DRAFT:
Volatile Fatty Acid (VFA) Emission Rate Technical Assessment
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Introduction

Volatile fatty acids (VFAs) are a group of compounds that include acetic acid (the lowest molecular weight VFA), propionic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, hexanoic acid and other higher molecular weight (MW) compounds. This paper reviews and compares the various studies that have attempted to characterize and/or quantify VFA emissions from manure. As noted below, VFA emissions are strongly dependent on the type of manure and the process conditions of the manure. This can be demonstrated by reviewing the biochemistry and air/water chemistry of VFAs, as well as the studies described below.

Chemistry

Cows and cow manure produce VFAs through the process of fermentation of starches and proteins in either their digestive systems or excreta. All VFAs are semi-volatile organic compounds (SVOCs), because of their low volatility (Henry's law constant) and water solubility, since their polar nature makes them more likely to stay in aqueous solution. From an air quality regulatory perspective, most VFAs meet the definition of Volatile Organic Compound (VOC), as they have not been listed as exempt by the U.S. EPA or the SJVAPCD. VFAs are very water soluble and, as such, are found at dominant concentrations in aqueous median such as manure and liquid solution. Hydrocarbons in anaerobic liquid environments, such as those found in dairy lagoons, are typically consumed and preferentially excreted as methane.

Studies

Studies related to VFAs from manure are listed in Table 1. Where possible, emission estimates are included. For each study, the test method and conditions are noted, as well as comments on the study or its potential application to estimating VFA emissions from dairies.

Conclusions:

For determining VFA emissions at local San Joaquin dairies, the Schmidt et al. study is the most appropriate. It is a study done at a local dairy. It measured VFA emissions at multiple process locations (feedlanes, corrals, lagoons, etc.) using an EPA-approved test method (see NOTES section after Table 1 for more discussion on the test method). Testing at all significant dairy area sources (corrals, flushed lanes, lagoons, etc.) with the U.S. EPA-validated chamber was non-detect for all samples collected, however detection limits were higher than desirable (60 ppbv to 260 ppbv). Two emission estimates were developed: 1) assuming that acetic acid was at the detection limit for all processes and that it represented 37% of the total VFAs; and 2) assuming a more realistic estimate of

	Study	Emission Factor (lb/hd-yr)	Test Methods and Conditions	Comments
7.	Miller and Varel	Cannot be estimated using this data	• Fresh and aged manure from an unknown source (presumably feedlot manure) collected and stored in containers and emissions measurements made in an enclosed chamber. • VFAs were only quantified in the liquid phase	• No measurements were made of gas-phase VFAs • Acetate, propionate, and butyrate comprised more than 98% of the total VFAs in both fresh and aged slurries.

NOTES:

Schmidt: Testing at all significant dairy area sources (corrals, flushed lanes, lagoons, etc.) with the USEPA validated chamber was non-detect for all samples collected, however detection limits were higher than desirable (60 ppbv to 260 ppbv). Areas on the San Joaquin Valley dairy that were sampled include: flushed lanes (pre- and post-flushed); feedlane pile; freestall bed; turnouts; heifer pens; milk parlor; separator solids, storage pile solids; bedding pile solids; primary lagoon. Concerns have arisen that the method used by Schmidt et al. cannot detect, or would dramatically underestimate, VFAs because of losses in the sampling system. These concerns are not supported by the facts. Researchers conducted VFA sampling using EPA-approved method for semi-volatile organic compounds (flux chamber with EAS (Environmental Analytical Services) method that is a modified TO-5 method with GC/HPLC-UV/VIS). There is approximately 8 feet of purged tubing used by Schmidt, while Koziel used approximately 1-2 inches. Further, the EPA chamber and tubing were operated in the dynamic mode (constant air movement in the chamber and tubing). Such dynamic environments are not conducive to losses. This is born out by the method testing that was carried out when the method was approved by EPA. Even sulfur compounds, which are highly reactive with stainless steel, can be measured using this method.

Table 1: Comparison of VFA studies

	Study	Emission Factor (lb/hd-yr)	Test Methods and Conditions	Comments
1.	Schmidt et al.	0.47 (most probable) to 1.42 (worst-case) Includes all dairy processes	• SJV dairy, all significant surfaces at the dairy (corrals, lanes, lagoons, etc., 11 total) • USEPA validated chamber method used for the flux measurement • All measurements were made in situ. • EPA-approved analytical method (EAS) used for SVOCs, such as VFAs • VFAs collected on sorbent materials and measured using GC/MS. • No enteric VFA emissions measured. • No samples detected from any source above method detection limits. • Emission estimate based on worst-case assumption of fluxes demonstrated to be below the detection limit. See Notes.	• San Joaquin Valley dairy • Uses EPA-approved methods for VFAs, including sampling train. • Includes every process source at the dairy. • Does not include enteric emissions. • Emissions calculated using the detection limit for VFAs (10 ug/m^2-min) for the worst case acetic acid emissions. Total VFAs are calculated by assuming 37% of VFAs are acetic acid (Koziel et al.). For a better estimate, CARB guidance on estimating emissions for non-detect samples, when all samples are non-detect, is that emissions are 1/3 of the detection level. This is the first reported number. • Future testing will include VFA flux testing at lower method detection limits.

	Study	Emission Factor (lb/hd-yr)	Test Methods and Conditions	Comments
5.	McGinn, et al	Characterized, not quantifiable	• Three feedlots in Southern Alberta, Canada with varying stocking densities. • Includes land application emissions • Measurements were taken from March to September. Rainfall general 1.5 to 2.6" per month. • Towers were placed at various locations were equipped with multiple sampling devices. • Ambient air measurements were performed. • VFAs collected on sorbent materials and measured using GC/MS.	• Characterization study for high-density beef feedlots and land application. • Acetic acid (54 to 67%), proprionic acid (12-22%), and butyric acid (16 to 22%) are most prevalent VFAs. Others are generally at less than 1% to 2%. • Greatest VFA concentration during pen (e.g. corral) cleaning. • Wetter manure pack (and higher related emissions) than likely in SJV. • Only concentrations reported. No surface emission flux rates or emission factors included. Cannot be used to calculate an emission factor for VFAs, even for Canadian beef operations.