Behaviour of Pharmaceutically Active Compounds in Contact with Reactive Media in Simulated Ground Water

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Science
in
Earth Sciences

Waterloo, Ontario, Canada, 2008

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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ABSTRACT:

Water treatment approaches for pharmaceutically active compounds (PhACs) are restricted by the chemically-variable nature of the PhACs themselves, each successful in treating only a small number; or the adaptability or expense of the treatment system. Minimal study has taken place concerning novel, affordable, amendable treatment media that can be employed on numerous scales and water types, with the potential to treat a variety of PhACs and other water contaminants. This study evaluates the removal of a suite of environmentally relevant pharmaceuticals from water in response to contact with reactive media and/or natural organic matter. Experiments were conducted with batch samples containing a media of interest in simulated ground water spiked with carbamazepine, caffeine, naproxen, gemfibrozil, ibuprofen, sulfamethoxazole and clofibrate, each at an environmentally relevant concentration of 2-2.5 $\mu g\ l^{-1}$. Media investigated included: Stelco-BOF slag (STB), woodchips (WC), Borden sand (BDS), zero valent iron (ZVFe), and granular activated carbon (GAC). Water samples were analyzed for basic water quality parameters and pharmaceutical concentrations were calculated by internal and external calibration of HPLC-MS/MS results. Calculated pharmaceutical removal efficiencies were based upon percent changes in concentration between initial and final measurements. Pharmaceutical removal was observed for all investigated media, with success varying between media and pharmaceutical types. The greatest percent removal, of >99.88% was observed for all PhACs, with concentrations dropping below the limits of detection (LOD) of 3-189 $ng\ l^{-1}$, in GAC and ZVFe-GAC mixtures; the smallest percentage removal when considering all media, of 0.0%, was exhibited by ibuprofen and naproxen in STB, BDS and WC samples. The greatest removal was observed within the first 24 hours for the majority of the drugs that showed measurable removals. Results also indicated that the addition of activated carbon to zero valent iron may enhance the reactivity and/or lifespan of the media.

ACKNOWLEDGEMENTS:

I would like to thank my supervisor Dr. Carol Ptacek for her guidance and contribution to this research; and for providing me the possibility of conducting research in what is becoming an increasingly consequential field. I would like to bestow my gratitude upon my thesis committee members, Dr. Will Robertson and Dr. David Blowes, for their insight and recommendations.

I would like to express notable gratitude to Laura Groza for her help in all aspects of laboratory work, her unfailing ability to address questions of any kind and her essential role in the HPLC pharmaceutical analyses. As well, I bestow my gratefullness upon Corina McDonald, for her assistance in laboratory analyses.

A special thanks goes to Matt Lindsay, for always seeming to have the answers, and for providing an incredible amount of encouragement, guidance and support.

I would like to thank Kelly Stafford for being a sounding board, consipirator and great ali.

Finally I would like to thank my parents, Frank and Connie Boonstra, and Mike Williams for their love and support.

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1 INTRODUCTION:

The body uses only a small portion of an administered pharmaceutical; the remaining portion is excreted. Often this excreted portion is relatively unaltered or scarcely modified by metabolism, being reduced, oxidized, hydrolyzed, alkylated, or dealkylated through phase I metabolism, or conjugated to polar molecules such as glucuronides through phase II metabolism, to assist with drug clearance from the body (Cunningham, 2004). These metabolic changes are often undermined during sewage treatment; and thus oxidation-reduction reactions as well as cleavage of conjugates can convert even metabolized compounds to the original active parent pharmaceutical, allowing its entrance into the aquatic environment (Herberer, 2001).

However, parent pharmaceuticals are not the only compounds of concern. Pharmaceutical metabolites, conjugated or otherwise are suspected to be present at environmentally higher concentrations than their parent compounds; and given the potentially more toxic nature of some of these compounds, or their ability to chemically revert to an active form; these compounds deserve further research as well (Dorne et al., 2007; Brody et al., 2005). For example, studies by Miao and Metcalfe (2003) indicate that hydroxylated carbamazepine metabolites occur at higher concentrations in wastewater than the parent pharmaceutical. Recent studies are thus investigating a broader scope, addressing not only parent pharmaceuticals but pharmaceutically active metabolites as well. A number of studies have indicated that pharmaceutically active compounds (PhACs), including both pharmaceuticals and their active metabolites, are neither efficiently removed by wastewater treatment, nor biodegraded; and thus, the unchanged compounds are often discharged from sewage treatment plants into receiving waters (Herberer, 2002;; Halling-Sørensen et al., 1998;

Daughton and Ternes, 1999; Wilken et al., 2000). During recharge these receiving waters along with other contaminated surface water, landfill leachate, manufacturing residues, and leaking city sewer systems are pathways for PhAC-contaminated effluent to leach to underlying aquifers (**Figure 1.0**). More than eighty micro-pollutants, including pharmaceutical compounds and drug metabolites, have been identified at concentrations up to 10 $\mu g\ l^{-1}$, in surface waters and municipal wastewaters (Jones et al., 2005; Castiligioni et al., 2006; Skoumal et al., 2006).

Recent studies have indicated the presence of a large number of pharmaceuticals and personal care products (PPCPs) in groundwater as well. **Table 1.0** briefly outlines some recent studies documenting the occurrence of PhACs and PPCPs in groundwater. An investigation of water supply systems found the occurrence of 26 PhACs; seven of which were present in drinking water, 16 in groundwater and post-treatment effluent, and three PhACs that were observed in both (Collier, 2007). Studies conducted in Berlin, Germany, indicate that PhACs have entered a cycle originating and concluding with humans. PhACs travel from administration, to excretion, entering municipal sewage treatment plants, then surface and groundwater recharge, and returning back to humans via drinking water (Herberer, 2001).

The concentrations of PhACs in groundwater have been observed in the $\mu g\ l^{-1}$ level; and while this level of exposure may pose little risk to adult humans, the same may not be true for fetuses, infants or children and other organisms. Children have been shown to have up to an eight fold greater risk of adverse effects to PhAC exposure; and are potentially being exposed to several PhACs contraindicated, or not established as safe for pediatric use (Collier, 2007). At the currently observed levels of documented PhAC exposures, it can take anywhere

from as little as 3.4 years to 34,000 years to ingest a single clinically used dose (Collier, 2007). Children, however, are not the only ones susceptible to low PhAC exposures, pregnant women are also at risk; or to be more precise, the developing infant. Women over the course of a pregnancy are inadvertently exposed to a number of drugs that are teratogenic, ingesting up to almost 13% of a single dose over 36 weeks (Collier, 2007). Post-natal exposure to PhACs during breast-feeding is also grounds for concern (Collier, 2007).

Whereas changes in physiological parameters are not immediately evident, sub-clinical doses are known to cause effects at the cellular and organ system levels; and thus, developing fetuses and children subjected to chronic exposure may undergo long-term alterations in organ systems and/or structural function. Developmental patterns for life, as well as growth, are established during the fetal period, and subtle changes attributed to chronic PhAC exposure during this time may manifest into evident physiological, morphological or cognitive outcomes (Collier, 2007). Therefore, whereas concentrations may appear low in ground and drinking water, chronic exposure to these low levels may harm the developing population, who is unable to process PhACs.

The potential risks of chronic low level PhAC release into the environment and the potential ecological effects are increasing researched and noted for their significance (Jørgensen and Halling-Sørensen, 2000; Stuer-Lauridsen et al., 2000; Kümmerer, 2004). The design of PhACs, to be persistent in the body and to cause a specific biological response, makes their release potentially harmful to aquatic flora and fauna. Whereas information concerning chronic toxicity of human PhACs to biota is still limited, previous and current investigations have indicated chronic toxicity for algae, invertebrates and fish species (Triebskorn, 2007). Research with aquatic organisms indicates that low concentrations of

PhACs have increased toxicity when present in a mixture with other PhACs, as they usually occur in the environment. Whereas the concentration of each component PhAC may be at a level independently confirmed to have little to no effect, the mixture itself may be toxic. The toxicity of the mixture follows the concept of concentration addition, with compounds acting in an additive fashion (Triebskorn et al., 2007). Recent investigations by Cleuvers (2004) supported such findings, indicating that diclofenac, ibuprofen, acetylsalicylic acid and naproxen show greater toxicities as a mixture than as individual compounds. The effect of chronic PhAC exposure must include the sensitivity of specific organisms, such as those in early development. Accordingly, the complete exposure pathway must be considered when evaluating the environmental risk assessment for PhAC release.

With the unknown potential consequences of chronic PhAC exposure it is not surprising that treatment of pharmaceuticals in water has been and is currently a focus of investigation. A great deal of data has been collected reflecting waste water and drinking water treatment for PhACs; **Table 1.2** briefly outlines some of the recent studies. Little exploration has occurred, however, concerning new passive techniques comprised solely of affordable, amendable treatment media that can be employed on numerous scales and water varieties, from surface and wastewater to groundwater treatment.

Thus the objective of this study was to assess the removal of environmentally relevant pharmaceuticals from water in response to contact with reactive media and/or natural organic matter that are highly available, affordable, and offer the advantage of being low maintenance passive systems. The investigation explores the potential sorption and/or chemical degradation of these PhACs by these media using pharmaceutically spiked batch reactors.

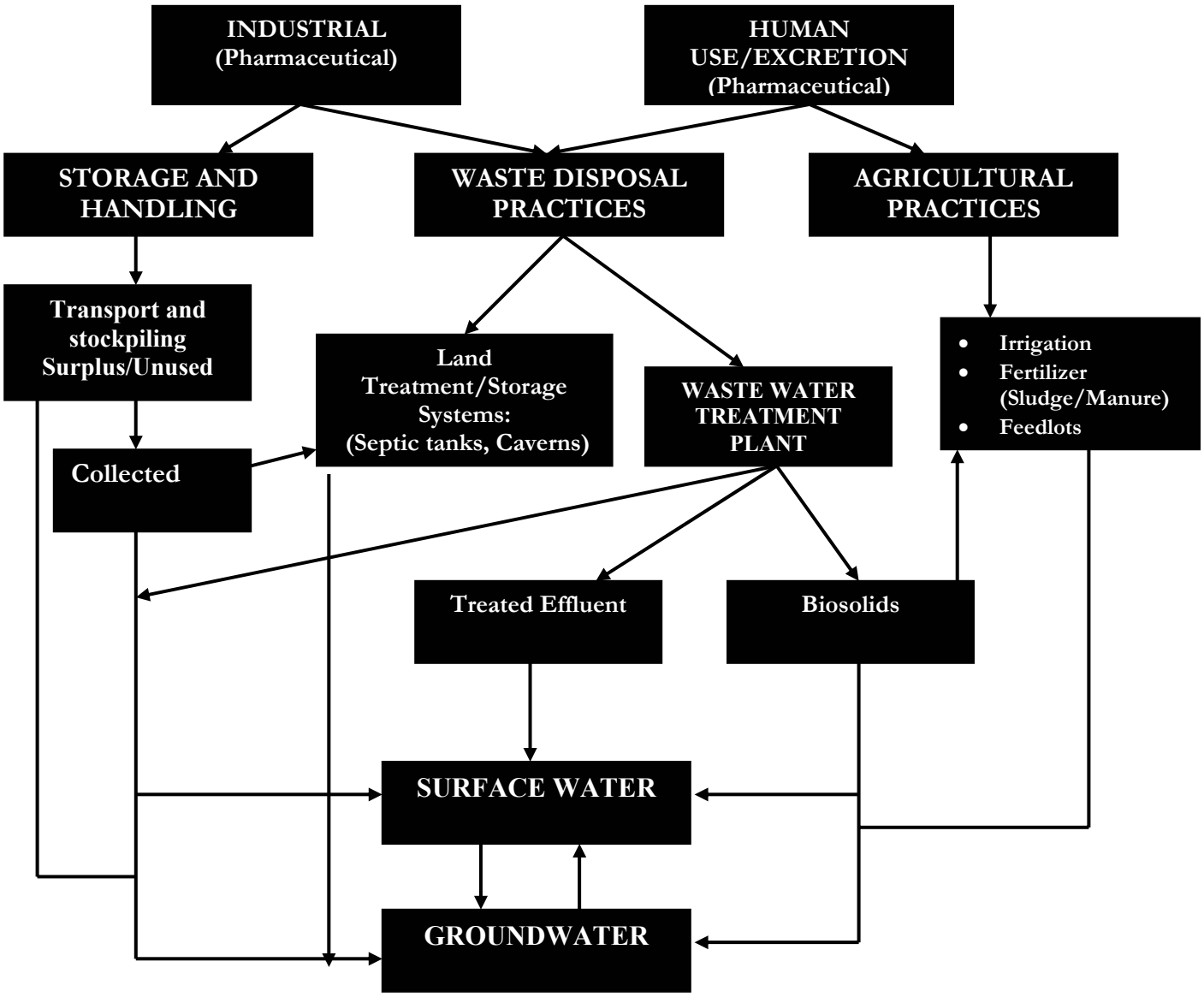

Figure 1.1 Potential sources of PhAC contamination to surface and ground water

Table 1.1: PhAC occurrence in groundwater indicated by previous studies

Pharmaceutically Active Compound	PhAC Use	Reference for ground water detection
Acetaminophen	Antipyretic	Hinkle et al., 2005; Heberer et al., 2002
Benzafibrate	Lipid regulator	Clara et al., 2004
Caffeine	Stimulant	Seiler et al., 1999; Buerge et al., 2003; Hinkle et al., 2005; Godfrey et al., 2007; Seiler et al., 1999
Carbamazepine	Anticonvulsant, Anti-manic, antidepressant	Seiler et al., 1999; Drewes et al., 2003 ; Buerge et al., 2003; Clara et al., 2004; Godfrey et al., 2007; Snyder et al., 2004 ; Heberer et al., 2002; Heberer et al. 2004; Godfrey et al.; Snyder et al., 2004
Cimetidine	Antiasthmatic	Kolpin et al., 2002
Codeine	Analgesic	Kolpin et al., 2002
Cotinine	Nicotine metabolite	Kolpin et al., 2002; Stackelberg, 2003; Godfrey el al., 2007;Barnes et al., 2004
Clofibric Acid	Lipid regulator	Heberer et al., 2002; Sheytt et al.., 2007 ; Heberer et al., 2004
Diclofenac	Non-steroidal anti-inflammatory (NSAID)	Heberer et al., 2002; Clara et al., 2004 ; Heberer et al., 2004
Diazepam	Anti-anxiety	Heberer et al., 2002
Diltiazem	Blood pressure control	Kolpin et al., 2002
Erythromycin-18	Antibiotic	Kolpin et al., 2002; Snyder et al. 2004
Fluoxetine	Antidepressant	Kolpin et al., 2002; Snyder et al, 2004
Fenofibrate	Lipid regulator	Heberer et al., 2002
Gemfibrozil	Lipid-regulator	Heberer et al., 2002
Ibuprofen	NSAID	Heberer et al., 2002; Snyder et al., 2004
Iopromide	Contrast agent	Herberer et al., 2002 ; Clara et al. 2004
Lincomycin	Antibiotic	Barnes et al., 2004
Metformin	Antihyperglycemic	Kolpin et al., 2002
Naproxen	Analgesic	Drewes et al., 2003
Nicotine	CNS stimulant; nicotinic agonist	Albaiges et al., 1986; Rogers et al., 1986
Paraxanthine	Caffeine metabolite	Kolpin et al., 2002, 2004
Primidone	Anti-convulsant	Heberer et al., 2002; Scheytt et al., 2007; Drewes et al., 2003; Heberer et al., 2004
Ranitidine	Histamine	Kolpin et al., 2002
Salbutamol	Bronchodilator	Castiglioni et al., 2005
Sulfamethoxazole	Antibiotic	Hartig et al., 1999; Huang et al.., 2002; Hinkle et al. 2005; Godfrey et al. 2007 ; Heberer et al., 2002; Godfrey et al., 2007 ; Snyder et al., 2004
Trimethoprim	Antibiotic	Kolpin et al., 2002; Godfrey et al., 2007; Herberer et al., 2002; Snyder et al., 2004 ; Snyder et al., 2004
Triclosan	Anti-bacterial	Snyder et al., 2004 ; Barnes et al., 2004
Warfarin	Anticoagulant	Kolpin et al., 2002

Table 1.2: Previously studied techniques for PhAC removal and/or degradation

Treatment Type	Treatment Systems	Source of study:
Drinking Water Treatment	Adsorptive and oxidative processes: Aluminum sulfate; ferric chloride coagulants,chemical lime softening, powder activated carbon, ozone and chlorination	Westerhoff et al., 2005
	Nanofiltration (NF) membranes: (Trisep) TS-80 and Desal HL, NF with subsequent GAC filtration	Verliefde et al., 2007
	Ozone – oxidant	Renato et al., 2007 ; Cornelissen et al., 2006 ; Wenyi et al., 2006
	Chlorine dioxide – oxidant	Hubera et al., 2005
	AOPs: Advanced Oxidation Processes Photo-fenton reagent	Pérez-Estrada et al., 2005
	*Clarification (chlorination): $FeCl_3$ / Disinfection: NaClO / Granular-activated-carbon (GAC) filtration	Gibbs et al., 2007
	Advanced Oxidation Processes: Ultrasound (sonolysis) and Thermal degradation (pyrolysis)	Constable et al., 2008. ASAP
	Adsorption: micelles pre-adsorbed on montmorillonite *Micelles of benzyldimethylhexadecylammonium (BDMHDA)	Groisman et al., 2006
Wastewater treatment	Anaerobic Biotransformation/Adsorption/Settling /Volatilization /Plant Uptake /Photolysis	Conn et al., 2006 Bagnati et al., 2006
	Free Chlorine (chlorination/oxidation)	Boyd et al., 2005
	Denitrifying biofilter; Denitrifying/nitrifying Bacteria and Denitrifying/nitrifying activated sludge, Activated sludge	Vieno et al., 2007; Aga et al., 2006 ; Lema et al., 2005; Benito et al., 2005; Hideshige et al., 2006; Kronberg et al., 2005
	Neutral and anion-exchange polymers: (adsorption) Polystyrene–divinylbenzene Phenol–formaldehyde aliphatic acrylic, Aliphatic methacrylic Polystyrene–divinylbenzene Polystyrene–divinylbenzene aromatic acrylic	Butler et al., 2006
	Chlorination: Hypochlorite	Bedner and MacCrehan, 2006
	Irrigation: Soil aquifer treatment using activated sludge	Ternes et al., 2007
	*Activated Sludge treatment (AST) and Membrane Bioreactor (MBR) – biodegradation	Bernhard et al., 2006; Alder et al., 2005
	*Urine source-separation followed by… Treatment technologies: electrodialysis, bioreactor treatment, nanofiltration, struvite precipitation, ozonation	Escher et al., 2006
	**Coagulation–flocculation technique / **Flotation technique	Carballa et al., 2005
	WWT: 1) primary settling process; 2) activated sludge – denitrification); 3) phosphorous removal, gravity filtration, 4) disinfection	Foster and Thomas, 2005
	**Up-flow anaerobic stage reactor (UASR) Biomass = anaerobic digested sewage sludge – methanogenic bacteria	Chelliapan et al., 2006
Drinking and waste water treatment	Ferrate(VI) ($FeVIO_4^{2-}$, Fe(VI)), - oxidants	Mishra et al., 2006
	Advanced Oxidation processes: **O_3 (ozonation) and O_3/H_2O_2 (perozonation)	Babuna et al., 2007
	Membrane bioreactor (MBR) / Membrane filtration: Activated carbon/Reverse osmosis/Nanofiltration/Ultrafiltration GAC	Cho et al., 2007

CHAPTER 2: REVIEW OF TREATMENT METHODS FOR THE REMOVAL OF PHACS FROM WASTEWATER AND DRINKING WATER

As the pharmaceutical industry grows, advancements and new PhACs enter the marketplace everyday; and coinciding with this increasing variety of treatments is the increase in use of prescription and non-prescription pharmaceuticals. This greater use is equated with greater excretion of parent PhACs and metabolites to the envrionment because the body uses only a small portion of an administered dose. Thus, with each administered dose, we are not only treating ourselves, but also releasing PhACs to the environment (Cunningham, 2004).

Both pharmaceutical compounds and pharmaceutical metabolites are a concern in the aquatic envrionment. Changes to parent pharmaceuticals by metabolism, such as reduction, oxidation, hydrolysis, alkylation, dealkylation or conjugation assist in drug clearance from the body (Cunningham, 2004). However, these changes can be reversed by sewage treatment or environmental reactions, or they can result in more toxic compounds; leaving parent or potentially more pharmaceutically active compounds to enter the aquatic environment (Heberer, 2001). Recent studies are thus investigating a broader scope, addressing not only parent pharmaceuticals but pharmaceutically active metabolites as well; all of these compounds are addressed under the umbrella term of pharmaceutically active compounds or PhACs.

Recent studies have indicated the presence of a large number of pharmaceuticals and personal care products in surface water, wastewater, drinking water and groundwater. Greater than eighty micropollutants, including PhACs have been identified at concentrations up to 10 $\mu g\ l^{-1}$ in municipal wastewater and surface waters (Heberer, 2002; Jones et al., 2005; Castiligioni et al., 2006; Skoumal et al., 2006), and recent studies are documenting

widespread groundwater occurrence (**Table 1.1**). Numerous studies have indicated that PhACs are neither efficiently removed by wastewater treatment, nor biodegraded; and thus, the primarily unchanged compounds are often discharged from sewage treatment plants into receiving waters (Herberer, 2002;; Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Wilken et al., 2000). During recharge these receiving waters along with other contaminated surface water, landfill leachate, manufacturing residues, and leaking city sewer systems offer avenues for PhAC-contaminated effluent to enter nearby aquifers (**Figure 1**).

The uncertain end results of chronic PhAC exposure to humans and the ecosystem have made investigations into PhAC treatment to reduce exposure increasingly popular. An abundant mass of data has been compiled regarding primarily wastewater and drinking water treatment for PhACs. An appraisal of this large body of research resulted in the formation of the following review. This review involves selected tables explicating distinct details of the overall review, including the frequency of investigation, the collective success of particular treatments and PhACs, and the mode of studies employed in the investigations; as well as a final inclusive table providing detailed description of recently investigated media and treatment systems, the PhACs and water type involved, procedural particulars and results of each study..

Forty-one journal articles were reviewed and summarized in a comparison chart. Investigations ranged from small laboratory-scale batch experiments to field scale analyses of full functioning waste- and drinking water treatment plants; a number of studies had both a laboratory and field component, but laboratory-scale investigations predominated (Figure 2.1).

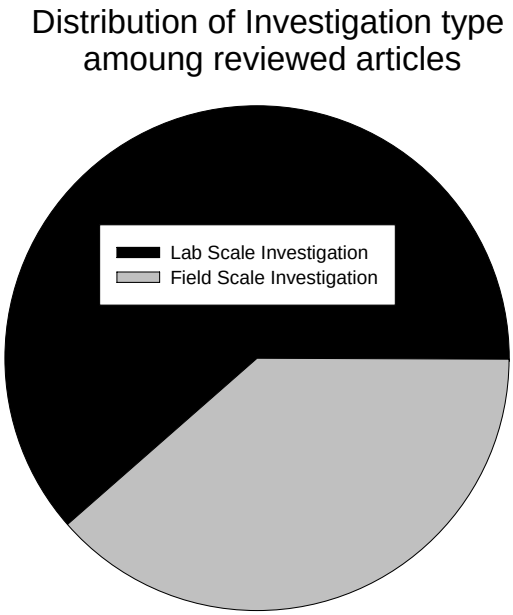

Figure 2.1 Distribution of investigation type amoung reviewed articles. Laboratory and field investigations were conducted in the reviewed studies; pie sections indicate the percentage of all investigations that were conducted at a laboratory-scale (black) or a field-scale (grey). Pilot-sized operations were considered laboratory-scale unless operated along side a full-scale operation.

Whether conducted in the laboratory or in the field, the basis for most investigations was the increasing ability to detect and quantify PhACs at environmentally relevant concentrations, as low as ng l^{-1}. Advances in technology and increased knowledge concerning appropriate handling, extraction and analysis of such compounds have greatly contributed to the increasing body of information concerning not only the occurrence of PhACs in the environment, but also the treatment of such compounds. For example, improvements from single quadrapole detectors and traditional ion trap systems to vastly improved ion trap systems and high sensitivity triple quadrapole detectors have provided improved assurance in the identification of trace concentrations of unknown compounds. Extraction procedures, such as solid-phase-extraction (SPE) were common amid the majority of analyses; as well as,

certain analytical devices such as high performance liquid chromatography (HPLC) and liquid chromatography tandem mass spectrometry (LC/MS/MS) and gas chromatography-mass spectrometry (GC/MS) systems. As depicted in **Figure 2.2** these analytical devices dominated the research; however, colourimetric methods, biological testing, IR and NMR analyses were also employed in a modest number of investigations.

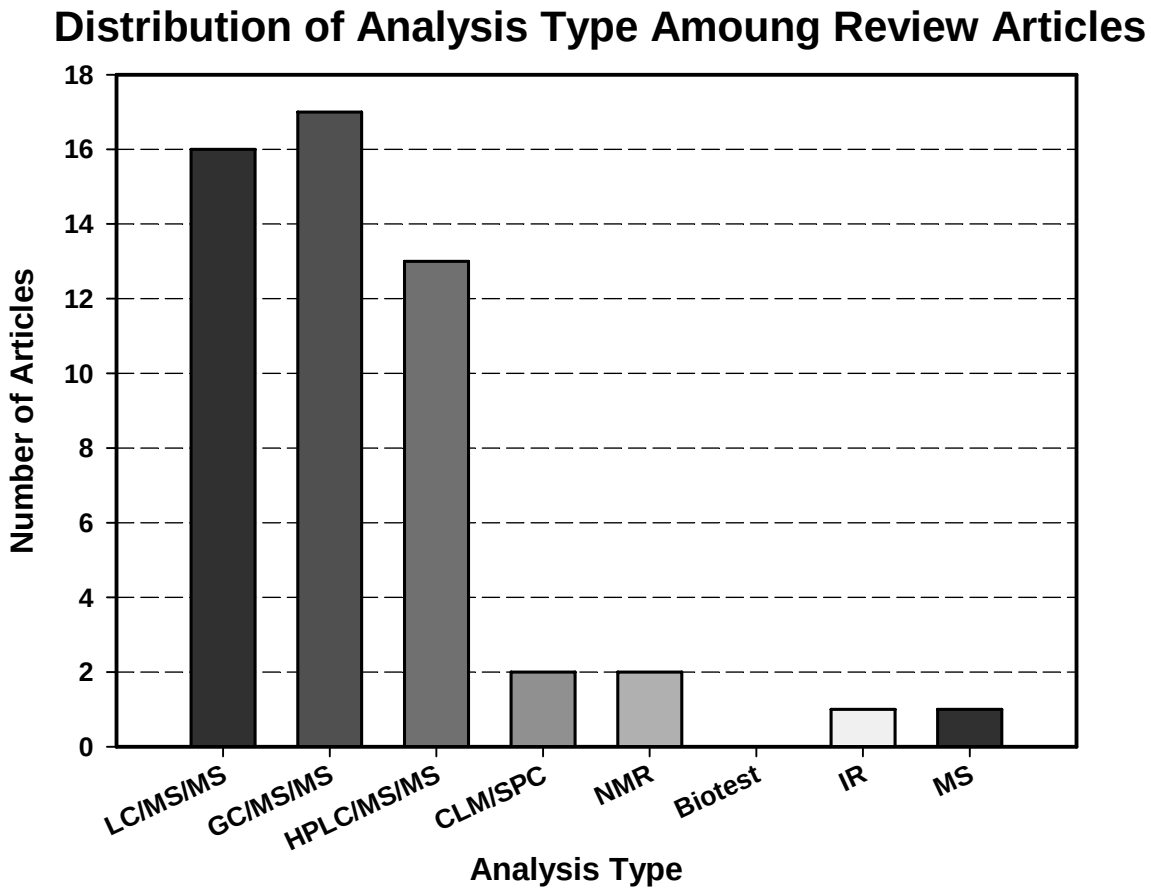

Figure 2.2. Distribution of analysis type among reviewed articles. LC, GC and HPLC represent liquid, gas and high performance liquid chromatography, respectively. MS/MS indicates tandem mass spectrometry. CLM and SPC denote colourimetric methods with spectrophotometry; and finally, MS, IR and NMR represent Mass Spectrometry (specific method not distinguished), Infrared Spectrometry and Nuclear Magnetic Resonance imaging, respectively. Biological tests (biotest) included the algal chlorophyll fluorescence test, the yeast estrogen screen (YES) and the umu test; biotests can be used to detect PhACs using the known toxilogical natures of the pharmaceuticals examined and the elimination of a test species or introduced toxicity.

An expanded variety of media and treatment systems, as well as, target PhACs and PPCPs were examined in the 41 studies. Treatment media and treatment systems ranged from full-scale functioning wastewater and drinking water facilities to lone compounds such as granular activated carbon (GAC) or filtration membranes. Oxidation techniques were the most commonly investigated treatments, including ozone, ferrate, chlorination media such as

chlorine dioxide, and advanced oxidation processes (AOPs) including photo-fenton reagents and ozone-peroxide mixtures. Of the 68 treatments evaluated, 32% of them were oxidative treatments. While oxidative techniques are described more distinctly in Figure 2.3, increasingly broad designations are used to describe less commonly explored media and system classifications. Coagulant and precipitants included ferric chloride, aluminum sulfate, aluminum polychloride, ferric sulfate, calcium oxide and chemical lime softening; disinfection media included chlorine dixoide, hypochlorite, free chlorine and NaClO; waste water treatments included tank-, biofilter- and wetland-based facilities; activated sludge encompassed a number of forms including denitrifying and nitrifying sludge; filtration techniques include nanofiltration (NO), ultrafiltration(UF) and reverse osmosis (RO); and finally, exchange polymers of various compositions, such as polystyrene and acrylic were investigated.

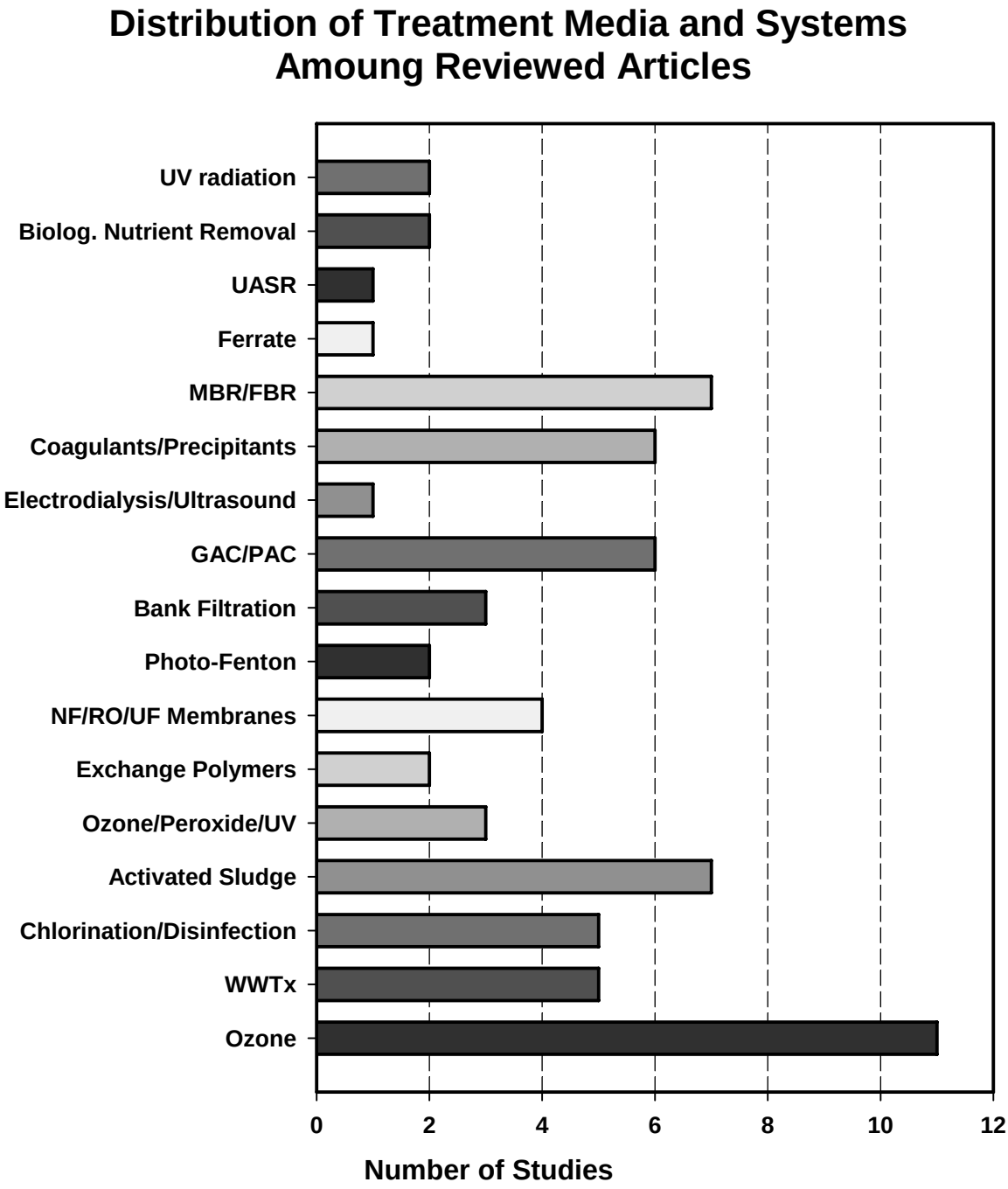

Figure.2.3. Distribution of treatment media and systems explored in the reviewed investigations. UASR =Up-flow anaerobic stage reactor; MBR = Membrane Bioreactor; FBR = Feedbed Bioreactor; GAC = granular activated carbon; PAC = powdered activated carbon; NF = nanofiltration; RO = reverse osmosis; UF = ultrafiltration; UV = ultraviolet radiation; WWTx = waste water treatment process.

The variety of treatment media and systems explored was surpassed by the collection of analytes investigated. Some studies were extremely focussed, studying one specific PhAC,

while other studies explored the treatment success of greater than 60 different PhACs and PPCPs. A total of 107 different PhACs and PPCPS were explored (Fig. 2.4). A number of PhACs were reoccurring between studies as a consequence of their environmental relevancy; these included: carbamazepine, ibuprofen, gemfibrozil, naproxen, benzafibrate, ketoprofen, estrogenic compounds and sulfonamide antibiotics including sulfamethoxazole.

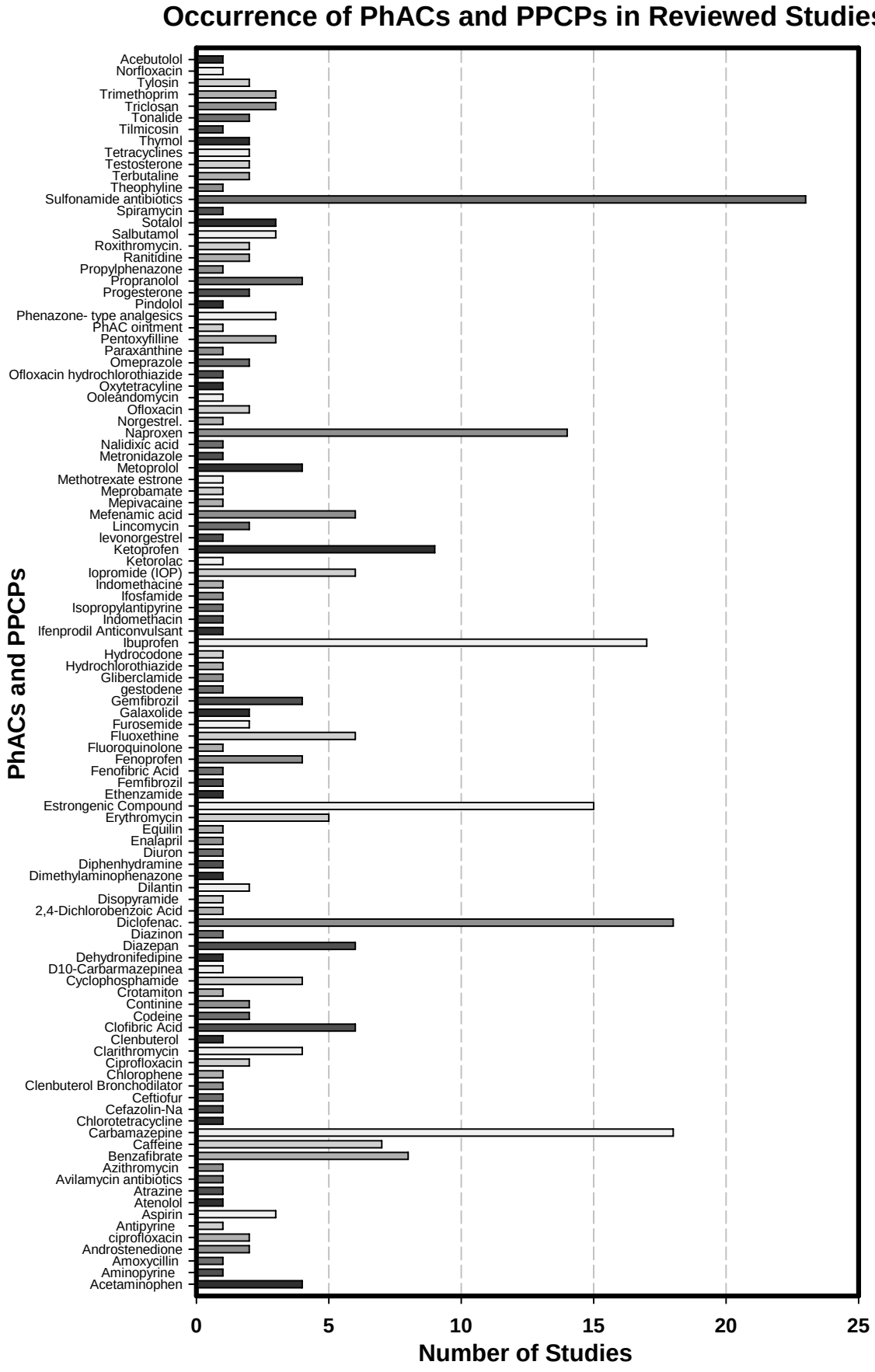
Occurrence of PhACs and PPCPs in Reviewed Studies
PhACs and PPCPs
Acebutolol
Norfloxacin
Tylosin
Trimethoprim
Triclosan
Tonalide
Tilmicosin
Thymol
Tetracyclines
Testosterone
Terbutaline
Theophyline
Sulfonamide antibiotics
Spiramycin
Sotalol
Salbutamol
Roxithromycin.
Ranitidine
Propylphenazone
Propranolol
Progesterone
Pindolol
Phenazone- type analgesics
PhAC ointment
Pentoxyfilline
Paraxanthine
Omeprazole
Ofloxacin hydrochlorothiazide
Oxytetracyline
Ooleandomycin
Ofloxacin
Norgestrel.
Naproxen
Nalidixic acid
Metronidazole
Metoprolol
Methotrexate estrone
Meprobamate
Mepivacaine
Mefenamic acid
Lincomycin
levonorgestrel
Ketoprofen
Ketorolac
Iopromide (IOP)
Indomethacine
Ifosfamide
Isopropylantipyrine
Indomethacin
Ifenprodil Anticonvulsant
Ibuprofen
Hydrocodone
Hydrochlorothiazide
Gliberclamide
gestodene
Gemfibrozil
Galaxolide
Furosemide
Fluoxethine
Fluoroquinolone
Fenoprofen
Fenofibric Acid
Femfibrozil
Ethenzamide
Estrongenic Compound
Erythromycin
Equilin
Enalapril
Diuron
Diphenhydramine
Dimethylaminophenazone
Dilantin
Disopyramide
2,4-Dichlorobenzoic Acid
Diclofenac.
Diazinon
Diazepan
Dehydronifedipine
D10-Carbarmazepinea
Cyclophosphamide
Crotamiton
Continine
Codeine
Clofibric Acid
Clenbuterol
Clarithromycin
Ciprofloxacin
Chlorophene
Clenbuterol Bronchodilator
Ceftiofur
Cefazolin-Na
Chlorotetracycline
Carbamazepine
Caffeine
Benzafibrate
Azithromycin
Avilamycin antibiotics
Atrazine
Atenolol
Aspirin
Antipyrine
ciprofloxacin
Androstenedione
Amoxycillin
Aminopyrine
Acetaminophen
0
5
10
15
20
25
Number of Studies

Figure 2.4. Occurrence of PhACs and PPCPs in reviewed studies. The figure shows the number of studies in which each PhAC or PPCP was investigated. Certain PhACs, such as sulfonamide antibiotics and estrogenic compounds were grouped together due to the sheer number of compounds in these categories.

The success of the investigated treatment media and systems was extremely variable. The variation occurred both within and amidst treatment types ranging from no removal to complete removal of the target analytes. The varying success of treatment media and systems was usually compound specific; underlying the fact that few techniques were efficient at removing analytes of varying chemical composition. Differing success between larger systems, such as WWTx plants, was dependent not only on the analytes, but also on characteristics of the plants themselves, such as solid retention time (SRT), hydraulic retention time (HRT), composition and seasonality. Figure 2.5 depicts the removal success of the different treatment media/systems explored in the reviewed studies, illustrating through a box diagram the upper and lower limits of percent removal achieved by each treatment type.

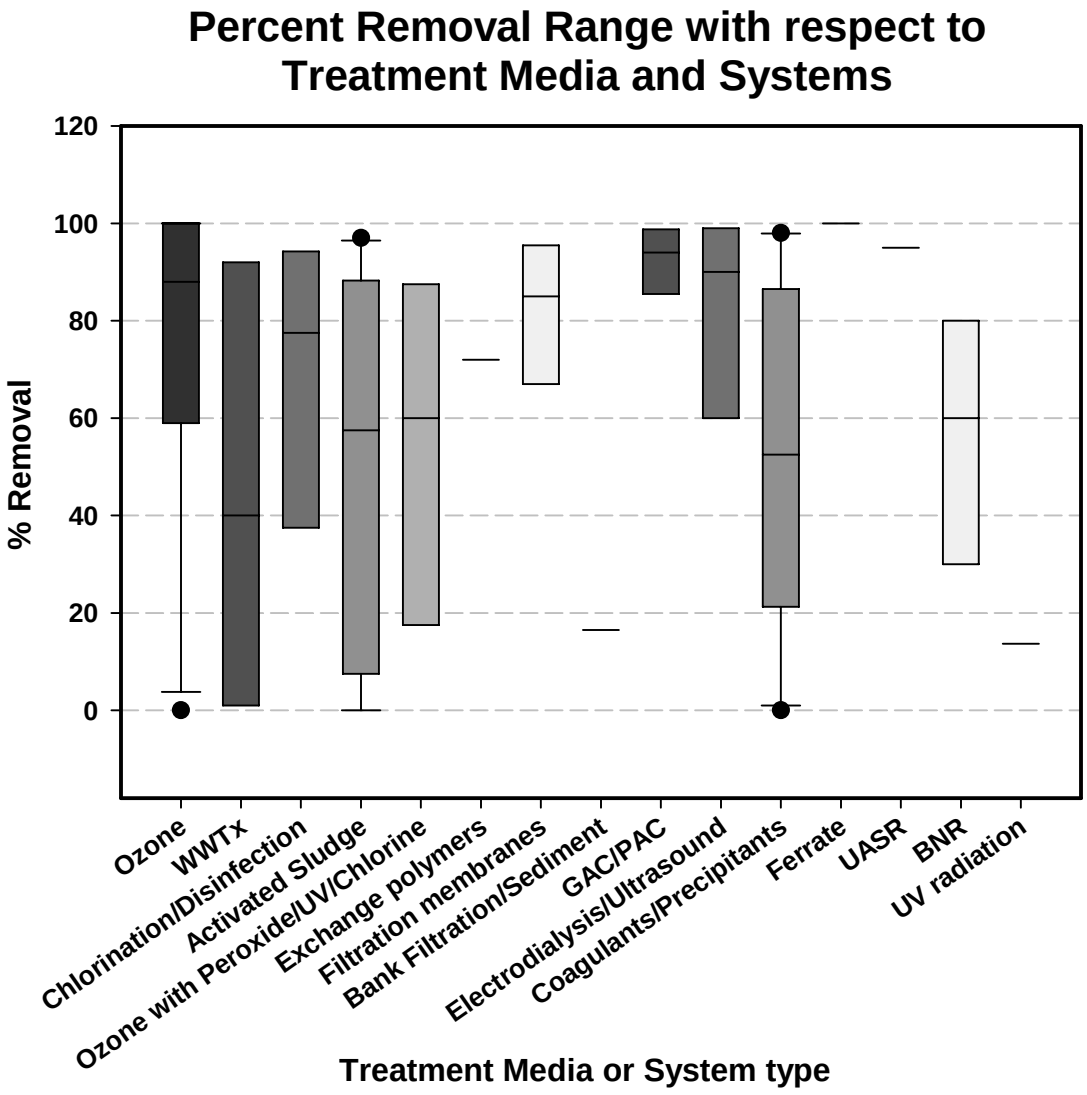

Figure 2.5. Percent removal range for a variety of PhACs and PPCPs with respect to treatment media or system. The range of % removals for each treatment type are displayed in a box plot which indicates the minimum, low quartile, median, upper quartile, and maximum % removal for each treatment type. Data points indicate outliers in the removal ranges. Note: Not all studies described removal success in terms of % removal and thus only comparative data is included in this figure. UASR = upflow anaerobic reactor; BNR = biological nutrient removal; GAC = granualr activated carbon; PAC = powdered activated carbon; WWTx = waste water treatment.

Common to all investigations concerning multiple target analytes was the observation that treatment success was highly variable between PhAC and PPCPs. Differences in chemical properties made each compound a unique removal challenge, showing varying levels of successful removal with different treatment approaches. Certain PhACs were

observed to be highly persistent, resistent to most treatment approaches, such as clofibric acid, whereas others, such as caffeine, showed consistently high removals. For the most part, both negligible and almost complete removals were seen for nearly all drugs, with variation occurring as a result of the type of treatment approach. Percent removals depicted in Figure 2.6 indicate the average percent removal seen for each PhAC/PPCP considering all possible treatments. Error bars indicate the standard deviation within the removal success.

When considering the percent removals with respect to PhAC/PCCP type depicted in Figure 2.6, one should note that some PhAC and PPCPs are more extensively researched than others. Thus, while a PhAC such as Tylosin may indicate 95% removal success, as compared to ibuprofen, with a removal range of 0 to 100%, the latter PhAC was evaluated many more times with a multitude of different treatment media. Figure 2.6 portrays the extensive variation in removal success for compounds, given their differences in chemical nature, with different treatments, as well as an overall indication of compounds that are particularly difficult to treat. Treatment success, or percent removals with respect to PhAC or treatment type as depicted in Figures 2.5 and 2.6 should be considered in conjunction with Figures 2.3 and 2.4 which indicate how extensively each PhAC/PPCP or treatment type has been explored. The following Table 2.1 has been included in this review to further allow appropriate weighting to be applied to the described removal data; the table shows the number of PhACs/PPCPs that have been examined with each treatment approach.

Table 2.1 Number of PhAC/PPCPs investigated with respect to each type of treatment. Some investigations used a group of compounds not indicating exact numbers, and thus the > sign indicates that more PhAC/PPCPs may have been investigated with that specific treatment media or system. The number indicated in the table is thus the minimun number of PhAC/PPCPs explored.

Treatment Type	Number of PhAC/PPCPs
Ozone	183
WWTx	>9
Chlorination/Disinfection	111
Activated Sludge	53
Ozone with Peroxide/UV/Chlorine	50
Exchange Polymers	>1
Filtration/Membranes	>48
Photo-Fenton oxidation	>2
Bank Filtration/Sediment	>14
GAC/PAC	>81
Electrodialysis/Ultrasound	>9
Coagulants/Precipitants	>70
MBR/FBR	>29
Ferrate	5
UASR	1
Biological Nutrient Removal	67
UV radiation	34

The final table, Table 2.2 the PhAC/PPCP treatment chart, briefly describes all 41 reviewed journal articles. The descriptions provide information pertaining to the investigated media and treatment systems, the PhACs and water types involved, as well as, procedural particulars and results of each study.

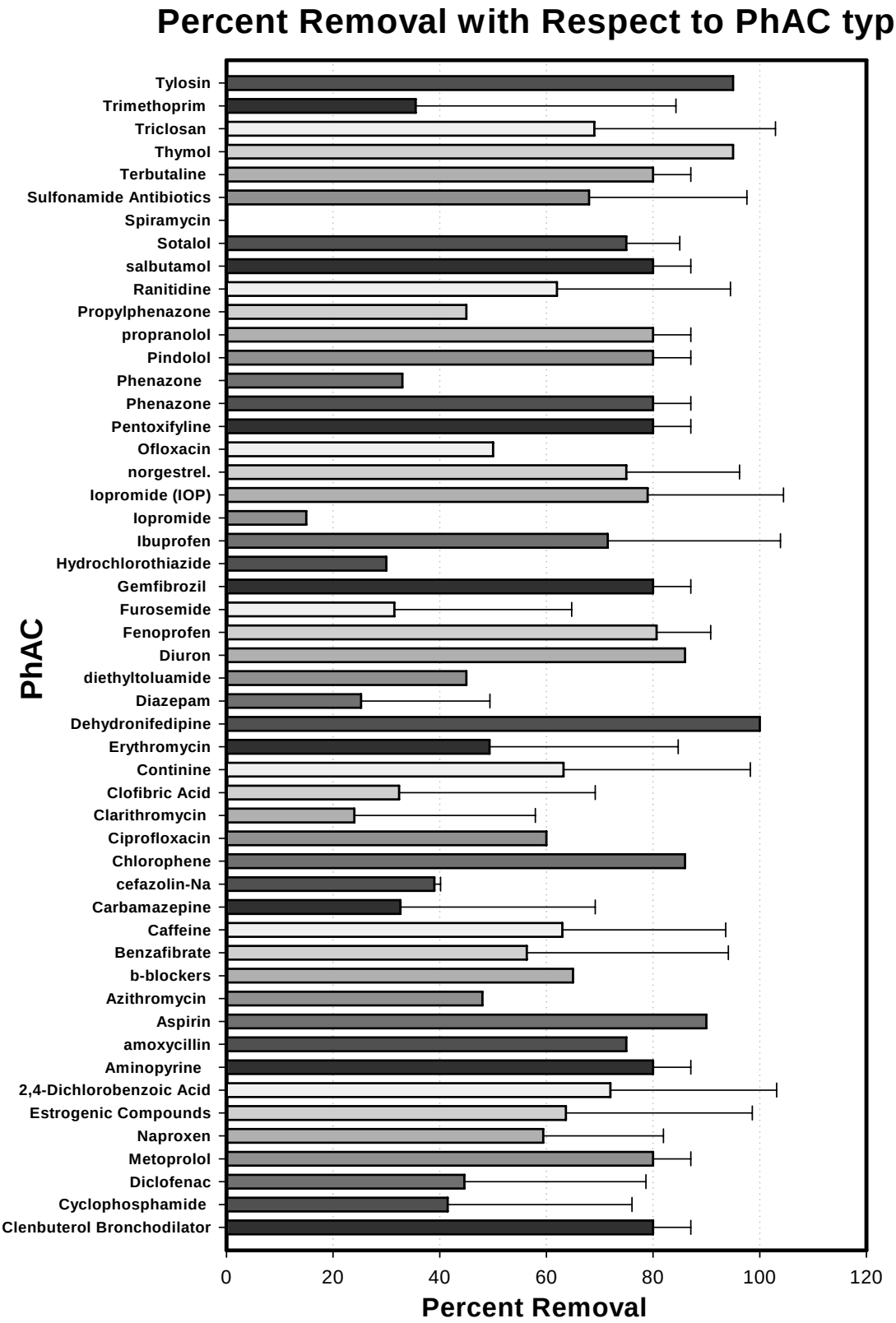

Figure 2.6. Percent removals, in literature pharmaceutical removal studies, with respect to PhAC/PPCP type. Bars represent the mean percent removal while error bars represent the standard deviation within the removal data set from this mean.

Table 2.2 Previously Explored Treatment Media and Systems for PhAC/PPCP Removal

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
Water Research 39 (2005) 3607–3617	**Oxidation of PhACs during water treatment with chlorine dioxide**			Hubera et al., 2005
Drinking water treatment Oxidation **Water:** Pure water - Water samples from German DWT plant Lake water - Water from Lake Zurich, Switzerland Groundwater - from Duebendorf, Switzerland	Azithromycin Clarithromycin Dehydro-erythromycin Roxithromycin Sulfamethazine Sulfamethoxazole Sulfapyridine Sulfathiazole Sulfapyridine Sulfathiazole Estrongenic Compound **Acidic**: Benzafibrate Clofibric Acid Diclofenac Fenoprofen Gemfibrozil Ibuprofen Ketoprofen Naproxen **Neutral** Caffeine Carbamazepine Cyclophosphamide Diazepam Dimethylaminophenazone Gliberclamide Ifosfamide Pentoxifyline Phenazone Propylphenazone Iopromide	Chlorine dioxide **Oxidant used for the disinfection. **Chlorite is the major reduction product; it is considered to be a blood poison (Condie, 1986). * ClO_2 is also used in waste water treatment disinfection ** ClO_2 more effectively inactivates protozoa (e.g., Cryptosporidium and Giardia) than chlorine and the halogenated disinfection byproducts are not formed under proper generation conditions (USEPA, 1999). ** ClO_2 is a stable free radical; reacts via an electron transfer rxn with water matrix components and micropollutants ** Highly selective oxidant for specific functional groups like phenolic moieties or tertiary amino groups (common to PhACs). Thus it is likely to oxidize many PhACs despite its lower oxidation potential than ozone and hypochlorous acid	** Samples were spiked with acidic and neutral PhACs up 1mg l^{-1} ***Lab experiments**: Room temperature in batch reactors with ClO_2 doses 0.95 and 11.5 mg l^{-1} and rxn time of 30 min. **Groundwater was spiked with 4 sulfonamide (1 mg l^{-1} each), 4 macrolide antibiotics (100 ng l^{-1} each) & 3 estrogens (1 mg l^{-1} each); then treated with 0.1 mg l^{-1} ClO_2 **ClO2 concentrations were determined using 3 different methods:** (1) The direct spectrophotometrical determination at 359nm (Hoigne´ and Bader, 1994), (2) ABTS method –a colorimetric method adapted from Pinkernell et al.(2000) (3) LGB method, a colorimetric methodusing lissamine green B (Chiswell and O'Halloran, 1991). ** sulfamethoxazole and diclofenac concentrations were measured with a Hewlett-Packard 1050 series **HPLC** equipped with an Ultra Aqueous C18 column and a variable wavelength detector.	** 4 of the 9 compounds showed an appreciable reactivity with ClO_2 : (2^{nd} order rate constants) sulfamethoxazole (6.7×10^3 $mol^{-1}s^{-1}$) roxithromycin (2.2×10^2 $mol^{-1}s^{-1}$) 17a-ethinylestradiol (2.0×10^5 $mol^{-1}s^{-1}$) diclofenac (1.05×10^4 $mol^{-1}s^{-1}$) **Comparison to Ozone and Chlorine:** ** ClO_2 reacted more slowly and with fewer compounds than ozone and faster than chlorine. It is effective to oxidize only certain compound classes such as the investigated classes of sulfonamide and macrolide antibiotics, and estrogens. ** EE2, roxithromycin, and SMX all indicate pH-dependent rate constants, with high reactivity at pH 7. This is due to their protonation state. ****ClO_2 reacts very selectively** with functional groups with high electron densities such as phenoxide ions and neutral tertiary amines, and thus non-protonated forms tend to be more reactive. ** The relatively high rate constant of the aniline derivative diclofenac indicates that the aniline group is also reactive to ClO_2. **Drinking Water treated for 30min with ClO_2: bezafibrate, carbamazepine, diazepam, and ibuprofen showed no reactivity, whereas diclofenac was readily oxidized. **Surface water can have a substantial ClO_2 demand, causing PhACs and water matrix to compete for ClO_2; in which case even highly reactive PhACs may not transform below a certain ClO_2 dose. ****Sulfonamides** -Oxidized more than 95% after 30 min of contact time. -Reactivity between sulfonamides varied more than expected and may be explained by differences in speciation. Reactivity seems strongly influenced by the protonation state of the acidic nitrogen **M**acrolides:** -Oxidized more slowly than the sulfonamides and only ~48% after 180 min. -Reactivity between macrolides was similar following their common reactive moiety (tertiary amino group). ****Estrogen:** -Estrogens reacted too fast to be detected after 5 min contact time. **Full mineralization is generally not achievable with oxidant doses commonly used in water treatment, thush it can only deactivate PhACs by selectively oxidizing functional groups crucial to their activity.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
Environ. Sci. Technol. 2006, 40, 7358-7366		**Occurrence and Fate of Organic Contaminants during Onsite Wastewater Treatment**		Conn et al., 2006
Wastewater treatment system Volatilization, Biotransformation, and sorption **Water:** Wastewater from 30 onsite treatment systems in Summit and Jefferson Counties, CO.	A range of OWCs: surfactants metabolites steroids stimulants metalchelating agents, disinfectants, antimicrobial agents, and PhAC compounds	**Tank-Based Tx** - Anaerobic Biotransformation - Adsorption - Settling **Biofilter-based Tx** - Aerobic biotransformation - Adsorption - Volatilization **Wetland-based Tx** - Biotransformation - Plant Uptake - Adsorption - Photolysis	The 30 onsite treatment systems were sampled twice: August to October 2003 and March to May 2004. At each site, grab samples of wastewater were collected **specific conductance, ammonia, carbonaceous biochemical oxygen demand (cBOD), and total dissolved solids were analyzed by standard methods **GC/MS ananlysis	** **Efficiencies** <1% to >99% depending on treatment type and physicochemical properties of the compound. **10 of 12 OWCs systems with additional aerobic treatment had lower median concentrations than anaerobic tank treatments. **Recirculation through **aerobic textile-media** biofilters, at 7of the sites increased sorption, volatilization, and aerobic biotransformation. **Biofilter-based** systems had greater removal efficiencies than tank-based systems; resulting in 96% reduction in 1,4-dichlorobenzene compared to 22% removal in tank-based treatment (Figure 4). -Volatilization in Biofilter Tx may effectively remove compounds with large Henry's Law constants (KH) due to increased air-water exchange and turbulence. **Nonvolatile OWCs removal during Confined unit Tx can occur by biotransformation and sorption. -Sorption to solids with subsequent removal by sedimentation or filtration was effective removal mechanisms in tank- and biofilter-based systems for compounds with large Kow's. **Surface water/groundwater interactions may be notable when onsite treatment systems are situated near streams. Shallow groundwater can discharge to streams within 5 years of recharge, a time period often deficient for degradation of recalcitrant compounds. Some compounds can volatilize and biodegrade in the unsaturated zone, but once in the saturated zone, low oxygen and nutrient conditions lead to long-term (>30 years) persistence and transport.
Water Research 39 (2005) 668–676		**Naproxen removal from water bychlorination and biofilm processes**		Boyd et al., 2005
Waste and Drinking water treatment Chlorination (oxidation) **Water:** Synthetic waters containing elevated concentrations of naproxen	Naproxen	Free Chlorine	Chlorine dosages:1, 5, and 10 mg l^{-1} yielding naproxen:chlorine molar ratios of 30:1, 6:1, and 3:1, respectively Bioreactor : 1-l glass feed jar, 2 peristaltic pumps and 30.5m of polypropylene tubing, covered with aluminum foil to minimize light exposure. -Feed bacteria for stimulating biofilm growth was collected from an urban storm water drainage canal All samples were prepared in triplicate and residual naproxen concentration was measured by **HPLC.**	**Formation of naproxen products was dependent on pH, chlorine dosage and contact time. **Naproxen readily reacted with free chlorine and formed disinfection products. **Formation of specific reaction products varied depending on water/wastewater characteristics and treatment operating conditions. **Bioreactor Results: Naproxen was not degraded biologically for the conditions of this study. **The naproxen solution containing chlorination products caused an adverse response by discharging biomass from the bioreactor. Thus naproxen chlorination products can potentially impact the performance of biofilm processes in natural and engineered aquatic environments. **The amount of biomass in the bioreactor decreased for 20 days following the addition of the chlorine–naproxen solution. **After 6 min.the original chromatographic peak for naproxen disappeared and new peaks appeared indicating the formation of intermediate products, which were further transformed/degraded until two peaks remained as visible end products after 7 days.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
				**End product, observable by HPLC at 254 nm, suggests that the naproxen is transformed, but not mineralized. ** ~30 min of contact time with free chlorine typically used for microbial inactivation in WWT systems may be too short for complete oxidation of PPCP contaminants such as naproxen. More time maybe needed for chemical reactions to reach completion at lower concentrations at treatment plants (1–100 mg l^{-1} or lower for naproxen, 0.5–1 mg l^{-1} for chlorine) or in the presence of natural organic matter. ** PhACs that occur in natural waters and sewage systems may not be completely oxidized by chlorination treatment processes, but instead only transformed to intermediate products. **Naproxen was more readily transformed by contact with chlorine at pH 5.0 (99.7% naproxen removal after 15 min reaction) and neutral pH 7.0 (99.2% naproxen removal) than at pH 9.0 (61.5% naproxen removal). **Aqueous chlorine exits primarily as hypochlorus acid (HOCl) at low pH , which favors NPX oxidation.
Water Research 41 (2007) 1001 – 1012			**Elimination of PhACs in sewage treatment plants in Finland**	Vienoa et al, 2007
Sewage Tx System **Water**: Sewage effluent	**b-blockers**: acebutolol, atenolol, metoprolol and sotalol; **antiepileptic:** carbamazepine; fluoroquinolone **antibiotics:** ciprofloxacin, norfloxacin, ofloxacin	Denitrifying biofilter Activated sludge	PhACs separated from aqueous media using SPE Extracts were chromatographed on a C18-column using Agilent 1100 HPLC-system (Agilent Technologies, Espoo, Finland) and detected with a Quattro Micro triple-quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with electrospray ionization source. Positive ions were acquired in the multiple reaction-monitoring mode.	**In the treatment plants:** ****Antibiotics:** -**Fluoroquinolones** were eliminated by >80%; main elimination process was sorption to sludge in STPs **-Ciprofloxacin and ofloxacin** were eliminated in average of 84% and 83%, respectively. ****Carbamazepine**: (CBZ) -CBZ was not eliminated, in fact higher concentrations were frequently found in the treated effluent. -This is most likely due to enzymatic cleavage of the glucuronic conjugate of CBZ and release of the parent compound in the treatment plant. Activated sludge has been found to have glucuronidase activity. **** Beta-blockers:** -Average elimination <65%; elimination varied greatly between the treatment plants. -Dilution of raw sewage by rainwater and a consequent decrease in the hydraulic retention time of a treatment plant was found to deteriorate the elimination of the b-blockers. -Highest average elimination rates were for atenolol (61%) and sotalol (65%). Avgerage elimination of Acebutolol was 47% and the lowest elimination rates were observed for metoprolol (29%). Elimination varied greatly between STPs. **No sludge samples were analyzed, thus it was not possible to differentiate between biodegration and sorption. ** Carbamazepine and the b-blockers may reach recipient water. There is a need to enhance their elimination in STPs.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
				**Denitrifying biofilter: caused no further elimination of the target compounds.
Water Research 40 (2006) 2259 – 2266		Ozone treatment and the depletion of detectable PhACs and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada		Hua et al., 2006
Drinking water treatment **Water:** Drinking water effluent	18 major PhACs (and metabolites) and 7-triazines herbicides. Caffeine Carbamazepine Cotinine - D10-Carbarmazepine	**Ozone** Has several purposes in DWT: Disinfection, Taste and odor removal, Degrade contaminants	**Pilot plant:** -Operates in real-time with the full-scale water treatment plant, -Allows parallel water treatment streams, i.e., conventional and ozone plus conventional treatment (Fig. 2). -2 L water samples were used for co-extracting neutral PhACs (carbamazepine, caffeine, cotinine) and atrazine using 6mL Supelclean C-18 SPE cartridges (Supelco, Canada). Sample Analysis: carried out on the same **LC-ESI-MS/MS** system	**Regardless of season, conventional coagulation/ flocculation/sedimentation and filtration without O_3, indicated no decrease in the water PhAC concentrations. ****Pretreatment of ozone:** -Range of mean removal percentages were 78–99%, 83–93%, 67–81%, and 66–96% for carbamazepine, cotinine, caffeine ,and atrazine, respectively (when ozonation was coupled with the flocculation-coagulation and dual media filtration) -It was not clear whether the large concentration decreases are a function of the initial O3 treatment or the coagulation/ flocculation/sedimentation process -O3 reacts rapidly with CBZ's double bond yielding several ozonation products containing quinazoline based functional groups. **Few Canadian DWTPs incorporate ozonation into conventional treatment
Chemosphere 63 (2006) 934–941		**Adsorption of the quinolone antibiotic nalidixic acid onto anion-exchange and neutral polymers**		Robberson et al., 2006
Wastewater treatment -Adsoption **Water:** Lab synthesized	Nalidixic acid (quinolone antibiotic)	**Neutral and anion-exchange polymers:** Polystyrene–divinylbenzene Phenol–formaldehyde Aliphatic acrylic Aliphatic methacrylic Polystyrene–divinylbenzene Polystyrene–divinylbenzene Aromatic acrylic **Polymers have maintained their structural integrity for >5 years in WTPs in China, lasting for >2000 regeneration cycles. In comparison, activated carbon requires replacement after 15–20 regeneration cycles.	*Bench-scale isothermal adsorption experiments at different pH values with different polymer types *Polymers were pre-washed with propanolo and dried in a dessicator with a vacuum pump *pH adjustments were accomplished using HCl and NaOH *Standards, samples and blanks were analyzed by a **Shimadzy UV-1601 spectrophotometer**	**Neutral form** (below pKa) of NA adsorbs to a greater extent on neutral polymers **Anionic form** (above pKa) of NA adsorbs more to anion-exchange polymers; due to electrostatic attraction between the anionic NA and the cationic surface of the polymer; **Aromatic ring interactions between NA and the surface of both neutral and anion-exchange polymers are important in the adsorption process; which has important implications for the treatment of PhAC-contaminated water, as many PhAC contaminants are ionizable and have aromatic rings in their structure. **There was more adsorption per gram of polymer to both neutral polymers (X16 and X761) than to the anion-exchange polymer (I402). Higher adsorption to the neutral polymers can be explained by expulsion of neutral NA from water due to the hydrophobic effect, as well as the lower affinity of neutral NA for the positively charged, hydrophilic I402 compared to neutral X16 and X761. **Greater NA adsorption on the polar X761 vs. the non-polar X16: X761 has an electronegative oxygen functional group not present on X16. NA has partial neg. and pos. charges due to carboxylic acid and amine functional groups, and thus likely interacts via dipole–dipole interactions with the polar X761, but not X16. **Greater adsorption by the anion-exchange polymer I402 vs. the two neutral polymers: Electrostatic attraction between anionic NA and the cationic surface of I402.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
				**Greater adsorption affinity of I402 at pH 7 vs. pH 5 and the lower adsorption affinity of X16 and X761 at pH 7 vs. pH 5 are also consistent with these results and can be explained by the deprotonation of NA above its pKa **Neutral aromatic polymer matrices more effectively remove NA than neutral aliphatic matrices below the NA pKa due to interactions between the aromatic rings on the NA and the polymer; **Anion-exchange polymers with styrenic matrices more effectively remove NA than those with acrylic matrices due to interactions between the aromatic rings on the polymer and the NA.
Water Research 40 (2006) 3297 – 3303		**PhAC chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment**		Nakada et al., 2006
Wastewater treatment **Water:** Wastewater effluent	aspirin, ibuprofen, naproxen, ketoprofen, fenoprofen, mefenamic acid, thymol, triclosan propyphenazone, crotamiton, carbamazepine, diethyltoluamide estrogens	**Activated Sludge**	**PhAC concentrations were measured in 24-h composite samples of influents and secondary effluents collected seasonally from five municipal STPs in Tokyo. ****GC-MS analysis.**	****Amide-type PhACs**: ketoprofen, and naproxen showed poor removal (<50% efficiency), likely due to their lower hydrophobicity (log Kow). ****Crotamiton** was very persistant during 2nd ary treatment and most abundant PhAC in the effluent, with concentrations from 245 to 968 ng/L ****Acidic PhACs**: -Aspirin and ibuprofen removed most efficiently, >90%, while ketoprofen and naproxen averaged <45%, with large variability (0% to 80%). ****Asprin removal mechanism**: -Likely microbial and chemical degradation, including conversion to salicylic acid.. **Ibuprofen: Higher removal efficiencies by STPs in Tokyo are likely due to longer SRT (~5 days) and hydraulic retention time (~9 h). ****Fenoprofen:** -Relatively high removal efficiencies (avg 85%) with large variability (65–95%). Lower removal efficiencies for ketoprofen and naproxen may be due to their less hydrophobic nature (log Kow<3) and persistence under microbial attack ****Phenolic PhACs:** -Thymol: high removal efficiency (~95%), likely volatizes during STx due to high VP (0.0022mmHg) -Ttriclosan: Wide range of removal efficiencies (45-93%), ~70% on average; Variability is similar to those observed in five EU countries (Paxeus, 2004). ****Amide-type PhACs:** (diethyltoluamide, propyphenazone, carbamazepine, and crotamiton) - Not efficiently removed: avg. removals <45% with large range in efficiency; poor removal is partly due to their hydrophilic nature (logKow <3) and chemical stability. - Secondary effluent concentrations were often higher than those in corresponding influents; possibly due to deconjugation of metabolic products.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
Environ. Sci. Technol. 2006, 40, 7367-7373		**Enhanced Biodegradation of Iopromide and Trimethoprim in Nitrifying Activated Sludge**		Batt et al., 2006
Wastewater Treatment Biodegradation in Nitrifying Activated sludge **Water:** Wastewater Effluent	Iopromide (IOP) Trimethoprim (TRI)	**Nitrifying Activated Sludge** -Biomass from the stage-2 activated sludge - Bioreactor with long SRT (49 days **Nitrifying Bacteria (NB)** - Can co-metabolize some organic micro-pollutants resistant to biodegradation -aerobic -chemolithoautotrophic **Two types:** 1) Ammonia oxidizing bacteria (AOB), 2) Nitrite-oxidizing bacteria (NOB). - Extremely slow-growing, thus growth in activated sludge is favored at longer SRT.	**Laboratory-scale bioreactors:** - Contain mixed liquor from nitrifying activated sludge; - - Biodegradation of IOP and TRI were conducted in 2 bioreactors: 1) No inhibition of nitrification 2) Nitrification was inhibited **** Full-scale municipal WWTP analysis:** -Conducted to corroborate the observed removal efficiencies **LC/MS/MS Analysis.** - LCQ Advantage ion trap mass spectrometer (ITMS) equipped with an ESI, operated in positive ion mode **SPE extraction with oasis HLB cartridges	**LAB SCALE:** - Much higher removal of IOP and TRI by nitrifying activated sludge than by conventional activated sludge - Inhibition of NB caused % removal to decrease from 97 to 86% for IOP, and from 70 to 25% for TRI. - IOP metabolite identified with non-inhibited NB was dehydroxylated iopromide at the two side chains. - With inhibition of NB a carboxylate metabolite was identified, formed by the oxidation of the primary alcohol on the side chain. **Full-scale WWTP: - Analysis corroborated observed removal efficiencies from lab-scale study; showing higher removal of TRI & IOP by nitrifying sludge (SRT 49 days) than by conventional (SRT of 6 days). -IOP removal reached 61% in nitrifying sludge and was negligible in conventional -TRI removal was ~1% in the conventional activated sludge, and ~50% in the nitrifying
Water Science & Technology Vol 52 No 8 pp 9–14 Q IWA Publishing 2005		**Removal of PhACly active compounds in nitrifying–denitrifying plants**		S. Sua´ rez, et al., 2005
Waster water treatment Nitrifying–denitrifying process in an activated sludge system. **Water:** Urban synthetic wastewater	Carbamazepine diazepam fluoxetine citalopram ibuprofen, Naproxen diclofenac estradiol ethinylestradiol	**Nitrifying and denitrifying activated sludge** **Activated sludge system:** -simultaneous removal of C & N - Has an anoxic zone for denitrifying followed by an aerobic one for nitrification & carbon removal. - Finally, suspended solids are separated from the effluent to levels below 0.1 g VSS/l in a sedimentation tank	*The unit was inoculated with 2 g VSS/l taken from a similar unit in a full-scale sewage treatment plant. * HRT was set to 1 day. *Temperature and pH were monitored but not controlled, in order to maintain the same operating conditions as in full scale plants. *SPE with oasis HLB cartridges ***GC/MS** analysis	**Overall Removal:** **Carbamazepine, diazepam and diclofenac were only removed to a small extent; higher removal rates observed for naproxen and ibuprofen (68% and 82%), respectively. **No adverse effects were observed on conventional parameters as observed in the evolution of carbon and nitrogen removal rates and suspended solids content ****Diclofenac** -Was only removed to a small extent; always below 20%. **Carbamazepine and diazepam**: -Were persistent with removal rates <10% **Naproxen:** 68% of the influent concentration removed **Ibuprofen:** highest removal observed at 82% **A differentiation between adsorption and degradation during the removal process was not performed.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
Environ. Sci. Technol. 2005, 39, 8300-8306		**Photo-Fenton Degradation of Diclofenac: Identification of Main Intermediates and Degradation Pathway**		Pearez-estrada et al., 2005
Advanced oxidation processes (AOPs) Water: Lab synthesized	diclofenac	**Photo-Fenton reagent** **AOPs:** - produce hydroxyl radicals (*OH), which are very reactive and cause the pollutant's mineralization in the final stages. **Photo-Fenton** - Low cost AOP - Easy-to-handle technology - Well adapted to small to-medium-scale renewable energy facilities.	* All experiments were performed in a compound parabolic collector (CPC) solar pilot plant *Three hydrolysis experiments were done at different pH (3, 7, and 9) to ensure results were not due to hydrolysis * **GC/MS and LC coupled with time-offlight MS (LC/TOF-MS)** *SPE: using Oasis HLB .	**Rapid and complete oxidation of diclofenac after 60 min, and total mineralization (disappearance of dissolved organic carbon, DOC) after 100 min exposure to sunlight. **Degradation takes place in the homogeneous phase governed by a precipitation-redissolution degradation process **** Photolysis experiments:** rapid decay of >70% of the diclofenac in the 1st 30 h of irradiation. No mineralization, with DOC concentration remaining stable throughout. -Such fast decomposition of diclofenac by direct photolysis suggests possible contribution of this reaction pathway to the photocatalytic process. ****"Dark" Fenton reaction** (Fe2+): Diclofenac concentration decreased quickly, reducing the initial amount by more than 50%. ****Photo-Fenton reaction** (Fe3+): The overall process started slowing down, but led to mineralization. At that moment, there are two effects present: (i) partial degradation of the main molecule, with subsequent apparition of some DPs, and (ii) rapid decrease of the pH, triggering precipitation of diclofenac - which is a very soluble (50 g/L at 25°C at pH 7) acidic PhAC (pKa 4.15) that becomes almost insoluble below pH 4. **From HPLC measurements to assess the process, diclofenac degradation took around 60 min and peroxide consumption up to this point was around 20 mM
Envrionment Science and Technology. Awaiting publishing		**Ultrasound-Induced Destruction of Low Levels of Estrogen Hormones in Aqueous Solutions**		XiangFu et al., ASAP
Advanced Oxidation Process Ultrasound (sonolysis) **Water:** MilliQ spiked with estrogens - No competing species such as natural organic matters (NOMs) were added.	**Estrogen Hormones:** 17R-estradiol, 17â-estradiol, ethinyl estradiol, estrone, equilin, gestodene, levonorgestrel, and norgestrel.	**Ultrasound :** *Waves pass through liquid, creating cavities due to oscillating acoustic pressures. Dissolved gases, organics & water vapor diffuse into the cavities from solution, cavities grow and ultimately implode. Generates temperatures up to 5200K and pressures >1000 atm inside collapsing cavity, and ~1900 K in the region between the solution and the collapsing bubble (19). ***Destruction of pollutants occurs via:** - Thermal degradation (pyrolysis) - Combustion reactions (if O2 is present). - Free radicals OH*, H*, HO2*) formed by thermolysis of water	*Batch reactor wuth a 1.1 W/mL sonication unit and a continuous flow reactor using a 2.1 W/mL sonication unit. * Temperature, pH, and pressure were studied in lab-scale systems. *Two types (0.6 and 2 kW) of sonication reactors (both of 20 kHz frequency) were used * SPE followed **GC/MS** analysis was used for quantitative analysis of the estrogens	**Degradation of estrogens follows pseudo first-order kinetics. **Reaction likely takes place in the interfacial region and in the bulk solution with radical species. **Low solution pH & T is more favorable for destruction of estrogens. **Increasing the fluid pressure is detrimental to reaction efficiency. **After 25 min of sonication, 60-90% of individual estrogen compounds were degraded, and ~80% of total estrogens **Low Henry's constant for estrogens implies little volatilization into the cavity thus pyrolysis inside the cavity is not important. **Due to their hydrophobicity (low solubility), estrogens would tend to diffuse into the cavity-liquid interface. The reaction likely takes place in the interfacial region where high temperature and pressure are produced upon cavity implosion causing thermal degradation or supercritical oxidation. Oxidative degradation by strong radicals in or near the interface is also possible.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
				*Does not require oxidants or catalysts, and does not generate additional waste as with adsorption (spent adsorbent) or ozonation (ozone off-gas) processes.
Chemosphere 65 (2006) 17–23		**Degradation of macrolide antibiotics by ozone: A mechanistic case study with clarithromycin**		Lange et al., 2006
Ozonolysis **Water:** Milli-Q-filtered (Millipore) water	clarithromycin (macrolide antibiotic:)	**Ozone** *Ozonide zwitterion decays via two routes: 1) looses dioxygen yielding the N-oxide 2) dissociates into the ozonide radical anion and the amine radical cation	**Lab-scale studies in which ozone and clarithromycin were mixed in appropriate ratios to achieve a desired product turnover to allow product analysis *Set amounts of ozone and clarithromycin were used to measure kinetic parameters ****HPLC-MS./MS** **1H-NMR spectra (in D2O) were run on a 500 MHz instrument (Bruker DRX-500 with XWIN-NMR software). **Growth inhibition experiments with Pseudomonas putida DOT-T1E were used to measure biological activity	**Only the free amine reacts with ozone ** Rate of reaction is pH dependent ** The main reaction is a transfer of an O-atom yielding the N-oxide **A minor product (10%, based on formaldehyde yields) is demethylated clarithromycin (identified by HPLC/MS–MS). -The dimethylamino group is thought necessary for drug binding to target receptor; thus changes to this functional group, like the formation of the N-oxide (no longer a proton acceptor), inactivates these drugs. This was shown by the growth inhibition of Pseudomonas putida. *Biological inactivation requires only 1 molecule of ozone, in contrast to mineralization which requires 100 X more. ($C_{38}H_{69}NO_{13}$ + $100O_3$ ↔ $38CO_2$ + 34 H2O + HNO3 + $100O_2$) **Amines react well with ozone, at a rate ~4 X 10^6 $M^{-1}s^{-1}$, only when the lone electron pair is not protonated or complexed by a transition metal ion such as Fe3+ in Fe(III)EDTA. **Reaction rate increases 10-fold (within the limits of error) per pH unit; since the concentration of free amine increases 10-fold per pH unit through deprotonation.
Chemosphere 65 (2006) 2130–2137		**Reactions of the amine-containing drugs fluoxetine and metoprolol during chlorination and dechlorination processes used in wastewater treatment**		Bedner et al., 2006
Wastewater Tx **Water:** Simulated wastewater (WW) And WW from operating plant	Amine-containing PhACs: fluoxetine and metoprolol	Chlorination: Hypochlorite – reacts rapidly with PhACs during disinfection to form N-chloramines; -Chloramines are important in disinfection processes due to their oxidizing ability and are considered "active chlorine" compounds. **Dechlorination is used in WWT following chlorination to reduce active chlorine residuals from entering the environment. Dechlorination is usually achieved with sulfur dioxide or sulfite salts.	**Studied the tendency of fluoxetine and metoprolol to react with hypochlorite in pure water using conditions that simulate wastewater disinfection. **Chlorination reactions were also investigated in WW collected from an operating treatment plant. **Reactivity of the chlorination products with sulfite was studied to simulate WW dechlorination. **Liquid chromatography (LC) with several detection modes including ultraviolet absorbance (UV), mass spectrometry (MS), and post-column reaction /reductive electrochemistry (EC) for determining active chlorine products.	**At 10μM, both PhACs reacted rapidly (<2 min) to form largely N-chloramine products, stable in aqueous solution for at least 1h **In WW similar reactivity was noted. ** Longer reaction times lead to complete reduction and formation of the parent PhAC amine. Dechlorination in WWT tends to be seconds long, thus these PhAC chlorination products may evade dechlorination and be released into the environment. ****Fluoxetine**: No peak at 5.8 min indicates that fluoxetine reacted completely to form one major product of increased hydrophobicity eluting at 21.2 min. Complete disappearance of the parent fluoxetine peak was also noted for 2 min and 30 min chlorination times. -Dechlorination: After 2 min, peak area of product has decreased to ~ 70% of peak area, indicating only a portion has been chemically reduced with this reaction time. At 5.8min a peak with the retention time of fluoxetine appears, which intensifies over the next 30min as the product peak decreases. Thus the chlorination product is

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				converted back to fluoxetine upon dechlorination, but only reaches ~70% of pre-chlorination concentration. ****Metoprolol**: Only one major product with greater hydrophobicity is formed (retention time of 11.3 min) containing active chlorine; thus it has been partially reduced. The chloramine has been completely reduced by 20 min. – -Dechlorination: Reduction by sulfite converts the chloramine product back to metoprolol. After 20 min peak area of metoprolol is ~90% of its pre-chlorination value ****Chloramines:** -have increased hydrophobicity relative to the parent amine caused by replacement of H with Cl. At neutral pH, both fluoxetine and metoprolol are protonated (pKa 10.1 and 9.2, respectively), also enhancing their hydrophilicity. -This increase my cause the chloramines to sorb to surfaces such as sediments, soils, and biological membranes. - can transfer their active chlorine to other reductants, reversing the chlorination reaction--freeing the bioactive parent PhAC
Chemosphere 66 (2007) 894–904		**Irrigation of treated wastewater in Braunschweig, Germany: An option to remove PhACs and musk fragrances**		Ternes et al., 2007
WWT Soil-aquifer treatment. (Irrigation) **Water:** Treated municipal wastewater	52 PhACs and two personal care products (PPCPs) betablockers, antibiotics, antiphlogistics, carbamazepine, musk fragrances, Iodinated contrast media (ICM) estrogens.	**Soil/Sediment Irrigation:** -inexpensive method to add water and nutrients. -digested sludge mixed into irrigation water; containing organic matter to improve water retention capacity of soil and the bulk of nutrients originally present in the sewage, (N and PO4). -secondary effluent is irrigated on agricultural fields. -In the vegetation period from March to October digested sludge is mixed with the effluent ***The irrigation machines are fed with an effluent/sludge mixture which they distribute over a distribution net of 100km. The mixture is irrigated to about 40 l m^{-2} at each application. About 500 l m^{-2} (in the winter time only effluents) are applied per year	*Water samples were taken as 24 h flow-proportional composite samples (cooled at 4 degC) from the outlet of the grit removal tank and the secondary clarifier, collected at midnight **water samples were collected from stainless steel lysimeters in the selected agricultural field at 3 different depths together with groundwater probes. **Several different analytical methods were used for PhAC detection – only references are given	**Most PPCPs while found in irrigated WW were never found in lysimeter or groundwater samples ****Groundwater and lysimeter** samples did contain diatrizoate, iopamidol, carbamazepine and sulfamethoxazole up to several µg/l; thus there were not removed by sorption or degradation ****Acidic PhACs, musk fragrances, estrogens and ß-blockers** were likely sorbed or transformed while passing through top soil layer. ****Estrogens:** Estrogenic effects are likely to disappear after irrigation, since the most potent steroid estrogens were not measurable. **Removal >90% was found for caffeine and ibuprofen. **Appreciable removal of: atenolol, metoprolol, propranolol, bezafibrate, trimethoprim, AHTN (tonalide) iohexol, iomeprol and iopromide. ****Removal Mechanism:** -Based on the phys–chemical properties (e.g. polarity) and literature data elimination of caffeine, ibuprofen and the ICM is likely caused by biodegradation -For ß-blockers, lipid regulators, antiphlogistics, iodinated contrast media and antibiotics the estimated Kd values indicate that sizeable non-specific sorption is not likely ****SRT =** important for the biodegradation of trace pollutants STP with a SRT of about 12–14 d a removal of three ICMs was observed, whereas in a previous case study with a SRT of about 4–6 d for the Wiesbaden STP no ICM removal occurred

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				(Ternes and Hirsch, 2000). -Removal via sorption is likely for polycyclic musk fragrances with Kd values of 150 and 180 l. -For estrogens sorption could also be significant, but as described in literature (see above) accompanied with biodegradation. **Compounds appear removed by top soil passage; formation of stable or even toxic transformation products products is however possible
Water Research 40 (2006) 3419 – 3428		**Biodegradation of persistent polar pollutants in wastewater: Comparison of an optimised lab-scale membrane bioreactor and activated sludge treatment**		Bernhard et al., 2006
Wastewater Treatment Biodegradation **Water:** Wastewater Ground-water	Carbamazepine Diclofenac Clofibric Acid Ibuprofen 2,4-Dichlorobenzoic Acid	*__Activated Sludge Tx (AST)__ *__Membrane Bioreactor (MBR)__ - higher sludge retention time (SRT) favouriing microbial adaptation. -compared to WWTP: higher SC and SRT; less sludge production, smaller footprint size and unsurpassed effluent quality in terms of turbidity, bacteria and viruses, and occasionally, in total dissolved organics, biological oxygen demand (BOD) and chemical oxygen demand (COD).	**Lab-scale membrane bioreactor **After primary treatment a fraction of preclarified WW was split to the MBR, which was run without an anoxic pretreatment stage. *Analysis by **GC-MS and LC-MS** after enrichment with SPE ** The MBR was filled in November 2003 with 21 L activated sludge of the WWTP Wiesbaden.	**__Non-degradable micropollutants__, such as EDTA and carbamazepine were not eliminated at all during WWT **__MBR__ indicated better removals compared to AST for poorly biodegradable P3, such as diclofenac, mecoprop and sulfophenylcarboxylates. ** Increased SRT and SC improved the adaptation rates of the microorganisms towards the degradable P3, whereas temperature and pH-values did not show a measurable effect. **Ibuprofen removal in the WWTP and the MBR were 97.371.3% and 98.870.7%, respectively; it rose from 90% to 95% by increasing the SRT up to 75 d ** **Diclofenac:** -AST removal between 0% and 60%; MBR removal in the range of 28% and 78% No adsorption of diclofenac to the activated sludge was observed. **** Clofibric acid**: -Removals in AST were between 0% and 50%. The MBR obviously removed clofibric acid in 9 out of 11 samples with a much higher efficiency compared to AST. Significant removals for the MBR could not be calculated due to concentrations below LOD. **** 2,4-Dichlorobenzoic acid:** -Removal by AST and MBR ranged from 36% to 96% and 56% to 100%, respectively. Others were dependent on the concentrations of 2,4-dichlorobenzoic acid in the influents. Lower concentrations (< 0.40 μg/l) cause less removal. **** Carbamazepine** -Not eliminated in WW treatment, neither by AST nor by MBR. It was present in all corresponding samples at an almost steady concentration level ranging from 0.81 to 1.46 mg l^{-1}.
Water Research 40 (2006) 2369 – 2374		**Water remediation by micelle–clay system: Case study for tetracycline and sulfonamide antibiotics**		Polubesova et al., 2006
Adsorption removal Water:	tetracycline and sulfonamide antibiotics	micelles pre-adsorbed on montmorillonite Micelles of benzyldimethylhexadecylammonium	**Batch Experiments **Isotherms of adsorption for micelle–clay complexes (final concentrations 12mM of BDMHDA and 10 g/L clay) were	**The micelle–clay complexes (1% w/w) removed 96–99.9% of antibiotics from their water solutions containing 5 to 50 mg l^{-1} of PhACs. **Column filters (quartz sand and BDMHDA micelle–clay complex at 100:1 w/w ratio)

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Lab synthesized		(BDMHDA) were used	measured for all antibiotics. **Initial concentrations of antibiotics were in the range of 5–50 mg l^{-1}. **Adsorption experiments were performed in triplicate. **Analysis by **HPLC** (Merck Hitachi 6200) equipped with a diode array detector. **SPE using 3M Empore TM SDS-RPS (47mm) extraction disks (Varian, CA, USA) and vacuum manifold.	-Removed 94–99.9% of PhACs from initial solutions containing 10 mg l^{-1}; and 89% of sulfamethizole from an initial solution containing 10 μg/L of this antibiotic. -Also efficient removal of antibiotics in the presence of dissolved soil organic matter removing 89–99% of tetracycline and sulfamethizol from initial solutions containing 10 mg $l^{-1}$of antibiotic and 8 mg l^{-1} of humic acid, or 9 mg l^{-1} of fulvic acid. **Adsorption isotherms were fitted by the Langmuir equation with R2 larger than 0.999; Implying that interactions btw adsorbed antibiotic molecules can be ignored. Electrostatic binding along with partitioning is suggested adsorption mechanism **Filters with activated carbon mixed with quartz were less efficient than micelle–clay–quartz systems, removing 45–58% of sulfonamides and 79–88% of tetracyclines from the initial solutions containing 10 mg l^{-1} of PhACs.

Environ. Sci. Technol. 2006, 40, 7222-7227	**Oxidation of Sulfonamide Antimicrobials by Ferrate(VI) [FeVIO42-]**	Sharma et al., 2006

Oxidation Water: Lab Synthesized	**Sulfonamide antimicrobials:** sulfisoxazole, sulfamethazine, sulfamethizole, sulfadimethoxine, and sulfamethoxazole.	**Ferrate(VI) (FeVIO42-, Fe(VI)),** -Powerful oxidizing agent; reduction potential of 2.20 & 0.70V in acidic and alkaline solutions, respectively -Under acidic onditions it has highest redox potential of all oxidants used in WWT. -Spontaneous decomposition of Fe(VI) in water gives molecular oxygen and Fe(III) -environmentally friendly chemical for coagulation, is infection, and oxidation -Can improve removal of natural organic matter -Unlike ozone, it does not react with bromide ion; thus carcinogenic bromate ion is not formed in the treatment of bromide containing water by.	**Rxn kinetics determined as a function of pH (7.0-9.7) and Temp. (15-45 °C) using a stopped-flow spectrophotometer equipped with a photomultiplier (PM) detector under pseudo-first-order conditions with sulfonamides in excess. **SMX and were dissolved in 1 g of CD3OD before introduction in the AMX-360 IS, a pulse Fourier Transform Nuclear Magnetic Resonance spectrometer with a 1H resonance frequency of 360.13 MHz. ****IR spectral analysis** ****MS spectral analysis**	**At a stoichiometric ratio of 4:1 (Fe(VI):SMX), complete removal of SMX was achieved. Oxidation products and kinetics suggest that attack of Fe(VI) occurs at the isoxazole moiety and the aniline moiety with minimal preference. **Oxidation of sulfonamides by Fe(VI) is first-order with respect to each reactant. Observed second-order rate constants decreased nonlinearly with increasing pH and may be related to the protonation of Fe(VI) and sulfonamides **HFeO4- has a faster reaction rate with the neutral sulfonamide species (SH) than with negatively charged ionized species (S-). Thus, pH dependence may be due to electrostatic interaction between Fe(VI) and sulfonamide species. It is expected that the attraction between the Fe(VI) species and SH will be stronger than that with S-. Neutral species (SH) (RSH) increase with a decrease in pH, and thus their overall contribution to reaction rate should be higher at lower pH. **Excess Fe(VI) (10-5 M or 2 mg l-1 K2FeO4) relative to sulfonamides in water, has a half life <5min at pH7 for most sulfonamides. Rate and thus T1/2's are pH dependent **Fe(VI) oxidation is the destruction of the aromatic ring (e.g. isoxazole ring), forming a oxidation product with differing biological binding property. Oxidation of the amino group and/or isoxazole ring may cause it to less effectively mimic p-aminobenzoic acid necessary for the synthesis folic acid. Thus byproducts are expected to be less toxic.

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Water Science & Technology 55 No 10 217–225, 2007		**Treatability of cefazolin antibiotic formulation effluent with O3 and O3/H2O2 processes**		Iskender et al., 2007
Advanced Oxidation Processes (AOPs) ozonation and perozonation Water: Lab simulated waste water (PhAC plant effluent)	cefazolin-Na (antibiotic)	**O3 **O3/H2O2	**Synthetic samples prepared by dissolving appropriateamount of cefazolin-Na powder in deionised water to an initial CODof 400 mg l^{-1}. **Ozonation and perozonation processes were applied in semi-batch mode to 1 L of synthetic cefazolin-Na formulation effluent in a 1.5 L-capacity bubble column **The experiments were carried out for 5, 10, 20, 40 and 60min at an initial pH of 11. **The acute toxicity tests run with the marine microalga haeodactylum tricornutum were performed as previously described by Okay et al. (2002). **Standard analytic method: APHA-AWWWA-WCPF,1989	**20 min of ozonation at a rate of 1,500 mg l^{-1}-h removed COD by 38%, removal efficiency of 40% was achieved via H2O2 enhanced ozonation **Both pretreatment alternatives underwent elevation of the BOD5/COD ratio from 0.01 to 0.08. The initially inert COD was reduced by 38% using ozonation and by 60% using H2O2 enhanced ozonation. In terms of the lowest achievable effluent. **COD levels after bio-treatment, ozonation was observed at 205 mg l^{-1}, while a residual COD of 135 mg $l^{-1}$was involved for perozonation. **According acute toxicity test, ozonated and perozonated samples exhibited more toxicity than the untreated effluent after 4 days. Synthetic cefazolin-Na WW showed less toxicity than ozonated and perozonated samples. **Penetration of synthetic cefazolin-Na effluent with its high molecular weight had more difficultly than the smaller and more bioavailable ozonated and perozonated samples in entering cells. The ease in entrance through the cell can cause a higher toxicity. **Activated sludge inhibition test demonstrated that both alternatives efficiently eliminated the inhibition of investigated formulation effluent.
Water Research 39 (2005) 3139–3152		**Removal of PhACs and fragrances in biological wastewater treatment**		Joss et al., 2005
Wastewater treatment Water: Municipal wastewater	Roxithromycin sulfamethoxazole. Diclofenac, Ibuprofen, Naproxen. Iopromide Galaxolide, Tonalide and Carbamazepine.	*__Activated Sludge__ *__Membrane Bioreactor__ (MBR) -is a 100 PE (population equivalents) pilot plant fed with primary effluent from the conventional activated sludge treatment plant 1 (CAS1) at a flow-rate variation proportional to full-scale inlet flow. __*Fixed Bed Reactor (FB)__ -Consists of eight Biostyrs reactors with a total volume of 1520m3.	__*Monitoring was performed at:__ 1) WWTP of Kloten/Opfikon, where (CAS1) treatment plant is run in parallel with a pilotscale membrane bioreactor (MBR). 2) WWTP of Altenrhein, where a lane of a CAS1 is run in parallel with a FB reactor * The pilot was run with SRTs of 1672, 3373 and 60–80 d and is equipped with stirred anaerobic and anoxic compartments followed by aerobic filtration compartments. *SPE (Oasis HLB, Waters). *Analysis using: -reversed-phase liquid -electrospray mass spectrometry in the positive ionization mode -GC/MS in single-ion monitoring mode (SIM). -Pressurized liquid extraction	**__Observed removal__ of PhACs was mainly due to biological transformation and varied from <10% (CBZ) to >90% (ibuprofen). **__Naproxen__ showed significant removal (50–80%), as did __SMX__ and its metabolite N4-acetyl-sulfamethoxazole; Partial removal is also seen for __Diclofenac__ (20–40%). **No removal is seen for __Carbamazepine.__ **No quantitative relationship between structure and activity could be set up for the biological transformation. **For compounds showing a sorption coefficient (Kd) <300 L/Kg, sorption onto secondary sludge was not relevant and their transformation can be assessed by comparing influent and effluent concentrations. __**In some samples output loads were greater than influent (values >100%).__ This may be due to either (i) sampling inaccuracy, (ii) inaccuracy of the sorption coefficient especially for primary sludge, or (iii) conjugate compounds not detected in the influent but re-transformed into the original compound during wastewater treatment (e.g. de-acetylation as occurs for N4-acetyl-SMX). **For most compounds removal did not show a clear dependency on __reactor configuration__, sludge age or temperature (except for iopromide and roxithromycin, where a significant variation but no clear correlation is seen).

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				Similar performance between the FB and the CAS1 indicates that total contact time between wastewater and sludge (HRT) has only a minor influence on removal **Result of **nutrient-removing WWTPs, show that no compounds are significantly degraded at low sludge ages (<2 days of sludge retention times) **Variation of **the sludge age** between 10 and 60–80 days showed no significant impact on the transformation efficiency of the seven PhACs studied in this work ****MBR plant** shows comparable removal plants equipped with 2nd ary clarification, indicating that micro- and ultrafiltration cannot remove micropollutants directly by sieving (molecular size is at least 100X smaller pore size) ****For SMX and iopromide (IP):** a correlation of removal and sludge age seems to be indicated in the data, however if inconclusive because: (i) the dependency is not confirmed by comparable sludge ages run in conventional plants, and (ii) both SMX and IP show unexplained removal variations
Water Research 39 (2005) 4790–4796		**Removal of cosmetic ingredients and PhACs in sewage primary treatment**		Carballa et al., 2005
Primary Sewage treatment: Coagulationflocculation and flotation **Water:** **Sewage Secondary solutions:** 1) contains musks & neutral PhACs 2) Contains acidic compounds spiked to 10L of urban WW **Secondary types of WW:** 1) Low fat (LF) WW, (60 mg l^{-1}) 2) High fat (HF) WW, (150 mg l^{-1})	Galaxolide, Tonalide, Carbamazepine, Diazepam, Ibuprofen, Naproxen and Diclofenac.	**Coagulation–flocculation:** -Enhance removal of suspended solids and colloids; addition of metal salts or organic compounds causes the agglomeration of these particles, allowing elimination by decantation or filtration Flotation technique: -finely suspended particles are separated by adhering to the surface of rising bubbles, -proved to be efficient, practical and reliable for the removal of fat, and other contaminants, such as oils, biomolecules or suspended solids from water . Lipophilic PPCPs can be removed from WW by flotation due to their solubilization in the lipid fractions or sorption onto small aggregates.	**Objective:** to improve the removal efficiencies of 3 groups of PPCPs (musks, neutral and acidic PhACs), with different sorption properties, during sewage primary treatment ***Coagulation–flocculation** -main parameters considered were the additives (ferric chloride, aluminum sulfate, and aluminum polychloride), their doses and the temperature (12 or 25 1C). -Assay carried out in a Jar-Test device, 1 l of liquid volume. The influence of three additives was studied: ****Flotation assays:** -Carried out in a unit consisting of a pressurized vessel of 2 l (where air was dissolved into the wastewater) and a flotation cell of 1 l **SPE of 500 ml samples using 60mg OASIS HLB cartridges ****GC/MS** used to determine the concentration of compounds in the SPE extract	****Coagulant-Flocculant assays**: -Initial fat content of WW and temperature were studied. -Musks were removed the most (35–60%), followed by Diazepam (40–50%) and diclofenac (20–45%) and, to a lesser extent, CBZ (20–35%), Ibuprofen (10–25%) and NPX (10–30%). Best results were usually at 25 1C, although in some cases the operation at 12 1C gave similar results. Removal of musks and neutral compounds was higher in HF wastewater **For compounds more hydrophilic than diclofenac, removals were less (with maximum reductions below 25%). ****Carbamazepine and Ibuprofen** were not removed under any tested condition. **Coagulant dose and temperature showed <5% difference in PPCPs removal in the considered range. **The use of an additive increased the removal efficiencies of all PPCPs tested except IBU and CBZ. ****Diclofenac** elimination was higher with ferric chloride and aluminum sulfate (around 70%) -With significant sorption affinity—was removed ~ 50–70% at both temperatures independent of dose and type of coagulant used. **Concentrations of **Diazepam and Naproxen** were reduced by 20–25%. For Diazepam there were no significant differences between ferric chloride and aluminum sulfate, Naproxen was only removed with ferric chloride. In both cases, PAX was the less effective additive (below 5%)

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				Coagulant enhanced the binding of Diclofenac to the suspended solids throughout the trivalent cations, thus allowing a further removal from the water phase. Diazepam and Naproxen removal was also improved by coagulant (20–25%), although to lesser extent due to their lower Kd values. **Flotation Assays: -Elimination of Diazepam was similar to musks (40–45%); no significant difference was observed between both temperatures. **According to its lower lipophilicity (logKow ~ 2.4), CBZ was removed to a lesser extent (~ 20%) independently of the temperature. **In the HF water removal by flotation was increased for CBZ and Diazepam, increasing to 35 & 50% respectivelt, uninfluenced by temperature *Anti-inflammatories: -Highest removal for Diclofenac (20–40%). -Temperature influenced removal significantly - Independent of the fat content, thus their removal patterns were similar to those observed in the assays with LF wastewaters: 20–45% for Diclofenac, 10–30% for Naproxen and 10–20% for Ibuprofen. ***Musks:** the highest values were obtained at 25 1C. ** The different affinities of PPCPs for organics can be clearly seen with HF WWs; removal of lipophilic substances, such as musks, is enhanced, while elimination of more polar compounds remains unchanged. **Physico-chemical properties** of the PPCPs, the presence of the other substances in the medium, fat globules, the colloidal matter or the flocs formed during coagulation–flocculation assays must all be considered.
Environ. Sci. Technol. 2006, 40, 357-363		**Removal of PhACs in Sewage Treatment Plants in Italy**		Castiglioni et al., 2006
Sewage Treatment Water: Sewage Surface receiving waters	clarithromycin atenolol erythromycin enalapril spiramycin diazepam lincomycin carbamazepine quinolines ciprofloxacin furosemide ofloxacin hydrochlorothiazide amoxycillin ethinylestradiol sulfamides sulfamethaxole omeprazole macrolides oleandomycin ranitidine tilmicosin bezafibrate tylosin		**Loads and **removal rates (RR)** were studied in six sewage treatment plants. **Sampled influents and effluents of all the STPs for mass balance calculations. **PhACs were measured by reversed-phase **HPLC-MS/MS,** after combined extraction by two SPE columns, an OasisMCX(60 mg, Waters Corp., Milford, MA) at pH 2.0 and a Lichrolut EN (200 mg, Merck, Darmstadt, Germany) at pH 7.0 **Three deuterated internal standards were used to quantify the PhACs,	****Total removal rates in the STPs were mostly lower than 40%.** **PhACs could be divided into 3 groups: 1) **RR higher in summer than in winter**; amoxicillin (median of about 75% in winter and 100% in summer), atenolol (10% and 55%), bezafibrate (15% and 87%), enalapril (18% and 100%), furosemide (8% and 54%), ibuprofen (38% and 93%), ranitidine (39% and 84%), and sulfamethoxazole (17% and 71%). 2) **RR similar in summer and winter**: ciprofloxacin (60%), hydrochlorothiazide (30%), and ofloxacin (50%),

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	clofibric acid tetracyclines oxytetracycline demethyl-diazepam cyclophosphamide 17â-estradiol methotrexate estrone ibuprofen salbutamol			3) **No removal:** carbamazepine, clarithromycin, erythromycin, lincomycin, salbutamol, and spiramycin, plus estrone. **STP effluents still contained PhACs that were discharged in the receiving water. **The total load of the 26 PhACs discharged through the STP effluents were in the range of 1-3g/day/1000 inhabitants; about 60-180 kg/day of PhAC substances reach surface **RRs were generally <40%, with the exception of the plant in Varese Lago (64%). In two plants (Varese Olona and Cagliari) the RR was zero. RR were 0%, 16%, 31%, and 39% in the four STPs sampled in winter and 0%, 31%, and 64% in those sampled in summer RR were higher in summer thandue to temperature-dependent increase of microbial activvity. *Greater attenuation (30 to 60%) was found for molecules also found in the particulate (hydrochlorothiazide, bezafibrate, spiramycin, clarithromycin, estrone, and erythromycin), indicating that attenuation may be due to both sorption and degradation -A second group of compounds with known persistence/stability in water had lower % attenuation (<30%) including: carbamazepine, atenolol, furosemide, enalapril, and ranitidine. - Atenolol, carbamazepine, enalapril, ranitidine, ofloxacin and ciprofloxin were sorbed to particulate suggesting sorption is important in their attenuation -Furosemide and ibuprofen, sulfamethoxazole, which degraded up to 70% in STPs and salbutamol and lincomycin which were not degraded at all, were not detected in the particulate, thus indicating a greater role for degradation.
Environmental Toxicology and Chemistry 24,. 1, (2005)25–30		**Tracking Acidic Pharmaceuticals Caffeine and Triclosan through the Wastewater Treatment Process**		Thomas et al., 2005
Waster water treatment (4 stages) Water: Wastewater effluent	Ibuprofen, Naproxen, Ketoprofen, Diclofenac, Caffeine, Triclosan, and Meclofenamic acid	**4 stages of WWT:** **all WWTPs were similar in design, consisting of: 1) a primary settling process; 2) an activated sludge biological nutrient removal process (with anoxic zones for denitrification); 3) an advanced treatment consisting of phosphorous removal, gravity filtration, 4) disinfection	**Field-scale analysis of WWT plant effluent **Extraction via SPE with Waters Oasis hydrophilic–lipophilic balance solid phase extraction columns, **The samples were concentrated in an evaporating centrifuge, spiked with 100 ng of internal standard, and derivatized with N,O-bis(trimethylsilyl) trifluoroacetamide. **Anyalysis by **GC/MS** -Samples (1 ml) were injected into an HP 5980 GC coupled to an HP 5971 mass selective detector and quantified against calibration standards (0.05–33 ng/ml) using selected ion monitoring mode. Method detection limits ranged from 6 to 45ng/L.	**The majority of compound removal (51–99%) occurs during **secondary treatment**; microbes present in a mixture of aerobic and anaerobic zones biodegrade organic matter not removed in primary treatment; removing a large quantity of fine particulate matter to which PhACs may be adsorbed. **A smaller portion (0–44%) is removed during **primary treatment**; suspended solids in the raw influent are mixed with polymet flocculant and allowed to settle and are then separated; removing large dense particles too small to be collected by the bar screens. ****Advanced treatment** removes a smaller portion (0–16%). ** **Qualitative methanol extraction** of collected particulates showed no detectable levels of the acidic drugs in the particulate, supporting the expectation from the total suspended matter data, that acidic drugs are present 98% in the aqueous phase. -Conversely, triclosan was found in the qualitative extraction of suspended matter collected during extraction.

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Water Research 40 (2006) 507 – 516		**Performance of an up-flow anaerobic stage reactor (UASR) in the treatment of PhAC wastewater containing macrolide antibiotics**		Shreeshivadasan et al., 2006
WWT up-flow anaerobic stage reactor (UASR) Water: Wastewater Real PhAC effluent	Macrolide antibiotics: Tylosin and Avilamycin antibiotics *Tylosin was PhAC of focus	****up-flow anaerobic stage reactor (UASR)** -Biomass = anaerobic digested sewage sludge – methanogenic bacteria -Each stage of the reactor is a separate compartment; this increases efficiency since recalcitrant substrates are in environments more conducive to their degradation. -Separating acidogenesis and methanogenesis benefits reactor performance **With no moving parts or mechanical mixing USAR is economically as a pre-treatment system. -Reactor configuration protects methanogenic biomass from toxic compounds in the influent	**Performance of the reactor was characterized in terms of its COD removal, Tylosin reduction, pH, VFA (volative fatty acid) production, methane yield and sludge washout. **Both reactors were seeded with anaerobic digested sewage sludge (Hexham Municipal sewage treatment plant). **Sample analysis included COD(chemical oxygen demand), pH, alkalinity, TKN, ammonium nitrogen (NH3-N), suspended solids (SS), volatile suspended solids (VSS), all according to Standard Methods (APHA, 1985) **Available PO4-P was measured by ion-chromatography, ** VFA by gas–liquid chromatography (Unicam 610 Series Gas Chromatograph with auto-injector and PU 4811 computing integrator) **Tylosin assay was performed by HPLC by injecting sample solutions onto a 20 cm Nucleosil C18 analytical column	**At a total **hydraulic retention time** (HRT) of 4 d and organic loading rate (OLR) of 1.86 kg $CODm^{-3}$ d^{-1}, no detectable levels of the acidic drugs in the particulate fraction were found;, COD reduction was 70–75%, suggesting the biomass had acclimated to the antibiotics; **Average reduction of 95% for Tylosin in the UASR, indicating efficient degradation in the anaerobic reactor system. **Similar COD removal efficiency occurred when tylosin was present at concentrations ranging from 0 to 400 mg l^{-1} (mean removal 93%), **At tylosin concentrations of 600 and 800 mg l^{-1} there was a slight decline in treatment efficiency to 85% and 75% removal, respectively. Tylosin caused only a minor inhibition effect on the microorganisms within the UASR. **VFA, biomass and pH data indicate different metabolic processes between Stages 1–4 of the UASR system, each stage favour a unique population of microorganisms. **At a reactor OLR of 1.86 kg $CODm^{-3}$ d^{-1} (HRT 4 d), soluble COD reduction was ~70–75%; When OLR was increased (by lowering the HRT) COD removal efficiency decreased, continuing to do so until only 45% soluble COD removal was observed at an OLR of 3.73 kg $CODm^{-3}$ d^{-1}. **Stages 2–4 showed a relatively minor contribution to total COD removal, stage 2 contributing ~10-15% and stages 3&4 only ~5%. **50–60% COD reduction occurred in Stage 1 of the UASR when HRT was set to 4 d ** Methanogenic biomass in Stages 2–4 could have been affected adversely by products and acidic conditions generated in Stage 1 ** While the COD removal profile showed reducing COD removal efficiency with increasing OLR, Tylosin removal efficiency remained relatively constant
Water Research 41 (2007) 1013 – 1021		**Occurrence and removal of PhACs and endocrine disruptors in South Korean surface, drinking, and waste waters**		Kima et al., 2007
Waste water And Drinking water treatment **Water:** Surface waters and Wastewater treatment plant **Water:**		Membrane bioreactor (MBR): - system consists of an activated sludge tank followed by commercially available plate and frame type membrane modules (Pure-Envitech Co., Ltd, Korea) and a hollow-fiber membrane module	**Full and Pilot-scale investigations ****LC–MS/MS** with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) **SPE - Waters HLB (hydrophilic–lipophilic balance) solid phase extraction cartridges	**Conventional drinking water treatment** methods were relatively inefficient for contaminant removal, while efficient removal (E99%) was achieved by GAC. **Observed removal appeared completely related to **GAC** at the DWTP; likely due to high sorption efficiencies of compounds with activated carbon based on hydrophobicity. **River water has low concentrations of natural organic matter (NOM) which results in less competition for the binding of micropollutants to the activated carbon ****Wastewater treatment processes:**

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WWT plant effluents in South Korea		Membrane filtration: Activated carbon Reverse osmosis Nanofiltration Ultrafiltration **GAC**		1) **Membrane bioreactors** (MBR) showed limited target compound removal; found to be efficient for hormones (e.g., estriol, testosterone, androstenedione) and certain PhACs (e.g., acetaminophen, ibuprofen, and caffeine) with approximately 99% removal; MBR treatment did not decrease the concentration of erythromycin, TCEP, trimethoprim, naproxen, diclofenac, and carbamazepine. 2) **Membrane filtration** processes using reverse osmosis (RO) and nanofiltration (NF) showed excellent removal (>95%) for all target analytes. **the combination of membranes with UV irradiation did not provide enhanced removal. **RO did not display higher removal percentages when compared with NF.
Water Research 39 (2005) 2654–2664		**Pathways and metabolites of microbial degradation of selected acidic PhAC and their occurrence in municipal wastewater treated by a membrane bioreactor**		Benito et al., 2005
WWTx **Water:** Municiple waterwater effluent	5 acidic PhACs: Ketoprofen Naproxen, Bezafibrate, Ibuprofen Diclofenac	**Activated Sludge -Since the sludge was withdrawn from a reactor treating real municipal wastewater in which all five PhACs were found (Quintana and Reemtsma, 2004), it had the opportunity to adapt to these substrates.	**Laboratory biodegradation tests were performed in batch cultures to investigate the biodegradation of these PhACs by activated sludge from a municipal WWTP **Initial experiments were conducted with the concentration of PhACs at 20 mg l^{-1} ****LC-MS/MS** - Ion-pair liquid chromatography was coupled to a triple quadrupole mass spectrometer (Quattro LC, Micromass, UK) with electrospray ionization operated in the negative ion mode.	**Initial Lab experiment (20 mg l^{-1}): -Only ketoprofen and the aniline control were degraded within 28 days; all other PhACs remained unaltered. -Ketoprofen transformation started on day 10 and it was completely transformed after 28 days; two new metabolites of relatively high intensity could be detected and tentatively identified by means of LC-MS. While the first metabolite reached its maximum around 14 days, the second one increased until the end of the experiment -Based on these metabolites, it is proposed that ketoprofen is degraded along the pathway known for biphenyls, biphenyl ethers and related compounds ****2nd Lab Experiment (Addition of carbon source for co-metabolic degradation): -**Ketoprofen and Diclofenac** were not degraded in this series over a period of 28 day; The other three PhACs showed variable degrees of transformation and mineralization; -**Bezafibrate** was completely transformed but not mineralized within 5 days; One metabolite was detected with rapidly increasing concentration during the 1st 5 days; DOC removal from bezafibrate over the 28 days was assessed as 30% -**Naproxen** degradation was slow; ~60% transformation within 28 days and only 1 metabolite (O-desmethyl-NPX) detected at low intensity. This ether cleavage is well documented for in mammalian and fungal metabolism, yet not for bacterial transformation. -Steady desmethyl-naproxen concentration during day 20–25 may due to steady demethylation of naproxen and mineralization of desmethyl-naproxen. LC-MS analysis of a sample taken day 39 shows neither naproxen nor desmethyl-naproxen present **Thus, incomplete removal seen in municipal

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				WWTP is a kinetic problem. *** Ibuprofen:** biodegradation started after a lag phase of a ~5 days and was completed after 22 days; 2 products were detected by LC-MS: two isomers of hydroxy-ibuprofen - Isomers do not accumulate, degrading easily as shown by their rapidly decreasing concentration with decreasing concentration of the parent compound ** None of the metabolites detected in the batch tests were found in treated municipal wastewater. This agrees with the results of the batch tests that indicated mineralization of most of the detected metabolites
	Water Research 39 (2005) 2219–2228	**Occurrence of acidic PhACs in raw and treated sewages and in receiving waters**		
Sewage Treatment **Water:** Sewage - mainly municipal with roughly 10% industrial inflow (e.g. from pulp and paper mills, and food and metal industry) Receiving Water	Ibuprofen, Naproxen, Ketoprofen, Diclofenac and Bezafibrate,	Treatment process consisted of combinations of biological and chemical processes Four of the plants used denitrification/nitrification (DN) process for nitrogen removal.	**SPE-LCMS ** SPE to separate Rx from waste water **Liquid chromatographic separation **Detection by a triple-quadrupole mass spec ****Risk to aquatic environment was estimated by a ratio of measured environmental concentration (MEC) and predicted no-effect concentration (PNEC).	** **Highest removal rate** was observed for ibuprofen and the lowest for diclofenac, 92% +/- 8% and 26% +/- 17%, respectively. **Due to the incomplete removal, the PhACs were found in rivers at the discharge points of the STP effluents. **Downstream of discharge points, concentrations decreased significantly mainly due to dilution in river. **Surface water concentration** indicated no aquatic risk; however, in dry seasons or during STP malfunctions ibuprofen could pose a risk in small river systems. ** Despite a high removal rate (81± 18%), **naproxen** was the most abundant PhAC in the two studied effluents. ** **Ketoprofen** was removed in an average of 78± 18% ** **Bezafibrate** removal (51±42%) varied significantly between STPs; even increasing at one site. This may be due to analytical inaccuracy or to deconjugation, since 22% of bezafibrate is glurcuronidated. ** Total removal of studied PhACs in STPs was 75–98%. ** **For ibuprofen, naproxen, ketoprofen, diclofenac and bezafibrate, the previously reported removal rates are**: 75–90%, 66–82%, 23–78%, 3–75% and 50–83%, respectively **Since sludge concentrations of PhACs were not determined, it's not possible to deduce whether the removal was due to biodegradation or adsorption to the sludge. ** **The DN process** had no significant effect on the removal rates of the PhACs. ** In the cities where part of the wastewater originates for instance from pulp and paper mills and metal industry, the removal rates of PhACs are lower.

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Science of the Total Environment 377 (2007) 255–272		**Efficiency of conventional drinking-water-treatment processes in removal of PhACs and other organic compounds**		Stackelberg et al., 2007
Drinking water treatment **Water:** Drinking water	**113 organic compounds (OC) analyzed** PhACs: Acetaminophen Caffeine Carbamazepine Codeine Continine Dehydronifedipine Diphenhydramine Erythromycin Fluoxetine Lincomycin Sufadimethoxine Sulfamethazine Sulfamethoxazole Sulfathiazole Diazinon	**Clarification:** Chemically treating water (with FeCl3) to destabilize colloidal particles (coagulation) and facilitate their flocculation (using microsand) and settling with other suspended sediments. **Disinfection:** Disinfection was conducted by the addition of NaClO **Granular-activated-carbon (GAC)** filtration: GAC Filters: 25.4 cm of sand and 91.4 cm of bituminous granular activated carbon (GAC filters)	**Field analysis measuring occurrence of five PhACs in SPR influent and effluent; samples were collected as 24 hour composite samples and stored at -18degC **SPE ** accelerated solvent extraction (ASE) ****HPLC/MS–ESI(+)** **** LC/MS – ESI (+)** ****HPLC/MS-MS – ESI (+)** ****GC/MS**	**OVERALL DRINKING WATER TREATMENT** ****Effectiveness of treatments** varied widely within and among classes of compounds; some hydrophobic compounds were strongly oxidized by free chlorine, and some hydrophilic compounds were partly removed through adsorption processes. ** **Effectiveness of a DWT depends on several factors:** -The quality of the source water, the type and mode of operation of each treatment process, and physiochemical characteristics of compounds ** **Hydrophilic compounds** (low log Kow and high solubility), such as PhACs, were detected at relatively low concentrations in dried-solids samples and were present in measurable concentrations in finished-water samples; thus little sorption ****CLARIFICATION:** -Accounted for only 15% of the reduction in average concentration of OCs -None of the 32 OCs showed a decrease >75% -**Mild degradation (25-75%)**: Sulfamethoxazole, acetaminophen, dehydronifedipine; which were not detected in the dried solids of settled sludge -Removal of these hydrophilic PhACs from the water phase may be due to ferric chloride coagulation, resulting in base or acid hydrolysis **-Less than 25%** removal of carbamazepine, caffeine, erythromycin–H2O, continine ****DISINFECTION:** -Accounted for 32% of the degradation or removal of OCs from the water phase. - **Significant removal:** Sulfamethoxazole, acetaminophen, erythromycin–H2O, and diazinon were significantly lowered decreasing by at least 75% (oxidation with free chlorine) -**Low removal:** Carbamazepine, caffeine, cotinine, and dehydronifedipine were found to have low reactivity with free chlorine, decreasing by <25% **GAC FILTRATION:** -Accounted for 53% of the removal of OCs from the water phase. - PhAC degradates erythromycin–H2O and dehydronifedipine, were lowered below detection limits - Carbamazepine, caffeine, cotinine, were decreased by 90% or more

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Environ. Sci. Technol. 2006, 40, 5095-5101		Monitoring the Removal Efficiency of PhACs and Hormones in Different Treatment Processes of Source-Separated Urine with Bioassays		Beate et al., 2006
Wastewater treatment Urine Source-Separation Urine Treatment technologies **Water:** Wastewater Raw stored urine and spiked urine	carbamazepine diclofenac, ibuprofen, propranolol, sulfamethoxazole, 17â-estradiol (E2) 17Rethinylestradiol (EE2)).	Urine source-separation -prevents wasting nutrients -prevents potentially hazardous micropollutants from entering the wastewater stream -promote sustainability of WW management because urine contains most of the nutrients and a majority of endocrine disrupting compounds and PhACs in domestic WW but constitutes <1% of total wastewater volume Treatment Technologies: electrodialysis, bioreactor treatment, nanofiltration, struvite precipitation, ozonation	* Removal efficiencies were determined with a combination of bioassays and chemical target analysis. **Biotest battery: 1) The algal chlorophyll fluorescence test with green algae for detecting phytotoxicity and baseline toxicity The yeast estrogen screen (YES) for detection of estrogenic endocrine disruption 3) Theumutest for genotoxicity **SPE **Chemical Analysis: **LC-MS/MS**	** **Filtration methods** (nanofiltration and electrodialysis) were highly efficient with respect to toxicity reduction. **Micropollutant degradation during **biological treatment** in a sequencing batch reactor was very compound specific. ****ELECTRODIALYSIS:** Diluate contained all remaining estrogenic activity, and removal efficiency with respect to estradiol equivalent concentrations (EEEZ) was >99%. Overall, 42-66% of the EEEQ was recovered in the diluate. This can be attributed to adsorption of ethinylestradiol to the membranes ****NANOFILTRATION** (NF): Toxicity reduction, expressed as removal efficiency, amounted to 84% for urine & 89% for urine spiked with PhACs. NF removed natural and xenobiotic compounds with a negative impact on growth and photosynthesis in algae. -**Removal efficiencies**: 59% for the basic propranolol ,96%for the acidic ibuprofen and diclofenac, and 74% for the neutral carbamazepine -**Retention depends on size, charge & polarity** ****BIOREACTOR:** -In the algal chlorophyll fluorescence test, no reduction of toxicity was observed in urine spiked with 10-5 M propranolol or 10-3 M ibuprofen, nor did the analytically determined concentrations decrease within 50 h. Note that biodegradation is highly dependent on the sludge ****** STRUVITE PRECIPITATION:** -PhAC Removal efficiency was 97 ± 2% measured by algae test; and estrogens was 98 ± 2% measured with the YES. -Removal was sightly higher if struvite was washed prior to re-dissolving it for the toxicity assay ****OZONATION:** -An ozone dose ~1 g/L-1 reduced algal toxicity only by 50-60%; while removing 99% of the estrogenic activity -Increasing ozone dose to 2.1 g/L improved the reduction of **algal toxicity** to only 75%. Thus, ozonation decreases estrogenicity of estrogenic compounds but does not lead to mineralization -Reduction was 70-90% higher in spiked urine. Micropollutants in urine dropped to below LOD at ozone doses of 0.6-1.3 gâL-1 -Partially degrades many PhACs, hormones, and other natural urine components, but does not lead to full mineralization, shows clear dose-dependency ***May create reactive species**; Umu test indicated no activity in the treated urine; however umu test was conducted with SPE extracts of the ozonation samples, and thus it's possible that potentially reactive and genotoxic constituents of the urine were removed.

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Environ. Sci. Technol. 2007, 41, 3708-3714		**Elimination of Selected Acidic Pharmaceuticals from Municipal Wastewater by an Activated Sludge System and Membrane Bioreactors**		Kimura et al., 2007
Waste Water Treatment Activated Sludge Membrane Bioreactor **Water:** Wastewater effluent	Clofibric acid, Diclofenac, Ibuprofen, Ketoprofen, Mefenamic acid, Naproxen	*Acivated Sludge *Membrane Bioreactor (MBR)	*Field analysis and Batch Elimination Test with Sludge Collected from the WWTP and MBRs -Used to investigate the degree of biodegradation /sorption of the PhACs. **Sampled from August to October at municipal WWTP *Solid retention times (SRTs) of the WWTP: 7 *SRT of MBR: 15 & 65 days *Measured the amount of adsorbed PhAC to sludge to investigate the elimination pathways –ultrasonic solvent extraction method *Sterilized sludges were also examined. ***GC/MS analysis**	***Elimination** was variable between compounds ***Membrane bioreactors** caused greater removal than seen at actual WWT plants ***Elimination success depended on SRT's;** better performance was seen in the MBR with a 65 day SRT as compared to the MBR with the 15 day SRT – this was particularly significant with diclofenac and ketoprofen ***BATCH ELIMINATION TESTS:** **-** revealed that the sludges in the MBRs had large specific sorption capacities due to their large specific surface areas. ****Elimination Mechanism:** -Despite the sorption capacities of sludges, the main **mechanism of elimination** of the PhACs was biodegradation. -Greater Ibuprofen and ketoprofen elimination in the experiments with **unsterilized sludges**, thus elimination mechanism is likely bidegradation -Initial removal of diclofenac was likely through sorption; biodegradation did not appear significant, occuring slowly if at all
Chemosphere 71 (2008) 1476–1485		**Behaviour and redox sensitivity of harmaceutical residues during bank filtration – Investigation of residues of phenazone-type analgesics**		Massmann et al., (2008)
Drinking Water treatment *Bank Filtration **Water:** Ground-water	Phenazone-type analgesics	*Sediment (oxic and anoxic) -microbes	*Field Analysis and Lab-scale column study *Water sampling of surface water, and wells (observation and production) conducted monthly ***HPLC-MS/MS PhAC analysis**	**GENERAL OBSERVATIONS:** ***Greater OXIC PhAC removal:** -Phenazone, 4-acetylaminoantipyrine (AAA), 4-formylaminoantipyrin (FAA) and 1,5-dimethyl-1,2-dehydro-3-pyrazolone (DP) were eliminated more efficiently under oxic conditions ***No Removal:** - 1-acetyl-1-methyl-2-dimethyloxamoyl-2-phenylhydrazide (AMDOPH) was not eliminated at all. **FIELD STUDY:** *PhAC elimination displayed strong seasonal variations. *Compounds were found to be more persistent under anoxic field conditions. *Microbially mediated degradation appeared only effective under oxic conditions (encountered in winter) *phenazone elimination was almost complete in column study(oxic conditions), but only 33% was eliminated in an undisturbed sediment core from the lake banks (largely anoxic) **COLUMN STUDY:** *Column study indicated elimination to be limited to uppermost dm of lake base, where oxygen is present.

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Chemosphere 70 (2008) 1525–1531		**Combined chemical treatment of pharmaceutical effluents from medical ointment production**		Kulik et al., 2008
Waste water treatment **Water:** Wastewater from PhAC plant -pretreated plant effluent	PhAC ointment	Fenton Chemical treatment with lime coagulation * $Fe_2(SO_4)_3$ *$7H_2O$ and CaO used as coagulant	*Lab-scale treatment * Batch experiments conducted in an Erlenmeyer flask *Permanent agitation for 1–6 h. *Catalyst ($Fe_2(SO_4)_3$ *$7H_2O$) was added first then reaction was initiated by adding H_2O_2 all at once *Experiments with non-catalyzed peroxide were conducted in same manner	*Fenton-like oxidation showed highest eficacy at H_2O_2/COD weight ratio of 2:1, H_2O_2/Fe2+ molar ratio of 10:1 and 2 h of treatment time. *Combining Fe(III) precipitation and lime coagulation improved COD and residual iron concentration reduction as well as BOD and BOD/COD ratios in pharmaceutical effluents. ***Combine treatment** enhanced the quality of pharmaceutical effluents and improved the biodegradability of pharmaceutical effluents. * Both iron (III) precipitation alone and in combination with lime coagulation (as second step in fenton oxidation) indicated < 2 mg /L residual Fe and no hydrogen peroxide in effluents. *COD removal of 87%, 94% and 96% and BOD7 removal of 79%, 92% and 95% were achieved.
		Removal of ibuprofen from wastewater: comparing biodegradation in conventional, membrane bioreactor, and biological nutrient removal treatment systems		Smook et al., 2008
Waste water treatment **Water:** Influent and effluent samples collected from WWTP and BNR	Ibuprofen	Conventional, membrane bioreactor (MBR) *Biological nutrient removal treatment systems (BNR)	BNR samples collected at: 1) Influent to the BNR; 2) Anaerobic tank; 3) Effluent from anoxic tank; 4) Effluent from aerobic Membrane tank **WWTP samples collected at:** 1) influent to primary clarifiers; 2) influent to aeration tanks; 3) influent to final secondary clarifiers; 4) effluent from final secondary clarifiers ***GC/MS analysis**	**Preliminary and Primary Treatment:** * Both plants indicated negligible removal of ibuprofen in preliminary and primary treatment **Aeration Tank:** *Ibuprofen removal >95% the aeration tank; aerobic biodegradation being the dominant mechanism. ***First order kinetic rate constants**, k_{biol}, for conventional tank and MBR were statistically similar (-6.8 ± 3.3 L/g SSpd and -8.4 ± 4.0 L/g SSpd, respectively) *BNR study indicated IBU is also anaerobically degraded. **Anaerobic Tank:** *%Removal of IBU in anaerobic tank was ~60%, and k values were similar at 1.07 1/h and 0.89 1/h for Trial 1 and Trial 2, respectively.
Water Researc 41 (2007) 2525 – 2532		**Bezafibrate removal by means of ozonation: Primary intermediates, kinetics, and toxicity assessment**		Dantas et al., 2007
Ozonation **Water:** Lab prepared water spiked with BZF	Benzafibrate	**Ozone** -Strong oxidant -Can attack organics by a direct (ionic) mechanism and a radical one - which originates from its decomposition in water to generate hydroxyl radicals (Sotelo et al., 1987). -Capable to degrade several xenobiotic compounds and transform refractory natural organic matter to biodegradable forms, i.e. biodegradable dissolved organic	Two different experimental approaches (absolute and competition method) are adopted to estimate the second-order kinetic constants for the ozone attack at pH 6.0, 7.0 and 8.0. *experiments were carried out in a 0.8 L reactor with a continuous supply of ozone gas stream *initial BZF concentration ranging from0.2 to 0.5mmol/L ***HPLC** analysis for BZF *BOD and COD used to measure biodegradability *Acute toxicity measured using	***Ozonation** efficiently degraded BZF: after 10 min of treatment (dose = 0.73mmolL_1 of ozone) complete BZF removal achieved *Only a small fraction was mineralized. ***Chloride release** corresponding to 100% of initial chlorine content in BZF molecule was observed. ***Mechanism:** LC–MS analyses showed that ozone reacts mainly with unchlorinated ring, forming aldehydic and ketonic intermediates. *Presence of species with 3 additional oxygen atoms suggested that hydroxylation of both aromatic rings may also occur *Ozonation improved the biodegradability and reduced the toxicity of water containing BZF.

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		carbon -Potential for toxicity by oxidized intermediates in the early stage of ozonation to bacteria and microbes	Microtox® M500 toxicity analyzer, using Vibrio fischeri strains	
		Evaluation of ozone-based treatment processes for wastewater containing microcontaminants using LC-QTRAP-MS and LC-TOF/MS		Gomez et al., 2008
Waster water treatment Ozonation **Water:** Effluent of secondary clarifier at WWTP	Ciprofloxacin Sulfamethoxazole Mepivacaine Caffeine; Codeine Omeprazole Carbamazepine Ketorolac Paraxanthine Atenolol; Sotalol Naproxen Indomethacine Propanolol Diazepan Metoprolol Ranitidine Fluoxethine Trimethoprim Metronidazole Antipyrine; Ofloxacin Salbutamol Ketoprofen Mefenamic Acid Terbutaline Fenofibric Acid Furosemide Diclofenac Benzafibrate Gemfibrozil Hydrochlorothiazide Chlorophene Diuron; Ibuprofen Mefenamic acid	**Ozone (O_3)** and **O_3 with H_2O_2**	*O3 treatments were conducted in a 5L-stirred tank agitated at 1,000 rpm with a four-blade turbine. * Same conditions were used for O3/H2O2, with equal volumes of H2O2 (30% w/v) injected every 5 min. to favour pollutant elimination via radicals. * **LC/MS** PhAC analysis	*__Removal >90%__ was seen for most analytes *__5 compounds:__ gemfibrozil, chlorophene, diuron, ibuprofen and mefenamic acid indicated lower removal efficiencies; however **still >86%** * **Combining O_3 with H_2O_2** enhances oxidizing ability causing nearly complete elimination of contaminants **OVERAL PhAC REMOVAL**: *Considering all contaminants 97% removal and 99% removal were seen for **O_3** and **O_3 with H_2O_2** respectively.
		Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H2O2		Kim et al., 2008
Waster water treatment Ozonation **Water:** Lab prepared spiked pure water	Acetaminophen Fenoprofen Antipyrine Ethenzamide Mefenamic acid Naproxen Ketoprofen Isopropylantipyrine Diclofenac Indomethacin Disopyramide Metoprolol Propranolol Ifenprodil Carbamazepine Sulfadimethoxine Sulfadimizine Sulfamethoxazole Sulfamonomethoxine Tetracycline Chlorotetracycline Oxytetracyline Clarithromycin Ceftiofur Cyclophosphamide	**O_3** **O_3 with H_2O_2** **O_3 with UV** **H_2O_2** with	*Same batch reactor with 22L of solution spiked with PhACs used for O_3 and UV studies * UV radiation source: 8W low-pressure mercury lamps emitting 254nm wavelength and intensity 0.384mW/cm2. *Experiments performed with and without H2O2 *Ozone experiments were started by sparging O3 continuously into the reactor filled with the tested water *LC-MS/MS analysis	***Ozone Based Treatments:** - **O_3** and **O_3**-based/UV-based AOPs removed a variety of the PPCPs effectively, -However, 2-QCA, DEET and cyclophosphamide showed relatively low degradability -DOC concentration did not decrease with PPCP concentration thus evaluation of intermediates is necessary -All 30 PPCPs degrades linearly with time, thus **pseudo first order K constants** were calculated to compare degradability. - **O_3 with UV** was most effective: k values of 11 PPCPs > 0.461/min, thus >90% was degraded within 5min. Degradation via direct photolysis by UV and OH radicals from photolysis of O3 -O3/H2O2 and O3/UV processes: k>0.077/min for most of the PPCPs except for cyclophosphamide. * **UV treatment**:: -Combining UV and O_3 or H_2O_2 (that can generate OH radicals) caused faster degradation of PPCPs

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	Clenbuterol Theophyline			than UV alone. -Only k value of **ketoprofen** was > 0.461/min; 18 PPCPs had k values < 0.077/min, thus 90%of the initial concentration was not degraded within 30min *UV/ H_2O_2 process: k values of 29 PPCPs except for cyclophosphamide were > 0.077/min, *Combining UV with O_3 or H_2O_2 (that can generate OH radicals) promotes the degradation of the PPCPs.
Water Research 42 (2008) 121 – 128		Phototransformation of selected pharmaceuticals during UV treatment of drinking water		Canonica et al., 2008
Drinking water treatment Phototransformation **Water:** **i)**Lab prepared, buffered at various pH values ii) DWT plant effluent: (1) water collected after sand filtration (2) water collected after GAC filtration	17a-ethinylestradiol (EE2) diclofenac sulfamethoxazole and iopromide	Ultraviolet radiation	* Clear aqueous sample in quartz tubes were irradiated by light emitted from a lamp situated in a cooling jacket at photoreactor centre. *Light is filtered through the cooling jacket and an aqueous solution containing the immersed sample tubes, serving as an optical filter and as a medium to control temperature. *UV radiation source: low-pressure mercury (LP Hg) lamp Heraeus Noblelight model TNN 15/32 *__HPLC PhAC analysis__	**Effect of pH** * pHdependent rate constants were observed for all PhACs except iopromide, may be due to acid–base equilibria **Effect of UV wavelength:** *Degradation appeared wavelength independent except for EE2 * At the UV-C (254nm) drinking water dose of 400 J/m^{-2} PhAC reduction at pH ~ 7.0 in pure water was: 0.4% for EE2, 27% for diclofenac, 15% for sulfamethoxazole, and 15% for iopromide **Effect of Natural water:** * For 3 of 4 PhACs the presence of natural water had little effect on phototransformation rates * EE2 phototransformation rates were greatly enhanced by the presence of natural water, increasing by a factor of 6.1; this could be due to formation of a carbonate radical or nitrogen dioxide forning a hydroxide radical.
Desalination 202 (2007) 156–181		**Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals**		Snyder et al., 2007
Waste water treatment: GAC Membranes and Filters Water: Spiked WWPT effluent	Acetaminophen Androstenedione Caffeine Carbamazepine Diazepam Diclofenac Dilantin Estradiol Estriol Estrone Ethinylestradiol Fluoxetine Gemfibrozil Hydrocodone Ibuprofen Iopromide Meprobamate Naproxen Pentoxifylline Progesterone Testosterone	**Activated Carbon** **Membranes and Filters**: microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis reversal, membrane bioreactors, and combinations of membranes	* GAC studied at bench-scale using small-scale column tests and at 2 full-scale utilities. *Membrane studies conducted in dynamic flow-through pilot skids or in operational full-scale utilities *__GC-MS/MS and LC-MS/MS__ used for PhAC analyses *Virgin and fouled membranes were evaluated	*Membrane characteristics and molecular properties of contaminant determine the degree of removal by membrane. *** Microfiltration and ultrafiltration** rejected few target compounds; some loss of steroidal type compounds was observed. ***Nanofiltration and Reverse osmosis** caused significant rejection of nearly all targets; but compounds were detectable at trace levels in permeates. *__GAC__ proved highly effective at removing all target chemicals; hydrophilic compounds broke through faster than hydrophobic compounds. Removal for nearly all compounds was >90%. *GAC efficacy is greatly decreased by the presence of natural organic matter (NOM); NOM competes for binding sites on the GAC, blocking pores within the GAC structure. *Full-scale applications indicated that GAC filters receiving regular regeneration had little breakthrough of contaminants; non-regenerated filters showed no removal *Powdered AC removal is dependent on dose,

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
				contact time, and contaminant molecular properties; it does provide the benefit over GAC of being fed as a new product into the treatment process, and is thus a new source of carbon. *Toxicological relevance of these treatments has yet to be established; ultimately these treatments may lead to decreased concentrations of disinfection byproduct precursors.
Environ. Sci. Technol. 2002, 36, 3855-3863		**Removal of Pharmaceuticals during drinking water treatment**		Ternes et al., 2002
Drinking water treatment Water: Native surface water and groundwater	Benzafibrate, Clofibric acid, Carbamazepine, Diclofenac	*Sediment/Sand (bank filtration) *Iron Chloride (flocculation) *Ozonation	*Investigated at lab and pilot scale and in real waterworks *Solid phase extraction and **GC-MS analysis of analytes** *Waterworks studies: batch tests (following OECD guidelines) consisting of ground water and surface water with different filter media; two waterworks setups investigated *Aerobic sorption studies: sand or gravel taken from the underground of a groundwater catchment *Sterile control were used to differentiate between biodegradation and sorption *Flocculation studies were conducted using a "jar-test" setup *GAC PhAC removal was studied via a pilot plexiglass filter operated in down flow mode with spiked ground water *Ozonation PhAC removal was studied via a lab-scale device; Ozone was bubbled into water in 2-L glass bottles simulating real waterworks conditions; varying bubbling time allowed specific doses to be given	**SEDIMENT:** *No significant PhAC removal in batch experiments with sand under natural aerobic and anoxic conditions; indicating low sorption and high persistence with non-adapted microbes. **FLOCCULATION:** *Lab-scale and waterworks studies of flocculation using iron (III) chloride showed little elimination of PhACs. * Relative concentrations of the PhACs (C/Co) ranged from 87 (clofibric acid) to 110% (benzafibrate); changes in concentration were within the RSD. **OZONATION:** ***** Removal is highly contaminant specific *Ozonation proved highly effective for some PhACs; at 0.5 mg l^{-1} ozone diclofenac and carbamazepine decreased >90%; at 1.5 mg l^{-1} bezafibrate was reduced by 50%; clofibric acid was stable even at 3 mg l^{-1} ozone. *Under waterworks conditions, removal efficiencies were similar. **GRANULAR ACTIVATED CARBON:** *GAC proved very effective in removing PhACs; providing the major elimination of all but clofibric acid *Efficiency of removal is decreased by the presence of competing compounds such as natural organic matter (NOM) *In the pilot scale experiment, carbamazepine showed the highest sorption potential of all PhACs, and clofibric acid had the lowest.
		Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan		Okuda et al., 2008
Wastewater Treatment **Water:** WWTP effluent	*66 PhACs including: antibiotics, analgesics, and psychoneurotic agents	Conventional activated sludge (CAS) Biologica nutrient removal (BNR) processes Ozonation "Title 22 process": coagulation, sedimentation and filtration followed by UV or chlorination disinfection after biological processes,	*12 WWP effluents were collected from 11 WWTPs in Japan *2 BNR processes were studied with simultaneous coagulation with PAC *Ozonation and biological activated carbon (BAC) followed one of the BNR processes *Grab samples were taken at the end of biological treatment (before and after coagulation), before and after ozonation and after BAC process	*80% removal of the total concentration of the individual pharmaceuticals during biological treatment; except carbamazepine and crotamiton which had efficiencies < 30%. *Total concentration of the individual PhACs was 1.5X greater in the CAS process effluent than that from BNR process. *Total concentration of the individual PhACs in WWTP effluent applying activated sludge then ozonation, decreased to <20%. *Physico–chemical treatment train (Title 22) treatment following CAS did not efficiently remove PhACs.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
			*SPE-LC/MS/MS PhAC analysis	*Ozonation followed by biological AC efficiently decreased all residual PhACs below LOQ *Sand filtration processes did not reduce PhAC concentration significantly *Individual PhAC effluent concentrations differed among the WWTPs, suggesting that the PhAC response differs between those followed by biological treatment and those followed by ozonation processes.
ESNT 39, 2005	**Fate of Endocrine-Disruptor, PhAC, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes**			Westserhoff et al., 2005
Drinking Water Treatment Water: 3 surface waters that provide raw water to WTPs and one model water	*62 Different EDC/PPCP's Acetominophen Andostenedione Caffeine CBZ Diazepam Diclofenac Dilantin Erythromycin-H2O Estradiol Estron Fluoxetine Femfibrozil Ibuprofen Iopromida Naproxen Progesteron Sulfamethoxazole Testosterone Triclosan Trimethoprim (note: All LC/MS.MS compounds)	Drinking water treatment: Adsorptive and oxidative processes to remove or transform organic materials. **Ozone/ Chlorination** *Inactivates microbes; *Oxidizes reduced metals and organic material. *Reactivity with oxidants is dictated by electron density effects and functional group degree of protonation. *Electron-donating (e.g., hydroxyl, amine) or electron-withdrawing (e.g., carboxyl) groups increases & decreases reactivity, respectively, for substituted aromatic rings (40). **With H2O2: Increases rate of ozone decay, increases HO* concentrations. HO* reacts less selectively with organic compounds than molecular ozone: combining O3/H2O2 (AOP) allows for more potential transformations.	*The transformation of several amine-containing antibiotics, diclofenac, and caffeine were observed in lab experiments with chlorine **LC/MS/MS or GC/MS/MS	**Decreased Endocrine disruptin compounds (EDC) and Personal care products (PPCPs) initial concentration by <10% to >90%; **EDC/PPCPs were likely transformed to oxidation byproducts. **Ozone oxidized steroids containing phenolic moieties (estradiol, ethynylestradiol, or estrone) more efficiently than those without aromatic or phenolic moieties (androstenedione, progesterone, and testosterone). ****EDC/PPCP reactivity with oxidants were separated into three general groups:** (1) Compounds easily oxidized (>80% reacted) by chlorine and always oxidized at least as efficiently by ozone; (2) Compouds poorly oxidized (<20% reacted) by chlorine or ozone; 6 of the 60 compounds (TCEP, BHC, chlordane, dieldrin, heptachlor epoxide, musk ketone) (3) Compounds reacting preferentially (higher removals) with ozone rather than chlorine.; 24 of the 60 compounds *The formation, fate, detection, and toxicity of oxidative byproducts from pesticide sand EDC/PPCPs is of potential concern (17, 27, 42). **Ozone oxidized most LC/MS/MS compounds by >80% except for atrazine, meprobamate, and TCEP, which do not contain aromatic moieties, and ibuprofen which has an electron-withdrawing functional group on an aromatic ring. **Several GC/MS/MS compounds exhibited minimal oxidation during ozonation (BHC, chlordane, dieldrin, heptachlor epoxide, mirex, or musk ketone). **Addition of small amounts of H_2O_2 prior to ozonation generally improved the extent of oxidation by 5-15%. Four compounds (including androstenedione and testosterone) indicated >20% higher oxidation in the presence of H_2O_2.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
		***Aluminum sulfate; ferric chloride** coagulants -Chemical coagulation employs aluminum- or iron-based salts, which precipitate as metal hydroxides *chemical lime softening - removes dissolved calcium and magnesium, using lime and soda ash to precipitate calcium carbonate at lower pH and magnesium hydroxide at pH >11 ***Powder Activated Carbon** -Activated carbon adsorbs many organic pollutants (33).	*Chemical coagulation and softening aid in removing suspended solids (i.e., turbidity) from the water and dissolved organic carbon (DOC). *A PAC slurry is added at dosages of 1 to 25 mg l^{-1} to a solids-contact, or flocculation, chamber that has contact times of 0.5 to 5 h; removal of PAC (with adsorbed compounds) occurs during sedimentation and filtration processes (34) Addition of 5 mg l^{-1} of powder activated carbon (PAC) with a 4-h contact time – reflective of conditions employed at WTPs, and capable of achieving partial, but not complete removal, thus allowing relationships between compound structure and removal to be studied.	**COAGULATION:** **Less than 25% of most of the EDC/PPCPs were removed. **Only 2 of the 28compounds analyzed by **LC/MS/MS** exhibited >20% removal during **alum coagulation:** (hydrocodone, 24%; erythromycin-H2O, 33%). **12 of 32 of the **GC/MS/MS** compounds exhibited >20% removal during **alum coagulation**; the highest removals were for PAHs. **For most EDC/PPCPs, **ferric coagulation** achieved comparable removals as equivalent alum dosages. **Average % removal: -for EDC/PPCPs detected by LC/MS/MS = 6% -for EDC/PPCPs dectected by GC/MS/MS = 26% (range: 0-83%) **GC/MS/MS compounds: - More hydrophobic PAHs were removed better (60-80%); - log Kow > 6.5 also had removals >20%; suggesting removal by partitioning onto suspended particulates or precipitated solids that had adsorbed DOC ****Chemical lime softening** -Achieved comparable EDC/PPCP removal as alum or ferric coagulation within experimental reproducibility (20%); likely having same removal mechanisms (sorption onto turbidity and precipitated solids). **Removed 50% to >98% of GC/MS/MS compounds (more volatile) and 10% to >95% of LC/MS/MS compounds (more polar); **POWDERED ACTIVATED CARBON:** (PAC) -higher PAC dosages improved EDC/PPCP removal ****3H-E2 removal:** - At a 1 mg l^{-1} PAC dosage in CRW, 3H-E2 removal was 32, 58, and 84% after contact times of 1, 4, and 24 h respectively - Increasing PAC dosage improved 3H-E2 removal, and the effect of contact time became less significant at PAC dosages of 5 and 25 mg l^{-1}. *CRW had ~45% less 3H-E2 adsorption capacity than nanopure water; thus the amount and characteristics of DOC in the source waters may be important for EDC/PPCP removal. *Partial removal was seen for nearly all EDC/PPCP compounds spiked into the source waters. *Appears that the percentage removal of EDC/PPCPs is independent of initial concentration. *Some competition between EDC/PPCPs may occur for adsorption sites

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
Water Research 41 (2007) 3227 – 3240		**Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutically active compounds in surface water**		Verliefde et al. 2007
Drinking water Treatment Nanofiltration and GAC **Water:** Surface water Two sources: 1) intake from Weesperkarspel treatment plant, Amsterdam 2) Surface water from the river Schie, Delft	Terbutaline Salbutamol Pindolol Propranolol Atenolol Metoprolol Sotalol Clenbuterol Phenazone Aminopyrine Carbamazepine Cyclophosphamid Pentoxyfilline Ibuprofen Clofibric Fenoprofen Gemfibrozil Ketoprofen Diclofenac Bezafibrate	**Nanofiltration membranes** 1) Trisep TS-80 membrane **2)** Desal HL **NF and Subsequent GAC filtration**	*Feed water recovery =amount of water produced/amount of feed water used *All experiments were carried out in a recycle mode with a single batch of water, with both permeate and concentrate recycled back into the feed reservoir. * Low feed water recovery (10%) * High feed water recovery (80%) *The pre-treated water from the river Schie is fed to an NF unit, operating at 80% recovery, with experiments carried out in a single-pass (once-through) mode. The GAC column is fed with the permeate of the NF unit. ***Removal efficiency** is greatest for negative charged solutes, then neutral and then positive. Again, rejection appears to be less determined by steric hindrance: ***Drawback of the NF/GAC:** Disposal of the concentrate stream from NF. Thus, the zero liquid discharge (ZLD) concept, which aims to decrease the volume of concentrated	*NF is affected by charge effects: -Negatively charged solutes are better removed than uncharged solutes, which are, in turn, better removed than positively charged solutes; due to charge attractions between neg. membrane and pos. charged solutes that allows solutes to dissolve and diffuse across membrane more easily. - Increasing feed concentrations of positively charged PhACs lead to increasing rejection values, due to membrane charge-shielding effects. *Often high rejection values for negatively charged PhACs, due to repulsive forces; the negative solutes cannot approach the negatively charged membrane surface and are thus prevented from permeating through the membrane **Rejection of **neutral** solutes by high-pressure membranes is mostly due to **steric hindrance** effects between the solutes and the membrane's polymeric matrix. ****Solute hydrophobicity influences the rejection of organic solutes in NF.** -Hydrophobic solutes can adsorb onto the membrane surface and partition into the membrane matrix, and thus exhibit lower rejection values than hydrophilic solutes of the same size ***Negatively** charged PhACs are independent of their hydrophobicity. Repulsions between solute and membrane inhibit negatively charged solutes from approaching the membrane surface, inhibiting potential hydrophobic interactions. *For the **neutral** and **positively** charged PhACs, there is a decrease in rejection with increasing solute hydrophobicity *Rejection >85% with the Trisep TS-80 membrane. **Rejection values were higher for the Trisep membrane than for the Desal membrane for all PhACs, except salbutamol. *Higher rejection values with the Trisep membrane are due to **steric hindrance effects** since the molecular weight cut off values of the Trisep membrane is lower *Rejection >75% for all PhACs with the Desal HL membrane; less than Trisep membrane *Removal efficiency of PhACs with the combination NF/GAC is extremely high. *Removal by adsorption on the **GAC** is high (>98%) for all PhACs, even with the short empty bed contact time used (3 min).; the largest part of the natural organic matter (NOM) is removed by NF ; this NOM normally competes with PhACs for adsorption sites on the carbon, so its removal increases the adsorption capacity of the GAC ***Removal efficiency** with **GAC** is slightly lower for smaller positively charged solutes; likely due to the higher GAC influent concentrations for these solutes, since they are less-efficiently removed during NF.

Treatment & Water Type	Drugs Treated	Treatment Media	Procedural Notes / Analysis	Results/Conclusions
				Removal efficiency is greatest for negative charged solutes, then neutral and then positive. Again, rejection appears to be less determined by steric hindrance: *__Drawback of the NF/GAC:__ Disposal of the concentrate stream from NF. Thus, the zero liquid discharge (ZLD) concept, which aims to decrease the volume of concentrated discharged is an important point of study. Efficient removal of all scaling ions in NF pre-treatment would enable the NF system to operate at 99% recovery, leaving only 1% of NF concentrate to be discharged. However, at higher recoveries a decrease in rejection is seen; thus more research into removal of PhACs at high feed water recoveries is necessary. *Drawback of the NF/GAC: Disposal of the concentrate stream from NF. Thus, the zero liquid discharge (ZLD) concept, which aims to decrease the volume of concentrated, discharge is an important point of study. Efficient removal of all scaling ions in NF pre-treatment would enable the NF system to operate at 99% recovery, leaving only 1% of NF concentrate to be discharged. However, at higher recoveries a decrease in rejection is seen; thus more research into removal of PhACs at high feed water recoveries is necessary.

3 INVESTIGATION:

The growing body of research concerning water treatments for pharmaceuticals indicated a wide range of success both between pharmaceutical and treatment types. What appeared absent from the literature was a passive treatment media or system that was highly available, affordable, easy to use, ecologically safe and capable of successfully treating a wide variety of pharmaceuticals, as well as, potentially other water contaminants. Thus the following study was conducted to explore the response of pharmaceuticals to novel passive treatment media.

Batch experiments were conducted consisting of a media of interest in simulated groundwater spiked with: carbamazepine, caffeine, naproxen, gemfibrozil, ibuprofen, sulfamethoxazole and clofibrate, each at a resultant concentration of 2-2.5 $\mu g\ l^{-1}$. Investigated media were selected based on their notable reactivity, affordability, availability, durability and ease of use, as well as, occupying a previously established role in water treatment.

3.1 Materials and Media

Simulated Ground Water: Simulated ground water was prepared by dissolving $CaCO_3$ into 20 l of milliQ water to make a final water composition of 0.104 g l^{-1} $CaCO_3$. Carbon dioxide gas was added to promote dissolution of the calcium carbonate, followed by bubbling with air to adjust the final pH to approximately 8 for use in the aerobic experiments. For the anaerobic experiments, the simulated groundwater was purged for a minimum of 30 min with Ar or N_2 gas prior to its use in the experiments. The simulated ground water was transferred into the 1000 ml reaction flasks.

Spike Stock Solution: A stock solution containing carbamazepine, clofibrate, ibuprofen, naproxen, caffeine, sulfamethoxazole, and gemfibrozil was prepared to allow simultaneous addition of seven PhACs to each reaction flask. Each PhAC was added to 50:50 methanol (MeOH):MilliQ water, resulting in a stock solution of 2.0 mg l^{-1} of each PhAC; resulting in an environmentally relevant concentration of 2.5 μg l^{-1} with the addition of 1 ml of the stock solution to each flask, with a minimal addition of methanol. Each PhAC was measured by mass prior to dissolution in the 50:50 MeOH:MilliQ water mixture. Due to light sensitivity, sulfamethoxazole was added last to the stock solution to minimize potential photo-degradation. After this final addition the stock was sonified 35 min on the day of preparation, and then a further 30 min on the first day of the experiment to ensure complete dissolution of the PhACs. The stock solution was maintained at 4°C in an amber glass bottle to minimize compound degradation.

Working Stock Simulated Groundwater for Final Batch: A stock AG water was prepared and distributed to each sample bottle for the batch experiments. Sodium chloride was added to this solution to result in a final concentraiton of 50 mg l^{-1} to improve the response of the Eh and pH probes, and to mimic natural groundwaters more closely. The water was spiked with the original spike stock solution containing 2 mg l^{-1} concentration of each pharmaceutical. An additional concentration of both sulphamethoxazole and caffeine were added to the working stock simulated groundwater, increasing their final concentrations to 4 mg l^{-1} .

Pharmaceutically Active Compounds: The target compounds investigated in this study were selected based on their environmental relevance, being either or both persistent in nature or commonly occurring. Investigated compounds included: sulfamethoxazole, carbamazepine, ibuprofen, gemfibrozil, naproxen, and caffeine. Information regarding each PhAC can be found in **Table 3.1**.

Reactive Media: Characterization, preparation methods as well as experimental proportions for each media are summarized in **Table 3.2.**

Table 3.1: Characterization of Pharmaceuticals

Feature:	Cabemazepine:	Gemfibrozil:	Naproxen:	Caffeine	Ibuprofen:
Molecular Weight	236.3 B (Trenholm et al,. 2006)	250.3 B	230.3 B	194.2 B	206.3 A (Scheytt et al., 2007)
Use	*Treatment of psychomotor and grand mal seizures, as well as trigeminal neuralgia *Anticonvulsant properties; appears to act by reducing polysynaptic responses and blocking the post-tetanic potentiation *principal metabolite (CBZ-10,11-epoxide) has anticonvulsant activity	Blood lipid regulator	Analgesic/anti-inflammatory	Stimulant	Analgesic/anti-inflammatory
Excreted Unchanged	1-3% C (Vieno et al., 2007)		1-10% D (Lindqvist, 2005)		1-10% D
Solubility (mg l^{-1})	17.7 mg l^{-1} B	19 mg l^{-1} B	15.9 mg l^{-1} B	21600 mg l^{-1} B	21 mg l^{-1} A
pKa	236.3 B	NA B	4.15 B	10.4 B	4.52 A
logKow	2.45 B	4.77 B	3.18 B	-0.07 B	3.5 3.97 A
Adverse Effects/ Teratogenic	*Potential fetal harm when administered during pregnancy *Rapid transplacental passage (30-60 min); accumulates in fetal tissue, concentrating specifically in liver, kidney, brain and lung			*Inability to be metabolized by fetur/infants; therefore can accumulate	
Risk Indicators	high volumes; long-term prescriptions; persistent (D)	long-term prescriptions; commonly detected			very high prescription and OTC volumes;
Drug Interactions	**Lithium:** May increase risk of neurotoxic effects **Oral contraceptives:** Decrease plasma concentration, thus less effective **CYP 3A4 inhibitors (inhibit CBZ metabolism)** : cimetidine, danazol, diltiazem, macrolides, erythromycin, troleandomycin, clarithromycin, fluoxetine, fluvoxamine, azoles nefazodone, loratadine, terfenadine, isoniazid, niacinamide, nicotinamide, propoxyphene, acetazolamide, verapamil, grapefruit juice, protease inhibitors, valproate. ***CYP 3A4 inducers (increase CBZ metabolism)**: Cisplatan, doxorubicin HCl, felbamate, rifampin, phenobarbital, phenytoin, primidone, methsuximide, theophylline **Other anticonvulsants:** Effect proper thryroid function	**HMG-CoA reductase inhibitors:** Increased risk of myopathy and rhabdomyolysi **Anticoagulants**: Bleeding complications due to alterations in prothrombin time	**ACE-inhibitors:** May diminish anti-hypertensice effect **Antacids/ Sulcrafate:** Delay NPX absorption **Other NSAIDs**: Reduce protein binding Increase side effects; Delay absorption **Cholestyramine:** Delay absorption **Diurectis**: Reduce naturetic effect of furosemide/thiazides, by inhibiting renal prostaglandin synthesis **Lithium:** Elevation is plasma lithium levels and decreased renal clearance **Methotrexate:** Competitively inhibit MTX; ↑toxicity **Warfarin:** GI bleeding due to synergistic effects	*Cytochrome P450-1A (**CYP1A$_2$**) is the major enzyme involved in the metabolism; thus ther eis potentiaol to interact with drugs that sutstrates for CYP1A$_2$, potentially inhibiting or inducing its function.	**ACE-inhibitors:** May diminish anti-hypertensice effect **Antacids/ Sulcrafate:** Delay NPX absorption **Other NSAIDs**: Reduce protein binding Increase side effects; Delay absorption **Cholestyramine:** Delay absorption **Diurectis**: Reduce naturetic effect of furosemide/thiazides, by inhibiting renal prostaglandin synthesis **Lithium:** Elevation is plasma lithium levels and decreased renal clearance **Methotrexate:** Competitively inhibit MTX; ↑toxicity **Warfarin:** GI bleeding due to synergistic effects

***Unless stated otherwise pharmaceutical information provided by RxList Inc. 2006**
***Kow = octanol-water coefficient *pKa = negative log of the acid dissociation constant**

Table 3.2: Characteristics, preparation and experimental proportions for Reactive Media

Batch ID	Media and Source	%Wt. to AG water		Preparation:	Previous Remediation Use:
		Prelim	Final		
ZVFe:Sand	Connelly Zero Valent Iron	2.5%	12.5%	* Hand sifted with a No. 8 sieve, to ensure consistent grain size, then measured and mixed in appropriate proportion with either sand or activated carbon	*PRB – chlorinated solvents, Cr, U, Tc, (Blowes et al, 2000) *Se(VI) (Sasaki et al, 2008) *Chorinated solvents (Song et al, 2005, Gillham et al, 1994; Farrel et al, 2000) *Carbothioate Herbicide (Joo et al, 2004) *Cr(VI) (Hoch et al, 2008; Lui et al, 2008; *Cr(VI) and Pb(II) (Ponder et al, 2000) *Carbon disulfide (Mcgeough et al, 2007) *As(V) (Kanel et al, 2006) *Atrazine, nirtophenols, N-nitrosodimethylamin, PCBs, alkyl-halides (Sweeny, 1981)
	Silica Sand	10%	N/A	*Massed in appropriate proportion to ZVI	
ST-BOF	Stelco BOF Slag	12.5 %	N/A	*Sifted with a No.8 hand sieve for smaller, more consistent grain size.	*PRB – PO_4, As, (Baker et al, 1998,)
WC	Wood Chips	1.88%	N/A	*Sifted with a No.12 hand sieve for smaller consistent media size.	*PRB – Acid mine drainage; sulfate reduction and metal sulfide precipitation; nitrate (Waybrant et al, 2002; Benner et al, 1999; Waybrant et al 1998)
BDS	Camp Borden Sand	12.5 %	N/A	*Washed with deionized water oven dried	
AC	Granular activated carbon	N/A	12.5%	*Rinsed with MilliQ water to remove fine particles and oven dried	*Drinking water treatment- removal of fine particulates, bacteria and odor/taste compromising compounds (Snyder et al., 2007)
ZVFe: AC 70:30 and 50:50	Connelly Zero Valent Iron	N/A	8.75% 6.25%	*Hand sifted and massed autonomously into 100 ml serum bottle	*As described Previously
	Granular Activated Carbon	N/A	3.75% 6.25%	* Rinsed with MilliQ and over dried * Massed autonomously into 100 ml serum bottle	*As described Previously

Note: ZVFe = zero valent iron; ST-BOF = stelco BOF-slag; WC = woodchips; BDS = Borden sand; AC = activated carbon.

3.2 Batch Test Procedures

Preliminary Batch Experiments: The batch experiments consisting of simulated groundwater, reactive media and/or aquifer sand and the stock solution, were carried out in 1000 ml reaction flasks. The reaction flasks were each equipped with two sampling ports and one access port. Caps with Teflon septa were used to seal each sampling port, allowing access by syringe for sample collection, as well as, addition of argon gas when needed. A ground glass stopper coated with vacuum grease sealed the access port of each vessel. Each flask was wrapped in aluminum foil to minimize light exposure.

All media were added to approximately 100 g dry weight within the 1000 ml reaction flasks (Table 3.2). Simulated ground water (800 g) was then added into each flask, followed by the addition of 1 ml of the PhAC stock solution. The volumes of simulated groundwater and PhAC stock solution were measured both by volume and gravimetrically. Subsequent to the addition of the stock solution oxygen was displaced from the vessels with argon gas. The sampling and access ports were secured with the caps and glass stopper, wrapped in aluminum foil and gently swirled by hand to mix the media and aqueous solution..

Final Batch Experiment: The final batch experiments consisting of the spiked stock simulated groundwater and the reactive media were carried out in a series of 100 ml amber serum bottles. Eighteen serum bottles were prepared for each media investigated, as well as a control set containing simply the spiked stock simulated groundwater.

All media were addedd in the appropriate proportions to a final dry weight of approximately 10 g into the amber serum bottles (**Table 3.2**). Once prepared all bottles were transferred into an anaerobic glove box (Coy) containing 95%N_2:5%H_2 to minimize ingress of

oxygen into the test mixtures. The transferred bottles were then allowed to equilibrate within the glove box for 24 hrs.

After the equilibration period, 80 g of spiked stock simulated groundwater was auto-dispensed into each bottle. The aliquots of stock simulated groundwater were measured both by volume and gravimetrically within the glove box. Following the final addition of the stock solution, each serum bottle was sealed using a lyophization stopper and then sealed with an aluminum crimp top (**Figure 3.2**).

3.3 Sample Collection and Preparation:

Preliminary Batch Sample Collection: Each reaction vessel was sampled via a syringe inserted through Teflon-septa of the sampling port cap. Samples were taken at predetermined time intervals starting from the time at which the PhAC stock solution had been added to the reaction flask. Aqueous samples were removed using a 20 ml glass syringe rinsed with 5% methanol and milliQ water prior to use. Anaerobic grade argon was injected via a syringe through the second sampling port during sample collection for the anaerobic samples to prevent introduction of air into the reaction vessels.

Final Batch Sample Collection: Samples were selected at random from the series of bottles prepared for each media and collected at predetermined time intervals. Upon sampling, the bottles were opened and aqueous samples were removed and measured via a glass syringe for PhAC samples and via disposable plastic syringes for anion and cation analysis (**Figure 3.2**).

Pharmaceutical Sample Collection and Preparation: Approximately 20 ml samples were taken for PhAC analysis using HPLC-tandem mass spectrometry. Samples were filtered through Sartorius 0.45 μm nylon syringe filters and collected into 125 ml amber glass bottles to minimize light exposure. The samples were then acidified to pH<2 with HPLC grade sulfuric acid (H_2SO_4) in preparation for solid phase extraction (SPE). The acidified samples were tested using litmus paper to ensure a pH of less than 2. Additional 50% sulfuric acid was added if needed.

In preliminary batches samples were kept in the freezer at -18°C until time of extraction, in final batch experiments samples were extracted via SPE within 3 days of collection.

The Preliminary Batch Experiment samples were diluted by 40 ml of nanopure to 20 ml of sample to obtain a consistent volume for the SPE step. Internal standards (IS) consisting of caffeine-D_3, carbamazepine-D_{10}, gemfibrozil-D_6, sulphamethoxazole-D_4, Mecoprop (MEC)-D_3, ibuprofen-D_3, and naproxen-C_{13} each at a concentration of 100 μg l^{-1} dissolved in 50:50 methanol was added to each sample. Sample extraction was conducted manually using 5 cm^3 Oasis HLB (hydrophilic-lipophilic balance) solid phase extraction cartridges within a vacuum manifold. The cartridges were conditioned with 3 ml of methanol followed by 3 ml of milliQ water. Following conditioning, the cartridges were loaded with 60 ml of sample at a flow rate of approximately 10 ml min^{-1}. After loading, the HLB cartridges were rinsed with 3 ml of 5% methanol and then finally extracted using 3 aliquots of 2 ml methanol, drawn through the columns into 7 ml amber glass bottles. An aliquot of 1 ml was then taken for HPLC-MS/MS analysis (**Figure 3.3**).

For the final batch samples, 0.2 ml of IS stock solution containing caffeine-D_3, carbamazepine- D_{10}, gemfibrozil- D_6, sulphamethoxazole- D_4, MEC-D_3, ibuprofen- D_3, and

naproxen- C_{13} each at a concentration of 10 μg l^{-1} dissolved in 50:50 methanol was added to the 20 ml undiluted PhAC sample. Samples were then manually extracted using 3 cm^3 Oasis HLB cartridges, deviating only from the previously described method in the volumes of solution. Two-milliliter aliquots of each solvent were employed for cartridge conditioning and elution of the final samples, and a total sample volume of 20 ml was loaded into each cartridge.

3.4 Analytical Methods and Water Chemistry:

Water Chemistry Analyses: Approximately 10 ml and 5 ml of sample were collected for cation and anion analysis, respectively. Samples were filtered through Sartorius 0.45 μm nylon syringe filters and collected into polypropylene bottles. The cation samples were preserved to pH <2 using trace-metal grade HNO_3. All cation and anion samples were kept at 4° until time of analysis. Samples were analysed for sodium, calcium, magnesium, potassium, iron and manganese using ICP-MS. Samples were analyzed for nitrate, phosphate, sulfate, fluroide and chloride using ion chromatography.

Alkalinity was measured on 1 to 3 ml of filtered sample using bromocresol green/methyl red indicator titrated with a Hach digital titrator with 1.6 or 0.6 N H_2SO_4.

Approximately 5 ml unfiltered aqueous samples were withdrawn for determination of pH and Eh. Immediately following sample collection the unfiltered samples were injected into inverted syringes holding either a pH or Eh probe. Data was collected for 20 to 30 min for each sample. The Ross combination pH electrode (Orion 815600) was calibrated prior to sampling with standard fresh pH 4 and 7 buffers, and then checked against a pH 10 buffer. The electrodes were again checked at the end of the sampling period with the pH 4 and 7 buffers. The Pt combination redox electrode (Orion 8156BNUWP) was checked against

ZoBell's (Nordstrom, 1977) and Light's (Light, 1972) solutions prior to and following analysis.

Pharmaceutical Analyses: PhAC analysis was conducted using high performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS).

Analyte separation was performed with an Agilent 1100 liquid chromatograph with a RP18, 50X4.6mm3µm column for the ESI positive PhACs and a XBD-C18, 150X4.6mm5µm column for the ESI negative PhACs. For gradient elution two different mobile phases were utilized. For the positive mode samples eluent A was a formulation of 5 mM Am Ac 0.1% formic acid in nanopure MilliQ water, and eluent B was a formulation of 100% methanol with 0.1% formic acid. For the negative mode, eluent A was composed of acetonitrile with water (30:70) and 6.9 mM acetic acid and eluent B was composed of 100% acetic acid. The mobile phase was pumped through the column at a flow rate of 1.25 and 1 ml min^{-1} for the positive and negative modes respectively. A sample injection volume of 15 µl and 10 µl were injected in a loop, with repeat injections between one to six times for the positive and negative modes respectively. The total elution time of the sample in positive mode was 4 min, while the time for a sample run in negative mode was 45 min.

An Applied Biosystems/MDS Sciex 4000 QTrap mass spectrometer with triple quadrapole capability was utilized to detect and quantify the PhACs in the samples. The nebulizer gas at the ionization source, as well as the collision gas used to fragment the parent ion was N_2. Ionization was conducted in two modes, either by a positive electrospray ionization source (ESI+) or by a negative electrospray ionization source (ESI-) depending on the PhAC analyzed. The drugs analyzed by positive mode were carbamazepine, caffeine and

sulfamethoxazole, and the drugs analyzed by negative mode were naproxen, clofibrate, gemfibrozil, and ibuprofen.

A multiple reaction monitoring scan (MRM) was applied for the purposes of quantification. Concentrations were quantified by means of a signal ratio between the original concentrations of the PhAC in comparison to the known concentration of the internal standard. This method of quantification allows for management of discrepancy caused by sample preparation and extraction. Each PhAC also was quantified using an external standard calibration curve. The calibration curves for the PhACs consisted of an eight point calibration, with nonlabelled working standards between 0.2 μg l^{-1} and 20 μg l^{-1}; all containing the same concentration of surrogate internal standard as the investigated samples.

3.5 Geochemical Modeling

Aqueous geochemistry was interpreted with the assistance of the geochemical equilibrium/mass transfer code MINTEQA2. Modifications to the MINTEQA2 database were made to ensure its consistency with WATEQ4F (Ball and Nordstrom, 1991). Calculated saturation indices provided by the model were employed to determine the mineral phases potentially controlling the aqueous concentrations of each mineral component. The indices designate mineral phases at equilibrium by a value of zero, while values greater than zero and less than zero signifiy supersatuartion and undersaturation, respectively. MINTEQA2 geochemical modeling was performed for each treatment media investigated.

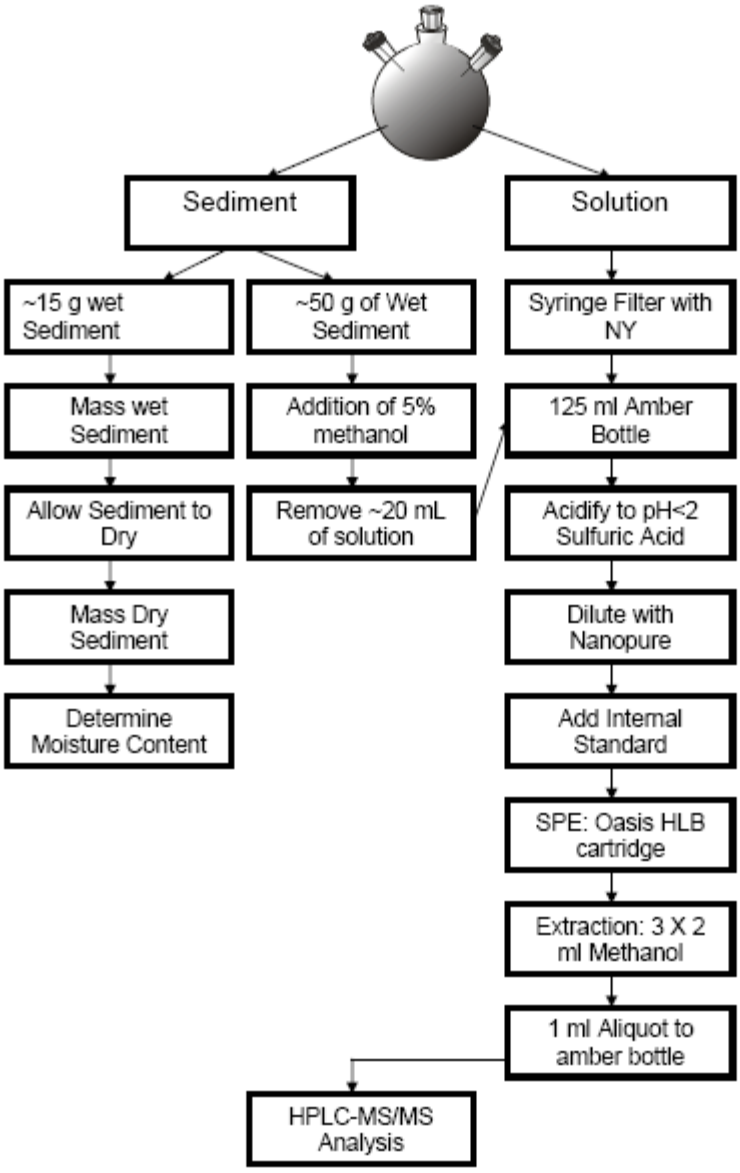

Figure 3.1 Procedural flow chart for preliminary batch experiments showing outline of method design for water and sediment-system sample preparation and analysis

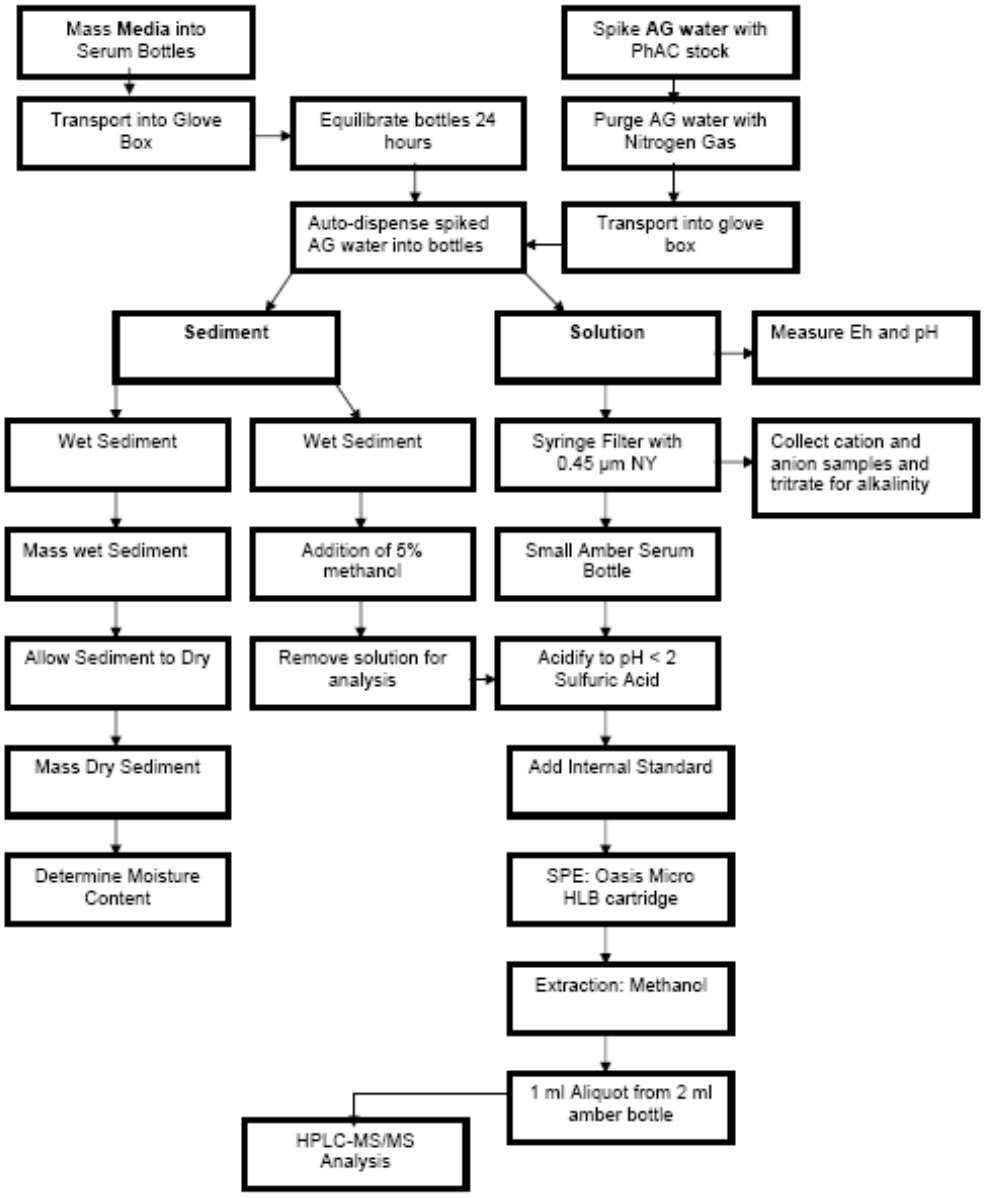

Figure 3.2 Procedural flow charts for the final batch experiment, indicating the general method designs for sample preparation and analysis.

3.6 Method Evaluation:

Linearity (R), range, sensitivity (limits of detection and quantitation), specificity, accuracy (analyte recoveries), precision (%RSD) and method recoveries were employed to evaluate the overall SPE-HPLC-MS/MS method.

Three sets of standards were made for calibration and statistical evaluation. Two sets of calibration standanrds were prepared in MeOH/MilliQ water (50:50, v/v); one prepared just prior to analysis using the same stock solution (containing all seven target pharmaceuticals) and IS as the samples; and the second being a set of calibration standards. The third set of standards, the quality control standards, also prepared just prior to analysis, was composed of MilliQ water spiked with the same stock solution and IS, as well as extracted by the same SPE procedure, as all experimental samples.

Sulfamethoxazole and clofibric acid results were not included in the final analyses due to disproportionate noise in the analytical results. Unable to confidently integrate the peaks for these pharmaceuticals it was decided to omit these analytes. Thus, for the purposes of analytical consistency all media and control analyses included carbazmazepine, caffeine, gemfibrozil, naproxen and ibuprofen.

3.6.1Linearity and Range

Standard curves were prepared within the analytical range for all of the pharmaceutical compounds analyzed. Linearity of the HPLC-MS/MS method was supported by R^2 values >0.999 and residuals less than 1% for each calibration point in the analytical range of the linear regression equations derived (Appendix VII). Quantification of analyte concentration was performed using the correlation between the analyte peak area divided by the internal

standard peak area, and the analyte concentration. The use of internal standards for quantification compensates for matrix effects and any loss of analyte through extraction and sample preparation.

Table 3.3 Calibration and linearity parameters for linear regressions

Calibration Standard Linear Regressions				
Curve	**%Residuals**	**Analytical range (μg l^{-1})**	**Calibrators (n)**	**R^2**
CBZ	0.50	0.1-20	8	0.9999
CAFF	0.50	0.1-20	8	0.9998
GEM	0.68	0.1-20	8	1.000
NPX	0.18	0.1-20	8	0.9998
IBU	0.02	0.1-20	8	0.9998

3.6.2 Accuracy and Precision

The accuracy and precision of the instrument and method was evaluated over the complete analytical range for all compounds analyzed (Table 3.4). Accuracy was assessed based upon the measured analyte recovery of the quality control standards with respect to the known spiked concentration. Analytical precision was assessed based upon the percent relative standard deviation between three (n = 3) replicate HPLC-MS/MS analysis of the same calibration standard samples. Potential amplification and supression of analyte peak areas, and thus concentrations may be the result of matrix effects introduced by the media and simulated groundwater composition, or by competition or common ion effects within the extraction column.

Table 3.4 Method accuracy and precision.. Accuracty was measured as the percent analyte concentration recovery of the quality control standards with respect to the known spiked concentration, at each concentration in the calibration range. Precision was calculated based upon the percent relative standard deviation (%RSD) between three (n = 3) replicate calibration standards run in the same sample set.

PhAC	Validation Characteristic	0.1 µg l^{-1}	0.2 µg l^{-1}	0.5 µg l^{-1}	1 µg l^{-1}	2 µg l^{-1}	5 µg l^{-1}	10 µg l^{-1}	20 µg l^{-1}
CBZ	**Accuracy %Recovery**	121.5	108.2	100.2	104.5	101.5	104.0	111.5	103.8
	Precision %RSD (n=3)	0.039	0.026	0.029	0.014	0.014	0.004	0.010	0.004
Caffeine	**Accuracy %Recovery**	94.0	108.0	117.0	104.0	111.0	106.0	114.0	112.0
	Precision %RSD (n=3)	0.117	0.022	0.009	0.027	0.016	0.035	0.017	0.046
Ibuprofen	**Accuracy %Recovery**	102.0	99.0	99.8	103.0	101.0	100.0	99.8	99.5
	Precision %RSD (n=3)	0.014	0.036	0.017	0.000	.007	0.011	0.019	n/a
Naproxen	**Accuracy %Recovery**	100.0	99.5	98.4	125.0	116.0	126.4	130.0	100.4
	Precision %RSD (n=3)	.0070	0.0107	0.0372	0.0205	0.0148	0.0107	0.0070	n/a
Gemfibrozil	**Accuracy %Recovery**	122	104.5	108.2	118	121.5	103	121	115
	Precision %RSD (n=3)	0	0.007	0.006	0.014	0.007	0.004	0.006	n/a

3.6.3 Sensitivity: Limits of quantification and Limits of detection

Limits of detection (LOD) were defined as the lowest observable concentration giving a signal to noise ration of 3:1; while, limits of quantification (LOQ) were defined as the lowest observable concentration denoting a signal to noise ratio of 10:1. The method detection and quantification limits for the samples analyzed fell within the ranges of 3-189 ng l^{-1} and 19.8-763 ng l^{-1} (Table 3.5) respectively.

3.6.4 Specificity:

Method specificity was assessed by the analysis of blank samples. Blank samples without analytes, blank samples without analytes or IS and control samples with known analyte concentrations were included in each sample series. No peaks indicating contamination of the

investigated analytes or internal standard were present upon analysis of blank samples. Control samples of known concentration dispersed between experimental samples indicated accurate measurements with respect to the analyte concentrations.

3.6.5 Matrix Effects:

Matrix effects due to the media or simulated groundwater composition can potentially affect the signal intensity (peak area) of measured parameters. While the use of an internal standard solution compensates for potential matrix effects during analyte quantification, matrix effects are apparent when calculating the absolute recovery of IS within the experimental samples. Evaluation of matrix effects was conducted based upon the extent of signal suppression (%) for the sample IS as compared to the average signal intensity of the IS in the spiked MilliQ water standards. Signal suppression was calculated using equation (1):

$$\textit{Signal suppression (\%)} = [1-I_s/I_x]*100 \qquad (1)$$

Where I_s is the signal intensity of the sample IS and I_x is the average signal intensity of the spiked MilliQ water IS. Signal suppression was investigated for all reactive media studied; the intensity reduction of the IS was usually in the range of 10-35% in the experimental samples with the exception of wood chips indicating a suppression of 84%.

3.6.6 Method Recoveries:

i) Absolute method IS recovery: Recoveries were determined by comparing the IS peak area of the calibration standards to that of the quality control standards, that experienced the entire

experimental procedure. Recoveries were calculated for concentrations from 0.05 to 20 μg l^{-1} and an average of these recoveries was taken for each analyte. The absolute method recoveries indicates losses due solely to experimental method and sample preparation and does not include signal suppression due to matrix effects caused by investigated media simulated groundwater composition.

ii) Relative Method Recovery: Compares the concentration specific ratio of the analyte peak area to IS peak area (ie. analyte peak area/IS peak area) of the calibration standards with the coordinating ratio of the quality control samples. This recovery indicates procedural losses and amplification due to sample analysis including all steps of the method (i.e., SPE and HPLC) which are not compensated or adjusted for by the surrogate IS concentrations.

iii) Absolute Analyte Recovery: Recoveries were determined by comparing the analyte peak area of the calibration standards to that of the quality control standards, which experienced the entire experimental procedure. Recoveries were calculated for concentrations from 0.05-20 μg l^{-1} and an average of these recoveries was taken for each analyte. The absolute method recoveries indicate losses solely due to experimental method and sample preparation and does not include signal suppression due to matrix effects caused by media or simulated groundwater composition. Unlike the relative method recovery, the absolute analyte recovery encompasses all losses and amplifications due to method and sample preparation, having no disparity compensated for by the relation to a surrogate IS.

Table 3.5 Method recoveries and sensitivity: Analytical limits and average recoveries for surrogate internal standard and analyte peak area in calibration and quality control standards

Method Recoveries				Analytical Limits	
PhAC	**Absolute IS Recovery**	**Relative Recovery**	**Absolute Analyte Recovery**	**LOD (ng l^{-1})**	**LOQ (ng l^{-1})**
Caffeine	101±10.3	120±3	121±8	0	19.8
Carbamazepine	89±6	106±2	104±12	3	37
Naproxen	86±5	113±10	109±2	139	763
Gemfibrozil	90±1	116±7	110±6	15	65
Ibuprofen	101±9	100±1	95±9	189	648

3.6.7 Sample Recoveries

iv) Absolute Sample IS Recovery: Recoveries were determined by comparing the IS peak area of the calibration standards to the IS peak area of the samples. Recoveries were calculated for every sample collected and a unique average of these recoveries was taken for each specific media. The absolute sample recoveries indicate losses due to experimental method, sample preparation as well as signal suppression and amplification due to matrix effects caused by the investigated media or simulated groundwater water composition. Sample recoveries were in an expected range of 78±7 to 126± 7% with the exception of carbamazepine in the woochip reaction vessel, having an extremely low recovery of 17%.

Table 3.6 Sample Recoveries. Average recovery of surrogate internal standard (IS) peak area for samples with respect to the media type of sample. Surrogate IS is added to all samples subsequent to sampling and prior to extraction, thus IS is not exposed to media but to sample preparation and extraction procedures.

Percent Sample Recoveries of Internal Standard											
PhAC	**Control 1**	**ZVFe: Sand**	**Control 2**	**Stelco BOF slag**	**Wood Chips**	**Borden Sand**	**Contro l 3**	**ZVFe 100%**	**GAC**	**ZVFe: GAC (50:50)**	**ZVFe: GAC (70:30)**
Caffeine	111.±12	115±12	94±13	93±10	102±9	111±14	104±9	120±21	97±7	93±7	89±12
Carbamazepine	79±6	80±5	73±6	64±5	17±2	63±7	83±7	72±6	83±8	81±9	76±21
Naproxen	103±11	101±7	93±22	94±20	78±7	95±22	100±10	99±7	84±9	85±12	78±12
Gemfibrozil	106±10	104±8	96±22	95±14	86±4	97±20	93±4	91±6	81±8	79±15	89±16
Ibuprofen	95±7	100±6	98±18	100±16	80±7	102±17	118±6	126±7	95±2	94±9	102±13

4 RESULTS AND DISCUSSION: PHARMACEUTICAL RESPONSE TO REACTIVE MEDIA

4.1 Overview and Analysis

Experiments were conducted with batch samples containing a media of interest in simulated groundwater spiked with carbamazepine, caffeine, naproxen, gemfibrozil, ibuprofen, sulfamethoxazole and clofibrate, each at a resultant concentration of 2-2.5 µg/L, to examine the potential sorptive or degradative capacity of the media with respect to these pharmaceuticals. Samples were collected at predetermined time intervals over the course of 10 or 15 days to observe the influence of different contact times on the removal process.

Media investigated included: Borden sand (BDS), Stelco-BOF slag (BOF), wood chips (WC), zero valent iron (ZVFe) and granular activated carbon (GAC). These media were selected based on their reactivity, affordability, availability, durability and ease of use. The media were also chosen based upon their application for the treatment of other contaminants. Borden sand, while not typically considered a reactive media, was investigated as a control, employed to reveal possible sorption or interactions of the pharmaceuticals with natural aquifer materials. Activated carbon, while already extensively investigated as a treatment media for removal of pharmaceuticals, was investigated in this study to explore the benefit of this media when applied as a mixture.

Two sets of batch experiments were conducted. A preliminary batch, conducted solely on the bench top in 1000 ml reaction flasks; and a final batch, consisting of a series of 100 ml serum bottles, constructed and sealed within an anaerobic glove box, remaining sealed until the time of sampling. While the initial preliminary batch experiments had the benefit of consistency in media, in that the same media was in contact with the same water for every sample extracted for that media; it had the potential for contamination at the time of sampling,

thus affecting all subsequent samplings, it did not provide a sufficiently anaerobic environment, and finally small difference in concentrations of pharmaceuticals occurred due to unique spiking of each reaction flask. The final batch experiments attempted to remedy the shortfalls of the preliminary batches; each vessel was sampled only once thus eliminating potential contamination; samples were prepared and sealed within a glove box, which provided as evident by measured Eh readings, a reducing environment; and preparation of a working stock solution of spiked simulated ground water ensured that every sample vessel had the identical concentrations of pharmaceuticals.

To ensure that the resultant changes in concentrations of pharmaceuticals with time in the final batch experiments were consistent, reproducible and not due to undefined variables, triplicate samples were prepared at every other sampling time for all media and controls. The standard deviation was then calculated between these replicate samples to verify that the noted change or stability in pharmaceutical concentration was consistent between replicate samples taken at the same time interval. Calculated deviations are depicted as error bars on the concentration versus time profiles in **Figures 4.1** and **4.2**, each bar representing the standard deviation from the mean, represented by the data point. Standard deviations were extremely small, in most cases so small that the majority of sampling times the error bars were not discernable. The small observed standard deviations are indicative of the high reproducibility of results throughout the experiment; thus verifying that the investigated media was triggering the same response or outcome on pharmaceutical concentrations among samples.

The change in concentrations of pharmaceuticals over time was plotted for all media in the initial batch experiments (**Figure 4.1**). Concentrations are plotted as C/C_0; C being the

measured concentration of the sample at the time of sampling, and C_0 being the initial concentration of the spiked reaction solution (as calculated using concentration and volumes of spike and reaction solution (see Appendix VIII). Concentrations were calculated by internal and external calibration of HPLC-MS/MS results.

Analogous information regarding all media investigated in the final batch experiments is depicted in **Figure 4.2**. Concentrations are again plotted as C/C_0 versus time; however in these experiments C_0 was established as the average concentration of the pharmaceutical in the control samples. This definition of C_0 was justified in the final batches while not in the initial batch experiments since the simulated ground water was spiked prior to distribution to each sample; and thus every sample, including the controls started with the identical initial concentration. Matching the analytical procedure for the preliminary batch experiment, concentrations were calculated by internal and external calibration of HPLC-MS/MS results. The analytical method accurately quantified the investigated pharmaceuticals, as indicated by the absolute method recoveries of 86-101%, the analyte recovery of the quality control standards, 95-121%, as well as the low %RSD of 0-0.117% (n=8), and % residuals of the calibration standards of less than 1% (-0.300-0.4268%) (Appendix VII). Observed removals of parent pharmaceuticals were not the consequence of compounded recovery effects due to matrix and analytical influences since consistent recoveries of surrogate internal standard occurred within media specific samples (**Table 3.6** in method validation); and percent removals were considered with respect to deviation from the apparent concentrations in control samples.

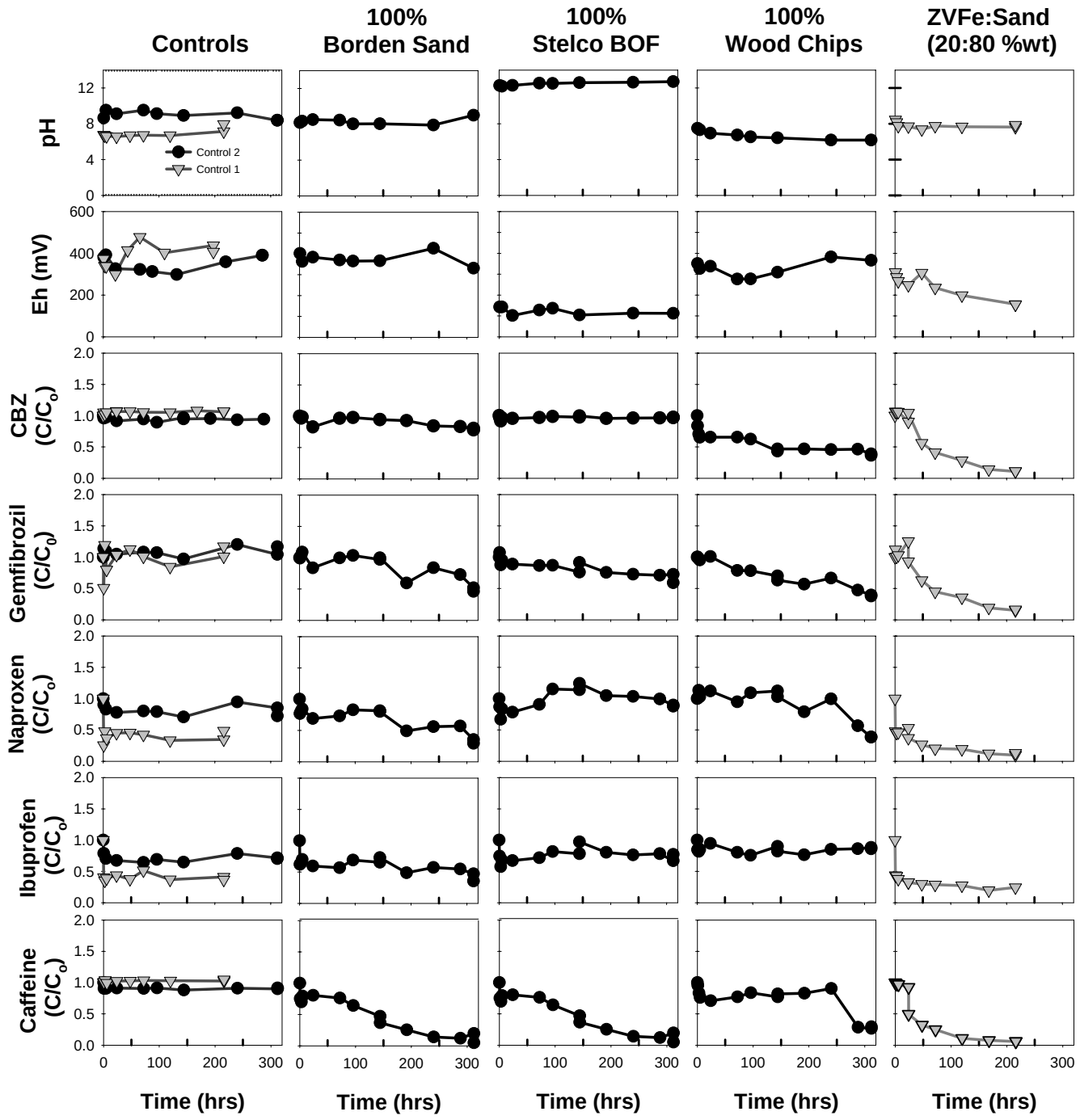

Figure. 4.1 Pharmaceutical concentration *versus* time plotted for all media in the initial batch experiments. Concentrations are expressed as C/C_o; C being the measured concentration of the sample at the time of sampling, andC_o being the initial concentration of the spiked reaction solution. C_o was calculated using concentration and volumes of the stock spike solution and the reaction solution as shown in Appendix VIII. Concentrations were calculated by internal and external calibration of HPLC-MS/MS results that were then corrected for earlier dilution and then subsequent concentration by SPE. Two controls are depicted in the figure, representative of the two preliminary batch experiments conducted. Control one denotes the control for the first preliminary batch including the ZVFe: sand reaction vessel; while control two denotes the second preliminary batch experiment involving WC, BOF and BDS.

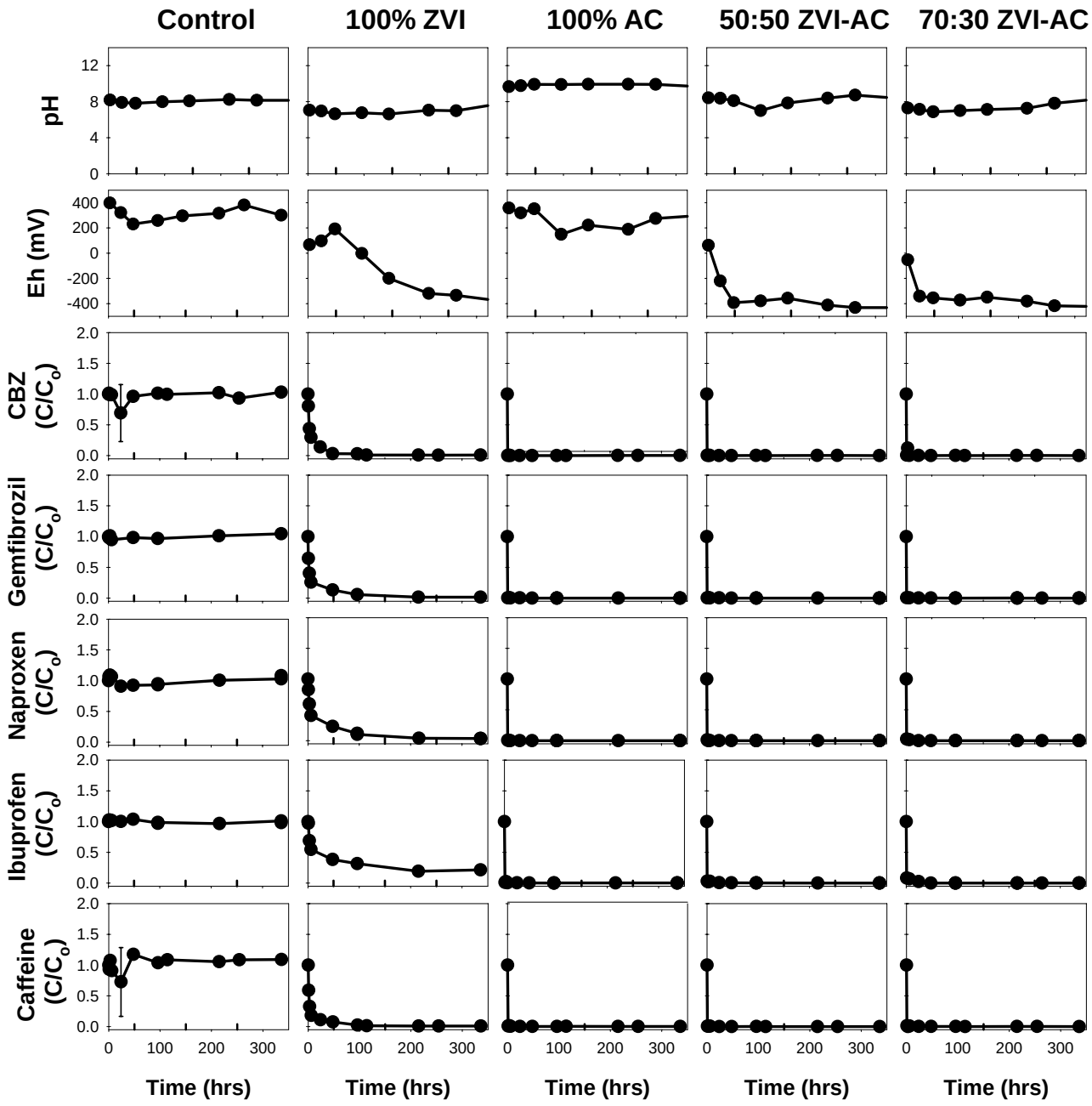

Figure. 4.2 Concentrations of pharmaceuticals *versus* time plotted for all media in the final batch experiments. Concentrations are plotted as C/C_o; C being the measured concentration of the sample at the time of sampling, and C_o being the initial concentration of the spiked reaction solution. C_o was calculated using concentration and volumes of the stock spike solution and the reaction solution as shown in Appendix VIII. Concentrations were calculated by internal and external calibration of HPLC-MS/MS results which were then corrected for earlier dilution and then subsequent concentration by SPE.

Percent removals of each pharmaceutical with respect to concentration for each of the media investigated are illustrated in Figure 4.3. Percent removal was calculated using equation (1).

$$\% \text{ Removal} = (1- C_f/C_o)*100 \quad (1)$$

Where C_f is the final pharmaceutical concentration in the treated effluent and C_o is the initial pharmaceutical concentration defined or calculated as described previously. Calculations for preliminary batches, where C_o is defined as the spiked pharmaceutical concentration, were further defined by equation 2:

$$R_m = R_{cc} – R_{cm} \quad (2)$$

where R_m = total percent removal by media, and R_{cm} and R_{cc} are the calculated percent removals of the media and the controls respectively, as calculated by equation one. Percent removals by media ranged from as little as 0.0% for Stelco-BOF-slag, Borden sand and wood chips to as great as 100.0% in samples containing granular activated carbon. In general, the controls exhibited little to no reduction in pharmaceutical concentration; with the exception of caffeine, which saw almost 50% reduction within the control vessels. The greatest percent removal was seen in the samples with GAC, either alone or in a mixture with ZVFe; concentrations decreased to below the LOD for all investigated pharmaceuticals before the first sampling. The smallest percentage removals when considering all media were exhibited by ibuprofen and naproxen, which indicated no removal when in contact with BOF and BDS.

Most removal was seen within the first 24 hours for the majority of the drugs which showed measurable removals.

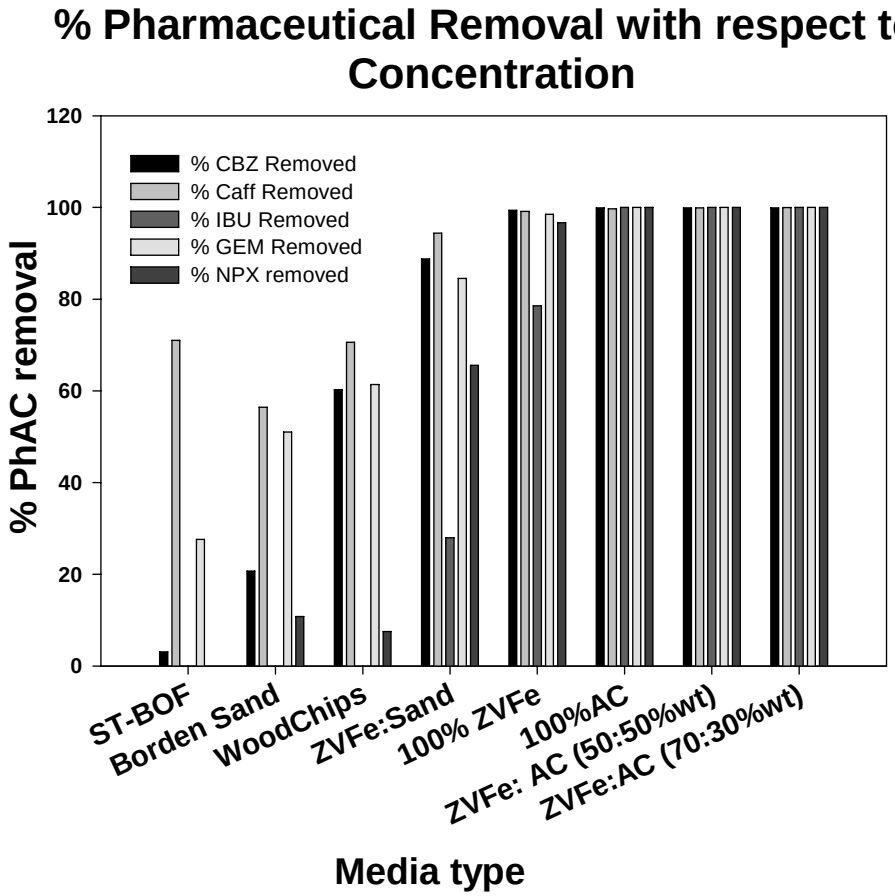

Figure 4.3 Percent removal of pharmaceuticals (CBZ, CAFF, IBU, GEM, NPX) by the investigated media. Percent removals were calculated using the equation %Removal = (1-C/Co)*100, where C= final Pharmaceutical concentration in solution and Co = the initial concentration in solution. Co was determined based upon spiked concentrations for preliminary batches and upon the average concentrations in the controls for the final batch experiments. Percent removal for preliminary batch samples were calculated as the resultant removal surpassing removal experienced by control samples; thus final percent removals were calculated as %Removal (preliminary batches) = Rm – Rc; where Rm is the percent removal in the treated sample and Rc was for the control.

4.2 Controls:

For each set of batch experiments conducted, a set of controls was also established. Controls consisted of simulated groundwater (from the same stock used for all samples), spiked with the same pharmaceutical stock (containing all seven compounds) in the same concentrations as the media samples. Control reaction vessels were prepared in a matching manner as the media reaction vessels, except for the absence of reactive media; and samples were collected and prepared for analysis correspondingly.

The initial control vessels contained approximately 2 ± 0.5 $\mu g l^{-1}$ of each pharmaceutical, and the solutions were initially near neutral in pH (pH 6.7-8.6). Eh measurements indicated oxidizing conditions and were in the range of 300-400 mV in the preliminary batch experiments, and in a slightly lower range of 230-400 mV in the final batch experiments, likely due to the anaerobic preparation of the samples. Concentration versus time profiles for all control experiments are shown in Figures 4.1 and 4.2 for the preliminary and final batch experiments, respectively. The $CaCO_3$ and NaCl composition of the simulated groundwater, as well as the trace amount of methanol introduced to each reaction flask via the pharmaceutical stock solution did not affect the concentrations of pharmaceuticals, as indicated by the narrow 95% confidence intervals (ranging from 0.017 to 0.29) (Appendix XIII). Little change was noted in the chemical composition of the water, including concentrations of cations, anions, pH (ranging from 6.7-9.5) and Eh (ranging from 230-400 mV) in the control flasks over the course of the experiments; indicating stability in the bulk geochemistry within the control vessels.

4.3 Reactive Media

Reactive Media -BOF Slag:

Stelco basic oxygen furnace (BOF) slag, an iron oxide byproduct of steel manufacturing demonstrated modest potential for use in pharmaceutical treatment. BOF slag is a coarse grained, homogenous product comprising high concentrations of Ca (portlandite, calcium oxides/silicates), Fe (FeO, ferrites, and silicates), Mg, Si, and Al in the form of oxides and silicates (Baker et al, 1998). In this study, BOF slag was investigated solely in the preliminary batch studies, where a series of sample volumes were drawn over the course of 15 days from a 1000 ml reaction flask containing BOF slag and simulated groundwater spiked with the aforementioned pharmaceuticals.

Initial spiked simulated groundwater solutions contained approximately 2-2.5 $\mu g\ l^{-1}$ concentrations of each investigated pharmaceutical, and measured initial pH values of approximately pH 8. Pharmaceutical removal, potentially through degradation or sorption mechanisms, resulted in percent removals from 0.0% for naproxen and ibuprofen up to 71% for caffeine (**Figure 4.3**). Profiles showing concentrations versus time are depicted in Figure 4.2.

The BOF-slag minimally influenced the solution concentrations of naproxen, ibuprofen, gemfibrozil and carbamazepine, showing percent removals of 0.0%, 0.0%, 27% and 3% respectively. Paired t-test calculations comparing control concentration profiles to the concentration profiles of the treated samples indicated little to no difference (Appendix XII).

Reaction with BOF slag did however result in more substantial decreases in the solution concentration of caffeine resulting in a percent removal of 71%. Paired t-test

calculations comparing the control caffeine concentration profile to the concentration profile of the treated samples indicated a more significant difference (Appendix XII).

Concentration changes or stability within the BOF reaction vessels were accompanied by an increase in pH to pH >12 and Eh values in the range of 100 to 150 (**Figure 4.2**). The increase in pH is attributed to the dissolution of portlandite [Ca $(OH)_2$] – the major soluble mineral phase in BOF slag (Baker et al, 1998). The dissolution reaction of portlandite (reaction 3) causes a substantial increase in pH and dissolved Ca^{2+} in solution:

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \qquad (3)$$

Geochemical analyses of water samples indicated a corresponding increase in concentrations of Ca^{2+} consistent with this reaction. Increases were also observed in concentrations of other cations such as K^+, Na^+ and Fe (Figure 4.5). . Anion analysis indicated increasing concentrations of all measured anions with time, including nitrate, fluoride, chloride and sulfate, with the exception of phosphate, of which none was detected (**Figure 4.4**). The stability of nitrate and sulfate are consistent with the oxidizing conditions created by the BOF slag media.

Back extractions of the treatment media were conducted to delineate the possible distribution of the pharmaceutical between the solution and the solid phases. Knowledge of this distribution provides insight into the potential mechanism responsible for pharmaceutical removal as a result of the media; for example, sorption or degradation (Appendix XI). The percent mass recovery from the BOF-slag for all of the evaluated pharmaceuticals was very similar, around 5%, with the exception of caffeine which was less than 1% (**Figure 4.8**). The

nearly complete mass recovery of carbamazepine, ibuprofen and naproxen indicates that the small removals noted for these pharmaceuticals is likely due to the roughly 5% sorbed to the reactive media, and not to degradation processes. For caffeine and gemfibrozil, the total masses were not accounted for by the recovery of sorbed and dissolved masses, with 94% and 37% of mass unaccounted for each of these compounds respectively. While these percentages may not reflect the actual percent of the drugs transformed, since back extractions may not have desorbed all of the compounds, they do indicate that sorption may not be the sole removal mechanism—that potentially another mechanism, such as oxidation reactions may be contributing to their removal. Previous studies have indicated high success using oxidative treatments such as ozone and chlorine dioxide with caffeine and gemfibrozil, indicating percent removals in the range of 91-93% and 88-98% for ozone and >60% and >90% for chlorine dioxide respectively (Gomez et al., 2008; Westerhoff et al., 2006); thus oxidation of these pharmaceuticals by BOF-slag is feasible. However, these same oxidative treatments showed similarly high success for the pharmaceuticals that in this study demonstrated only slight removal due to BOF-slag, likely due to sorption not oxidation. The reactivity of BOF as an oxidative treatment may be limited by the phase of the media itself; being limited to surface reactions as a solid media, unlike gaseous or liquid treatment media. Similarly, neither the elevated pH conditions nor the high content of oxide minerals appear to promote extensive removal of the pharmaceuticals investigated.

Reactive Media – Wood Chips:

Organic carbon rich reactive mixtures containing such media as wood chips have been investigated in the past for the treatment of nitrate and acid mine drainage employed within

containerized wastewater treatment systems (e.g. Roberston et al., 2000) and permeable reactive barriers (PRBs) to enhance bacterial sulfate reduction and metal sulfide precipitation (e.g. Benner et al., 1999). Bench-top batch experiments were conducted to evaluate the effectiveness of wood chips in the removal of the suite of pharmaceuticals when present in simulated groundwater. Experiments including wood chips were conducted exclusively in the preliminary batch studies.

Pharmaceutical removal, potentially through degradation or sorption mechanisms, resulted in percent removals from 0.0 % for ibuprofen up to 82% for caffeine (**Figure 4.3**). The rate at which this removal occurred is illustrated by concentrations versus time profiles (**Figure 4.1**).

Wood chips resulted in minimal change in solution concentrations of ibuprofen and naproxen and only a moderate change in concentrations of caffeine, carbamazepine and gemfibrozil, showing percent removals of 0.0%, 7.5% 71%, 60% and 61% respectively. Paired t-test calculations comparing controls to the concentration profiles of the treated samples indicated little statistical difference for naproxen (Appendix XII) at the 5% level. Paired t-test values for caffeine, gemfibrozil and ibuprofen did indicate significant statistical difference at the 5% level; however, probabilities were still greater than 1% for gemfibrozil and caffeine, thus at the 1% significance level the samples were not statistically different. The reduction in carbamazepine however had a p-value close to zero, indicating significant statistical difference at even the 0.1% significance level (Appendix XII).

The moderate reduction of pharmaceutical concentrations within the wood chip reaction vessel was accompanied by a decrease in pH from 7.5 to 6.17 possibly due to organic matter decomposition and the production and release of organic acids such as formate and

acetate. The Eh of the reaction vessel did not vary greatly over the course of the study, falling from approximately 350 mV to 280 mV and then returning back to approximately the starting value by the end of the 15 days (Figure 4.1). Due to the reducing nature of organic matter a greater decrease in Eh was expected, thus suggesting possible ingress of oxygen into the reaction vessel, despite purging with argon gas. Geochemical analysis of anions did however indicate elevated concentrations of phosphate, up to 8.5 $mg\ l^{-1}$ (as PO_4), indicating that degradation of organic matter was potentially leading to the release of phosphate (Waybrant et al., 2002). Increases in concentrations of Mn and Fe were also observed potentially due to release through degradation of organic matter (**Figure 4.4**). Concentrations of Ca and alkalinity (**Figure 4.5** and **4.7**) were observed to increase over the course of the experiment, consistent with dissolution of carbonate minerals.

Back extractions of wood chips were conducted to help elucidate the possible distribution of pharmaceuticals between solution and solid phases. The percent mass recovery of pharmaceuticals from the wood chips ranged from as low as 1.5% for carbamazepine to as high as 16% for ibuprofen (**Figure 4.8**). The complete mass recovery of ibuprofen indicates that the approximately 16% of mass back extracted from the wood chips accounted for all ibuprofen removal. Ibuprofen, found in previous studies to degrade primarily by biodegradation is generally thought to have low sorption potential due to its low log K_{ow} value (Smook et al., 2008; Ternes et al., 2004). Wood chips do appear to adsorb a small percentage of ibuprofen, however, the total ibuprofen removal in the vessel containing woodchips was actually no more than the observed decrease in the control vessel; thus, wood chips do not appear to be a promising treatment media for ibuprofen. The total masses of carbamazepine, caffeine, naproxen and gemfibrozil were not accounted for by the recovery of sorbed and

dissolved masses. The back extractions recovered approximately 10% of the mass of each pharmaceutical, with the exception of carbamazepine, indicating that sorption to wood chips is occurring and contributing to pharmaceutical removal. For carbamazepine, back extractions recovered as little as 1.5% of the pharmaceutical from the woodchips (Appendix XI).

A large measure of uncertainty was encountered in the woodchip sample analysis. Sample recoveries of internal standard were extremely low, as low as 17% for D_{10}-carbamazepine and MINTEQA2 calculated high charge balance errors, up to 98.75%. This uncertainty may be due to interference resulting from the high total organic carbon (TOC) contributed by the woodchips to the water; this natural organic matter can potentially complex with the analyzed constituents thus interferring with the determination of their substantiality in the system. Future analysis regarding woodchips and other media rich in organic matter would benefit from the use of standard additions to help counteract descrepancies caused by organic matter interferences.

Reactive Media – Borden Sand:

Camp Borden, a Canadian forces base northwest of Toronto, is extensively used for groundwater research. Following numerous investigations at this site the aquifer and sediments in this area are well characterized. Due to the extensive interest and characterization of media from this research location, Borden sand was chosen to investigate the potential sorption of each of the investigated pharmaceuticals to common aquifer media, in this case, sand. In the preliminary bench top batch experiments Borden sand was investigated in the same manner as previous media to evaluate its influence on the removal of

the suite of pharmaceuticals when present in simulated groundwater. Borden sand was investigated solely in the preliminary batch studies.

The reaction vessel initially contained simulated groundwater with 2-2.5µg/L concentration of each investigated pharmaceutical, and pH values of approximately pH 8. Pharmaceutical removal, likely due to sorption, resulted in percent removal from 20% for carbamazepine up to 66% for caffeine (**Figure 4.3**). **Figure 4.1** displays concentration versus time profiles for this media.

A moderate influence on the solution concentration of carbamazepine, gemfibrozil, naproxen and ibuprofen was noted, showing percent removals of 20%, 51%, 64% and 53% respectively (**Figure 4.3**). Due to the characteristically low organic carbon content of Borden sand (organic carbon fraction, foc = 0.021%) and the hydrophobicity of the pharmaceuticals this removal was greater than anticipated. Thus solid-water distribution coefficients (K_d) were calculated for the pharmaceuticals from predicted organic-carbon distribution coefficient (K_{oc}) values using equation 4 (Schwarzenbach et al., 2003), to delineate the theoretical sorptive behaviour of the pharmaceuticals. K_{oc} values for each pharmaceutical were determined as described by Carballa et al. (2008) using the pH dependent octanol-water distribution coefficient (D_{ow}), which accounts for the pH of the system, as well as the pK_a of the pharmaceutical (equation 5).

$$K_d = K_{ow} * f_{oc} \quad (4)$$

$$LogK_{oc} = 0.74 * logD_{ow} + 0.15 \quad (5)$$

$$LogD_{ow} = logK_{ow} \quad (6)$$

$$LogD_{ow} = logK_{ow} + log[1/1+10^{pH-pKa}] \quad (7)$$

The D_{ow} is calculated based upon the type of pharmaceutical. For neutral compounds such as carbamazepine or caffeine, D_{ow} is calcuated using equation 6 (Carballa et al., 2008); while determination of D_{ow} for acidic compounds, such as ibuprofen, is calculated using equation 7 (Carballa et al., 2008). Calculated K_d values for the pharmaceuticals indicated that at simulated groundwater conditions gemfibrozil should show the greatest sorption, followed in order by carbamazepine, ibuprofen, caffeine and finally naproxen. This trend was not observed for the experimental results, since despite its hydrophilic nature, caffeine showed the greatest removal and carbamazepine removal was lower than the less hydrophobic compounds.

The removal of the pharmaceuticals relative to each other was not the only unexpected result with respect to Borden sand. As previously mentioned the amount of removal was greater than anticipated given the low f_{oc}. A recent investigation by Ran et al. (2003) noted that prior studies (Curtis et al., 1986a,b; Roberts et al., 1986; Goltz and Roberts, 1987; Ball and Roberts, 1991a,b; Ptacek and Gillham, 1992) all indicated that organic compound uptake by Borden sand was slow, and that measured K_d values tended to be greater than those calculated based upon K_{ow} and f_{oc} values. The Ran et al. study proposed that kerogen, a condensed type of natural organic matter (NOM), was present in the Borden aquifer material; and that it was this NOM that played the leading role in the uptake of organic chemicals. The K_{oc} values for Borden sand were higher than those determined by a K_{oc}-K_{ow} correlation, due to the kerogen having a condensed rigid physical nature and reduced chemical composition capable of trapping organic chemicals. Larger organic chemicals have less accessibility to the kerogen and are thus less likely to be trapped within the parallel aromatic sheets of the NOM. Sorption to kerogen in Borden sand may explain the higher than expected pharmaceutical

removal within this study; and further explain why caffeine, having the smallest molecular weight, indicated the greatest removal, while less removal was seen by the other pharmaceuticals, all having larger molecular weights.

Table 4.1 Solid-water distribution coefficients ($\mathbf{K_d}$) were calculated for each pharmaceutical in Borden sand using the relationship between $\mathbf{K_d}$ and $\mathbf{K_{oc}}$ and $\mathbf{f_{oc}}$ as described by equation 4. $\mathbf{K_{oc}}$ values were calculated as described by equations 5, 6 and 7. Calculations were based upon a pH value of pH 8. Gemfibrozil was assumed to be neutral at these pH conditions since no $\mathbf{pK_a}$ value could be found for this pharmaceutical in the literature.

Pharmaceutical	pK_a	pH	$logK_{ow}$	$logD_{ow}$	$logK_{oc}$	K_{oc}	f_{oc} (%)	K_d
Carbamazepine	14	8	2.45	2.45	1.96	91.83	0.021	0.02
Caffeine	10.4	8	-0.07	-0.07	0.098	1.25	0.021	0.00026
Naproxen	4.15	8	3.18	-0.6	-0.29	0.51	0.021	0.00011
Gemfibrozil	n/a	8	4.77	4.77	3.68	4784.10	0.021	1.00
Ibuprofen	4.52	8	3.97	0.52	0.53	3.43	0.021	0.00072

While the final percent removals with respect to concentration were higher than expected, paired t-test calculations, comparing controls to concentration profiles of treated samples, did in fact indicate no statistical difference in the pharmaceutical concentrations at the 5% level for the majority of the pharmaceuticals (Appendix XII). Caffeine was the only pharmaceutical to show a significant decrease in solution concentration, resulting, as previously noted, in a 66 % removal. Paired t-test calculations comparing controls to the concentration profiles of caffeine in treated samples indicated significant statistical difference at the 5% level (Appendix XII). Over the course of the experiment, there was little change in the bulk chemical composition of the water. The pH in the reaction vessel was for the most part stable, ranging from 7.9 to 9.0, similar to control vessels (**Figure 4.1**). The pH stability is likely the result of pH buffering due to the high carbonate content of the Borden sand and dissolved carbonate in the simulated groundwater. Eh measurements over the course of the

investigation also mirrored control samples, ranging from 330 mV to 430 mV (Figure 4.1). Similarly results of anion and cation geochemical analysis deviated little from those of the controls, with the exception of an initial increase and subsequent decrease in Fe concentration, possibly due to the dissolution of iron mineral components (**Figure 4.4** and **Figure 4.5**).

Back extractions of Borden sand conducted to interpret the possible apportioning of pharmaceuticals between solution and solid phases recovered approximately 1-3% of the mass of each pharmaceutical investigated. The greatest mass recovered was for caffeine which showed the greatest overal removal. While caffeine recovery from the sand was less than expected, at only 3% of the total mass, adsorption is still considered the probable removal mechanism. This is the most conceivable removal mechanism when one considers the scarcity of strong oxidants or reductants in Borden sand. The small amount of mass recovered from the sand for the other pharmaceuticals was expected due to the insignificant changes in pharmaceutical concentration between control and treated samples. This is supported by a study conducted by Ternes el al. (2002) that found no significant removal in pharmaceuticals in batch experiments with sand under natural aerobic and anaerobic conditions; as well as, Carrara et al. (2008) who found minimal pharmaceutical removal specifically in Borden sand.

Reactive Media – Zero Valent Iron (ZVFe):

Zero valent iron (ZVFe) has been investigated extensively and is used for the treatment of a wide range of water contaminants. Laboratory and field applications of ZVFe, including permeable reactive barriers (PRBs) containing ZVFe, have been used to treat chlorinated solvents, Cr(VI), U, Tc, Se, Pb(II), carbon disulfide, As(V), carbothioate herbicides, atrazine, nitrophenols, PCBs and other alkly-halides (Table 3.2). Zero valent iron a strong reducing

agent relative to many redox-labile compounds, such as hydrogen ions, carbonates, sulfates, nitrates, oxygen and alkyl halides, due to the standard reduction potential of -0.440 V for its reduction reaction with dissolved aqueous Fe^{2+} (eq. 6, Matheson et al., 1994). Zero valent iron reduces a large number of contaminants through a reaction known as a dissolving metal reduction; a reaction equivalent to iron corrosion, where the contaminant is acting as the oxidizing agent (Matheson et al, 1994). An example of this reaction is shown in equation 7 for the treatment of an alkyl halide. In an anaerobic environment water alone can act as the oxidant; and the corrosion of iron results in oxidative dissolution of the metal and production of ferrous iron (Fe^{2+}) and H_2 (eq 8); thus three possible reductants are present: Fe^0, Fe^{2+} and H_2 (Matheson et al., 1994).

$$Fe^{2+} + 2e^- \leftrightarrow Fe^0 \quad (6)$$

$$Fe^0 + R\text{-}X + H^+ \leftrightarrow Fe^{2+} + R\text{-}H + X^- \quad (7)$$

$$Fe^0 + 2H_2O \leftrightarrow Fe^{2+} + H_2 + 2OH^- \quad (8)$$

The reductive potential, availability, affordability and ease of use of ZVFe as a treatment media, has made it a popular choice for the remediation of a number of contaminants. To our knowledge the use of ZVFe in the treatment of pharmaceuticals has not been explored. Thus, bench top batch experiments were conducted to evaluate the influence of ZVFe on the behaviour of the suite of experimental pharmaceutical compounds when present in simulated groundwater. Zero valent iron was investigated in both the preliminary batch studies, where a

series of samples was drawn over the course of 10 days from the same 1000 ml reaction flask, and the final batch studies, where a series of 100 ml serum bottles were assembled and sealed inside a glove box, drawn on only at the time of sampling, then wasted.

Initial spiked simulated groundwater in both preliminary and final batches contained approximately 2-2.5 $\mu g\ l^{-1}$ concentration of each pharmaceutical, with the exception of caffeine, which was increased to approximately 4.5$\mu g\ l^{-1}$ in final batch samples. Initial water chemistry exhibited pH values of approximately pH 7 for the preliminary batch experiments and approximately pH 8 for the final batch experiments (**Figures 4.1** and **4.2**). Pharmaceutical removal, potentially through degradation or sorption mechanisms, resulted in percent removals from 27% for ibuprofen and up to 94% for caffeine in the preliminary ZVFe-sand reaction mixture; and from 79% for ibuprofen and up to 99% for caffeine and carbamazepine in the 100% ZVFe final batch reactions (**Figure 4.3**). Concentration versus time profiles depicted in Figures 4.1 and 4.2 indicate that most removal was seen within 6 days in the preliminary batches and within 24 hours in the final batch samples.

The preliminary batch samples composed of ZVFe and silica sand in a ratio of 20:80 indicated little to moderate amendment to the solution concentrations of ibuprofen and naproxen with percent removals of 28% and 66% respectively. The statistical weight of these reductions, by paired t-test calculations, indicates no statistical difference between the control and treated samples for naproxen and borderline statistical differences for ibuprofen, at the 5% level (Appendix XII). Greater % removals of 89%, 85% and 94% were seen for carbamazepine, gemfibrozil, and caffeine, respectively. Paired t-test results comparing controls to the concentration profiles of the treated samples supported the significance of

these changes for carbamazepine and caffeine, with p values less than alpha even at the 1% level (Appendix XII).

The final batch samples, prepared within a glove box and composed of 100% ZVFe caused much greater and more rapid decreases in pharmaceutical concentrations for each of the pharmaceuticals studied. Overall, while the removals were accelerated and larger, the general removal trend remained similar with the least percent removal occurring once again for ibuprofen and then naproxen. Percent removals of 78.6%, 96.6%, 98.5, 99.1% and 99.4% for ibuprofen, naproxen, gemfibrozil, caffeine, and carbamazepine, respectively, all indicated significant statistical difference at the 1% level between control and treated samples with p values of 0.000 for all pharmaceuticals (**Figure 4.3**; Appendix XII).

The greater percent removals seen in the final batch experiments are likely due to one or a combination of two things: the increased wt % of ZVFe from 2.5% to 12.5% with respect to the solution mass, or the more fully anaerobic nature of the samples. A number of studies have indicated that the reaction kinetics of contaminant degradation by ZVFe are controlled by the available reactive surface area of the metal, with linear relationships between the first-order rate constant and the specific surface area (McGeough et al, 2007, Farrel et al., 2000; Joo et al., 2004; Johnson et al., 1996). The final batch samples having a greater proportion of ZVFe would thus have a larger amount of reactive surface area, therefore, accounting for at least in part to the faster and greater removals exhibited by the pharmaceuticals in the final batch. However, O_2 exposure may have played a role in decreasing the efficiency of the preliminary batch as well. While the preliminary batches were sparged with argon gas upon sampling, O_2 entry into the system was apparent by the unexpectedly high Eh values that declined to only 150 mV. Eh values in the final batch dropped as low as -380 mV; indicating

a much more reducing environment. The presence of O_2 in the preliminary batch may have decreased the degradation potential of the ZVFe by competing with the pharmaceuticals (Joo et al., 2004). Oxygen reduction by ZVFe (eq 8 and 9) produces Fe^{2+} that with further oxidation produces Fe^{3+}. This oxidation is expectedly coupled with subsequent precipitation of particulate iron oxyhydroxides that may have coated the ZVFe surface, decreasing the available reactive surface area and consequently the reaction rate (Blowes et al., 1997; Pratt et al., 1997; Joo et al., 2004).

As previously noted, even under anaerobic conditions iron corrosion can occur, with water acting as the oxidant (equation 8). This reaction produces hydroxide and thus should result in an increase in pH. The pH in the preliminary and final batch samples did not however show a significant increase in pH. Preliminary batch samples remained in the range of pH 7.37 to 8.45, and only a small increase from 7.04 to 7.72 occurred in the final batch samples (**Figures 4.1** and **4.2**). Thus, while the decrease in Eh values in both batches indicates the gradual dissolution of Fe^0 to Fe^{2+}, the steady pH measurements indicate that the hydroxide produced by iron corrosion is potentially balanced by additional processes within the system, possibly by the formation of iron hydroxides (Matheson et al., 1994).

Geochemical speciation calculations using MINTEQA2 indicated the water was supersaturated with respect to iron oxide and hydroxide phases thus supporting this hypothesis. An initial increase in concentration of total iron was observed during the experiment. According to speciation analysis using MINTEQA2 almost 100% of this total iron is present as Fe^{2+}, and thus this increase in concentration suggests that ZVFe corrosion occurred (**Figure 4.5**). Geochemical analyses also indicated corresponding initial increases in total Mn, indicated by MINTEQA2 to exist primarily as Mn^{2+}, in both preliminary and final

batches, and decreases in nitrate concentration in the final batch samples, both indicative of a reducing environment. Subsequent decreases in Mn and Fe concentrations over the course of the experiment, as well as a significant decrease in dissolved Ca and alkalinity suggests the formation of secondary carbonate minerals (**Figures 4.5** and **4.7**). MINTEQA2 calculations indicate the water is slightly supersaturated with respect to siderite in both ZVFe experiments, suggesting precipitation of carbonate containing minerals may be limiting concentrations of these dissolved constituents (**Figure 4.6**).

Back extractions of ZVFe performed to delineate the possible distribution of the pharmaceuticals between solution and solid phases recovered less than 1% of the mass of all pharmaceuticals investigated with the exception of ibuprofen, where approximately 2% was recovered. The small amount of mass recovered from the ZVFe accounts for very little of the mass loss in the reaction vessels, thus implying that an alternative removal mechanism is occurring. To the best of our knowledge ZVFe has not been previously explored in the treatment of pharmaceuticals, and thus one can only predict that removal mechanisms are by means of reduction as confirmed in the treatment of other contaminants such as chlorinated solvents, Cr(VI) and Se (Gillham, 1994, Blowes et al., 1997; Farrell et al., 2000; Ponder et al., 2000; Lui et al, 2008; Song et al., 2005; Sasaki et al., 2008).

Reactive Media – Granular Activated Carbon (GAC) and GAC: ZVFe mixtures:

Granular activated carbon (GAC) has been used extensively in drinking water treatment systems due to its high sorption capacity. It is employed to capture fine particulate matter and bacteria, and to counteract compounds that may cause unpleasant odors or taste (Stackelberg et al., 2007). Its ability to sorb many organic contaminants has lead to its distinction as one of

the best available technologies for the treatment of regulated organic pollutants by the USEPA (Westerhoff et al., 2005). GAC generally facilitates contaminant removal by sorption, based upon hydrophobic interactions; thus the media most effectively removes non-polar contaminants. In this study GAC was investigated, both alone and as a mixture with ZVFe, in the final batch studies, where a series of 100 ml serum bottles were filled and sealed inside a glove box, each opened and appraised only at the time of sampling.

The reaction vessels at the outset enclosed simulated groundwater with approximately 2-2.5 μg/L concentration of each investigated pharmaceutical, with the exception of caffeine, which was increased to approximately 4.5μg/L in final batch samples. Initial water chemistry of the input solution was similar to that of the controls, with pH values of approximately 8 and Eh values in the range of 300-400 mV.

Pharmaceutical removal, expectedly by sorption, resulted in final concentrations below LOD for all pharmaceuticals investigated and thus recorded percent removals of 100% (**Table 4.3**). Concentrations versus time profiles depicted in **Figure 4.2** indicate that pharmaceutical removal occurred rapidly, decreasing to levels below detection before the first sampling time at 1 hr. Integrated peak analyses indicated below-detection concentrations as low as 3.48×10^{-4} μg l^{-1} for caffeine. However, removal was to such an extent for some pharmaceuticals, that no peak was distinguishable for pharmaceuticals such as carbamazepine. Paired t-test calculations, conducted simply for reasons of consistency, predictably supported that the removals were statistically significant even at the 0.1% significance level when comparing controls to the concentration profiles of the treated samples (Appendix XII). Pharmaceutical removal within the GAC reaction vessel was followed by some slight alterations in water chemistry over the 15 days of the experiment.

The pH of the system increased to 9.7 where it remained for the duration of experiment; while the Eh starting initially around 360 mV, decreased to 100 mV by day 3 and then continually increased returning to approximately 300 mV by the end of the study (**Figure 4.2**).

Previous laboratory studies investigating pharmaceutical removal support the above findings that GAC efficiently removes pharmaceuticals (Stackelberg et al., 2007; Westerhoff et al., 2005; Snyder et al., 2007; Ternes et al., 2002). In a study conducted by Snyder et al. (2007) GAC was capable of removing nearly all evaluated pharmaceuticals by greater than 90%, while both caffeine and carbamazepine showed greater than 90% removals in the study be Stackelberg et al. (2007).

While the results of the final batch experiments provided little information from which to explore trends and patterns, due to the sudden decrease in concentration, previous studies, such as the one conducted by Westerhoff et al. (2005), allowed some general conclusions to be reached concerning the contaminant-specific removal effectiveness of activated carbon. Such studies indicated that at low doses of powdered activated carbon (PAC) a trend was identified between the log K_{ow} of the contaminant and the % removal; higher removals being seen for those compounds with high log K_{ow} values. Also, protonated bases appeared to have superior removal, while deprotonated acids and compounds with low log K_{ow} values tended to be the most challenging to remove.

If one considers solely the percent removals of pharmaceuticals from the final batch experiments, as well as some previously conducted investigations one may consider the USEPA to be correct in saying that GAC is one of the best available technologies for the treatment of many regulated organic pollutants. However, activated carbon studies conducted in the laboratory such as this one do not accurately reflect the true potential of this media

when used in the field. In the Stackelberg et al. (2007) study, removals extended from16 to 93% for spiked surface-water samples, where it was acknowledged that the presence of organic carbon affected pharmaceutical removal by PAC, by competing for adsorption sites. Specifically, correlations between the removal efficiency and the aromatic carbon content, and the molecular weight and hydrophobicity of the DOC were observed. Similar observations were made by Ternes et al. (2002) and Snyder et al. (2007) where it was noted that AC efficiency was deeply diminished by the presence of natural organic matter that competes for binding sites and blocks pores within the AC structure. It has also been recognized that the efficacy of GAC filter banks is dependent upon the age and the condition of the GAC; and thus its effectiveness in application such as drinking water treatment (DWT) varies widely within and among classes of compounds (Stackelberg et al., 2007). Saturated GAC may not allow for adsorption of contaminants; and desorption from GAC is possible during equilibration with aqueous phase concentrations, being that in GAC systems adsorbed contaminant concentrations equilibrate with influent-phase concentrations (Westerhoff et al., 2005; Stackelberg et al., 2007). In fact DWT plants with high total organic carbon using GAC filtration without frequent replacement or regeneration experience very little pharmaceutical removal (Snyder et al., 2007); thus indicating that GAC has finite life when used in the field.

GAC and ZVFe mixtures:

Given the potential downfalls and coinciding enormous potential of AC as a treatment media for pharmaceuticals, further investigations were conducted on AC when used in conjunction with another promising treatment media, ZVFe.

Two mixtures of GAC and ZVFe were investigated in the final batch studies, with one series of 100 ml serum bottles containing a mixture of ZVFe: GAC in the ratio 50:50%wt and the other 70:30%wt. With the exception of caffeine, which was increased to an approximate concentration of 4.5 $\mu g l^{-1}$, an initial concentration of 2-2.5 $\mu g\ l^{-1}$ of each investigated pharmaceutical was spiked in to the artifical groundwater distributed to both series of reaction vessels. The initial input solution water chemistry was similar to that of the controls indicating pH values of approximately 8 and Eh values in the range of 300-400 mV.

Pharmaceutical removal within these reaction vessels paralleled that of the 100% GAC sample vessels, resulting in final concentrations below LOD for all investigated pharmaceuticals; thus, percent removals were recorded as 100% (**Figure 4.3**). No visible peak was present to integrate in late time analyses for ibuprofen, while the lowest concentration to be integrated below detection limits was that of $6.38 \times 10^{-6}\ \mu g\ l^{-1}$ for caffeine. Also following the GAC reaction samples, concentrations versus time profiles depicted in **Figure 4.2** indicate that pharmaceutical removal was very rapid, decreasing to levels below detection before the first sampling time at 1 hour. Paired t-test calculations supported that the removals were statistically significant even at the 0.1% significance level when comparing controls to the concentration profiles of the treated samples (Appendix XII).

While the rapid decline of pharmaceutical concentration in these reaction vessels provided minimal insight into mechanisms of pharmaceutical removal, subsequent changes in water chemistry did provide information regarding potential benefits of pairing these two media. The decrease in Eh values in both the 50:50 wt% and 70:30 wt% ZVFe-GAC mixtures were more rapid and consistently lower than in the reaction flask containing ZVFe alone. Paired t-test analysis comparing the Eh, as well as the pH, values measured in these mixtures

to that of the 100% ZVFe samples indicate that the difference in these two parameters between sample types is significant at the 5% level. In the 50:50 wt% and 70:30 wt% ZVFe-GAC reaction vessels Eh values decreased to -220 mV and -340 mV within one day, further decreasing as low as -430 mV and -420 mV by day 15, respectively. Eh values in the 100% ZVFe reaction vessels decreased less rapidly and less extensively, reaching only 100 mV by day one, declining only to -380 mV by day 15 of the experiment. These results indicate the presence of a more reducing environment in the ZVFe-GAC mixture reaction vessels than for the GAC media alone.

The slight difference in pH between the mixture reaction vessels and the 100% ZVFe vessels is also of interest; further supporting the suggestion that the environment may well be more favourable to contaminant reduction or iron corrosion. The pH in the 100% ZVFe vessels starts at pH 7.04 increasing and decreasing modestly throughout the experiment resting at a final value of pH 7.72 by day 15. As mentioned previously the generation of hydroxyl by iron corrosion should lead to an expected increase in pH, and the absence of such an increase indicates that alternative processes within the system likely balance hydroxyl production. In the 50:50 wt% ZVFe-GAC reaction vessels the pH was measured at a higher pH of pH 8.42 by hour 3, a value largely maintained throughout the study, ending on day 15 with a pH of 8.4. In the 70:30 wt% ZVFe-GAC reaction vessels pH measurements started similarly to that of 100% ZVFe at pH 7.28, however, increasing consistently throughout the experiment to pH 8.26 by the last day. The consistently higher pH values in the 50:50 wt% ZVFe-GAC vessels, as well as the steadily increasing pH in the 70:30 wt% vessels implies that increases in pH due hydroxyl production may not be counteracted.

The faster, more extensive decreases in Eh in the ZVFe-GAC mixtures in this study potentially indicate a greater reducing environment, where improved iron corrosion (or contaminant reduction) reactions are converting more Fe^0 to Fe^{2+}. The higher pH values, and decreasing saturation indices for iron (oxy)hydroxides, as calculated by MINTEQA2, suggest that hydroxide is being produced and that iron (oxy)hydroxides, that may offset the pH affect of this hydroxide production, are either not being formed or are being sequestered in some fashion (Figure 4.6). The strongly undersaturated conditions of numerous mineral phases, such as lepidocrocite, goethite, maghemite, calcite, aragonite and ferrihydrate, and the dramatic decreases in aqueous Ca^{2+}, Fe^{2+}+ and Mn^{2+} in these reaction vessels, alludes that the GAC in the mixture may in fact be adsorbing one or both the reaction products of iron corrosion, or other competing compounds within the water (Figure 4.4). As noted in previous studies, available surface area on ZVFe tends to decrease over time, as iron corrosion products of Fe^{2+} and Fe^{3+} form iron oxyhydroxides which can coat the ZVFe surface (Joo et al., 2004). Thus the adsorption of these products or competing compounds to GAC may prevent or slow the formation of this coating, leaving a greater available surface area for contaminant reduction. Past studies evaluating ZVFe have identified contaminant degradation rates as dependent on the extent of available reactive surface area (Johnson et al., 1996; McGeough et al, 2007, Farrel et al., 2000; Joo et al., 2004). Thus, the addition of GAC may increase both the efficiency as well as the life span of ZVFe treatment systems for both pharmaceuticals as well as other contaminants.

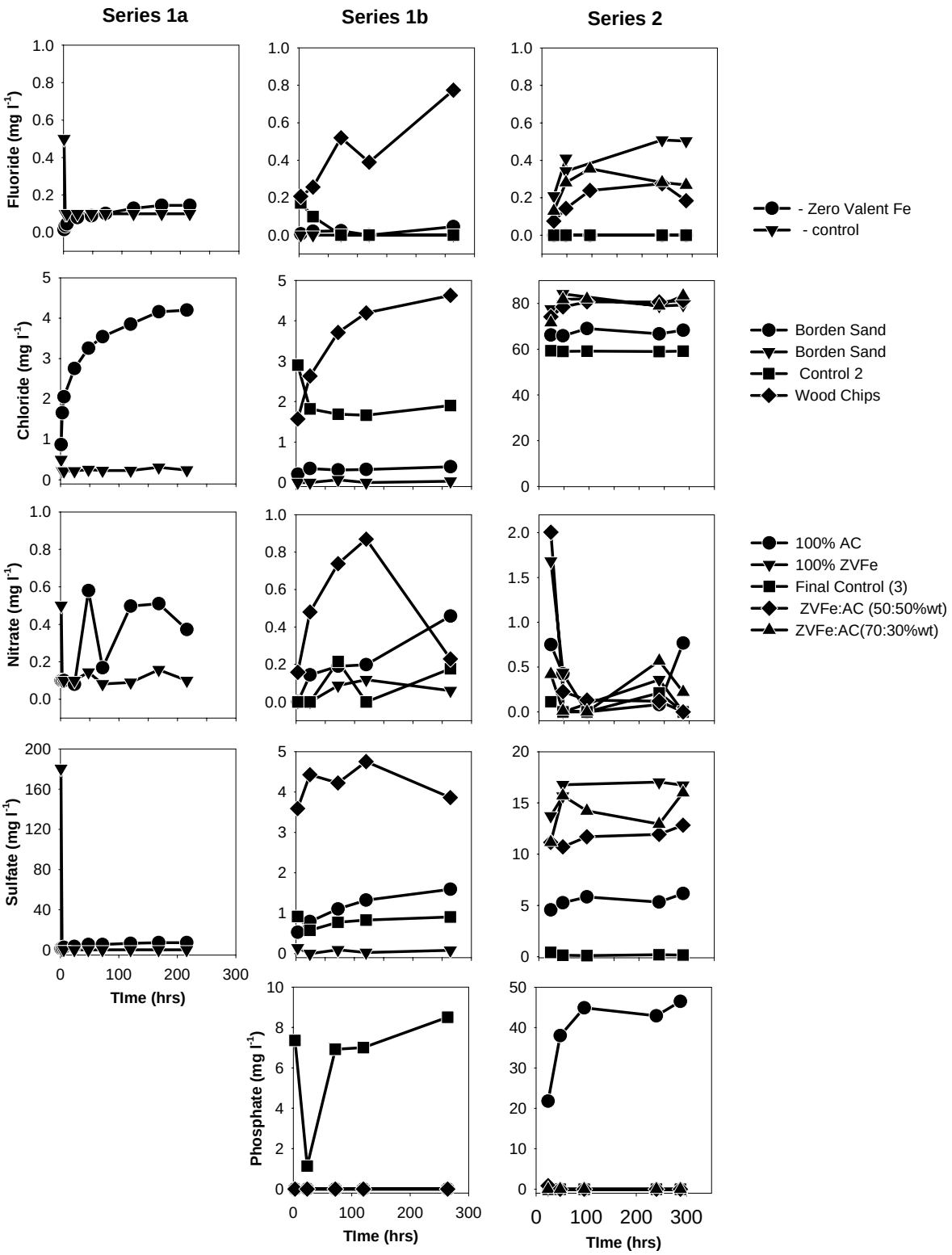

Figure 4.4 Concentrations of anions as a function of time for preliminary (series 1a and 1b) and final batch experiments (series 2).

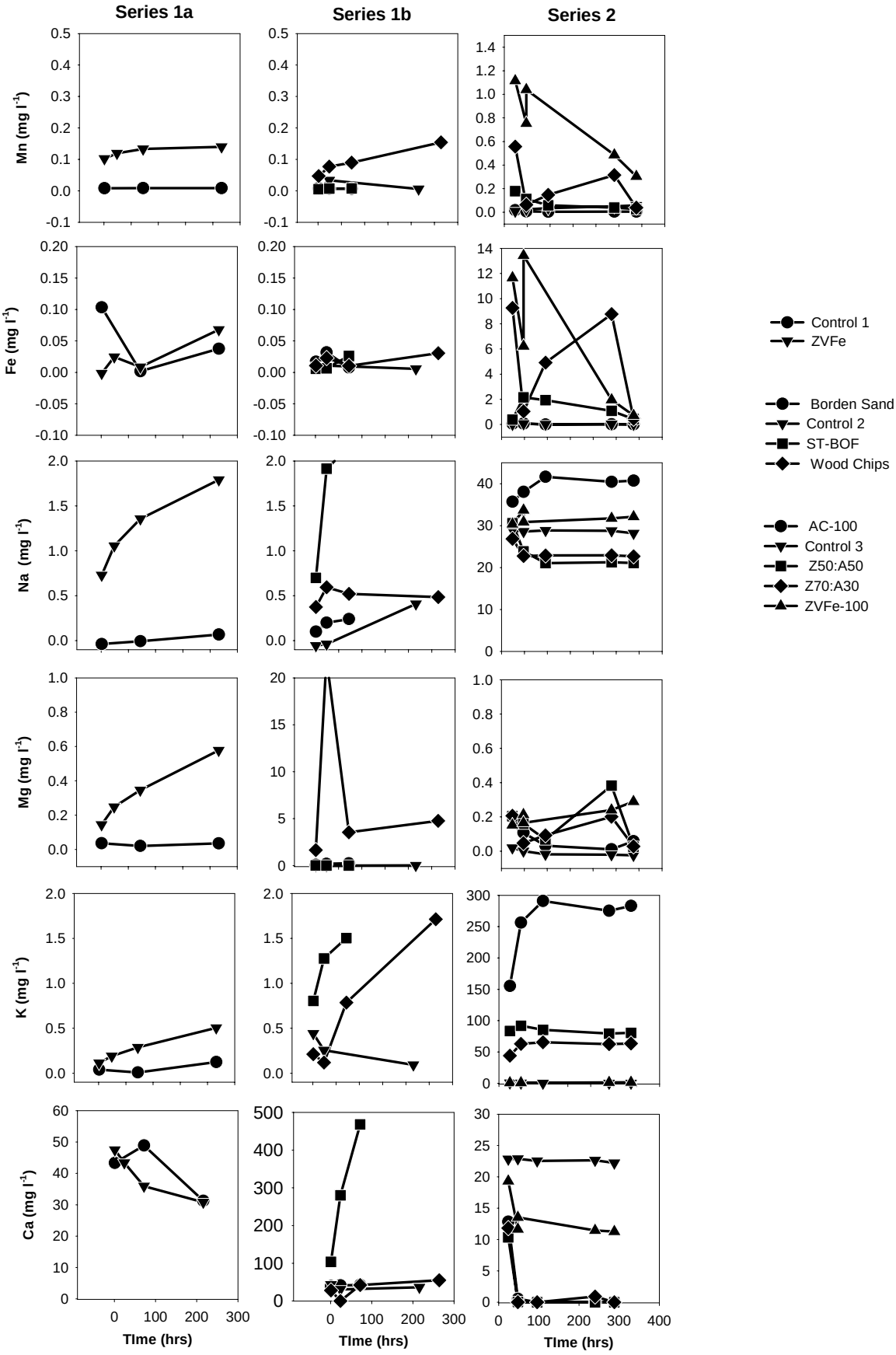

Figure 4.5 Concentrations of cations as a function of time for for preliminary (series 1a and b) and final batch experiments (series 2).

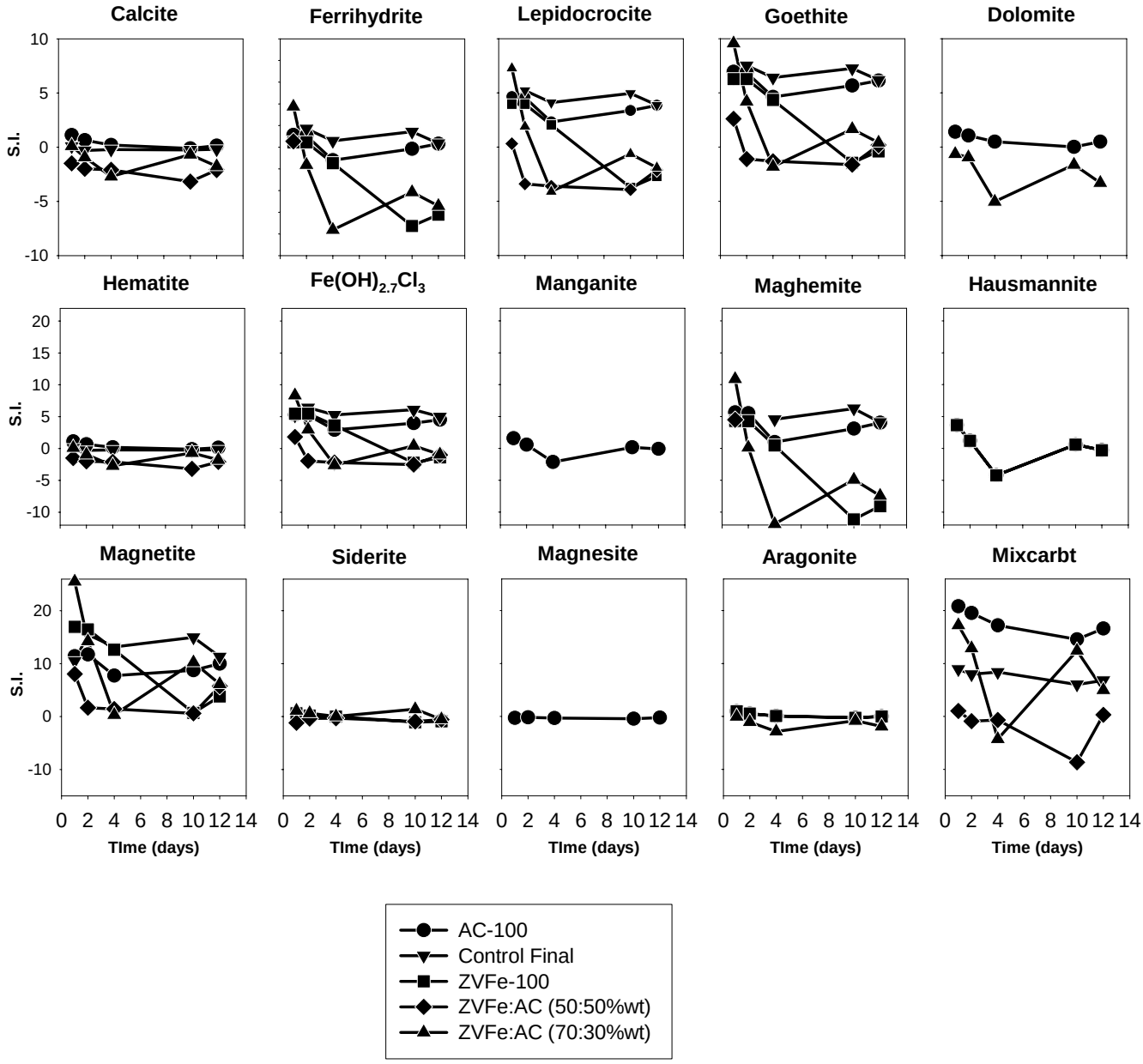

Figure 4.6 MINTEQA2 calculated Saturation Indices (S.I.) for selected mineral phases for all batch experiments.

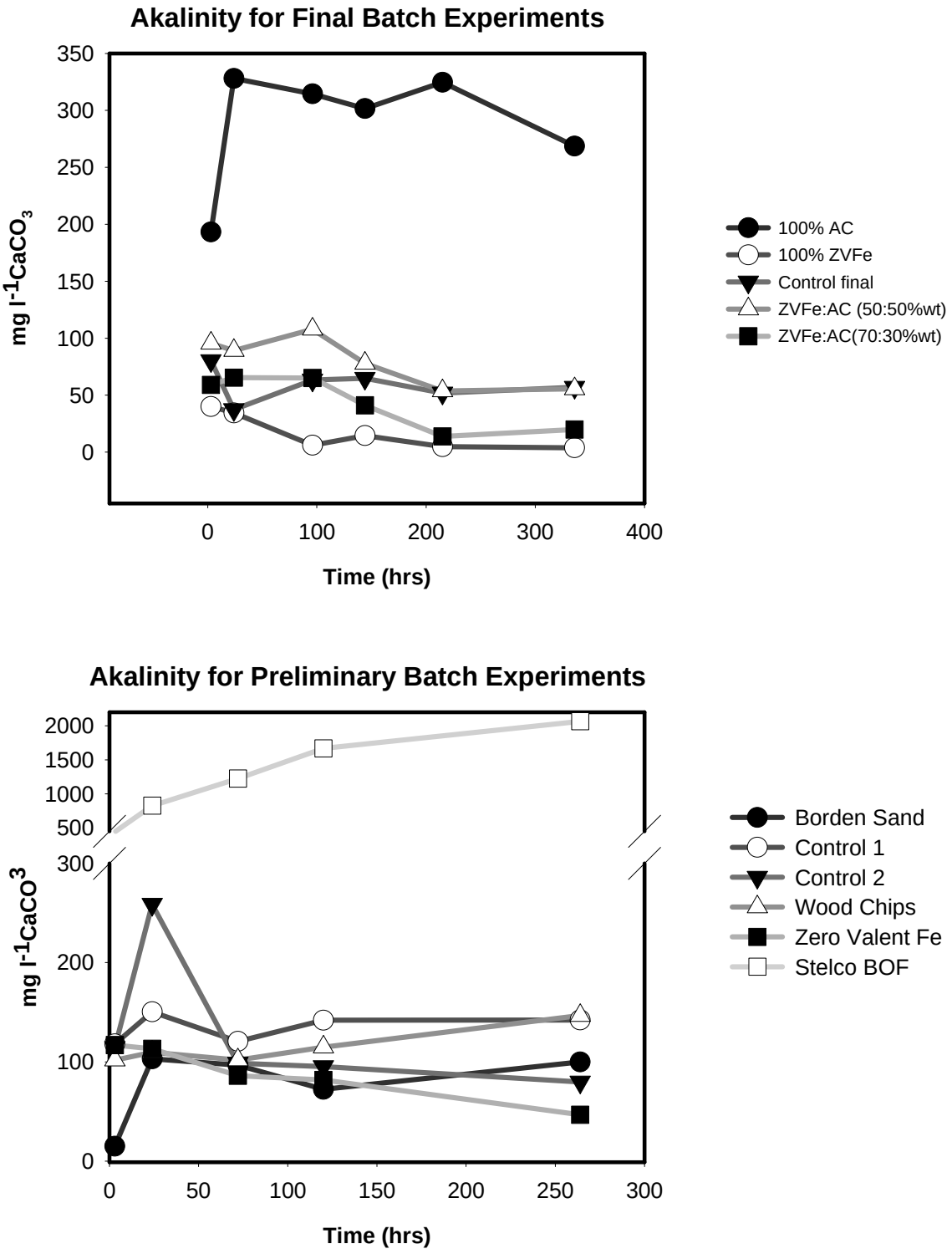

Figure 4.7 Akalinity measurements for Preliminary and Final Batch Experiments

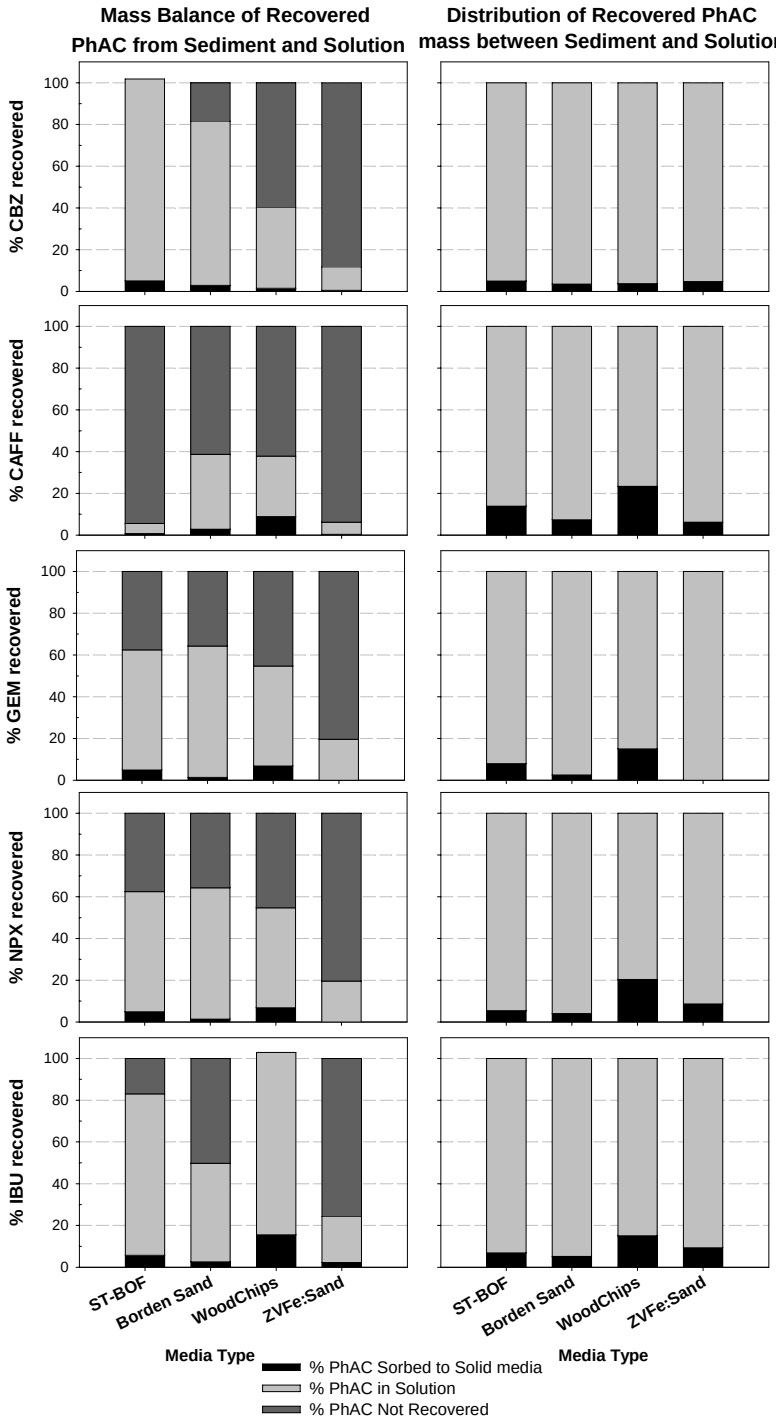

Figure 4.8 Calculated Mass balances and distributions of recovered pharmaceuticals. The left bank of figures indicates the distribution of pharmaceuticals between the solid, solution and what was unaccounted for, while the right hand bank of figures indicates purely the distribution of the recovered pharmaceutical mass between solution and solid phases. The mass of pharamceutical bound to solid was calculated from the concentration back extracted from a sediment sample. Moisture contents were determined for sediment sample to calculate the dry mass. This dry mass was then used to calculate the amount of pharmaceutical per gram of sediment by dividing the HPLC calculated mass by the dry mass. Knowing the mass of sorbed pharmaceutical per gram of media, it was then possible to calculate the total mass of sorbed pharmaceutical by multiplying this by the total known mass of sediment in the reaction vessel. (Appendix X).

4.4 Evaluating the Promise of each Media in Pharmaceutical Water Treatment

When considering the success of a treatment media with respect to a contaminant, one must consider more than simply the percent removal. As previously mentioned, success is also a measure of affordability, availability, durability and ease of use. Since the bulk of the media evaluated in this study were selected with these criteria in mind, assuming that these standards are met, one can consider the effectiveness of each media based upon three experimental criteria: the removal efficiency, as measured by percent removal; the statistical significance of this removal, as calculated by paired t-test analyses; and media limitations, as noted by previous investigations. **Table 4.3** summarizes the findings of this investigation in terms of these three experimental traits. Based upon specific definitions of these qualifications, conclusions were drawn as to the potential of each media in the treatment of each pharmaceutical. The media were considered a promising treatment if they indicated a statistically significant percent removal greater than 75%, with to the best of our knowledge no deleterious limitations. Statistical significance was defined by a p-value less than alpha at a 5% significance level ($\alpha = 0.05$), therefore indicating that the observed removal could not be ascribed to chance alone 95% of the time. Limitations were considered deleterious if they resulted in either decreased water quality, or environmental harm; for example, the production of reactive species as seen in chlorination and ozonation processes (Dantas, 2007; Huber et al., 2005; Virender et al., 2006; Skender et al., 2007).

The evaluation of the investigated media revealed that GAC and ZVFe, both independently and combined hold promise as pharmaceutical water treatments, having surpassed the defined demands. While both media do on their own experience limitations regarding maintenance of their reactive surfaces, as formerly noted the combination of the

two media may just prove to remedy this inadequacy. According to removal alone, GAC appeared to be an excellent treatment, exhibiting exceptional removal of all the pharmaceuticals. However, as previously noted, earlier studies have identified GACs limitations in the field, having both a limited lifespan and efficiency, influenced by GAC age and condition, as well as, the molecular weight and hydrophobicity of the DOC and aromatic carbon content of the treated water (Stackleberg et al., 2007). Meanwhile, albeit zero valent iron did not show as high of pharmaceutical removals as GAC, it is not bounded by these like limitations, and has the added benefit of successfully treating other important contaminants such as chlorinated solvents, or PCBs (see **Table 3.2**). Thus, ZVFe holds the potential to be a maintenance-free passive treatment media for the treatment of water experiencing both pharmaceutical as well as further types of contamination.

In general, while fulfilling many desired treatment qualities, the success of the other investigated treatment media was highly dependent upon the type of pharmaceutical, as illustrated by the wide range of percentage removals. As a point of comparison between the media investigated in this study and those accounted for in the review, percent removals for the pharmaceuticals specifically evaluated in this study by previously investigated treatments are listed in **Table 4.3**. As with all treatments, investigated in this study or otherwise, the achievement of each treatment is reliant on numerous provisions, and proper evaluation is dependent on consideration of all these stipulations.

Table 4.2 Experimental Results Summary

MEDIA	ST-BOF	Borden Sand	Wood Chips	ZVFe:Sand	100% ZVFe	100%AC	ZVFe:AC (50:50)	ZVFe:AC (70:30)
				Carbamazepine				
%Removal	3.0	20.7	60.3	88.8	99.4	100	99.95	99.93
Paired t-test (statistical significance?)	Insignificant	Insignificant	Significant	Significant	Significant	Significant	Significant	Significant
Possible Limitation(s):	Reactivity Surface Area	Reactivity	Reactivity	Available reactive surface area	Available reactive surface area	Available reactive surface area and competition for adsorptive sites		
Potential PhAC Treatment?	No	No	No	Yes	Yes	Yes	Yes	Yes
	Caffeine							
%Removal	71.0	56.40	70.60	94.41	99.13	99.73	99.91	99.96
Paired t-test (statistical significance?)	Significant	Significant	Significant	Significant	Significant	Significant	Significant	Significant
Possible Limitation(s):	Reactivity Surface Area	Reactivity	Reactivity	Available reactive surface area	Available reactive surface area	Available reactive surface area and competition for adsorptive sites		
Potential PhAC Treatment?	No	No	No	Yes	Yes	Yes	Yes	Yes
	Ibuprofen							
%Removal	0	0	0	27.94	78.59	99.97	99.96	100
Paired t-test (statistical significance?)	Significant	Insignificant	Significant	Significant	Significant	Significant	Significant	Significant
Possible Limitation(s):	Reactivity Surface Area	Reactivity	Reactivity	Available reactive surface area	Available reactive surface area	Available reactive surface area and competition for adsorptive sites		
Potential PhAC Treatment?	No	No	No	No	Yes	Yes	Yes	Yes
	Gemfibrozil							
%Removal	27.6	51.01	61.4	84.5	98.51	99.95	99.96	99.83
Paired t-test (statistical significance?)	Insignificant	Insignificant	Significant	Insignificant	Significant	Significant	Significant	Significant
Possible Limitation(s):	Reactivity Surface Area	Reactivity	Reactivity	Available reactive surface area	Available reactive surface area	Available reactive surface area and competition for adsorptive sites		
Potential PhAC Treatment?	No	No	No	Yes	Yes	Yes	Yes	Yes
	Naproxen							
%Removal	0	10.8	7.5	65.6	96.66	99.95	99.97	99.84
Paired t-test (statistical significance?)	Significant	Insignificant	Insignificant	Insignificant	Significant	Significant	Significant	Significant
Possible Limitation(s):	Reactivity Surface Area	Reactivity	Reactivity	Available reactive surface area	Available reactive surface area	Available reactive surface area and competition for adsorptive sites		
Potential PhAC Treatment?	No	No	No	No	Yes	Yes	Yes	Yes

Note: Removals reported as 100% indicate that no visible peak was present for the analyzed pharmaceutical. Percent removals greater than 99% reported for 100%AC, 100%ZVFe and ZVFe-AC 50:50 % wt and 70:30%wt all had final concentrations falling below detection limits.

Table 4.3 Success of Previously studied Treatments in the Removal of Investigated PhACs. When more than one study is recorded for removal efficiencies, superscripts denote which percent removal coincides with which study.

Treatment Type	Success/Percent Removal					Source
	Carbamazepine	Caffeine	Gemfibrozil	Naproxen	Ibuprofen	
DWT: -GAC -Clarification/ Chlorination	85%*	88%				Stackelberg et al., 2007
Chlorine dioxide (oxidation)	Little [a] >95%[b]	>60% [b]	Little [a] >90% [b]	>80% [b]	Little [a] 25-75% [b]	Huber et al., 2005[a] Westerhoff et al, 2006 [b]
Anaerobic sludge with O_3 pretreatment	~20%					Carballa et al., 2007
Anaerobic sludge	0%					Carballa et al., 2007
Ozone coupled with flocculation, coagulation and dual filtration	78-99%	67-81%				Hua et al., 2006
Ozone	98% [a] 99% [b] >97%[c]	93% [a] 91% [c]	88% [a] 98% [c]	91% [c]	84% [a] 80% [c]	Gomez et al., 2008[a] Westerhoff et al, 2006 [b] Ternes et al., 2002 [c]
Ozone with H_20_2	100%	98%	100%		96%	Gomez et al., 2008
STP (overall process)	-121% 0-45%				60-95%	Suarez et al., 2008
Biological WWT	0% [a]				≥90% [a] >95% [b]	Joss et al., 2005 [a] Smook et al., 2008 [b]
Conventional activated sludge Denitrifying sludge Ditch oxidation processes	-44% [a] -193% [b] -32% [c]		98% [b]	<50% [c]	100% [b]	Vieno et al., 2007 [a] Lindqvist et al., 2005 [b] Nakada et al., 2006 [c]
Primary sewage Tx: -Coagulation, flocculation and flotation	20-35%			10-30%	10-25%	Carballa et al., 2005
Membrane bioreactor				49%	96%	Quintana et al., 2005

5 SUMMARY AND CONCLUSIONS:

Little is known of the potential consequences of chronic PhAC exposure. Thus, it is not unanticipated that treatment of pharmaceuticals in water has been and is in recent times a focus of investigation. The review of numerous articles has unearthed a large mass of information concerning this new field, and amid this information are common discoveries and common limitations. To date most treatments appear to be limited by the chemically-variable nature of the PhACs themselves, each treatment method successful in the removal of only a small number of compounds; or limited by the adaptability or expense of the treatment media. There exists minimal information on novel, affordable, amendable treatment media that can be employed on numerous scales and water varieties, with the potential to treat a variety of PhACs as well as other water contaminants.

The aim of this study was to evaluate the removal of a suite of environmentally relevant pharmaceuticals from water in response to contact with reactive media and/or natural organic matter. The study explored the potential sorption and/or chemical degradation of these PhACs by affordable and readily available media, already employed in the treatment of other water contaminants, using batch reactor style experiments.

The experiments were conducted with batch samples containing a media of interest in simulated ground water spiked with carbamazepine, caffeine, naproxen, gemfibrozil, ibuprofen, sulfamethoxazole and clofibrate, each at an environmentally relevant initial concentration of 2-2.5 μg/L. Investigated media included: Stelco-BOF slag, wood chips, Borden sand, zero valent iron (ZVFe), and granular activated carbon (GAC). Samples were collected at predetermined time intervals over the course of 10 or 15 days to observe the influence of different contact times on the removal process. Samples were analyzed for basic

water chemistry and pharmaceutical concentrations were calculated by internal and external calibration of HPLC-MS/MS results.

Removal efficiencies, based on the change in concentration, were calculated for all batch reactors. In general, the controls exhibited 0% removal and narrow confidence intervals. For each of the reactive media, at least a small percentage of removal was seen for at least three of the five pharmaceuticals studied. The greatest percent removal, of 100%, was observed for all pharmaceuticals with concentrations dropping below the LOD, in GAC and ZVFe-GAC mixtures; the smallest percentage removal when considering all media, of 0%, was experienced by ibuprofen and naproxen in BOF, BDS and WC samples. Most removal was observed within the first 24 hours for the majority of the drugs that showed measurable removals.

For the most part minimal to no removal was observed for any of the three controls or Borden sand over the course of the experiment. Indicating that little attenuation of the pharmaceuticals was occurring due to the composition of the groundwater or duration of the study, and supporting previous research, asserting that Borden sand possessed little sorptive capacity with respect to the investigated pharmaceuticals (Carrara et al., 2008). The one exception was ibuprofen, which in the preliminary batch experiments showed a 50% decrease in concentration, potentially indicating its oxidative sensitivity. Decreases in pharmaceutical concentrations in the Borden sand reaction vessels ranged from zero to 56%, however all showed removals that were designated as statistically insignificant by paired t-test analysis at the 5% significance level.

Despite notable changes in water chemistry pharmaceutical removal in the ST-BOF and WC reaction vessels proved to be moderate, ranging similarly from no removal for

ibuprofen up to 71% removal for caffeine. Removal within these vessels appeared to be highly dependent upon the type of pharmaceutical, as indicated by the wide range of removal efficiencies. Sorption to reactive media appeared to be a potential removal mechanism for Borden sand, Stelco BOF-slag and woodchips as suggested by results of sediment back extractions, media properties and water chemistry.

More consistently successful removal was observed for the ZVFe and GAC reaction vessels, both independently and as mixtures. While ZVFe in the preliminary batch experiment showed slightly more variable success, with percent removals ranging from 28 to 94%, increasing the concentration and control of the redox environment proved to likewise increase the efficiency of the media, increasing and narrowing the range of percent removal up to 79 to 100%. Removal demonstrated in the ZVFe reaction vessels did not appear as dependent on pharmaceutical type as previously mentioned media, as indicated by more precise range of removal effciencies. Recovery of pharamaceuticals from sediment back extractions suggests that sorption is not a significant removal mechanism for this media.

GAC and GAC-ZVFe mixture reaction vessels indicated 100% removal for all pharmaceuticals, decreasing their concentrations to below LOD before the first sampling time. While the removal efficiency of the GAC was impressive, and supported by previous studies, such as Snyder et al., (2007) that found the media capable of removing all evaluated PhACs by >90%, previous studies have also indicated that GAC is greatly limited by availability of adsorption sites as controlled by age, condition and presence of competing compounds (Ternes et al., 2002; Snyder et al., 2007).

The limitation of GAC with respect to reactive surface area is also a consideration for ZVFe, that has indicated in previous studies to be bounded by available reactive surface area.

Available surface area tends to decrease over time, as products of oxidative dissolution coat the ZVFe surface (Joo et al., 2004). So while the percent removals in the ZVFe-GAC mixtures were impressive, they were not the sole result of interest in these reaction vessels. Water chemistry, including Eh, pH, anion and cation analysis, in combination with MINTEQA2 results suggested that the addition of activated carbon may prove beneficial for the reactivity and life span of ZVFe.

This investigation demonstrated itself to be a stepping stone into the investigation of novel treatment media for pharmaceutical contamination in all water types. Further exploration into the reaction intermediates and removal mechanisms of all the involved media would prove useful in understanding each media's full potential. In particular, GAC and ZVFe independently, or more importantly as mixtures, merit further research concerning their effectiveness with an even wider variety of pharmaceutical compounds, and a more in depth exploration of the benefits of their potentially symbiotic relationship.

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APPENDIX: SUPPLEMENTAL INFORMATION

Appendix I: Stock Solution Preparation for Batch Tests

Table 1.1 PhAC masses for preparation of PhAC working stock solution. Each drug was massed as a solid, than dissolved in 1000 ml 50:50 wt% methanol and nanopure water with subsequent sonification to ensure dilution. Exact masses of each PhAC are listed.

PhAC	Mass Added To Solution (ng)
Carbamazepine	1.995×10^{-6}
Clofibrate	2.206×10^{-6}
Ibuprofen	2.001×10^{-6}
Naproxen	1.976×10^{-6}
Caffeine	1.970×10^{-6}
Sulfamethoxazole	1.973×10^{-6}
Gemfibrozil	1.942×10^{-6}

Table 1.2 Masses of isotope-labeled-PhAC standards for preparation of surrogate internal standard working stock solution. Each standard contained the isotope labeled PhAC dissolved in 50:50 wt% methanol-nanopure water. Each standard was measured both volumetrically and gravimetrically and combined to form a final volume of 20 ml with the addition of 50:50 wt% methanol-nanopure water.

Solution	Concentration of Standard	Mass of Standard Added
IS STOCK ONE		
MeOH:Nanopure	5050 % wt	18.6
Caffeine-D3	1×10^{6} ngL^{-1}	0.182
Gemfibrozil-D6	1×10^{6} ngL^{-1}	0.182
Carbamazepine-D10	1×10^{6} ngL^{-1}	0.182
Sulfamethoxazole-D4	1×10^{6} ngL^{-1}	0.183
MEC-D3	1×10^{6} ngL^{-1}	0.183
Ibuprofen-D3	1×10^{6} ngL^{-1}	0.184
Naproxen-C13	1×10^{6} ngL^{-1}	0.184
IS STOCK TWO		
MeOH:Nanopure	5050 % wt	18.6
Caffeine-D3	1×10^{6} ngL^{-1}	0.180
Gemfibrozil-D6	1×10^{6} ngL^{-1}	0.183
Carbamazepine-D10	1×10^{6} ngL^{-1}	0.181
Sulfamethoxazole-D4	1×10^{6} ngL^{-1}	0.183
MEC-D3	1×10^{6} ngL^{-1}	0.180
Ibuprofen-D3	1×10^{6} ngL^{-1}	0.182
Naproxen-C13	1×10^{6} ngL^{-1}	0.180

Appendix II: Composition of Quality Control Standards

Table A2. Quality control standards were prepared gravimetrically and volumetrically using a hand pipette. Standard PhAC stock solutions were used and adjusted to the appropriate concentration using nanopure water.

Final Concentration of Quality Control Standard (ngl^{-1})	Concentration of Stock PhAC (ngl^{-1})	Volume of Stock PhAC added (nl)	Volume of Nanopure water (nl)
10×10^3	200×10^3	1000×10^3	19.0×10^6
5×10^3	200×10^3	500×10^3	19.5×10^6
2×10^3	200×10^3	200×10^3	19.8×10^6
1×10^3	100×10^3	200×10^3	19.8×10^6
0.5×10^3	50×10^3	200×10^3	19.8×10^6
02×10^3	20×10^3	200×10^3	19.8×10^6
0.1×10^3	10×10^3	200×10^3	19.8×10^6
0.05×10^3	5×10^3	200×10^3	19.8×10^6
0.02×10^3	2×10^3	200×10^3	19.8×10^6
0.01×10^3	1×10^3	200×10^3	19.8×10^6
0.005×10^3	0.5×10^3	200×10^3	19.8×10^6

Appendix III: Composition of Reaction Flasks for Preliminary Batch Experiments.

Table A3. Media was massed into each flask, followed by the addition of Simulated Ground (AG) water and subsequent spiking with the PhAC working stock solution containing all investigated PhACs. Total mass includes reaction flask, caps, tubing, stopper and experimental contents.

Reactive Media Type	Mass of Reactive Media (g)	Mass of AG water (g)	Mass of PhAC stock added (g)	Total mass including vessel (g)
Control One	0	800.04	0.95	1189.10
ZVFe	100.03	800.01	0.95	1210.04
Control Two	0	799.24	1.08	1174.68
ST-BOF	100.09	800.31	0.90	1176.95
Borden Sand	103.18	800.61	102	1289.13
Wood Chips	15.05	800.51	1.01	1205.44

Appendix IV: Time and Volume and Reactive Media Data for Final Batch Samples.
Table A4. A set of 18 Sample vessels was constructed for each investigated media and control. The volume of spiked AG water, as well as the time of the addition was recorded for every sample in the sample sets. The contribution of reactive media in each sample vessel is also indicated by the recorded mass of each component.

Sample	ZVFe	AC	AG water	Spike Time	Sample Time		
	(mg)	(mg)	(mg)		Day	Time	Duration (hrs)
1	0	0	83.049	10:34	3	12:58	48.10
2	0	0	82.598	10:26	5	12:20	96.08
3	0	0	82.886	10:38	5	12:25	96.07
4	0	0	82.787	10:29	2	13:35	24.13
5	0	0	83.019	10:41	1	11:41	0.04
6	0	0	85.637	10:33	10	10:05	215.98
7	0	0	83.037	10:47	12	12:30	264.07
8	0	0	83.202	10:48	1	13:48	0.13
9	0	0	82.982	10:30	7	12:00	144.06
10	0	0	83.051	10:43	10	10:15	215.98
11	0	0	82.975	10:31	15	13:25	336.12
12	0	0	82.716	10:39	2	13:30	24.12
13	0	0	83.102	10:42	15	13:45	336.13
14	0	0	83.338	10:40	1	16:40	0.25
15	0	0	83.116	10:46	5	12:07	96.06
16	0	0	82.21	10:36	2	16:20	24.24
17	0	0	83.255	10:44	15	13:40	336.12
18	0	0	82.971	10:35	10	10:20	215.99
19	10.07	0	83.306	11:09	10	10:35	215.98
20	10	0	83.12	12:27	2	13:47	24.06
21	10	0	82.893	12:23	5	12:40	96.01
22	10	0	83.267	11:10	1	17:13	0.25
23	10.03	0	82.667	12:22	5	12:50	96.02
24	10.01	0	86.095	11:07	15	14:40	336.15
25	10.06	0	82.659	12:21	15	14:30	336.09
26	10.07	0	83.209	12:26	7	13:20	144.04
27	10.05	0	83.214	11:08	5	12:55	96.07
28	10.05	0	82.91	12:25	2	14:46	24.10
29	10	0	83.177	12:24	3	13:35	48.05
30	10.05	0	82.597	11:05	12	13:00	264.08
31	10.03	0	84.892	11:14	15	14:35	336.14
32	10.06	0	83.12	11:07	1	12:07	0.04
33	10.01	0	82.352	12:20	1	15:20	0.13
34	10.01	0	82.884	11:12	10	10:45	215.98
35	10	0	83.253	11:06	10	10:50	215.99
36	10.04	0	82.84	11:11	2	13:50	24.11
37	0	10	82.895	10:57	10	11:00	216.00
38	0	10.03	83.312	10:52	1	11:52	0.04
39	0	10	83.477	11:04	1	14:17	0.13
40	0	9.99	83.619	10:59	2	15:00	24.17
41	0	10	83.144	10:51	15	15:00	336.17

42	0	10.02	83.1	10:58	15	15:20	336.18
43	0	10.02	83.449	10:53	2	13:42	24.12
44	0	10.01	83.37	10:55	3	14:00	48.13
45	0	10.05	83.165	10:50	10	11:15	216.02
46	0	10.03	83.184	10:56	2	13:38	24.11
47	0	9.99	82.551	11:00	5	13:25	96.10
48	0	9.99	82.804	11:01	15	15:25	336.18
49	0	9.99	83.335	10:52	7	13:45	144.12
50	0	10.06	83.146	10:54	1	16:58	0.25
51	0	10.06	83.003	11:02	10	11:20	216.01
52	0	10.05	83.457	11:03	5	13:20	96.10
53	0	10.01	83.208	10:49	12	13:15	264.10
54	0	10.03	83.254	10:58	5	13:00	96.08
55	4.99	4.96	83.289	9:26	2	12:14	24.12
56	4.99	5.07	83.918	9:23	10	11:46	216.10
57	5	4.95	82.97	9:27	5	13:40	96.18
58	5.03	4.99	83.114	9:19	1	12:20	0.13
59	5.04	5.05	83.36	9:20	2	12:12	24.12
60	5.08	5	83.169	9:32	15	12:40	336.13
61	5	4.98	82.896	9:31	3	12:30	48.12
62	4.99	5.01	84.118	9:30	10	11:35	216.09
63	5.09	4.97	82.809	9:28	7	12:35	144.13
64	5.07	4.97	83.628	9:29	2	12:00	24.10
65	5.07	5	83.46	9:24	5	13:55	96.19
66	5.07	5.03	82.944	9:17	1	15:17	0.25
67	5	5	83.379	9:25	15	13:00	336.15
68	5.02	4.97	83.318	9:31	15	12:55	336.14
69	5.05	5.09	83.541	9:25	12	12:30	264.13
70	5	5.04	82.85	9:18	1	10:18	0.04
71	5.02	5.05	83.539	9:22	5	13:48	96.18
72	5.04	4.98	83.568	9:21	10	11:50	216.10
73	7.07	3	81.41	9:37	15	13:10	336.15
74	7.04	2.97	81.918	9:36	1	10:36	0.04
75	7.02	3.05	83.752	9:39	2	12:47	24.13
76	7.06	2.94	83	9:37	10	12:05	216.10
77	7.06	2.97	83.546	9:45	10	12:15	216.10
78	6.99	2.98	83.775	9:47	1	12:47	0.13
79	7.07	2.98	83.456	9:34	12	13:00	264.14
80	7.05	2.98	84.052	9:46	1	15:50	0.25
81	7	2.98	82.926	9:44	7	13:30	144.16
82	7.08	2.97	83.659	9:40	15	13:10	336.15
83	7	2.98	83.631	9:41	2	13:25	24.16
84	6.99	2.97	82.941	9:42	15	13:30	336.16
85	7.06	2.97	83.602	9:43	10	12:20	216.11
86	7.01	2.97	82.783	9:35	3	12:50	48.14
87	7.07	3	82.981	9:38	2	12:30	24.12
88	7.07	3.01	83.141	9:33	5	12:40	96.13
89	6.99	2.97	82.932	9:34	5	12:50	96.14
90	6.99	3.06	83.176	9:43	5	12:55	96.13

Appendix V: Results for Preliminary Batch Experiments.

Raw data from the HPLC/MS is recorded, including analyte and IS peak areas and calculated concentrations. Concentrations are based upon linear regressions of (analyte peak area / IS peak area) versus time. Factored HPLC/MS concentrations represent final calculated experimental concentrations after dilutions and/or concentration have been compensated for. (Sample ID: c = control 1; Co, K = control 2; BDS = Borden Sand; ZVFe = zero valent iron; WC = wood chips; BOF = stelco BOF slag).

Table A5.1 Gemfibrozil Results

GEM sample	Analyte Area	IS peak area	Analyte area / IS area	HPLC calculated concentration	Factored HPLC Concentration	C/Co
				($\mu g l^{-1}$)	($\mu g l^{-1}$)	
BDS43	6.37E+05	9.31E+04	6.84E+00	8.17E+00	2.45E+00	9.91E-01
BDS44	6.50E+05	9.12E+04	7.13E+00	8.53E+00	2.56E+00	1.03E+00
BDS45	9.85E+05	1.31E+05	7.52E+00	8.98E+00	2.69E+00	1.09E+00
BDS48	7.66E+05	1.32E+05	5.80E+00	6.90E+00	2.07E+00	8.37E-01
BDS51	1.10E+06	1.59E+05	6.92E+00	8.21E+00	2.46E+00	9.96E-01
BDS54	1.01E+06	1.41E+05	7.16E+00	8.54E+00	2.56E+00	1.04E+00
BDS57	1.15E+06	1.71E+05	6.73E+00	8.01E+00	2.40E+00	9.71E-01
BDS60	1.13E+06	1.63E+05	6.93E+00	8.23E+00	2.47E+00	9.98E-01
BDS63	9.22E+05	2.20E+05	4.19E+00	4.92E+00	1.48E+00	5.97E-01
BDS66	8.08E+05	1.38E+05	5.86E+00	6.93E+00	2.08E+00	8.40E-01
BDS69	6.73E+05	1.32E+05	5.10E+00	6.01E+00	1.80E+00	7.29E-01
sedBDS72	5.41E+05	1.47E+05	3.68E+00	4.27E+00	1.28E+00	5.18E-01
bds95	4.81E+05	1.30E+05	3.70E+00	3.81E+00	1.14E+00	4.62E-01
c1	5.95E+05	1.72E+05	3.46E+00	3.90E+00	1.17E+00	5.08E-01
c2	1.42E+06	1.79E+05	7.93E+00	9.16E+00	2.75E+00	1.19E+00
c3	9.73E+05	1.82E+05	5.35E+00	6.13E+00	1.84E+00	7.98E-01
c10	1.03E+06	1.49E+05	6.91E+00	7.96E+00	2.39E+00	1.04E+00
c13	1.26E+06	1.69E+05	7.46E+00	8.64E+00	2.59E+00	1.12E+00
c31	8.38E+05	1.29E+05	6.50E+00	7.74E+00	2.32E+00	1.01E+00
c16	8.92E+05	1.58E+05	5.65E+00	6.49E+00	1.95E+00	8.45E-01
c19	1.02E+06	1.51E+05	6.75E+00	7.76E+00	2.33E+00	1.01E+00
c22	9.54E+05	1.23E+05	7.76E+00	8.98E+00	2.69E+00	1.17E+00
c25	1.40E+06	1.53E+05	9.15E+00	1.06E+01	3.18E+00	1.38E+00
c34	9.75E+05	1.39E+05	7.01E+00	8.38E+00	2.51E+00	1.09E+00
Co37	1.79E+05	9.38E+04	1.91E+00	2.14E+00	6.42E-01	2.45E-01
Co38	7.91E+05	9.55E+04	8.28E+00	9.94E+00	2.98E+00	1.14E+00
Co39	7.05E+05	8.85E+04	7.97E+00	9.56E+00	2.87E+00	1.09E+00

Co46	1.23E+06	1.61E+05	7.64E+00	9.16E+00	2.75E+00	1.05E+00
Co49	1.05E+06	1.33E+05	7.89E+00	9.43E+00	2.83E+00	1.08E+00
Co52	1.04E+06	1.33E+05	7.82E+00	9.38E+00	2.81E+00	1.07E+00
Co55	1.39E+06	1.95E+05	7.13E+00	8.49E+00	2.55E+00	9.71E-01
Co58	1.36E+06	1.55E+05	8.77E+00	1.05E+01	3.15E+00	1.20E+00
Co61	1.39E+06	1.82E+05	7.64E+00	9.13E+00	2.74E+00	1.04E+00
Co64	1.30E+06	1.53E+05	8.50E+00	1.02E+01	3.06E+00	1.17E+00
Co67	1.20E+06	1.70E+05	7.06E+00	8.39E+00	2.52E+00	9.59E-01
Co70	6.98E+05	1.56E+05	4.47E+00	5.25E+00	1.58E+00	6.00E-01
cO96	9.84E+05	1.20E+05	8.20E+00	8.67E+00	2.60E+00	9.91E-01
q28	1.07E+06	1.46E+05	7.33E+00	8.49E+00	2.55E+00	9.71E-01
q29	4.66E+05	1.58E+05	2.95E+00	3.27E+00	9.81E-01	3.74E-01
q30	9.09E+04	1.56E+05	5.83E-01	4.84E-01	1.45E-01	5.53E-02
Sediments:						
SBDS75	6.55E+04	1.44E+05	4.55E-01	3.40E-01	1.02E-01	3.89E-02
SBOF76	1.70E+05	1.56E+05	1.09E+00	1.12E+00	3.36E-01	1.28E-01
sWC97	2.27E+05	1.29E+05	1.76E+00	1.73E+00	5.19E-01	1.98E-01
Sz77	1.87E+04	1.30E+05	1.44E-01	<0	0.00E+00	
BOF74	1.62E+05	1.31E+05	1.24E+00	1.17E+00	3.51E-01	1.34E-01
BOF40	5.90E+05	9.01E+04	6.55E+00	7.82E+00	2.35E+00	1.07E+00
BOF41	5.20E+05	9.67E+04	5.38E+00	6.38E+00	1.91E+00	8.76E-01
BOF42	5.23E+05	8.99E+04	5.82E+00	6.93E+00	2.08E+00	9.52E-01
BOF47	7.93E+05	1.46E+05	5.43E+00	6.46E+00	1.94E+00	8.87E-01
BOF50	7.17E+05	1.35E+05	5.31E+00	6.30E+00	1.89E+00	8.65E-01
BOF53	8.37E+05	1.56E+05	5.37E+00	6.32E+00	1.90E+00	8.68E-01
BOF56	7.66E+05	1.63E+05	4.70E+00	5.53E+00	1.66E+00	7.60E-01
BOF59	8.73E+05	1.55E+05	5.63E+00	6.65E+00	2.00E+00	9.13E-01
BOF62	8.80E+05	1.88E+05	4.68E+00	5.51E+00	1.65E+00	7.57E-01
BOF65	7.78E+05	1.73E+05	4.50E+00	5.29E+00	1.59E+00	7.27E-01
BOF68	6.19E+05	1.40E+05	4.42E+00	5.17E+00	1.55E+00	7.10E-01
BOF71	7.29E+05	1.62E+05	4.50E+00	5.27E+00	1.58E+00	7.24E-01
BOF93	4.92E+05	1.19E+05	4.13E+00	4.30E+00	1.29E+00	5.91E-01
WC81	8.51E+05	1.24E+05	6.86E+00	8.19E+00	2.46E+00	1.00E+00
WC82	8.26E+05	1.23E+05	6.72E+00	7.99E+00	2.40E+00	9.78E-01
WC83	9.69E+05	1.48E+05	6.55E+00	7.79E+00	2.34E+00	9.54E-01
WC84	8.89E+05	1.29E+05	6.89E+00	8.24E+00	2.47E+00	1.01E+00
wc85	8.47E+05	1.38E+05	6.14E+00	6.44E+00	1.93E+00	7.89E-01
wc86	7.09E+05	1.16E+05	6.11E+00	6.39E+00	1.92E+00	7.82E-01
WC87	6.87E+05	1.26E+05	5.45E+00	5.71E+00	1.71E+00	6.99E-01

WC88	6.04E+05	1.22E+05	4.95E+00	5.16E+00	1.55E+00	6.32E-01
WC89	5.52E+05	1.24E+05	4.45E+00	4.64E+00	1.39E+00	5.68E-01
WC90	6.64E+05	1.28E+05	5.19E+00	5.44E+00	1.63E+00	6.66E-01
WC91	4.31E+05	1.15E+05	3.75E+00	3.86E+00	1.16E+00	4.73E-01
WC92	3.57E+05	1.14E+05	3.13E+00	3.22E+00	9.66E-01	3.94E-01
WC94	3.83E+05	1.27E+05	3.02E+00	3.09E+00	9.27E-01	3.78E-01
z7	1.06E+06	1.42E+05	7.46E+00	8.61E+00	2.58E+00	1.12E+00
z8	1.07E+06	1.59E+05	6.73E+00	7.74E+00	2.32E+00	1.01E+00
z9	1.17E+06	1.71E+05	6.84E+00	7.92E+00	2.38E+00	1.03E+00
z12	1.18E+06	1.42E+05	8.31E+00	9.63E+00	2.89E+00	1.25E+00
z32	8.67E+05	1.44E+05	6.02E+00	7.15E+00	2.15E+00	9.30E-01
z15	6.85E+05	1.61E+05	4.25E+00	4.84E+00	1.45E+00	6.30E-01
z18	5.05E+05	1.64E+05	3.08E+00	3.44E+00	1.03E+00	4.48E-01
z21	3.97E+05	1.61E+05	2.47E+00	2.71E+00	8.13E-01	3.53E-01
z24	2.23E+05	1.58E+05	1.41E+00	1.47E+00	4.41E-01	1.91E-01
z27	1.68E+05	1.47E+05	1.14E+00	1.15E+00	3.45E-01	1.50E-01
z36	1.52E+05	1.30E+05	1.17E+00	1.24E+00	3.72E-01	1.61E-01

Table A5.2 Caffeine Results

Caffeine Sample	Analyte peak area	IS peak area	analyte area/IS area	HPLC calculated concentration	Factored HPLC concentration	C/Co
				($\mu g l^{-1}$)	($\mu g l^{-1}$)	
Co1	147000	17300	8.49711	7.85	2.355	1.007271
Co2	171000	19600	8.72449	8.05	2.415	1.032934
Co3	153000	18300	8.360656	7.72	2.316	0.99059
Co10	149000	17300	8.612717	7.95	2.385	1.020103
Co13	145000	16800	8.630952	8.03	2.409	1.030368
Co16	138000	15900	8.679245	8.06	2.418	1.034217
Co19	153000	17700	8.644068	8.04	2.412	1.031651
Co22	123000	14300	8.601399	7.95	2.385	1.020103
Co25	154000	17500	8.8	8.14	2.442	1.044482
Co31	163000	18500	8.810811	8.13	2.439	1.043199
Co34	136000	15800	8.607595	8	2.4	1.026518
Co78	113000	13100	8.625954	8.02	2.406	1.029085
Z7	135000	16200	8.333333	7.72	2.316	0.990167
Z8	120000	14600	8.219178	7.59	2.277	0.973493
Z9	129000	15800	8.164557	7.59	2.277	0.973493
Z12	125000	16000	7.8125	7.2	2.16	0.923472
Z32	112000	20100	5.572139	5.03	1.509	0.645147
Z15	71900	16700	4.305389	3.85	1.155	0.493801
Z18	48800	16800	2.904762	2.49	0.747	0.319367
Z21	36200	15700	2.305732	1.91	0.573	0.244976

Z24	23000	19500	1.179487	0.837	0.2511	0.107354
Z27	18400	20000	0.92	0.588	0.1764	0.075417
Z36	15600	20500	0.760976	0.436	0.1308	0.055921
sedZ77	9020	17200	0.524419	0.207	0.0621	0.02655
K37	32000	7050	4.539007	4.06	1.218	0.457551
K38	109000	12600	8.650794	8.02	2.406	0.903832
K39	111000	12800	8.671875	8.08	2.424	0.910594
K46	136000	15600	8.717949	8.11	2.433	0.913974
K49	141000	16300	8.650307	8.04	2.412	0.906086
K52	131000	15000	8.733333	8.09	2.427	0.911721
K55	161000	19100	8.429319	7.8	2.34	0.879038
K58	127000	14600	8.69863	8.04	2.412	0.906086
K61	138000	16000	8.625	8.02	2.406	0.903832
K64	133000	15200	8.75	8.09	2.427	0.911721
K67	140000	16200	8.641975	7.98	2.394	0.899324
K70	98600	11700	8.42735	7.78	2.334	0.876784
K96	138000	16100	8.571429	7.95	2.385	0.895943
ST40	80700	13300	6.067669	5.03	1.509	0.681264
ST41	82800	14600	5.671233	4.7	1.41	0.636569
ST42	75300	11800	6.381356	5.28	1.584	0.715124
ST47	107000	16500	6.484848	5.4	1.62	0.731377
ST50	88500	14400	6.145833	5.08	1.524	0.688036
ST53	69600	13300	5.233083	4.32	1.296	0.585102
ST56	50400	12900	3.906977	3.2	0.96	0.433409
ST59	45600	14700	3.102041	2.52	0.756	0.341309
ST62	31900	14300	2.230769	1.78	0.534	0.241084
ST65	20000	14600	1.369863	1.05	0.315	0.142212
ST68	14300	11900	1.201681	0.909	0.2727	0.123115
ST71	23800	13400	1.776119	1.4	0.42	0.189616
ST93	10600	16300	0.650307	0.439	0.1317	0.059458
sedST74	8840	12600	0.701587	0.486	0.1458	0.065824
BD43	90900	13100	6.938931	5.78	1.734	0.690837
BD44	92900	13600	6.830882	5.67	1.701	0.677689
BD45	119000	17300	6.878613	5.75	1.725	0.687251
BD48	84400	14300	5.902098	4.89	1.467	0.584462
BD51	94000	16500	5.69697	4.7	1.41	0.561753
BD54	82300	15800	5.208861	4.3	1.29	0.513944
BD57	88300	17600	5.017045	4.13	1.239	0.493625
BD60	83100	16500	5.036364	4.15	1.245	0.496016
BD63	68000	21000	3.238095	2.63	0.789	0.314343
BD66	67800	19300	3.512953	2.86	0.858	0.341833
BD69	63700	17900	3.558659	2.91	0.873	0.347809
BD72	56000	16300	3.435583	2.79	0.837	0.333466
BD95	56900	16500	3.448485	2.81	0.843	0.335857

sedBD75	16900	15900	1.062893	0.794	0.2382	0.0949
W81	134000	15700	8.535032	7.96	2.388	0.960579
W82	107000	14300	7.482517	6.94	2.082	0.83749
W83	113000	16500	6.848485	6.39	1.917	0.771118
W84	108000	16800	6.428571	5.97	1.791	0.720434
W85	116000	16700	6.946108	6.48	1.944	0.781979
W86	121000	16100	7.515528	6.98	2.094	0.842317
W87	114000	16400	6.95122	6.48	1.944	0.781979
W88	109000	14800	7.364865	6.85	2.055	0.826629
W89	106000	14200	7.464789	6.95	2.085	0.838697
W90	124000	15300	8.104575	7.58	2.274	0.914722
W91	41200	15000	2.746667	2.42	0.726	0.292035
W92	36300	14000	2.592857	2.26	0.678	0.272727
W94	40900	14500	2.82069	2.48	0.744	0.299276
sedW97	14000	11900	1.176471	0.903	0.2709	0.10897
Q28	140000	14400	9.722222	8.15	2.445	
Q29	55600	24200	2.297521	1.84	0.552	
Q30	14100	12400	1.137097	0.854	0.2562	

Table A5.3 Carbamazepine Results

CBZ sample	Analyte peak area	IS peak area	Analyte area / IS area	HPLC calculated concentration	Factored HPLC Concentration	C/Co
Co1	1.35E+05	2.29E+04	5.90E+00	8.44E+00	2.53E+00	1.05E+00
Co2	1.39E+05	2.43E+04	5.72E+00	8.18E+00	2.45E+00	1.02E+00
Co3	1.40E+05	2.37E+04	5.91E+00	8.45E+00	2.54E+00	1.05E+00
Co10	1.27E+05	2.11E+04	6.02E+00	8.56E+00	2.57E+00	1.07E+00
Co13	1.43E+05	2.39E+04	5.98E+00	8.54E+00	2.56E+00	1.07E+00
Co16	1.33E+05	2.22E+04	5.99E+00	8.57E+00	2.57E+00	1.07E+00
Co19	1.35E+05	2.28E+04	5.92E+00	8.46E+00	2.54E+00	1.05E+00
Co22	1.07E+05	1.81E+04	5.91E+00	8.48E+00	2.54E+00	1.05E+00
Co25	1.32E+05	2.18E+04	6.06E+00	8.62E+00	2.59E+00	1.08E+00
Co31	1.24E+05	2.08E+04	5.96E+00	8.53E+00	2.56E+00	1.06E+00
Co34	1.26E+05	2.10E+04	6.00E+00	8.57E+00	2.57E+00	1.07E+00
Co78	9.53E+04	1.61E+04	5.92E+00	8.44E+00	2.53E+00	1.05E+00
Z7	1.38E+05	2.31E+04	5.97E+00	8.51E+00	2.55E+00	1.06E+00
Z8	1.30E+05	2.18E+04	5.96E+00	8.51E+00	2.55E+00	1.06E+00
Z9	1.27E+05	2.13E+04	5.96E+00	8.51E+00	2.55E+00	1.06E+00
Z32	1.06E+05	2.09E+04	5.07E+00	7.24E+00	2.17E+00	9.03E-01
Z12	1.19E+05	2.03E+04	5.86E+00	8.36E+00	2.51E+00	1.04E+00
Z15	7.38E+04	2.34E+04	3.15E+00	4.52E+00	1.36E+00	5.62E-01
Z18	5.30E+04	2.29E+04	2.31E+00	3.32E+00	9.96E-01	4.13E-01
Z21	3.57E+04	2.25E+04	1.59E+00	2.27E+00	6.81E-01	2.84E-01
Z24	1.89E+04	2.41E+04	7.84E-01	1.12E+00	3.36E-01	1.41E-01
Z27	1.48E+04	2.43E+04	6.09E-01	8.76E-01	2.63E-01	1.10E-01

Z36	1.20E+04	1.93E+04	6.22E-01	8.95E-01	2.69E-01	1.12E-01
sedZ77	1.80E+03	1.92E+04	9.38E-02	1.43E-01	4.29E-02	1.86E-02
K37	2.64E+04	1.39E+04	1.90E+00	2.71E+00	8.13E-01	2.98E-01
K38	8.71E+04	1.42E+04	6.13E+00	8.77E+00	2.63E+00	9.60E-01
K39	9.12E+04	1.47E+04	6.20E+00	8.84E+00	2.65E+00	9.71E-01
K46	1.22E+05	1.96E+04	6.22E+00	8.91E+00	2.67E+00	9.74E-01
K49	1.13E+05	1.93E+04	5.85E+00	8.37E+00	2.51E+00	9.16E-01
K52	1.16E+05	1.92E+04	6.04E+00	8.58E+00	2.57E+00	9.45E-01
K55	1.33E+05	2.33E+04	5.71E+00	8.17E+00	2.45E+00	8.93E-01
K58	1.12E+05	1.81E+04	6.19E+00	8.87E+00	2.66E+00	9.68E-01
K61	1.17E+05	1.93E+04	6.06E+00	8.66E+00	2.60E+00	9.48E-01
K64	1.23E+05	2.02E+04	6.09E+00	8.67E+00	2.60E+00	9.53E-01
K67	1.22E+05	2.05E+04	5.95E+00	8.48E+00	2.54E+00	9.31E-01
K96	1.29E+05	2.14E+04	6.03E+00	8.64E+00	2.59E+00	9.43E-01
ST40	7.22E+04	1.40E+04	5.16E+00	7.52E+00	2.26E+00	9.70E-01
ST41	7.33E+04	1.51E+04	4.85E+00	7.09E+00	2.13E+00	9.13E-01
ST42	6.76E+04	1.32E+04	5.12E+00	7.50E+00	2.25E+00	9.63E-01
ST47	9.08E+04	1.79E+04	5.07E+00	7.42E+00	2.23E+00	9.54E-01
ST50	8.47E+04	1.64E+04	5.16E+00	7.53E+00	2.26E+00	9.72E-01
ST53	8.76E+04	1.67E+04	5.25E+00	7.65E+00	2.30E+00	9.87E-01
ST56	8.86E+04	1.71E+04	5.18E+00	7.58E+00	2.27E+00	9.75E-01
ST59	1.01E+05	1.91E+04	5.29E+00	7.70E+00	2.31E+00	9.95E-01
ST62	9.43E+04	1.86E+04	5.07E+00	7.41E+00	2.22E+00	9.54E-01
ST65	9.16E+04	1.79E+04	5.12E+00	7.46E+00	2.24E+00	9.63E-01
ST68	9.11E+04	1.78E+04	5.12E+00	7.50E+00	2.25E+00	9.63E-01
ST71	1.08E+05	2.09E+04	5.17E+00	7.57E+00	2.27E+00	9.72E-01
ST93	8.76E+04	1.70E+04	5.15E+00	7.53E+00	2.26E+00	9.69E-01
sedST74	1.76E+04	2.09E+04	8.42E-01	1.22E+00	3.66E-01	1.60E-01
BD43	7.98E+04	1.34E+04	5.96E+00	8.71E+00	2.61E+00	9.89E-01
BD44	8.70E+04	1.49E+04	5.84E+00	8.52E+00	2.56E+00	9.69E-01
BD45	1.13E+05	1.90E+04	5.95E+00	8.66E+00	2.60E+00	9.87E-01
BD48	8.28E+04	1.66E+04	4.99E+00	7.27E+00	2.18E+00	8.28E-01
BD51	1.00E+05	1.72E+04	5.81E+00	8.54E+00	2.56E+00	9.65E-01
BD54	8.92E+04	1.51E+04	5.91E+00	8.66E+00	2.60E+00	9.81E-01
BD57	1.06E+05	1.86E+04	5.70E+00	8.35E+00	2.51E+00	9.46E-01
BD60	9.85E+04	1.76E+04	5.60E+00	8.18E+00	2.45E+00	9.29E-01
BD63	8.17E+04	2.15E+04	3.80E+00	5.54E+00	1.66E+00	6.31E-01
BD66	8.65E+04	1.70E+04	5.09E+00	7.42E+00	2.23E+00	8.45E-01
BD69	9.06E+04	1.80E+04	5.03E+00	7.36E+00	2.21E+00	8.36E-01
BD72	7.85E+04	1.62E+04	4.85E+00	7.07E+00	2.12E+00	8.05E-01
BD95	8.18E+04	1.74E+04	4.70E+00	6.85E+00	2.06E+00	7.81E-01
sedBD75	9.19E+03	1.71E+04	5.37E-01	7.79E-01	2.34E-01	9.09E-02
W81	2.90E+04	5.81E+03	4.99E+00	7.31E+00	2.19E+00	8.37E-01
W82	2.25E+04	5.35E+03	4.21E+00	6.15E+00	1.85E+00	7.05E-01
W83	1.86E+04	4.77E+03	3.90E+00	5.69E+00	1.71E+00	6.54E-01

W84	1.59E+04	4.06E+03	3.92E+00	5.73E+00	1.72E+00	6.57E-01
W86	1.38E+04	3.71E+03	3.72E+00	5.44E+00	1.63E+00	6.24E-01
W87	1.19E+04	4.63E+03	2.57E+00	3.75E+00	1.13E+00	4.32E-01
W88	1.11E+04	3.98E+03	2.79E+00	4.08E+00	1.22E+00	4.68E-01
W89	1.13E+04	4.04E+03	2.80E+00	4.08E+00	1.22E+00	4.70E-01
W90	1.24E+04	4.55E+03	2.73E+00	3.99E+00	1.20E+00	4.58E-01
W91	1.04E+04	3.77E+03	2.76E+00	4.03E+00	1.21E+00	4.63E-01
W92	9.86E+03	4.25E+03	2.32E+00	3.38E+00	1.01E+00	3.90E-01
W94	8.51E+03	3.93E+03	2.17E+00	3.16E+00	9.48E-01	3.64E-01
sedW97	4.36E+02	4.86E+03	8.97E-02	1.22E-01	3.66E-02	1.68E-02
Q28	1.25E+05	2.20E+04	5.68E+00	8.30E+00	2.49E+00	1.01E+00
Q29	5.52E+04	2.32E+04	2.38E+00	3.48E+00	1.04E+00	4.25E-01
Q30	1.04E+04	2.15E+04	4.84E-01	7.00E-01	2.10E-01	8.79E-02

Table A5.4 Ibuprofen Results

IBU sample	Analyte	IS peak	Analyte area / IS area	Calculated concentration	Factored HPLC concentratin	C/Co
ID	Area	Area		C	C*3/10	
BDS433	2.23E+05	5.59E+04	3.99E+00	5.29	1.587	0.622597
BDS44	2.17E+05	5.26E+04	4.13E+00	5.49	1.647	0.646136
BDS45	3.47E+05	7.76E+04	4.47E+00	5.95	1.785	0.700275
BDS48	2.84E+05	7.44E+04	3.82E+00	5.06	1.518	0.595528
BDS51	3.83E+05	1.03E+05	3.72E+00	4.82	1.446	0.567281
BDS54	3.78E+05	8.39E+04	4.51E+00	5.86	1.758	0.689682
BDS57	4.26E+05	9.96E+04	4.28E+00	5.56	1.668	0.654374
BDS60	4.18E+05	8.79E+04	4.76E+00	6.2	1.86	0.729698
BDS63	3.80E+05	1.18E+05	3.22E+00	4.14	1.242	0.48725
BDS66	3.13E+05	8.33E+04	3.76E+00	4.86	1.458	0.571989
BDS69	2.84E+05	7.88E+04	3.60E+00	4.65	1.395	0.547273
BDS72	2.35E+05	7.54E+04	3.12E+00	4	1.2	0.470773
bds95	2.02E+05	8.47E+04	2.38E+00	3.02	0.906	0.355434
c1	1.60E+05	6.35E+04	2.52E+00	3.22	0.966	0.406737
c10	1.86E+05	8.42E+04	2.21E+00	2.79	0.837	0.352421
c13	2.10E+05	8.75E+04	2.40E+00	3.06	0.918	0.386526
c31	1.89E+05	7.09E+04	2.67E+00	3.46	1.038	0.437053
c19	1.80E+05	7.68E+04	2.34E+00	2.97	0.891	0.375158
c2	2.36E+05	7.50E+04	3.15E+00	4.07	1.221	0.514105
c22	1.62E+05	7.03E+04	2.30E+00	2.93	0.879	0.370105
c25	2.24E+05	8.76E+04	2.56E+00	3.26	0.978	0.411789
c3	1.68E+05	7.32E+04	2.30E+00	2.91	0.873	0.367579
c34	1.65E+05	8.02E+04	2.06E+00	2.61	0.783	0.329684
c78	2.45E+05	8.06E+04	3.04E+00	3.89	1.167	0.491368
					0.959182	

Co37	7.44E+04	5.43E+04	1.37E+00	1.67	0.501	0.185281
Co38	2.75E+05	5.19E+04	5.30E+00	7.1	2.13	0.787722
Co39	2.52E+05	5.29E+04	4.76E+00	6.36	1.908	0.705621
Co46	4.40E+05	9.45E+04	4.66E+00	6.07	1.821	0.673447
Co49	3.32E+05	7.62E+04	4.36E+00	5.8	1.74	0.643491
Co52	3.46E+05	7.43E+04	4.66E+00	6.22	1.866	0.690089
Co55	5.19E+05	1.16E+05	4.47E+00	5.83	1.749	0.64682
Co58	4.91E+05	9.08E+04	5.41E+00	7.08	2.124	0.785503
Co61	4.89E+05	9.90E+04	4.94E+00	6.45	1.935	0.715607
Co64	3.95E+05	8.12E+04	4.86E+00	6.35	1.905	0.704512
Co67	4.36E+05	9.30E+04	4.69E+00	6.11	1.833	0.677885
Co70	2.48E+05	8.27E+04	3.00E+00	3.83	1.149	0.424926
cO96	2.87E+05	6.92E+04	4.15E+00	5.4	1.62	0.599112
					1.815	
q28	4.22E+05	8.11E+04	5.20E+00	6.84	2.052	
q29	1.84E+05	8.35E+04	2.20E+00	2.78	0.834	
q30	5.32E+04	8.72E+04	6.10E-01	0.631	0.1893	
SBDS75	5.28E+04	7.99E+04	6.61E-01	0.674	0.2022	
SBOF76	7.12E+04	8.11E+04	8.78E-01	0.967	0.2901	
Sz77	4.38E+04	7.27E+04	6.02E-01	0.594	0.1782	
sWC97	8.73E+04	6.92E+04	1.26E+00	1.51	0.453	
sBOF74	8.92E+04	7.73E+04	1.15E+00	1.36	0.408	
BOF40	2.07E+05	4.91E+04	4.22E+00	5.59	1.677	0.745333
BOF41	1.91E+05	5.81E+04	3.29E+00	4.32	1.296	0.576
BOF42	1.95E+05	5.05E+04	3.86E+00	5.11	1.533	0.681333
BOF47	3.10E+05	8.15E+04	3.80E+00	5.04	1.512	0.672
BOF50	3.34E+05	8.23E+04	4.06E+00	5.38	1.614	0.717333
BOF53	4.32E+05	9.18E+04	4.71E+00	6.13	1.839	0.817333
BOF56	4.22E+05	9.34E+04	4.52E+00	5.88	1.764	0.784
BOF59	4.99E+05	8.97E+04	5.56E+00	7.29	2.187	0.972
BOF62	4.91E+05	1.06E+05	4.63E+00	6.04	1.812	0.805333
BOF65	4.52E+05	1.03E+05	4.39E+00	5.72	1.716	0.762667
BOF68	3.53E+05	7.83E+04	4.51E+00	5.87	1.761	0.782667
BOF71	3.87E+05	9.95E+04	3.89E+00	5.03	1.509	0.670667
BOF93	3.00E+05	6.76E+04	4.44E+00	5.78	1.734	0.770667
WC81	3.57E+05	6.55E+04	5.45E+00	7.13	2.139	0.847129
WC82	3.64E+05	6.92E+04	5.26E+00	6.89	2.067	0.818614
WC83	4.14E+05	7.57E+04	5.47E+00	7.17	2.151	0.851881
WC84	3.98E+05	6.56E+04	6.07E+00	7.97	2.391	0.946931
WC89	3.46E+05	6.68E+04	5.18E+00	6.78	2.034	0.805545
WC91	2.96E+05	6.05E+04	4.89E+00	6.39	1.917	0.759208
WC90	3.54E+05	6.14E+04	5.77E+00	7.58	2.274	0.900594

WC92	2.96E+05	5.58E+04	5.30E+00	6.94	2.082	0.824554
WC94	2.91E+05	5.91E+04	4.92E+00	6.44	1.932	0.765149
wc85	3.88E+05	7.08E+04	5.48E+00	7.18	2.154	0.853069
wc86	3.44E+05	6.22E+04	5.53E+00	7.26	2.178	0.862574
WC87	3.61E+05	6.37E+04	5.67E+00	7.43	2.229	0.882772
WC88	3.54E+05	6.41E+04	5.52E+00	7.23	2.169	0.85901
z7	1.84E+05	6.79E+04	2.71E+00	3.47	1.041	0.438131
z8	1.91E+05	7.22E+04	2.65E+00	3.38	1.014	0.426768
z9	2.08E+05	8.79E+04	2.37E+00	3	0.9	0.378788
z32	1.70E+05	8.42E+04	2.02E+00	2.57	0.771	0.324495
z15	1.62E+05	8.61E+04	1.88E+00	2.35	0.705	0.296717
z18	1.57E+05	8.59E+04	1.83E+00	2.28	0.684	0.287879
z21	1.46E+05	8.31E+04	1.76E+00	2.18	0.654	0.275253
z24	1.07E+05	8.25E+04	1.30E+00	1.56	0.468	0.19697
z27	1.36E+05	8.60E+04	1.58E+00	1.94	0.582	0.244949
					0.525	

Table A5.5 Naproxen Results

NPX sample	Analyte Peak Area	IS peak area	Analyte area / IS area	HPLC Calculated concentration	Factored HPLC concentratin	C/Co
				($\mu g l^{-1}$)	($\mu g l^{-1}$)	
1ppb	4.77E+04	5.15E+04	9.26E-01	1.16	0.348	
1ppb	5.38E+04	6.11E+04	8.81E-01	1.1	0.33	
BDS43	1.47E+05	3.23E+04	4.55E+00	6.46	1.938	0.769964
BDS44	1.45E+05	3.03E+04	4.79E+00	6.8	2.04	0.810489
BDS45	2.29E+05	4.60E+04	4.98E+00	7.08	2.124	0.843862
BDS48	1.94E+05	4.74E+04	4.09E+00	5.79	1.737	0.690107
BDS51	2.76E+05	5.98E+04	4.62E+00	6.16	1.848	0.734207
BDS54	2.64E+05	5.08E+04	5.20E+00	6.96	2.088	0.829559
BDS57	3.11E+05	6.09E+04	5.11E+00	6.84	2.052	0.815256
BDS60	2.96E+05	5.88E+04	5.03E+00	6.74	2.022	0.803337
BDS63	2.53E+05	8.06E+04	3.14E+00	4.14	1.242	0.493445
BDS66	1.83E+05	5.13E+04	3.57E+00	4.72	1.416	0.562574
BDS69	1.73E+05	4.79E+04	3.61E+00	4.78	1.434	0.569726
BDS72	1.19E+05	5.22E+04	2.28E+00	2.96	0.888	0.352801
bds95	8.83E+04	4.64E+04	1.90E+00	2.47	0.741	0.294398
c1	9.69E+04	6.48E+04	1.50E+00	1.98	0.594	0.253305
c2	1.73E+05	6.38E+04	2.71E+00	3.74	1.122	0.478465
c3	1.26E+05	5.97E+04	2.11E+00	2.86	0.858	0.365885
c10	1.39E+05	5.41E+04	2.57E+00	3.53	1.059	0.451599
c13	1.56E+05	6.01E+04	2.60E+00	3.56	1.068	0.455437
c31	1.11E+05	4.63E+04	2.40E+00	3.32	0.996	0.424733

c16	1.06E+05	5.48E+04	1.93E+00	2.6	0.78	0.332623
c19	1.12E+05	5.63E+04	1.99E+00	2.71	0.813	0.346695
c22	1.27E+05	4.61E+04	2.75E+00	3.79	1.137	0.484861
c25	1.71E+05	5.38E+04	3.18E+00	4.39	1.317	0.56162
c34	1.34E+05	4.88E+04	2.75E+00	3.81	1.143	0.48742
c78	2.03E+05	4.95E+04	4.10E+00	5.44	1.632	0.695949
Co37	5.13E+04	3.50E+04	1.47E+00	1.95	0.585	0.219101
Co38	1.93E+05	3.43E+04	5.63E+00	8.04	2.412	0.903371
Co39	1.55E+05	2.99E+04	5.18E+00	7.4	2.22	0.831461
Co46	2.87E+05	5.54E+04	5.18E+00	6.92	2.076	0.777528
Co49	2.19E+05	4.37E+04	5.01E+00	7.14	2.142	0.802247
Co52	2.33E+05	4.72E+04	4.94E+00	7.04	2.112	0.791011
Co55	3.37E+05	7.16E+04	4.71E+00	6.29	1.887	0.706742
Co58	3.61E+05	5.77E+04	6.26E+00	8.42	2.526	0.946067
Co61	3.31E+05	5.87E+04	5.64E+00	7.57	2.271	0.850562
Co64	2.61E+05	5.43E+04	4.81E+00	6.44	1.932	0.723596
Co67	3.03E+05	6.06E+04	5.00E+00	6.7	2.01	0.752809
Co70	1.59E+05	5.59E+04	2.84E+00	3.73	1.119	0.419101
cO96	2.03E+05	4.14E+04	4.90E+00	6.62	1.986	0.74382
q28	3.49E+05	5.33E+04	6.55E+00	9.24	2.772	
q29	1.55E+05	5.71E+04	2.71E+00	3.73	1.119	
q30	3.26E+04	5.31E+04	6.14E-01	0.72	0.216	
SBDS75	2.05E+04	4.88E+04	4.20E-01	0.389	0.1167	
SBOF76	5.56E+04	5.53E+04	1.01E+00	1.2	0.36	
BOF74	5.75E+04	4.44E+04	1.30E+00	1.63	0.489	
sWC97	3.62E+04	4.46E+04	8.12E-01	0.953	0.2859	
Sz77	1.39E+04	4.44E+04	3.13E-01	0.241	0.0723	
BOF40	1.45E+05	3.21E+04	4.52E+00	6.43	1.929	0.868137
BOF41	1.34E+05	3.81E+04	3.52E+00	4.97	1.491	0.671017
BOF42	1.33E+05	3.06E+04	4.35E+00	6.16	1.848	0.831683
BOF47	2.09E+05	5.10E+04	4.10E+00	5.8	1.74	0.783078
BOF50	2.37E+05	5.02E+04	4.72E+00	6.72	2.016	0.907291
BOF53	3.49E+05	5.50E+04	6.35E+00	8.54	2.562	1.153015
BOF56	3.35E+05	5.34E+04	6.27E+00	8.45	2.535	1.140864
BOF59	4.01E+05	5.88E+04	6.82E+00	9.21	2.763	1.243474
BOF62	3.96E+05	6.85E+04	5.78E+00	7.76	2.328	1.047705
BOF65	3.57E+05	6.24E+04	5.72E+00	7.67	2.301	1.035554
BOF68	2.84E+05	5.18E+04	5.48E+00	7.35	2.205	0.992349
BOF71	2.99E+05	6.03E+04	4.96E+00	6.63	1.989	0.89514
BOF93	2.19E+05	4.55E+04	4.81E+00	6.5	1.95	0.877588
WC81	2.74E+05	4.43E+04	6.19E+00	8.34	2.502	1.00361

WC82	2.77E+05	3.97E+04	6.98E+00	9.42	2.826	1.133574
WC83	3.23E+05	5.08E+04	6.36E+00	8.56	2.568	1.030084
WC84	2.96E+05	4.28E+04	6.92E+00	9.33	2.799	1.122744
wc85	2.73E+05	4.72E+04	5.78E+00	7.87	2.361	0.947052
wc86	2.55E+05	3.82E+04	6.68E+00	9.08	2.724	1.092659
WC87	2.55E+05	3.73E+04	6.84E+00	9.33	2.799	1.122744
WC88	2.55E+05	4.05E+04	6.30E+00	8.57	2.571	1.031288
WC89	2.01E+05	4.15E+04	4.84E+00	6.57	1.971	0.790614
WC90	2.56E+05	4.20E+04	6.10E+00	8.28	2.484	0.99639
WC91	1.45E+05	4.13E+04	3.51E+00	4.71	1.413	0.566787
WC92	8.99E+04	3.71E+04	2.42E+00	3.2	0.96	0.385078
WC94	9.85E+04	4.04E+04	2.44E+00	3.22	0.966	0.387485
z7	1.43E+05	5.29E+04	2.70E+00	3.73	1.119	0.476982
z8	1.42E+05	5.49E+04	2.59E+00	3.55	1.065	0.453964
z9	1.50E+05	5.72E+04	2.62E+00	3.6	1.08	0.460358
z12	1.52E+05	5.08E+04	2.99E+00	4.14	1.242	0.529412
z32	1.08E+05	5.12E+04	2.11E+00	2.89	0.867	0.369565
z15	9.04E+04	5.78E+04	1.56E+00	2.08	0.624	0.265985
z18	7.41E+04	6.07E+04	1.22E+00	1.59	0.477	0.203325
z21	6.33E+04	5.42E+04	1.17E+00	1.51	0.453	0.193095
z24	4.14E+04	5.34E+04	7.75E-01	0.951	0.2853	0.121611
z27	3.47E+04	5.33E+04	6.51E-01	0.773	0.2319	0.098849
z36	3.86E+04	4.66E+04	8.28E-01	1.02	0.306	0.130435

Appendix VI: Results for Final Batch Experiments:

Raw data from the HPLC/MS is recorded, including analyte and IS peak areas and calculated concentrations. Concentrations are based upon linear regressions of (analyte peak area / IS peak area) versus time. Factored HPLC concentrations represent final calculated experimental concentrations after dilutions and/or concentration have been compensated for. Percent removals calculated as indicated in Appendix VI are also shown. (Samples type (ie. Type of reactive media) are listed as a subheading within sample ID column).

Table A6.1 Ibuprofen Results

IBU sample ID	Analyte peak area	IS peak area	Analyte / IS area	HPLC Calculated concentration	Corrected HPLC concentration	C/Co	%Removal WRT concentration
Control				($\mu g l^{-1}$)	($\mu g l^{-1}$)		
5	2.22E+06	1.24E+05	1.79E+01	1.28E+01	1.28E+00	1.02E+00	-2.30
8	2.58E+06	1.44E+05	1.79E+01	1.28E+01	1.28E+00	1.02E+00	-2.38
14	2.44E+06	1.37E+05	1.78E+01	1.27E+01	1.27E+00	1.02E+00	-1.77
	2.30E+06	1.31E+05	1.76E+01	1.25E+01	1.25E+00	1.00E+00	-0.32
1	2.38E+06	1.31E+05	1.82E+01	1.30E+01	1.30E+00	1.04E+00	-3.81
2	2.17E+06	1.27E+05	1.71E+01	1.22E+01	1.22E+00	9.76E-01	2.37
3	2.26E+06	1.33E+05	1.70E+01	1.21E+01	1.21E+00	9.71E-01	2.90
15	2.52E+06	1.46E+05	1.73E+01	1.23E+01	1.23E+00	9.86E-01	1.37
6	2.22E+06	1.31E+05	1.69E+01	1.21E+01	1.21E+00	9.68E-01	3.17
11	2.48E+06	1.40E+05	1.77E+01	1.27E+01	1.27E+00	1.01E+00	-1.22
13	2.46E+06	1.43E+05	1.72E+01	1.23E+01	1.23E+00	9.83E-01	1.70
ZVFe-100							
32	2.13E+06	1.25E+05	1.70E+01	1.22E+01	1.22E+00	9.74E-01	2.63
33	1.63E+06	1.35E+05	1.21E+01	8.62E+00	8.62E-01	6.90E-01	31.01
28	1.49E+06	1.56E+05	9.55E+00	6.82E+00	6.82E-01	5.46E-01	45.43
29	1.04E+06	1.55E+05	6.71E+00	4.79E+00	4.79E-01	3.83E-01	61.66
21	7.10E+05	1.30E+05	5.46E+00	3.90E+00	3.90E-01	3.12E-01	68.80
23	7.85E+05	1.38E+05	5.69E+00	4.06E+00	4.06E-01	3.25E-01	67.50
27	7.90E+05	1.43E+05	5.52E+00	3.95E+00	3.95E-01	3.16E-01	68.44
19	4.45E+05	1.32E+05	3.37E+00	2.41E+00	2.41E-01	1.93E-01	80.74
24	5.22E+05	1.35E+05	3.87E+00	2.76E+00	2.76E-01	2.21E-01	77.91
25	4.86E+05	1.38E+05	3.52E+00	2.51E+00	2.51E-01	2.01E-01	79.88
31	5.09E+05	1.32E+05	3.86E+00	2.75E+00	2.75E-01	2.20E-01	77.97
AC-100							
38	2.08E+04	1.15E+05	1.81E-01	1.29E-01	1.29E-02	1.03E-02	98.97
39	6.81E+04	1.59E+05	4.28E-01	3.05E-01	3.05E-02	2.44E-02	97.56
50	1.01E+04	1.33E+05	7.59E-02	5.36E-02	5.36E-03	4.29E-03	99.57
40	9.19E+03	1.39E+05	6.61E-02	4.66E-02	4.66E-03	3.73E-03	99.63
44	4.76E+03	1.37E+05	3.47E-02	2.42E-02	2.42E-03	1.94E-03	99.81
47	8.18E+02	1.35E+05	6.06E-03	3.72E-03	3.72E-04	2.97E-04	99.97

52	1.73E+03	1.40E+05	1.24E-02	8.22E-03	8.22E-04	6.57E-04	99.93
54	1.77E+03	9.29E+04	1.91E-02	1.30E-02	1.30E-03	1.04E-03	99.90
37	5.03E+03	1.51E+05	3.33E-02	2.32E-02	2.32E-03	1.85E-03	99.81
41	6.81E+03	1.78E+05	3.83E-02	2.67E-02	2.67E-03	2.14E-03	99.79
42	9.83E+02	9.71E+04	1.01E-02	6.62E-03	6.62E-04	5.30E-04	99.95
48	6.00E+03	1.50E+05	4.00E-02	2.80E-02	2.80E-03	2.24E-03	99.78
Z50:A50							
70	7.54E+04	1.35E+05	5.59E-01	3.98E-01	3.98E-02	3.19E-02	96.81
58	4.02E+04	1.11E+05	3.62E-01	2.58E-01	2.58E-02	2.06E-02	97.94
66	6.36E+04	1.17E+05	5.44E-01	3.88E-01	3.88E-02	3.10E-02	96.90
55	1.72E+04	1.53E+05	1.12E-01	7.97E-02	7.97E-03	6.37E-03	99.36
61	9.27E+03	1.23E+05	7.54E-02	5.32E-02	5.32E-03	4.26E-03	99.57
57	6.17E+03	1.38E+05	4.47E-02	3.13E-02	3.13E-03	2.51E-03	99.75
65	5.26E+03	1.25E+05	4.21E-02	2.94E-02	2.94E-03	2.36E-03	99.76
71	4.68E+03	1.33E+05	3.52E-02	2.45E-02	2.45E-03	1.96E-03	99.80
62	1.06E+03	1.08E+05	9.81E-03	6.40E-03	6.40E-04	5.12E-04	99.95
60	2.39E+03	1.48E+05	1.61E-02	1.09E-02	1.09E-03	8.74E-04	99.91
67	5.84E+03	1.45E+05	4.03E-02	2.82E-02	2.82E-03	2.25E-03	99.77
68	1.22E+03	1.42E+05	8.59E-03	5.53E-03	5.53E-04	4.42E-04	99.96
Z70:A30							
74	9.36E+04	9.58E+04	9.77E-01	1.04E+00	1.04E-01	8.32E-02	91.68
80	1.02E+05	1.24E+05	8.23E-01	8.53E-01	8.53E-02	6.82E-02	93.18
87	5.75E+04	1.51E+05	3.81E-01	3.08E-01	3.08E-02	2.46E-02	97.54
86	1.24E+04	9.25E+04	1.34E-01	3.11E-03	3.11E-04	2.49E-04	99.98
88	9.03E+03	1.25E+05	7.22E-02	< 0	0.00E+00	0.00E+00	100.00
90	6.08E+03	1.26E+05	4.83E-02	< 0	0.00E+00	0.00E+00	100.00
89	1.69E+04	1.32E+05	1.28E-01	< 0	0.00E+00	0.00E+00	100.00
76	7.62E+03	1.22E+05	6.25E-02	< 0	0.00E+00	0.00E+00	100.00

Table A6.2 Gemfibrozil Results

GEM sample ID	Analyte peak area	IS peak area	Analyte / IS area	HPLC Calculated concentration	Factored HPLC concentratin	C/Co	%Removal WRT Concentration
Control							
14	6.33E+06	2.97E+05	2.13E+01	2.17E+01	2.17E+00	9.50E-01	4.988583507
1	6.64E+06	3.01E+05	2.21E+01	2.24E+01	2.24E+00	9.83E-01	1.660468084
2	6.64E+06	2.98E+05	2.23E+01	2.26E+01	2.26E+00	9.93E-01	0.670601579
3	5.46E+06	2.64E+05	2.07E+01	2.10E+01	2.10E+00	9.22E-01	7.802523794
15	6.09E+06	2.74E+05	2.22E+01	2.26E+01	2.26E+00	9.91E-01	0.918434548
6	6.58E+06	2.90E+05	2.27E+01	2.31E+01	2.31E+00	1.01E+00	-1.146970709
11	6.48E+06	2.79E+05	2.32E+01	2.36E+01	2.36E+00	1.04E+00	-3.536747841
13	6.96E+06	2.98E+05	2.34E+01	2.37E+01	2.37E+00	1.04E+00	-4.11574088
17	6.71E+06	2.81E+05	2.39E+01	2.43E+01	2.43E+00	1.06E+00	-6.448231167
ZVFe-100							
32	3.74E+06	2.58E+05	1.45E+01	1.47E+01	1.47E+00	6.46E-01	35.37390337

33	2.43E+06	2.67E+05	9.10E+00	9.25E+00	9.25E-01	4.06E-01	59.42093855
22	1.64E+06	2.81E+05	5.84E+00	5.93E+00	5.93E-01	2.60E-01	73.97318084
29	9.27E+05	3.13E+05	2.96E+00	3.01E+00	3.01E-01	1.32E-01	86.78624955
21	2.91E+05	2.67E+05	1.09E+00	1.11E+00	1.11E-01	4.87E-02	95.12927168
23	3.87E+05	2.62E+05	1.48E+00	1.50E+00	1.50E-01	6.60E-02	93.40336063
27	3.51E+05	2.84E+05	1.24E+00	1.26E+00	1.26E-01	5.52E-02	94.47838445
19	9.63E+04	2.57E+05	3.75E-01	3.84E-01	3.84E-02	1.68E-02	98.31702783
24	9.08E+04	2.81E+05	3.23E-01	3.31E-01	3.31E-02	1.45E-02	98.5469188
25	8.31E+04	2.78E+05	2.99E-01	3.07E-01	3.07E-02	1.35E-02	98.65483319
31	1.00E+05	2.69E+05	3.72E-01	3.81E-01	3.81E-02	1.67E-02	98.33022566
AC-100							
38	2.09E+04	2.54E+05	8.23E-02	8.65E-02	8.65E-03	3.80E-03	99.62044704
39	4.41E+04	2.64E+05	1.67E-01	1.73E-01	1.73E-02	7.57E-03	99.242639
50	1.10E+04	2.54E+05	4.33E-02	4.69E-02	4.69E-03	2.06E-03	99.79417573
40	1.79E+04	2.48E+05	7.22E-02	7.63E-02	7.63E-03	3.35E-03	99.66549253
44	9.65E+02	2.40E+05	4.02E-03	7.00E-03	7.00E-04	3.07E-04	99.96928562
47	3.01E+03	2.43E+05	1.24E-02	1.55E-02	1.55E-03	6.80E-04	99.93199601
52	2.05E+03	2.59E+05	7.92E-03	1.10E-02	1.10E-03	4.81E-04	99.95192796
54	2.01E+03	2.63E+05	7.64E-03	1.07E-02	1.07E-03	4.69E-04	99.95314245
37	4.03E+02	2.31E+05	1.74E-03	4.69E-03	4.69E-04	2.06E-04	99.97943148
41	1.91E+03	2.81E+05	6.80E-03	9.82E-03	9.82E-04	4.31E-04	99.95691078
42	5.45E+02	2.70E+05	2.02E-03	4.97E-03	4.97E-04	2.18E-04	99.9782105
48	2.37E+03	3.05E+05	7.77E-03	1.08E-02	1.08E-03	4.74E-04	99.95257233
Z50:A50							
70	2.76E+04	2.42E+05	1.14E-01	1.19E-01	1.19E-02	5.21E-03	99.4788565
58	6.93E+03	2.22E+05	3.12E-02	3.46E-02	3.46E-03	1.52E-03	99.84806814
66	1.50E+04	2.24E+05	6.70E-02	7.10E-02	7.10E-03	3.11E-03	99.68872894
55	2.74E+03	2.64E+05	1.04E-02	1.35E-02	1.35E-03	5.91E-04	99.94094642
61	4.78E+03	2.43E+05	1.97E-02	2.29E-02	2.29E-03	1.00E-03	99.89952939
57	5.04E+02	2.33E+05	2.16E-03	5.11E-03	5.11E-04	2.24E-04	99.9775661
65	1.23E+03	2.14E+05	5.75E-03	8.76E-03	8.76E-04	3.84E-04	99.96158865
71	3.90E+03	2.59E+05	1.51E-02	1.82E-02	1.82E-03	7.99E-04	99.92009024
62	9.91E+03	2.18E+05	4.55E-02	4.91E-02	4.91E-03	2.15E-03	99.78458531
60	5.15E+03	3.20E+05	1.61E-02	1.93E-02	1.93E-03	8.45E-04	99.91547323
67	1.73E+03	3.34E+05	5.18E-03	8.18E-03	8.18E-04	3.59E-04	99.96412049
68	1.31E+03	2.96E+05	4.43E-03	7.41E-03	7.41E-04	3.25E-04	99.96748112
Z70:A30							
74	2.37E+04	1.61E+05	1.47E-01	1.48E-01	1.48E-02	6.49E-03	99.35087719
80	1.91E+04	2.34E+05	8.16E-02	7.92E-02	7.92E-03	3.47E-03	99.65263158
87	1.10E+04	2.46E+05	4.47E-02	4.07E-02	4.07E-03	1.79E-03	99.82149123
86	4.90E+03	1.44E+05	3.40E-02	2.96E-02	2.96E-03	1.30E-03	99.87017544
88	2.63E+03	1.78E+05	1.48E-02	9.69E-03	9.69E-04	4.25E-04	99.9575
90	3.21E+03	1.87E+05	1.72E-02	1.22E-02	1.22E-03	5.35E-04	99.94649123
89	5.16E+03	1.97E+05	2.62E-02	2.15E-02	2.15E-03	9.43E-04	99.90570175
76	7.21E+03	1.77E+05	4.07E-02	3.66E-02	3.66E-03	1.61E-03	99.83947368

Table A6.3 Naproxen Results

NPX sample ID	Analyte peak area	IS peak area	Analyte / IS area	HPLC Calculated concentration	Corrected HPLC concentratin	C/Co	%Removal WRT Concentration
Control				(μgl^{-1})	(μgl^{-1})		
14	6.33E+06	2.97E+05	2.13E+01	2.17E+01	2.17E+00	9.50E-01	4.99
1	6.64E+06	3.01E+05	2.21E+01	2.24E+01	2.24E+00	9.83E-01	1.66
2	6.64E+06	2.98E+05	2.23E+01	2.26E+01	2.26E+00	9.93E-01	0.67
3	5.46E+06	2.64E+05	2.07E+01	2.10E+01	2.10E+00	9.22E-01	7.80
15	6.09E+06	2.74E+05	2.22E+01	2.26E+01	2.26E+00	9.91E-01	0.92
6	6.58E+06	2.90E+05	2.27E+01	2.31E+01	2.31E+00	1.01E+00	-1.15
11	6.48E+06	2.79E+05	2.32E+01	2.36E+01	2.36E+00	1.04E+00	-3.54
13	6.96E+06	2.98E+05	2.34E+01	2.37E+01	2.37E+00	1.04E+00	-4.12
17	6.71E+06	2.81E+05	2.39E+01	2.43E+01	2.43E+00	1.06E+00	-6.45
ZVFe-100							
32	3.74E+06	2.58E+05	1.45E+01	1.47E+01	1.47E+00	6.46E-01	35.37
33	2.43E+06	2.67E+05	9.10E+00	9.25E+00	9.25E-01	4.06E-01	59.42
22	1.64E+06	2.81E+05	5.84E+00	5.93E+00	5.93E-01	2.60E-01	73.97
29	9.27E+05	3.13E+05	2.96E+00	3.01E+00	3.01E-01	1.32E-01	86.79
21	2.91E+05	2.67E+05	1.09E+00	1.11E+00	1.11E-01	4.87E-02	95.13
23	3.87E+05	2.62E+05	1.48E+00	1.50E+00	1.50E-01	6.60E-02	93.40
27	3.51E+05	2.84E+05	1.24E+00	1.26E+00	1.26E-01	5.52E-02	94.48
19	9.63E+04	2.57E+05	3.75E-01	3.84E-01	3.84E-02	1.68E-02	98.32
24	9.08E+04	2.81E+05	3.23E-01	3.31E-01	3.31E-02	1.45E-02	98.55
25	8.31E+04	2.78E+05	2.99E-01	3.07E-01	3.07E-02	1.35E-02	98.65
31	1.00E+05	2.69E+05	3.72E-01	3.81E-01	3.81E-02	1.67E-02	98.33
AC-100							
38	2.09E+04	2.54E+05	8.23E-02	8.65E-02	8.65E-03	3.80E-03	99.62
39	4.41E+04	2.64E+05	1.67E-01	1.73E-01	1.73E-02	7.57E-03	99.24
50	1.10E+04	2.54E+05	4.33E-02	4.69E-02	4.69E-03	2.06E-03	99.79
40	1.79E+04	2.48E+05	7.22E-02	7.63E-02	7.63E-03	3.35E-03	99.67
44	9.65E+02	2.40E+05	4.02E-03	7.00E-03	7.00E-04	3.07E-04	99.97
47	3.01E+03	2.43E+05	1.24E-02	1.55E-02	1.55E-03	6.80E-04	99.93
52	2.05E+03	2.59E+05	7.92E-03	1.10E-02	1.10E-03	4.81E-04	99.95
54	2.01E+03	2.63E+05	7.64E-03	1.07E-02	1.07E-03	4.69E-04	99.95
37	4.03E+02	2.31E+05	1.74E-03	4.69E-03	4.69E-04	2.06E-04	99.98
41	1.91E+03	2.81E+05	6.80E-03	9.82E-03	9.82E-04	4.31E-04	99.96
42	5.45E+02	2.70E+05	2.02E-03	4.97E-03	4.97E-04	2.18E-04	99.98
48	2.37E+03	3.05E+05	7.77E-03	1.08E-02	1.08E-03	4.74E-04	99.95
Z50:A50							
70	2.76E+04	2.42E+05	1.14E-01	1.19E-01	1.19E-02	5.21E-03	99.48
58	6.93E+03	2.22E+05	3.12E-02	3.46E-02	3.46E-03	1.52E-03	99.85
66	1.50E+04	2.24E+05	6.70E-02	7.10E-02	7.10E-03	3.11E-03	99.69
55	2.74E+03	2.64E+05	1.04E-02	1.35E-02	1.35E-03	5.91E-04	99.94
61	4.78E+03	2.43E+05	1.97E-02	2.29E-02	2.29E-03	1.00E-03	99.90

57	5.04E+02	2.33E+05	2.16E-03	5.11E-03	5.11E-04	2.24E-04	99.98
65	1.23E+03	2.14E+05	5.75E-03	8.76E-03	8.76E-04	3.84E-04	99.96
71	3.90E+03	2.59E+05	1.51E-02	1.82E-02	1.82E-03	7.99E-04	99.92
62	9.91E+03	2.18E+05	4.55E-02	4.91E-02	4.91E-03	2.15E-03	99.78
60	5.15E+03	3.20E+05	1.61E-02	1.93E-02	1.93E-03	8.45E-04	99.92
67	1.73E+03	3.34E+05	5.18E-03	8.18E-03	8.18E-04	3.59E-04	99.96
68	1.31E+03	2.96E+05	4.43E-03	7.41E-03	7.41E-04	3.25E-04	99.97
Z70:A30							
74	2.37E+04	1.61E+05	1.47E-01	1.48E-01	1.48E-02	6.49E-03	99.35
80	1.91E+04	2.34E+05	8.16E-02	7.92E-02	7.92E-03	3.47E-03	99.65
87	1.10E+04	2.46E+05	4.47E-02	4.07E-02	4.07E-03	1.79E-03	99.82
86	4.90E+03	1.44E+05	3.40E-02	2.96E-02	2.96E-03	1.30E-03	99.87
88	2.63E+03	1.78E+05	1.48E-02	9.69E-03	9.69E-04	4.25E-04	99.96
90	3.21E+03	1.87E+05	1.72E-02	1.22E-02	1.22E-03	5.35E-04	99.95
89	5.16E+03	1.97E+05	2.62E-02	2.15E-02	2.15E-03	9.43E-04	99.91
76	7.21E+03	1.77E+05	4.07E-02	3.66E-02	3.66E-03	1.61E-03	99.84

Table A6.4 Carbamazepine Results

CBZ sample ID	Analyte peak area	IS peak area	Analyte / IS area	HPLC Calculated concentration	Corrected HPLC concentratin	C/Co	%Removal WRT Concentration
Control				($\mu g l^{-1}$)	($\mu g l^{-1}$)		
C5	3.89E+05	2.36E+04	1.65E+01	2.43E+01	2.43E+00	1.01E+00	-1.33
C8	4.45E+05	2.76E+04	1.61E+01	2.37E+01	2.37E+00	9.88E-01	1.17
C14	3.95E+05	2.46E+04	1.61E+01	2.37E+01	2.37E+00	9.88E-01	1.17
C4	4.05E+05	2.66E+04	1.52E+01	2.25E+01	2.25E+00	9.38E-01	6.17
C16	5.24E+04	2.02E+04	2.59E+00	3.82E+00		0.00E+00	
C1	4.33E+05	2.76E+04	1.57E+01	2.31E+01	2.31E+00	9.63E-01	3.67
C15	4.11E+05	2.51E+04	1.64E+01	2.41E+01	2.41E+00	1.00E+00	-0.50
C3	4.30E+05	2.49E+04	1.73E+01	2.55E+01	2.55E+00	1.06E+00	-6.34
C2	4.36E+05	2.74E+04	1.59E+01	2.34E+01	2.34E+00	9.76E-01	2.42
C10	4.25E+05	2.51E+04	1.69E+01	2.49E+01	2.49E+00	1.04E+00	-3.84
C7	4.06E+05	2.67E+04	1.52E+01	2.24E+01	2.24E+00	9.34E-01	6.59
C17	4.50E+05	2.63E+04	1.71E+01	2.52E+01	2.52E+00	1.05E+00	-5.09
C13	4.87E+05	2.95E+04	1.65E+01	2.44E+01	2.44E+00	1.02E+00	-1.75
ZVFe-100							
Z32	2.83E+05	2.12E+04	1.33E+01	1.93E+01	1.93E+00	8.05E-01	19.52
Z33	1.67E+05	2.29E+04	7.29E+00	1.05E+01	1.05E+00	4.38E-01	56.21
Z22	1.16E+05	2.36E+04	4.92E+00	7.11E+00	7.11E-01	2.96E-01	70.35
Z20	5.43E+04	2.12E+04	2.56E+00	3.69E+00	3.69E-01	1.54E-01	84.61
Z28	3.41E+04	2.65E+04	1.29E+00	1.86E+00	1.86E-01	7.76E-02	92.24
Z36	5.82E+04	2.05E+04	2.84E+00	4.09E+00	4.09E-01	1.71E-01	82.94
Z29	3.98E+04	2.44E+04	1.63E+00	2.35E+00	2.35E-01	9.80E-02	90.20
Z21	1.24E+04	2.22E+04	5.59E-01	7.96E-01	7.96E-02	3.32E-02	96.68
Z23	1.44E+04	2.30E+04	6.26E-01	8.96E-01	8.96E-02	3.74E-02	96.26
Z27	1.39E+04	2.57E+04	5.41E-01	7.73E-01	7.73E-02	3.22E-02	96.78

Z19	3.12E+03	2.21E+04	1.41E-01	1.97E-01	1.97E-02	8.21E-03	99.18
Z34	3.47E+03	2.31E+04	1.50E-01	2.10E-01	2.10E-02	8.76E-03	99.12
Z35	3.69E+03	2.39E+04	1.54E-01	2.16E-01	2.16E-02	9.01E-03	99.10
Z30	2.65E+03	1.95E+04	1.36E-01	1.89E-01	1.89E-02	7.88E-03	99.21
Z25	2.61E+03	2.47E+04	1.06E-01	1.45E-01	1.45E-02	6.05E-03	99.40
Z24	2.61E+03	2.50E+04	1.04E-01	1.43E-01	1.43E-02	5.96E-03	99.40
AC-100							
A38	1.48E+03	2.73E+04	5.42E-02	7.11E-02	7.11E-03	2.96E-03	99.70
A39	2.21E+03	2.73E+04	8.10E-02	1.10E-01	1.10E-02	4.59E-03	99.54
A50	4.16E+02	2.32E+04	1.79E-02	1.88E-02	1.88E-03	7.84E-04	99.92
A46	6.51E+01	3.25E+04	2.00E-03	< 0	0.00E+00	0.00E+00	100.00
A43	8.42E+01	2.70E+04	3.12E-03	< 0	0.00E+00	0.00E+00	100.00
A40	9.84E+02	2.44E+04	4.03E-02	5.12E-02	5.12E-03	2.13E-03	99.79
A44	1.76E+02	2.68E+04	6.57E-03	2.46E-03	2.46E-04	1.03E-04	99.99
A54	2.21E+02	2.63E+04	8.40E-03	5.09E-03	5.09E-04	2.12E-04	99.98
A52	2.14E+02	2.66E+04	8.05E-03	4.56E-03	4.56E-04	1.90E-04	99.98
A47	1.36E+02	2.48E+04	5.48E-03	8.65E-04	8.65E-05	3.61E-05	100.00
A49	3.30E+02	2.44E+04	1.35E-02	1.25E-02	1.25E-03	5.21E-04	99.95
A37	6.21E+02	2.68E+04	2.32E-02	2.64E-02	2.64E-03	1.10E-03	99.89
A51	7.76E+02	2.33E+04	3.33E-02	4.11E-02	4.11E-03	1.71E-03	99.83
A53	5.33E+02	2.35E+04	2.27E-02	2.56E-02	2.56E-03	1.07E-03	99.89
A41	1.04E+02	3.10E+04	3.35E-03	< 0	0.00E+00	0.00E+00	100.00
A42	1.23E+02	2.74E+04	4.49E-03	< 0	0.00E+00	0.00E+00	100.00
A48	4.68E+02	2.91E+04	1.61E-02	1.62E-02	1.62E-03	6.75E-04	99.93
Z50:A50							
AZ70	1.18E+03	2.42E+04	4.88E-02	7.86E-02	7.86E-03	3.28E-03	99.67
AZ58	3.50E+02	2.07E+04	1.69E-02	3.14E-02	3.14E-03	1.31E-03	99.87
AZ66	1.05E+03	2.47E+04	4.25E-02	6.92E-02	6.92E-03	2.89E-03	99.71
AZ64	1.87E+02	2.99E+04	6.25E-03	1.57E-02	1.57E-03	6.55E-04	99.93
AZ55	3.15E+02	2.64E+04	1.19E-02	2.40E-02	2.40E-03	1.00E-03	99.90
AZ59	2.46E+02	2.80E+04	8.79E-03	1.94E-02	1.94E-03	8.09E-04	99.92
AZ61	2.38E+02	2.38E+04	1.00E-02	2.12E-02	2.12E-03	8.84E-04	99.91
AZ57	3.70E+02	2.20E+04	1.68E-02	3.12E-02	3.12E-03	1.30E-03	99.87
AZ71	4.38E+02	2.34E+04	1.87E-02	3.40E-02	3.40E-03	1.42E-03	99.86
AZ65	3.13E+02	2.43E+04	1.29E-02	2.54E-02	2.54E-03	1.06E-03	99.89
AZ63	1.04E+02	2.34E+04	4.44E-03	1.30E-02	1.30E-03	5.42E-04	99.95
AZ62	7.63E+02	2.21E+04	3.45E-02	5.72E-02	5.72E-03	2.39E-03	99.76
AZ56	5.06E+02	2.24E+04	2.26E-02	3.97E-02	3.97E-03	1.66E-03	99.83
AZ72	4.20E+02	2.43E+04	1.73E-02	3.20E-02	3.20E-03	1.33E-03	99.87
AZ69	2.96E+02	2.58E+04	1.15E-02	2.34E-02	2.34E-03	9.76E-04	99.90
AZ60	3.94E+02	2.71E+04	1.45E-02	2.79E-02	2.79E-03	1.16E-03	99.88
AZ68	5.75E+01	2.83E+04	2.03E-03	9.46E-03	9.46E-04	3.94E-04	99.96
AZ67	1.13E+02	3.04E+04	3.72E-03	1.19E-02	1.19E-03	4.96E-04	99.95
Z70:A30							

ZZ74	1.68E+03	1.78E+04	9.44E-02	1.46E-01	1.46E-02	6.09E-03	99.39
ZZ78	5.05E+01	2.52E+01	2.00E+00	2.96E+00	2.96E-01	1.23E-01	87.66
ZZ80	1.35E+03	2.99E+04	4.52E-02	7.29E-02	7.29E-03	3.04E-03	99.70
ZZ87	4.47E+02	2.82E+04	1.59E-02	2.98E-02	2.98E-03	1.24E-03	99.88
ZZ75	3.41E+02	2.57E+04	1.33E-02	2.60E-02	2.60E-03	1.08E-03	99.89
ZZ83	2.40E+02	2.54E+04	9.45E-03	2.04E-02	2.04E-03	8.51E-04	99.91
ZZ86	2.07E+02	1.92E+04	1.08E-02	2.23E-02	2.23E-03	9.30E-04	99.91
ZZ88	4.89E+02	2.37E+04	2.06E-02	3.69E-02	3.69E-03	1.54E-03	99.85
ZZ90	4.89E+02	2.52E+04	1.94E-02	3.50E-02	3.50E-03	1.46E-03	99.85
ZZ89	2.72E+02	2.41E+04	1.13E-02	2.31E-02	2.31E-03	9.63E-04	99.90
ZZ81	1.66E+02	2.31E+04	7.19E-03	1.71E-02	1.71E-03	7.13E-04	99.93
ZZ76	4.29E+02	2.55E+04	1.68E-02	3.13E-02	3.13E-03	1.31E-03	99.87
ZZ77	6.60E+02	2.16E+04	3.06E-02	5.15E-02	5.15E-03	2.15E-03	99.79
ZZ85	4.23E+02	2.39E+04	1.77E-02	3.25E-02	3.25E-03	1.36E-03	99.86
ZZ79	6.48E+02	2.93E+04	2.21E-02	3.90E-02	3.90E-03	1.63E-03	99.84
ZZ82	3.69E+02	2.75E+04	1.34E-02	2.62E-02	2.62E-03	1.09E-03	99.89
ZZ73	1.94E+02	2.89E+04	6.71E-03	1.63E-02	1.63E-03	6.80E-04	99.93
ZZ84	2.03E+02	2.55E+04	7.96E-03	1.82E-02	1.82E-03	7.59E-04	99.92
QA/QC							
Q91	4.12E+05	2.61E+04	1.58E+01	2.32E+01	2.32E+00	9.67E-01	3.25
Q92	1.95E+05	2.54E+04	7.68E+00	1.13E+01	1.13E+00	4.71E-01	52.88
Q93	7.47E+04	2.01E+04	3.72E+00	5.48E+00	5.48E-01	2.29E-01	77.15

Table A6.5 Caffeine results

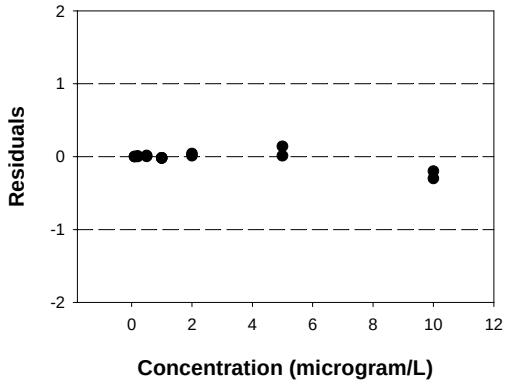
CAFF sample ID	Analyte peak area	IS peak area	Analyte / IS area	HPLC Calculated concentration	Corrected HPLC concentratin	C/Co	%Removal WRT Concentration
Control				(μgl^{-1})	(μgl^{-1})		
C5	7.84E+05	2.09E+04	3.75E+01	3.88E+01	3.88E+00	9.31E-01	11.62
C8	8.61E+05	1.99E+04	4.33E+01	4.48E+01	4.48E+00	1.07E+00	-2.05
C14	7.47E+05	2.04E+04	3.66E+01	3.79E+01	3.79E+00	9.09E-01	13.67
C12	6.66E+05	1.57E+04	4.24E+01	4.40E+01	4.40E+00	1.06E+00	-0.23
C4	7.98E+05	1.90E+04	4.20E+01	4.35E+01	4.35E+00	1.04E+00	0.91
C16	6.88E+04	1.98E+04	3.47E+00	3.33E+00		0.00E+00	
C1	8.65E+05	1.83E+04	4.73E+01	4.89E+01	4.89E+00	1.17E+00	-11.39
C15	7.60E+05	1.89E+04	4.02E+01	4.15E+01	4.15E+00	9.96E-01	5.47
C3	7.86E+05	1.81E+04	4.34E+01	4.50E+01	4.50E+00	1.08E+00	-2.51
C2	8.16E+05	1.95E+04	4.18E+01	4.33E+01	4.33E+00	1.04E+00	1.37
C9	8.07E+05	1.84E+04	4.39E+01	4.53E+01	4.53E+00	1.09E+00	-3.19
C6	8.19E+05	1.89E+04	4.33E+01	4.49E+01	4.49E+00	1.08E+00	-2.28
C10	7.98E+05	1.89E+04	4.22E+01	4.36E+01	4.36E+00	1.05E+00	0.68
C18	7.85E+05	1.86E+04	4.22E+01	4.37E+01	4.37E+00	1.05E+00	0.46
C7	7.41E+05	1.69E+04	4.38E+01	4.53E+01	4.53E+00	1.09E+00	-3.19
C11	8.44E+05	2.02E+04	4.18E+01	4.32E+01	4.32E+00	1.04E+00	1.59
C17	8.92E+05	1.95E+04	4.57E+01	4.73E+01	4.73E+00	1.13E+00	-7.74
C13	9.31E+05	2.10E+04	4.43E+01	4.60E+01	4.60E+00	1.10E+00	-4.78

ZVFe-100							
Z32	4.32E+05	1.93E+04	2.24E+01	2.46E+01	2.46E+00	5.90E-01	43.96
Z33	2.17E+05	1.72E+04	1.26E+01	1.37E+01	1.37E+00	3.29E-01	68.79
Z22	1.42E+05	1.98E+04	7.17E+00	7.64E+00	7.64E-01	1.83E-01	82.60
Z20	6.33E+04	1.53E+04	4.14E+00	4.32E+00	4.32E-01	1.04E-01	90.16
Z28	7.55E+04	1.76E+04	4.29E+00	4.74E+00	4.74E-01	1.14E-01	89.20
Z36	6.72E+04	1.47E+04	4.57E+00	4.79E+00	4.79E-01	1.15E-01	89.09
Z29	5.38E+04	1.72E+04	3.13E+00	3.20E+00	3.20E-01	7.68E-02	92.71
Z21	2.45E+04	2.06E+04	1.19E+00	1.04E+00	1.04E-01	2.49E-02	97.63
Z23	2.52E+04	1.89E+04	1.33E+00	1.21E+00	1.21E-01	2.90E-02	97.24
Z27	2.23E+04	2.28E+04	9.78E-01	8.14E-01	8.14E-02	1.95E-02	98.15
Z26	1.61E+04	2.18E+04	7.39E-01	5.45E-01	5.45E-02	1.31E-02	98.76
Z19	1.13E+04	1.99E+04	5.68E-01	3.54E-01	3.54E-02	8.49E-03	99.19
Z34	1.47E+04	2.24E+04	6.56E-01	4.54E-01	4.54E-02	1.09E-02	98.97
Z35	1.30E+04	2.33E+04	5.58E-01	3.44E-01	3.44E-02	8.25E-03	99.22
Z30	1.35E+04	2.40E+04	5.63E-01	3.53E-01	3.53E-02	8.47E-03	99.20
Z25	1.28E+04	2.52E+04	5.08E-01	2.88E-01	2.88E-02	6.91E-03	99.34
Z31	1.34E+04	2.32E+04	5.78E-01	3.66E-01	3.66E-02	8.78E-03	99.17
Z24	1.43E+04	2.25E+04	6.36E-01	4.33E-01	4.33E-02	1.04E-02	99.01
AC-100							
A38	8.75E+03	1.55E+04	5.65E-01	3.54E-01	3.54E-02	8.49E-03	99.19
A39	1.17E+04	1.56E+04	7.50E-01	5.58E-01	5.58E-02	1.34E-02	98.73
A50	5.73E+03	1.48E+04	3.87E-01	1.56E-01	1.56E-02	3.74E-03	99.64
A46	4.94E+03	1.91E+04	2.59E-01	1.30E-02	1.30E-03	3.12E-04	99.97
A43	5.04E+03	1.71E+04	2.95E-01	5.39E-02	5.39E-03	1.29E-03	99.88
A40	6.02E+03	1.53E+04	3.93E-01	1.62E-01	1.62E-02	3.89E-03	99.63
A44	5.16E+03	1.50E+04	3.44E-01	1.07E-01	1.07E-02	2.57E-03	99.76
A54	4.98E+03	1.72E+04	2.90E-01	4.71E-02	4.71E-03	1.13E-03	99.89
A52	5.79E+03	1.63E+04	3.55E-01	1.21E-01	1.21E-02	2.90E-03	99.72
A47	6.02E+03	1.63E+04	3.69E-01	1.35E-01	1.35E-02	3.24E-03	99.69
A49	6.47E+03	1.68E+04	3.85E-01	1.53E-01	1.53E-02	3.67E-03	99.65
A37	5.51E+03	1.39E+04	3.96E-01	1.64E-01	1.64E-02	3.93E-03	99.63
A51	5.96E+03	1.54E+04	3.87E-01	1.56E-01	1.56E-02	3.74E-03	99.64
A45	4.96E+03	1.71E+04	2.90E-01	4.77E-02	4.77E-03	1.14E-03	99.89
A53	5.51E+03	1.59E+04	3.47E-01	1.11E-01	1.11E-02	2.66E-03	99.75
A41	6.83E+03	1.80E+04	3.79E-01	1.46E-01	1.46E-02	3.50E-03	99.67
A42	6.07E+03	1.50E+04	4.05E-01	1.75E-01	1.75E-02	4.20E-03	99.60
A48	4.84E+03	1.86E+04	2.60E-01	1.45E-02	1.45E-03	3.48E-04	99.97
Z50:A50							
AZ70	9.47E+03	1.71E+04	5.54E-01	2.82E-01	2.82E-02	6.77E-03	99.36
AZ58	5.94E+03	1.20E+04	4.95E-01	2.19E-01	2.19E-02	5.25E-03	99.50
AZ66	8.76E+03	1.54E+04	5.69E-01	2.98E-01	2.98E-02	7.15E-03	99.32
AZ64	5.94E+03	1.95E+04	3.05E-01	2.22E-02	2.22E-03	5.33E-04	99.95
AZ55	5.40E+03	1.74E+04	3.10E-01	2.75E-02	2.75E-03	6.60E-04	99.94
AZ59	5.57E+03	1.79E+04	3.11E-01	2.82E-02	2.82E-03	6.77E-04	99.94
AZ61	5.60E+03	1.74E+04	3.22E-01	3.94E-02	3.94E-03	9.45E-04	99.91
AZ57	5.14E+03	1.65E+04	3.12E-01	2.85E-02	2.85E-03	6.84E-04	99.94

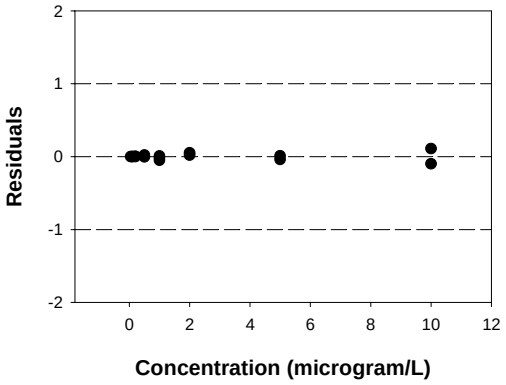
AZ71	5.51E+03	1.63E+04	3.38E-01	5.77E-02	5.77E-03	1.38E-03	99.87
AZ65	5.94E+03	1.46E+04	4.07E-01	1.29E-01	1.29E-02	3.09E-03	99.71
AZ63	4.30E+03	1.66E+04	2.59E-01	< 0	0	0	100
AZ62	4.44E+03	1.68E+04	2.64E-01	< 0	0	0	100
AZ56	5.46E+03	1.68E+04	3.25E-01	4.37E-02	4.37E-03	1.05E-03	99.90
AZ72	5.56E+03	1.82E+04	3.05E-01	2.30E-02	2.30E-03	5.52E-04	99.95
AZ69	4.07E+03	1.71E+04	2.38E-01	< 0	0	0	100
AZ60	5.86E+03	1.94E+04	3.02E-01	1.98E-02	1.98E-03	4.75E-04	99.95
AZ68	6.32E+03	1.74E+04	3.63E-01	8.27E-02	8.27E-03	1.98E-03	99.81
AZ67	5.24E+03	1.84E+04	2.85E-01	2.39E-03	2.39E-04	5.73E-05	99.99
Z70:A30							
ZZ74	1.11E+04	1.36E+04	8.16E-01	5.54E-01	5.54E-02	1.33E-02	98.74
ZZ78	3.14E+03	0.00E+00	#DIV/0!	< 0	0	0	100
ZZ80	1.31E+04	1.92E+04	6.82E-01	4.13E-01	4.13E-02	9.91E-03	99.06
ZZ87	7.71E+03	2.07E+04	3.72E-01	9.33E-02	9.33E-03	2.24E-03	99.79
ZZ75	6.84E+03	1.67E+04	4.10E-01	1.31E-01	1.31E-02	3.14E-03	99.70
ZZ83	7.65E+03	1.96E+04	3.90E-01	1.12E-01	1.12E-02	2.69E-03	99.74
ZZ86	4.77E+03	1.38E+04	3.46E-01	6.45E-02	6.45E-03	1.55E-03	99.85
ZZ88	6.04E+03	1.73E+04	3.49E-01	6.94E-02	6.94E-03	1.66E-03	99.84
ZZ90	5.74E+03	1.81E+04	3.17E-01	3.48E-02	3.48E-03	8.35E-04	99.92
ZZ89	6.13E+03	1.83E+04	3.35E-01	5.42E-02	5.42E-03	1.30E-03	99.88
ZZ81	5.07E+03	1.81E+04	2.80E-01	< 0	#VALUE!	#VALUE!	#VALUE!
ZZ76	5.59E+03	1.68E+04	3.33E-01	5.10E-02	5.10E-03	1.22E-03	99.88
ZZ77	6.93E+03	1.48E+04	4.68E-01	1.92E-01	1.92E-02	4.61E-03	99.56
ZZ85	5.56E+03	1.54E+04	3.61E-01	8.08E-02	8.08E-03	1.94E-03	99.82
ZZ79	7.39E+03	1.91E+04	3.87E-01	1.08E-01	1.08E-02	2.59E-03	99.75
ZZ82	6.01E+03	1.88E+04	3.20E-01	3.86E-02	3.86E-03	9.26E-04	99.91
ZZ73	5.10E+03	1.74E+04	2.93E-01	1.01E-02	1.01E-03	2.42E-04	99.98
ZZ84	4.61E+03	1.63E+04	2.83E-01	2.66E-04	2.66E-05	6.38E-06	100.00
QA/AC							
Q91	3.99E+05	1.72E+04	2.32E+01	2.40E+01	2.40E+00	5.76E-01	45.33
Q92	1.95E+05	1.58E+04	1.23E+01	1.25E+01	1.25E+00	3.00E-01	71.53
Q93	6.99E+04	1.26E+04	5.55E+00	5.51E+00	5.51E-01	1.32E-01	87.45

Appendix VII: Residuals for HPLC Calibration Linear Regressions

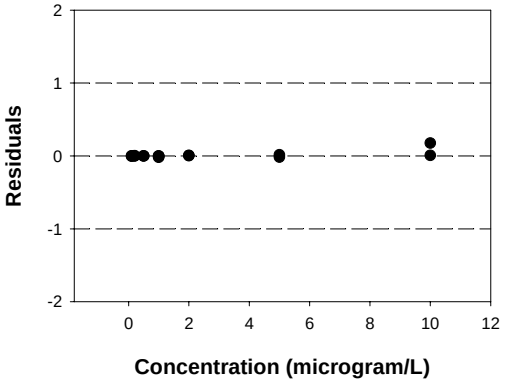
Residual for Ibuprofen Linear Regression



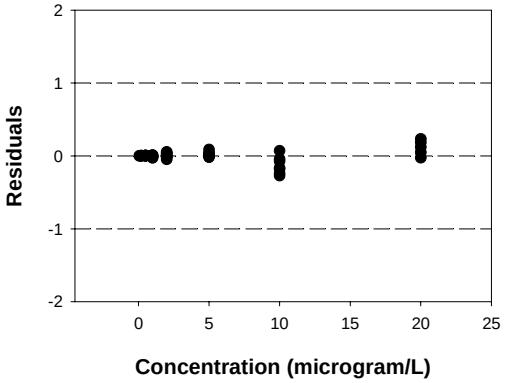
Residual for Naproxen Linear Regression



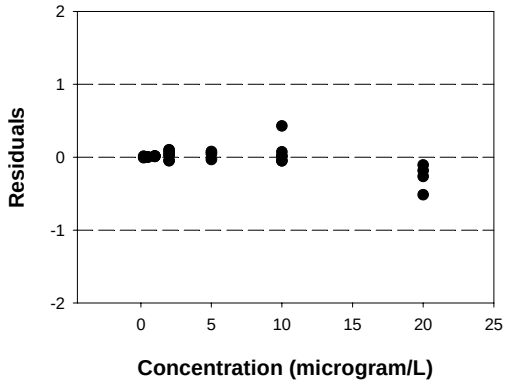
Residual for Gemfibrozil Linear Regression



Residual for Carbamazepine Linear Regression



Residual for Caffeine Linear Regression



Appendix VIII: Calculation of Expected Concentration for Preliminary Batches. Expected concentration are calculated for preliminary batches using the mass of PhAC in the PhAC working stock solution, the volume of this stock added as well as the total volume of the reaction vessel sample solution.

Table A8.1 Calculation of initial carbamazepine spiked concentration (expected concentration) in preliminary reaction vessel. This concentration is used as C_o in percent removal calculations.

Reaction flask	Mass Carbamazepine in stock (mg)	Vol. Stock Added	Vol. of Sample	Expected Drug Concentrationn ($mg\ l^{-1}$)	Expected Concentration ($\mu g l^{-1}$)
Control 1	1.9950	0.0010	0.8004	0.0024	2.3679
Control 2	1.9950	0.0011	0.7992	0.0027	2.6958
DK BOF	1.9950	0.0009	0.8004	0.0023	2.2931
ST BOF	1.9950	0.0009	0.8003	0.0022	2.2435
ZVFe	1.9950	0.0010	0.8000	0.0024	2.3690
BDS	1.9950	0.0010	0.8006	0.0025	2.5417
WC	1.9950	0.0010	0.8005	0.0025	2.5171

Table A8.2 Calculation of initial gemfibrozil spiked concentration (expected concentration) in preliminary reaction vessel. This concentration is used as C_o in percent removal calculations.

Reaction flask	Mass Gemfibrozil in stock (mg)	Vol. Stock Added	Vol. of Sample	Expected Drug Concentration ($mg\ l^{-1}$)	Expected Concentration ($\mu g l^{-1}$)
Control 1	1.9420	0.0010	0.8004	0.0023	2.3050
Control 2	1.9420	0.0011	0.7992	0.0026	2.6242
DK BOF	1.9420	0.0009	0.8004	0.0022	2.2322
ST BOF	1.9420	0.0009	0.8003	0.0022	2.1839
ZVFe	1.9420	0.0010	0.8000	0.0023	2.3061
BDS	1.9420	0.0010	0.8006	0.0025	2.4742
WC	1.9420	0.0010	0.8005	0.0025	2.4502

Table A8.3 Calculation of initial naproxen spiked concentration (expected concentration) in preliminary reaction vessel. This concentration is used as C_o in percent removal calculations.

Reaction flask	Mass Naproxen in stock (mg)	Vol. Stock Added	Vol. of Sample	Expected Drug Concentration ($mg\ l^{-1}$)	Expected Concentration ($\mu g l^{-1}$)
Control 1	1.9760	0.0010	0.8004	0.0023	2.3453
Control 2	1.9760	0.0011	0.7992	0.0027	2.6701
DK BOF	1.9760	0.0009	0.8004	0.0023	2.2713
ST BOF	1.9760	0.0009	0.8003	0.0022	2.2221
ZVFe	1.9760	0.0010	0.8000	0.0023	2.3465
BDS	1.9760	0.0010	0.8006	0.0025	2.5175
WC	1.9760	0.0010	0.8005	0.0025	2.4931

Table A8.4 Calculation of initial ibuprofen spiked concentration (expected concentration) in preliminary reaction vessel. This concentration is used as C_o in percent removal calculations.

Reaction flask	Mass Ibuprofen in stock (mg)	Vol. Stock Added	Vol. of Sample	Expected Drug Concentration ($mg\ l^{-1}$)	Expected Concentration ($\mu g l^{-1}$)
Control 1	2.0010	0.0010	0.8004	0.0024	2.3750
Control 2	2.0010	0.0011	0.7992	0.0027	2.7039
DK BOF	2.0010	0.0009	0.8004	0.0023	2.3000
ST BOF	2.0010	0.0009	0.8003	0.0023	2.2503
ZVFe	2.0010	0.0010	0.8000	0.0024	2.3762
BDS	2.0010	0.0010	0.8006	0.0025	2.5493
WC	2.0010	0.0010	0.8005	0.0025	2.5247

Table A8.5 Calculation of initial caffeine spiked concentration (expected concentration) in preliminary reaction vessel. This concentration is used as C_o in percent removal calculations.

Reaction flask	Mass Caffeine in stock (mg)	Vol. Stock Added	Vol. of Sample	Expected Drug Concn ($mg\ l^{-1}$)	Expected Concentration ($\mu g l^{-1}$)
Control 1	1.9700	0.0010	0.8004	0.0023	2.3382
Control 2	1.9700	0.0011	0.7992	0.0027	2.6620
DK BOF	1.9700	0.0009	0.8004	0.0023	2.2644
ST BOF	1.9700	0.0009	0.8003	0.0022	2.2154
ZVFe	1.9700	0.0010	0.8000	0.0023	2.3393
BDS	1.9700	0.0010	0.8006	0.0025	2.5098
WC	1.9700	0.0010	0.8005	0.0025	2.4855

Appendix IX: Percent Removal Calculations with respect to concentration

Percent removal was calculated using equation (1).

$$\% \text{ Removal} = (1 - C_f / C_o) * 100 \qquad (1)$$

Where C_f is the final PhAC concentration in the treated effluent and Co is the initial PhAC concentration. C_o is defined as the average control concentration for the Final batch experiements; and defined by the known spiked concentration as calculated in the tables in appendix VIII. Calculations for preliminary batches, where Co is defined as the spiked PhAC concentration, were futher defined by equation 2,

$$R_m = R_{cc} - R_{cm} \qquad (2)$$

Where R_m = total percent removal by media, and R_{cm} and R_{cc} are the calculated percent removals of the media and the controls respectively, as calculated by equation one. This second equation is applied so that percent removals include only that removal due to the media itself and not removal seen in the controls.

Appendix X: Calculation of Moisture Content for Sediment Back Extractions and Mass of PhAC sorbed to Solid

Table A10. Table of measured and calculated quantities used in the computation of moisture content and solid-phase sorbed PhACs. This calculation of sorbed PhACs contributes to mass balance calculations in Appendix XI.

Drug	Media Type	MeOH mass	Wet Mass	Dry Mass	Moisture Content	Sediment Sample Mass	Calc. Dry Mass	HPLC [Rx] from media	Mass recovery from media	Rx Mass per g media	Mass of Media in vessel	Mass of Rx Sorbed to Media
Unit		g	g	g	%	g	g	$\mu g l^{-1}$	ug	$\mu g g^{-1}$	g	ug
CBZ	ST-BOF	100.08	10.55	8.24	21.90	51.00	39.83	0.36	0.04	0.00	100.09	0.09
CBZ	Borden Sand	100.10	7.59	5.86	22.79	52.00	40.15	0.23	0.02	0.00	103.18	0.06
CBZ	Wood Chips	100.05	5.58	0.87	84.41	14.00	2.18	0.04	0.00	0.00	15.05	0.03
CBZ	ZVFe	100.52	14.71	11.76	20.05	52.00	41.57	0.04	0.00	0.00	100.03	0.01
CAFF	ST-BOF	100.08	10.55	8.24	21.90	51.00	39.83	0.05	0.01	0.00	100.09	0.01
CAFF	Borden Sand	100.10	7.59	5.86	22.79	52.00	40.15	0.23	0.02	0.00	103.18	0.06
CAFF	Wood Chips	100.05	5.58	0.87	84.41	14.00	2.18	0.26	0.03	0.01	15.05	0.18
CAFF	ZVFe	100.52	14.71	11.76	20.05	52.00	41.57	0.03	0.00	0.00	100.03	0.01
IBU	ST-BOF	100.08	10.55	8.24	21.90	51.00	39.83	0.41	0.04	0.00	100.09	0.10
IBU	Borden Sand	100.10	7.59	5.86	22.79	52.00	40.15	0.20	0.02	0.00	103.18	0.05
IBU	Wood Chips	100.05	5.58	0.87	84.41	14.00	2.18	0.45	0.05	0.02	15.05	0.31
IBU	ZVFe	100.52	14.71	11.76	20.05	52.00	41.57	0.18	0.02	0.00	100.03	0.04
NPX	ST-BOF	100.08	10.55	8.24	21.90	51.00	39.83	0.36	0.04	0.00	100.09	0.09
NPX	Borden Sand	100.10	7.59	5.86	22.79	52.00	40.15	0.12	0.01	0.00	103.18	0.03
NPX	Wood Chips	100.05	5.58	0.87	84.41	14.00	2.18	0.29	0.03	0.01	15.05	0.20
NPX	ZVFe	100.52	14.71	11.76	20.05	52.00	41.57	0.07	0.01	0.00	100.03	0.02
GEM	ST-BOF	100.08	10.55	8.24	21.90	51.00	39.83	0.35	0.04	0.00	100.09	0.09
GEM	Borden Sand	100.10	7.59	5.86	22.79	52.00	40.15	0.10	0.01	0.00	103.18	0.03
GEM	Wood Chips	100.05	5.58	0.87	84.41	14.00	2.18	0.20	0.02	0.01	15.05	0.14
GEM	ZVFe	100.52	14.71	11.76	20.05	52.00	41.57	0.00	0.00	0.00	100.03	0.00

Appendix XI: Mass Balance Calculations of Recovered PhACs

Table A11. Measured and calculated quantities indicating the calculation of distribution of recovered PhAC between solid and solution phases.

Drug	Media Type (g)	Final Rx concentration is solution	Vol of Rxn flask sample	Final Rx mass in Rxn flask	Expected Initial Concentration	Expected Initial mass in rxn flask	Solid %Rx recovered	Solution %Rx recovered	Transformed
		ug/L	L	ug	Ug/L	ug	%	%	%
CBZ	ST-BOF	2.17	0.80	1.74	2.24	1.80	5.03	96.75	-1.78
CBZ	Borden Sand	2.00	0.80	1.60	2.54	2.04	2.92	78.68	18.40
CBZ	Wood Chips	0.98	0.80	0.78	2.52	2.01	1.51	38.94	59.55
CBZ	ZVFe	0.27	0.80	0.21	2.37	1.90	0.56	11.23	88.21
CAFF	ST-BOF	0.11	0.80	0.09	2.22	1.80	0.77	4.77	94.46
CAFF	Borden Sand	0.91	0.80	0.73	2.51	2.04	2.85	35.88	61.27
CAFF	Wood Chips	0.73	0.80	0.59	2.49	2.01	8.84	29.04	62.12
CAFF	ZVFe	0.14	0.80	0.11	2.34	1.90	0.38	5.83	93.79
IBU	ST-BOF	1.73	0.80	1.39	2.25	1.80	5.72	77.31	16.98
IBU	Borden Sand	1.20	0.80	0.96	2.55	2.04	2.56	47.21	50.24
IBU	Wood Chips	2.20	0.80	1.76	2.52	2.01	15.51	87.41	-2.91
IBU	ZVFe	0.53	0.80	0.42	2.38	1.90	2.27	22.16	75.56
NPX	ST-BOF	1.99	0.80	1.59	2.22	1.80	5.04	88.68	6.28
NPX	Borden Sand	0.89	0.80	0.71	2.52	2.04	1.48	34.93	63.59
NPX	Wood Chips	0.97	0.80	0.77	2.49	2.01	9.79	38.38	51.83
NPX	ZVFe	0.23	0.80	0.19	2.35	1.90	0.92	9.79	89.29
GEM	ST-BOF	1.29	0.80	1.03	2.18	1.80	4.92	57.51	37.57
GEM	Borden Sand	1.28	0.80	1.03	2.47	2.04	1.29	62.94	35.77
GEM	Wood Chips	0.97	0.80	0.77	2.45	2.01	6.77	47.94	45.28
GEM	ZVFe	0.37	0.80	0.30	2.31	1.90	0.00	19.63	80.37

Appendix XII: Paired T-test Results for Treatments

Table A12. Table of paired t-test results for all media investigated. Paired T-test were calculated between control samples and treated samples to verify the statistical significance on any change in concentration. The significance level , alpha, was set at 5% ($\alpha = 0.05$). If the probability of attaining a statistically similar value (p) is less than alpha, then one rejects the null hypothesis that the results are statistically similar and the results cannot be ascribed to chance alone; thus the difference in results between the compared sample sets are described as "statistically significant at the 5% level".

	ZVFe: sand	ZVFe 100%	Z70:Z30	Z50:A50	AC100%	BOF	BDS	Wood Chips
Carbamazepine								
T value	3.455	10.158	13.417	13.350	12.649	-1.651	0.936	8.982
P value	0.006	0.000	0.000	0.000	0.000	0.130	0.371	0.000
Degrees of freedom	10.000	18.000	18.000	18.000	17.000	10.000	10.000	10.000
p value< or > alpha	less	less	less	less	less	greater	greater	less
Caffeine								
T value	4.372	10.401	12.659	12.636	2.523	5.178	7.665	2.7181
P value	0.001	0.000	0.000	0.000	0.021	0.000	0.000	0.0187
Degrees of freedom	10.000	18.000	18.000	18.000	18.000	11.000	11.000	12.0000
p value< or > alpha	less	less	less	less	less	less	less	less
Gemfibrozil								
T value	2.059	8.333	10.899	10.898	10.899	1.631	1.361	2.580
P value	0.066	0.000	0.000	0.000	0.000	0.129	0.199	0.024
Degrees of freedom	10.000	11.000	11.000	11.000	11.000	12.000	12.000	12.000
p value< or > alpha	greater	less	less	less	less	greater	greater	less
Naproxen								
T value	-0.399	7.659	10.724	10.742	10.721	-3.552	1.039	2.052
P value	0.698	0.000	0.000	0.000	0.000	0.004	0.319	0.063
Degrees of freedom	10.000	11.000	11.000	11.000	11.000	12.000	12.000	12.000
p value< or > alpha	greater	less	less	less	less	less	greater	greater
Ibuprofen								
T value	2.467	6.779	10.976	10.954	10.972	-2.398	0.982	-4.202
P value	0.039	0.000	0.000	0.000	0.000	0.034	0.346	0.001
Degrees of freedom	8.000	11.000	11.000	11.000	11.000	12.000	12.000	12.000
p value< or > alpha	less	less	less	less	less	less	greater	less

Appendix XIII: Confidence Intervals for Controls

Table A13. Confidence Intervals for Controls:

	Control (Final Batch)				Control (Preliminary 1)				Control (Preliminary 2)			
	Avg.	**S.D.**	**C.I.**	**n**	**Avg.**	**S.D.**	**C.I.**	**n**	**Avg.**	**S.D.**	**C.I.**	**n**
CBZ	2.398	0.085	0.039	18	2.506	0.036	0.021	11	2.404	0.508	0.287	13
CAFF	4.394	0.270	0.125	18	2.403	0.035	0.020	12	2.402	0.031	0.017	12
GEM	2.278	0.103	0.067	18	2.455	0.390	0.230	11	2.703	0.405	0.220	13
NPX	2.348	0.157	0.092	18	1.084	0.243	0.143	11	2.058	0.352	0.199	12
IBU	1.250	0.030	0.018	18	0.939	0.136	0.080	11	1.815	0.199	0.139	13

Note: all were calculated on 95% confidence intervals with alpha = 0.05

Appendix XIV: MINTEQA2 Speciated and Unspeciated Charge differences and Mineral Saturation Indices

Table A14. The following table depicts the results of geochemical modeling with the mass-transfer code MINTEQA2. Saturation indices calculation by MINTEQA2 were employed to determine potential mineral phases controlling aqueous geochemistry in the reaction vessels. Saturation indices of zero value indicate equilibrium with respect to the mineral phase; while values greater than 0 indicate supersaturation and values less than zero indicate undersaturation.

Control 3	**Time 1**	**Time 2**	**Time 4**	**Time 7**	**Time 8**		
Unspeciated charge difference	10	4.681	5.862	0.5201	8.179		
Speciated charge difference	10.32	5.113	5.58	3.507	8.521		
NAME	**Sat. Index**	**Sat. Index**	**Sat. Index**	**Sat. Index**	**Sat. Index**	**Change**	**Final State**
Aragonite	-0.064	-0.439	-0.357	-0.384	-0.338	Becomes less saturated	Undersaturation
Calcite	0.081	-0.295	-0.212	-0.239	-0.194	Becomes less saturated	Undersaturation
Ferrihydrite	0.542	1.699	0.581	1.432	0.353	Becomes less saturated	Supersaturation
Boehmite	0.243	0.702	0.573	1.682	0.47	Becomes more saturated	Supersaturation
Gibbsite	0.737	1.197	1.067	2.177	0.964	Becomes more saturated	Supersaturation
Disapore	1.965	2.425	2.295	3.405	2.192	Constant	Supersaturation
Lepidocrocite	4.062	5.219	4.101	4.952	3.873	Constant	Supersaturation
Magnesium-Ferrite	4.894	6.971	4.748	5.601	4.055	Constant	Supersaturation
Maghemite	4.48	6.794	4.559	6.26	4.101	Constant	Supersaturation
$Fe(OH)_{2.7}Cl_3$	5.18	6.421	5.279	6.1	4.997	Constant	Supersaturation
Goethite	6.361	7.519	6.401	7.251	6.172	Constant	Supersaturation
Mixed Carbite	8.912	7.962	8.365	6.038	6.826	Becomes less saturated	Supersaturation
Magnetite	10.467	15.511	13.147	14.969	11.312	Constant	Supersaturation
Hematite	14.721	17.036	14.8	16.501	14.342	Constant	Supersaturation
Pyrolusite	55.117	51.965	50.3	52.131	53.15	Constant	Supersaturation

100% AC	**Time 1**	**Time 2**	**Time 4**	**Time 7**	**Time 8**		
Unspeciated charge difference	9.949	14.78	15.28	0.7808	9.7		
Speciated charge difference	9.08	13.19	0.2901	1.9	7.4		
NAME		**Sat. Index**	**Sat. Index**	**Sat. Index**	**Sat. Index**	**Change**	**Final State**
Octacaphosphate	0.976	-0.934	-2.334	-3.439	-2.658	Becomes less saturated	Undersaturation
Hausmannite	3.667	1.193	-4.214	0.601	-0.285	Becomes less saturated	Undersaturation
Magnesite	-0.295	-0.174	-0.305	-0.458	-0.22	Constant	Undersaturation
Bixbyite	3.223	1.206	-4.231	0.403	-0.081	Becomes less saturated	Undersaturation
Mangnitite	1.582	0.573	-2.145	0.171	-0.07	Becomes less saturated	Undersaturation
Aragonite	0.975	0.512	0.065	-0.255	-0.011	Becomes less saturated	Undersaturation
Calcite	1.12	0.657	0.21	-0.11	0.134	Becomes less saturated	Supersaturation
Ferrihydrite	1.127	1.053	-1.198	-0.148	0.319	Becomes less saturated	Supersaturation
Dolomite	1.407	1.065	0.487	0.014	0.496	Becomes less saturated	Supersaturation
Whitlockite	3.38	1.932	0.926	0.104	0.573	Becomes less saturated	Supersaturation
Manganese Phosphate	0.897	0.503	0.354	0.51	0.577	Becomes less saturated	Supersaturation
Lepidocrocite	4.647	4.573	2.322	3.372	3.839	Becomes less saturated	Supersaturation
Maghemite	5.65	5.502	1	3.101	4.034	Becomes less saturated	Supersaturation
$Fe(OH)_{2.7}Cl_3$	5.335	5.223	2.932	3.98	4.512	Becomes less saturated	Supersaturation
Goethite	6.946	6.872	4.621	5.672	6.138	Constant	Supersaturation
Magnesium Ferrite	9.299	9.209	4.807	6.818	7.588	Becomes less saturated	Supersaturation
Magnetite	11.408	11.737	7.732	8.747	9.986	Becomes less saturated	Supersaturation
Hematite	15.892	15.743	11.241	13.342	14.275	Constant	Supersaturation
Mixed Carbite	20.817	19.568	17.213	14.555	16.621	Becomes less saturated	Supersaturation
Pyrolusite	58.785	57.225	51.759	56.211	56.13	Constant	Supersaturation

100% ZVFe	Time 1	Time 2	Time 4	Time 10	Time 12
Unspeciated charge difference	92.21	80.2	99.43	100	100
Speciated charge difference	4.721	9.661	1.663	5.486	5.024

NAME	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Iron Hydroxide	0.72	0.26	-3.607	-15.548	-12.445	Becomes less saturated	Undersaturation
Maghemite	4.305	4.287	0.457	-11.124	-9.034	Becomes less saturated	Undersaturation
Magnesium Ferrite	3.005	2.883	-1.327	-12.427	-8.823	Becomes less saturated	Undersaturation
Ferrihydrite	0.454	0.445	-1.469	-7.26	-6.215	Becomes less saturated	Undersaturation
Lepidocrocite	3.974	3.965	2.051	-3.74	-2.695	Becomes less saturated	Undersaturation
Rhodocrocite	-0.889	-1.205	-1.602	-2.157	-1.734	Becomes less saturated	Undersaturation
$Fe(OH)_{2.7}Cl_3$	5.467	5.485	3.633	-2.231	-1.405	Becomes less saturated	Undersaturation
Siderite (D)	0.152	-0.265	-0.473	-1.531	-1.349	Becomes less saturated	Undersaturation
Siderite (C)	0.606	0.189	-0.019	-1.077	-0.895	Becomes less saturated	Undersaturation
Goethite	6.274	6.265	4.35	-1.441	-0.396	Becomes less saturated	Undersaturation
Hematite	14.546	14.528	10.699	-0.883	1.207	Becomes less saturated	Supersaturation
Magnetite	16.956	16.495	12.628	0.687	3.79	Becomes less saturated	Supersaturation
Pyrolusite	41.649	42.175	38.193	27.475	28.793	Becomes less saturated	Supersaturation

Z70:A30	Time 1	Time 2	Time 4	Time 10	Time 12
Unspeciated charge difference	92.95	100	100	100	100
Speciated charge difference	16.27	13.96	18.48	0.7604	80.13

NAME	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Jarosite	0.463	-15.422	-29.336	-23.091	-28.265	Become less Saturated	Undersaturation
Maghemite	10.893	0.143	-11.854	-4.906	-7.424	Become less Saturated	Undersaturation
Magnesium Ferrite	12.389	2.349	-13.273	-3.357	-6.133	Become less Saturated	Undersaturation
Ferrihydrite	3.749	-1.627	-7.625	-4.151	-5.41	Become less Saturated	Undersaturation
Ankerite-Dolomite(T)	-0.27	-1.305	-4.376	-0.959	-3.441	Become less Saturated	Undersaturation
Dolomite	-0.644	-0.944	-5.026	-1.617	-3.297	Become less Saturated	Undersaturation
Ankerite	0.732	-0.794	-3.19	0.231	-2.785	Become less Saturated	Undersaturation
ANK-DOL(IMN)	0.488	-0.553	-3.619	-0.203	-2.685	Become less Saturated	Undersaturation
Ankerite-Dolomite (I)	0.49	-0.545	-3.616	-0.199	-2.681	Become less Saturated	Undersaturation
Aragonite	-0.038	-1.073	-2.851	-0.821	-1.903	Become less Saturated	Undersaturation
Lepidocrocite	7.269	1.893	-4.105	-0.631	-1.89	Become less Saturated	Undersaturation
Calcite	0.107	-0.928	-2.706	-0.676	-1.758	Become less Saturated	Undersaturation
Rhodochrosite	0.218	-0.765	-1.532	-0.17	-0.952	Become less Saturated	Undersaturation
$Fe(OH)_{2.7}Cl_3$	8.335	2.975	-2.612	0.442	-0.927	Become less Saturated	Undersaturation
Siderite(D)	1.122	0.631	0.012	1.404	-0.531	Become less Saturated	Undersaturation
Wustite	0.668	0.175	-1.807	1.163	-0.311	Become less Saturated	Undersaturation
Siderite(C)	1.576	1.085	0.466	1.858	-0.077	Become less Saturated	Undersaturation
Goethite	9.568	4.193	-1.806	1.668	0.409	Become less Saturated	Supersaturation
Hematite	21.135	10.384	-1.613	5.336	2.817	Become less Saturated	Supersaturation
Mixed Carbite	17.247	12.875	-4.294	12.419	4.997	Become less Saturated	Supersaturation
Magnetite	25.527	14.26	0.324	10.253	6.14	Become less Saturated	Supersaturation
Pyrolusite	46.393	35.666	25.459	29.398	29.626	Become less Saturated	Supersaturation

Z50:A50	Time 1	Time 2	Time 4	Time 10	Time 12
Unspeciated charge difference	99.89	100	100	100	100
Speciated charge difference	5.409	7.951	7.721	5.381	14.32

NAME	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Lepidocrocite	0.309	-3.399	-3.614	-3.928	-2.123	Become less saturated	Undersaturation
Calcite	-1.492	-1.997	-2.085	-3.182	-2.093	Become less saturated	Undersaturation
$Fe(OH)_{2.7}Cl_3$	1.824	-1.937	-2.181	-2.5	-1.008	Become less saturated	Undersaturation
Siderite (D)	-1.174	-0.379	-0.319	-0.931	-0.557	Become more saturated	Undersaturation
Goethite	2.608	-1.1	-1.314	-1.628	0.176	Become less saturated	Supersaturation
Mixed Carbite	1.034	-0.914	-0.667	-8.665	0.303	Become less saturated	Supersaturation
Hematite	7.215	-0.202	-0.63	-1.258	2.351	Become less saturated	Supersaturation
Magnetite	8.042	1.664	1.432	0.621	5.759	Become less saturated	Supersaturation
Pyrolusite	36.58	27.178	26.323	25.952	28.265	Become less saturated	Supersaturation

Borden Sand	Time 1	Time 2	Time 4	Time 10	Time 12
Unspeciated charge difference	99.89	100	100	100	100
Speciated charge difference	5.409	7.951	7.721	5.381	14.32

NAME	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Lepidocrocite	0.309	-3.399	-3.614	-3.928	-2.123	Become less saturated	Undersaturation
Calcite	-1.492	-1.997	-2.085	-3.182	-2.093	Become less saturated	Undersaturation
$Fe(OH)_{2.7}Cl_3$	1.824	-1.937	-2.181	-2.5	-1.008	Become less saturated	Undersaturation
Siderite (D)	-1.174	-0.379	-0.319	-0.931	-0.557	Become more saturated	Undersaturation
Goethite	2.608	-1.1	-1.314	-1.628	0.176	Become less saturated	Supersaturation
Mixed Carbite	1.034	-0.914	-0.667	-8.665	0.303	Become less saturated	Supersaturation
Hematite	7.215	-0.202	-0.63	-1.258	2.351	Become less saturated	Supersaturation
Magnetite	8.042	1.664	1.432	0.621	5.759	Become less saturated	Supersaturation
Pyrolusite	36.58	27.178	26.323	25.952	28.265	Become less saturated	Supersaturation

ST-BOF	Time 1	Time 2	Time 4
Unspeciated charge difference	46.76	28.54	35.29
Speciated charge difference	92.75	88.09	93.16

NAME	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Portlandite	-1.95	-1.596	-0.738	Becomes more saturated	Undersaturation
Cerargyrite	-0.089	0.24	-0.561	Becomes less saturated	Undersaturation
Todorokite	-0.903	-3.406	-0.481	Becomes more saturated	Undersaturation
Pyrocrocite	-0.351	-0.353	-0.215	Becomes more saturated	Undersaturation
Magnesite	0.504		0.025	Becomes less saturated	Supersaturated
Gold Oxide	0.926	1.177	0.173	Becomes less saturated	Supersaturated
Nickel Hydroxide	0.49	0.87	0.384	Becomes less saturated	Supersaturated
$Fe(OH)_{2.7}Cl_3$	0.461	0.567	0.634	Becomes more saturated	Supersaturated
Huntite	1.423	0.662	0.741	Becomes less saturated	Supersaturated
Nsutite	1.092	0.618	1.052	Constant	Supersaturated
Lepidocrocite	1.058	1.103	1.261	Becomes more saturated	Supersaturated
Artinite	2.204	1.216	1.705	Becomes less saturated	Supersaturated
Magnetite	1.69	2.061	2.385	Becomes more saturated	Supersaturated
Brucite	2.468	1.9	2.447	Constant	Supersaturated
Aragonite	2.385	2.886	3.139	Becomes more saturated	Supersaturated
Calcite	2.529	3.03	3.284	Becomes more saturated	Supersaturated
Goethite	3.358	3.403	3.56	Constant	Supersaturated
Dolomite	3.615	3.696	3.891	Constant	Supersaturated
Manganite	4.143	3.905	4.192	Constant	Supersaturated
Gold Metal	5.723	6.085	5.434	Constant	Supersaturated
Magnesium Ferrite	7.205	6.728	7.59	Constant	Supersaturated
Bixbyite	8.346	7.87	8.443	Constant	Supersaturated
Hematite	8.714	8.804	9.119	Constant	Supersaturated
Hausmannite	12.4	11.923	12.634	Constant	Supersaturated
Mixed Carbite	27.154	29.41	30.525	Constant	Supersaturated
Pyrolusite	60.298	59.824	60.259	Constant	Supersaturated

ZVFe	Time 1	Time 2	Time 4	Time 10
Unspeciated charge difference	24.35	9.7	10.23	37.37
Speciated charge difference	25.51	10.21	9.697	4.107

NAME	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Manganite	-0.701	-1.347	-3.397	-4.074	Becomes less saturated	Undersaturation
Dolomite	-0.367	-0.998	-2.109	-2.108	Becomes less saturated	Undersaturation
Aragonite	0.71	0.267	-0.421	-0.563	Saturated to unsaturated	Undersaturation
Calcite	0.855	0.411	-0.276	-0.418	Saturated to unsaturated	Undersaturation
Rhodocrocite	0.055	0.256	-0.338	-0.03	Saturated to unsaturated	Undersaturation
Aluminun Hydroxide	-2.307	-1.844	-1.403	-0.005	Becomes more saturated	Undersaturation
Aluminum Sulphate	-10.084	-7.465	-4.535	1.04	Unsaturated to Saturated	Supersaturation
Ferrihydrate	-0.317	-0.284	0.869	1.648	Unsaturated to Saturated	Supersaturation
Iron Hydroxide	-7.114	-6.329	-1.751	1.997	Unsaturated to Saturated	Supersaturation
Boehmite	-0.093	0.37	0.811	2.209	Unsaturated to Saturated	Supersaturation
Gibbsite (C)	0.401	0.865	1.306	2.703	Becomes more saturated	Supersaturation
Hercynite	-6.343	-4.697	-1.543	3.443	Becomes more saturated	Supersaturation
Disapore	1.629	2.093	2.534	3.931	Becomes more saturated	Supersaturation
Lepidocrocite	3.203	3.236	4.389	5.168	Becomes more saturated	Supersaturation
$Fe(OH)_{2.7}Cl_3$	3.688	3.895	5.253	6.036	Becomes more saturated	Supersaturation
Maghemite	2.763	2.829	5.135	6.692	Becomes more saturated	Supersaturation
Magnesium Ferrite	3.597	3.315	4.859	6.988	Becomes more saturated	Supersaturation
Goethite	5.503	5.536	6.689	7.467	Becomes more saturated	Supersaturation
Mixed Carbite	15.599	12.698	8.592	9.158	Becomes less saturated	Supersaturation
Hematite	13.004	13.07	15.376	16.934	Becomes more saturated	Supersaturation
Magnetite	9.121	9.906	14.484	18.232	Becomes more saturated	Supersaturation
Pyrolusite	54.458	53.127	49.957	47.869	Becomes less saturated	Supersaturation

Woodchips	**Time 1**	**Time 2**	**Time 4**	**Time 10**
Unspeciated charge difference	97.82	98.11	97.81	96.81
Speciated charge difference	98.75	98.71	97.87	96.32

NAME	**Sat. Index**	**Sat. Index**	**Sat. Index**	**Sat. Index**	**Change**	**Final state**
MIXCARBT	1.059	-0.157	-6.861	-6.968	Becomes less saturated	Undersaturation
Magnesium Ferrite	4.354	4.117	-2.499	-1.826	Becomes less saturated	Undersaturation
Ferrihydrite	0.906	0.936	-1.68	-1.172	Becomes less saturated	Undersaturation
Aluminum Hydroxide	-1.213	-0.882	0.196	-0.165	Becomes more saturated	Undersaturation
Brushite	0.646	0.522	0.397	0.564	Constant	Supersaturation
Octaphosphate	3.088	2.216	0.42	0.622	Becomes less saturated	Supersaturation
Monetite	0.978	0.853	0.728	0.896	Constant	Supersaturation
Whitlockite	3.322	2.575	0.903	0.938	Becomes less saturated	Supersaturation
Alumnite	-6.348	-5.089	1.013	1.025	Becomes more saturated	Supersaturation
Maghemite	5.209	5.269	0.037	1.054	Becomes less saturated	Supersaturation
Zinc Phosphate	0.221	1.341	-3.091	1.08	Becomes more saturated	Supersaturation
Boehmite	1.002	1.333	2.41	2.05	Becomes more saturated	Supersaturation
Lepidocrocite	4.426	4.456	1.84	2.349	Becomes less saturated	Supersaturation
Aluminum Sulphate	-4.362	-2.832	3.323	2.52	Becomes more saturated	Supersaturation
Gibsite (C)	1.496	1.827	2.904	2.544	Becomes more saturated	Supersaturation
Strengite	3.018	3.422	2.103	3.078	Constant	Supersaturation
$Fe(OH)_{2.7}Cl_3$	5.32	5.35	2.97	3.586	Becomes less saturated	Supersaturation
Disapore	2.724	3.055	4.132	3.772	Becomes more saturated	Supersaturation
Goethite	6.725	6.756	4.14	4.648	Becomes less saturated	Supersaturation
Manganese phosphate(C)	4.673	4.874	4.714	4.818	Constant	Supersaturation
Varscite	2.63	3.335	5.709	5.816	Becomes more saturated	Supersaturation
Magnetite	13.022	13.737	6.978	7.835	Becomes less saturated	Supersaturation
Hematite	15.45	15.511	10.279	11.296	Becomes less saturated	Supersaturation
Pyrolusite	51.435	50.013	46.379	47.352	Becomes less saturated	Supersaturation

Control 1	Time 1	Time 2	Time 4	Time 10
Unspeciated charge difference	42.02	10.11	2.752	12.84
Speciated charge difference	49.25	14.77	9.326	13.57

NAME	Sat. Index	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Aluminite	1.74	-3.664	-2.93	-10.806	Becomes less saturated	Undersaturation
Aluminum Sulphate	1.68	-0.567	0.421	-7.3	Becomes less saturated	Undersaturation
Aluminum Hydroxide (A)	-0.737	-0.566	-0.336	-1.57	Becomes less saturated	Undersaturation
Aragonite	-1.121	-0.983	-1.24	0.232	Becomes more saturated	Supersaturation
Calcite	-0.976	-0.838	-1.095	0.377	Becomes more saturated	Supersaturation
Boehmite	1.477	1.648	1.878	0.644	Becomes less saturated	Supersaturation
Gibbsite (C)	1.971	2.142	2.372	1.139	Becomes less saturated	Supersaturation
Disapore	3.199	3.37	3.6	2.367	Becomes less saturated	Supersaturation
Pyrolusite	48.621	47.284	45.496	54.515	Becomes more saturated	Supersaturation

Control 2	Time 1	Time 2	Time 4
Unspeciated charge difference	16.65	21	11.56
Speciated charge difference	17.41	22.64	11.98

NAME	Sat. Index	Sat. Index	Sat. Index	Change	Final State
Manganite	-0.532	0.315	-1.104	Becomes less saturated	Undersaturation
Aragonite	0.685	0.921	0.332	Becomes less saturated	Supersaturation
Calcite	0.829	1.066	0.477	Becomes less saturated	Supersaturation
Ferrihydrite	0.901	0.743	0.694	Becomes less saturated	Supersaturation
Lepidocrocite	4.421	4.263	4.214	Constant	Supersaturation
Maghemite	5.198	4.883	4.785	Constant	Supersaturation
Magnesium ferrite	3.654	4.273	4.886	Becomes more saturated	Supersaturation
Goethite	6.72		6.514	Constant	Supersaturation
Mixed Carbite	9.023	11.727	10.481	Becomes more saturated	Supersaturation
Magnetite	11.355	11.365	10.853	Constant	Supersaturation
Hematite	15.439	15.124	15.026	Constant	Supersaturation
Pyrolusite	56.045	56.411	55.356	Constant	Supersaturation