Literature Assignment

Şimşek Uygun, B.; Albek, E. A. Seasonal Monitoring of Organochlorine Pesticides in Water, Soil, and Sediment in a Small Pond and Determining Ecotoxicological Risk Assessment, Environmental Quality Management 2022, 32 (2), 295–307.

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Research Purpose:

The goal of this research was to determine the concentration of organochlorine pesticides in surface water, soil, and sediment.

What is the concentration of organochlorine pesticides in the surface water, soil, and sediment of the Borabey pond and nearby watershed?

Analyte Properties:

Organochlorine pesticides (OCPs) are a subsection of a larger identity called persistent organic pollutants (POPs). These OCPs are hydrophobic, which leads to their higher abundance in soils samples compared to water samples. This also leads to the half-life of OCPs to be much longer in soils compared to water, which implies that uncontained OCPs can directly impact plants outside of their intended range, even in a drought. The OCPs enter the environment after being administered to nearby farmland via diffusion into soil, air, and water. While the original purpose of the OCPs is to eliminate insects and specific plants from interfering with crops, when they leech into natural landscapes, they have negative effects on the local flora and fauna. As pesticides, OCPs are toxic to native plants as well, which could drastically impact the survival of infected local flora. The OCPs analyzed in this method includes α - β hexachlorocyclohexane (HCH), heptachlor epoxide, aldrin, dieldrin, dichlorodiphenyltrichloroethane (DDT) and metabolites pp-dichlorodiphenyldichloroethane (DDD), op-DDD and pp-DDT.

Sampling Plan:

The sampling strategy was judgemental as the researchers deemed the pond to be sufficiently mixed for only a few locations to represent the pond. Replicate grab samples were obtained for each matrix.

Sampling:

- Using a pre-cleaned glass bottle with a Teflon-coated spoon, 8 total water samples were collected from 0.3m below the water's surface. In two locations, four repeat samples per location
 - A pre-cleaned glass bottle and Teflon-coated spoon help prevent any additional interferences.
 - By going just below the surface, this reduces large debris collection.
 - Repeat samples can be used to analyze precision.
- The top 10 cm of bed sediment was collected using a Teflon-coated, aluminum foil-wrapped spoon. In two locations, four repeat samples per location
 - The top layers of sediment would have the greatest concentration from leeching from the water.
 - The extra wrapped spoon allows for an extra layer of protection between samples as the aluminum can be replaced and the spoon underneath also rinsed.
- Soil samples were collected from three locations within the watershed, four repeat samples per location.
 - Repeat samples can be used to analyze precision.
 - This allows the researchers to compare the area around the pond to the pond itself.
- Each sample was packed with ice cassettes and shipped to the research center.
 - This slows any degradation of the analytes during transport.
- Water samples were filtered through a hexane-filtered paper.
 - Removes debris from samples.
- Soil and Sediment (separate): 10 g taken from each sample.
 - Sets a similar starting mass between solid samples before drying and homogenizing.
- Soil and Sediment (separate): Dried with a milling dryer.
 - Removes excess water while also homogenizing.

Instrumental Technique:

The instruments used were the Thermo TSQ 8000 Gas Chromatographer-Mass Spectrometer/Mass Spectrometer (GC-MS/MS) and Agilent 6460 Liquid Chromatographer-Mass Spectrometer/Mass Spectrometer (LC-MS/MS).

By using MS, they could identify the compounds based on any expected fragmentations along with the molecular mass.

To prepare the samples for these instruments, each type of matrix had different steps involved.

Analysis Preparation:

Water:

- NaCl was added to 1L of sample. Transferred to separatory funnel.
 - The NaCl addition is to help extract a separate analyte they were analyzing.
- 50mL of hexane was added and shaken for 20 minutes then allowed to stand for 5 minutes.
 - A large initial dose of organic solvent to begin the extraction of the analyte.
- Organic phase was drained into an Erlenmeyer flask.
 - Removes the extracted analyte to be processed later.
- 30mL of hexane was added to the funnel and shaken for 5 minutes.
 - Removes analyte from the aqueous layer and into the organic layer.
- Organic phase was drained into the Erlenmeyer flask.
 - Removes the extracted analyte to be processed later.
- The last two steps were repeated three times.
 - Increases extraction efficiency.
- The sample was passed through a filter paper with Na₂SO₄.
 - Removing any excess water remaining.

- Vacuum evaporated at 45°C until extract completely evaporated.
 - Evaporates the hexane liquid and concentrates the analyte.
- Samples were removed with nitrogen gas purging until 2 mL sample remained.
 - Removes impurities and other gases from the atmosphere.
- Sample transferred to GC instrument.

Soil and Sediment:

- Extracted via Soxhlet extraction.
 - Transfers analyte from the solid matrix and into a heated solvent.
- Cleaned with a silica column.
 - Removes interferences.
- Extract was reduced to 1 mL.
 - Increases concentration to increase chance of detection.
- Sample transferred to GC and LC instruments.

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Discussion:

The first point to critique is the complete lack of quality control measures listed. No blanks, certified reference materials, LOD, or LOQ were mentioned throughout the paper. I would have suggested several steps that fall under that category. Some of the simplest ones would include transport blanks, field blanks, and equipment blanks, especially when considering the variety of matrices involved in sampling. Due to the liquid and solid samples being treated differently, there is also a need for method blanks as there are two separate methods being used. Without the quality control steps, there is no guarantee that the samples were not contaminated at any point in the method, from sampling to analysis.

As for the analytical question, what is the concentration of organochlorine pesticides in the surface water, soil, and sediment of the Borabey pond and nearby watershed? There were seven OCPs that were analyzed in the water, soil, and sediment in and around the pond, which were detailed in the analyte properties. Of the seven, α -HCH was the highest concentration of OCPs in Borabey pond at a concentration of 13.8 ppt in water and 1.08 µg/kg in the sediment. Within the watershed soil, α -HCH still held the highest concentration of the POCs at 51.93 µg/kg. While they were able to answer the analytical question, there is no confirmation that the samples were not contaminated at any point due to a lack of blanks.

The samples were appropriate for the analytical question as they represented the pond in several different manners. By using a judgemental sampling plan, they limited the locations of sampling within the pond and nearby watershed to only seven locations for three matrices.

In the area of greenness, there were many steps done well and some steps that could be improved. The most noticeable step I would change is the replicate grab samples. At the end of the analysis, they averaged the results per matrix type as they concluded that the results were very similar. This could be made greener by instead taking composite samples which would reduce the number of samples that need to be analyzed from 50 to 3. An example of a green step that they included was using the Soxhlet extraction technique. This is greener in energy when compared to the intense heat required for other solid extraction methods such as digestion, which they may have considered due to the second group of analytes they were researching being heavy metals.