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Profiling Volatile Emissions from Sewage Sludge Land-Applied Across Washington State (USA) Using Headspace Sampling with Gas Chromatography-Mass Spectrometry (GC-MS) Determination

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Background

Some eight million tons of sewage sludge is generated in the U.S. annually, with more than half of that applied to forest and agricultural lands as the primary method of disposal.[1] Noxious emissions from these wastes provoke public concerns for the safety of this disposal method, yet little is known about the volatile constituents of sludge once land-applied. To address this, we collected sludge disposed in forest and farm lands across Washington State (USA) and profiled their volatile emissions over seasonal and daily temperature regimes of the region. We also profiled volatile emissions at the more extreme 100°C with the aim of defining the total volatile potential of these wastewater residues.

Methods

- Land-applied sewage sludge samples (N=18) and a non-sludged soil were collected from forest and farm lands across Washington State (Figure 1).
- Samples used to develop the method ("method samples") were incubated over a range of temperatures (0-100ºC) and times (15-120 min) to assess volatile evolution and determine optimum incubation times.
- All samples were then incubated in triplicate for 60 min at 25ºC & 100ºC.
- Volatile compounds were measured via headspace sampling with gastight syringe followed by GC-MS analysis.
- Compounds were identified by comparison of measured mass spectra to reference spectra in the NIST Mass Spectral Library.
- Only compounds with > 80% spectral match were considered.
- Compounds were sorted into functional classes as follows: acids (ACID), alcohols (ALC), aldehydes (ALD), aliphatics (ALH), aromatics (ARH), esters (EST), ethers (ETH), halogen-containing (HAL), ketones (KET), nitrogen-containing (NIT), sulfur-containing (SUL), terpenoids (TER).
- As an initial assessment of potential risks, detected compounds were cross-referenced with the United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS) database.

Findings

- Volatile profiles generally increased in complexity and intensity with temperature (Figures 2 & 3).
- Volatile profiles varied with sludge source and application site but were predominated by aliphatic hydrocarbons (Figures 2 & 3).
- Unique compounds detected, and those with GHS codes, increased with temperature in method samples 1 & 2 (Figure 2).

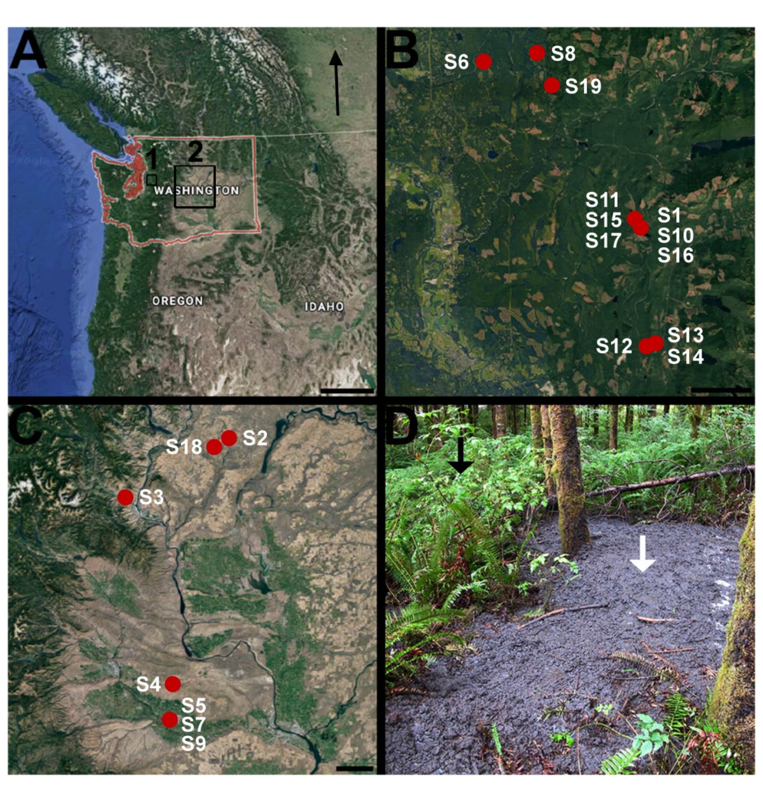

Figure 1. Sampling sites (panel A). Insets 1 & 2 are blown up in panels B & C, respectively. A representative site where sludge (white arrow) has been applied to forested land (black arrow) is shown in panel D.

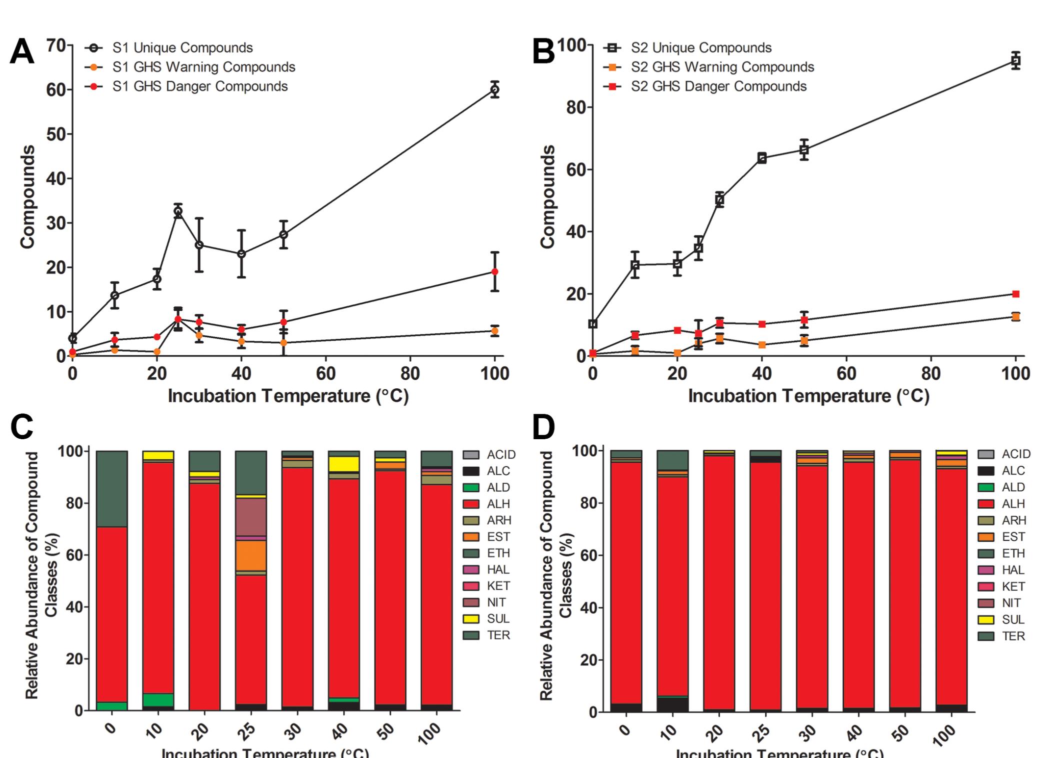

Figure 2. Unique volatile compounds, as well as those with GHS codes, evolved from method samples 1 (panel A) and 2 (panel B) with temperature. Compound class evolution for samples 1 (panel C) and 2 (panel D) are presented as average total chromatographic area (N=3).

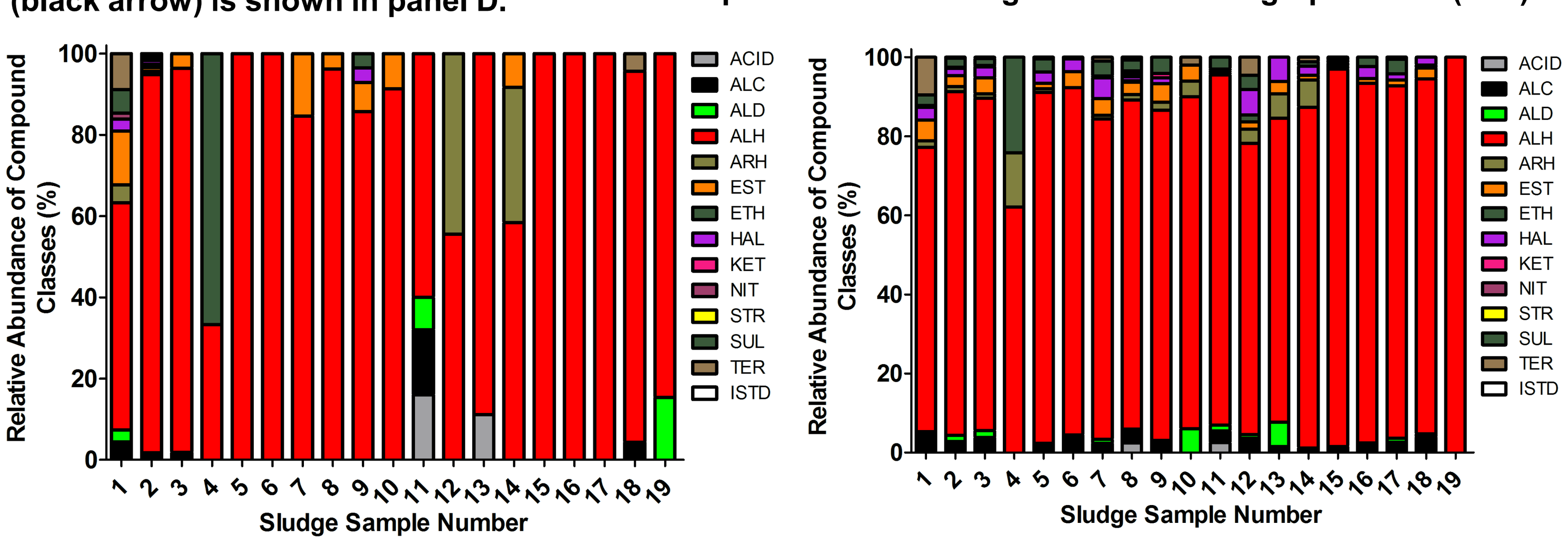

Figure 3. Distribution of compound classes detected in all sludge samples incubated at 25 °C (left panel) and 100°C (right panel). Sample 19 is a control soil collected from a forest site receiving no sludge application.

Findings Continued

- Total number and concentration of volatile compounds in "method" samples 1 & 2 generally increased with temperature (Figures 2, 4, & 5).
- Total number of GHS codes associated with detected compounds varied over the sample set but generally increased with temperature (Figure 6).
- 568 unique volatile compounds were identified over the sample set, with 26% of those classified as hazards in the GHS database.
- Total number of volatile compounds detected varied over the sample set but generally increased with temperature (Figure 7).
- Concentration of volatile compounds detected increased with temperature, with samples 1, 2, & 3 evolving the largest concentrations (Figure 8).
- 40% of detected compounds did not meet ID criteria and were excluded.

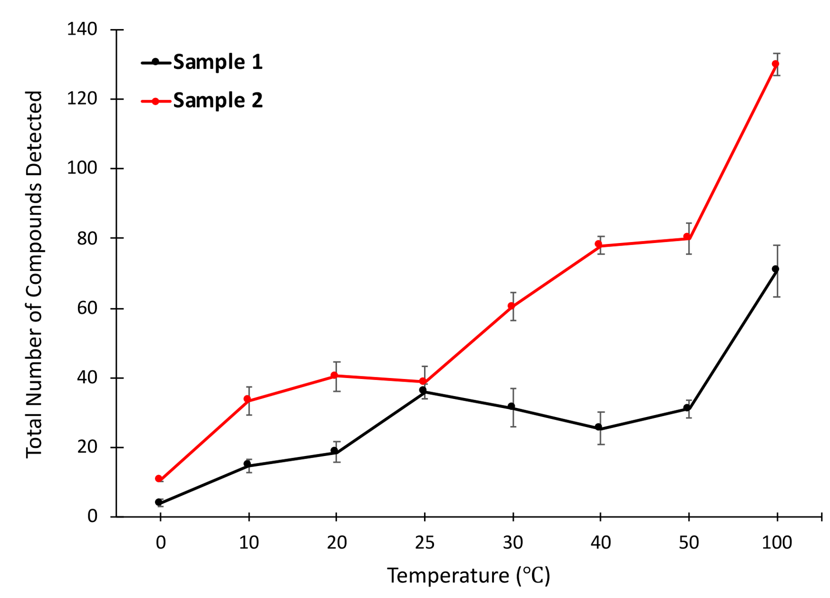

Figure 4. Total number of volatile compounds detected with temperature for "method" samples 1 and 2.

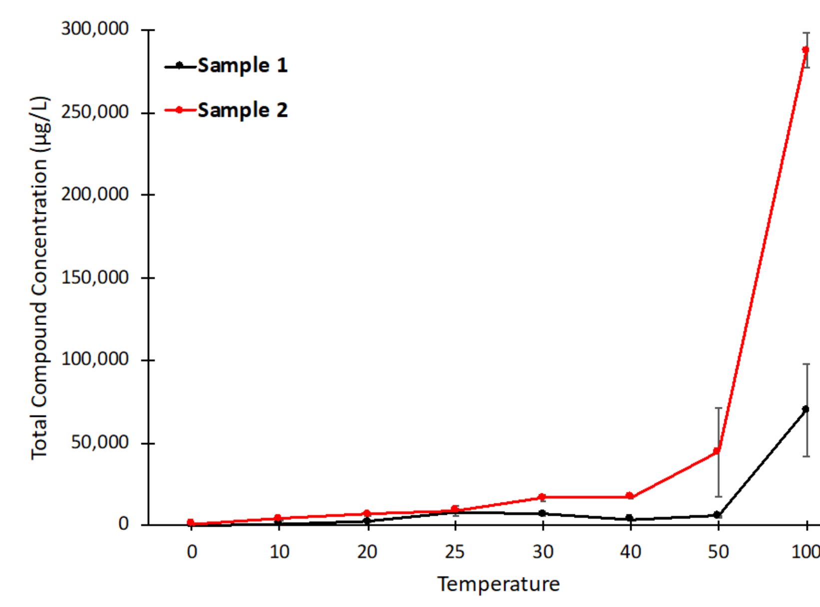

Figure 5. Total concentration of volatile compounds detected with temperature for "method" samples 1 and 2.

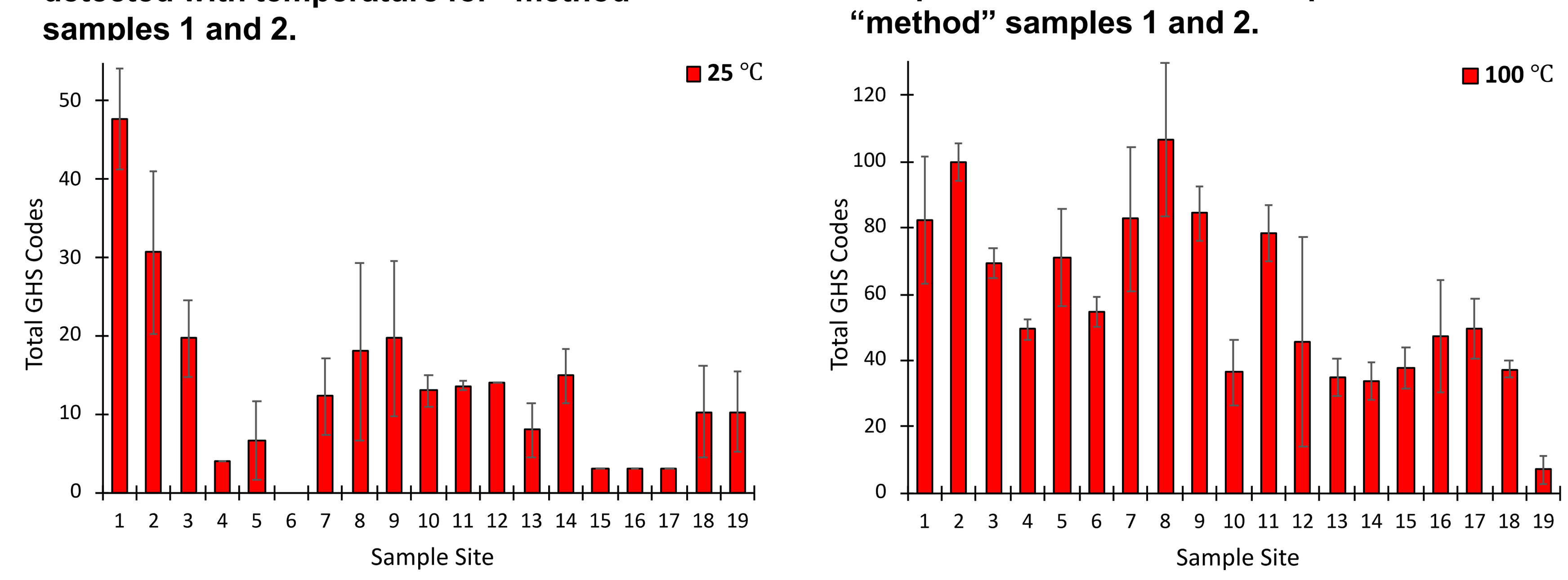

Figure 6. Total number of GHS codes for volatile compounds detected in all samples at 25 ℃ (left panel) and 100 ℃ (right panel). Sample 19 is a control soil collected from a non-sludged site.

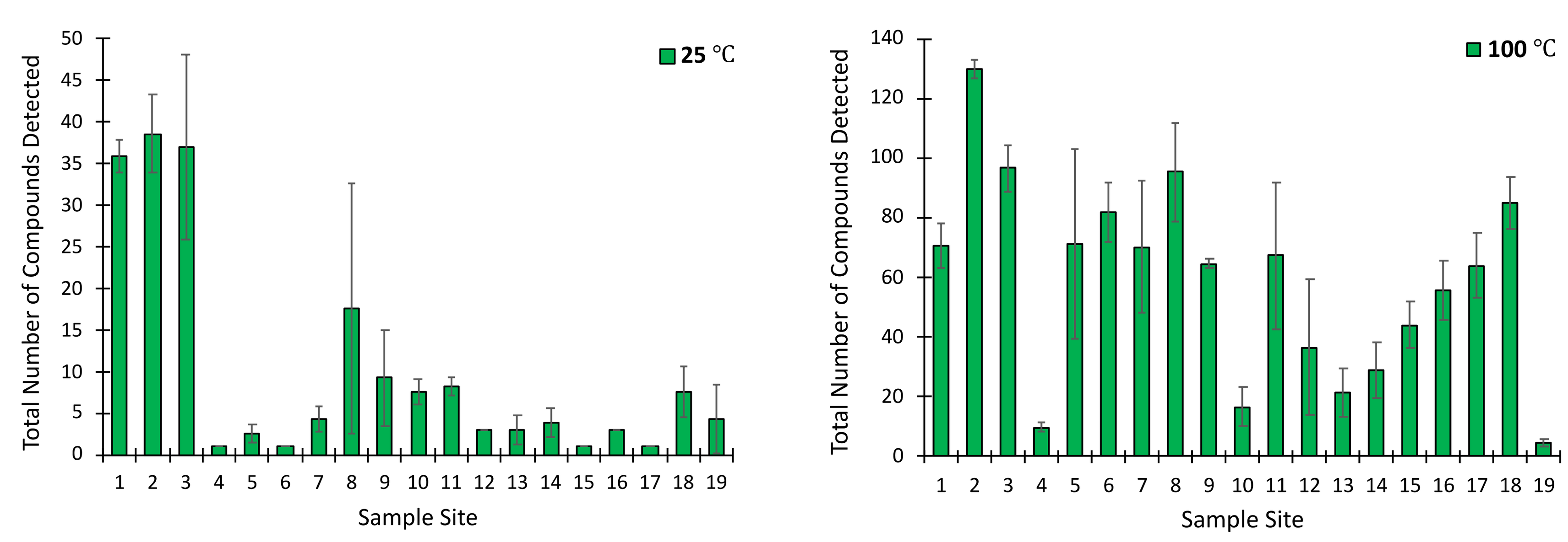

Figure 7. Total number of volatile compounds detected in all samples at 25 ℃ (left panel) and 100 ℃ (right panel).

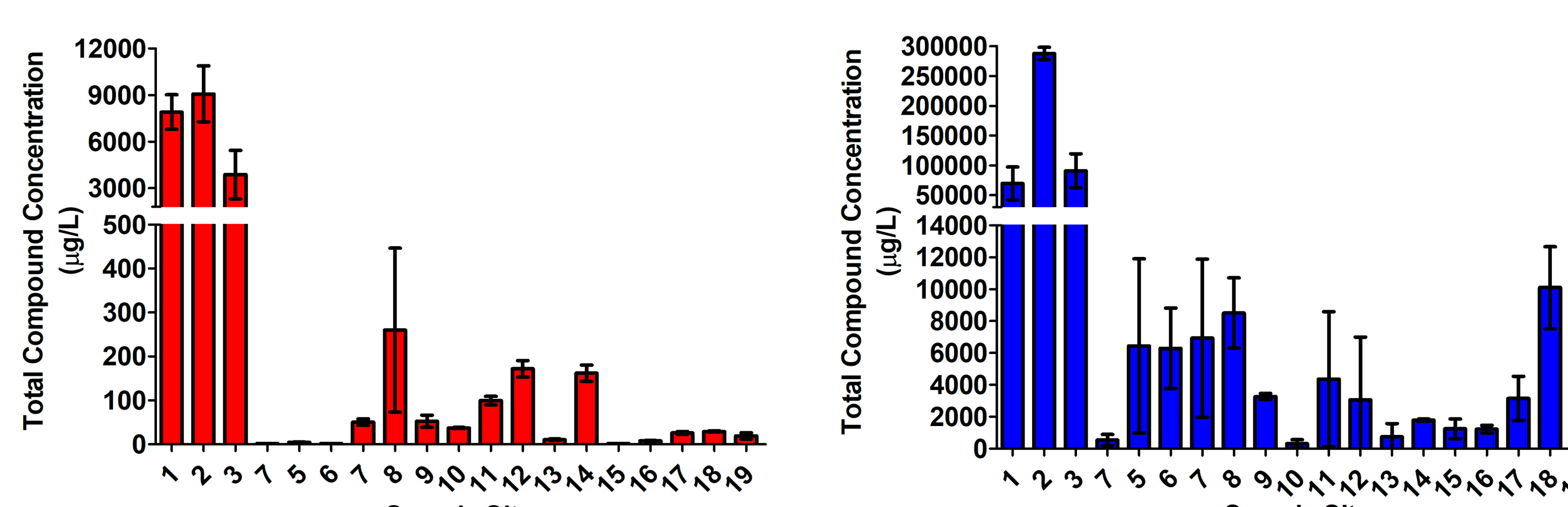

Figure 8. Total concentration of volatile compounds detected for all samples at 25 ℃ (left panel) and 100 ℃ (right panel).

Conclusions & Future Work

- Results demonstrate the complexity and variability of volatile compound emissions from land-applied sewage sludges over relevant daily and seasonal temperature regimes, and at the more extreme 100 ℃.
- Volatile concentrations, combined with the number of volatile compounds detected with GHS hazard codes, suggest that this sludge disposal method may pose some risks to environmental and human health.
- This is the first effort to assess volatile profiles of sludge once land-applied.
- Work is ongoing to profile sludge from these same sites several years after application to assess changes in volatile emissions with time.

References

Gaylor, MO; Mears, GL; Harvey, E; La Guardia, MJ; Hale, RC. Polybrominated Diphenyl Ether Accumulation in an Agricultural Soil Ecosystem Receiving Wastewater Sludge Amendments. *Environ. Sci. Technol.* 2014, 48, 7034-7043.