Degradation of some illicit compounds in sewage sludge batch tests

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ABSTRACT
The batch tests enabled determination of the degradation of the compounds at different temperatures and times, using various sludge types after characterisation. Removal rates of cocaine (91.0%), benzoylecgonine (90.6%), heroin (97.9%), morphine (99.7%), 6 monoacetylmorphine (93.3%) and diazepam (99.7%) were measured after 3 hours equilibration; partition coefficients (Kd) for these six substances ranged from 1.2 – 68.1 Kg L⁻¹. The degradation of compounds at 19 ± 0.5°C was relatively greater but it still occurred slowly at 4 ± 0.5°C at between 5 and 10%. Work encompassed in this study directly measures illicit drug removal rates in laboratory studies for the first time. The application of batch studies in calculating removal rates in sewage works is an improvement over prior studies where assumptions on removal rates at STW were made.

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Introduction
Emerging priority contaminants groups like ‘illicit drugs and their metabolites’ have no safe-levels because of the insufficient information on their biodegradability and persistence after their disposal of chemicals and degradation products to lands or receiving waters via sewage treatment works. Studies in the literature have confirmed the enrichment of the sewage sludge partitioning of chemicals onto sludge solids or suspended in solution is due to their hydrophilicity/lipophilicity properties compared to influent sewage [1-3]. Understanding of the fate and behaviour of pollutants during sewage treatment will show the degradation possibility of compounds that are completely or partially degraded in aqueous and solid phases, sorbed to sludge solids or mineralised. In a study reported by Strachan et al [4], organic contaminants are located within the fraction of large organic wastes (biomass) which are repository of living and dead micro-organisms required for degradation processes.

Investigations on the levels of removal of organic residues from a wastewater plant studies have shown toxicity correlation of wastewater effluents on aquatic organisms to determine the response levels with degree of contamination [5-7]. Biodegradability studies of organic priority pollutants and reduction in toxicity of these pollutants in wastewaters treatment processes have also been carried out [8,9]. Also evaluated were 22 priority pollutants belonging to the class of phthalates, pesticides, polycyclic aromatic hydrocarbons and phenols in an activated sludge pilot plant [8,10]. About 80-99% removal efficiency was recorded from the parallel and spiked treatments of between 50-150 µg L⁻¹ concentrations. The results indicated a degradation of phenols, enrichment of PAHs to about 64% from the mass balance calculations while pentachlorophenol was associated with the solid phases. Table 1 presents percent sewage sludge disposal in the last 3 years, and the subsequent transport of these residual organic pollutants in the sewage which enters the environment and becomes the issue of current concern.

Sewage is a complex association of wastes of human excreta containing mixtures of fats, sugars, lignin, protein, cellulose, humid materials, amino acids and fatty acids. Wang et al [12] studied the partitioning mechanism of the organic residues within the biomass and sorption onto the sludge surface as a two-stage process. Determination and prioritisation of typical sewage sludge can be a complex task because of many synthetic organic materials with various residues of diverse origins due to 1) interferences of co-contaminants in complex matrices, sample extraction and clean ups, sensitive techniques needed to determine low concentrations 2) the fate and behaviour of sludge-derived residues after disposals requires investigation to monitor persistence and environmental impacts and 3) bio-transformation arising from degradation of residues generates toxic by-products, but unavailability of some compounds, sorped onto sewage solids to bacteria for degradation can be significant as little is known about the final fate of these organics [13-17]. Difficult isolation of sludge samples arises also from non-uniformity of extraction procedures and variability in obtaining grab samples as a representative of all various genotoxins in the sludge matrix [18-20]. Different processes or techniques are often adopted for specific effluents depending on the origins of the contaminants. Generally factors often considered, though contaminants can be lost during treatments in a complex variety of ways are: 1) sorption/association with sewage solid surfaces 2) abiotic processes/hydrolysis involving chemical degradation 3) volatilisation and 4) biodegradation [10].

Humans are typically exposed to numerous organic and inorganic pollutants, as by-products from treatment of waste water from domestic, agricultural and industrial sources which
constitutes sewage [21]. The presence of intestinal pathogenic bacteria and animal parasites in sewage sludge has been confirmed from several investigations [22,23]. However, sewage sludge may contain relatively large amounts of heavy metals as well as organic pollutants such as phthalates, polychlorinated biphenyls (PCBs), alkylphenols, and organochlorine pesticides compared to normal environmental levels in soil, water, and air [2]. Increasing amounts of sewage sludge are used for land filling and agricultural land including pastures grazed by ruminants following the ban on ocean dumping of sludge [24]. The potential health risk imposed due to the presence of organic and inorganic compounds found in sewage sludge is of concern in humans [25,26] if they are delivered at high enough doses to cause effects through the consumption of products derived from animals grazing on contaminated pastures [27]. Adverse effects which have been reported in humans include perturbation of male reproductive tract, certain male and female cancers, declined fertility, thyroid dysfunction and ill impacts on the male reproductive tract, certain male and female cancers, declined fertility, thyroid dysfunction and ill impacts on the

In the literature, degradation studies of pharmaceuticals have identified degradates of anti-inflammatory, analgesics and blood-lipid regulators. In batch studies of acetylsalicylic acid with suspended activated sludge, the decrease of about 70-99% in concentration after 6, 24 and 72 h was observed but no metabolites were detected using GCMS [34]. The degradation studies of anti-inflammatory and blood-lipid regulators such as bezafibrate, diclofenac, naproxen and ketoprofen in activated sludge were carried out, but only ketopofenbiotransformed into 3-(hydroxyl-carboxy-methyl) hydratropic acid and 3-(keto-carboxyl- methyl) hydratropic acid [34]. Biodegradation of trimethoprim showed resistance to degradation in a reactor filled with activated sludge, but its degradation in a nitrification process was completed in 3 days. In a similar study, Ternes et al [34] investigated degradability of estrogens in aerobic batch reactors at two different concentrations using GCMS. The 17β-estradiol was oxidised to estrone without any detectable degradates. Also, 16α-hydroxy-estrone was similarly degraded without degradation products. In a subsequent work, the biodegradation studies of trimethoprim, anti-tumoursalciplatin, cyclophosphamide, cytarabine, X-ray contrast agents, iodopamide and diatrizoate has been carried out but not all the details of metabolites identification were reported [34].

Concerning the degradability of illicit drugs, apart from sample degradation, biodegradation is a natural process that has been reported by the stability experiment conducted by Georgshe et al [35] and which observed that the concentration of cocaine and ecgoninemethylster changed in surface water by 40 and 95% after 5 and 24 h test period respectively Batch tests using sewage sludge samples obtained from two sewage treatment works were aimed to determine the effects of these compounds physico-chemical properties and biological sludge characteristics on biodegradation. Degradation of cocaine was observed with a concomitant production of metabolites like ecgoninemethylster, cocaethylene and other short chain compounds. Degradation was determined to be both biotic and abiotic processes with the mixed liquor solids concentration involving both intracellular and extracellular enzyme activities which influenced compounds degradation. However, increased degradation of the drugs led to the bio-accumulation of the related metabolites which were in turn degraded, but some showed possibilities of bio-combination of residues that may result in their escape from complete removal from the sewage treatment processes to the receiving waters in a complex-interplay of interactions. The capability is also outlined of furthering our understanding of fate and behaviour of drugs with particular reference to illicit drugs, abused pharmaceutical and environmental processes in our quest to understand the overall issues of drugs and make available exposure data for the aquatic realm.

**Experimental**

**Experimental preparation**

A simple experiment to simulate conditions in actual STWs was designed to use raw sewage in batch studies to provide natural bacterial species and population that can allow continuous degradation of metabolites slowly and naturally in contrast to utilising synthetic activated sludge. Three hours duration for the degradation studies was chosen as this permitted an intensive subsampling and processing allowing data-intensive assessments for an anticipated fast (min hr⁻¹) degradation rate. Only 6 compounds used in spiking (batch) studies were cocaine and its metabolite benzoylecgonine; heroin and its metabolites 6-monoacetylmorphine and morphine and diazepam as shown below in Table 5.

**Chemicals and Materials**

Standard compounds of cocaine, benzoylecgonine, heroin, 6-acetylmorphine, morphine and diazepam, were purchased under license from both Sigma Aldrich (Gillingham Dorset, UK) and LGC standards (Teddington Middlesex, UK). Analar grade hydrochloric acid (HCl), ammonium hydroxide (NH₄OH) and methanol (MeOH) used for pH adjustment and sample preparations were obtained from Aldrich. A derivatizing agent, N, O, bis (trimethylsilyl) trifluoroacetamide (BSTFA with 1% trimethylchlorosilane, TMCS) was purchased from Cerrillant (Round Rock, TX, USA). The choice of BSTFA as a silylating agent for derivatization is due to its faster reaction and volatility of its by-products. Pyridine was also purchased from Aldrich and was used to provide appropriate derivatization reaction medium. Reagent water was from a Millipore milliQ water purification system (ELGA labwater, UK). Stock solutions of each chemical at 100 µg L⁻¹ were prepared in methanol and were stored at -20°C in the dark at pH = 2 with 37% HCl until analysis [35], while working solutions were prepared from appropriate dilutions. Oasis HLB® sorbent in a 47mm SPE disc format and disc holder were purchased from Waters (Elstree Herts, UK). A Phenomenex SPE Vacuum Manifold (Macclesfield Cheshire, UK) with 12 ports and a self-cleaning and drying vacuum were used for loading and elution of samples with appropriate solvent mixtures.

**Description of the RAF Molesworth Sewage Treatment (STW) studied with sampling location**

Royal Air Force (RAF) base Molesworth is located in Molesworth, Suffolk, approximately 20 miles from Cambridge. There are no residents on the base. However, the base operates 24 hours per day with approximately 1,200 personnel (over 2 shifts), with an overnight staffing around 400 personnel. The STW is located within the RAF base and utilises activated sludge for secondary biological treatment. The plant is consented to discharge a maximum of 360 m³ day⁻¹ (0.1Mgal day⁻¹). The average volume treated by the works is approximately 78.4 m³ day⁻¹ (0.02 Mgal day⁻¹). RAF Molesworth has separate wastewater and surface water drainage networks and wastewater is pumped from across the base to a biological treatment works where it is treated prior to discharge to a
tributary of ‘Cock Brook’. The existing works which is shown schematically in the diagram below in Fig. 1 has four different stages: pre-treatment, primary treatment, secondary treatment and reed beds. The sewage plant process starts from terminal pumping station where sewage is pumped to a raised inlet works and screened. A storm overflow diverts excess flow to the storm tanks and settled material accumulates in the storm tanks which are always manually cleared. Wastewater gravitates to a primary tank which removes coarse materials and a recently installed the submerged aerated filter (SAF process) removes biochemical oxygen (BOD), ammonia and finely dispersed solids. This new process replaced the previous plastic media filter system. Humus tanks are used to remove any secondary settleable material. The recirculation pumping system has not been used as it was not installed to ensure the required wetting rate of the old plastic media filter was maintained. The reed beds polish the final effluent to required quality standards before being finally discharged to the neighbouring rivers.

The supernatant constitutes the effluents that are passed forward. The excess secondary sludge, the solids from primary sedimentation and sedimentation of solid wastes and liquid stream in humus tanks are recycled back into the inlet of the plant. Co-settled sludge is pumped from the primary sludge well to a sludge storage tank. Decant liquors can be removed from the tank by an adjustable decant arm. The sampling points for the analysis are: (i) inlet to the grit removal unit (influent wastewater), (ii) inlet to primary sedimentation tank (primary sludge), (iii) inlet to submerged aerated filter reactor (SAF-1), (iv) mixed SAF, (v) secondary sedimentation unit (humus sludge) and (vi) outlet of sedimentation unit (effluent) [36].

Figure 1: Diagram of the Molesworth sewage treatment work at RAF showing location of the sampling points (SP1=primary sludge tank; SP2 =submerged aerated filter tank; SP3 = mixed submerged aerated filter tank and SP4 = humus tank [36]

The physico-chemical characterization of the wastewaters and recovery studies

Total suspended solids (TSS), chemical oxygen demand (COD), organic carbon (OC), ash and pH were determined by standard methods [37-39].

Recovery rates of the drugs depended on the nature of the samples collected from each RAf sampling point: primary sludge (PS), submerged aerated filter -1 (SAF-1), mixed secondary aerated filter (MSAF) and humus sludge (HS) and Stoke Bardolph STW sampling points: influent wastewater -1, influent wastewater – 2, primary effluent, secondary effluent – North, secondary effluent – South, and secondary effluent – New. Recovery experiment for 1L of wastewater were spiked at mixed concentrations of 100 ug mL\(^{-1}\), while the liquid phase of the raw sewage samples were spiked with known concentration of drugs (50 mg L\(^{-1}\)) and analysed in exactly similar ways as in the full batch studies.

Experimental batch studies

During primary and secondary wastewater processes, the fate of cocaine, benzoycgonine, heroin, 6-monoacetylmorphine, morphine and diazepam were determined under different conditions in a series of jar tests. In a series of experiments with 250 mL of the aliquots of raw sewage in the conical flasks spiked with 1 mL of 12.5 mg of separate standard of drugs (not a mixture). Background concentrations of the six analytes were measured and none of the compounds under investigation were detected in the original sludge samples. The initial concentration was thus 50 mgL\(^{-1}\)equivalents for each of the six drugs of interest and each batch test was initially 0.5 mg of drug in 10 mL of raw wastewater or sewage samples.

The choice of 12.5 mg/250 mL of sample for each of the selected compounds was used to achieve optimal experimental strategy that would provide evidence of the presence of residual compounds at concentration in the lower ng L\(^{-1}\) range for the batch test after 3h duration. Therefore adequate spiking concentration for batch experiments was selected after initial trial experiment to determine adequate concentration that would allow measurable concentration of parent drug and associated degradation products. No possible evaporation occurred during the batch studies as aluminium foil caps were securely placed on the flasks with the jar tests carried out in the incubator to maintain a typical activated sludge plant constant temperature. Batch experiments were conducted at two temperatures of 19±0.5°C and lower abiotic temperature at 4±0.5°C. Sample were agitated using magnetic stirrer throughout to obtain homogenous sample of which 10 mL of batch sample was removed at every 15 min intervals. These subsamples were centrifuged (1500rpm for 5 min) and filtered using 0.45 µm cellulose acetate Whatman and the aqueous phase was extracted by solid phase extraction using Oasis HLB (500mg/6 mL) adsorbent (made up of a divinylbenzene/N-vinylpyrrolidone copolymer with both hydrophilic and hydrophilic properties) with very good recovery data[40] compared to other adsorbents such as MCX\(^{©}\) (500mg/6mL) [41], Isolute ENV+\(^{®}\) (500mg/6 mL) and Isolute PH\(^{®}\) (1000mg/6 mL) adsorbents [42], and Bond Elut Certify\(^{®}\) adsorbent [43]. The choice was based on the use of Oasis HLB\(^{®}\) (500mg/6 mL) in the extraction of cocaine and its metabolites in waste and surface water in the literature, and it was recommended as most suitable adsorbent for organic compounds because of its lower solvents usage, time, stability to pH range and over 75% recovery for most analytes in aquatic medium was achieved[35]. The solid phase was extracted by shaker extraction for 15 min after initial drying with about 2 g of anhydrous sodium sulphate followed by addition of 2 x 5 mL each of ethyl acetate and dichloromethane.

Gas chromatography mass spectrometry analyses were performed with an Agilent 6890GC coupled to Agilent 5975 inert XL mass selector detector (MSD; 2564,7 eV), using a capillary column (HP5-MS) (30.0 x 0.25mm x 0.25 um film thickness) with helium as carrier gas (1 mL min\(^{-1}\)). With sample injection in splitless mode, the analyte separation was achieved with the temperature programming: 50°C (hold 2min), rise to 300°C at 10°C min\(^{-1}\) and then held at 300°C for 3 min. The standard software supplied by the Agilent Chemstation (manufacturer) was used for data acquisition and analysis. The mass spectrometer was in electron impact (EI) ionization mode at 70eV. Quantitation was determined using total ion corresponding area (TIC) with the EI mass spectra recorded in
Operational issues encountered with batch studies.

Municipal STWs contain lot of different trace polluting substances received from many sources as earlier mentioned, therefore carrying out degradation studies of drugs and the analysis of their metabolites using solid phase extraction (SPE), derivatization, detection and confirmation by gas chromatography mass spectrometry (GCMS) in highly contaminated sewage samples would normally be met with some operational issues. To guarantee accurate and reproducible data in highly polluted sewage, some operational issues and treatment options were anticipated (see below). Considerable efforts were made to enable a simple, robust and complete picture of the degradation studies to model a chemical fate in the STW and our most suitable options in the situation are presented:

1. On the basis of precautionary measures after ensuring none of the compounds under investigation were detected in the original sludge, the samples from different processing units of RAF Molesworth STW in Cambridge were obtained to minimise unnecessary drug-drug interferences that may influence some chemical properties of drugs or inhibit their biodegradability potential.

2. Studies on samples from Stoke Bardolph STW, Nottingham were also conducted to see expected variability since the configuration of municipal treatment works vary in design capacity and location but both are considered for effects of degradation in different treatment facilities or sludge types.

3. The spiking concentration of 12.5 mg of each drug in 250 mL flasks was considered adequate after initial random degradation studies to allow measurable concentration in the lower ugL\(^{-1}\) range after 3h period of exposure.

4. Pre-selection of environmentally relevant compounds for batch studies were based on the initial results of the analysis of survey of water effluents from Stoke Bardolph, Nottingham STW which showed the presence of these drugs in the samples collected as well as their concentrations in other UK wastewater as reported in the literature.

Discussion

Spike recovery studies and characterizations of compounds.

The recoveries for the compounds were only done for the liquid phase of the sewage and since these recovery data were used for both liquid and solid phases it would introduce uncertainty. However, the aqueous phase data ranged between 75.8 – 96.2 % from different sewage matrices and are presented in Table 2 and the final results were adjusted for each drug accordingly to reflect the recovery rates. The results compares well with other discovery experiments carried out in other places, like the average levels of cocaine and its metabolites (benzoylcegonine, BZE) in the River Po which have shown recoveries of > 90% for the two compounds [35].

In a related investigation, 500mL of wastewater samples were filtered through micro-fibre filters and extracted by Strata-X™ SPE cartridge, the filtrate was adjusted to pH 6 with HCl with recovery for most analytes found in the region of 50-65% [44]. Cocaine (COC), benzoylcegonine (BE) and ecegoninemethylester (EME) have been determined on 100mL and 500mL in wastewater and surface water by a method that involved the use of SPE and LC-MS analysis [44] and the overall method variability was ≤10% for the influents, ≤ 5% for effluents and recoveries in wastewater were ≥ 80%.

Due to variability in the overall composition of wastewaters as a result of continuous discharges and potential matrix effects on degradation studies, the sewage sludge characterizations for wastewaters and sewage samples were analysed for total suspended solids (TSS), organic carbon (organic C), ash and chemical oxygen demand (COD) and results are shown below in Table 3.

Table 3 above shows the mean results as presented and explained in the worked calculation above to illustrate the total COD, organic C and TSS contents achieved from different samples collected from the two different STWs. The highest effluent COD concentration from both STWs was 6.2 mgdm\(^{-3}\)O\(_2\), and this was below the consent limit of 15 mg L\(^{-1}\) BOD shown in Table 4 [36], while the highest concentration of COD observed for influents were 216.8 mgdm\(^{-3}\)O\(_2\) (RAF Molesworth STW) and 48 mgdm\(^{-3}\)O\(_2\) (Nottingham STW), indicating the nature of sewage and different treatment processes can influence the kinetics of degradation [45]. The COD values obtained from the influent and effluent samples collected from Stoke Bardolph Nottingham and Molesworth STWs therefore compares well with the values reported for primary effluent (309 mgdm\(^{-3}\)O\(_2\) COD), food processing sewage (7249 mgdm\(^{-3}\)O\(_2\) COD), swine waste (67,444 mgdm\(^{-3}\)O\(_2\) COD), secondary effluent (35 mgdm\(^{-3}\)O\(_2\) COD), lagoon (27089 mgdm\(^{-3}\)O\(_2\) COD) and effluent (71 mgdm\(^{-3}\)O\(_2\) COD) in a study [46]. This would indicate that the values produced in this work are in line with typical STW [46], ensuring sewage characteristics in the current batch studies can be assumed to be representative of most municipal sewage types.

Similar studies carried out in two other places have also reported a range of 65 – 686 mgdm\(^{-3}\)O\(_2\) [47] and 86 – 2852 mgdm\(^{-3}\)O\(_2\) of COD [48] in sewage. In this current work, the difference in influent and effluent results as reported may form a basis of empirical relationship between COD removal and the quality of treatment processes of sewage or wastewaters and these functions may be used to develop a gauge for sewage treatment to confirm adequate efficiency so that effluent quality is sufficiently good.

Treatment of organic matter in an activated sludge plant has also produced 22.7 – 253 mg L\(^{-1}\) TSS [49] in a study, but in Nottingham and Molesworth STWs, the remaining suspended particulates after treatments represent the final effluent (TSS) concentrations found to be 5.5 mg L\(^{-1}\) (Molesworth STW) and 10.0 mg L\(^{-1}\) (Stoke Bardolph STW, Nottingham) compared to influent (TSS) concentrations of 797.9 mg L\(^{-1}\) (Stoke Bardolph, Nottingham) and 36243.0 mg L\(^{-1}\) (Molesworth STW) while 897.0 - 77386.5 mg L\(^{-1}\) of TSS were observed for sewage sludges from both STWs. However, it is important to note the large difference in the levels of TSS from influent and effluent from the two STWs as quoted as this was evidence of extent of removals. Since domestic sewage differs in strength due to strong temporal variation, function controlling sludge characteristic can only be measured when effluent performance is compared to influent data and this was satisfactory with respect to our experimental results of TSS from both STWs. In addition, the TSS found in the effluents of the two STWs was significantly less than the 30 mg L\(^{-1}\) consent limit set by UK Environment Agency Compliance - Discharge Consent as presented in Table 4 [36].

In our current work, the average concentration of organic carbon found in all the four sewage types collected from Molesworth STW was 0.94 g per 1.0 gram of sewage samples. The levels of organic carbon were expectedly higher in the sludge due to myriads of materials as they facilitate compound degradation and removal, since the extent of drug removal to particulates/solids depends on the amenability of drugs to
degradation on association to biological solids and possible volatilisation [50]. Unfortunately, direct comparison and evaluation of the organic carbon from sewage sample from the Stoke Bardolph STW Nottingham was impossible due to inability to obtain raw sewage due to site restrictions.

**Batch experimental results**

**Evaluation of degradation and removal of drugs in primary and secondary sludge treatment samples**

For our batch tests, a 3h contact time was selected (though 2h was average period of a process unit in RAF Molesworth STW under the hydraulic conditions) to extensively monitor the degradation processes. Samples of primary sludge and SAF-1 (250 mL) at 19± 0.5°C were spiked with 12.5 mg of each drug (cocaine, benzoylecgonine, heroin, morphine, 6-monoacetylmorphine and diazepam). The samples were mixed thoroughly and 2 x 10 mL aliquots were removed at timed interval (15 min) over a period of 3h. Results show the degradation of cocaine in both primary and secondary aerated sludge increased with exposure time with corresponding increment in their degradation products.

A very rapid abiotic removal was observed in the first 15 min of cocaine degradation in primary sludge in batch studies. This observation was rather different from generally accepted positions from the literature that no significant degradation occurs in primary sedimentation [51]. But over a period of 3h, the cocaine showed decline in concentration with its uneven distribution between both solid and aqueous phases in a pattern that reflects their hydrophobic/hydrophilic nature. As compounds become lesser in concentration, the degradation products such as egocine methyl ester and cocaethylene were simultaneously identified and quantified. As degradation progressed the degradation products pattern could not be properly followed due to their diffuse nature of being further degraded as they areformed. The benzoylecgonine (a principal hydrolysis product) could not be detected possibly due non – hydrolysis as cocaine has been reported to be stable in pond water in pH = 2 at 25°C for 5 days [35] or low detection. But the presence of egocine methyl ester and cocaethylene (other biodegradation products of cocaine) were observed confirming the presence of bio-degradation processes in primary sludge. However, compound removal from aqueous phase in sewage may not indicate their complete degradation.

However, the partition fractions of each batch test with drug and their related metabolites were analysed and related to sludge types under the same condition. Similar degradation was observed in both sludges showing that biological aeration sludge in secondary treatment had little influence. The sorption behaviour of compounds was assessed by solid-water partition coefficient (K<sub>s</sub> L/Kg) as calculated by C<sub>sorbed</sub>/SS.C<sub>soluble</sub>,where C<sub>sorbed</sub> = chemical concentration in sorbed phase, C<sub>soluble</sub> is concentration in aqueous SS = suspended solids). The K<sub>s</sub> values were calculated for each time period from batch studies data, the 2-3 HRT is the usual processing time in the Molesworth STW. The observed low solid-water partition coefficient for cocaine (K<sub>s</sub>&lt; 14) in both sludges indicated low sorption as the removal mechanism but since recovery experiment for the solid could not completed, further experiment is needed for confirmation. From the results, the K<sub>s</sub> values for cocaine and other drugs ranged from 1.2 – 68.1 were however generally very much lower than the range of 12300 – 37700 L/Kg calculated for detected ten quinolone and fluoroquinolone antibiotics in a municipal SWT [52].

Over 98% removal of cocaine was achieved in 3h. Comparing removal efficiencies from concentration of cocaine in raw primary sewage and SAF-1 gave about 10% difference in 2h. Also in every 15 min, empirical relationship exists between cocaine dissolved, sorbed and degraded as they all relate to each other and added up to 12500 ug. This approach was later applied in mass balance calculations to capture the degradation process and transport of compounds in STW units.

The pattern of degradation observed for cocaine was the same for benzoylecgonine (BZE) but with relatively higher degradation in primary sludge. As one of the major human metabolites of cocaine, its biodegradation studies in aquatic environment become important to understand the final fate of cocaine. In the current study, its sorption potential (K<sub>s</sub>&lt; 2.5) indicated biodegradation as predominant removal process compare to sorption to solids. But the removal efficiencies of BZE in both PS and SAF-1 also showed 10% difference in 2h.

Also, morphine is one of the metabolites of heroin; it was selected primarily to monitor its biodegradability and its final fate. Therefore, the result of a relative higher degradation of morphine within a biological secondary aerated sludge compare to primary sludge was observed from our batch studies, but like cocaine and BZE, a lower sorption potential of 0.1 – 1.3 made degradation a significant removal process with 85 – 99% and 94 – 100% removal of morphine.

Though many of the biological wastewater units have different characteristics, yet most compounds tend to exhibit general tendencies to accumulate to solids and sediments. But the removal rate of morphine appears to be related to degradation processes and less of sorption. Gradual removal rate of morphine in both primary and secondary sewage with the decline in the concentration of morphine may be due to biodegradation mechanism.

In this current work, comparable removals of benzoylecgonine with cocaine infer that sorption may not be the only removal mechanisms. Gradual decline in the concentration profile of benzoylecgonine, morphine, 6-MAM and diazepam were apparent but degradation products of the two compounds could not be identified in both primary and SAF-1. However, the measurement of the degradation products of heroin (morphine and 6-MAM) provided evidence of degradation in PS and SAF-1. Again, degradation products occurring simultaneously limited the accurate measurements of all metabolites as the degradation was going on.

Another human metabolite of heroin studied in both primary and secondary treatment sludge was 6-monoacetylmorphine (6-MAM). The idea was to observe the 6-MAM trend of degradation to know its final fate. Unlike the four compounds studied earlier, 6-ACM showed similar degradation in the primary sludge with corresponding low sorption potential (K<sub>s</sub>&lt; 9) and removal efficiency of between 98 – 100% in PS, but removal rates were relatively slower after 2h of exposure in SAF-1 (19 – 86%) from the result shown. In real time, after 2h treatment there are possibilities of most compounds in aqueous phase to pass on to the next treatment tank due to the average 2 HRT for RAF Molesworth. However, the observed variability in degradation pattern may likely make the removal of 6-MAM faster in primary sludge than in SAF-1. Heroin and diazepam follow the pattern observed in cocaine. The heroin has over 96% removal in both sludges, but, diazepam showed more removal in primary sludge.

**Removal of drugs during primary sewage treatment**

Figure 2 further demonstrates the degradation as a removal mechanism for all drugs at different rates with decline in various compounds concentrations distributed between aqueous and solid phases.
Table 1: Sewage sludge disposal in England, 2008-2011 [11]

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<td>1</td>
<td>255</td>
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*EfW = Energy from waste

Table 2: Recovery data for the compounds in aqueous phase (%) (n=3, mean ± STD).

<table>
<thead>
<tr>
<th>Drug</th>
<th>Aqueous matrix</th>
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<tbody>
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<td></td>
<td>PS</td>
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<tr>
<td>Cocaine</td>
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<tr>
<td>Benzoylecgonine</td>
<td>96.2±0.8</td>
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<tr>
<td>Heroin</td>
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<td>6-monoacetylmorphine</td>
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<td>Morphine</td>
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<tr>
<td>Diazepam</td>
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</tbody>
</table>

Note: PS (primary sludge); SAF-1 (submerged aerated filter-1); MSAF (mixed SAF); HS (humus sludge) and SB (Stoke bardolph primary influent)

Table 3: Characterization of wastewaters from RAF Molesworth and Nottingham STWs (June 2011)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>pH (Temp;°C)</th>
<th>TSS (mg/L)</th>
<th>Organic C (g)</th>
<th>Ash content (g)</th>
<th>COD (mgdm⁻³O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molesworth STW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>InfWW</td>
<td>8.5 (17.1)</td>
<td>36243.0</td>
<td></td>
<td></td>
<td>216.8</td>
</tr>
<tr>
<td>EffWW</td>
<td>7.8 (18.7)</td>
<td>5.5</td>
<td></td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>PS</td>
<td>5.7 (14.4)</td>
<td>77386.5</td>
<td>0.95</td>
<td>0.07</td>
<td>162.6</td>
</tr>
<tr>
<td>MSAF</td>
<td>5.7 (14.4)</td>
<td>8465.0</td>
<td>0.93</td>
<td>0.05</td>
<td>138.0</td>
</tr>
<tr>
<td>SAF-1</td>
<td>7.1 (14.6)</td>
<td>70793.5</td>
<td>0.95</td>
<td>0.07</td>
<td>82.0</td>
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<tr>
<td>HS</td>
<td>7.1 (14.2)</td>
<td>3563.5</td>
<td>0.94</td>
<td>0.06</td>
<td>52.4</td>
</tr>
<tr>
<td>Nottingham STW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>InfWW-1</td>
<td>8.4 (12.7)</td>
<td>797.9</td>
<td></td>
<td></td>
<td>36.0</td>
</tr>
<tr>
<td>InfWW-2</td>
<td>8.1 (12.1)</td>
<td>599.1</td>
<td></td>
<td></td>
<td>28.6</td>
</tr>
<tr>
<td>1 EffWW</td>
<td>7.7 (12.2)</td>
<td>897.0</td>
<td></td>
<td></td>
<td>48.0</td>
</tr>
<tr>
<td>2 EffWW</td>
<td>7.7 (12.3)</td>
<td>9.7</td>
<td></td>
<td></td>
<td>6.2</td>
</tr>
<tr>
<td>2 EffWW (north)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2 EffWW (south)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 EffWW (new)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: InfWW = influent wastewater; EffWW = effluent wastewater; PS = primary sludge; MSAF = mixed SAF; SAF-1 = secondary aeration filter; HS = Humus sludge; InfWW-1 = primary influent -1; InfWW = primary influent -2; 1 EffWW = primary effluent; 2 EffWW = primary influent (north); 2 EffWW = primary influent (south); 2 EffWW = primary influent (new).

Table 4: UK Department for Environment, Food and Rural Affairs [36]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Consent Limit (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biochemical Oxygen Demand (BOD)</td>
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</tr>
<tr>
<td>Ammoniacal Nitrogen expressed as N (NH₄-N)</td>
<td>5</td>
</tr>
<tr>
<td>Total Suspended Solids (TSS)</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 5: Data of illicit compounds and a pharmaceutical used in batch studies [44].
Table 6: Data of water-solid distribution coefficients of drugs in both PS and SAF at 19± 0.5°C (K<sub>d</sub>, Kg/L).

<table>
<thead>
<tr>
<th>Time(min)</th>
<th>COC</th>
<th>BZE</th>
<th>HER</th>
<th>6MAM</th>
<th>MOR</th>
<th>DIAZ</th>
<th>COC</th>
<th>BZE</th>
<th>HER</th>
<th>6MAM</th>
<th>MOR</th>
<th>DIAZ</th>
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</thead>
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<td>15</td>
<td>3.2</td>
<td>2.9</td>
<td>18.2</td>
<td>1.6</td>
<td>3.1</td>
<td>10.5</td>
<td>12.2</td>
<td>6.5</td>
<td>9.7</td>
<td>2.3</td>
<td>3.3</td>
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<td>5.3</td>
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<tr>
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<td>1.2</td>
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<td>10.7</td>
<td>9.9</td>
<td>8.2</td>
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<td>9.9</td>
<td>8.1</td>
<td>16.1</td>
<td>1.8</td>
<td>5.6</td>
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<td>7.0</td>
<td>-</td>
<td>18.7</td>
<td>5.2</td>
<td>7.4</td>
<td>51.5</td>
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<tr>
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<td>0.0</td>
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<td>6.4</td>
<td>18.6</td>
<td>10.2</td>
<td>-</td>
<td>12.0</td>
<td>6.3</td>
<td>7.9</td>
<td>46.0</td>
</tr>
<tr>
<td>135</td>
<td>4.4</td>
<td>15.6</td>
<td>0.0</td>
<td>2.2</td>
<td>5.0</td>
<td>21.2</td>
<td>8.1</td>
<td>-</td>
<td>18.7</td>
<td>5.4</td>
<td>5.5</td>
<td>43.4</td>
</tr>
<tr>
<td>150</td>
<td>4.0</td>
<td>18.9</td>
<td>0.0</td>
<td>3.1</td>
<td>7.4</td>
<td>29.5</td>
<td>12.4</td>
<td>8.7</td>
<td>24.4</td>
<td>7.0</td>
<td>8.1</td>
<td>46.1</td>
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<tr>
<td>165</td>
<td>3.6</td>
<td>25.7</td>
<td>0.0</td>
<td>5.1</td>
<td>6.7</td>
<td>32.2</td>
<td>8.8</td>
<td>8.2</td>
<td>12.8</td>
<td>5.3</td>
<td>7.3</td>
<td>69.9</td>
</tr>
<tr>
<td>180</td>
<td>2.7</td>
<td>31.9</td>
<td>0.0</td>
<td>7.1</td>
<td>4.6</td>
<td>66.7</td>
<td>10.6</td>
<td>6.3</td>
<td>15.1</td>
<td>5.2</td>
<td>5.1</td>
<td>68.1</td>
</tr>
</tbody>
</table>

Opiates

- Benzoylecgonine 1.3
- Heroin 1.7
- 6-monoacetylmorphine 1.6
- Morphine 0.9

Benzodiazepine

- Diazepam 2.9
Figure 2: Degradation of compounds in primary sludge at time (A) 15 min and (B) 3h, demonstrating the change in distribution/partitioning as drugs degrade at 19± 0.5°C.

In Figure 3, it can also be seen that all drug concentrations falls rapidly within the first hour of exposure to sewage with significant removals within the time of contact but slows down as biodegradation advances. Diazepam showed slower degradation but greater pattern of distribution in the aqueous phase as biodegradation progressed over 3 hour periods.

Figure 3: Plot showing combined concentrations of drugs in aqueous and solid phases in primary sewage sludge at 19± 0.5°C.

The concentration of compounds decreases with concurrent accumulation of metabolites such as ecgoninemethylester, benzoylecgonine and cocaethylene for cocaine, morphine and 6-monoacetylmorphine for heroin and nordiazepam for diazepam which were in turn being further biodegraded. A second experiment to evaluate the significance of adsorption or degradation on retention time and its effects on removal rates was carried out. The results in Figure 4 below shows the removal rates of different compounds due to their different association with primary sewage solids (suspended solids concentration of 77387 mg L⁻¹) and different degradation rates.

Figure 4: The effect of retention time on the removal of compounds during primary treatment processes.

The two mechanisms were significant in the removal of compounds in the primary sedimentation unit over the range of retention times with more than 80% removal achieved within the first hour of contact.

Removal of drugs during secondary sewage treatment:

All six compounds exhibited significant but different removal rates over 3h retention time and the results are presented in Figure 5.

Figure 5: Degradation of compounds in SAF-1 sludge at time (A) 15 min and (B) 3h, demonstrating the change in distribution/partitioning as drugs degrade at 19± 0.5°C.

The illustration of combined concentrations of drugs in aqueous and solid phases in the same secondary sewage sample at 19± 0.5°C is shown in Figure 6. Most compounds expectedly showed greater degradation in biological secondary sewage compared to the pattern observed in primary sludge in Figure 6.

In Figure 7, the effect of retention time on the removal of compounds during the secondary sewage processes can be seen with 6-monacetylmorphine, benzoylecgonine and cocaine showing average removal rate in the first hour of contact. Since others exhibited maximum removals at the same period of exposure, it was found that the removal of compounds at 19±

Table 7: Adsorption of compounds onto sludge of different suspended solids concentration (%) in 3h

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Suspended solids (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>77386.5 (PS)</td>
</tr>
<tr>
<td>Cocaine</td>
<td>0.08</td>
</tr>
<tr>
<td>Benzoylecgonine</td>
<td>0.51</td>
</tr>
<tr>
<td>Heroin</td>
<td>0.00</td>
</tr>
<tr>
<td>Morphine</td>
<td>0.59</td>
</tr>
<tr>
<td>6-monoacetylmorphine</td>
<td>0.03</td>
</tr>
<tr>
<td>Diazepam</td>
<td>4.06</td>
</tr>
</tbody>
</table>
0.5°C was favourable being the normal operational temperature of most STWs.

Figure 6. Plot showing combined concentrations of drugs in aqueous and solid phases in secondary sewage sludge (SAF-1) at 19±0.5°C.

Figure 7: The effect of retention time on the removal of compounds during secondary treatment.

Comparison of Kd values to LogKow data.

The octanol-water partition coefficient (Log Kow) is a laboratory-measured property of a substance that is recognized and are used extensively in environmental chemistry as it provides a thermodynamic measure of the tendency of the substance to prefer a non-aqueous or oily phase rather than water (i.e. its hydrophilic/lipophilic balance). But the water-solid partition coefficient (Kd) measured for the selected illicit drugs and abused pharmaceuticals in the current work were generally higher compared with literature Log Kow data range of 0.9 – 2.9 in Table 5 as against 1.2 – 69.9 in Table 6 for the drugs. Again, calculating of Kd changes at the timed interval of 15 minutes for 3h could introduce uncertainties as the values would be higher with higher recoveries from the sludge types. However, Table 6 below generally show the relatively higher Kd values in secondary sludge compared to primary sludge with diazepam showing greater values in both sludge types.

Evaluation of biotic versus abiotic degradation

Further batch tests to evaluate biotic and abiotic degradation were carried out with a 250 mL of unfiltered primary sludge samples of the same suspended solids concentration (77387 mgL⁻¹) measured in a flask, refrigerated at 4±0.5°C for 30 min to inhibit biological activity before the sample was spiked with drugs. Both biologically active and inactive samples were taken at 15 min for 3h. Results show the cocaine faster degradation process at biotic temperature of 19±0.5°C and a relatively slowly abiotic process at 4±0.5°C were observed. The low temperature inhibited the biological process as gradual transformation of initial compound concentration to degradation products at the low temperature have demonstrated biodegradation process and chemical hydrolysis as two major removal mechanism, as there is no loss through volatilization [53]. Since gradual decline in the levels of cocaine were observed in spite of microbial inhibition, therefore it was correct to assume that bio-degradation was part of the removal processes and not only chemical degradation and reported in the performance differences of both activated sludge and trickling filters experiment [54].

Several reports of biological degradations such as the fate and behaviour of endocrine disrupters in wastewaters treatment processes in which the degradation of nonylphenolic surfactants in activated sludge batch tests and their removals were not by biological processes alone have been shown [55]. In the behaviour of the s-triazine herbicides, atrazine and simazine, during primary and secondary biological waste water treatment [56], the removal of s-triazine was also not by bio-degradation as the primary degradation products in the two experiments were not obvious hence their removal was sorption to the solids. However, the observed rapid abiotic removal of cocaine was in contrast to the observation of Gheorghe et al (35) in their “analysis of cocaine and its principal metabolites in waste and surface water using solid-phase extraction and liquid chromatography-ion trap tandem mass spectrometry” where cocaine was reported to be stable for 5 days at 20°C. Stability of cocaine and benzoylecgonine may be influenced by matrices due to differences in bacteria population that may aid biodegradation. Apart from chemical hydrolysis of cocaine to benzoylecgonine, another bio-degradation product of cocaine is ecgoninemethylester at pH = 2 and its formation may or may not be as rapid depending on the matrix composition. However, significant removal of cocaine and other compounds may still not indicate complete degradation as some might undergo partitioning into solid phase. Since the recovery experiment for the solid phase was not separately conducted and this may have introduced uncertainty. Further study is therefore needed to confirm set conclusions to understand the partition of cocaine especially in primary sludge [54].

Nevertheless, treatment processes may use temperature strategy to optimise the removal of compounds from convective sewage works during degradation.

Figure 8 further demonstrates how microbial inactivity has slowed down metabolic processes with obvious relative slower changes in concentrations observed indicating the degradation of compounds were both biological and chemical with an increase degradation products and greater partitioning in solid phases.

Figure 8: Degradation of compounds in primary sludge at abiotic conditions (4±0.5°C) demonstrating the change in distribution/partitioning at time (A) 15 min and (B) 3h.
In the current work, the effect of suspended solids on the removal of compounds was done by evaluating the levels of compounds adsorbed onto the solids in primary sludge at 19±0.5°C. The changes suggest chemical degradation of compounds indicating that the degradation was both biological and chemical. The temperature change affects the rate of removal of compounds with the $K_d$ values of diazepam, heroin, morphine and benzoylecgonine showing greater sorption at 19±0.5°C while 6-monoacetylmorphine and cocaine were better sorped at 4±0.5°C.

### Evaluation of suspended solids on the removal of compounds

High removals of organic compounds during primary treatment have largely depended on water-solid partition coefficient ($K_d$) values which normally determine the degree of partitioning of compounds between aqueous and solid phases [52]. One of the major removal mechanisms of compounds is the association with the suspended and settleable solids which are removed in sludge after sedimentation in the primary sludge. In the secondary treatment processes, transformation or accumulation of organic pollutant onto the sewage sludge matrix depends on factors like:

i. Sorption onto the surfaces of the biological solids or association with fats and oils
ii. Chemical degradation such as hydrolysis
iii. Biodegradation
iv. Volatilisation

In the current work, the effect of suspended solids on the removal of compounds was done by evaluating the levels of compounds adsorbed onto the solids in primary sludge at 19±0.5°C.

The results in Table 7 indicate that in PS, 0.08% of cocaine was sorbed onto solids, further showing adsorption as one of the removal mechanisms with significant removal of diazepam in both primary and secondary sewage samples, compared to cocaine, benzoylecgonine and 6-monoacetylmorphine removals in secondary sludge. Heroin and morphine exhibited negligible associations with the suspended solids and therefore have minimal removals in both primary and secondary sludge samples.

Figure 9 below further confirmed the degradations were temperature independent as chemical hydrolysis did occur for all compounds at low temperature.

**Figure 9: Plot showing combined concentrations of compounds in aqueous and solid phases in abiotic conditions (4±0.5°C).**

Inhibition of the biological activities in the samples was expected at 4±0.5°C to slow the metabolic processes. Observed changes in the concentration indicating that the degradation was chemical with possible biological processes may be involved. No changes in the concentrations would have been observed if degradation were only biological, but that was not the case here as metabolic processes though were slowed down compared to degradation at 19±0.5°C. The changes suggest chemical degradation of compounds indicating that the degradation was both biological and chemical. The temperature change affects the rate of removal of compounds with the $K_d$ values of diazepam, heroin, morphine and benzoylecgonine showing greater sorption at 19±0.5°C while 6-monoacetylmorphine and cocaine were better sorped at 4±0.5°C.

Further comparison of the effects of adsorption on the removal of compounds at abiotic (4±0.5°C) and biotic (19±0.5°C) temperatures exhibited similar adsorption pattern (Fig. 10). However, heroin, cocaine and benzoylecgonine showed greater adsorption at chilling temperature whereas morphine and diazepam exhibited better adsorption at biotic temperature. The sorption by organic compounds has therefore be reported with log $K_{ow}$< 2.5 (low sorption potential), log $K_{ow}$> 2.5 and < 4.0 (medium sorption potential) and log $K_{ow}$ > 4.0 (high sorption potential) for chemicals that partition to organic phases to estimate a clear relationship with the degree of partitioning of contaminants during treatment [10].

The solid-water partition coefficients ($K_d$) in the current study were in the range for cocaine (0.2 – 0.9), benzoylecgonine (0.2 – 2.5), morphine (0.2 – 1.3), 6-monoacetylmorphine (0.1 – 0.5), heroin (0.7 – 1.7) and diazepam (2.1 – 13.7). The association of diazepam with biological solids may have exhibited adsorption as an important removal mechanism during primary and secondary wastewater treatment while other drugs have no significant adsorption. Also, removal efficiencies above 75% in primary sludge and biological secondary sludge for all the compounds were observed. The $K_d$ values of compounds studied in this work showed positive correlation with their removal efficiencies as reported for ten quinolone and fluoroquinolone antibiotics in sludge samples [52].

### Effect of nature of sludge on degradation

The effects of degradation of compounds with respect to the nature of sludge sample show results obtained from the primary sludge samples collected at Molesworth and Stoke Bardolph Nottingham STWs.

The ability of sewage treatment works to design removal processes that enable interactions with natural solid particles (sediments, microorganisms, clay) and added materials (coagulants, active carbon) in facilitating the physical-chemical removals of compounds by flotation, settling or by biodegradation are dissimilar. Even difference in bacteria population and diversity could exist in different municipal treatment works giving rise to different degradation rates.
Municipal treatment works vary in design capacity and location and this has almost certainly resulted in variations in degree of degradation (Figure 11).

Figure 11: Degradation of cocaine in (a) Molesworth and (b) Nottingham STWs, comparing reductions in parent drug over 3h as drugs degrade at 19± 0.5°C.

The similarity in degradation and removal profiles as shown from the two STWs where samples were collected surprisingly showed no significant effects of nature of primary sludge samples on degradation, the only difference is the morphine data. Both have high values after 15 mins, and low values after 3hours. Variability in the values of TSS and COD as shown in the characterization (Table 3) is based on Stoke BardolphSTW Nottingham and Molesworth STWs suggesting many treatment processes exist with different requirements based on peculiar inflow variability to solve problematic situation by adjusting operating conditions.

The degradation products (metabolites) found for cocaine were benzoylecgonine, ecgonine methyl ester and cocaethene and heroin produced morphine and 6-monoacetylmorphine. Attempt to quantify these products were difficult due to their diffuse nature as these compounds were futher being degraded simultaneously as they were been generated from initial corresponding drugs. While other polar degradation products could also not be detected and accurately measured possibly due to the method of analysis or incomplete derivatisation, duplicate measurement of the concentration levels of drugs dissolved in aqueous phase and those sorbed to solid phase were removed from initial concentration to obtain degradation levels.

Finally, benzoylecgonine, morphine and diazepam showed relatively higher degradations in sludge-samples from Molesworth compared to Stoke BardolphSTW Nottingham samples. But as part of the operational challenges encountered as mentioned above, inability to obtain extensive samples from different processing units of the Stoke BardolphSTW, Nottingham limited the empirical comparison between the STWs to only TSS and COD contents. The primary wastewater effluent from primary sedimentation tank was the only access we had due to site restrictions.

Conclusions
In the current work, six representative compounds of classes of illicit drugs (cocaine, benzoylecgonine, heroin, 6 monoacetyl morphine, morphine and diazepam (pharmaceutical) were studied and these drugs exhibited comparable removals when in contact with both primary and biological secondary treatment sludge during the batch studies of 3h exposure time. The compounds were comparably dissolved, degraded, adsorbed and distributed between both solid and aqueous phases in a pattern that reflects their hydrophobic nature as degradation progressed. Observed rapid removals were exhibited in the first few minutes of contact with both primary and secondary sewage samples with increase in the degradation products as compounds exposed to microbial and chemical hydrolysis but the rate slows down as availability of nutrient source reduces. Elements of this work reaffirm existing knowledge and data derived from batch studies, removal rates and their application to Molesworth and Stoke Bardolph STWs are the novel aspects of this thesis. The main conclusions for the novel work are presented in 4 bullet points:

- A number of degradation batch studies of cocaine, benzoylecgonine, heroin, morphine, 6-monoacetylmorphine and diazepam on sludge samples at two different temperatures showed consistent duplicates results with the degradation of compounds at 19 ± 0.5°C relatively greater but still occurred slowly at 4 ± 0.5°C, demonstrating that degradation was both biotic and abiotic but the degradation of compounds at 19 ± 0.5°C was faster than at 4 ± 0.5°C, by between 5 and 10%. Both biological and chemical degradations affects the removal of compounds in different rates at 4 ± 0.5 °C, the degradation/partitioning is therefore temperature dependent.
- The characterization of the sewage sludge of RAF Molesworth and Stoke Bardolph STW, Nottingham demonstrated strong variation in concentration strengths of TSS, CODs and occasional pH changes. In the RAF Molesworth STW, the TSS was 36243.0 mg L⁻¹ (influent) and 5.5 mg L⁻¹ (effluent), while Stoke Bardolph had 797.9 mg L⁻¹ (influent) and 8.6 mg L⁻¹ (effluent). The COD at RAF Molesworth was 216.8 mgdm⁻³O₂ (influent) and 1.8 mgdm⁻³O₂ (effluent), while Stoke Bardolph had 36.0 mgdm⁻³O₂ (influent) and 3.6 mgdm⁻³O₂ (effluent). The pH ranges of 7.8 and 8.4 were found between the influent and effluent wastewaters of the two STWs. Also, the average ash and organic carbon contents of the sewage samples were 0.94 g/g and 0.06 g/g, respectively.

Work encompassed directly measures illicit drug removal rates in laboratory studies for the first time and improvement over prior study where assumptions on removal rates were made. With refinement, the capabilities of the current experimental batch data in generating removal rates of drugs have however been clearly demonstrated and applied, the conceptual approach developed may be very useful to obtain influent information of any organic compounds in real life (STWs) situations.

References


