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Solid Phase Extraction of Herbicides from Groundwater and Soils

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Introduction

The purpose for this experiment was to compare relative concentrations of the herbicide atrazine in soil and ground water samples. Atrazine is commonly found in groundwater and is known to be toxic to aquatic life with long lasting effects. This experiment aims to identify whether or not atrazine is present in the groundwater as well as to examine how long atrazine can persist in soil. Previous studies have shown atrazine and other related herbicides persisting with little to no degradation for up to 16 weeks. Soil and groundwater samples were obtained from a farm where atrazine is used seasonally to treat a field before and after corn has been planted. Weekly groundwater samples were taken and representative samples were taken from his field. To analyze water samples, solid phase extraction and gas chromatography-mass spectrometry (GC-MS) were used. Soil extracts were first filtered and then analyzed with GC-MS

Experimental

- Overall Solid Phase Extraction (SPE) procedure:
  - Begins with the cleaning and rinsing the SPE column
    - 3:1 Hexanes:Isopropanol (3 mL)
  - Condition the column
    - Methanol (3mL) followed by water (3 mL)
  - Add sample
    - Contains the analyte and sample matrix
  - Wash column with DI water to further remove unwanted compounds
  - Use 3:1 hexanes:isoproponal (1.8 mL) to elute the analyte from the column, which pre-concentrates the solution
- Analysis
  - Began by locating the internal standard, acenaphthene d-10, on a chromatogram produced by GC-MS
  - Obtained atrazine solution from local store and identified its retention time and fragmentation pattern
  - Sampled farm, which uses atrazine mixture as herbicide
    - Obtained stream and groundwater samples
  - Water samples extracted with SPE
  - Soil samples were agitated by sonication or vigorous stirring in solvent, filtered, and diluted via evaporation
    - Solvents consisted of acetone and 2:1 acetone:hexanes

Results and Discussion

Solid phase extraction was completed and successful when extracting acenaphthene d-10 (**Figure 2**) and atrazine (**Figure 3**) from samples with known matrices and analyte concentrations. This was important for confirming the adequacy of the method being performed. When using SPE on liquid samples, there were some complications with eluting the analyte. Elution by gravity should occur, however, the nonpolar qualities of the packing in the column would in some cases not allow the small remaining quantities of sample (usually water) to fully pass through the column. So when the nonpolar solvent (3:1 hexanes:isopropanol) was put on the column to elute the analyte, there was no movement through the column due to the lack of interaction between hexanes and water.

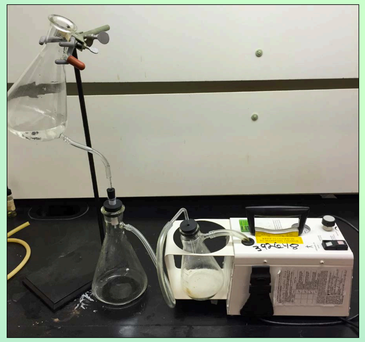

Figure 1. Apparatus used for solid phase extraction

It was observed that “flushing” the SPE column with nitrogen gas allowed for the elution solvent to drain by gravity.

Solid phase extraction was not used for soil samples. The solvent being used would have prevented the nonpolar interactions of the analyte and packing phase resulting in no retention of the herbicide. Atrazine was extracted successfully from pre-treated soils, which validated the extraction method. When performing extractions on environmental samples, no atrazine was found however, an unexpected compound was located and identified as S-[(2E)-1,3-Diphenyl-2-butenyl] dimethylthiocarbamate (**Figure 4**). Thiocarbamates are commonly used in agriculture as insecticides, herbicides, and fungicides.

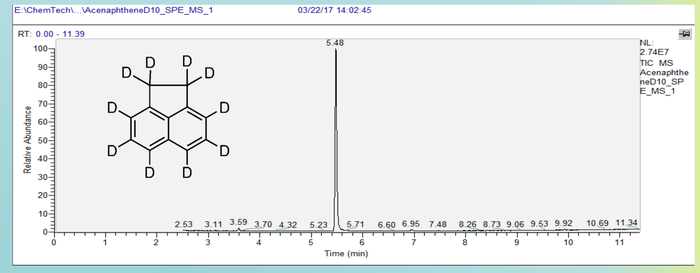

Figure 2. GC-MS chromatogram showing acenaphthene d-10 (5.48 min), identified with the NIST MS library.

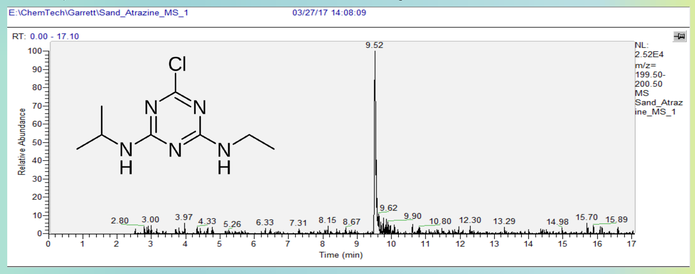

Figure 3. GC-MS chromatogram showing the retention time (9.52 min) of atrazine, identified with the NIST MS library

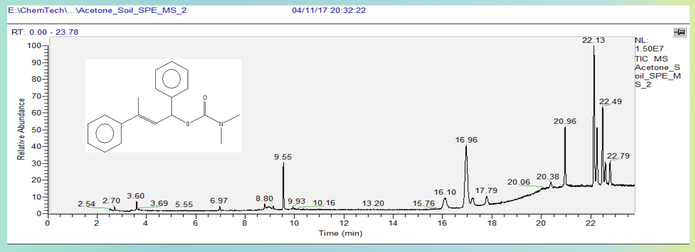

Figure 4. GC-MS chromatogram showing the results from soil agitation with 2:1 acetone:hexanes. The thiocarbamate compound shown was found at 22.49 min.

Acknowledgements & References

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