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Memorandum

Air Quality Program

~~January 14, 2019~~ February 14, 2019

To: 460 Rulemaking Stakeholders

From: Gary Palcisko, Toxicologist, Science and Engineering Section
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Subject: Petition to remove ammonium sulfate from the list of toxic air pollutants in WAC 173-460-150

On July 25, 2017, Far West Agribusiness Association (Far West) petitioned Ecology to remove ammonium sulfate from the list of toxic air pollutants in WAC 173-460-150. Far West contended that ammonium sulfate should not be considered a toxic air pollutant (TAP). As part of the current rulemaking, Ecology agreed to evaluate the petition and supporting information provided by consultants for Simplot and Two Rivers Terminal (Arcadis, 2018; Weeks D., 2018), and existing literature around the short-term respiratory effects of ammonium sulfate. The McGregor Company and Far West Agribusiness Association each sent a letter supporting the removal of this chemical from the list.

As part of response to Far West's petition, Ecology reviewed and considered:

- The basis for including ammonium sulfate on the existing list of TAPs
- Information about potential health effects associated with inhalation of ammonium sulfate
- Levels of short-term exposure that could pose mild adverse respiratory effects
- Public health implications of removing ammonium sulfate from the list of TAPs

Based on our review, Ecology proposes to remove ammonium sulfate from the TAP list during the current rulemaking because this action is not likely to result in increased hazards from new sources of air pollution.

This decision was informed by the following key considerations:

- The primary study used to determine the reference level (which forms the basis for the ASIL) observed slight changes in airway function after exposure to sulfuric acid and ammonium bisulfate, but not after exposure to ammonium sulfate;
- Sulfates of greater acidity than ammonium sulfate appear to be more likely to cause short-term respiratory effects;
- Ammonium sulfate as a constituent of ambient particulate matter is not unequivocally known to be more toxic than other forms of particulate matter; and
- Existing regulations that address particulate matter emissions from new and existing sources likely address emissions of ammonium sulfate.

Removing ammonium sulfate from the list of TAPs would not likely result in an increase in short-term respiratory hazards from new sources of air pollution.

Basis of ammonium sulfate ASIL

The ammonium sulfate acceptable source impact level (ASIL = 1-hr average concentration of 120 $\mu g/m^3$) is based on California Environmental Protection Agency Office of Environmental Health Hazard Assessment's (OEHHA's) acute Reference Exposure Level (REL) for "sulfates" (CalEPA, 1999). An REL is exposure level "that is not likely to cause adverse health effects in a human population, including sensitive subgroups, exposed to that concentration (in units of micrograms per cubic meter or $\mu g/m^3$) for the specified exposure duration on an intermittent basis." Acute RELs are intended to be protective of infrequent one-hour exposures that occur once every two weeks in a year (CalEPA, 2015).

OEHHA derived the REL based primarily on a human exposure study in which 17 people with asthma were exposed to 1000, 450, and 100 $\mu g/m^3$ sodium chloride, sulfuric acid, ammonium bisulfate, sodium bisulfate, and ammonium sulfate for 16 minutes (Utell et al., 1983). The key results of the study were that:

- Sulfuric acid exposures at 1000 $\mu g/m^3$ caused significant decreases in airway conductance and forced expiratory volume (FEV).
- Ammonium bisulfate exposure at 1000 $\mu g/m^3$ caused significant decreases in airway conductance
- Sulfuric acid exposure at 450 $\mu g/m^3$ caused significant decreases in airway conductance.
- **No significant decreases in airway function for ammonium sulfate at an exposure level of 1000 $\mu g/m^3$**.[1]
- Results support the concept of a relationship between the acidity of the sulfate aerosol, and the degree of induced bronchoconstriction. Inhalation of more acidic sulfates (i.e., sulfuric acid and ammonium bisulfate) produced the most significant bronchoconstriction. Exposure to the less acidic sulfate aerosols, sodium bisulfate and ammonium sulfate caused no significant change in lung function.

[1]Unlike other sulfates, subjects were not exposed to ammonium sulfate levels less than 1000 $\mu g/m^3$.

Based on the results of this study, OEHHA used the no observable adverse effects level (NOAEL) for ammonium bisulfate (450 μg/m^3) as the point of departure[2] in deriving the REL for "sulfates." No uncertainty factors or modifying factors were used to adjust this exposure concentration because the study focused on a sensitive human subpopulation (i.e., people with asthma). OEHHA adjusted the sixteen minute exposure duration in the study to derive a one-hour average concentration according to Haber's Law in which:

$C^n \times t = k$

Where:

C = concentration (450 μg/m^3)
n = chemical specific regression coefficient (OEHHA assumed n = 1)
t = time (16 minutes)
k = a constant defining the incidence and severity of a toxic effect (no mild adverse effect in this case) related to concentration and time.

In this case:

$$120\,\frac{\text{ug}}{\text{m3}}\ (1\text{hr}) = \frac{450\,\frac{\text{ug}}{\text{m\^{}3}}\ x\ 16\ minutes}{60\ \text{minutes}}$$

OEHHA determined that the resulting REL was protective of mild effects after short-term exposures to "sulfates" including ammonium sulfate. It is worth noting that the acute REL for sulfuric acid is also set at 120 μg/m^3 based on similar assumptions even though there was a small but significant decrease in airway conductance at the 450 μg/m^3 sulfuric acid exposure level (OEHHA, 1999). OEHHA considered 450 μg/m^3 to be a NOAEL instead of a lowest observable adverse effects level (LOAEL) for the purpose of deriving the sulfuric acid acute REL.

Summary of ammonium sulfate human inhalation exposure studies

A review of the literature revealed a few human inhalation exposure studies evaluating the respiratory effects of ammonium sulfate (Table 1). While these studies varied in design, they measured lung function parameters among normal (i.e., healthy) individuals and / or asthmatics after short-term exposure to ammonium sulfate. Exposure levels varied from a low of 70 μg/m^3 to a high of 1000 μg/m^3. These studies found no significant adverse effects at levels less than 1000 μg/m^3.

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[2] The point of departure refers to a point on a concentration-response curve that corresponds to a low or no adverse effect level. Typically, uncertainty and modifying factors are applied to the point of departure to determine an even lower reference level in which adverse health effects are unlikely in an exposed individual or population.

Studies in which human subjects were exposed to ammonium sulfate at 1000 μg/m^3 produced inconsistent results. Utell et al., 1983 reported no respiratory effects after normal and asthmatic subjects' exposure to ammonium sulfate levels as high as 1000 μg/m^3, but two other studies reported slight changes in respiratory function among normal adults. In a report submitted to the National Institute for Occupational Safety and Health, Frank et al. reported a slight decreases in pulmonary flow resistance and dynamic lung compliance (measures of lung function) among four adults. These effects did not occur until 1.5 to 2 hours into the exposure. The authors also noted that effects were partially reversed after 30 minutes recovery. Utell et al., 1982 reported that sulfates, including ammonium sulfate, inhaled for 16 minutes produced a small but significant decrease in expiratory flow in healthy and asthmatic subjects. The authors also noted that bronchoconstriction induced by carbachol (a chemical known to cause bronchoconstriction) was potentiated by sulfates "more or less in relation to their acidity."

Studies that evaluated multiple sulfate compounds suggest that ammonium sulfate appears to be less potent in producing reduced lung function relative to more acidic sulfates (i.e., ammonium bisulfate or sulfuric acid). The increased deposition of hydrogen ions on airway surfaces may be responsible for these observations (EPA, 1989). In a review of the biological effects resulting from exposure to secondary aerosols, Schlesinger and Cassee suggest that the secondary aerosols likely to be of toxicological significance are those that have strong acidity. These aerosols include sulfuric acid, ammonium bisulfate, and nitric acid (Schlesinger and Cassee, 2003).

Table 1. Summary of ammonium sulfate short-term human exposure studies

Study Authors	**Number Exposed**	**Broad description of subjects**	**Ammonium Sulfate Exposure Duration and Concentrations**	**Key Conclusion**
Frank et al., 1977	4/12	Adult Normal	2 hour exposures 1000 μg/m^3	A slight decrease in pulmonary flow resistance and decreased dynamic lung compliance
Avol et al., 1979	16	5 Normal 5 Sensitive to ozone 6 Asthmatics	2 hour exposures on multiple days Up to 337 μg/m^3	No significant deleterious changes in pulmonary function or clinical symptoms
Utell et al., 1982	16	Normal	16 minutes 1000 μg/m^3	"small but significant decrease in expiratory flow in healthy subjects. Carbachol induced bronchoconstriction was potentiated by sulfate aerosols

Study Authors	Number Exposed	Broad description of subjects	Ammonium Sulfate Exposure Duration and Concentrations	Key Conclusion
				more or less in relation to their acidity”
Utell et al., 1983	10	Asthmatics	16 minutes 1000 $\mu g/m^3$	No significant decrease in lung function
Stacy et al., 1983	13	Normal adult males	4 hours 133 $\mu g/m^3$	No significant effects
Kulle et al., 1984	20	Non-smokers	4 hours 500 $\mu g/m^3$	No significant effects
Koeing et al., 1983	17	Seniors 9 Asthmatic 8 Normal	40 minutes 70 $\mu g/m^3$	No significant effects

Ammonium sulfate as a component of ambient PM

As described previously, the “sulfate” REL derived by OEHHA was primarily based on respiratory effects from exposure to acidic sulfates (i.e., sulfuric acid and ammonium bisulfate). Ecology has not identified alternative toxicity values from other agencies for use in assessing short-term mild health hazards related to ammonium sulfate inhalation. Because it appears that acidity may play a key role in short-term respiratory effects, a short-term level of ammonium sulfate exposure that is higher than the “sulfate” REL and the ASIL may be tolerable. It is unclear what represents the highest level below which mild adverse respiratory effects would not be expected after short-term one-hour exposures to ammonium sulfate.

Sulfates have long been a concern for human health based on their presence in ambient particulate matter (EPA, 1975). Sulfates in ambient air typically form from secondary reactions of other air pollutants (e.g., sulfur dioxide and ammonia). These sulfate particles exist as part of complex mixture of multiple types of particles. Researchers conducted studies with the aim of identifying whether certain sources and components of $PM_{2.5}$ are more harmful than others (Lippmann et al., 2013; Vedal et al., 2013). While some studies suggest that there are differences in the degree of responses posed by different particle types, these results have been inconsistent. EPA determined that the existing “evidence does not indicate that any one source or component is consistently more strongly related with health effects than $PM_{2.5}$ mass” (EPA, 2018). Thus efforts to control $PM_{2.5}$ emissions regardless of the source or component are necessary for public health protection (Adams et al., 2015; EPA, 2018).

Public health implications of removing ammonium sulfate from the list of TAPs

By removing ammonium sulfate from the list of TAPs, local air agencies would not specifically consider peak short-term impacts posed by new sources of ammonium sulfate emissions. To determine the public health implications of this action, we consider:

- Our experience over the past ten years regulating new sources of ammonium sulfate emissions.
- Other regulatory requirements that relate to emissions of particulate air pollutants.

Ammonium sulfate has been on the list of toxic air pollutants since 2009. Since that time, Ecology is aware of only one industry that has been affected: bulk fertilizer manufacturers and distributors.

Ammonium sulfate is a common constituent of fertilizer. Approximately 1.8 million tons were used in the United States in 2014 (USDA, 2018), and Washington State Department of Agriculture reports show that about 20,000 tons were distributed by licensed bulk fertilizer licensee and registrants in Washington between July 2017 through June 2018. (WSDA, 2019). Currently there are at least 19 bulk fertilizer distributors registered with Ecology and at least 13 facilities with active air permits. According to WSDA, there are potentially dozens of additional (mostly small) facilities throughout the state (B Perry personal communication, 2018).

Ammonium sulfate is delivered to bulk fertilizer distributors by rail where they are conveyed, mixed, stored, and distributed. Although ammonium sulfate granules tend to be larger than 1 mm in size (EPA, 1976), smaller particles may be formed through mechanical processes. Therefore, $PM_{2.5}$ and PM_{10} emissions are possible. The most likely scenarios that cause emissions at bulk fertilizer facilities would be:

- Unloading granulated ammonium sulfate from rail cars
- Mixing and blending fertilizers
- Loading fertilizer mixtures into trucks
- Disturbances of dust on roads or surfaces from spills

Ecology staff visited several bulk fertilizer facilities[3] during the spring and summer of 2018 to observe emissions that are produced at a typical operating facility. In general, staff found that the facilities produced very little dust. Generally, material from railcars are dropped directly to underground conveyance systems minimizing exposure to ambient air. Some conveyance point transfers may occur outdoors (bucket elevator to overbin belt conveyor), but this is mostly via enclosed conveyance. Minimal emissions were observed during August 23, 2018 site visit to Wilbur-Ellis, Moses Lake facility.

Mixing and blending is through an enclosed process, so emissions are expected to be minimal. Truck loading is performed indoors or under coverings. Loading is performed through drop-down shoots directly onto trucks which are then covered with tarps before leaving the facility.

[3] Note that no ammonium sulfate chemical plants are located in Washington, but if they were, they would need to comply with EPA’s air toxics rule in 40 C.F.R. Part 63, Subpart FFFF.

Some trucks are equipped with a small hole on top of for the drop-down shoots to convey materials into the mostly enclosed truck cargo area with minimal exposure. Trucks are loaded directly from overtop drop-down shoots which would only cause a spill if trucks were overfilled. Indoor spills (from truck filling or other indoor movement of materials) are swept into grates back into underground conveyors. In addition to using tarps on trucks, some facilities use signage to discourage outdoor spills. Some sites are paved or have fugitive dust corrective action plans as part of their operations and maintenance (O&M) manual. The plan outlines housekeeping requirements such as cleaning up spilled material in a timely manner to minimize plant haul road fugitive emissions.

Observations made at these facilities confirm that methods to control dust and particulate emissions in general would address emissions of ammonium sulfate. Aside from regulating ammonium sulfate as a TAP, other existing regulations address emissions of ammonium sulfate particulate from bulk fertilizer facilities. Table 2 summarizes portions of existing state regulations that would serve to ensure that emissions of ammonium sulfate from existing, new, or modified sources be reasonably minimized.

Table 2. Rule provisions in Chapter 173-400 WAC that address emissions of ammonium sulfate particulate

Rule Section	**Sub-section**	**Description**
WAC 173-400-040 General standards for maximum emissions.	(2) Visible emissions.	No person shall cause or allow visible emissions (exceeding 20 percent opacity as determined by Ecology method 9A) for more than 3 minutes in any one hour.
WAC 173-400-040 General standards for maximum emissions.	(3) Fallout.	No person shall cause or allow the emission of particulate matter from any source to be deposited beyond the property under direct control of the owner or operator of the source in sufficient quantity to interfere unreasonably with the use and enjoyment of the property upon which the material is deposited
WAC 173-400-040 General standards for maximum emissions.	(4) Fugitive emissions.	The owner or operator of any emissions unit engaging in materials handling, construction, demolition or other operation which is a source of fugitive emission: (a) If located in an attainment area and not impacting any nonattainment area, shall take reasonable precautions to prevent the release of air contaminants from the operation. (b) If the emissions unit has been identified as a significant contributor to the nonattainment status of a designated nonattainment area, the owner or operator shall be required to use reasonable and

Rule Section	Sub-section	Description
		available control methods, which shall include any necessary changes in technology, process, or other control strategies to control emissions of the air contaminants for which nonattainment has been designated.
WAC 173-400-040 General standards for maximum emissions.	(9) Fugitive dust.	(a) The owner or operator of a source or activity that generates fugitive dust must take reasonable precautions to prevent that fugitive dust from becoming airborne and must maintain and operate the source to minimize emissions. (b) The owner or operator of any existing source or activity that generates fugitive dust that has been identified as a significant contributor to a PM-10 or PM-2.5 nonattainment area is required to use reasonably available control technology to control emissions. Significance will be determined by the criteria found in WAC 173-400-113 (4).
WAC 173-400-110 New source review (NSR) for sources and portable sources.	(5) Exemptions based on emissions.	New or modified sources that increase emissions by more than the following amounts of PM must obtain preconstruction approval: • $PM_{2.5}$ = 0.5 tpy • PM_{10} = 0.75 tpy

Summary

The ASIL for ammonium sulfate was based on California OEHHA’s acute REL for “sulfates.” The REL was derived from a study in which no adverse effects were seen after ammonium sulfate exposure, but effects were observed from similar exposure to other more acidic sulfates. As the REL is intended to protect against short-term mild impacts, it is possible that relative to the more acidic sulfates, higher levels of ammonium sulfate could be tolerated before short-term mild adverse effects occur.

In addition to the fact that brief exposures to ammonium sulfate is less likely to cause mild short-term adverse respiratory effects relative to more acidic sulfates, other air pollution regulations likely address potential emissions from ammonium sulfate sources. Because ammonium sulfate is emitted as particulate matter, general air pollution standards and permitting requirements would address emissions of this pollutant even if it was no longer regulated under Chapter 173-460 WAC.

Given that ammonium sulfate is less likely than acidic sulfates to cause mild short-term respiratory effects at exposures greater than the ASIL, and existing regulations aimed at limiting and controlling particulate emissions appear to be an effective general approach to protecting public health, Ecology recommends removing ammonium sulfate from the list of TAPs regulated under WAC 173-460-150 as it likely presents an unnecessary regulatory requirement providing minimal public health benefit.

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