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Uncertainties in the Current Knowledge of Some Atmospheric Trace Gases Associated with U.S. Agriculture: A Review

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ABSTRACT

Approximately 80 different crop species are grown in the United States in widely differing geographic areas, climatic and edaphic conditions, and management practices. Although the majority of cultivated acreage in the United States is planted with only about 10 primary crops, uncertainties associated with trace gas emissions arise from: (1) limited data availability, (2) inaccurate estimates because of large temporal and spatial variability in trace gas composition and magnitude of trace gas emissions from agricultural activities, (3) differing characteristics of pollutant emissions from highly dispersed animal feed-lots, and (4) limited understanding of the emissions of semi-volatile organic compounds (SVOCs) associated with agriculture. Although emission issues are of concern, so also is atmospheric deposition to cropping systems, including wet and dry nitrogen, minerals, and organic compounds. These can have feedback effects on trace gas emissions. Overall, the many gaps in our understanding of these aspects of agricultural systems deserve serious attention.

IMPLICATIONS

Emissions of trace gases including gaseous nitrogen and SVOCs from animal and cropping systems have become a serious environmental and political problem. Compliance with increasingly stringent federal and state air pollution regulations pose both technical and economic challenges to agricultural operations. Our current knowledge of agricultural emissions and their impacts on regional and global scale air quality and climate forcing are fraught with many uncertainties that require urgent attention.

INTRODUCTION

According to a report by the U.S. National Research Council, there is convincing evidence that changes in agricultural crop production and animal activities are increasing the emissions of trace gases into the atmosphere (see <http://books.nap.edu/catalog/10586.html>). Such emissions not only alter the air quality but some of them also play a very important role in climate change or forcing. These concerns were underscored by the focus of a 2006 global-level Workshop entitled "Agricultural Air Quality: State of the Science" (see <http://www.esa.org/AirWorkshop>), which among others, included the contents of this paper.

Regarding atmospheric emissions at the global scale, agriculture (including crop production, animal rearing, biomass combustion, and soils) is both a source and a sink for a number of carbon (C) and nitrogen (N) trace gases. U.S. agriculture includes 10 primary crops cultivated over most of the arable area nationwide and some 70 other important agronomic and horticultural species, as well as dozens of species of regional economic importance. On the basis of the five principal crops, the United States has the largest harvested area (ha) and highest production (Mt) per capita in the world and contributes 21% of global crop production.¹

Climatic, edaphic, abiotic, and biotic growth regulating factors, as they vary across 8 different temperature zones and 11 distinct orders of soil, lead to substantial variability in crop management practices, and associated agricultural fluxes of trace gases. At the regional and national scales, agriculture is a major, but poorly understood, source of atmospheric C and N trace gases.²

Anthropogenic emissions of ammonia (NH₃), oxides of nitrogen (NO_x), and nitrous oxide (N₂O), respectively, account for 43 Mt (36%), 31.1 Mt (26%), and 3.2 Mt

(~3%) of N annually to the total global budget (natural plus anthropogenic sources).³ Of the total anthropogenic emissions, NH₃ accounts for 55%, NO_x for 40%, and N₂O for approximately 5%. Agriculture contributes approximately 50% of total N, stationary and mobile source fossil fuel combustion each contribute 15%, and biomass burning contributes another 10%. It was estimated that during 1990, China emitted 8449 Gg NH₃-N yr⁻¹; India 7608 Gg NH₃-N yr⁻¹; Latin American countries, African nations, the former Soviet Union, and western European countries 6284, 5415, 3403, and 2879 Gg NH₃-N yr⁻¹, respectively; and the United States emitted 2898 Gg NH₃-N yr⁻¹.³

In addition to the N species, agricultural emissions of semi-volatile organic compounds (SVOCs) are a rapidly emerging issue of major concern. For example, on a leaf dry-weight basis, emissions of formic acid can be as high as 500 ng · g⁻¹ · hr⁻¹, and acetic acid up to 400 ng · g⁻¹ · hr⁻¹. Total terrestrial vegetation emits between 14 and 256 Gmol · yr⁻¹ of formic acid and 9–94 Gmol · yr⁻¹ of acetic acid. Biomass burning emits directly between 55–202 Gmol · yr⁻¹ of formic acid and 182–650 Gmol · yr⁻¹ of acetic acid.⁴ These large ranges of estimated emissions reflect the serious limitations of our current knowledge of SVOC emissions in agriculture because of substantial uncertainties in both measurements and the underlying science.

There are several principal sources of uncertainty in determining the contributions of both emissions and deposition of trace gases associated with agriculture. Emission inventories of trace gases are uncertain because of: (1) measurement methods for atmospheric trace gas concentrations and fluxes; (2) spatial and temporal sparsity of existing concentration data; (3) lack of sufficient information on sources, emissions, and transport, and fate of SVOCs or volatile organic compounds (VOCs); and (d) validation of regional scale assessments. Many of these issues pertain to all classes of agriculturally sourced trace gases. However, we focus here on the burgeoning problems of nitrogenous gases and the often short-lived SVOCs.

N SPECIES

The dominant atmospheric trace gaseous N species are nitric oxide (NO), nitrogen dioxide (NO₂), N₂O, and NH₃. Particulate ammonium (NH₄⁺), nitrate (NO₃⁻), nitric acid vapor (HNO₃), and organic N species are also of importance. NO and NO₂ are major reactants in the atmospheric photochemistry leading to the production of phytotoxic ozone (O₃) and other oxidants,⁵ NO₂ and NH₃ can have adverse direct effects on plant foliage.⁶ Excess atmospheric N deposition to soils can lead to substantial effects on the structure and function of native and forested ecosystems because of excess fertilization.⁷ Such atmospheric deposition to cropping systems that are subjected to commercial fertilizer application⁸ is not likely to cause detrimental impacts, although it may contribute to N contamination of ground and surface waters.

NO emissions from agriculture have been linked to application of organic and synthetic N fertilizers. However, it has not proven possible to use simple relationships

between fertilizer N application rates and NO emissions across locations with differing climate, soil, crop, and management conditions. In general, high N application rates; warm climates; and coarse, textured, and neutral soils with high C content favor NO emissions.¹ In the atmosphere, NO is largely converted to NO₂ through photochemical reactions and leads to the formation of a suite of oxidants.⁹

In addition to NO, approximately 24% of anthropogenic N₂O emissions come from fertilized soils,¹⁰ although natural emissions from native soils and agricultural soils in the tropics have not been separated.¹¹ In general, there is a strong increase of N₂O emissions with N application rates, warm climates, fine soil texture, restricted drainage, neutral to acidic conditions, and high organic C and N contents.¹ On a global scale, N₂O emissions from synthetic and manure-based fertilizer sources appear to be approximately equal. In that context, fertilizer use in developed countries has remained roughly the same since 1980. However, in developing countries it has increased by 60% in the last decade, and the trend is predicted to continue into the future.¹¹

There are no nationwide monitoring networks in the United States to quantify agricultural emissions of NO, N₂O, or NH₃ (see below). In contrast, the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) has been monitoring the wet deposition of NH₄⁺ and NO₃⁻ since 1978 and currently has some 250 sites across the United States (see <http://nadp.sws.uiuc.edu/>). Similarly, since 1987 the Clean Air Status and Trends Network (CASTNET) has been monitoring dry deposition of NO₃⁻, NH₄⁺, and HNO₃ (but not NH₃, NO, NO₂, or N₂O) at 70 sites primarily in the eastern United States (see <http://www.epa.gov/castnet/>). Unfortunately, there are only a few sites where both dry and wet deposition of N species are measured concurrently. Nevertheless, informative comparisons can be made between the two sets of data at those sites (Table 1).

Atmospheric NH₃ reacts with both sulfuric acid (H₂SO₄) and HNO₃ molecules to form the corresponding fine particle NH₄⁺ salt aerosols that are a regional-scale problem. Both salts are deliquescent, the NO₃⁻ more so than the sulfate (SO₄²⁻). Accumulation of ammonium sulfate ((NH₄)₂SO₄) and ammonium nitrate (NH₄NO₃) in the atmosphere not only results in a reduction in visibility, but also increases in cloud condensation or nucleation.⁵ It may also contribute to the observed increases in the nighttime air temperatures in the United States.¹²

Results presented in Table 1 show that ambient sulfur dioxide (SO₂) concentrations in the United States have declined by -15 to -95% between 1989 and 2004 at almost all of the CASTNET monitoring locations. There was also a decline (-8 to -45%) in particulate SO₄²⁻ (dry deposition) concentrations at those locations. A similar temporal trend in SO₄²⁻ (-7 to -59%) was observed in the NADP/NTN weekly precipitation (wet deposition) data at the collocated sites. However, NH₄⁺ behaved differently. A comparison of the time trends of the dry deposition data (Table 2) of the NH₄⁺ concentrations in CASTNET with the wet deposition data in NADP/NTN

Table 1. Seasonal Kendall's trend test: Comparison of CASTNET SO₄²⁻ concentrations in the particle phase (dry deposition), CASTNET SO₂ concentrations, and NTN SO₄²⁻ concentrations in precipitation (wet deposition) from December 1989 to November 2004.

Site ID		CASTNET SO ₄ ²⁻ Trend		CASTNET SO ₂ Trend		NTN SO ₄ ²⁻ Trend	
CASTNET	NADP	Direction and Significance	Magnitude (%)	Direction and Significance	Magnitude (%)	Direction and Significance	Magnitude (%)
Eastern sites							
SND152	AL99	▼	-17	▼	-48	▽	-15
CAD150	AR03	▼	-22	▼	-50	▼	-19
GAS153	GA41	▼	-17	▼	-53	▽	-7
BVL130	IL11	▼	-38	▼	-52	▼	-40
VIN140	IN22	▼	-42	▼	-67	▼	-38
MCK131	KY03	▼	-37	▼	-64	▼	-55
CVL151	MS30	▼	-25	▼	-70	▽	-14
COW137	NC25	▼	-18	▼	-44	▼	-27
WST109	NH02	▼	-45	▼	-63	▼	-33
WSP144	NJ99	▼	-33	▼	-36	▼	-34
OXF122	OH09	▼	-36	▼	-53	▼	-35
KEF112	PA29	▼	-36	▼	-51	▼	-35
PSU106	PA42	▼	-30	▼	-57	▼	-39
VPI120	VA13	▼	-31	▼	-15	▼	-32
SHN418	VA28	▼	-25	▼	-61	▼	-29
PAR107	WV18	▼	-38	▼	-95	▼	-59
Western sites							
GRC474	AZ03	▼	-18	▼	-72	▼	-24
GLR468	MT05	▼	-25	▼	-47	▼	-44
PND165	WY06	▽	-8	▽	5	▽	-20

Notes: ▲ = increasing trend, statistically significant ($p \leq 0.10$); ▼ = decreasing trend, statistically significant; △ = increasing trend, not statistically significant; ▽ = decreasing trend, not statistically significant.

Table 2. Seasonal Kendall's trend test: Comparison of CASTNET NH₄⁺ concentrations in the particle phase (dry deposition) and NTN NH₄⁺ concentrations in precipitation (wet deposition) from December 1989 to November 2004.

Site ID		CASTNET Trend		NTN Trend	
CASTNET	NADP ^a	Direction and Significance	Magnitude (%)	Direction and Significance	Magnitude (%)
Eastern sites					
SND152	AL99	▼	-17	△	9
CAD150	AR03	▽	-10	▽	-15
GAS153	GA41	▼	-14	▲	22
BVL130	IL11	▼	-30	△	11
VIN140	IN22	▼	-36	△	18
MCK131	KY03	▼	-24	△	16
CVL151	MS30	▼	-30	△	8
COW137	NC25	△	4	△	9
WST109	NH02	▼	-20	▽	-3
WSP144	NJ99	▼	-27	△	5
OXF122	OH09	▼	-32	△	9
KEF112	PA29	▼	-11	▽	-8
PSU106	PA42	▼	-17	△	4
VPI120	VA13	▼	-13	▽	-10
SHN418	VA28	▽	-3	▽	-1
PAR107	WV18	▼	-18	▼	-18
Western sites					
GRC474	AZ03	▼	-12	▲	47
GLR468	MT05	▽	-2	▲	41
PND165	WY06	▽	-8	▲	46

Notes: ▲ = increasing trend, statistically significant ($p \leq 0.10$); ▼ = decreasing trend, statistically significant; △ = increasing trend, not statistically significant; ▽ = decreasing trend, not statistically significant.

networks showed that although there was a declining trend at the CASTNET sites (-2 to -36%), there was an increase at several NADP/NTN sites ($+4$ to 22%), with statistically significant increases at the western sites ($+41$ to $+47\%$; Table 2). The underlying reasons for the increasing trends in NH_4^+ at the three western sites are difficult to explain at this time. Current changes in both crop and animal agricultural production practices merit further attention in this regard.

The NADP/NTN data on wet deposition of N species are likely to be underestimates. There is evidence to show a measurable loss of N species in weekly precipitation samples compared with daily or event samples, likely because of volatilization and/or microbial consumption.¹³ An examination of annual data from an agricultural site with collocated daily and weekly samplers of precipitation showed a loss of approximately 17% of NH_4^+ and 8% of NO_3^- in the weekly compared with the daily sampling (Table 3). Losses are thus diminished when precipitation samples are collected frequently, and even further, under in situ refrigeration versus ambient conditions.¹³

There are also uncertainties associated with measurements of N gas fluxes over crop canopies. The most frequently used methods consist of various types of chambers (e.g., static and dynamic), micrometeorological techniques (e.g., flux gradient, eddy covariance), and mass balance (e.g., use of applied ^{15}N as a tracer). The advantages and limitations of these methods have been considered.¹ The selection of the appropriate measurement method will depend on the intended use of the data. For example, environmental as well as chemical and biological factors affect NH_3 volatilization from fertilized soils. Therefore, it is advisable to use techniques that cause minimal disturbance to the field environment, and micrometeorological and ^{15}N balance approaches are the most advisable. However, ^{15}N balance techniques produce estimates of total N loss. Hence, for determining NH_3 loss and denitrification, a combination of ^{15}N balance and micrometeorological techniques would be the most appropriate approach because they provide estimates of both loss and flux. Similar considerations apply to the quantification of the fluxes of other N species.

Isotopic enrichment or relative ratios of stable elemental isotopes (e.g., ^{13}C : ^{12}C ; ^{15}N : ^{14}N ; $^{18,17}\text{O}$: ^{16}O ; ^{34}S : ^{32}S) in atmospheric and receptor (plants, soils, etc.) samples have been used to identify the contributions of

Table 3. Comparison of precipitation-weighted mean concentrations and total annual wet deposition for AIRMoN (daily) and NADP/NTN (weekly) samples in 2004 from the Bondville, IL, sampling site.

	NH_4^+	SO_4^{2-}	NO_3
AIRMoN ^a mean concentration	0.38 mg/L	1.51 mg/L	1.16 mg/L
NADP/NTN ^a mean concentration	0.32 mg/L	1.44 mg/L	1.07 mg/L
AIRMoN total deposition	3.79 kg/ha	15.0 kg/ha	11.6 kg/ha
NADP/NTN total deposition	3.19 kg/ha	14.4 kg/ha	10.7 kg/ha
Percent difference in total deposition (AIRMoN-NADP/NTN)	+18.8	+4.2	+8.4

Notes: ^aAIRMoN = Atmospheric Integrated Research Monitoring Network.

Table 4. Some examples of passive sampling of ambient agricultural trace gases.

Trace Gas	Absorbent/Adsorbent
CO	Y-type zeolite
CO ₂	Barium hydroxide
H ₂ S	Silver nitrate
NO	Chromium trioxide + TEA
NO ₂	TEA, sodium carbonate + glycerol
N ₂ O	Molecular sieve
HNO ₃	Nylon
NH ₃	Phosphoric acid, citric acid
O ₃	Sodium nitrite, DPE
Organic compounds	Triolein, polyurethane

Notes: Modified from: Krupa and Legge.¹⁸ H₂S = hydrogen sulfide, TEA = triethanolamine, DPE = 1-2-di-(4-pyridyl) ethylene.

specific sources (crop, soil, animal operations, etc.) to wet and dry deposition of air pollutants at a regional scale or at a given location.¹⁴ For example, development of analytical methodology for measuring ^{18}O , ^{17}O , and ^{15}N in NO_3 offers a powerful tool. However, because the isotope data represent relative (delta) but not absolute values, clear separation must exist in the composition of individual sources for the contributions of their emissions to be apportioned. That problem can be resolved by combining the isotope data with detailed trace element profiles and analyzing the entire dataset using multivariate methods such as positive matrix factorization (PMF).¹⁵

There are several models available for scaling N gas emission or deposition data from a given plot or study location to the regional scale.¹⁶ Such model results require validation, because this extrapolation of data can result in large uncertainties because of significant spatial and temporal variations in the trace gas concentrations. In U.S. agriculture, there is a significant diversity in the distribution of cropping systems, even within a single region. Variation in climatic and edaphic factors and management practices within and across regions also contribute to uncertainty. There is also the complexity of temporally regulated fluxes. One approach to resolving these uncertainties is to couple aircraft and ground-based measurements,¹⁷ directly linking spatial scales, or to use inexpensive passive samplers of trace gas concentrations at many locations, allowing spatial and temporal averaging (Table 4; also Krupa and Legge¹⁸). Passive samplers allow the quantification of the time-integrated (e.g., 1 day to 1 week) concentrations of a trace gas. Currently methods are available for the passive sampling of NO, NO₂, N₂O, and NH₃. At a given site, a set of passive samplers can be deployed at different heights above the surface to calculate the net deposition of a given N species using, for example, a time-averaged gradient method.¹⁹ Such data can be used to calibrate and validate the relationships and reduce the corresponding uncertainty between remotely sensed (e.g., aircraft) and surface-based measurements of trace gas fluxes.

Passive sampler-based regional assessments are generally accomplished by Kriegering and by Geographic Information System (GIS) methods.^{20,21} However, to characterize the spatial characteristics of the N gas of interest, the

data requirements for applying these methods must be followed.^{22,23} The theoretical minimum sample number (measurement locations)²⁴ must be calculated from covariance analysis of the passive sampler data from clustered sites (spatial autocorrelation).²⁵ Currently, application of this type of spatially aggregated data often fails to meet these standards, leading to considerable uncertainty in derived spatial distribution and transport characteristics.

N trace gases and their chemically transformed products (e.g., O₃) have considerable capacity for direct and indirect harm, and a substantial role in atmospheric chemistry and in climate forcing. Krupa and Moncrief⁸ concluded that atmospheric N deposition to cropping systems that are subjected to commercial fertilizer application is not likely to cause detrimental impacts. A different aspect is the role of N deposition on arable lands, and how the effect of the added N on plant growth acts as a feedback to the atmosphere.²⁶ Analogous to what has been observed with the effects of elevated CO₂ on plants,²⁷ one should expect an altered climate in response to this inadvertent anthropogenic forcing. Even if the direct effect on the crops themselves is small, because crops are often deliberately fertilized with N, its atmospheric deposition could affect adjacent uncultivated land, resulting in climate effects over the cropland. "The cycles of nitrogen, carbon, and other key nutrients are inextricably linked. Their interactions are likely to provoke key nonlinear behaviors in the evolving Earth system."²⁸ In discussing the diverse aspects of climate forcing, as opposed to a top-down (global averages to regional scale variability²) approach to modeling, Pielke et al.²⁹ describe a new paradigm, a bottom-up approach for assessing the role of agriculture in the climate system and in climate change. In this approach of scaling from regional to larger spatial dimensions, aspects such as changes in the land use practices can be accounted for and consequently lead to improvement in reliability by reducing the variability imposed by temporal and spatial considerations. Nevertheless, within the overall subject, the large uncertainties in N gas budgets between agricultural systems and the atmosphere suggest that considerable further work is urgently needed.

SVOCs

Emissions of SVOCs from agriculture are a major emerging concern. SVOCs are compounds that exhibit a significant ambient distribution in gas, liquid, or solid phases and are commonly or adsorbed to solid substrates.³⁰ SVOCs include acids, alkanes, carbonyls, lipids, N-substituted aromatic compounds, terpenoids, organochlorine and other pesticides, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs), and polybrominated diphenyl ethers (PBDFs), among others. The broad range of compounds and vapor pressures involved (10⁻⁶ to 10¹ Pa) requires a host of often incompatible sampling and analytical procedures.³¹

SVOCs are deposited to surfaces and revolatilized repeatedly with diurnal and seasonal changes in ambient

Table 5. Pesticide fluxes from soil + plants within 1 day of application.

Compound	Soil Flux (g/ha/day) (% applied)	Plant Flux (g/ha/day) (% applied)
Herbicide		
Trifluralin	1440 (50%)	381 (15%)
Insecticide		
Diazinon	6 (0.4%)	218 (4.8%)
<i>p,p'</i> -DDT	11 (0.8%)	11 (<1%)
Dieldrin	69 (2.8%)	41 (1.6%)

Notes: Modified from Woodrow et al.⁵⁰ and Bedos et al.³⁴

temperatures. This facilitates transport across the landscape. Adsorption to particles further enhances transport, with redistribution from smaller to larger particles increasing with time.³² Gas-phase concentrations increase with vapor pressure as the particulate matter contributions decline, and thus, larger compounds are dispersed farther in warm weather.

Among SVOCs, emission of pesticides is due to volatilization, governed by their physicochemical properties and partitioning between environmental compartments. These properties are well known for purified active ingredients, but often not so for commercial preparations. Emission without volatilization can occur by re-entrainment of particles from wettable powders and spray drift of liquid particles during application.

Depending on the physicochemical properties, in certain cases volatilization of a pesticide from vegetation can be larger than from the soil because of greater roughness and surface area (Table 5). Available soil moisture often increases volatilization, but postfumigation irrigation may depress emissions by acting as a cap. Volatilization is largest immediately after application, but measurements cannot generally be made at that time. In wind tunnel tests, 44% of chlorpyrifos and 25% of parathion-methyl were lost to volatilization by 12 days after application,³³ with initial emissions of chlorpyrifos of approximately 1 mg · m⁻² · hr⁻¹. Literature values³⁴ for a range of such materials are from ng to μg · m⁻² · sec⁻¹.

Models and measurements often conflict in describing transport of SVOCs. The former may indicate limited transport whereas the latter indicates long distance transport.³⁵ In North Dakota, a broad spectrum of organochlorines, triazine, and herbicides were found in regional air.³⁶ The relative absence of PCBs indicated that agriculture dominated the atmospheric SVOC. Aircraft measurements using relaxed eddy accumulation (REA) over agricultural and forested surfaces in Ontario found fluxes of atrazine from -1.1 to +2.5 ng · m⁻² · sec⁻¹ and of metolachlor of -0.02 to +0.56 ng · m⁻² · sec⁻¹ (negative away from the ground surface).¹⁷ Compounds with higher vapor pressure were not observed in these measurements taken roughly 2 months after regional applications. In the agricultural San Joaquin Valley of California, pesticides are volatilized from plant surfaces at low elevation and deposited at cooler, higher elevations or at night. Pesticides used during the winter season were found in winter-spring precipitation (wet deposition). Pesticides

used in the summer were found many kilometers away and at greater elevation both in the air and in dry deposition in the forested Sierra Nevada Mountains.^{37,38} Uncertainties in these results arise from the sampling and analytical methods used, the diversity in the surface cover over the transport pathway, and dynamic partitioning between the particle and gas phases.

As with pesticides, direct (biogenic) emissions of SVOCs from vegetation are poorly understood except for the monoterpenes (C_{10}) emitted in substantial quantities from certain genera. Sesquiterpenes (C_{15}) have also been shown occasionally to be emitted in equivalent quantities.^{39,40} Reported values of emissions range from 0 to approximately $50 \mu\text{g} \cdot \text{g}^{-1} \cdot \text{hr}^{-1}$ (leaf dry-weight basis) in aromatic species such as tomatoes.⁴⁰ Plants emit carbonyl compounds, largely aldehydes, including some high-molecular-weight species. Cotton and alfalfa were found to emit mixed hexenals and larger aldehydes.⁴¹

Emissions from forests account for 15–30% of the European budget of tropospheric organic acids. As noted previously, emissions of formic acid on a leaf dry-weight basis range from 0 to $500 \text{ ng} \cdot \text{g}^{-1} \cdot \text{hr}^{-1}$, and of acetic acid from 0 to $400 \text{ ng} \cdot \text{g}^{-1} \cdot \text{hr}^{-1}$. Total terrestrial vegetation emits between 14 and $256 \text{ Gmol} \cdot \text{yr}^{-1}$ of formic acid and between 9 and $94 \text{ Gmol} \cdot \text{yr}^{-1}$ acetic acid.⁴ Additional organic acids are derived from atmospheric oxidation of biogenic volatile alkenes, yielding mostly formic, acetic, and pyruvic acids.

Crop species are often sinks. Plant cuticles, including both epicuticular and intracuticular waxes, absorb SVOCs, but absorption and re-emission are species-specific.^{42,43} Particulate-bound PAHs are more characteristic of soil than plants because of re-entrainment and washoff, whereas gaseous species are associated more with plant leaves.⁴³ Zucchini, (*Cucurbita pepo*) is unusual in its ability to extract SVOCs from soil,⁴⁴ with transport to the shoot and perhaps beyond into the boundary layer. Biogenic sources of PAHs have been suggested in the savanna ecosystem of Brazil.⁴⁵ In both zucchini and the Brazilian savanna, volatilization rates remain unknown. Uncertainties in the data reflect large differences in emissions from closely related plants and complex and poorly characterized environmental impacts on emissions, partitioning, and uptake of SVOCs by the vegetation-atmosphere system.

Another substantial agricultural source of SVOCs may be concentrated animal feeding operations (CAFOs). Ruminant animals are globally estimated to emit approximately $2.5 \text{ Gmol} \cdot \text{yr}^{-1}$ of acetic acid.⁴ Emissions of SVOC from commercial dairies in California's Central Valley were evaluated by a panel of concerned citizens and experts.⁴⁶ The panel found extremely limited data availability, particularly in the areas of organic acids, amines, and phenols. Estimates for total VOC emissions from dairies ranged from 2.3 to $18.2 \text{ kg} \cdot \text{cow}^{-1} \cdot \text{yr}^{-1}$ on the basis of various combinations of partial measurements on several California dairies, cattle and dairy operations in other states, and laboratory manure slurry studies. Estimates of amines ranged from 0.09 to $5 \text{ kg} \cdot \text{cow}^{-1} \cdot \text{yr}^{-1}$, of acids 0.5 to $17 \text{ kg} \cdot \text{cow}^{-1} \cdot \text{yr}^{-1}$, and of phenols from 0 to $1.2 \text{ kg} \cdot \text{cow}^{-1} \cdot \text{yr}^{-1}$. The large uncertainties suggested a

need for further studies, particularly of process-based emissions, under locally relevant conditions.

Mechanical drying of poultry litter (20–110 °C) resulted in emissions of aldehydes, sulfur compounds, ketones, alkanes, pyridines, and furans.⁴⁷ Swine CAFO emissions include butyric and isovaleric acids and *p*-cresol, among other odorous SVOCs.⁴⁸ As an odor constituent, *p*-cresol became increasingly dominant with distance, downwind from the cattle or the swine.

Uncertainties in estimates of emissions from animal agriculture reflect the difficulties typical of the quantification of SVOCs as well as: (1) sampling and analytical methods, particularly for unknown, low volatility compounds; (2) uncertain spatial sampling requirements among the diverse areas of modern CAFOs; (3) temporal and spatial characterization of the activities of modern CAFOs; and (4) seasonal, diurnal, and management effects on emissions. A specific data gap involves accounting for emissions from manure transported off-site for land spreading or other methods of disposal.

In the context of anthropogenic sources of SVOCs, among the most toxic emissions from incomplete combustion are PAHs, including benzo(a)pyrenes (BAPs), emissions of which increase with the amount of green biomass in the fuel. Estimates of PAHs (sum of 19 congeners) of 5–685 $\text{mg} \cdot \text{kg}^{-1}$ fuel depend on fire intensity.⁴⁹ Open-field agricultural burns are generally of low intensity. Increasing combustion efficiency reduces total organic emissions but increases the fraction of PAHs.⁴⁹ Emissions of dioxins and furans (PCCD/F) decline with burn efficiency, becoming negligible above 1000 °C.⁴⁹ Fuel mix influences emission of PAHs, with barley and wheat straw emitting more PAHs (including BAP) than straw of other grains or wood combustion.⁴⁹

Biomass burning emits directly between 55–202 $\text{Gmol} \cdot \text{yr}^{-1}$ of formic acid and 182–650 $\text{Gmol} \cdot \text{yr}^{-1}$ of acetic acid.⁴ Formic acid is also formed from atmospheric oxidation of formaldehyde emitted directly during biomass combustion.⁴⁹ Uncertainties arise from the occasional and spatially disperse nature of burns and the diversity of burn pile geometries and fuels, as well as the pervasive sampling and analytical difficulties associated with SVOCs. As biomass burning from intentional and accidental fires may affect large land areas, uncertainties in this regard require considerable further attention.

CONCLUSIONS

The large diversity and distribution of crops grown within the U.S. landscape, coupled with the similarly diverse climatic zones, soil orders, and management practices, result in significant uncertainties in deriving regional-scale estimates of trace N gas emissions and their total atmospheric deposition. For N gases this is compounded by the associated temporal variability and lack of nationwide measurement networks, with the exception of wet deposition. There are uncertainties with the methods used to collect wet deposition with in situ losses during weekly sampling. Although there are many site-specific flux studies of N gases (dry deposition), such results are difficult to extrapolate to the regional scale by modeling

without validation of the results. Aircraft measurements and the application of passive trace gas sampling offer approaches to resolving the problem. However, careful attention should be paid in designing experiments using those methods.

SVOCs are also highly diverse. Evaluation of their occurrence and distribution is therefore experimentally difficult and expensive. Process-oriented measurements directed towards specific classes of SVOCs will be required to provide sufficient information to model emissions under specific conditions. Total SVOC emissions from agricultural operations remain an important area of great uncertainty at this time.

Although we have emphasized N and SVOC trace gases, the diversity and dynamic nature of U.S. agriculture lead to rather large uncertainties in emissions from this sector. As agricultural-urban interface issues increase in frequency and intensity, it is hoped that considerable further research funding will be made available in this arena.

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