function by fine particulate ammonium sulfate aerosols, but this report is unavailable for evaluation because it is an unpublished, non peer-reviewed report. The BMU (2004) document states:

> "At 1 mg ammonium sulfate/m^3 a decrease in pulmonary flow resistance and decreased dynamic lung compliance were found in 4 healthy volunteers after 120 min of exposure (Frank et al., 1977)."

No details about the study are known, such as the particle size of the aerosol; the identity of the negative controls, if any; whether the reported effects were statistically significant or not compared to a negative control; the number of volunteers tested; etc. Accordingly, this one sentence cannot be used as support for the erroneous inclusion of ammonium sulfate into the "sulfates" REL category based on the mis-reading of the Utell et al. (1983) study.

4 Ammonium Sulfate Fertilizer is Prepared and Used as Large Particle Solids or Liquids

Inhalation of fine particle ammonium sulfate aerosols has not been shown to adversely affect the pulmonary function of normal or asthmatic human volunteers. However, even if the Utell et al. (1983) had shown adverse effects in the human volunteers, that information and the OEHHA-derived REL would not be relevant to the manufacture, processing, packaging, distribution and use of ammonium sulfate fertilizers.

The health concern about sulfuric acid and certain acidic sulfates is due to their presence in ambient air as small particles ($PM_{2.5}$) from power plant emissions. Such small particles do not arise to any significant degree from the manufacture, processing, packaging, distribution and use of ammonium sulfate fertilizers.

USEPA (1979) measured the particle size distribution of the uncontrolled emissions of ammonium sulfate at four manufacturing plants from the drying step where small particle emissions would be excepted to be the highest. They measured particles before the scrubbers to define uncontrolled emissions. Then they measured emissions at the scrubber outlets to determine the air pollution control efficiencies. The fraction of particles less than 2.5 microns varied from 0% (<0.1%) to 15%, and the efficiency of removal of those particles varied from 97.3% removal to 99.9% removal. Some fine particles were present at the scrubber inlet, but those particles were effectively removed by the control equipment and not present at the scrubber outlet. Human health is adequately protected by the NAAQS for $PM_{2.5}$ if any small particles were to escape the air pollution controls.

The particle sizes of dust generated during packaging, distribution and use of solid ammonium sulfate would be far greater because the product sold is granular in nature.

5 No Other Regulatory Entities Except OEHHA Have Derived A Health-Based Criterion for Ammonium Sulfate in Air

OEHHA is unique in having derived this REL value based primarily on effects with sulfuric acid and applying it to a category of substances, including the non-acidic ammonium sulfate. No other criteria were identified from other regulatory entities.

6 USEPA Does Not Regulate Ammonium Sulfate Aerosols

The following support documents for the Clean Air Act regulation of particulate matter do not mention ammonium sulfate even once. Ammonium sulfate is not an air pollution concern for public health. It is not a consideration in the setting of Federal standards for $PM_{2.5}$.

- USEPA (2010) Quantitative Health Risk Assessment for Particulate Matter supporting the 2012 revision of the NAAQS for $PM_{2.5}$
- USEPA (2009) Risk Assessment to Support the Review of the PM Primary National Ambient Air Quality Standards
- USEPA (2006) Provisional Assessment of Recent Studies on Health Effects of Particulate Matter Exposure
- USEPA (2005) Particulate Matter Health Risk Assessment for Selected Urban Areas

Ammonium sulfate is also not listed as a Hazardous Air Pollutant under the Clean Air Act and is not assessed in the National Air Toxics Assessment program.

7 USEPA Does Not Regulate Acidic Sulfate Aerosols

USEPA has been concerned in the past about acidic sulfates, such as sulfuric acid and ammonium bisulfate, because $PM_{2.5}$ includes many species including acidic sulfates. (Ammonium sulfate is not a member of this category.) However, USEPA has never specifically regulated acidic sulfates. The regulation of $PM_{2.5}$ adequately protects public health from the health effects of all small particles less than 2.5 microns in diameter, including acidic sulfates.

Note, again, that ammonium sulfate is not an acidic sulfate. Acidic sulfates, like ammonium bisulfate, are also not listed as a Hazardous Air Pollutant under the Clean Air Act and is not assessed in the National Air Toxics Assessment program.

8 Ammonium Sulfate is Generally Recognized as Low in Toxicity

USEPA has not derived Reference Doses, Reference Concentrations, or Regional Screening Levels for ammonium sulfate. Ammonium sulfate is not included in human health risk assessments because of its low order of toxicity.

The Occupational Safety and Health Administration does not have a Permissible Exposure Level (PEL) for ammonium sulfate, nor does the American Conference of Governmental Industrial Hygienists have a Threshold Limit Value (TLV) for ammonium sulfate.

The United States Food and Drug Administration has approved sulfate as a food additive and has classified ammonium sulfate as "Generally Recognized as Safe" for use in foods per 21 Code of Federal Regulations, Chapter 21, Subchapter B, Section 184.1143.

The National Institute for Public Health and the Environment of the Netherlands (RIVM) assess sulfate to determine the Maximum Permissible Risk (MPR) level and concluded that sulfate was non-toxic: "For the purpose of human-toxicological MPRs in the framework of soil contamination, sulfate can be considered non-toxic."

9 Summary

In summary, the Washington DOE listed ammonium sulfate as a "Toxic Air Pollutant," because of a mis-reading of the study by Utell et al. (1983) by the California OEHHA when they derived and published an REL in 2008 for a category of "sulfates" that included ammonium sulfate. OEHHA made a simple error by not noting that ammonium sulfate caused *no effects* in the airway conductance in asthmatic volunteers. This is not a matter of scientific interpretation or expert opinion. It is a simple matter of error in fact.

Supporting documentation is provided here that demonstrates that other regulatory authorities do not consider ammonium sulfate to be toxic.

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