Estimating the Mass of Pharmaceuticals Harbored in Municipal Solid Waste Landfills by Analyzing Refuse Samples at Various Ages and Depths

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Analytical Question and Goals

- This paper looks to determine the presence of 55 different pharmaceuticals (antibiotics and non-antibiotics) harbored in the largest landfill in Shanghai by analyzing refuse excavated at different depths.

Three main goals were further identified

a) Report the occurrence of pharmaceuticals in landfill refuse
b) Reveal age- and depth-related variations in pharmaceutical concentrations
c) Estimate the mass of pharmaceuticals based on their concentrations in different samples

How Many Pharmaceuticals are Harbored in MSW Landfills?
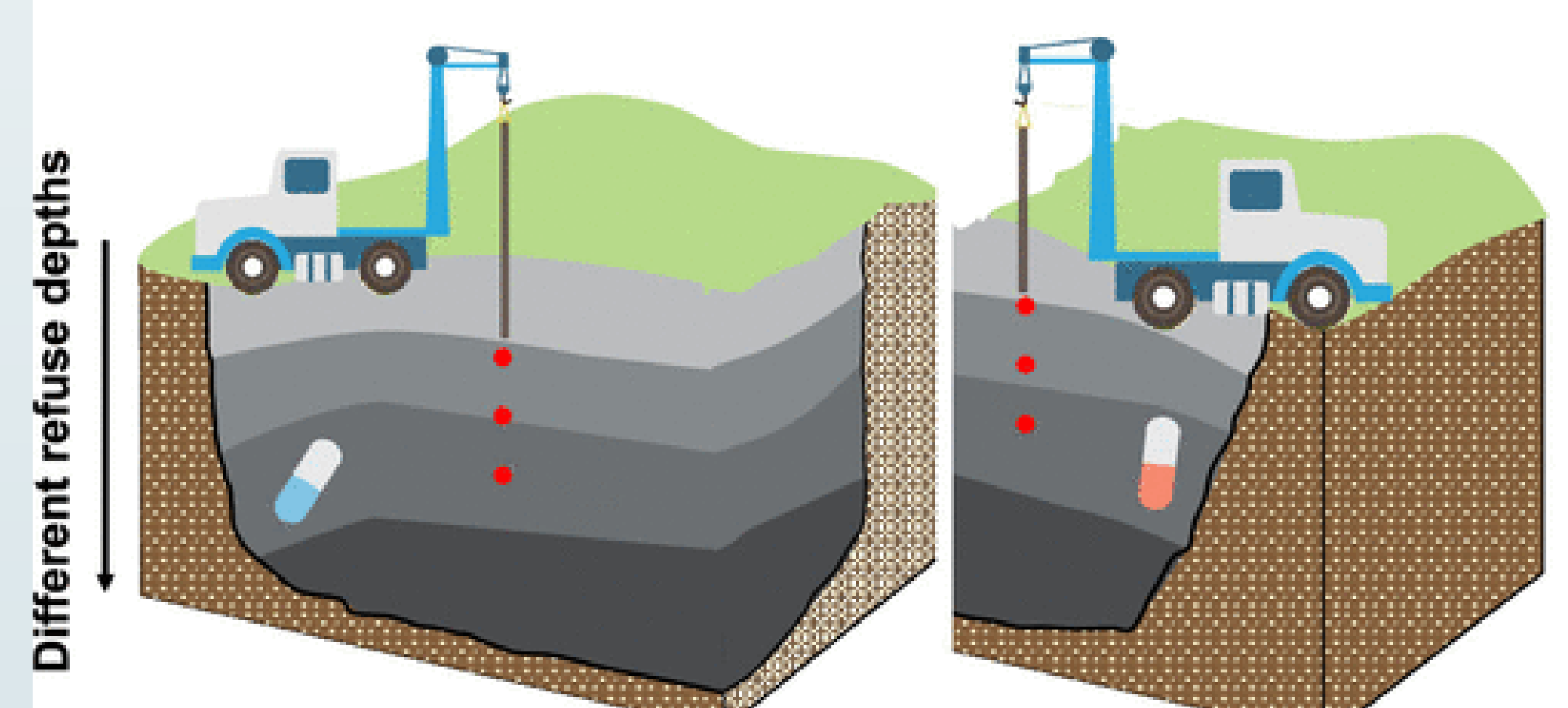
Cell #2 (landfill age: ~13 year)   Cell #5 (landfill age: ~25 year)
Six landfill cells with different ages (• sampling sites)

Figure 1. Diagram of landfill cells indicating different depths[1]

Sample Matrix and Analytes

Two sample matrices were identified which included :

1. Solid Refuse Samples
   Soil like properties retrieved from the landfill which contain pharmaceuticals
2. Aqueous Leachate samples
   Water leachate samples collected from the leachate of the refuse samples in liquid form which contain pharmaceuticals

The analytes of interest are a group of 55 pharmaceuticals which are or have been commonly prescribed. These include antibiotics (Quinolone, Tetracycline, Sulfonamides, and more) and non-antibiotics (Antidepressants, Painkillers, Stimulants, and more)

Sampling Plan

Considering the high heterogeneity of a landfill, it is very important to collect refuse samples which can represent the entire lot. The landfill is divided into separate cells, six of these cells were selected for sampling with landfill ages of 7-27 years.

Sample Type: Composite Sampling

Refuse samples collected from different boreholes at the same depth were mixed manually to reduce heterogeneity.

Sampling Strategy: Random Sampling

To ensure the sample was representative of landfill refuse, two or three random boreholes in each cell.

Sampling Strategy: Stratified + Judgmental Sampling

Sampling was conducted at different depths in each borehole. Data was available on the age- and depth-relationship from the landfill which is how the depths at which to sample were chosen. The boreholes were drilled using a bucket auger rig. Once the auger rig reached the desired depth (2, 5, and 8 m), refuse samples were collected. Leachate samples were also collected when available during drilling.

Storage, Transport and Preservation

The collected refuse samples were placed in fresh polyethylene bags, while the leachate samples were placed in fresh polyethylene bottles. The samples were transported to the lab in iceboxes.

Figure 2. Landfill refuse samples in polyethylene bags (left), drilling rig used to sample (right)[1]

Further Sampling Steps

- Lyophilization
  - Used to dry the refuse samples before further treatment
- Sieving
  - Refuse samples sieved through a 60-mesh (0.25mm) then 100-mesh (0.15mm) screen to obtain fine particles and mix uniformly

Is the Current Sampling plan Appropriate?

The current sampling plan is adequate as this is to their knowledge the first study that estimated the pharmaceutical mass in municipal solid waste (MSW) landfills. The plan addressed how heterogenous the landfill was by selecting a random sampling strategy coupled with composite sampling type. In future work more boreholes should be drilled in each cell to ensure a more representative sample. The plan also addressed the stratified aspect of the landfill by sampling at different depths at which the age of the refuse was known. This was also to ensure homogeneity of the sample and collect data with respect to goal b).

Analytical Techniques after sampling

Techniques for Refuse samples

- Spiking
  - Triplicate pretreated refuse samples (0.5 g) were placed in a 50 mL centrifuge tube and spiked with 100 uL internal standard mixture and stored at 4°C for 8 h.
- Extraction and pH adjustment
  - Samples treated with 2 mL of 0.1M Na_2EDTA-McIlvaine buffer (pH 4.0)
  - Vortexed for 5 min, mixed with 5 mL acetonitrile-methanol solution, vortexed for 5 min, centrifuged for 10 min, then supernatants collected
  - The extraction was repeated twice
- Dilution, filtration and further pH adjustment
  - Supernatants diluted in 200 mL of Milli-Q water
  - Filtered through glass fiber filters
  - Adjusted to pH 2.5-3.0 using 0.1M H_2SO_4
- Solid–phase extraction
- UPLC-ESI-MS/MS used to quantify pharmaceuticals

Techniques for Leachate Samples

- Filtering
  - Leachate samples were filtered through glass fiber filters
- Dilution
  - The sample (10 mL) was diluted with Milli-Q water to 100 mL and 0.1 g of Na_2EDTA added
- pH adjustment
  - Samples adjusted to pH 2.5-3.0 with 0.1 M H_2SO_4
- Spiking
  - Sample spiked with 100 uL of internal standard mixture
- Solid–phase extraction
- UPLC-ESI-MS/MS used to quantify pharmaceuticals

Conclusions

- The results revealed the presence of 42 pharmaceuticals in the landfill refuse with median concentrations ranging from 0.30-116 ug/kg.

- Different pharmaceuticals exhibited diverse concentration trends with age
  - Which relates to changes in policy and consumption over time

- The estimated mass of pharmaceuticals estimated from the concentrations was determined to be 80-220 tons with 95% probability.
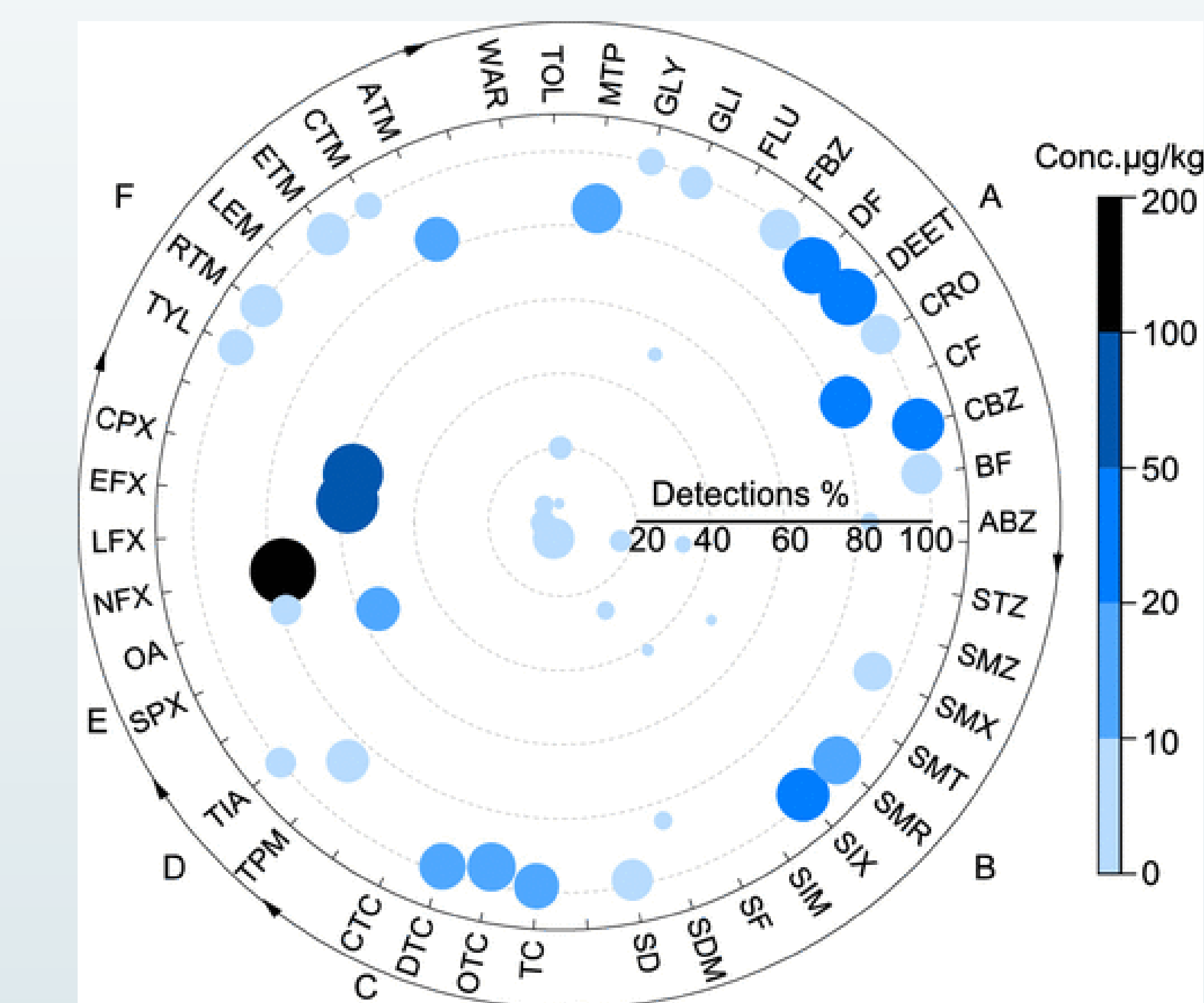

Figure 3. Detection frequency and median concentrations of investigated pharmaceuticals in landfill refuse samples. (A: non-antibiotics, B-F: different families of antibiotics. [1]

- I chose this article because the research of pharmaceuticals contaminants in the environment is a very recent concern and a topic which is very interesting
  - I wanted to further my knowledge on the research of detecting pharmaceuticals in soil like samples
- The chemical analysis was interesting because it seemed to be very simple and well outlined
  - There were no unnecessary steps identified and all the analytical techniques could be performed by CHEM 3140 students

References

[1]Yu, X.; Zhao, W.; Lyu, S.; Cai, Z.; Yu, G.; Wang, H.; Barcelo, D.; Sui, Q.. Estimating the Mass of Pharmaceuticals Harbored in Municipal Solid Waste Landfills by Analyzing Refuse Samples at Various Ages and Depths. *Environ. Sci. Technol.* **2023**, *57, 15*, 6063-6071.
https://doi.org/10.1021/acs.est.2c09455