

Supplemental Information for Manuscript:

Characterization of Indoor Amines in Poultry Farms: A Brief View of Chemical Exposures to Chickens and Farmers

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Section S1. Experimental Site



Figure S1. Satellite image of the commercial farm.

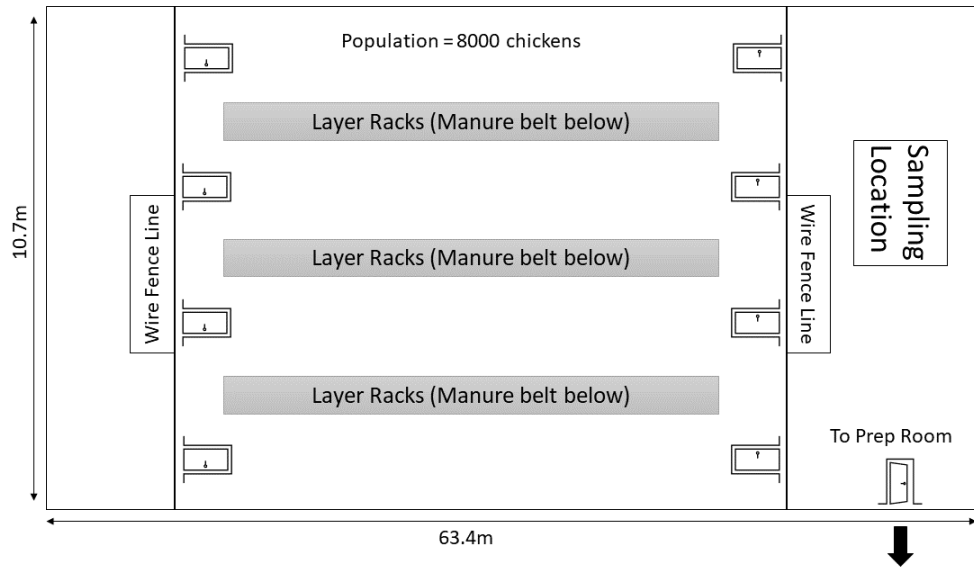


Figure S2. The sketched layout of the poultry farmhouse.



Figure S3. Picture of a litter bedding sample.

Section S2. Choice of PILS Solvent

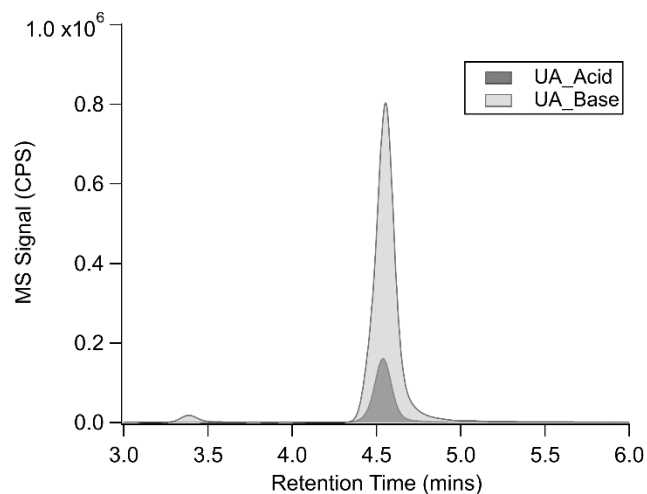


Figure S4. MS response of derivatized UA in chicken litter extracted by both acidic and basic solvents. Dark shade: acid scrubber. Light shade: basic buffer.

The goal of this experiment is to explore which solvent to use to collect particle samples. Here, we picked two portions of the litter sample for extraction. Both portions had the same mass and had similar amounts of chicken manure clusters. One extraction solvent was the acidic scrubber (0.1% formic acid), and another solvent was the basic buffer (sodium borate, pH = 9). The two extractions were performed in 100-ml beakers on an orbital shaker for one hour. An equal amount of extract is added to the derivatization matrix.

Although an internal standard was not used, the signal of UA in the basic buffer is significantly more intense than the acidic scrubber. Therefore, the basic buffer was used as the PILS solvent to collect particle samples.

Section S3. LC-MS Settings and E-AIM Parameters

S3.1 Detailed Instrumental Settings

Table S1. LC-MS instrument parameters	
Injection volume	1 μ L
Solvent A	0.1% (v/v) Formic Acid in MQ Water
Solvent B	0.1% Formic Acid in ACN
Gradient	See Table S2
Column	Luna Omega C18 column

	150 mm x 2.1 mm x 3 μ m
Acquisition Time	16 min
Scanning Mode	Positive
Spray Voltage	3.5 kV
Sheath Gas Flow Rate	40 a.u.
Aux Gas Flow Rate	8 a.u.
Sweep Gas Flow Rate	0 a.u.
Capillary Temp	275 $^{\circ}$ C
Capillary Voltage	35 V
Tube Lens	90 V

Table S2. LC gradient for TsCl derivatives			
Time /min	Flowrate μ L/min	Solvent A	Solvent B
0.00	400	80.0	20.0
2.00	400	80.0	20.0
16.00	400	1.0	99.0

S3.2 E-AIM Input Parameters

Table S3.E-AIM Model 2 Comprehensive Mode Inputs	
Temperature (K)	298.15
Relative Humidity	0.3
H ⁺ (mol/m ³)	7.74E-06
SO ₄ ²⁻ (mol/m ³)	3.20E-06
NO ₃ ⁻ (mol/m ³)	1.42E-06
NH ₄ ⁺ (MOL/m ³)	8.55E-08
NH ₃ (mol/m ³)	3.89E-04

DMA (mol/m ³)	1.35E-03
PUT (mol/m ³)	1.14E-08
CAD (mol/m ³)	1.14E-06

Section S4. PILS Multi-Instrument Intercomparison and Quality Control

In this intercomparison experiment, the aim was to compare the collection efficiency of our PILS-LCMS method for NH₃ and other ANCs with a dedicated NH₃ analyzer (Model 17i, ThermoFisher). We also discovered the effect of the PILS gas denuder on the collection of chemicals in gas and particle phases. **Table S4** summarizes the results of all experiments. The standard error of PILS (6.7%) is determined from the relative standard deviation (RSD) of the NH₄HSO₄ measurement, with the gas denuder on. This error value serves as the error bar of the chemical quantification in the main text.

Chemicals	NH ₃ Gas (ppb)		NH ₄ HSO ₄ Particles (NH ₃ equivalent, ppb)		DMA (ppb)	
	On	Off	On	Off	On	Off
PILS	Below LOD	73.0±3.7	59.6±4.2	32.5±8.3	0.55±0.29	14.91±7.43
Thermo 17i	118.1±6.2	123.6±1.4	85.8±16.5	28.1±2.3	N/A	N/A
Efficiency (PILS/17i)	Below LOD	59.1%	71.8%	115.6%	N/A	N/A

S4.1 Ammonia Gas

The PILS and the NH₃ analyzer sampled the same NH₃ source in this experiment. NH₃ was generated from the photolysis of ammonium carbonate and was diluted with zero air. We separated this experiment into two sessions: one with the PILS gas denuder attached, and another one with the denuder detached. Each session lasted 8 minutes and was equivalent to four LC-MS samples. PILS samples were transferred back to the University of Alberta for TsCl derivatization and MS analysis. We did not obtain any significant NH₃ signal when the denuder was attached, while the gas collection efficiency was 59.1% without the denuder (**Figure S5A**). Therefore, the PILS denuder can effectively remove gaseous species from the sample intake at this level of NH₃ concentration.

S4.2 Ammonium Particles

A Teflon chamber was used to hold NH_4HSO_4 particles generated from a homemade NH_3 generator. This experiment was carried out in the same manner as the gas experiment. With the intended PILS setup (with the gas denuder mounted), our measurements show that PILS has collected 71.8% of NH_4^+ .

According to the onsite scanning mobility particle sizer (SMPS), we note that some particles generated from this experiment are smaller than 30nm. Hence the PILS would have a reduced collection efficiency. **Figure S6** shows the size distribution collected by the SMPS.

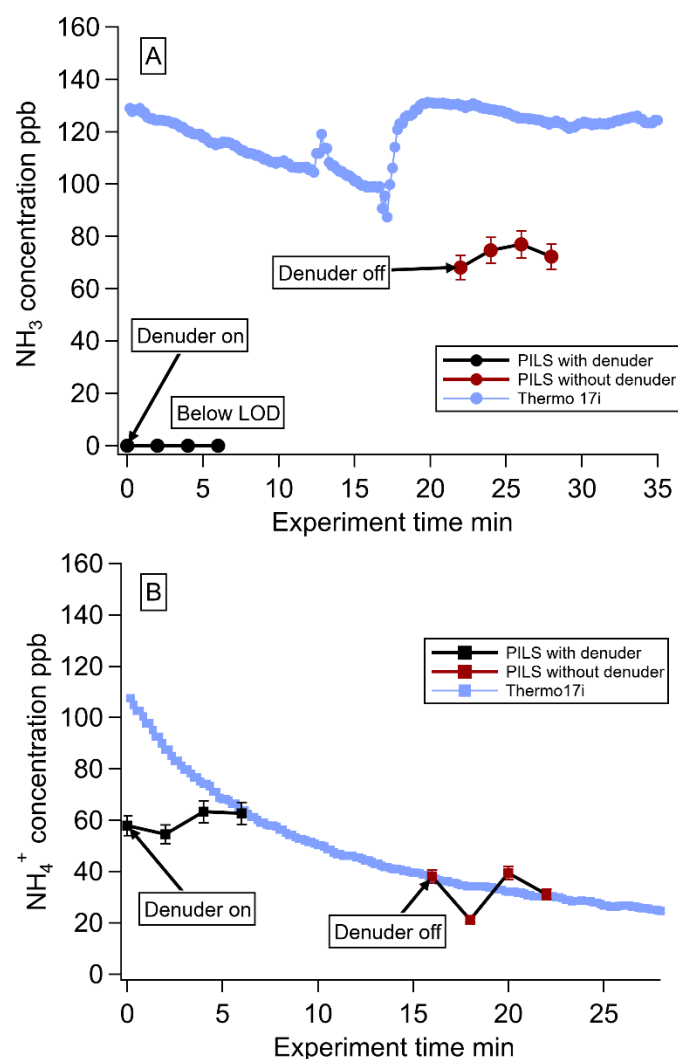


Figure S5. Time-resolved comparison between PILS and ThermoFisher 17i, A) NH_3 comparison, and B) NH_4^+ comparison

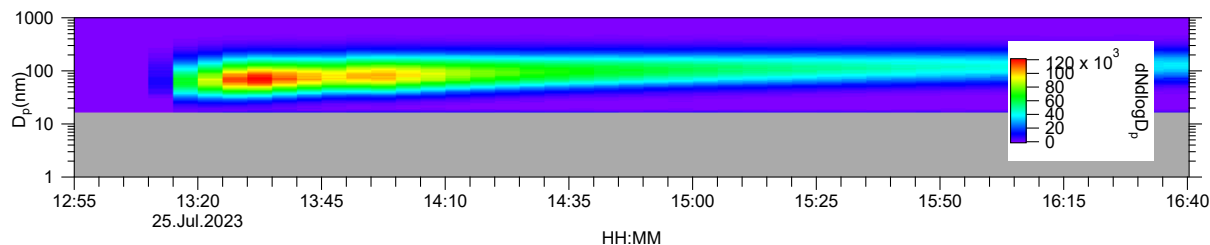


Figure S6. Particle size distribution of the entire experimental period.

S4.4 Autosampler Queue Time Corrections

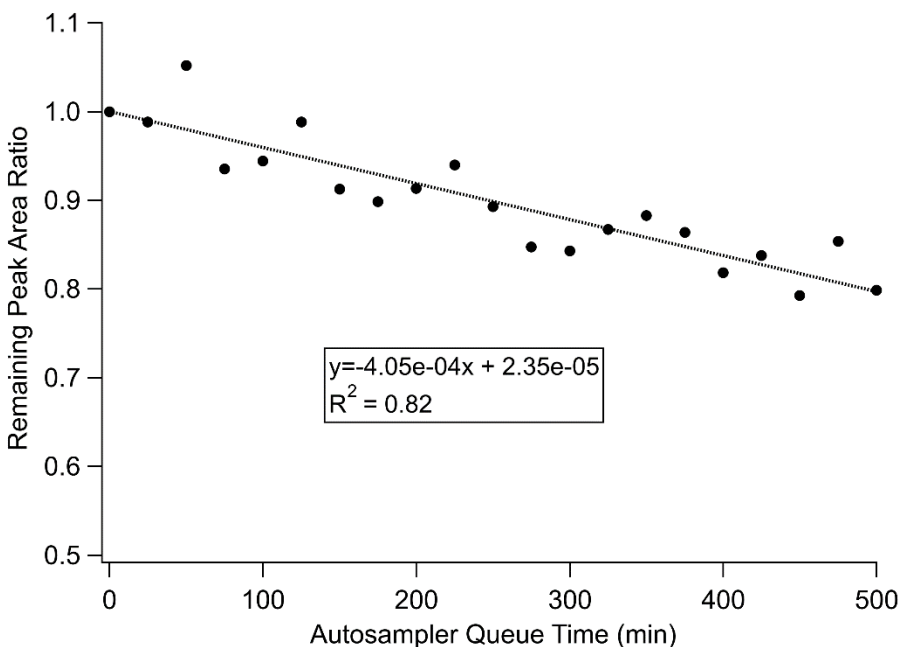


Figure S7. Repetitive measurement of a single uric acid LC-MS peak over time. The queue time is equivalent to the length of the sequence to obtain the time-resolved data.

This result shows the loss of UA peak area over time as the sample queues up on the LC autosampler. The sample used in this experiment is one of the litter extract samples, contains a high concentration of UA, and has the same matrix effect as the samples mentioned in the main text. The loss of signal is primarily due to double derivatization as we have observed a signal growth of double derivatized UA.

Section S5. Chemical Identification by HR-MS

S5.1 Derivatization by TsCl

TsCl-derivatization includes a loss of the HCl molecule. Therefore, the mass-to-charge ratio of a derived compound in ESI-positive mode can be calculated by the following equations:

$$[M + H]^+ = M_{molecule} + M_{TsCl} - M_{HCl} + 1 \quad (1)$$

$$[M + H]^+_{double-derivatized} = M_{molecule} + 2 \times M_{TsCl} - 2 \times M_{HCl} + 1 \quad (2)$$

There are also chances of double-derivatization (**equation 2**), or other adduct ions present in the ESI-positive mode, such as NH_4^+ or Na^+ . The double derivatization is kinetics-driven. Excess TsCl in the sample matrix can further react with derivatized products if there are available TsCl-active amino groups.

Figure S8 shows the high-resolution mass spectrum of selected ANCs in the sample, which also indicates the signature peak profile of sulfur-containing compounds due to the presence of ^{34}S . These peaks are also confirmed by simulated isotopic profiles with a resolution of 100,000 MS in Thermo FreeStyle™.

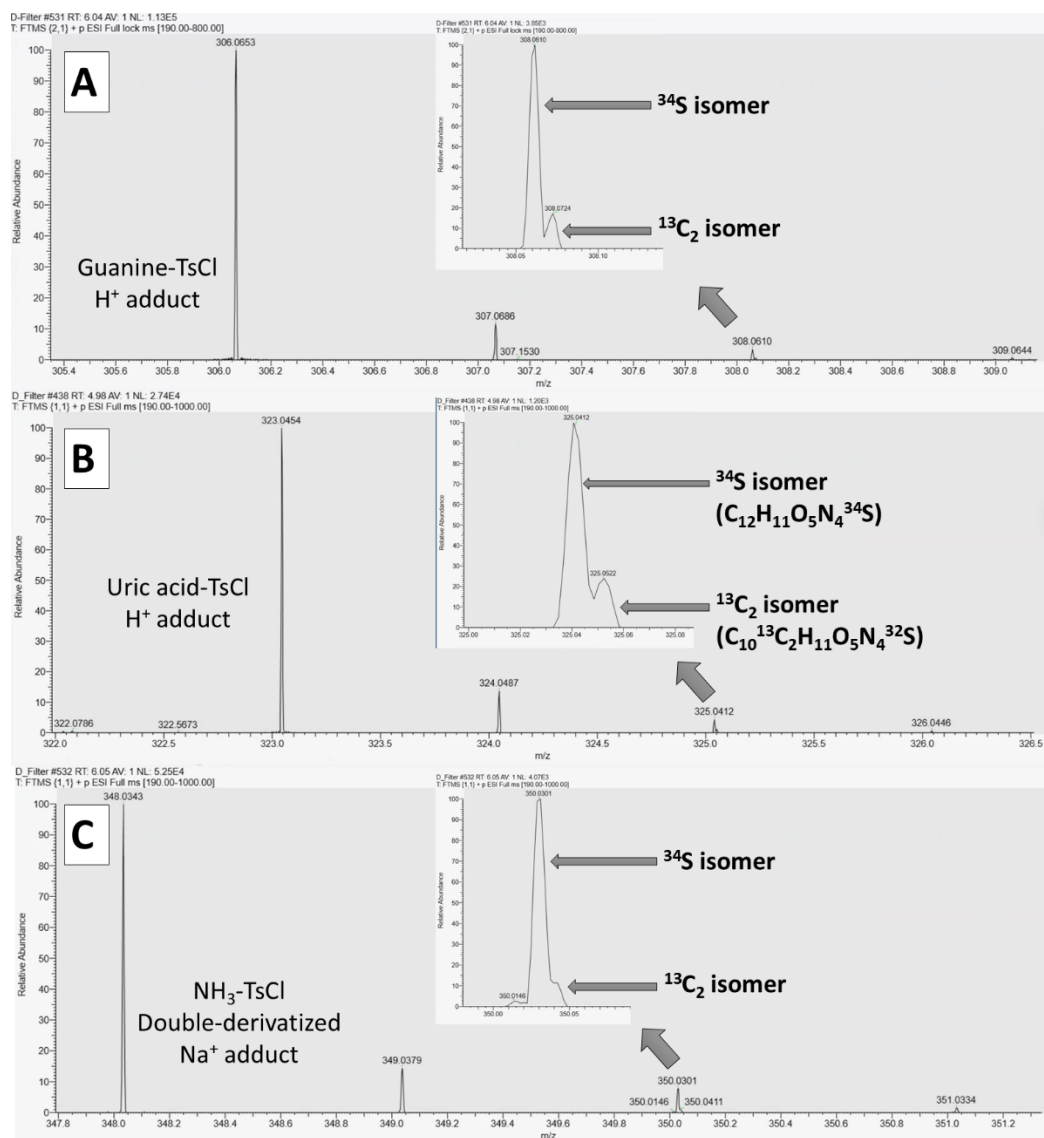


Figure S8. Mass spectrum of selected ANCs, A) guanine, B) uric acid, and C) ammonia/ammonium.

S5.2 Proposed Identity of ANCs

m/z (TsCl-derived)	Molecular Formula (Without TsCl)	Proposed Identity	Confirmation with Standard
200.0739	C ₂ H ₇ N	Dimethylamine	√
258.1155	C ₅ H ₁₃ NO	3-ethoxypropylamine	
306.0653	C ₅ H ₅ N ₅ O	Guanine	√
323.0441	C ₅ H ₄ N ₄ O ₃	Uric Acid	√
325.212	C ₇ H ₂₆ O ₂ N ₂	Unknown	
341.1349	C ₉ H ₁₈ N ₂ S	Cyclohexylethylthioure a	
343.0778	NH ₄	*Ammonium	√
344.0196	C ₇ H ₃ O ₄ N	Unknown	
397.12503	C ₄ H ₁₂ N ₂	Putrescine	√
411.1402	C ₅ H ₁₄ N ₂	Cadaverine	√
477.0547	C ₁₂ H ₁₀ O ₅ N ₄ S	Unknown	
499.0367	C ₁₀ H ₄ O ₃ N ₁₀ S	Unknown	
631.0639	C ₁₁ H ₁₂ O ₁₀ N ₁₀ S	Unknown	
313.30	C ₄ H ₆ N ₄ O ₃ **	Allantoin	√
316.14	CH ₄ N ₂ O**	Urea (unknown cluster)	√

* Double derivatization, with NH₄⁺ adduct

** Confirmed by standard resolution MS

Section S6. List of Acronyms

AAC: Airborne amino chemicals

ALA: Allantoin

CAD: Cadaverine

CCAC: Canadian Council on Animal Care

DMA: Dimethylamine

E-AIM: Extended Aerosol Inorganic Model

ESI: Electrospray ionization

GUA: Guanine

IAQ: Indoor air quality

LC-MS: Liquid chromatography mass spectrometry

LOD: Limit of detection / detection limit

NRSL: Natural Resource Analytical Laboratory at the University of Alberta

OPC: Optical particle counter

PILS: Particle-into-liquid sampler

PM: Particulate matter

PRC: Poultry Research Center at the University of Alberta

PUT: Putrescine

SMPS: Scanning mobility particle sizer

TPM: Total particle mass

TsCl: p-toluenesulfonyl chloride

UA: Uric acid

VOC: Volatile organic compounds