Fate and Availability of Emerging Contaminants in Sewage Sludge-Amended Soil

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Abstract

Concerns regarding the effects of organic pollutants like PPCPs on agricultural areas, which raises the amount of dissolved bioavailable pollutants that plants may absorb, are developing. This study's objectives were to address this issue and offer some potential fixes. DGT is a passive sampling instrument with the capacity to assess time-weighted averages of bioavailable compounds in soil, water, and sediments. When a study was first conducted to address this issue, it was concluded that since there was no restock of MEP, PRP, PHBA, and ETP, their sorption to DGT decreased from days 14 to 21 owing to biodegradation. This prompted a follow-up study that looked at the sewage slurry for 21 days with and without NaN3, while the same samplers were deployed 24 hours prior to the retrieval day to look at the available chemicals at the end of each week. The results showed that a longer period, possibly longer than 21, may be required to further reduce bioavailable PCPs in the sewage cakes amended soils by giving more time for degradation and desorption. It was discovered that NaN3 prevents PCP degradation, but a 24-hour deployment reveals that MEP, ETP, and PRP require a longer period for desorption and degradation before being used by farmers. A significant concentration of BPA, PHBA, MEP, NP, and BHT were found in the sludge slurry made in a ratio of 15g of sludge cakes to MQ water in a ratio of 3:37 for the later investigation. Of these, 2589 ngL-1 was adsorbed to DGT in 7 days, whereas 681 ngL-1 was adsorbed on the day 21. Yet, at that time, MEP grew from 19 ngL-1 to 1497 ngL-1 and PHBA increased from 859 ngL-1 to 2114 ngL-1. According to this study, there should be at least 28 days between the application of sludge cakes to farmland and cropping, which is thought to be safer with lower levels of toxins.

INTRODUCTION

According to Kasprzyk-Hordern et al. (2009), wastewater treatment facilities using the activated wastewater sludge treatment method may remove personal care products (PCPs) and pharmaceutical substances with up to 85% efficiency (Grassi et al., 2012; Tran and Gin, 2017). While some of these organic pollutants are discharged back into the environment via discharge to surface waters, others can be degraded or sorb during the wastewater treatment process (Ifelebuegu & Ezenwa, 2010;

Council, 2016). Although sewage sludge solids have a great attraction for organic matter, the pollutant load that sorbs onto them might endanger agricultural systems when sludge is used as fertilizer (Yu and Wu, 2011; Yu et al. According to studies, most sewage applications for agricultural use are made by farmers who are unaware of the developing pollutants present in the sludge (Petrie et al., 2014). (Petrie et al., 2014). Poor knowledge of the fate of organic pollutants in soils and their toxicity to terrestrial species has resulted from the lack of appropriate investigations on the features of sewage sludge used in agriculture (Porter, 2002; Stuart et al., 2011; Maier et al., 2014; Petrie et al., 2014).

The constituent compounds that make up the PCP group have often been described as "emerging organic pollutants" (Mailler et al., 2014; Chen, 2016), which are also known as everyday home or lifestyle items and are primarily intended for human external use (Sorensen et al., 2015a). They can be found in items including scents, disinfectants, UV filters, and insect repellents as additives or preservatives (Petrie et al., 2014; Wang et al., 2014; Sorensen et al., 2015a, 2015b). When used, many PCPs are often discharged into the wastewater treatment process without being metabolically altered, which leaves most of their components in the environment in their original forms (Carbajo et al., 2014; Arlos et al., 2015; Vanraes et al., 2015). Nonetheless, a percentage can bioaccumulate in the body after usage and be eliminated through the urine as metabolites or in their original form (Barrett, 2005; Tolls et al., 2009). Although little to no information on production and consumption trends, studies have revealed that a sizable quantity of these chemicals are generated and consumed yearly (Eriksson, Auffarth, Eilersen, Henze, & Ledin, 2003; Lee, 2010; Sarpila & Räsänen, 2011). According to Pal et al. (2014) and other studies, there are more new toxins being released into the environment as a result of human activity. This is due to the widening spectrum of consumer goods, which includes cosmetics and personal care items. There are several thousand chemical compounds used in cosmetic compositions, and the yearly output is in the thousands.

To extend the shelf life of skincare and cosmetic products, several PCP elements as parabens are often employed (Crinnion, 2010; Ma et al., 2013; Ocaa-González, Villar-Navarro, Ramos-Payán, Fernández-Torres, & Bello-López, 2015). Even though some of their components have been found to mimic oestrogen (Oishi, 2001; Golden et al., 2005; Liao, Liu, and Kannan, 2013) and others have been connected to skin cancer, breast cancer, reproductive issues, and hormonal imbalance, they are also used as anti-bacterial ingredients in cosmetics. In addition to being employed as preservatives in moisturisers and lipsticks, some synthetic antioxidants, such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), are also utilised in the manufacturing of food (Darbre et al., 2004; Ye, Bishop, Reidy, Needham, & Calafat, 2006). The International Agency for Research on Cancer (IARC) has designated several of these substances, including butylated hydroxytoluene and diethylstilbestrol, as carcinogens and mutagens (Soni et al., 2002; Konduracka et al., 2014; Roeder, 2014). Any environmental concerns must be recognised and quantified in light of some of these compounds' persistence and unrestricted usage.

However, it has been said in other research that neither temperature nor sludge retention time (SRT) affect the rate at which PCPs are removed throughout the treatment process (Carballa, Omil, Ternes, & Lema, 2007). Application guidelines must be followed in

order to minimise the risk of pathogens and heavy metals in sewage sludge that farmers use as fertiliser (Xu et al., 2009; Yang et al., 2011; Verlicchi and Zambello, 2015). This practise is currently not regulated for organic contaminants (Jones-Lepp & Stevens, 2007). The revised Sludge usage in Agriculture Regulations 1989 govern the use of sludge cakes as fertilisers and soil improvers on agricultural operations. To prevent consuming infections that might be hazardous to human health, such as those found in infected salad crops and vegetables, sewage sludge is to be reused for certain crops and plant kinds. Also, according to EU laws, sewage sludge must not be applied excessively by farmers and must not be put directly onto grassland; instead, both the soil and the sludge must be tested for a variety of metals (Blöc & European Commission, 2005; DEFRA, 2012).

MATERIALS AND METHODOLOGY

Diffusive Gradients in Thin-film (DGT) Preparation

Due to its properties, including Time Weighted Average sampling, size, production costs, and sorption, DGTs have been employed for this investigation. The 0.45um, 25mm diameter GH Polypro (GHP) membrane filters were acquired from muncipal Corporation, India, and the DGT mouldings from the DGT Laboratory. They were manufactured in Laboratory using HLB resins for the 0.56mm binding gel and agarose powder for the 0.8mm diffusive gel. In order to make diffuse gels, 0.9g of agarose powder was dissolved in 60 ml of boiling Milli Q water to produce a 1.5% agarose solution. The diffusive gels and HLB Hydrophilic-Lipophilic Balance Binding were made using the normal DGT preparation process.

Sludge and MWHC

According to information from the WWTP, the sludge cake's average dry solids content (dried at 1050C) was 23.3%, and its pH was 7.90. To estimate the sludge to water ratio to be employed in the laboratory experiment, the Maximum Water Holding capacity was determined. The next approach was utilised to figure out the MWHC;

In a filter (Whatman 54 toughened 110mm diameter) that has been put in a plastic funnel, 10g of oven-dried sludge at 1050C was added. Deionized water was used to immerse this funnel in a beaker for two hours. The filter with the funnel was taken out and put in the cylinder to dry for an additional two hours beneath the fume cupboard. The filter paper containing the moist sludge was weighed, and it was thought that the filter paper weighed 3.5g. Then, using the straightforward equation, the maximum water holding capacity was determined.

$$MWHC = \frac{\text{Mass of Wet Sludge} - \text{Mass of Dry Sludge}}{\text{Mass of Dry Sludge}} \quad (1)$$

The above was repeated for 3hrs and the average MWHC was found to be 132%.

Deployments and Sampling

Laboratory Deployment

The temperature of the lab where all three tests were conducted was 20°C. Sludge and milli-Q water were combined in Experiment A at a 60:740 ratio. Before DGT deployment, this sludge and water were combined and left for an hour. On days 7, 14, and 21 of the deployment period, 12 o-DGTs were removed in groups of four. At the same time, a parallel system B was

put up, but it included 240 L of sodium azode (NaN3) to prevent bacterial growth and deterioration over time. Additionally, 12 o-DGT samples were included in this system. The third system, C, was initially constructed without DGT and with simply sludge and milli-Q water. On the sixth, thirteenth, and twentieth days, four DGTs were introduced for just 24 hours prior to the retrieval of other samplers, whereas the other samplers were recovered simultaneously. The main goal of this approach was to give a spot sampling equivalent by understanding uptake during 24 hours in comparison to continuous sampling over 7 days.

DGT Extraction Process

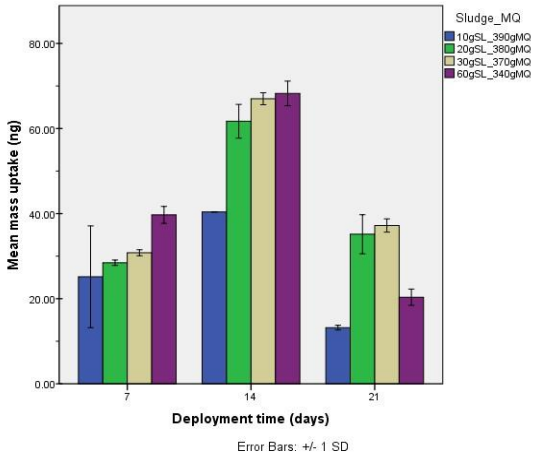
All DGT samples were extracted and prepared according to conventional DGT procedures for LCMS analysis. The resin gels were put into 15 ml clear amber vials, and then 50 l of mixed internal standards and 5 ml of Acetonitrile (ACN) were added to each vial. After 30 minutes of centrifuging, the solvent was decanted. Without the IS, this procedure was repeated with 3ml of ACN, and it was finished with a 2ml rinse of acetonitrile organic solvent. For storage and preservation, 10 ml of the extract were dried in the nitrogen and reconstitute with 1 ml of acetonitrile. ACN was used to create the 200-L aliquot of the extract for LCMS analysis in the proportion of 80/20 for MQ sol/ACN. Acetonitrile organic solvent served as the extraction and mobile phase for the LCMS analysis, however the study also included 5mM NH3OH as a buffer.

Experimental Study

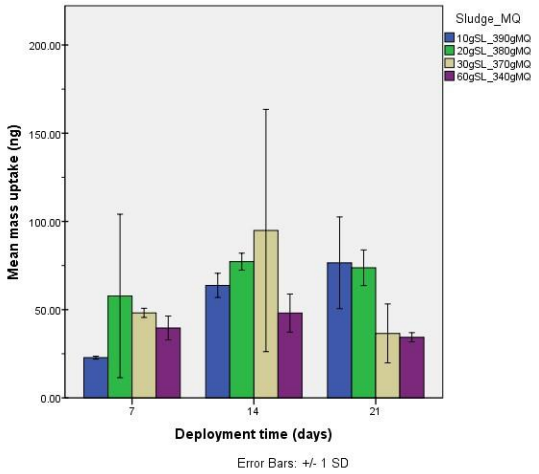
Studies have shown that a wide range of PCPs can be detected within sludge (Xu et al., 2009; Yang et al., 2011; Verlicchi & Zambello, 2015). The initial experiment investigated the use of DGT samplers to determine the sorption/desorption and degradation of PCPs in the sludge/water system. DGTs were deployed in a sludge cake slurry and sampled after 7 days, 14 days and 21 days of contact time. The following compounds Methylparaben (MEP), Ethylparaben (ETP), 4-hydroxybenzoic acid (PHBA) and Propylparaben (PRP) were investigated. The study also investigated the use of NaN3 to inhibit microbial activity and hence degradation. Sludge to water ratios was varied from 1/39 to 3/17 with a replicate of one of the experiments spiked with sodium azide to inhibit microbial activity. The preliminary study suggested that PCP ingredients are readily available in a soluble state for sorption into the binding gel. There was a noticeable reduction in mass uptake between 14 and 21 days for some compounds which could be attributable to degradation of the target analytes or desorption rate from the sludge and its mobility (Menezes-Blackburn et al., 2016). With these results in mind suggesting that bioavailable fraction of PCPs reduce overtime or degrade over the period suggest that PCPs might not pose a risk to the on-going use of sewage sludge for agricultural purposes. However, these preliminary results required a further investigation which led to this repeat study. The mass uptake for the compounds are shown in Figure 4a-d below;

Figure 4(a-d): Mass uptake for MEP, ETP, PHBA, PRP (ng) by o-DGT at various sludge ratios; 10g Sludge: 390g MilliQ water, 20gSl:380gMQ, 30gSl:370gMQ, 60gSl:340gMQ, measured on 7th, 14th and 21st days.

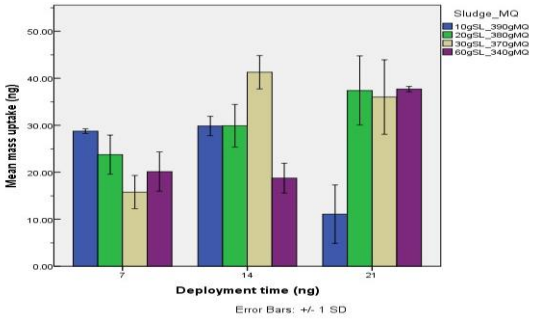
Mass uptake for MEP (ng) by o-DGT (a)



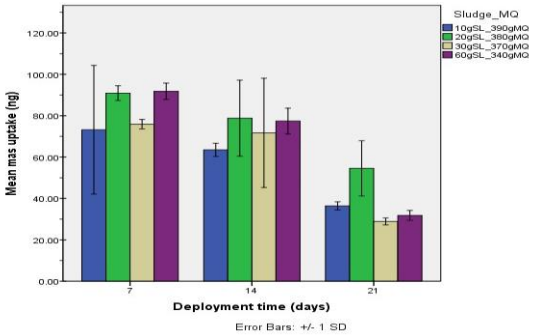
Mass uptake for ETP (ng) by o-DGT (b)



Mass uptake for PHBA (ng) by o-DGT (c)



Mass uptake for PRP (ng) by o-DGT (d)



Study Design

Sewage sludge cake was collected from LWWTW and prepared to form a slurry, with sludge to water ratio of 3:37 based on the water holding capacity earlier calculated for the preliminary experiment. 15g of sludge was used for each experimental design while 12 o-DGT samplers were deployed in each sampling pot and retrieved on the 7th, 14th and 21st day in duplicates respectively. A control experiment was spiked with 0.03%v Sodium Azide NaN3, mixed thoroughly to inhibit bacterial growth. This was aimed at controlling or reducing the biodegradation of the target compounds. A little paste of the slurry was put on the o-DGT open surface, before being concealed in the paste.

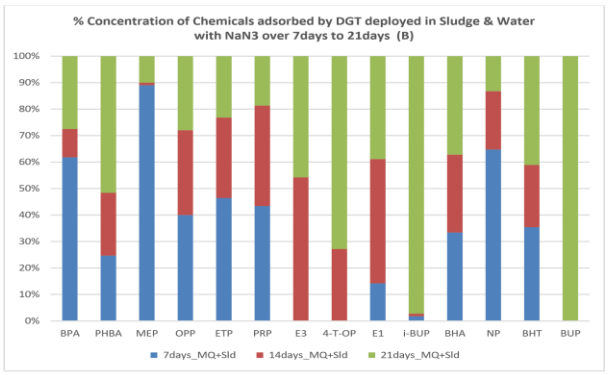
Upon removal, the DGT binding Gels were removed while the analytes of interest were extracted using organic solvent Acetonitrile before preparing the samples for Liquid

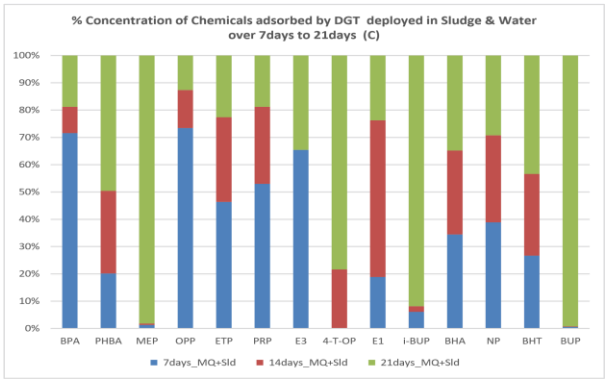
Chromatography-Mass spectrometry (LCMS) instrumental analysis. As an extension to this, another set of experiments were run simultaneously to quantify chemical uptake by the o-DGT over 24 hours rather than allowing accumulation over 7, 14 and 21 days. o-DGTs were deployed in quadruplicate for 24 hours on the 6th, 13th and 20th days for retrieval on the 7th, 14th and 21st days respectively. It was expected that this approach would give us concentration that is available at the time rather than 7days /14days/21days time-weighted average concentration.

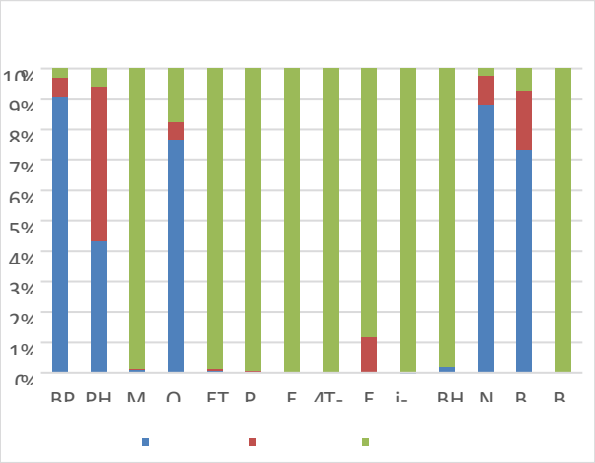
RESULTS AND DISCUSSION

The goal of this laboratory experiment utilizing sewage sludge cake with or without sodium azide (NaN3) was to gain insight into how bioavailability and potential biodegradation may play a role throughout the treatment process as well as following sludge use as a fertilizer for plants. Some of the compounds were found during the first 7 days of the investigation, while others weren't found until the last week of the experiment because of a variety of affinities between the study chemicals and organic matter (i.e., a range of solubilities in water). The proportion of compounds that are adsorbed onto the o-DGT with regard to deployment time is shown in Figure 5. Only a small number of compounds, including BPA, PHBA, BHT, OPP, and NP, were visible in the experiment A, which only deployed o-DGT for 24 hours. The bulk of the compounds did not dissociate from the sludge matrix until the 15th to 20th day of the deployment. Results from experiments B and C, however, indicate that some of the chemicals may have deteriorated quickly and that this may have had a detrimental influence on their detection throughout the course of the 24-hour DGT deployment period. Another possibility is that o-DGT won't be able to absorb a reportable concentration throughout the course of 24 hours.

Figure 5. (A) Chemical concentrations in sludge cakes used by farmers to remediate soil under various circumstances are shown in Figure 5. (A) On day 0, all the DGTs were placed into 15g of sludge cake with 3:37 sludge/water ratios. (B) On day 0, all the DGTs were placed into a controlled medium containing 0.03% v Sodium Azide NaN3 to prevent bacterial development, and they were recovered on days 7, 14 and 21. (C) On the sixth, thirteenth, and twenty-first days, the DGTs were deployed for 24-hour uptakes, respectively.





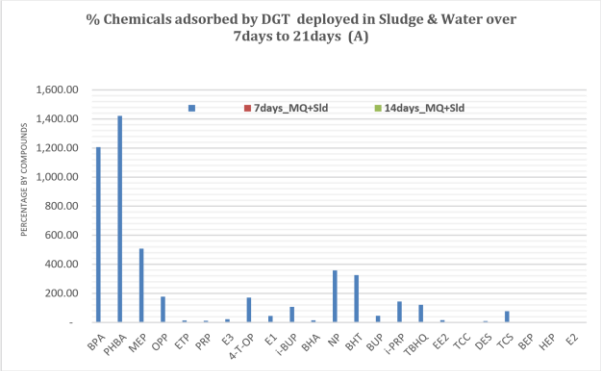


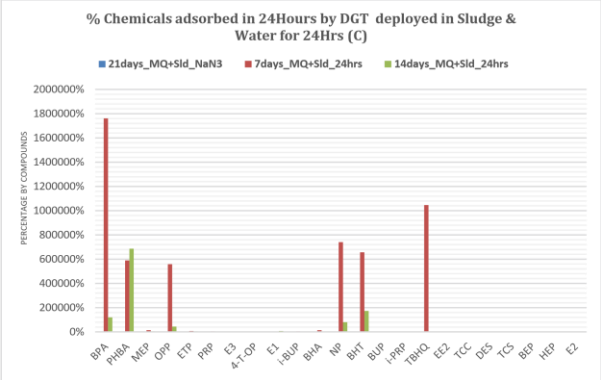
Out of the 23 substances that were initially examined, 8 were not reported. These substances, including TBHQ, EE2, BEP, HEP, E2, TCC, DES, and TCS, were undetectable. Below is a graph of the chemical sorption to the DGT during a 21-day period in the laboratory experiment, where the DGTs were deployed for 21 days and collected in batches on the 7th, 14th, and 21st days. The combination was made up of 15g sludge cakes that had been produced for agricultural use by the local farmers in a 3:37 sludge/water ratio. The amount of dissolved bioavailable chemicals that are accessible for plant uptake is measured by DGT in the sludge slurry. Throughout the absorption phase, there is a predicted loss of concentration, which would cause chemical desorption from the sludge slurry. The goal is to understand how these chemicals behave after being applied for agricultural use and to estimate how long it could take for the altered soil to appreciably reduce the chemicals before farmers can safely use the land. If these substances can't be broken down, some of them could wind up in the waterways.

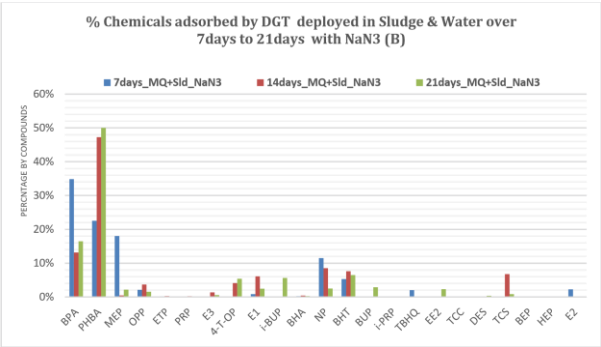
Figure 6A demonstrates that DGT absorbed 51% of the total BPA within 7 days of deployment whereas PHBA was absorbed 50% over a 14-day period. This revealed that BPA desorption, with a log Kow of 3.64, was faster in the early stages of sampling than PHBA desorption, with a log Kow of 1.39. However, the desorbed concentration from the sludge slurry may have been depleted or degraded during the course of the subsequent 14 days, leading to a decrease in the concentration of BPA. The results indicate that sodium azide prevented microbially mediated degradation throughout the experiment, which may possibly explain why some of these chemicals were discovered in low amounts in the activated sludge. When DGT was deployed into the sludge for 24 hours, it became evident that sorption was chemically dependent since certain substances, like BPA, NP, BHT, and OPP, tend to dissociate fast while others, including E3, PRP, ETP, 4-T-OP, i-BUP, and BUP, do not dissociate until 14 days had passed. This shows how the chemicals would separate from the sludge matrix after being injected into the soil. However, some variation in the actual environment should be anticipated owing to temperature changes and different soil bacteria that might facilitate biodegradation.

Figure 6C demonstrates that the majority of the chemicals were found in the sludge slurry during the 24-hour sample on day 21 of the sampling experiment, perhaps as a result of biodegradation or desorption from it. This may suggest that it will take some time for some of the chemicals to completely desorbate from the cake before the farmers can use them after putting them to their field. Additionally, it reveals that these substances may have a significant affinity for organic matter, whereas chemicals with a weaker affinity for organic matter may desorbate early and degrade before crops and plants can absorb the bioavailable substances.

Figure 6(A-C): Percentage of chemicals absorbed by DGT from sludge slurry from sludge cakes prepared for agricultural use under various circumstances (All the DGTs were deployed in 3:37 sludge/water ratios of 15g sludge cake).







To learn more about the behaviours of the discovered substances throughout the sample period, some of them are categorised below. These have also been chosen to include some of the chemicals that were the subject of prior trials so that conclusions can be drawn and perhaps a recommendation can be made as to when it would be safe for farmers to start planting their crops after the soil has been treated with sludge cakes. Figure 7 demonstrates that, with the exception of PHBA and MEP, most of the compounds examined showed an early desorption in sludge slurry without any inhibitor. This shows that given the quantities of 2114 ngL-1 and 1497 ngL-1 and their application to agricultural land, additional time may be needed for these 2 chemicals to properly desorbate from the sludge cake. The concentrations adsorbed by DGT were greater on the seventh deployment day, according to other substances, and there was a subsequent decline in the concentrations, which may have been caused by the degradation of bioavailable concentrations. However, the behaviour of PHBA in Figure 8 with the addition of NaN3 may be interpreted in a manner similar to that of Figure 8 without the inhibitor, with the exception that the concentrations were greater due to regulated or decreased biodegradation. BPA, on the other hand, saw a rise in concentration during weeks 2 and 3, from 470ngL-1 to 1202ngL-1, whereas all the other chemicals exhibit chemical depletion. BPA displayed this pattern in both situations, suggesting that NaN3 slows the degradation.

Figure 7: Time Weighted Average Concentrations (ngL^{-1}) of chemicals in sludge cakes adsorbed by o-DGT in MQ water & Sludge mixture without the inhibitor NaN_3

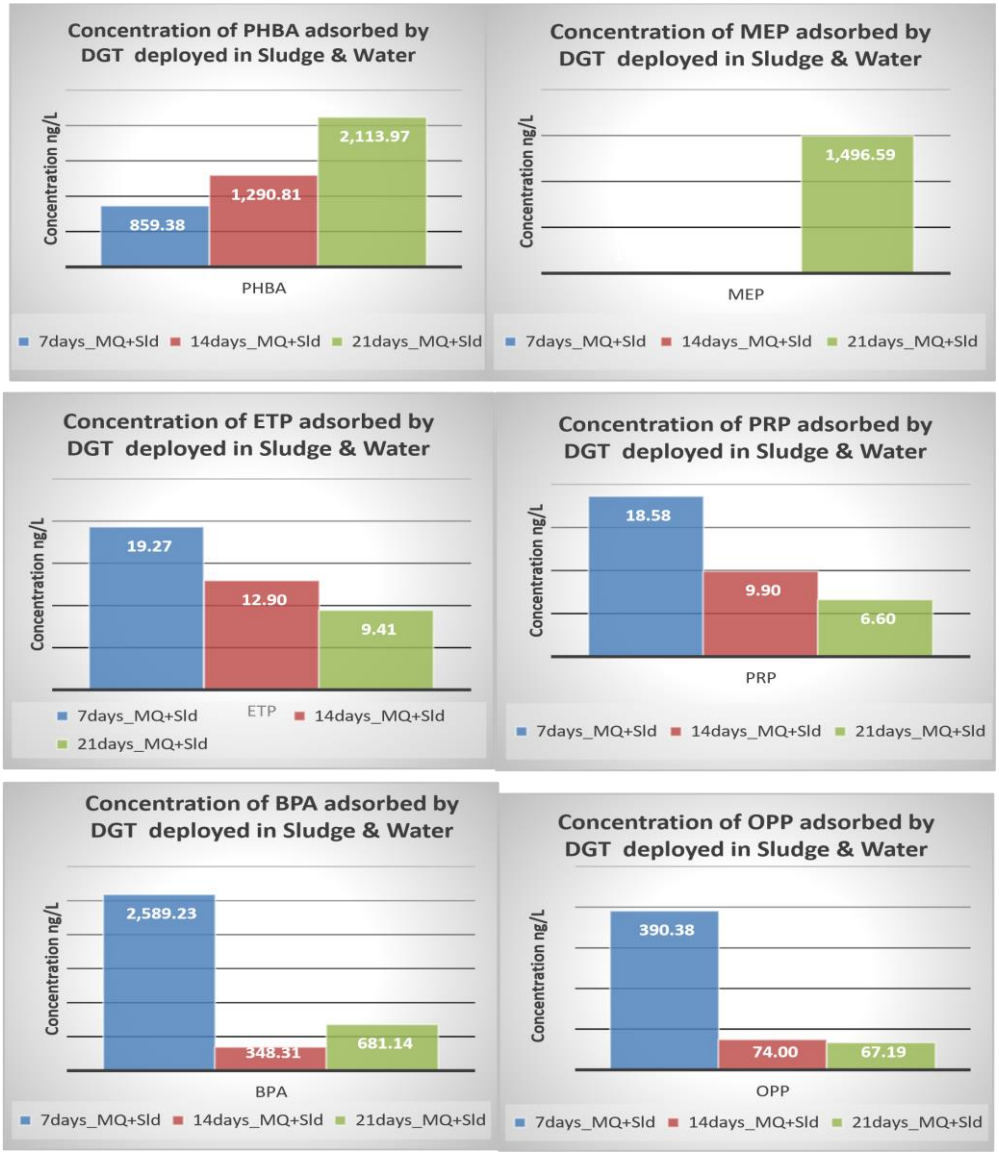


Figure 8: Time Weighted Average Concentrations (ngL-1) of chemicals in sludge cakes adsorbed by o-DGT in MQ water & Sludge mixture with the inhibitor NaN_3

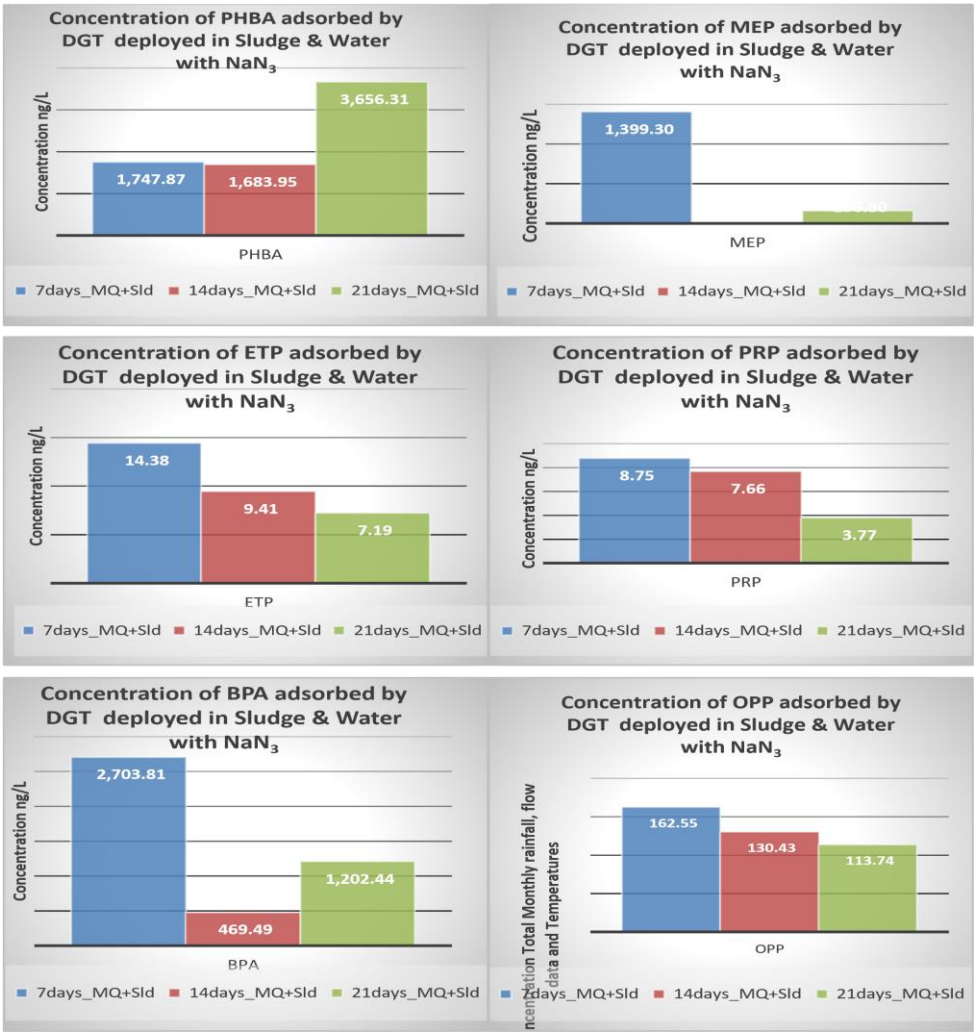
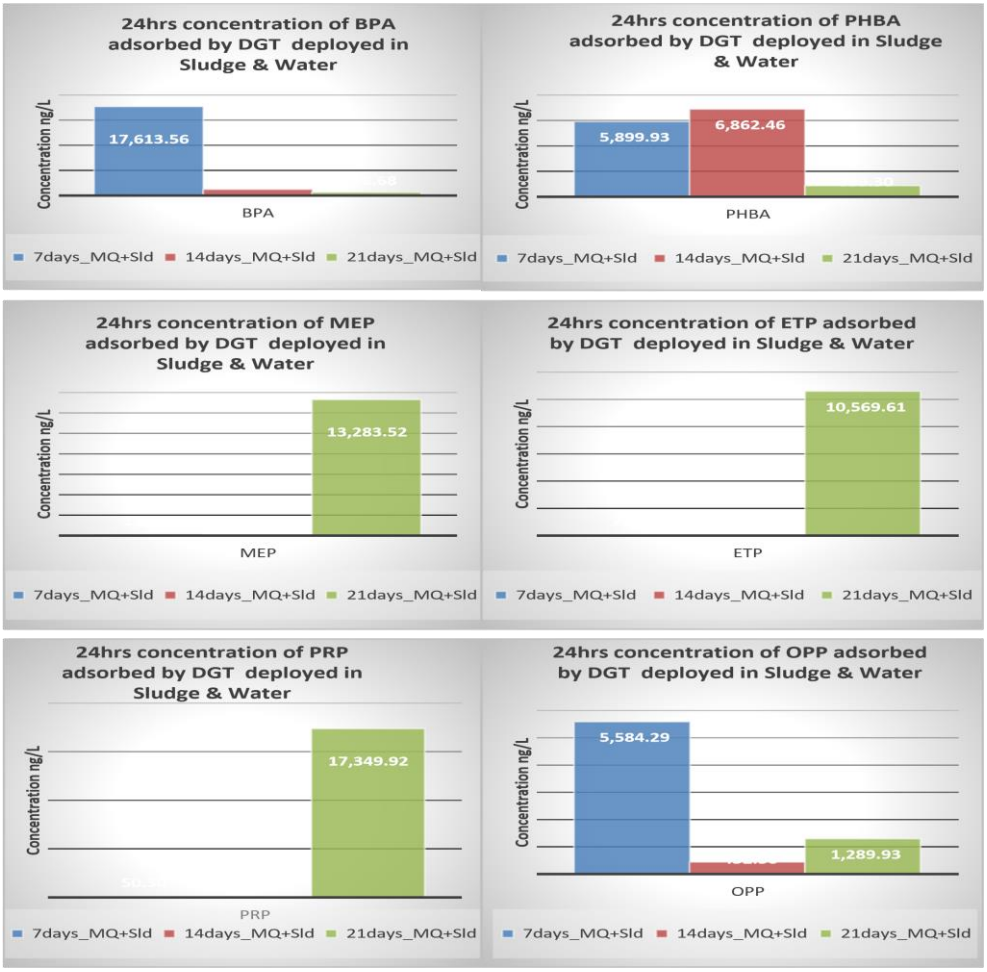


Figure 9: 24hrs Concentrations (ngL-1) of chemicals in sludge cakes adsorbed by o-DGT in MQ water & Sludge mixture without the inhibitor NaN_3



Even though the concentration on day 14 was lower than that on day 21, BPA levels dropped from day 7 to day 21. The same pattern was seen with MEP and BHT. OPP, NP, and TBHQ declined during the time under both settings, but PHBA rose over the course of 7 days to 21 days. These patterns are a result of these chemicals' respective solubility and partition coefficients (Kow, Koc). For instance, PHBA's solubility of 5000 mg L-1 and LogKow of 1.39 both indicate an increasing tendency over time. MEP, however, also has a comparable LogKow of 2 and a solubility of 2500 mg L-1. Over the course of 21 days, this compound's concentration was seen to decrease alongside NaN3, which prevents biodegradation. Although MEP concentrations were very low until 21 days had passed, as can be observed in Figure 7 when NaN3 was not administered, suggesting a mix of degradation if considered in light of Figure 8 or delayed desorption from the sludge slurry.

While early desorption was shown in BPA and OPP, and the adsorbed concentration suggests deterioration during the duration, DGT samplers deployed for 24 hours revealed that MEP, ETP, and PRP were more readily accessible on the 21st day compared to the other chemicals. The information in figure 9 above describes the concentration of chemicals that were present at the start of the study, how

rapidly some of them deteriorated, and how some of them had a sluggish desorption rate, resulting in a higher concentration at the end of the study than it had been earlier. While those who desorbed quickly were seen to have gotten worse with time. In comparison with the first study that Methylparaben (MEP), Ethylparaben (ETP), Propylparaben (PRP) and 4hydroxybenzoic acid (PHBA) and concluded that PCP ingredients are readily available for plant uptake, the reduction was between the day 14 to 21, the 2nd study for similar compounds also suggest that reduction in PCP bioavailability, MEP and PHBA full desorption or degradation could take longer than 14 days. It implies that bioavailability of ETP and PRP reduced from week 1 to week 3 suggesting that these could fully degrade if allowed a week further or 2 under the influence of environmental climatic factors such as temperature or precipitations while available surface area resulting from the soil to sludge ratio also play an important role.

CONCLUSION

Sludge cakes that had been processed for agricultural use were used in this investigation. Operators of treatment facilities have a big obligation to make sure that sewage sludges are disposed of properly to prevent the return of pathogens and organic pollutants into the environment. Although its usage in agriculture, particularly for the remediation of agricultural soils, is gaining popularity. In order to fully establish the environmental, economic, and ecotoxicology impact of various disposal avenues, End-of-Waste Criteria and Life Cycle Assessment were proposed (Kacprzak et al., 2017), where the current state-of-the-art method, agricultural reuse, and incineration seem more advantageous. The bioavailable portion of chemicals present that would be accessible for plant absorption after the agricultural soils are supplemented with the sludge cakes was quantified in this study using DGT as a technique.

Analysis of the overall absorption over 21 days revealed that DGT absorbed 100% of the TBHQ, 72% of the BPA, 73% of the OPP, 65% of the E3, and 53% of the PRP within the first 7 days of the sample period. The 21st day, however, saw the removal of 50% of the total PHBA adsorbed by DGT, as well as 98% PHBA, 78% 4-T-OP, 92% i-BUP, 35% BHA, 43% BHT, 99% BUP, 98% i-PRP, and 100% TCC, DES, and TCS. The observed concentrations give information on biodegradation and sorption/desorption behavior. This supports EU-27 recommendations of sludge reuse or incineration since it implies that retaining the treated soil for more than 3 weeks will considerably reduce organic pollutants before farmers plant their crops (Kelessidis & Stasinakis, 2012). Concerns from local resident organizations, landowners, and food merchants played a major role in the decision-making process that would require advanced technology to lower the quantity of germs in the sludge. Conclusion: Contaminants must be chemically dissociated from the sludge matrix, and the presence of microbial activity would promote biodegradation. Utilizing sludge cakes from several batches that had been exposed to various climatic conditions before beginning the laboratory research on the cakes may account for the difference between the first and later investigations.

Thus, it can be concluded that DGT is an effective method for determining how much of dissolved bioavailable chemicals are accessible for plant uptake. By allowing more time between the application of sludge cakes and planting, the danger of chemical contamination would be decreased. This result confirms the

theories of other researchers. Werle and Wilk (2010) also looked at the potential thermal use of sewage sludge for generating energy by gasification, pyrolysis, combustion, and co-combustion. Although this is a good concept, research has shown that areas close to the treatment facilities, particularly reed beds, increase eutrophication, supporting assertions that agricultural land yields where sewage sludge is sprayed are higher than those on areas where inorganic fertilizers are applied (Singh & Agrawal, 2008).

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