

## Important Air Emissions from Dairy Operations vis-à-vis the Prevailing Federal Statutes

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### Executive Summary

Potential emissions from animal feeding operations (AFOs) that are regulated under the federal clean air act (CAA) as criteria pollutants include ozone (regulated via volatile organic compounds (VOCs), and nitrogen oxides (NO<sub>x</sub>)), and particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>). Under the CAA, any source emitting 100 tons/yr of any of these emissions requires an operation permit. The limit drops to 50, 25, and 10 tons/yr for serious, severe, and extreme nonattainment areas, respectively. Ammonia (NH<sub>3</sub>) and hydrogen sulfide (H<sub>2</sub>S) are the other key emissions from AFOs that are currently regulated under two other federal statutes: CERCLA and EPCRA. An operation emitting 100 lb/day of NH<sub>3</sub> or H<sub>2</sub>S must report release under both CERCLA and EPCRA. AFOs are, however, exempt from CERCLA for emissions from normal manure handling on farms except from other forms of releases such as from: burst anhydrous ammonia tank, breached lagoon or holding pond, and manure spills. Research is in progress under the auspices of the ‘national air emissions monitoring study – NAEMS’ to establish credible tools and approaches for estimating emissions of these pollutants from AFOs.

Emissions of some VOCs are also, individually or in group, regulated under hazardous air pollutants (HAPs) federal statutes, which is mostly important at the local scale (property line or nearest dwellings). Sources emitting at least: (i) 10 tons/year of any HAP, or (ii) 25 tons/year of two or more HAPs, are permitted under EPA’s Title V as *major sources* and also require operation-permits. Amongst the major VOCs emissions identified in dairy operations, five (2-butanone, p-Cresol, phenol, methyl isobutyl ketone or hexone, and methanol) are HAPs. According to available data, only dairy operations with herds of at least 16,300 (lactating cows) or 34,600 (dry cows) may qualify as *major sources* of methanol. In addition, only dairy operations with herds of at least 2 and 90 million, respectively, qualify as *major sources* of 2-butanone and hexone. Available data thus effectively excludes most dairy operations from considerations as *major sources* for regulation under the EPA’s HAPs statutes.

With respect to VOCs as precursors for ozone formation, available data indicate that only dairy operations with herds of at least 1.4 million lactating dairy cows or 2.0 million dry dairy cows could potentially emit at least 10 tons/yr of ROG (in extreme ozone nonattainment areas). Given that only about 3.4% of dairies in the US exceed a herd of 500 cows, this essentially

insulates most dairy operations in the US today against regulation for VOCs emissions under CAA even in extreme ozone nonattainment regions.

Disclaimer: The current available VOCs emissions data from dairies, however, do not include emissions from silage, which are significant sources of VOCs in dairies according to unpublished data. Therefore, the herd size limits presented in this report, will adjust downwards when VOCs emissions from silage are eventually incorporated into the current estimates.

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## 1.0 Introduction

In order to protect public's health and damage to the environment and property, the US-EPA established the National Ambient Air Quality Standards (NAAQS) for six air pollutants under the Clean Air Act (CAA). These six pollutants are termed "criteria air pollutants" because they are regulated by developing human health and environmentally-based criteria for setting permissible levels. The EPA thus developed and maintains two sets of legal standards under the NAAQS: the primary standards are based on human health, while the secondary standards are intended to prevent environmental and property damages. These six pollutants are:

1. Ozone, O<sub>3</sub> (with VOCs and NO<sub>x</sub> as precursors)
2. Particulate Matter (PM<sub>10</sub> or PM<sub>2.5</sub>)
3. Carbon Monoxide, CO
4. Nitrogen Oxides, NO<sub>x</sub>
5. Sulfur Dioxide, SO<sub>2</sub>
6. Lead, Pb

To achieve NAAQS, EPA regulates emissions by issuing permits to *major sources* of the respective pollutants. In addition to these six criteria pollutants, however, EPA also regulates *major sources* of another 188 listed hazardous air pollutants (HAPs) under the CAA. The list of the 188 HAPs (which is modified by EPA regulation from time to time) is found in Section 112 of the 1990 CAA. The most likely candidates of the HAPs list from AFOs are the volatile organic compounds (VOCs). For purpose of regulation, the definitions of *major sources* under EPA's Title V are sources emitting at least either: (i) 100 tons/year of any of the criteria pollutants (These limits can drop to 50, 25, and 10 tons/yr for serious, severe, and extreme non-attainment areas, respectively; EPA, 2009), (ii) 10 tons/year of any HAP, or (iii) 25 tons/year of any two or more HAPs. Although livestock operations and other agricultural sources have not usually been regulated under the CAA this is not to mean that they are exempt from the statutes. For any operation whose emissions meet statutory or regulatory definitions of *major source*, provisions of the act could apply (Copeland, 2008). Such *major sources* are, in general, required to obtain operating permits that specify emission limitations, compliance schedule, and reporting requirements. They must also control those emissions to a level no less than the maximum achievable control technology (MACT), as determined by EPA or state permitting authorities.

Finally, there are two other federal regulations that currently target potentially hazardous hydrogen sulfide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>), which are important in dairy operations. These are: the comprehensive environmental, compensation and liability act (CERCLA) also known as superfund established in 1980, and the emergency planning and community right-to-know act (EPCRA) established in 1986. These two acts only have *reporting requirements* for major sources releasing at least 100 lb/day of either H<sub>2</sub>S or NH<sub>3</sub>. However, CAFOs are, in general, exempt for emissions from normal manure handling on farms but they need to comply with this legislation when other forms of releases such as from burst anhydrous ammonia tank, breached lagoon or holding pond, and manure spills; occur on their facilities. Superfund provides broad federal authority to clean up releases of hazardous substances that may endanger public health or the environment. In general, the EPA identifies parties responsible for contamination and compels the parties to clean up the sites or alternatively clean up releases from a special trust fund where responsible parties cannot be found. EPCRA on the other hand is meant to inform the public of potential harmful releases into their environment from specific sources.

## **2.0 Concern-emissions from Animal Feeding Operation (AFOs)**

Prompted by public concerns of probable pollution from AFOs, EPA in 2001 considered what information is needed to define and support feasible regulation of air emissions from AFOs. Acting together with USDA, EPA asked the National Research Council (NRC, 2003) of the National Academy of Sciences (NAS) to evaluate the scientific information needed to address these issues. A 16-person ad hoc committee was appointed, with its terms of appointment spelled under a Statement of Task defined by the NAS and the sponsoring agencies. The Statement of Task directed the committee to:

1. Review and evaluate the scientific basis for estimating the emissions to the atmosphere of various specified substances from confined livestock and poultry operations;
2. Review the characteristics of the agricultural animal industries, methods for measuring and estimating air emissions, and potential best management practices for mitigating emissions; and
3. Evaluate confined animal feeding production systems in terms of biologic systems; and identify critical short- and long-term research needs and recommend methods and modeling approaches for estimating and measuring air emissions and potential mitigation technologies.

This ad hoc committee identified important emissions from AFOs and noted that air emissions from AFOs are of varying concern at different spatial scales, as shown in Table 1 (NRC, 2003). The committee recommended that owing to these differing effects, concentrations, and spatial distributions; a logical plan of action was to establish research priorities to provide detailed scientific information on: (i) the contributions of AFO emissions and potential effects and, (ii) subsequent implementation of control measures. The committee further recommended that USDA and EPA should first focus their efforts on the measurement and control of those emissions of *major concern*. The National Academy of Sciences study (NRC, 2003) culminated into the 2007-2009 national air emissions monitoring study (NAEMS) that set to establish science-based approaches for estimating and measuring the following emissions of *major concern* from AFOs: ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>), and volatile organic compounds (VOCs).

**Table 1.** Committee’s Scientific Evaluation of the Potential Importance<sup>a</sup> of AFO Emissions at Different Spatial Scales

| Emissions         | Global, National, and Regional | Local—Property Line or Nearest Dwelling | Primary Effects of Concern         |
|-------------------|--------------------------------|---|------------------------------------|
| NH <sub>3</sub>   | Major <sup>a</sup>             | Minor                                   | Atmospheric deposition, haze       |
| N <sub>2</sub> O  | Significant                    | Insignificant                           | Global climate change              |
| NO <sub>x</sub>   | Significant                    | Minor                                   | Haze, atmospheric deposition, smog |
| CH <sub>4</sub>   | Significant                    | Insignificant                           | Global climate change              |
| VOCs              | Insignificant                  | Minor                                   | Quality of human life              |
| H <sub>2</sub> S  | Insignificant                  | Significant                             | Quality of human life              |
| PM <sub>10</sub>  | Insignificant                  | Significant                             | Haze                               |
| PM <sub>2.5</sub> | Insignificant                  | Significant                             | Health, haze                       |
| Odor              | Insignificant                  | Major                                   | Quality of human life              |

<sup>a</sup>Relative importance of emissions from AFOs at spatial scales based on committees’ informed judgment on known or potential impacts from AFOs. Rank order from high to low importance is major, significant, minor, and insignificant.

In addition to the NRC (2003) study and recommendations, a more recent report by Oregon Dairy Air Quality Task Force (2008), in particular identified methanol as a hazardous air pollutant that may be of *major concern* from dairy operations. Methanol, which is emitted from cow’s enteric fermentation and considered a HAP by EPA, is also a VOC. The singling of methanol as a HAP of *major concern* from AFOs in this report seems like a contradiction because according to the earlier NRC report, the potential effects of VOCs were identified as insignificant at global, national, or regional scales and only minor at the local scale. In view of

this obvious contradiction, this report further examined the critical nature of VOCs and methanol emissions from dairy operations.

### **3.0 Common VOCs identified in the livestock operations and relative magnitudes**

Major VOCs that have been identified in AFOs include organic sulfides, disulfides, C<sub>4</sub> to C<sub>7</sub> aldehydes, trimethylamine, C<sub>4</sub> amines, quinoline, dimethylpyrazine, C<sub>3</sub> to C<sub>6</sub> organic acids, limited amounts of C<sub>4</sub> to C<sub>7</sub> alcohols, ketones, aliphatic hydrocarbons, and aromatic compounds (NRC, 2003). In general, other than being potentially hazardous and responsible for ozone formation, VOCs are also responsible for odor in livestock operations. Mackie et al. (1998) identified six major groups of odorous compounds which include volatile fatty acids (VFA), NH<sub>3</sub>, volatile amines, phenols and indoles, as well as sulfur containing compounds. In livestock operations, these compounds could be emitted from several unit operations including the barns, silage mounds, waste storage facilities or from manure applied on land (NRC, 2003).

Several researchers have identified and in some cases also quantified volatile organic compounds in livestock operations. Most studies, however, seem to have been conducted on swine operations most probably because of strong odor emissions from these sources (Beck et al., 2007; Willig et al., 2004; Schiffman et al., 2001; Oehrl et al., 2001; Zahn et al., 1997). Comparatively few studies exist on VOCs emissions from dairy operations. Rabaud et al. (2003) identified 35 compounds in the air from a dairy (that housed 600 head of milk cows, 400 heifers, and 200 dry cows.) located in northern California including acids, alcohols, aldehydes, esters, ketones, halogenates and amines. The ten compounds with the highest concentrations included 1-propanol, butylamine, acetic acid, Dimethyl sulfoxide (DMSO), ethyl ether, methyl isobutyrate, pyridine, diethylamine, ethyl hexanone, and ethanol with maximum concentrations ranging from 170 - 750  $\mu\text{g m}^{-3}$ . Sunesson et al. (2001) identified 70 compounds in the air at eight dairy farms in northern Sweden including alcohols, aldehydes, carboxylic acids, esters, hydrocarbons and monoterpenes. The ten compounds with the highest concentrations in descending order were: 2-butanone,  $\Delta^3$ -Carene,  $\alpha$ -Pinene, ethyl acetate, ethyl butyrate, 2-butanol, p-cresol, 1-butanol, propylene glycol, and phenol with respective average concentrations of 50, 50, 50, 40, 40, 30, 30, 20, 20, and 10  $\mu\text{g m}^{-3}$  (ranging between 40 and 1570  $\mu\text{g m}^{-3}$ ). The total average concentration for all the 70 identified compounds was 485  $\mu\text{g m}^{-3}$ , and ranged from 40 to 1570  $\mu\text{g m}^{-3}$ . It is important to note the stark differences between the lists of the ten most important

VOCs (Table 2) from the US study (Rabaud et al., 2003) and the Sweden study (Sunesson et al., 2001). The differences in the VOCs emissions in US and Sweden may be attributed to the differences in the diet fed to the animals in the two different countries or due to differences in the methods of measurements. However, the most important note is that, only three VOCs (2-butanone, p-Cresol, and phenol) are listed under the EPA HAPs; all which were identified in the Sweden study.

**Table 2.** Comparison of top-ten VOCs in two studies conducted in USA and Sweden.

| <b>Rabaud et al. (2003): USA</b> | <b>Sunesson et al. (2001): Sweden</b> |
|----------------------------------|---------------------------------------|
| 1-Propanol                       | 2-Butanone                            |
| Butylamine                       | $\Delta^3$ -Carene                    |
| Acetic acid                      | $\alpha$ -Pinene                      |
| Dimethyl sulfoxide               | Ethyl acetate                         |
| Ethyl ether                      | Ethyl butyrate                        |
| Methyl isobutyrate               | 2-Butanol                             |
| Pyridine                         | p-Cresol                              |
| Diethylamine                     | 1-Butanol                             |
| Ethyl hexanone                   | Propylene glycol                      |
| Ethanol                          | Phenol                                |

Some other studies have quantified the VOCs in the liquid manure. Miller and Varel (2001) identified 14 compounds in manure samples from a cattle-feedlot located at the USDA research center in Nebraska. Liquid phase samples (20% slurry mixture) contained L-lactate, alcohols, VFA, phenols, indoles, aromatics, and benzoates with the highest liquid concentrations of ethanol (37mM) and acetic acid (100mM) after incubation. In addition, these researchers noted that ethanol in the manure slurries consisted of 95%, with propanol and butanol being the next most abundant alcohols in the manure slurries and comprising roughly 3% and 1%, respectively, of the total alcohol. The results of this research do not indicate any potential air quality concerns from volatilization of methanol from storage of manure slurries. This study further confirmed that cow manure potential for methanol emissions is very low. Unpublished research data, however, indicate that substantial emissions of methanol, in a dairy, originate from silage (Krauter et al, 2009; Frank Mitloehner: personal communication).

### 3.1 Potential Regulation of VOCs as HAPs

A couple of studies have estimated emissions rates or fluxes from dairy operations. One study conducted in Washington State by Filipy et al. (2006) identified 82 VOCs at a lactating cow pen stall and 73 VOCS from the manure lagoon both located on the university dairy research farm. In general, these compounds included alcohols, aldehydes, ketones, esters, ethers, aromatic hydrocarbons, halogenated hydrocarbons, terpenes, amines and other nitrogen containing compounds, and sulfur-containing compounds. The respective concentrations increased with ambient temperatures and it was thus seasonal. The concentrations of most detected compounds were below published odor detection thresholds. Emissions rates of ethanol and dimethyl sulfide were estimated at  $1026 \pm 513$  and  $13.8 \pm 10.3 \mu\text{g cow}^{-1} \text{ s}^{-1}$ , respectively. Emissions rates from the manure lagoon for acetone, 2-butanone, methyl isobutyl ketone, 2-methyl-3-pentanone, dimethyl sulfide, and dimethyl disulfide were respectively,  $3.03 \pm 0.85$ ,  $145 \pm 35$ ,  $3.46 \pm 1.11$ ,  $25.1 \pm 8.0$ ,  $2.19 \pm 0.92$ , and  $16.1 \pm 3.9 \text{ ng cow}^{-1} \text{ s}^{-1}$ .

A more recent study in a controlled environmental chamber (Sun et al., 2008) estimated emissions of methanol at 0.7 g/cow/h from lactating dairy cows and 0.33 g/cow/h from dry cows. This translates into approximately 6.1 kg/cow/yr and 2.9 kg/cow/yr for the lactating and dry cows, respectively. Given the legal limit of 10 ton/year for any stand-alone HAP, this implies that a dairy operation housing approximately 1,630 lactating cows or alternatively approximately 3460 dry cows may be subject to permit for potential release of methanol. A lactating cow appears to be equivalent to slightly over two dry cows with respect to potential methanol emissions. It is important to note that these values were estimated for cows kept under the conventional manure scrape collection system. For systems with the conventional manure flushing systems, the authors estimated a 90% reduction of both ethanol and methanol emissions (because both are very soluble in water), implying that only dairy operations with herds of 16,300 (lactating cows) or 34,600 (dry cows) may be subject to methanol legal limit under the EPA HAPs statutes (Title V). These extrapolations, however, assume uniform emissions all round the year, which is factually not the case. In addition, available estimates do not include emissions from silage stacks, which are significant based on unpublished data (Krauter et al., 2009; Frank Mitloehner, University of California-Davis - personal communication). Based on the start-of-the-science today, therefore, it is apparent that a lot more work is needed for accurate estimations of methanol emissions from dairy operations and other livestock operations.

The fluxes of the other two HAPs identified and quantified in a dairy operation in Washington (Filipy et al., 2006), namely 2-butanone and methyl isobutyl ketone were respectively,  $145 \pm 35$  and  $3.46 \pm 1.11 \text{ ng cow}^{-1} \text{ s}^{-1}$ . Based on the emissions factors of 2-butanone and methyl isobutyl ketone, only dairies with herds of at least 2 and 90 million animals, respectively, would be regulated as a major source of these two HAPs. These numbers should also be interpreted with caution because data: (i) is limited as it was collected for short intervals of time and thus not representative of the year round emissions, and (ii) do not also include emissions from silage.

### **3.2 Federal regulations of VOC as precursors for Ozone Formation**

Other than regulation of individual or groups of VOCs under HAPs, reactive VOCs (commonly referred to as reactive organic gases – ROG) and  $\text{NO}_x$  are also regulated as precursors of ozone formation. Under CAA, sources emitting 10 tons/yr of VOCs or  $\text{NO}_x$  are defined as major sources in extreme nonattainment areas, and are subject to CAA requirements (Copeland, 2008). This section discusses EPA's VOCs definition for purpose of regulation with respect to ozone formation.

#### **3.2.1 Definition of a Volatile Organic Compound**

For regulatory purposes EPA defines VOC as “any volatile compound of carbon,” unless specifically exempted. EPA regulations thus include a list of compounds that are explicitly exempted from regulation as VOCs, even though they are “compounds of carbon. These include a short list of compounds such as carbon monoxide and carbon dioxide that historically have not been regulated as VOCs, and a longer list of compounds that EPA has classified as “negligibly reactive.” Negligibly reactive compounds are compounds that, based on scientific studies, have been found “not to contribute appreciably to ozone formation.” This list of compounds (often referred to as “VOC-exempt compounds”) is established and modified by regulation. The list of exempt compounds is found at 40 C.F.R. 51.100(s) and in Table 4 in this document.

**Table 3. EPA List of hazardous air pollutants (HAPs)**

|   |   |   |  |
|---|---|---|--|
| Acetamide                                   | 1,2-Dibromo-3-chloropropane                   | Methyl chloroform (1,1,1-Trichloroethane)                   | Styrene  |
| Acetonitrile                                | Dibutylphthalate                              | Methyl ethyl ketone (2-Butanone)( <u>See Modification</u> ) | Styrene oxide                                  |
| Acetophenone                                | 1,4-Dichlorobenzene(p)                        | Ethylene dichloride (1,2-Dichloroethane)                    | 2,3,7,8-Tetrachlorodibenzo-p-dioxin            |
| 2-Acetylaminofluorene                       | 3,3-Dichlorobenzidene                         | Ethylene glycol   | 1,1,2,2-Tetrachloroethane                      |
| Acrolein                                    | Dichloroethyl ether (Bis(2-chloroethyl)ether) | Ethylene imine (Aziridine)                                  | Tetrachloroethylene (Perchloroethylene)        |
| Acrylamide                                  | 1,3-Dichloropropene                           | Ethylene oxide  | Titanium tetrachloride                         |
| Acrylic acid                                | Dichlorvos                                    | Ethylene thiourea   | Toluene  |
| Acrylonitrile                               | Diethanolamine                                | Ethylidene dichloride (1,1-Dichloroethane)                  | 2,4-Toluene diamine                            |
| Allyl chloride                              | N,N-Dimethylaniline                           | Formaldehyde  | 2,4-Toluene diisocyanate                       |
| 4-Aminobiphenyl                             | Diethyl sulfate                               | Hepachlor   | o-Toluidine                                    |
| Aniline                                     | 3,3-Dimethoxybenzidine                        | Hexachlorobenzene   | Toxaphene (chlorinated camphene)               |
| Asbestos                                    | o-Anisidine                                   | Dimethyl aminoazobenzene                                    | 1,2,4-Trichlorobenzene                         |
| Benzene (including benzene from gasoline)   | 3,3'-Dimethyl benzidine                       | Methyl iodide (Iodomethane)                                 | 1,1,2-Trichloroethane                          |
| Benzidine                                   | Dimethyl carbamoyl chloride                   | Methyl isobutyl ketone (Hexone)                             | Trichloroethylene                              |
| Benzotrichloride                            | Dimethyl formamide                            | Methyl isocyanate   | 2,4,5-Trichlorophenol                          |
| Benzyl chloride                             | 1,1-Dimethyl hydrazine                        | Methyl methacrylate   | 2,4,6-Trichlorophenol                          |
| Biphenyl                                    | Dimethyl phthalate                            | Methyl tert butyl ether                                     | Triethylamine                                  |
| Bis(2-ethylhexyl)phthalate (DEHP)           | Dimethyl sulfate                              | 4,4-Methylene bis(2-chloroaniline)                          | Trifluralin                                    |
| Bis(chloromethyl)ether                      | 4,6-Dinitro-o-cresol, and salts               | Methylene chloride (Dichloromethane)                        | 2,2,4-Trimethylpentane                         |
| Bromoform                                   | 2,4-Dinitrophenol                             | Methylene diphenyl diisocyanate (MDI)                       | Vinyl acetate                                  |
| 1,3-Butadiene                               | 2,4-Dinitrotoluene                            | 4,4'-Methylenedianiline                                     | Vinyl bromide                                  |
| Calcium cyanamide                           | 1,4-Dioxane (1,4-Diethyleneoxide)             | Naphthalene   | Vinyl chloride                                 |
| Caprolactam( <u>See Modification</u> )      | 1,2-Diphenylhydrazine                         | Nitrobenzene  | Vinylidene chloride (1,1-Dichloroethylene)     |
| Captan                                      | Epichlorohydrin (1-Chloro-2,3-epoxypropane)   | 4-Nitrobiphenyl   | Xylenes (isomers and mixture)                  |
| Carbaryl                                    | 1,2-Epoxybutane                               | 4-Nitrophenol   | o-Xylenes                                      |
| Carbon disulfide                            | Ethyl acrylate                                | 2-Nitropropane  | m-Xylenes                                      |
| Carbon tetrachloride                        | Ethyl benzene                                 | N-Nitroso-N-methylurea                                      | p-Xylenes                                      |
| Carbonyl sulfide                            | Ethyl carbamate (Urethane)                    | N-Nitrosodimethylamine                                      | Antimony Compounds                             |
| Catechol                                    | Ethyl chloride (Chloroethane)                 | N-Nitrosomorpholine   | Arsenic Compounds (inorganic including arsine) |
| Chloramben                                  | Ethylene dibromide (Dibromoethane)            | Parathion   | Beryllium Compounds                            |
| Chlordane                                   | Hexachlorobutadiene                           | Pentachloronitrobenzene (Quintobenzene)                     | Cadmium Compounds                              |
| Chlorine                                    | Hexachlorocyclopentadiene                     | Pentachlorophenol   | Chromium Compounds                             |
| Chloroacetic acid                           | Hexachloroethane                              | Phenol  | Cobalt Compounds                               |
| 2-Chloroacetophenone                        | Hexamethylene-1,6-diisocyanate                | p-Phenylenediamine  | Coke Oven Emissions                            |
| Chlorobenzene                               | Hexamethylphosphoramide                       | Phosgene  | Cyanide Compounds <sup>1</sup>                 |
| Chlorobenzilate                             | Hexane  | Phosphine   | Glycol ethers <sup>2</sup>                     |
| Chloroform                                  | Hydrazine                                     | Phosphorus  | Lead Compounds                                 |
| Chloromethyl methyl ether                   | Hydrochloric acid                             | Phthalic anhydride  | Manganese Compounds                            |
| Chloroprene                                 | Hydrogen fluoride (Hydrofluoric acid)         | Polychlorinated biphenyls (Aroclors)                        | Mercury Compounds                              |
| Cresols/Cresylic acid (isomers and mixture) | Hydrogen sulfide( <u>See Modification</u> )   | 1,3-Propane sultone   | Fine mineral fibers <sup>3</sup>               |
| o-Cresol                                    | Hydroquinone                                  | beta-Propiolactone  | Nickel Compounds                               |
| m-Cresol                                    | Isophorone                                    | Propionaldehyde   | Polycyclic Organic Matter <sup>4</sup>         |
| p-Cresol                                    | Lindane (all isomers)                         | Propoxur (Baygon)   | Radionuclides (including radon) <sup>5</sup>   |
| Cumene                                      | Maleic anhydride                              | Propylene dichloride (1,2-Dichloropropane)                  | Selenium Compounds                             |
| 2,4-D, salts and esters                     | <b>Methanol</b>                               | Propylene oxide   |  |
| DDE   | Methoxychlor                                  | 1,2-Propylenimine (2-Methyl aziridine)                      |  |
| Diazomethane                                | Methyl bromide (Bromomethane)                 | Quinoline   |  |
| Dibenzofurans                               | Methyl chloride (Chloromethane)               | Quinone   |  |

### 3.2.2 Effective VOCs Definition per 40 CFR Part 51.100(s) (as amended through January 18, 2007)

Effectively, according to EPA regulations, **VOC** means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. This includes any such organic compounds besides those identified in Table 4; the VOCs in this table are those with negligible photochemical reactivity.

### 3.2.3 Regulation test of VOCs for ozone formation

The mean concentration of total VOC (TVOC) for the outdoor environment, the dwellings, and the stables measured in cattle farms in Northern Germany were  $100 \mu\text{g m}^{-3}$ ,  $763 \mu\text{g m}^{-3}$ ,  $322 \mu\text{g m}^{-3}$  in spring and  $143 \mu\text{g m}^{-3}$ ,  $544 \mu\text{g m}^{-3}$ ,  $595 \mu\text{g m}^{-3}$  in autumn, respectively. There was no significant difference in season (Beck et al. 2007). In all these studies, only VOCs concentrations in the ambient air were determined. This seems typical of most studies. However, legal limits are stipulated as fluxes (mass/year), which are not possible to calculate from concentrations only. Although this data is informational, it is not very helpful in determining if legal limits are exceeded.

In addition, because regulation of VOCs stems from the need to curb or reduce ozone, only the component of VOCs that is reactive with NO<sub>x</sub> (aka reactive organic gases or ROGs) is important. Until 1980, ROG flux from dairy operations was based on a 1938 study by Ritzman et al., which estimated methane emissions at 160 lb/hd/year. This methane estimate was subsequently incorrectly assumed as the total organic gases (TOG) flux for the purpose of estimating ROG flux. A 1980 EPA study speciating TOG from livestock operations estimated ROG as 8% of the TOG with major constituents being ethyl alcohol (2%), isopropyl alcohol (2%), propyl acetate (2%), ethyl amine (91%), and trimethyl amine (1%). Based on the 1980 EPA study, the emission factor for ROG flux was adjusted to 12.8 lb/hd/yr ( $184.1 \mu\text{g/hd/s}$ ) being 8% of 160 lb/head/yr TOG factor. Recent studies in California (Shaw et al., 2009) in controlled environmental chambers has estimated TOG fluxes of 12 and 18  $\mu\text{g/cow/s}$  from dry and lactating cows, respectively. These estimates are approximately ten-fold lower than the value that has been in use since 1938. In addition, these studies also estimated that only about 1.3% of this TOG flux was ROG ( $0.16 \mu\text{g/cow/s}$  from dry cows and  $0.23 \mu\text{g/cow/s}$  from lactating cows),

which is approximately six-fold lower than the historical 8% used for estimating ROG from TOG flux.

**Table 4. EPA Exempted VOCs due to their negligible photochemical reactivity**

|  |  |
|--|--|
| Methane  | 1,1,1,2,3-pentafluoropropane (HFC-245eb)   |
| Ethane   | 1,1,1,3,3-pentafluoropropane (HFC-245fa)   |
| Methylene chloride (dichloromethane)                           | 1,1,1,2,3,3-hexafluoropropane (HFC-236ea)  |
| 1,1,1-trichloroethane (methyl chloroform)                      | 1,1,1,3,3-pentafluorobutane (HFC-365mfc)   |
| 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)                | Chlorofluoromethane (HCFC-31)  |
| Trichlorofluoromethane (CFC-11)                                | 1-chloro-1-fluoroethane (HCFC-151a);   |
| Dichlorodifluoromethane (CFC-12)                               | 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a)   |
| Chlorodifluoromethane (HCFC-22)                                | 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane<br>(C4F9OCH3 or HFE-7100)  |
| Trifluoromethane (HFC-23)                                      | 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-<br>heptafluoropropane ( (CF3)2CFCF2OCH3)                                      |
| 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114)               | 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane<br>(C4F9OC2H5 or HFE-7200)   |
| Chloropentafluoroethane (CFC-115)                              | 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-<br>heptafluoropropane ( (CF3)2CFCF2OC2H5)                                      |
| 1,1,1-trifluoro-2,2-dichloroethane (HCFC-123)                  | Methyl acetate   |
| 1,1,1,2-tetrafluoroethane (HFC-134a)                           | 1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane (n-<br>C3F7OCH3, HFE-7000)   |
| 1,1-dichloro-1-fluoroethane (HCFC-141b)                        | 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-<br>(trifluoromethyl) hexane (HFE-7500)                                |
| 1-chloro-1,1-difluoroethane (HCFC-142b)                        | 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea)   |
| 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124)                  | Methyl formate (HCOOCH3)   |
| Pentafluoroethane (HFC-125)                                    | Perfluorocarbon compounds which fall into these<br>classes:  |
| 1,1,2,2-tetrafluoroethane (HFC-134)                            | (i) Cyclic, branched, or linear, completely<br>fluorinated alkanes;  |
| 1,1,1-trifluoroethane (HFC-143a)                               | (ii) Cyclic, branched, or linear, completely<br>fluorinated ethers with no unsaturations;                              |
| 1,1-difluoroethane (HFC-152a)                                  | (iii) Cyclic, branched, or linear, completely<br>fluorinated tertiary amines with no unsaturations;                    |
| Parachlorobenzotrifluoride (PCBTF)                             | and  |
| Cyclic, branched, or linear completely methylated<br>siloxanes | (iv) Sulfur containing perfluorocarbons with no<br>unsaturations and with sulfur bonds only to carbon and<br>fluorine. |
| Acetone  |  |
| Perchloroethylene (tetrachloroethylene)                        |  |
| 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-<br>225ca)     |  |
| 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-<br>225cb)     |  |
| 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee)           |  |
| Difluoromethane (HFC-32)                                       |  |
| Ethylfluoride (HFC-161)  |  |
| 1,1,1,3,3,3-hexafluoropropane (HFC-236fa)                      |  |
| 1,1,2,2,3-pentafluoropropane (HFC-245ca)                       |  |
| 1,1,2,3,3-pentafluoropropane (HFC-245ea)                       |  |

Based on these more recent data obtained with the current state-of-the-art instrumentation and research methods (Shaw et al., 2009), only dairy operations with respective herds of 1.4 and 2.0 million of lactating dairy cows and dry dairy cows could surpass 10 tons/yr emissions of ROG allowable in extreme non-attainment areas. Given that only about 3.4% of dairies exceed a herd of 500 cows in the US (NASS-USDA, 2008); this basically excludes all dairy operations units today for regulation for VOCs emissions (as precursors of ozone formation) under CAA. It

is important to once again emphasize that these estimates have neither considered the diurnal and seasonal variations of emissions nor included emissions from silage.

#### **4.0 Summary and Conclusions**

Potential emissions from AFOs that may be regulated under the federal CAA as criteria pollutants are ozone (as VOCs and NO<sub>x</sub>), and particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>). Under the CAA, any facility emitting 100 tons/yr of these emissions are subject to permit. This limit drops to 50, 25, and 10 tons/yr for serious, severe, and extreme nonattainment areas, respectively.

Ammonia and hydrogen sulfide are the other potential emissions from AFOs that are currently regulated under two other federal statutes: CERCLA and EPCRA. Any facility emitting 100 lb/day of ammonia or hydrogen sulfide has release reporting requirements under both CERCLA and EPCRA. AFOs are, however, exempt from CERCLA for emissions from normal manure handling on farms except from other forms of releases such as from: burst anhydrous ammonia tank, breached lagoon or holding pond, and manure spills. Currently research under the auspices of the 'national air emissions monitoring study – NAEMS' is on-going to establish credible tools to estimate these emissions from AFOs to aide regulation.

The VOCs are also directly regulated under HAPs either individually or in groups. Although emissions of VOCs as HAPs from AFOs are insignificant at the regional, national, or global scale, they cannot be neglected at the local scale (property line or nearest dwellings). Sources emitting at least: (i) 10 tons/year of any one HAP, or (ii) 25 tons/year of any two or more HAPs, are also permitted under EPA's Title V as major sources and requires permitting. Amongst the major VOCs emissions from dairy operations, five (2-butanone, p-Cresol, phenol, methyl isobutyl ketone or hexone, and methanol) are listed as HAPs (Table 3). According to available data, only dairy operations with herds of 16,300 (lactating cows) or 34,600 (dry) may be subject to methanol legal limit under the EPA HAPs statutes (Title V). On the other hand only dairy operations with herds of 2 and 90 million may be subject to this statute for 2-butanone and hexone, respectively: when each is considered individually. These data suggests that almost all dairy operations in the US today may be exempt from considerations as major sources of VOCs as HAPs.

With respect to VOCs are precursors for ozone formation, available data suggests that only dairy operations with herds of 1.4 million lactating dairy cows or 2.0 million dry dairy cows

could potentially emit at least 10 tons/yr of ROG (legal limit in extreme nonattainment areas). This data also essentially excludes all dairy operations today against regulation for VOCs emissions (as precursors of ozone formation) under CAA.

It is important to note that the available data on the emissions of VOCs from dairies (either as HAPs or precursor of ozone formation) do not include emissions from silage. Based on unpublished data, emissions of VOCs from silage are significant sources of VOCs in dairies. It is instructive therefore; that the herd size limits presented in this report will adjust downwards when VOCs data from silage become available.

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