Analysis of Pharmaceuticals in Food Crops Grown in Urine- and Struvite-Fertilized Soil by Liquid Chromatography-Tandem Mass Spectrometry

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Introduction

There is interest in the agricultural field to recover and reuse nutrients in an energy efficient manner. Urine is a cost effective, renewable resource that can be used as a valuable source of fertilizer because it is rich in nitrogen, phosphorus and potassium. However, urine may also contain high levels of pharmaceuticals, [1] which may be of concern due to the potential to introduce pharmaceuticals into the environment if urine is to be land-applied to fertilize agricultural soil.[2] Previous research has focused on pharmaceutical uptake in wastewater treated crops.[3] As fertilizers derived from urine become more widely used, it is important to understand the fate of the pharmaceuticals in the environment. The goal of this study is to utilize developed analytical methods to measure the levels of pharmaceuticals in urine, struvite, lysimeter water, and food crops.

Figure 1. Urine collection, storage and application

Fertilization with urine may be cause for concern. It may lead to further release of pharmaceuticals into the environment; thus, pharmaceutical levels needs to be determined in urine and related matrices, as shown in Figure 2.

Figure 2. Matrices analyzed in project

LC-MS/MS

All spectra was acquired using a Agilent 6410 triple quad mass spectrometer equipped with an 1100 HPLC system. Separation is achieved using a beta basic column and ionization is achieved in positive mode using electrospray ionization. A representive separation of the pharmaceuticals in this study can be seen in Figure 3 below.

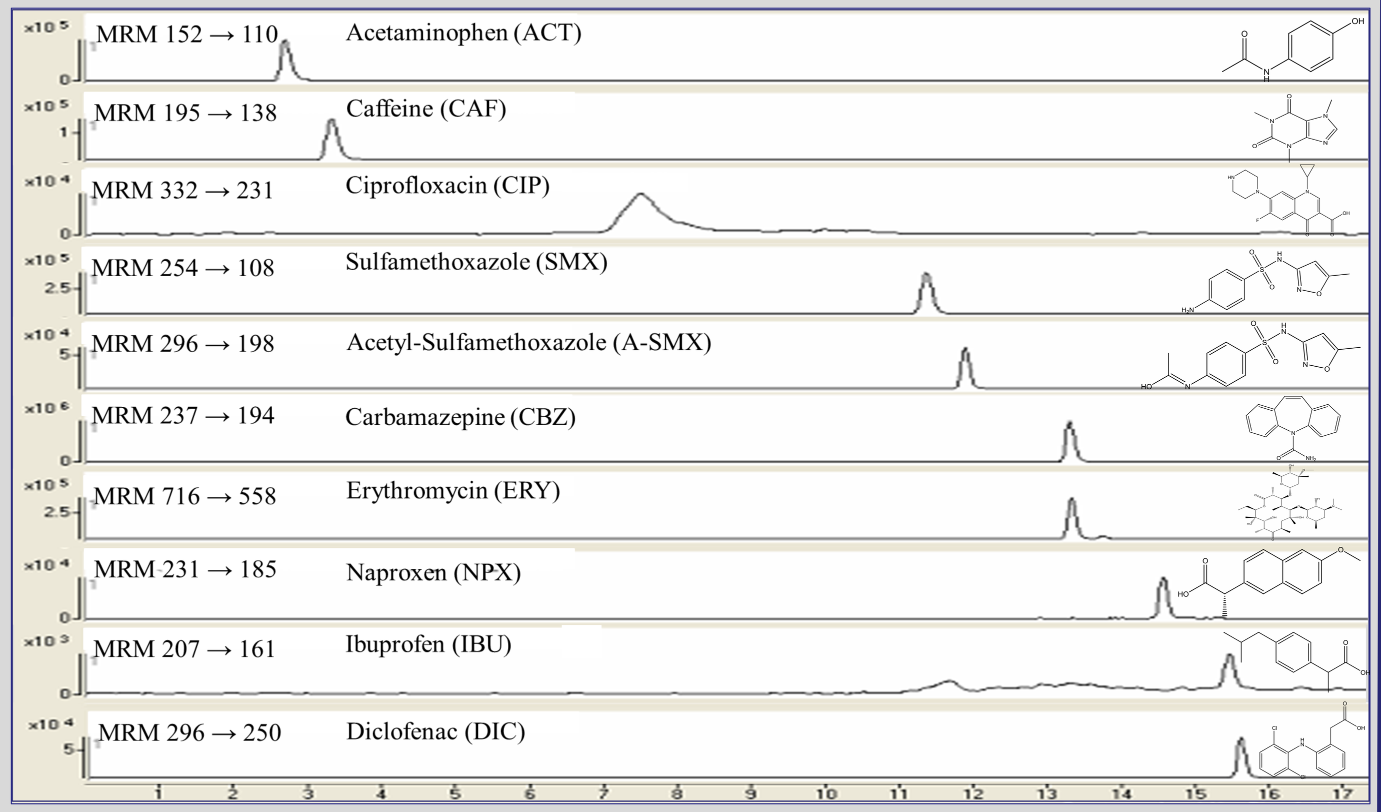

Figure 3. Separation of pharmaceuticals in a 50 ppb standard. Separation is achieved using a Betabasic-18 (2.1x100 mm) column and a 0.3 % formic acid in water and acetonitrile gradient

Field Plot Treatments

In order to explore the uptake of pharmaceuticals using urine derived fertilizer three different treatments were assessed. First, struvite precipitated from unspiked urine. Second, unspiked urine, and third, ~1 mg/L pharmaceutical spiked urine was applied as fertilizer to one set of field plots.

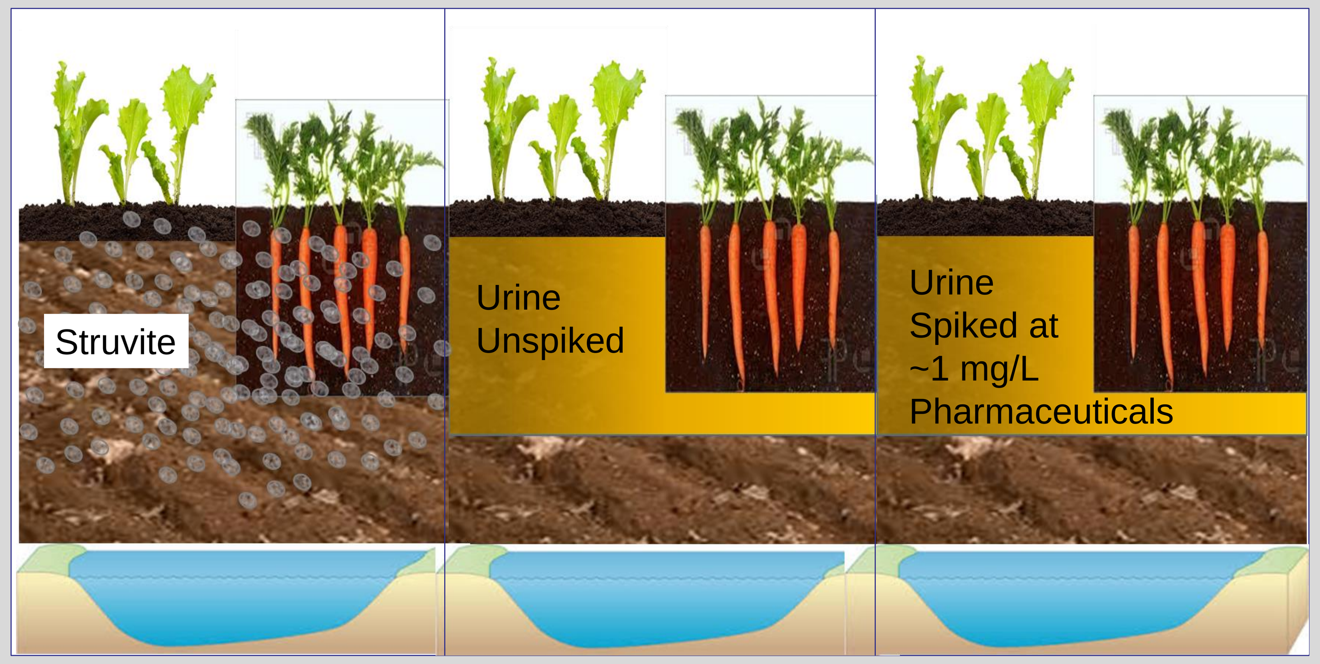

Figure 4. Depiction of the three different treatments (from left to right): fertilization with struvite (precipitated from the unspiked urine), fertilization with unspiked urine, fertilization with urine spiked at 1 mg/L.

Pharmaceuticals Levels in Each Matrix

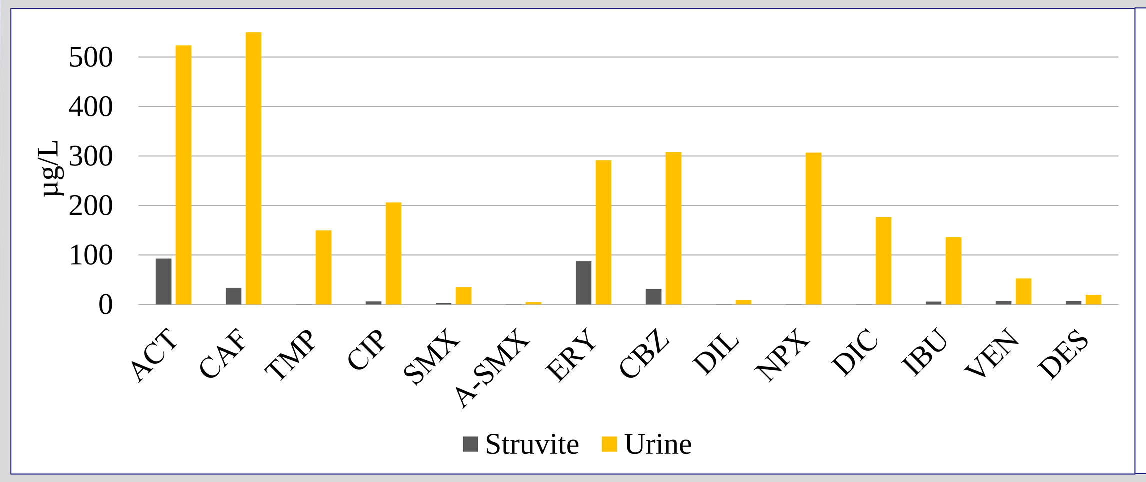

Figure 5. Pharmaceuticals in Struvite and Urine

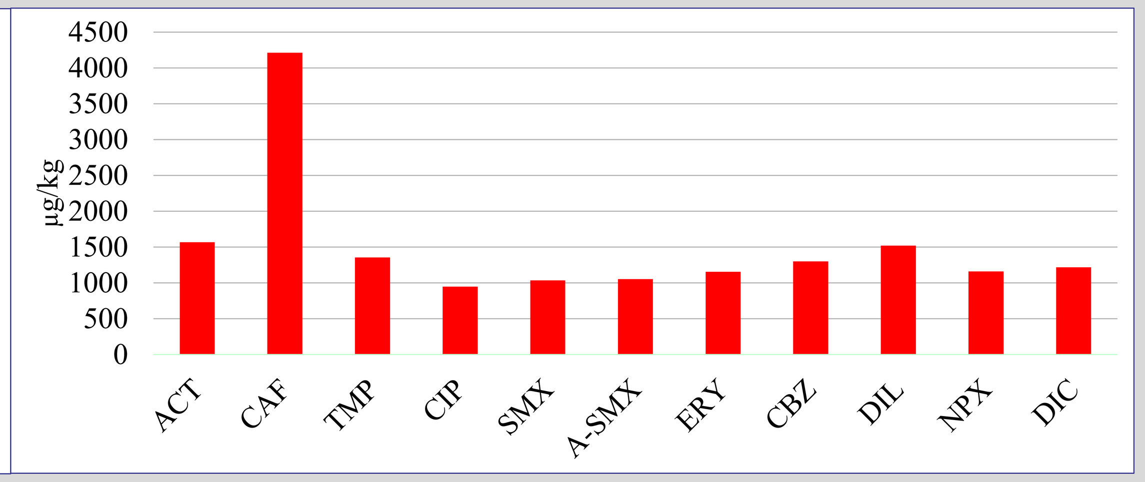

Figure 6. Pharmaceuticals in Spiked Urine

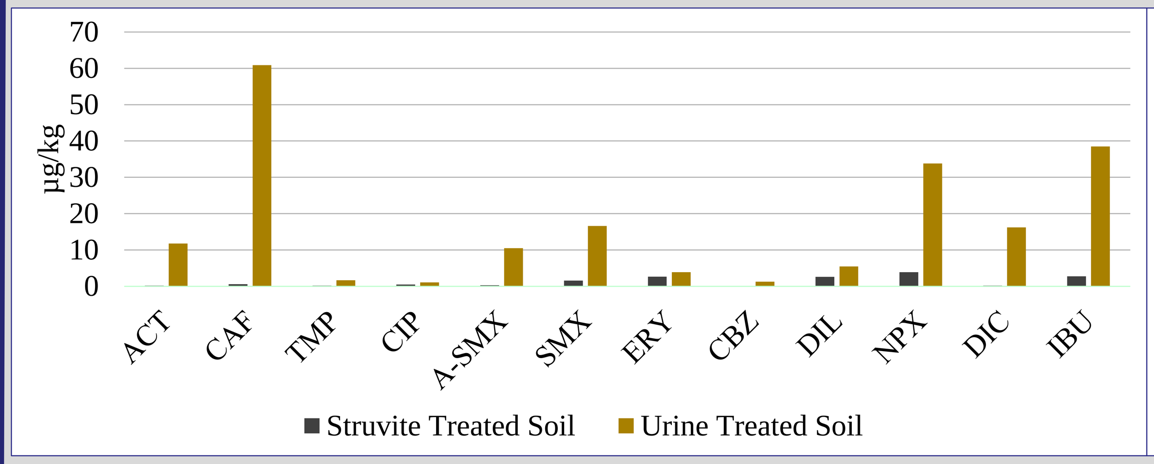

Figure 7. Pharmaceuticals in Soil Treated with Struvite and Urine

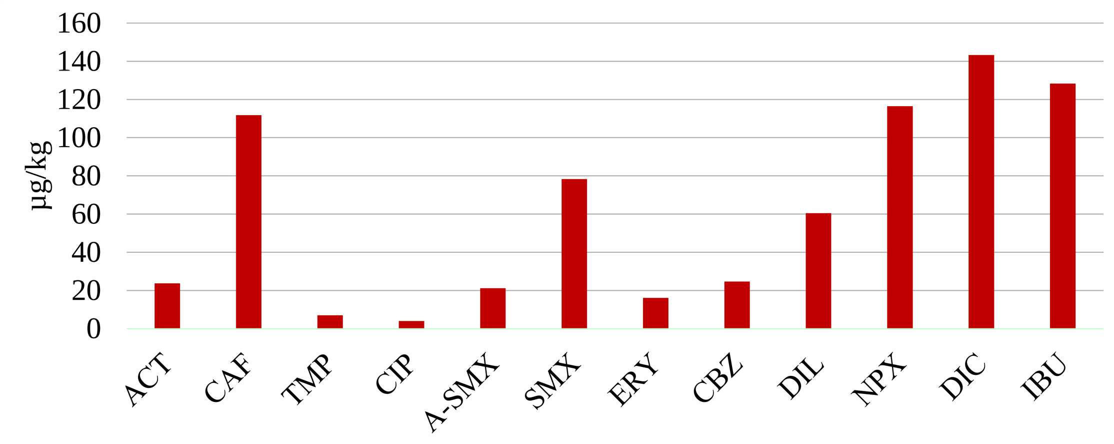

Figure 8. Pharmaceuticals in Soil Treated with Spiked Urine

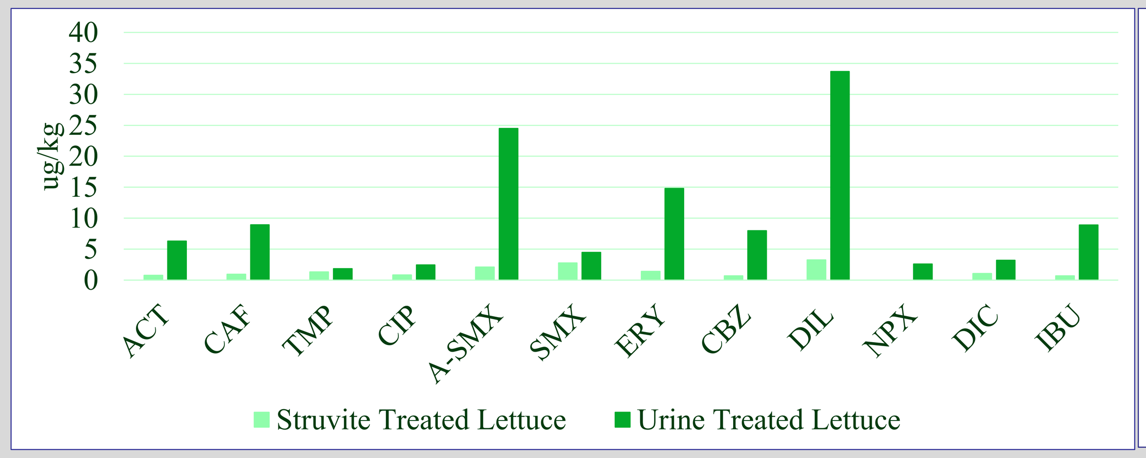

Figure 9. Pharmaceuticals in Lettuce Treated with Struvite and Urine

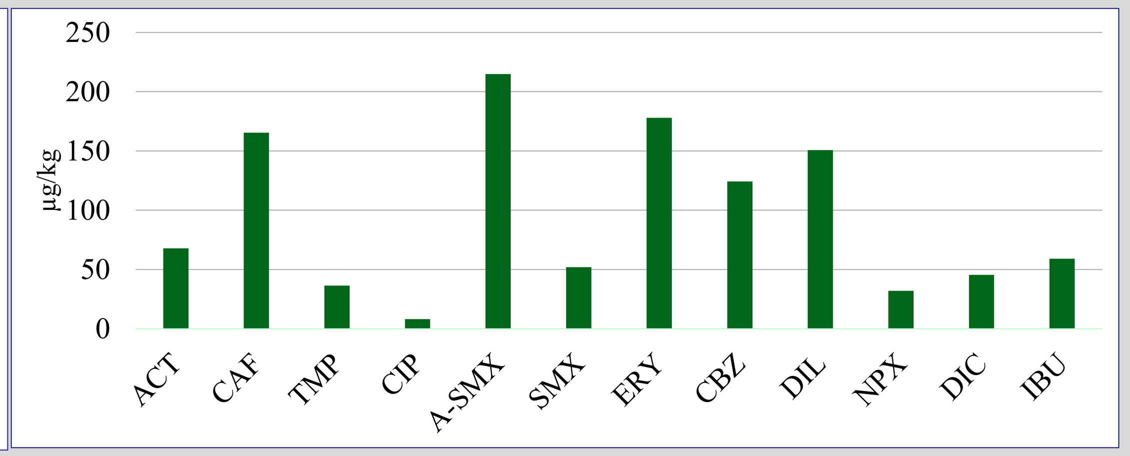

Figure 10. Pharmaceuticals in Lettuce Treated with Spiked Urine

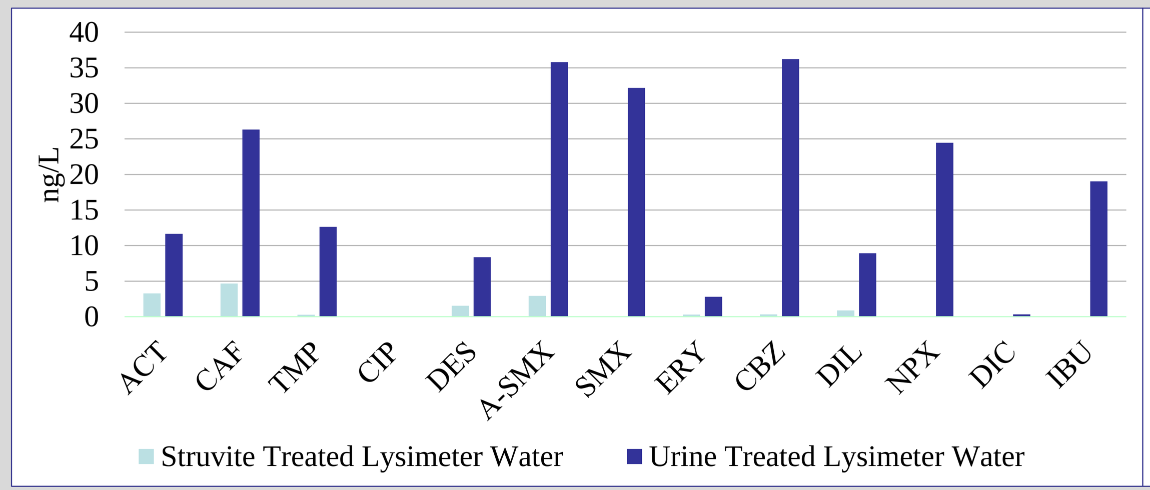

Figure 11. Pharmaceuticals in Water Treated with Struvite and Urine

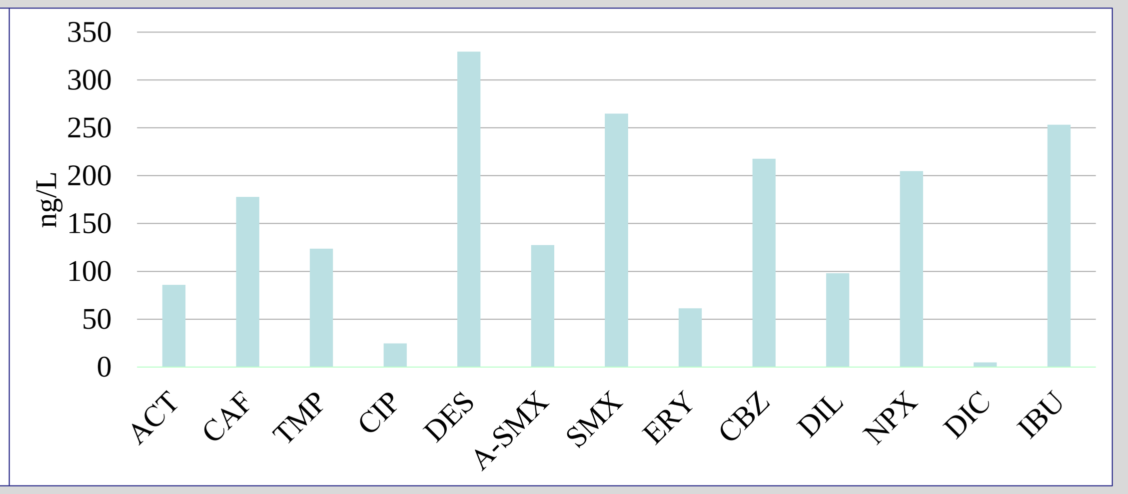

Figure 12. Pharmaceuticals in Water Treated with Spiked Urine

Transport of Pharmaceuticals

In order to assess the distribution of pharmaceuticals under the different treatment conditions the total mass of pharmaceuticals found in each matrix in each condition were summed. As shown in figure 11 below the pharmaceuticals from the urine fertilizer accumulate mostly in the water, while the pharmaceuticals from the struvite fertilizer accumulate mostly in the soil.

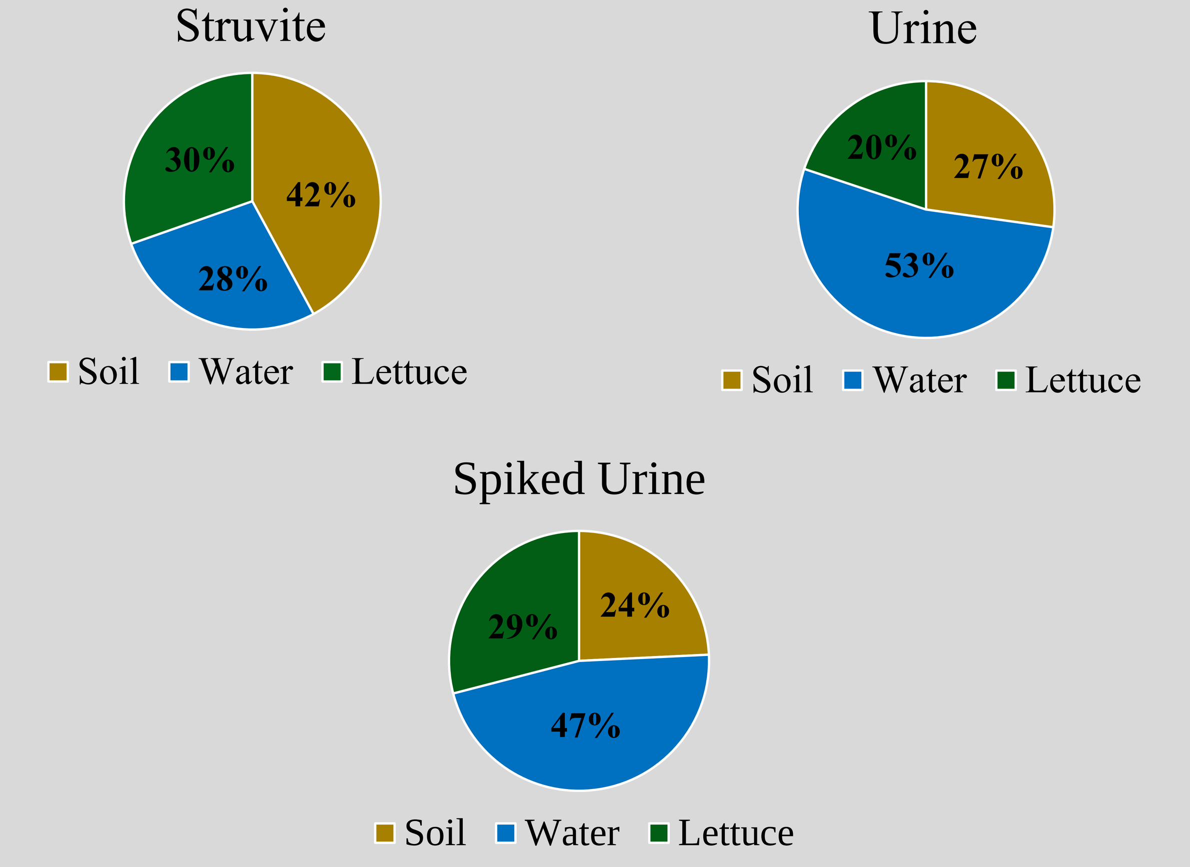

Figure 11. Distribution of Pharmaceuticals per Treatment.

Conclusion

Using sample clean-up and LC/MS/MS methods developed in our lab the first part of the field study is completed and there has been successfully detection and quantification of many pharmaceuticals in the different sample matrices of interest. All target pharmaceuticals were detected in urine. Acetaminophen, caffeine, and ibuprofen were detected in all matrices. These results show that, in general, the higher the concentration of pharmaceuticals in urine, the higher their potential for plant uptake, as observed in lettuce. More in depth field study is necessary to better understand the fate, transport, and plant uptake behavior of pharmaceuticals from urine land-application.

Future Work

- Complete the field study by analyzing the carrots exposed to the different fertilizers
- Assess the difference in uptake between the different fertilizers
- Assess the difference in uptake between the lettuce and carrots
- Do an untargeted study to observe what other pharmaceuticals may be present
- Potentially extend the study to other crops

References

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